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APPLICATION OF THENOYL TRIFLUORACETONE (TTA) EXTRACTION TO THE PREPARATION OF RADIOISOTOPES I.

Purification of Scandium and Preparation of Ca^{45}

Abraham Broido

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ABSTRACT

A rapid method is proposed for the purification of scandium and the preparation of carrier-free Ca^{45} from neutron bombarded scandium. The method depends on the extraction of the metal-TTA chelates into benzene from an aqueous solution of controlled pH. The equilibrium constants for the reactions at room temperature ($\sim 25^{\circ}$ C) are

$$K_{Sc} = \frac{[ScT_3]_B \, [H^+]_A^3}{[Sc^{+3}]_A \, [HT]_B^3} = 0.9$$

and

$$K_{Ca} = \frac{[CaT_2]_B \, [H^+]_A^2}{[Ca^{+2}]_A \, [HT]_B^2} = 1 \times 10^{-12}$$

The purification of scandium from several elements including rare earths was demonstrated by a single batch extraction at pH $\sim$ 1.5.

The preparation of carrier-free Ca^{45} was demonstrated and its radiation characteristics were confirmed.

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APPLICATION OF THENOYL TRIFLUORACETONE (TTA) EXTRACTION TO THE PREPARATION OF RADIOISOTOPES I.

Purification of Scandium and Preparation of Ca^{45}

Introduction

Among the procedures in demand for the radioisotope production program is a routine production method for the purification of carrier-free Ca^{45}. This isotope can be made from scandium, a mono-isotopic element, which, on neutron irradiation, undergoes the following reactions [1]

(1) Sc^{45} (n, γ) Sc^{46} (85d, β, γ)

(2) Sc^{45} (n, p) Ca^{45} (180d, β)

This report presents the development of a satisfactory method for the pre-bombardment purification of scandium and the preparation of carrier-free Ca^{45} from bombarded scandium based on the use of the chelating agent TTA (thenoyl trifluoracetone)*. The method herein described meets the following requirements:

(1) Quantitative recovery of the extremely small quantity of Ca^{45} ($\sim 10^{-8}$ gms per gm of scandium) with a high degree of purity, both chemical and radiochemical, is possible.

(2) The specific activity of the product may be kept high if purified reagents are used.

(3) The procedure is simple and easily operable by the remote control techniques which are made necessary by the gamma radiation from Sc^{46} formed during the bombardment**.

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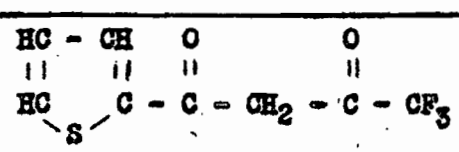
* 

** The scandium activity can be cut down by approximately a factor of ten without appreciably affecting Ca^{45} production by cutting out slow neutrons with a cadmium shield during pile irradiation. [2]

[redacted]

(4) No critical adjustments of reagents are necessary on the γ-active material.

Equilibrium Constants

(a) Discussion

Sc and Ca in an aqueous solution may be extracted with a TTA solution in benzene in accordance with the following reactions [3]:

$$(3) \quad Sc^{+3} + 3\,HT \rightleftharpoons ScT_3 + 3\,H^+$$

$$(4) \quad Ca^{+2} + 2\,HT \rightleftharpoons CaT_2 + 2\,H^+$$

where HT represents TTA.

The system at equilibrium may be characterized by the equilibrium constants:

$$(5) \quad K_{Sc} = \frac{\left[ScT_3\right]_B \left[H^+\right]_A^3}{\left[Sc^{+3}\right]_A \left[HT\right]_B^3}$$

$$(6) \quad K_{Ca} = \frac{\left[CaT_2\right]_B \left[H^+\right]_A^2}{\left[Ca^{+2}\right]_A \left[HT\right]_B^2}$$

where the brackets represent the corresponding thermodynamic activities, and the subscripts A and B refer to the aqueous and benzene phases, respectively.

In the determination of these constants, a benzene solution of TTA was added to an aqueous solution of the radioelement and the solutions mixed until equilibrium was attained. Aliquots of both phases were then taken for radioactivity determination and the pH of the aqueous phase was measured. No absolute determination of radioactivity is necessary since only the ratio of concentrations of the radioelement in the two phases is required. The cation to TTA ratio is kept low so the TTA concentration in the benzene phase will change significantly only due to ionization at high pH.

Reid[4] gives the value of Ka, the acid constant of the encl form of TTA, as 5×10^{-5} at 25° and the value for the encl/keto ratio in water as 0.016. From these values and the value of the distribution coefficient for TTA, given by Reas and King[5], the concentration of TTA left in the benzene phase equilibrated with aqueous phases at fairly high pH was calculated. The activity coefficients for TTA in benzene have been determined by Reas and King[5]. The activity coefficients for the substances in the aqueous phase were obtained from Kielland's tables[7].

(b) Determination

The Sc^{46} tracer was obtained from a scandium sample which had been bombarded in the pile and from which Ca^{45} had been extracted by Khym.[1] Necessary pH adjustments were made by adding appropriate quantities of NaOH or HCl. The distribution of scandium between the benzene and water phases was determined at room temperature at two concentrations of scandium, two concentrations of TTA and several different pH values as indicated in Table I. Preliminary experiments has shown that equilibrium was reached within five minutes with any method of fairly vigorous agitation.

No carrier-free Ca^{45} was available with which to check the extraction of calcium as a function of its concentration until after a Sc-Ca separation was actually completed. The first experiments with calcium were made with a neutron-bombarded calcium sample which has a specific activity of 1 mc Ca^{45} per gram of calcium. The results are tabulated below (Table II).

TABLE I

Distribution of Scandium between HCl-Aqueous and TTA-Benzene Phases

Original Conc. Sc in Aqueous Phase	$[HT]_B$	α	$\frac{[Sc]_B}{[Sc]_A}$	K_{Sc}
10^{-4} M	0.20 M	5.0	>100	
10^{-4} M	0.20 M	2.1	>100	
10^{-4} M	0.20 M	1.30	9.5	1.0
10^{-4} M	0.20 M	1.15	2.6	0.8
2.1×10^{-2} M	0.44 M (a)	1.25	40	0.7
2.1×10^{-2} M	0.50 M (b)	0.22	.072	1.0
			K_{ave} =	0.9

(a) 0.5 M minus 3 x 0.02, the amount that reacted with the extracted scandium

(b) Actually 0.5 - (3 x 0.072 x 0.021) = 0.496.

TABLE II

Distribution of Calcium between Aqueous and TTA-Benzene Phases

Original Ca Conc. in Aqueous Phase	$[HT]_B$	pH	$\frac{[Ca]_B}{[Ca]_A}$	K_{Ca}
2.5×10^{-2} M	0.20 M	3.5	< 0.01	-
2.5×10^{-2} M	0.20 M	5.7	< 0.01	-
2.5×10^{-2} M	0.19 M	6.4	0.065	0.8×10^{-12}
2.5×10^{-2} M	0.185 M	6.5	0.18	1.3×10^{-12}
carrier-free	0.05 M (?)	7.9	> 50	-
carrier-free	0.47 M	6.7	1.3	0.9×10^{-12}
carrier-free	0.5	1.4	< 0.01	-
				$K_{ave} = 1 \times 10^{-12}$

(c) Application

From an examination of the values of K_{Sc} and K_{Ca} it may be seen that with TTA concentrations of 0.1 to 1 M, Sc will be extracted appreciably at pH values close to 1, while Ca will not be extracted until the pH approaches 6 or 7. It may also be noted that as an ion is extracted, H^+ is liberated. Thus, if Sc is extracted with TTA an amount of H^+ equivalent to three times the molarity of the scandium will be liberated. If, for instance, the Sc is at a concentration of 0.5 mg/ml and before extraction the pH of the aqueous phase is adjusted to any value between 3 and 11 with NaOH, the pH at equilibrium will always be about 1.5. At this pH, if equal volumes of the Sc solution and a benzene solution 0.5 M in TTA are used, only about 0.3% of the Sc will be left in the aqueous phase.

To simplify remote control handling, the aqueous phase may be separated from the organic phase by gravity filtration through a sintered glass disc, the benzene phase being washed several times with water. By this time, the Sc concentration in the aqueous phase will be low enough to permit close-up handling and, for further extraction, the pH can be adjusted accurately to any desired value. For this pH adjustment, advantage may be taken both of the residual scandium concentration and of the buffering action of TTA[3]. As a final step, the Ca^{45} may, if desired, be extracted at pH $\sim$ 8, and re-extracted into a small volume of dilute acid.

Purification of Scandium

Although, by careful adjustment of conditions, calcium can be separated from the impurities present in the original scandium sample, it is obvious that the separation will be greatly simplified if a pure scandium sample is used. Further a degree of purity much greater than that usually desired is necessary for work of this type. For example, one of the first attempts to

TABLE III

Spectrographic Analysis* of "Pure" Scandium

S = Strong W = Weak F = Faint
M = Moderate T = Trace V = Very

Element	"Pure" Sc	Aqueous Residue	Conc. HCl
Ag	-	FT	
Al	-	FT	FT
B	-	T	FT
Be	-	VFT	-
Ca	FT	VS	VS
Ce	-	M	-
Cr	-	FT	FT
Er	-	VFT	-
Fe	-	T	T
Gd	-	FT	-
Lu	-	FT	-
Mg	FT	T	T
Mn	-	FT	FT
Nd	-	FT	-
Ni	-	FT	-
Pb	-	FT	-
Sc	VS	FT	-
Si	-	FT	-
Sm	-	FT	-
Y	-	VW	-
Yb	-	S	-
Zn	-	M	-

*Analysis performed by C. Feldman and H. Murray of this laboratory.

prepare Ca^{45} was made on a scandium sample which was shown to be spectrographically pure except for traces of calcium and magnesium (Table III, column 1). After bombardment, the extraction of all but 1 part in 10^6 of the scandium yielded a residue which contained long-lived impurities in quantities of about 10 times the activity of the calcium produced. These activities resulted from the bombardment of impurities undetected in the original scandium sample.

To purify the scandium before pile irradiation, samples may be extracted into TTA and then re-extracted into a minimum concentration of HCl. Those elements less extractable than scandium will remain in the first aqueous phase, while those more extractable will not re-extract into the HCl. To indicate the great variety of impurities present in the "pure" scandium sample of column 1, column 2 shows the analyses on the aqueous phase from which most of the scandium has been extracted. Column 3 shows the analysis on the hydrochloric acid solution used in these experiments. Feldman and Murray (8) of the spectrographic laboratory have made estimates which indicate the Yb and Zn impurities to be of the order of 0.1% of the original scandium while the other impurities range down to less than 10 ppm. Thus it can be seen that TTA provides a relatively simple way of purifying scandium even from its rare earth impurities*.

Preparation of Ca^{45} from Sc

The following general flow sheet was used to prepare several samples of "carrier-free" Ca^{45} from scandium. The results of a sample run, the first in which Ca^{45} was produced in large enough quantity to turn over to the Production Division for distribution, are given in Table IV.

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* The effectiveness of purifying the Sc target sample for Ca^{45} production by this method prior to irradiation has now been demonstrated by A. F. Rupp (9) and H. W. Kohn (2).

Irradiated Sc_2O_3: (1)	Dissolve in HCl and evaporate off excess acid. Add H_2O to 0.5 mg Sc/ml and transfer to Stang Precipitator (10), while drawing air upward through a sintered glass disc. Add equal volume of 0.5 M TTA in benzene and stir 10 minutes. Break vacuum, and allow aqueous phase to flow out by gravity.

(2) Benzene phase: Contains Sc and more extractable cations (Note 1)

(3) Aqueous phase: Contains Ca^{45} and all salts not extractable at pH 1.5. Add NaOH to final pH 5 and extract with 0.5 M TTA in benzene.

(4) Benzene phase: Contains Sc and all cations extractable between pH 1 and pH 5.

(5) Aqueous phase: Contains Ca^{45}, anions, alkali metals. Add 0.5 M TTA in benzene; add NaOH to neutralize 90% of TTA; final pH = 8.2.

(6) Benzene phase: Ca^{45} (Note 2). Add water (Note 4)

(7) Aqueous phase: Anions, alkali metals, etc. (Discard) (Note 3)

(8) Benzene phase: (Discard) (Note 3)

(9) Aqueous phase: (Ca^{45} prep) (Note 5)

Notes

(1) As a check on possible calcium loss here, calcium carrier was added and the extraction repeated. The quantitatively recovered calcium carrier contained no Ca^{45} activity.

(2) Up to this point the benzene phases may be washed with water. Washing with water here will extract the Ca^{45}, so, if washing is necessary a solution of the Na salt of TTA at pH 8 should be used.

(3) If more quantitative recovery of the Ca^{45} is desired, fraction 8 may be alternately shaken with fractions 7 and 9 until the desired recovery is attained.

(4) If there are no radiochemical impurities in fraction 5, dilute acid may be used here.

(5) The final solution may be extracted with benzene to remove last traces of TTA.

TABLE IV

Results of Sample Run [a] in Preparation of Ca^{45}

Fraction	% of Element in Fraction		Impurities (μc)
	Sc	Ca	
2[b]	> 99.9[c]	< 0.1	-
3	~10^{-3}[d]	> 99	~300
4	-	< 0.1	~270
5	-	> 99	~3
6	-	> 99	-
7	-	< 1	-
8	-	< 1	-
9	-	> 99	< 0.1

(a) This 0.270 g sample of Sc_2O_3 was prepared for bombardment by A. F. Rupp and E. E. Beauchamp of the Technical Division and the scandium was extracted by them (fraction 2). Fraction 3 was turned over to the author for study.

(b) These numbers refer to the flow sheet above.

(c) Residual HCl from solution step made the pH slightly higher so this extraction was repeated. Normally ~ 99.7% of the scandium will extract at this step.

(d) Estimated from spectrographic analysis (See Table III).

(e) Checked by re-extracting this fraction with water.

The data on this preparation may be summarized as follows:

Pile Yield:	Actual yield 31 μc (196 days in pile, 150 days decay) - corresponding to a saturation yield of 374 μc Ca^{45}/g Sc_2O_3.*
Radiopurity:	Absorption curve analysis - < 0.3% hard beta impurity. β-ray spectrometer** - no other measurable radiations. Radiochemical analysis*** (for Ca and Sc) - no impurities detected.
Chemical purity:	Solids ~ 1 mg. (may be reduced on ignition). Spectrographic analysis**** - very strong in Ca, with faint traces of Al, B, Cr, Fe, Mg, Mn, Na, Si and Sr. No Sc, Rare Earths, Zn, Ni, Ag, Hg, Pb, Ba, Zr.
Radiations observed:	Absorption curve - 1 β-ray - 0.24 Mev, No γ. β-ray spectrometer** - 1 β-ray - 0.248 ± 0.010, no γ.

Acknowledgment

The author wishes to take this opportunity to thank Dr. P. C. Tompkins, who suggested the problem and in whose group the work was performed, for his valuable suggestions and criticisms.

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*Such excellent agreement with Khym's value of 371 μc Ca^{45}/g Sc_2O_3 is quite accidental.

**Determinations made by R. T. Overman and W. C. Peacock. (11)

***Analysis performed by B. Warren of the Analytical Group.

****Compare with HCl analysis, Table III.

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