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Special Review of
Declassified Reports UCRL-432
ADDENDUM #1
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REPORT PROPERLY DECLASSIFIED

M Green 3-25-80
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Larry Bolden

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CHEMICAL SEPARATIONS

Element separated: Bismuth

Procedure by: Meinke

Parent material: Tracer Pa^{228} and daughters

Time for sep'n: ~ 1 1/2 hours

Milking experiment

Equipment required: Centrifuge, stirrers, tank H_2S

Yield: ~ 60%

Degree of purification: Factor of at least 10^3 from Pa and at least 100 from other activities. Factor of at least 5 from Pb.

Disadvantages: Gives a thick plate - rather bad for alpha pulse analysis.

Procedure: Purified tracer Pa in benzene - TTA solution (procedure 91-1 with DIPK and TTA extractions only).

(1) Stir organic layer 10 min with equal volume 6 N HCl (daughter into acid layer - most of Pa remains with organic layer).

(2) Wash the acid layer three times with double volume .4 M TTA in benzene, stirring 5 min each. (Removes Pa).

(3) Dilute acid layer to ~ 2 N and add ~ 1/2 mg Bi carrier. Bubble in H_2S gas to ppt Bi and Pb sulfides. Centrifuge.

(4) Again add 1/2 mg Bi carrier and repeat sulfide pptn. Centrifuge and combine ppts of (3) and (4).

(5) Dissolve sulfide ppts in few drops hot conc. HCl. Dilute to at least 1 N acid and reppt sulfides by bubbling in H_2S. Centrifuge.

(6) Repeat step (5), four times.

(7) Dissolve sulfide ppt in few drops conc HCl, dilute to ~ 6 cc and boil to rid solution of H_2S.

(8) Add 1 mg Pb carrier and ppt $PbSO_4$ by adding some SO_4^{-2} (H_2SO_4, $(NH_4)_2SO_4$, etc.) Discard prepicitate.

(9) Repeat step (8) three times.

(10) Add H_2S to supn from last pptn and centrifuge out the Bi_2S_3 formed.

(11) Dissolve the Bi_2S_3 in hot conc. HCl, dilute to known volume and plate aliquot for counting. Caution: Do not flame the $BiCl_3$ plate or much of the activity may be lost.

Remarks:

In step (3) if the acidity is greater than 2 N the Bi will not ppt.

See Prescott and Johnson's Qualitative Chemical Analysis (1933) p 157 for notes on $PbSO_4$.

In some experiments no Bi - Pb sepn is required and the solution of step (7) can be plated directly.

8/9/49
P-18-140

CHEMICAL SEPARATIONS

Element separated: Radium

Procedure by: Meinke

Target material: Thorium (~10 gm metal)

Time for sep'n: ~ 8 hrs.

Type of bbdt: 184" full energy particles

Equipment required: Standard plus centrifuges of:
250 ml capacity
50 ml capacity
15 ml capacity
Tank HCl

Yield: 25-50%

Degree of purification: At least 10^7 from Thorium, and at least 10^4 from other alpha activities present in high yield.

Advantages: Can be used to separate Ra with Ba carrier from large amounts of target material and (if coupled with column separation) to give weightless fraction of Ra.

Procedure:

(1) Dissolve the thorium metal target in concentrated HNO_3 with drops of .2 M $(NH_4)_2SiF_6$ soln added to make the sol'n ~ .05 M SiF_6^{-2}. (A large beaker should be used to prevent bubbling over in the vigorous reaction. The solution needs to be heated to start the reaction but once started the reaction proceeds vigorously.) Continue adding conc. HNO_3 and $(NH_4)_2SiF_6$ solution until target completely dissolves (may be an hour or two for 25 mil pieces of Th.)

(2) Evaporate off most of HNO_3 leaving $Th(NO_3)_4$ crystals. Caution: Do not evaporate to dryness or the nitrate will turn to ThO_2 which is harder than the original Th metal to dissolve. If some ThO_2 is accidentally formed use the same combination of conc. HNO_3, $(NH_4)_2SiF_6$ and heat to dissolve it. ThO_2 is considerably easier to dissolve immediately after forming than after prolonged heating and standing. (See 90- 4).

(3) Add 6 mg Ba^{++} carrier to the crystals and dilute with water to ~30 cc. Transfer to 250 ml centrifuge bottle.

(4) Add ~16 cc conc. NH_4OH (precipitating $Th(OH)_4$) dilute to 200 cc with water and digest for several minutes.

(5) Centrifuge and pour off supn (containing Ba and Ra plus other activities.)

(6) Dissolve ppt (amounting to ~125 cc volume) in ~16 cc conc. HNO_3.

(7) Add 3 mg Ba^{++} carrier, dilute to ~ 30 cc.

(8) Add ~ 20 cc conc. NH_4OH ppting the $Th(OH)_4$ dilute to ~ 200 cc with water and digest for several minutes.

(9) Centrifuge and pour off supn.

(10) Repeat steps 6 through 9.

(11) Combine the three supernatants from steps 5, 9 and 10. Evaporate combined solutions until ~ 200 cc. volume and transfer to 250 ml cent. bottle.

(12) Add 5 mg La^{+++} carrier and precipitate the $La(OH)_3$ plus $Th(OH)_4$ from any Th^{+4} remaining by the addition of conc NH_4OH. Discard ppt.

(13) Evaporate the supn to ~ 40 cc and repeat step 12.

(14) Add Na_2CO_3 solution to the supn to ppt $BaCO_3$ (carries Ra) digest for several minutes. Centrifuge.

(15) Dissolve $BaCO_3$ ppt in minimum of conc. HCl (one or two cc's probably enough).

(16) Place in ice bath. Add double or triple volume of ether and bubble in HCl gas until water and organic layers become miscible and the Ba ppts out as the $BaCl_2$. Centrifuge.

(17) Dissolve the ppt in minimum of H_2O.

(18) Repeat steps 16 and 17 twice (total of 3 $BaCl_2$ pptns). Caution: HCl-ether mixtures spatter readily when warmed.

(19) The $BaCl_2$ can be used for α counting or further purification can be made using a resin column.

Remarks:

Usually about 50 gms of Th metal can be bombarded at once in the cyclotron to produce the Ra^{225}. Hence the large centrifuge is necessary for the separation of the original $Th(OH)_4$ pptns and purifications.

The $Th(OH)_4$ ppt is very bulky-occupying more than half of the tube in step 4. However, with the Ba^{++} carrier added and the two reprecipitations of the thorium it is believed much of the Ra is recovered in the supernates.

The amounts of NH_4OH and HNO_3 used should be calculated rather closely so as to allow little excess, otherwise when the supn's are evaporated to ~ 40 cc (step 13) the solution will be saturated with NH_4NO_3 and interfere with the $BaCO_3$ pptns.

In step 13 some of the yield is lost through the solubility of some of the $BaCO_3$. This might be recovered by destroying the NH_4NO_3 and reducing the volume drastically before the carbonate precipitation.

Originally Ba and Ca were added as holdback carriers in the $Th(OH)_4$ ppts. The Ca, however, did not separate as well from the Ba as expected in the later parts of the procedure.

When working up 50 gms of Th, 10 gms at a time, residues might be combined and further recovery of Ba lost in the original procedure might be made. Also the $BaCO_3$ ppt of step 14 (first 10 gms) can be dissolved in conc. HNO_3 and used as carrier for the various steps of succeeding 10 gm portions - thus reducing the total amount of Ba in the final sample.

10 grams is about the maximum amount of thorium practical to work up at one time by this procedure using 250 ml centrifuge bottles.

If carrier free Ra is needed, $BaCO_3$ can be pptd from the water soln of the end of step 18. This $BaCO_3$ can be dissolved in acid pH 1-2 and absorbed on Dowex 50 resin. The Sr, Ba & Ra can then be eluted in that order by citrate at pH 7.5-8.0 (See E. R. Tompkins AECD-1998). This column procedure, however, has not been included in the runs made to date.

8/24/49

CHEMICAL SEPARATIONS

Element separated: Actinium
(Procedure designed for Ac^{225} & Ac^{226})

Procedure by: Hyde

Target material: Thorium metal
(Two 25 mil foils 1 1/2" square bombarded on edge) About 25 grams Th.

Time for sep'n: 24 hours

Type of bbdt: protons from 184"

Equipment required: beakers, centrifuge cones, 250 ml separatory funnel, resin column, automatic sampler, pH meter.

Yield: Not known - estimated 75%

Degree of purification: Complete separation from all other elements by factor of at least 10^4.

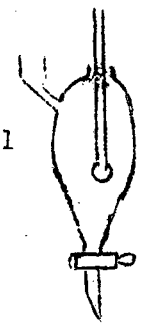
Procedure:

(1) Dissolve thorium in hot conc. HNO_3. Add 1 drop 1 N HF occasionally to catalyze dissolution.

(2) Evaporate solution nearly to crystallization. Cool. Transfer to 250 ml pear-shaped separatory funnel. One which has been modified to provide a side funnel as shown in figure 1 is recommended.

(3) Add 1-2 volumes penta ether (dibutoxytetraethylene glycol)*. Stir. Let settle. Drain aqueous layer into original beaker. Drain pentaether layer into bottle for storage.**

Fig. 1



(4) Return aqueous layer to funnel. Add solid ammonium nitrate with stirring until solution is saturated. Add 2-3 volumes pentaether. Stir. Drain aqueous into 50 ml centrifuge cone. Drain pentaether layer into storage bottle.

(5) Repeat pentaether extraction once again after adding 0.5 ml conc. HNO_3 to replace that extracted by solvent.

(6) Aqueous layer in 50 ml centrifuge cone centrifuged to separate last cc's of pentaether, which are pipetted off.

(7) Add NH_4OH to ppt last amounts of thorium as $Th(OH)_4$. This serves to carry the actinium out of the salted solution. Wash twice with H_2O.

* It is quite important that the solution be cool before the solvent is added as pentaether is rapidly decomposed by hot nitric acid.

** Pentaether is used to extract the bulk of the thorium away. The thorium serves as its own salting agent in the first pass which extracts the bulk of it and reduces the aqueous volume greatly. Subsequent extractions must be aided by NH_4NO_3 salting.

(8) Dissolve mixed hydroxides in minimum amoun[illegible] Dilute to 5 ml. Adjust pH to 1.5 --- 2.5*** check [illegible] pH meter using 1 drop glass electrode. Add 10 m[illegible] benzene [illegible] Stir. Recheck and if necessary readjust pH. [illegible] 10-20 minutes.

(9) Centrifuge. Pipet off benzene layer containing thorium.

(10) To aqueous add 10 ml fresh TTA. Stir, check pH. Stir 10-20 minutes. Centrifuge. Pipet off benzene layer.

(11) To aqueous layer containing actinium, rare earth and other activities add NH_4OH to adjust pH to between 5.5-7.0***.

(12) Add 10 ml TTA-benzene. Stir. Recheck pH. Contact 20 minutes.

(13) Pipet benzene layer containing actinium and rare earths into clean 50 ml centrifuge cone. Re-extract activity into 2.5 ml 0.1 N HCl by 2 minutes of stirring.

At this point the only likely impurities are rare-earth fission products. If these do not interfere, this solution may be considered the final solution. If separation from rare earths is desired the following resin separation is recommended.

(14) Add a few mg of ammonium form colloidal dowex 50 resin to the dilute HCl solution. Warm to $\sim 60^{\circ}C$ in water bath for 2-3 minutes. Centrifuge.

(15) If assay of supernate indicates nearly complete adsorption on resin, pipet the resin on to the top of a short resin column. Elute with 5% citrate solution of pH 3.8 - 4.0. Use a mechanical sampler to take samples every 20 minutes.

The rare earth and actinium peaks can not be predicted accurately enough to eliminate the necessity of alpha and beta counts to determine their location. The rare earth fractions come off in the first samples as indicated by the beta counts. The actinium peak is located by the alpha counts of Ac^{225}. The elution of Bi^{213} and its associated Po^{213} daughter alpha activity in the early fractions obscures the location of the actinium peak unless samples are pulse analyzed or unless the 47-minute Bi^{213} is allowed to decay before counting.

My experience with a column 6 cm x 2 mm of colloidal resin eluted with pH 3.9 citrate at a rate of 1 drop per 2.5 minutes was that the rare earth fraction came off within two hours and the actinium fraction, well separated from the rare earths, started to come off after 5 hours and was spread over 2-3 hours. Others (Orth & Street) report much more rapid elution under essentially the same conditions.

*** An equal volume of TTA-benzene will extract thorium essentially completely from an aqueous solution of pH >1. Actinium extraction is 0 at pH 2.5 or less, is 10% at pH 4 and rises sharply to essentially complete extraction at pH 5.5 or greater. See Hagemann AECD 1933.

7/6/49

P-18-46

[illegible]

CHEMICAL SEPARATIONS

Element separated: Actinium

Procedure by: Meinke

Parent material: Tracer Pa^{230}

Time for sep'n: 3-4 hrs.

Milking experiment

Equipment required: Standard, centrifuge

Yield: ~ 40%

Degree of purification: Factor of at least 10^7 from Pa, U and Th.

Advantages: Can separate very small amounts of Ac from large amounts of Pa, U and Th activity. In one experiment separated 500 d/m Ac^{226} from 10^7 total d/m of Pa^{230} and about equivalent amounts of U and 30 minute Th^{226}.

Procedure:

Pa^{230} in 6 N HNO_3 after DIPK extractions (procedure 91-1)

(1) Take 10 cc of Pa soln and add 1/4 mg La^{+++} and 5 mg Ce^{+++} carriers.

(2) Add 10 drops of conc HF to ppt the fluorides. Centrifuge.

(3) Metathesize ppt to La and Ce hydroxides by adding several ml of conc KOH soln. Centrifuge out the hydroxides and wash once with 5 ml alkaline water.

(4) Dissolve ppt in few drops 6 N HCl and dilute to 5 cc.

(5) Add 1/4 mg Zr^{+4} carrier and H_3PO_4 to make 3 N PO_4^{-3}. Discard ppt.

Steps 2 through 5 are repeated alternately or consecutively until the desired degree of purification is obtained. For the purifications noted above, 10 fluoride pptns and 9 phosphate pptns were made. After the 10th fluoride ppt had been metathesized to the hydroxide, the following procedure was used:

(6) Dissolve hydroxide ppt in 10 M HNO_3, make .01 M Fe^{+++} and oxidize Ce^{+++} to Ce^{++++} with solid sodium bismuthate (warm to speed up reaction.) (Ce^{+4} will now carry on the $Zr_3(PO_4)_4$ ppt.)

(7) Repeat step (5).

(8) Repeat (2) and (3).

(9) Dissolve ppt in few drops 6 N HCl, dilute to known volume and plate aliquot for counting.

Remarks:

The fluoride cycles decontaminate primarily from ~~Actinium~~ Pa, [redacted] from Th. If further purification is required include more cycles in procedure.

Only one milking can be made from a given batch of Pa by this procedure since it is difficult to again get the Pa into an extractable form once fluoride ion has been added.

It has been found that the $LaCl_3$ solution makes a more adherent and thinner plate than the LaF_3 ppt. The amount of La^{+++} carrier used in step (1) should be determined by the amount of bulk that can be tolerated on the final plate.

8/9/49
P-18-139

[redacted]

CHEMICAL SEPARATIONS

Element separated: Thorium

Procedure by: Meinke

Target material: Tracer Pa separated from 60" bbdt of ionium.

Time for sep'n: Several hours.

Type of bbdt: (Milking expt.)

Equipment required: Stirrers and TTA

Yield: As high as 50% possible.

Degree of purification: Decontaminate from 10^7 c/m Pa, 10^6 c/m U and 10^5 c/m Ac.

Advantages: Gives carrier-free Th, a thin plate for pulse analysis and good purification although not speed.

Procedure:

(1) Nitric acid used throughout. Make sample 6 N acid and TTA extract (with .4M TTA in benzene) 5 times with double volume of TTA -- stirring 5 minutes for each extraction. (Removes Pa into TTA ~ 70% or more per pass).

(2) Evaporate to dryness (wash twice with water and take these washings also to dryness) and take up in acid pH 1.0. TTA extract with equal volume (.25M TTA in benzene) stirring 15 minutes. (Th into TTA but not U or Ac.)

(3) Repeat TTA extn of (2) with fresh TTA and combine the extns.

(4) Wash TTA with equal volume of pH 1.0 soln for 15 min. (U contamination into acid.)

(5) Wash TTA with 6 N acid (equal volume) and stir 15 min. (Th into acid).

(6) Repeat parts (2), (3), and (4). (Repeat wash as in (4) if necessary for further U purification.)

(7) Plate out the .25 M TTA on Pt plates and flame.

Remarks: See curves of Hagemann for % extn into TTA vs pH for Th and Ac. At pH of 1 Th should go into the TTA almost completely but U should only go in less than 10% -- perhaps as little as 2%. Ac will not go into TTA until about pH 3 or so and of course Pa goes in up to about 6 or 8N acid.

pH conditions for separating Th from U by TTA extns are quite critical!

Equivalent and molecular weight of TTA is 222 gms.

8/24/49

P-18-254

CHEMICAL SEPARATIONS

Element separated: UX_1 (Thorium)

Procedure by: D. B. Stewart

Target material: $UO_2(NO_3)_2.6H_2O$ in which UX_1 has come to equilibrium

Time for sep'n: 24 hrs.

Equipment required: 40 ml centrifuge cone

Yield: 50,000 - 10,000 c/m from 20 g UNH.

Degree of purification: factor of $\sim 10^6$ from U.

Advantages: Good yield with small amount of inert carrier (Very voluminous insoluble precipitate) (Uranium does not precipitate at all)

Procedure:

(1) Dissolve 20 g $UO_2(NO_3)_2.6H_2O$ in 20-30 ml 0.01 N HNO_3 in a 40 ml centrifuge cone and warm solution to about 80°C in a hot water bath. Add 0.5 mg - 1 mg Zr carrier as nitrate.

(2) Add 5 ml of a saturated solution of m-nitrobenzoic acid in water and continue warming for about 1 hr. Let stand overnight.

(3) Centrifuge, decant supernatant, and wash $Zr(C_6H_4NO_2COO)_4$ twice with 0.01 N HNO_3 + m-Nitrobenzoic acid.

Remarks:

Saturated solution of m-nitrobenzoic acid made up by dissolving 400 mg. of the material in 100 ml H_2O. Heat to 80°C. Allow to stand several hours & filter to remove excess and impurities.

7/28/49
P-18-'81

CHEMICAL SEPARATIONS

Element separated: Thorium

Procedure by: Meinke

Parent material: Tracer Pa and daughters (both α & K)
Milking experiment

Time for sep'n: ~ 3/4 hr.

Equipment required: standard

Yield: Only ~ 40-50% Th per cycle

Degree of purification: 2-3% Ac carried per cycle - other elements decontaminated by factor of at least 100.

Advantages: Good procedure if Th present in ~ same amount as other activities.

Procedure:

Pa daughters in 6 N HCl after milking from Pa in TTA (91-1).

(1) To ~ 10 cc daughter soln add 1/2-1 mg Zr^{+4} carrier and enough H_3PO_4 to make ~ 4 M in $PO_4^{\equiv}$. Centrifuge ppt (carries Th^{+4}).

(2) Add to the ppt 3 mg La^{+++} carrier and dilute with 1 N HCl. Add HF, digest and centrifuge.

(3) Metathesize the fluoride ppt to hydroxide by adding conc KOH. Centrifuge. Wash once with alkaline water.

(4) Dissolve in HCl and repeat steps 1-3 reducing amount of La carrier.

(5) Plate as the $LaCl_3$ soln, flame and count.

Remarks:

$Zr_3(PO_4)_4$ ppt quite specific for carrying Th^{+4} from other elements in the heavy region. Yield lost in the LaF_3-$La(OH)_3$ pptns.

Do not use this procedure if more purification needed than given by 2 cycles since the Th yield will be very low.

$LaCl_3$ soln when evaporated sticks to Pt plates much better than the ppts encountered in this procedure.

8/12/49
P-18-151

Solution of Thorium Metal and Thorium Dioxide

Thorium metal can be dissolved rapidly in conc HCl but a considerable amount of black insoluble residue is formed in the process. If a few drops of $(NH_4)_2SiF_6$ solution (enough to make ~ 0.5 M) are added to the HCl before solution is started the black residue is dissolved, leaving only a small residue of thorium oxide (<1%) in the clear solution.

Thorium metal can be dissolved in conc. HNO_3 with the addition of $(NH_4)_2SiF_6$ (or HF) to .05 M. The metal becomes passive to ~~the~~ solution from time to time requiring further additions of acid and $SiF_6^{=}$.

If the excess HNO_3 is evaporated off care should be taken not to allow the solution to go completely to dryness or difficultly soluble ThO_2 will be formed.

If it is desired to dissolve ThO_2, the HNO_3-$(NH_4)_2SiF_6$ solution should be used and the mixture heated with stirring for several hours. ThO_2 when first formed is much more soluble than after prolonged heating.

Note: A bombardment of 50 mg 13% ionium (Th^{230}) in thorium (Th^{232}) mixture in the dioxide form should be mentioned here. The hydroxide was pptd and heated in a Pt crucible until only the dioxide remained. This dioxide was then packed into a Pt "boat" 1" x 1/2" x .085" and wet with a few drops of sodium silicate soln. The mixture was then dried under a heat lamp, more silicate added and again dried. The boat was then flamed over a Fisher burner.

It was found that a target prepared this way could withstand considerable mechanical shock and also the high target temperature produced by the 60" cyclotron deuteron beam without breaking the silica crust.

It was also found that the target material could be rather easily scraped out of the boat and mostly dissolved in 5 or 6 hours -- after several additions of HNO_3-$SiF_6^{=}$ soln.

[redacted]

Newton, Hyde, Meinke

8/15/49

P-18-202

CHEMICAL SEPARATIONS

Element separated: Protactinium

Procedure by: Meinke

Target material: ~ 10 gms Th metal

Time for sep'n: 1 1/2-2 hrs.

Time of bbdt: 60" D^+ bbdt and 184" bbdt all particles

Equipment required: Centrifuge Kjeldahl flasks, dry ice and stirrers.

Yield: Roughly 10% through entire chemistry

Degree of purification: Separate from all elements by a factor of at least 10^3. For further purification from Cb and Zr do more DIPK washes.

Advantages: Gives carrier-free Pa on weightless plates for pulse analysis and counting. Purification can be made more extensive by repeating individual steps.

Procedure:

(1) Nitric acid used except where indicated otherwise. Dissolve Th metal in conc. HNO_3 ~ .01 M in $(NH_4)_2SiF_5$ soln (25 cc acid and 3 or 4 drops of 1/5 M $SiF_6^{=}$ soln usually sufficient to dissolve 10 gms Th.)

(2) Dilute to ~ 4 N acid and Th^{+4} con. less than 0.65 M (Greater con. of Th salt interfers with pptn.)

(3) Add to 40 cc $Th(NO_3)_4$ soln in 4 N HNO_3 an excess of $Mn(NO_3)_2$. (1/2 cc of 50% soln sufficient.)

(4) Add 1.5 cc $KMnO_4$ soln (40 mg/cc). (Pa carried quantitatively on 1.5 gm/liter MnO_2 ppt.)

(5) Digest over water bath, centrifuge and pour off supn.

(6) To ppt. add few drops of 4 N acid and dissolve in a few drops of sat. soln of $NH_2OH \cdot HCl$.

(7) Dilute to required volume and repeat pptns. three times, reducing volume each time. Final volume is a few cc's.

(8) Make soln 6 N HNO_3 or HCl. Extract with 2-3 times volume of diisopropyl ketone (DIPK) shaking together for 1/2 min. in Kjeldahl flasks and separating phases by freezing aqueous layer with dry ice - acetone mixture. (Pa into DIPK ~ 60% yield/pass).

(9) Wash DIPK layer with 3 washs of an equal volume of soln 1 N HNO_3 and 3 N NH_4NO_3 in successive flasks.

(10) Pa then washed into 2 successive portions of .1 N HNO_3.

(11) DIPK extn repeated once and .1 N solns combined and made 6 N HNO_3.

(12) Equal volume of TTA (.4 M in benzene) stirred for 5 min. with the 6 N acid - (Pa into TTA.)

(13) Organic layer washed once with equal volume 6 N HNO_3.

(14) The Benzene-TTA plated out on platinum.

Remarks: The am't of F^- introduced by the .01 M $(NH_4)_2SiF_6$ is not enough to complex an appreciable amount of the Pa. Traces of Pa coppt with good yield from 1 - 5 N HNO_3 soln less than .65 M Th^{+4} on 1.5 gm/liter MnO_2 with good separation from macro am't of Th. A concentration factor of at least 10 can be obtained by these pptn cycles.

Any Th and fission product that extract into DIPK are washed out in the acid-salt washes. 0.1 N HNO_3 used to wash Pa out of DIPK keeps Pa from hydrolyzing to the colloid state.

The Pa must never get very near a neutral pH or it will go into the non-extractable colloid.

TTA separates Pa from all elements formed in bbdt except Zr, Cb, and Hf. DIPK extracts only Pa and U at these cons. MnO_2 carries Pa, Zr, Cb and maybe some others, but does eliminate things like I which might solvent extract through the other chemical procedures.

[redacted]

8/24/49

[redacted]

P-18-258

CHEMICAL SEPARATIONS

Element separated: Protactinium

Procedure by: Meinke

Target material: $Th(NO_3)_4$ or thorium metal

Time for sep'n: 2 minute minimum, average 15 min. with metal

Type of bbdt: 60" & 184" - all particles

Equipment required: stirrer

Yield: 40-80%

Degree of purification: Factor of at least 100 from all elements present except Zr, Cb, Hf.

Advantages: Fast, weightless plate & Pa, good for alpha pulse analysis. Zr & Cb fission products coming through procedure make Geiger counting of Pa impossible without more chemistry.

Procedure:

(1) Dissolve Th metal in conc. HNO_3 ~.05 M in $(NH_4)_2SiF_6$ soln. (25 cc. acid and 3 or 4 drops of 1/5 M $SiF_6^{=}$ sol'n sufficient to dissolve 10 gms Th.) $Th(NO_3)_4$ can be dissolved directly in 4 N HNO_3.

(2) Dilute to ~ 4 N acid.

(3) Add equal volume of TTA (.4 M in benzene) and stir for 5 minutes. (Pa, Zr, Cb into organic layer).

(4) If want somewhat better purification wash TTA layer with equal volume of 4 N HNO_3. (May lose up to half Pa yield in this wash.)

(5) Plate out benzene-TTA layer on platinum.

Remarks: TTA separates Pa from all elements formed in bbdt except Zr, Cb, & Hf.

This method used for excitation function work where as many as 16 foils are worked up simultaneously. Identical amounts of reagents are added and each sample subjected to the same procedure, giving approximately equal chemical yields for each foil (to within 5 or 10%).

6/22/49

[redacted]

CHEMICAL SEPARATIONS

Element separated: Protactinium (~2 mg)

Procedure by: Crane

Removal of macro amounts of Pa from rare earths, Mn, Zr, iron

Time for sep'n: Several days

Yield: ~ 80%

Equipment required: anion exchange resin, beakers, hot plate, centrifuge

Advantages: Takes Pa out of colloidal state

Procedure:

(1) Add ten times as much Zr^{+4} as you have Pa (~ 20 mg of Zr^{+4}) make 3 M in HF and allow to stand for several hours. Then add excess Ba^{+2} ion; Pa carries on the $BaZrF_6$ ppt.

(2) Check floride solution for Pa activity. If carrying not complete add 10 mg Zr^{+4} and digest at low temperature for a few hours.

(3) Combine $BaZrF_6$ + Pa ppts and dissolve in conc. HNO_3 + boric acid.

(4) Dilute and precipitate Zr + Pa as hydroxide with KOH.

(5) Redissolve ppt in conc. HCl. Boil this solution for a few hours then make HCl 8 M and absorb on anion exchange resin (Dow A-1 used in 20 cm x 1 cm^2 column; flow rate ~ 1 drop/min). Wash resin with 8 M HCl.

(6) Elute with 4 M HCl. Pa will come off in ~15 column volumns. (Uranium requires ~ 45 column volumns).

Alternate step for (1): If desired and solution of Pa does not contain too much Zr^{+4} and other floride complex ions the Pa solution may be absorbed directly on the resin from a 3 M HF soln, washed with conc HCl and eluted with 4 M HCl.

(7) Final solutions of HCl are then concentrated, made 6 M HCl and Pa extracted into equal volume diisopropyl ketone.

(8) The Pa is taken back into .1 volume 0.1 M HNO_3 solution and made 4 M in HCl to keep Pa from forming colloid.

8/17/49

P-18-242

CHEMICAL SEPARATIONS

Element separated: Uranium

Procedure by: Crane

Target material: ∾20 gr of Th metal

Time for sep'n: Several hrs.

Type of bbdt: 184" bbdt

Equipment required: Centrifuge, Kjeldahl flasks, dry ice and stirrers.

Yield: ∾ 90%

Degree of purification: Separate all elements in Th fission by factor greater than 10^6.

Advantages: Gives carrier free Uranium.

Procedure:

(1) Nitric acid used except where indicated otherwise. Dissolve Th metal in conc. HNO_3 & ∾ .05 M in $(NH_4)_2SiF_6$ (50 cc acid and ∾6 drops 1/5 M $SiF_6^{=}$ — Solution usually sufficient to dissolve 20 gram Th metal).

(2) Evaporate to near dryness & redissolve in 1 M HNO_3 and saturate with NH_4NO_3.

(3) Ether extract uranium using 3 separate portions of ether and combining; wash twice with .1 M HNO_3 + 10 M NH_4NO_3.

(4) Extract uranium back into water solution. Add La^{+++} carrier ∾ 1 mg/cc solution

(5) ppt hydroxide with NH_4OH. (carries uranium)

(6) Dissolve in 6 M HNO_3 and add Zr^{+4} scavenger (∾ 1 mg/cc), dilute to 3 N acid.

(7) Add iodic acid to ppt $ZrO(IO_3)_2$ to scavenge solution.

(8) Remove supernatent and ppt La^{+3} as hydroxide.

(9) Dissolve in 1 M HNO_3. Saturate with NH_4NO_3 and ether extract using 3 separate portions of ether and combining.

(10) Wash twice with .1 M HNO_3 + 10 M NH_4NO_3 and re-extract uranium into water.

Remarks: Use one part ether, two parts salt solution in extraction. Wash with equal volume salt solution. Re-extract into half volume water.

In step 7 do not add excess iodic acid or La will also be pptd. Add just enough to ppt the Zr as $ZrO(IO_3)_2$, otherwise much yield will be lost. For ether extraction of uranium see: A. S. Newton, Phys. Rev. 75 209 (1949).

6/16/49