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Collected Radiochemical Procedures

(Radiochemistry Group CNC-11)

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CHEMISTRY OF THE ELEMENTS ON THE BASIS OF ELECTRONIC CONFIGURATION

The properties of the chemical elements are largely dependent on the sizes of the atoms (or their ions) and on electronic configuration. Electronically, the elements may be arranged into three classes:

(1) The *regular* (or *representative*) *elements*, in which the outermost shell is being built up to a maximum of 8 electrons; i.e., elements in which the *s* and *p* subshells (orbitals) are being filled.

(2) The elements of the *short transition series*, in which the next to the outer shell is being built up from 8 to 18 electrons as a result of the filling of *d* orbitals.

(3) The elements of the *long transition series* (the *rare earths* or *lanthanides* and the *actinides*), in which *f* orbitals are being filled and the second from the outermost shell is being built up from 18 to 32 electrons.

I. General Properties of Regular (or Representative) Elements.

The regular elements (with the exception of the H-He period) exist in periods (series) in which *s* and *p* orbitals are being filled and the number of electrons in the outer shell increases regularly from 1 to 8; e.g., Li $1s^2\ 2s$; Be $1s^2\ 2s^2$; B $1s^2\ 2s^2\ 2p$; . . . Ne $1s^2\ 2s^2\ 2p^6$. Underlying the outer shell is one which contains either 8 or 18 electrons For the periods Li-Ne and Na-A, there are 8 electrons in the underlying shell; for the remainder of the complete periods, the first and second elements possess 8 electrons in the next to outer shell and the rest of the elements 18 electrons. This change in configuration results from the intervention of transition series between the second and third elements, beginning with the third complete period. Thus, between calcium (atomic number 20) and gallium (atomic number 31) there occurs the scandium-copper transition series. Included with the regular elements on the basis of similarity in general properties are zinc, cadmium, and mercury, elements having an . . . 18, 2 configuration, and which may be regarded as the terminal elements of the various short transition series.

General Properties of Regular (or Representative) Elements

1	2	3	4	5	6	7	8
$_{1}$H							He
$_{3}$Li	Be	B	C	N	O	F	Ne
$_{11}$Na	Mg	Al	Si	P	S	Cl	Ar
$_{19}$K	Ca	Ga	Ge	As	Se	Br	Kr
$_{37}$Rb	Sr	In	Sn	Sb	Te	I	Xe
$_{55}$Cs	Ba	Tl	Pb	Bi	Po	At	Rn
$_{87}$Fr	Ra						

Examination of the elements which make up any one of the regular series shows that, in general, there is a definite transition from active metal to active nonmetal to noble gas as the *s* and *p* orbitals are being filled. It should be emphasized, however, that this transition from active metal to nonmetal becomes less marked with increasing series number. Thus, whereas silicon is completely nonmetallic in character, germanium, the corresponding element of the next series, possesses some distinctly metallic characteristics. This diminishing trend is, of course, most pronounced in the last complete series; for example, astatine, a member of the halogen family, can be precipitated as a sulfide from hydrochloric acid solution.

The diminishing trend from active metal to active nonmetal with increasing series number has its effect on group relationships. Variations in properties within a group of elements are attributable chiefly to differences in sizes of atoms (or ions). Generally, the metallic character (or reactivity) of the members of any group as manifested by ionization or electrode potential values, and by the basic nature of the oxides which these elements form, becomes more pronounced with increasing atomic size.

Notable exceptions to this generalization exist, however. One such exception, which well illustrates the effect of size in determining properties within a group, is found in a comparison of the ionization and electrode potentials of the alkali metals. As would be expected, the ease with which an electron is removed from the gaseous atom increases in a regular fashion from lithium to cesium, as shown by the decreasing values for the corresponding ionization potentials (Li. 5.36 volts . . . Cs. 3.87 volts). On the other hand, although the electrode potentials increase regularly from sodium to cesium, the potential for the lithium electrode, instead of being the lowest as might be predicted from the ionization potentials alone, is actually equal to that of cesium. This apparent anomaly results from the large quantity of energy liberated by the hydration of the very small lithium ion; the tendency for the alkali metal ions to polarize water molecules and form stable hydrates increases markedly with decreasing ionic size.

Other noteworthy reversals of trend occur in the aluminum and the zinc groups. The values for the third ionization potentials and for the electrode potentials (for the reaction $M = M^{+++}(aq) + 3e^-$) of the members of the former group are shown below:

	THIRD IONIZATION POTENTIAL, VOLTS	ELECTRODE POTENTIAL, VOLTS
Al	28.31	+1.67
Ga	30.6	+0.52
In	27.9	+0.34
Tl	29.7	−0.72

The great decrease in reactivity from aluminum to gallium may reasonably be attributed to the existence of the first short transition series between these elements. As a result of the generally steady decrease in size in this series, arising from the filling of the *3d* orbitals, there occurs a regular increase in effective nuclear charge, which in gallium is manifested by a larger ionization potential than would be normally anticipated. The much lesser reactivity of thallium as compared with indium is explained in a similar manner, except that in this case two series intervene, in each of which a relatively steady decrease in size occurs: namely, the third short transition series and the lanthanides. An analogous explanation accounts for the somewhat noble chemical nature of mercury in contrast to the relatively reactive character of zinc and cadmium.

The change from a shell of 8 electrons underlying the valence shell to one of 18, which results from the intervention of a short transition series, also may affect basicity relationships. On the basis of size alone, the hydroxide of aluminum (the ionic radius of Al^{3+} ion is 0.50 A) would be expected to possess weaker basic characteristics than gallium hydroxide (the ionic radius of Ga^{3+} ion is 0.62 A). However, gallium hydroxide is a distinctly weaker base than is aluminum hydroxide. The inversion noted above is not found in the other groups of regular elements.

It has been mentioned that size differences are chiefly accountable for variations in properties between members of a group. Generally, the first (and smallest) group member exhibits the widest divergence from group similarities. This effect is most pronounced in the first three groups of regular elements, where lithium, beryllium, and boron differ markedly from the other members of their respective groups. For example, lithium, on the basis of solubility of its salts, ability to form complex compounds, and other properties, bears a much closer resemblance to magnesium than it does to the other alkali metals. In like manner, beryllium and boron are more similar to aluminum and silicon, respectively, than to the other members of their groups.

Regular series metals which possess a shell of 8 electrons adjacent to the valence shell have only one stable oxidation state, corresponding to the number of valence electrons. On the other hand, metals with an underlying shell of 18 electrons are capable of existing in more than one oxidation state. Thus, oxidation states of +1 and +3 for thallium, +2 and +4 for tin and lead, and +3 and +5 for antimony and bismuth are common. The existence of variable oxidation states for these elements has been attributed in part to the superior shielding of the valence electrons from the attractive force of the nucleus by an underlying shell of 18 electrons as compared with one of 8.

The ions of the regular elements are colorless and diamagnetic. They are generally much inferior to transition metal ions in their ability to form complex compounds. The tendency for complex compound formation is most marked in ions of large charge and relatively small size.

2. General Properties of Elements of Short Transition Series.

The elements of the short transition series exist in periods in which the number of electrons

GENERAL PROPERTIES OF ELEMENTS OF SHORT TRANSITION SERIES

	d^1s^2	d^2s^2	d^3s^2	d^4s^2	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$
3*d*	$_{21}$Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4*d*	$_{39}$Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5*d*	$_{57}$La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

in the outer shell remains essentially constant at s^2 and the next to the outer shell is being built up from 8 to 18 electrons; i.e., the *d* orbitals are being filled. Although, on the basis of electronic structure, the elements of the scandium group are members of short transition series, their chemistry is ordinarily discussed with that of the rare earths. These elements are found in minerals containing the rare earths and go along with the latter in most analytical procedures. Zinc, cadmium, and mercury, with completed *d* orbitals, are the terminal elements of the various short transition series and do not possess the general characteristics of transition elements.

All the transition elements are metals. Many of the ions they form are colored and paramagnetic as a result of the presence of unpaired electrons. The elements have a great tendency to form stable complex ions. Inasmuch as electrons in both the outer *s* and inner *d* orbitals are available for chemical binding, most of the transition elements possess variable oxidation states.

For the first six groups (scandium through iron group), the maximum oxidation state exhibited corresponds to the sum of the outer *s* and inner *d* electrons. Beyond the iron group, except for zinc, cadmium, and mercury, there appears to be no correlation between electronic configuration and the maximum oxidation state. A maximum oxidation state of eight, the highest attained by any element, is reached at the iron group. Only two members of this group, ruthenium and osmium, form compounds in which this state is exhibited; e.g., RuO_4 and OsO_4. It should be emphasized that the highest oxidation state is not always the most characteristic one of the element. In general, within a transition group where the elements exhibit variable oxidation states, the highest state becomes more stable with increasing atomic number and the lower states less stable. Thus the dichromate and permanganate ions in acid media are much more powerful oxidizing agents than the tungstate and perrhenate ions. In any series of compounds (e.g., halides, oxides), formed by a transition element, the ionic character of the compound decreases with increasing oxidation state of the element. This may be illustrated by a consideration of the oxides of chromium, some properties of which are shown below.

OXIDATION STATE OF CHROMIUM	OXIDE	CHARACTER	IONS FORMED
+2	CrO	basic	Cr^{2+}
+3	Cr_2O_3	amphoteric	Cr^{3+} CrO_2^-
+6	CrO_3	acidic	$Cr_2O_7^=$ $CrO_4^=$

Transition elements show both vertical (group) and horizontal relationships. The horizontal similarities are generally marked in the lower oxidation states, as illustrated by the fact that in the first series the +2 and +3 states are characteristic of the elements chromium through copper. Horizontal relationships are most striking in the series of elements frequently referred to as the "transition triads." Thus, iron, cobalt, and nickel are metals which possess similar physical properties and analogous oxidation states of 2, 3, and 4, with the exception of iron which also exhibits a +6 state. The second and third transition triads are so similar in properties that they are classified as the "platinum" metals and their chemistry is ordinarily discussed as a unit. The vertical similarities between the various pairs of platinum metals result from the lanthanide contraction, a phenomenon which has important consequences insofar as transition element chemistry is concerned.

From cerium, element 58, to lutetium, element 71, successive electrons are added to the 4*f* subshell, whereas the existing 5*d* and 6*s* levels remain practically unchanged. The filling of this level deep within the atom, accompanied by the corresponding regular increase in nuclear charge, results in a rather regular decrease in the atomic volumes (and also the ionic radii) of the rare-earth elements, which is known as the "lanthanide contraction." As a consequence of this contraction, significant irregularities in group trends exist between elements of the second and the third transition series; most of the irregularities occur immediately following the rare earths.

Within a regular group of metals, e.g., the alkali or alkaline earth group, the ionic radius of the characteristic ion increases regularly with increasing atomic number. No such regular increase is observed in several of the transition groups. In fact, in groups containing elements which are not far removed from the rare earths, the ionic radius of the third member is quite similar to that of the corresponding ion of the second member:

Ti^{4+}, 0.65 A	V^{5+}, 0.6 A	Cr^{6+}, 0.5 A
Zr^{4+}, 0.8 A	Nb^{5+}, 0.7 A	Mo^{6+}, 0.62 A
Hf^{4+}, ca. 0.8 A	Ta^{5+}, 0.72 A	W^{6+}, 0.65 A

Inasmuch as chemical properties within a group are in large measure related to the size of the members, it is not surprising to find that the second and third members of the transition groups are much more closely related to each other than to the first member. Mention has already been made of the remarkable similarity of the platinum metals. Zirconium and hafnium are so analogous chemically that their separation has proved until recently to be an exceedingly difficult task. The pairs, niobium and tantalum, and molybdenum and tungsten, are much more similar to each other than to vanadium and chromium, respectively.

Whereas within a regular group of elements, with the exceptions already noted, electropositivity as expressed by ionization or electrode potential values increases with increasing atomic number, the same situation does not prevail among the transition groups. Indeed, as a consequence of the lanthanide contraction, the last member of the group is ordinarily considerably less reactive than the first. The large increase in nuclear charge with increase in atomic number is not accompanied by a corresponding increase in atomic size, and thus the valence electrons are more firmly bound by the nucleus.

3. General Properties of Elements of Long Transition Series.

The long transition series are characterized by the filling of *f* orbitals. In the rare earths, or lanthanides, the 4*f* level is being filled, and in the actinides the 5*f*. Although it is still undetermined where the first 5*f* electron appears in the latter series, there is sufficient evidence to suggest that the 5*f* series begins with actinium in the same sense that the 4*f* series begins with lanthanum.

a. The Rare-Earth or Lanthanide Series.

The rare earths are remarkably similar in chemical behavior. They possess the usual properties of transition elements: they are all metals, many of their compounds are colored and paramagnetic, they form complex compounds but much less readily than do the elements of short transition series, and some of the elements possess more than one oxidation state.

THE RARE-EARTH OR LANTHANIDE SERIES

$_{58}$Ce	$4f^2\ 6s^2$ (first, second, third shells, 4*s*, 4*p*, 4*d*, and 5*s*, 5*p* levels filled)
$_{59}$Pr	$4f^3\ 6s^2$
$_{60}$Nd	$4f^4\ 6s^2$
$_{61}$Pm	$4f^5\ 6s^2$
$_{62}$Sm	$4f^6\ 6s^2$
$_{63}$Eu	$4f^7\ 6s^2$
$_{64}$Gd	$4f^7\ 5d\ 6s^2$
$_{65}$Tb	$4f^9\ 6s^2$
$_{66}$Dy	$4f^{10}\ 6s^2$
$_{67}$Ho	$4f^{11}\ 6s^2$
$_{68}$Er	$4f^{12}\ 6s^2$
$_{69}$Tm	$4f^{13}\ 6s^2$
$_{70}$Yb	$4f^{14}\ 6s^2$
$_{71}$Lu	$4f^{14}\ 5d\ 6s^2$

The close relationship between the rare-earth elements results from the existence of the 4*f* orbitals. Three electrons are readily lost from the atom to give the characteristic tripositive state of the configuration $4f^n$. The 4*f* electrons in the ion are not readily available for chemical binding and are relatively uninfluenced by the electrical fields of neighboring atoms.

The rather regular decrease in size of the tripositive ions with increase in atomic number (lanthanide contraction), arising from the successive filling of the 4*f* orbitals, has already been noted and some chemical consequences of this contraction have been described. As would be expected, the basicity of the oxides decreases regularly from cerium to lutetium. This, together with the regular increase of hydrated ionic radius from cerium to lutetium, has been of considerable significance in the successful separation of the rare earths by ion exchange methods.

The oxidation states other than +3 which exist may be correlated directly with electronic configuration. Three configurations, namely, $4f^0$, $4f^7$, and $4f^{14}$, are particularly stable among the rare-earth ions. It is not surprising, therefore, that in an ion of oxidation state other than +3 one of these configurations is attained, or nearly so. The so-called anomalous oxidation states of the rare earths and their configurations in the ground state are shown below:

Ce^{4+}	**$4f^0$**
Pr^{4+}	**$4f^1$**
Sm^{2+}	**$4f^6$**
Eu^{2+}	**$4f^7$**
Tb^{4+}	**$4f^7$**
Yb^{2+}	**$4f^{14}$**

The existence of these "anomalous" oxidation states has been useful in the separation of elements which possess them from other rare earths. Thus cerium may be oxidized to the +4 state and separated from the other rare earths by precipitation as the iodate. Both dipositive europium and ytterbium, which are similar in properties to the alkaline earth metal ions, may be removed from rare-earth mixtures by precipitation as sulfates.

The rare-earth elements are active metals possessing electrode potentials of the order of that of magnesium. Qualitatively the activity decreases with increasing atomic number.

Chemically, scandium, yttrium, and lanthanum resemble the rare earths. The order of decreasing ionic size for M^{3+} and decreasing basicity of the oxides is the following: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc.

b. The Actinide Series

The existence of a $5f$ series of elements having actinium as its prototype is derived largely from chemical evidence. The exact place at which the $5f$ level begins to fill is in doubt; however, spectroscopic data strongly indicate that the ground state of the neutral uranium atom is $5f^3\,6d\,7s^2$ (beyond radon).

THE ACTINIDE SERIES

$_{90}$Th	$6d^2\,7s^2$ (or $5f\,6d\,7s^2$) (first, second, third, fourth shells, $5s$, $5p$, $5d$, and $6s$, $6p$ levels filled)
$_{91}$Pa	$5f^2\,6d\,7s^2$ (or $5f\,6d^2\,7s^2$)
$_{92}$U	$5f^3\,6d\,7s^2$
$_{93}$Np	$5f^4\,6d\,7s^2$ (or $5f^5\,7s^2$)
$_{94}$Pu	$5f^6\,7s^2$ (or $5f^5\,6d\,7s^2$)
$_{95}$Am	$5f^7\,7s^2$
$_{96}$Cm	$5f^7\,6d\,7s^2$
$_{97}$Bk	$5f^8\,6d\,7s^2$ (or $5f^9\,7s^2$)
$_{98}$Cf	$5f^{10}\,7s^2$
$_{99}$Es	$5f^{11}\,7s^2$
$_{100}$Fm	$5f^{12}\,7s^2$
$_{101}$Md	$5f^{13}\,7s^2$
$_{102}$No	$5f^{14}\,7s^2$
$_{103}$Lw	$5f^{14}\,6d\,7s^2$

The +3 state is characteristic of all the actinide elements. (The tripositive state of thorium is incapable of existence in aqueous solution.) The first elements (U-Am) in this series are capable of being oxidized to oxidation states up to +6; in this respect the actinides differ from the rare earths. That the actinides possess more oxidation states above the +3 state than do the rare-earth elements is related to the fact that the $5f$ and $6d$ levels lie so close together that the energy required for the shift from one level to another is sometimes of the order of magnitude of chemical binding energies.

From uranium to americium the stability of the +6 state decreases regularly; this is accompanied by a corresponding increase in stability of the +3 state. At americium, the latter state becomes the predominant one, and the only oxidation state so far shown to exist for curium is +3. This is entirely consistent with the proposal that tripositive curium possesses a $5f^7$ configuration, analogous to the $4f^7$ configuration of gadolinium, its rare-earth homologue.

americium, antimony, arsenic

PURIFICATION OF AMERICIUM FOR GAMMA COUNTING

K. Wolfsberg and W. R. Daniels

1. Introduction

This procedure has been used for the separation of americium from samples of up to 2 g of debris from underground detonations. Purification of the sample involves the isolation of a fraction containing both americium and curium and consists of the following sequence of major steps: an initial fluoride precipitation; hydroxide precipitations; extraction of lanthanides and actinides into HDEHP (di-2-ethylhexyl orthophosphoric acid) from 0.05*M* HNO_3; back-extraction of only the lighter lanthanides and actinides into 0.8*M* HNO_3; passage through an anion column to remove contaminants such as Te, Zr, and Pu; additional fluoride and hydroxide precipitations; and finally, adsorption of the remaining lanthanides and actinides on a cation exchange column and elution with ethanol-HCl solution, and collecting the Am-Cm fraction. The determination of ^{240}Am and ^{241}Am can be effected by gamma ray counting in the presence of Cm.

2. Reagents

HNO_3: fuming; concd; 4*M*; 0.8*M*; 0.05*M*
$HClO_4$: concd
HF: concd
HCl: concd
HCl-HF: 4*M* in each acid
H_3BO_3: saturated aqueous solution
NaOH: 6*M*
NH_4OH: concd
$NH_2OH \cdot HCl$: solid
Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_3 in 6*M* HCl
Te(VI) carrier: 10 mg Te/ml, added as $Na_2TeO_4 \cdot 2H_2O$ in 3*M* HCl
Nd carrier: 5 mg Nd/ml, added as $NdCl_3 \cdot 6H_2O$ in H_2O
0.5*M* HDEHP: dilute 645 g of di-2-ethylhexyl orthophosphoric acid (about 94% purity) to 4 liters with *n*-heptane
EtOH-HCl reagent: 20% absolute ethanol - 80% concd HCl - 0.1% $NH_2OH \cdot HCl$; saturated with HCl gas
Anion exchange resin: Bio-Rad AG 1-X10, 100-200 mesh
Cation exchange resin: Bio-Rad AG 50W-X4, (H^+ form), nominal minus 400 mesh, batch selected to give satisfactory separation
Cation exchange resin: Bio Rad AG 50W-X4, 200-400 mesh (H^+ form)

3. Procedure

Step 1. From 4 to 24 hours prior to beginning Step 2, prepare a cation exchange column containing Bio-Rad resin AG 50W-X4, minus 400 mesh (H^+ form). Treat the resin (a quantity equivalent to a resin volume of 25 ml when centrifuged from a slurry in water) three times with 50 ml of concd HCl and three times with EtOH-HCl reagent. This treatment is performed in a Buchner funnel with a medium frit and the resin is sucked dry between treatments. Slurry the resin with EtOH-HCl and transfer to a glass column (9 mm o.d. x 38 cm long, filling to a height of more than 32 cm under 10 psi of air pressure. Pass EtOH-HCl reagent through the column until the column is ready to be used. Just prior to use of the column in Step 12 reduce the height of the resin to 30 cm.

Step 2. Treat about 2 g of ground debris in a Vycor or Teflon beaker with 10 ml of fuming HNO_3, 20 ml of concd $HClO_4$, and 25 ml of concd HF. Boil to heavy fumes of $HClO_4$. Repeat treatment and boiling 1 or 2 times. Add 40 ml of 4*M* HNO_3, transfer the solution to 40-ml Vycor centrifuge tubes, centrifuge, transfer the supernates to clean Vycor tubes, and discard the residues Make the supernates about 4*M* in HF, centrifuge, and discard the supernates. Wash the precipitates three times with 4*M* HCl-4*M* HF, combining them in a single centrifuge tube.

Step 3. Treat the precipitate with 5 ml of saturated H_3BO_3 and 2 ml of concd HNO_3 and boil. If the sample is not dissolved, add 2 ml of H_3BO_3 and 1 ml of HNO_3 and boil again. If a small quantity of solid still remains, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the residue (Note 1).

Step 4. Dilute the solution to at least 20 ml with H_2O and make basic with 6*M* NaOH. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of 6*M* NaOH, boiling the mixture, then wash with H_2O. Discard the washes.

Step 5. Dissolve the precipitate in about 3 ml of concd HCl, dilute to 20 ml with H_2O, and make basic with concd NH_4OH. Centrifuge, wash the precipitate with H_2O, and discard the wash.

Step 6. Dissolve the precipitate in about 1 ml of concd HNO_3. Boil the solution to incipient dryness. (A flash evaporator is useful for this purpose.) Dissolve the residue in 10 ml of 0.05*M* HNO_3 and transfer the solution to a 40-ml long-tapered centrifuge tube. Add 10 ml of

0.5*M* HDEHP in heptane. Plug the tube with a plastic stopper, shake vigorously for 20-30-sec, and centrifuge for about 15 sec. Draw off and discard the aqueous (lower) phase, and also discard any interface. Scrub the organic phase twice with 10-ml portions of 0.05*M* HNO_3. Back-extract the Am and the lighter tripositive lanthanides and actinides with two 10-ml portions of 0.8*M* HNO_3. Wash the combined back-extract with 10 ml of heptane and discard the wash. Transfer the solution to a 125-ml erlenmeyer flask and boil to incipient dryness (Note 2).

Step 7. Add 10 ml of concd HCl, 1 drop of concd HNO_3, and 1 drop each of Te(IV) and Te(VI) carriers. Heat the solution, but avoid boiling, and pass through an AG 1-X10, 100-200 mesh anion column (8 mm o.d. by 10 cm long) which has been pre-equilibrated with 10 ml of concd HCl. Collect all effluents in an erlenmeyer flask.

Step 8. Boil to about 2 ml, add 10-20 mg of Nd carrier (or any tripositive lanthanide carrier), and dilute to about 20 ml with H_2O. Add 4 ml of concd HF, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of 4*M* HCl-4*M* HF and discard the wash.

Step 9. Dissolve the precipitate in a mixture of 1-2 ml each of saturated H_3BO_3 and concd HCl, dilute the solution to 15 ml with H_2O, and make basic with 6*M* NaOH. Centrifuge and discard the supernate. Wash the precipitate with 15 ml of H_2O and discard the wash.

Step 10. Dissolve the precipitate in 1 ml of concd HCl, add about 100 mg of $NH_2OH{\cdot}HCl$, dilute to 15 ml with H_2O, and reprecipitate the hydroxides with concd NH_4OH. Centrifuge and discard the supernate. Wash the precipitate with 15 ml of H_2O and discard the wash.

Step 11. Dissolve the precipitate in 3-5 drops of concd HCl and dilute to about 30 ml with H_2O. Add the equivalent of 1-2 ml of centrifuged Bio-Rad AG 50W-X4, 200-400 mesh, cation resin (H^+ form) in water-slurry form, stir for 1 min, and centrifuge. Discard the supernate, wash the resin with 30 ml of H_2O, and discard the wash.

Step 12. Slurry the resin from Step 11 in 1-2 ml of H_2O and transfer to the top of the cation exchange column prepared in Step 1. Complete the transfer with a small H_2O wash. Allow the resin to settle and draw off the H_2O. Start eluting with EtOH-HCl reagent (Note 3) under about 10 psi of air pressure. The elution curve shown in Fig. 2 of the procedure for "Concentration of Transplutonium Actinides from Nevada Soil Samples" by K. Wolfsberg and W. R. Daniels is reproducible on a volume basis. Collect the Am-Cm fraction.

Notes

1. If a large amount of solid remains, add 20 ml of 6*M* NaOH and boil for about 2 min. Centrifuge, discard the supernate, and wash the precipitate with H_2O, discarding the wash. Treat the solid with 2-5 ml of saturated H_3BO_3 and 2 ml of concd HNO_3, boil, centrifuge, and combine the supernate with the original one.

2. If the heavier lanthanides and actinides are to be recovered, one should adapt Steps 8 and 9 of the procedure for "Concentration of Transplutonium Actinides from Nevada Soil Samples" by K. Wolfsberg and W. R. Daniels for the back-extraction of all the tripositive lanthanides and actinides.

3. The $NH_2OH{\cdot}HCl$ in the EtOH-HCl reagent ensures that all the Ce present remains in the +3 condition and that no trace of this element elutes early as a +4 species.

ANTIMONY

D. C. Hoffman and J. W. Barnes

1. Introduction

In this procedure for the determination of antimony in fission-product solutions, the antimony is first converted to the +5 state. Decontamination from the bulk of the molybdenum activity present is then effected by MoS_3 precipitation in the presence of fluoride ion which strongly complexes Sb(V), thus keeping it in solution. After reduction of antimony to the tripositive state, separation from tin is effected by precipitation of Sb_2S_3 in the presence of tin carrier and fluoride ion, the latter this time keeping the tin in solution as a fluoro complex. Tellurium, which precipitates along with antimony, is removed by precipitation with hydrogen sulfide from concentrated hydrochloric acid solution, the antimony remaining in solution. The antimony is then absorbed on a Dowex 1-X10 anion exchange column from $0.9M$ hydrochloric acid solution. The last traces of molybdenum are removed with a wash of the acid. The antimony is eluted from the column by means of a 20% ammoniacal tartrate solution and is again precipitated as a sulfide. The sulfide is dissolved in concentrated hydrochloric acid and then converted to the metal by reduction with Cr(II) chloride. In this form it is weighed and counted. The chemical yield is about 50%, and six analyses can be performed in about 8 hr.

2. Reagents

Sb carrier: 10 mg Sb/ml, added as $SbCl_3$ in $6M$ HCl, standardized
Mo carrier: 10 mg Mo/ml, added as Na_2MoO_4 in H_2O
Sn carrier: 10 mg Sn/ml, added as $SnCl_2 \cdot 2H_2O$ in $6M$ HCl
Te^{4+} carrier: 10 mg Te/ml, added as Na_2TeO_3 in $12M$ HCl
Te^{6+} carrier: 10 mg Te/ml, added as $Na_2H_4TeO_6$ in $3M$ HCl
HCl: concd; $6M$; $1M$; $0.9M$
HI: concd
HF: concd
H_2SO_4: concd
H_2S: gas
Br_2-H_2O: saturated solution
NH_4OH: concd
$CrCl_2$ solution (Oxsorbent)
$NaKC_4H_4O_6 \cdot 4H_2O$: 20% aqueous solution
Aerosol solution: 1% in H_2O
Methanol: absolute
Dowex 1-X10 anion resin, 100-200 mesh (obtained in purified form from Bio-Rad Laboratories, Richmond, Calif.)

3. Preparation and Standardization of Carrier

Dissolve 18.7 g of $SbCl_3$ in $6M$ HCl and make the solution up to a volume of 1 liter with the acid.

Pipet 5 ml of the above carrier solution into a weighed filter beaker. (This beaker has a 15-ml, fine-porosity, sintered-glass crucible sealed into the side near the top so that the operations which follow — reduction, filtration, drying, and weighing — may be carried out in this one vessel.) Add 5-10 ml of $CrCl_2$ solution (Oxsorbent). After conversion to Sb metal is complete, filter and wash the precipitate with small portions of H_2O and absolute methanol. Dry the filter beaker containing the Sb at 100° for 1 hr. Cool and weigh.

4. Procedure

Step 1. To a 40-ml short-taper centrifuge tube add 2 ml of Sb carrier, a few drops of Mo carrier, the sample, and 2 ml of Br_2-H_2O. Boil off the Br_2 and make the solution approximately $1.5M$ in HCl. Add 1 ml each of concd HF and concd H_2SO_4 per 25 ml of solution. Bring to boiling, saturate with H_2S to precipitate MoS_3, add some filter paper pulp, centrifuge, and pour the supernate through a filter into a 90-ml centrifuge tube. Wash the filter with 2-3 ml of $1M$ HCl and permit the washings to drain into the same centrifuge tube.

Step 2. To the solution add 1 ml Sn carrier, 2 drops of Mo carrier, 2 ml of concd HI, boil for about 2 min, and add 5 ml of H_2O. Saturate with H_2S to precipitate Sb_2S_3, add a few drops of aerosol solution, and centrifuge. Discard the supernate, wash the precipitate with $1M$ HCl, and discard the washings.

Step 3. Dissolve the precipitate in 4 ml of concd HCl, boil off H_2S, and remove any undissolved MoS_3 precipitate by filtering the solution through No. 41 Whatman paper into a clean 40-ml short-taper centrifuge tube. To the filtrate add 4 drops of Sn carrier, 4 drops of Te^{4+} carrier, 2 drops of Te^{6+} carrier, and 1 ml each of concd HI and concd HF. Boil for about 2 min (until the original vigorous reaction subsides). Dilute to 25 ml with 1*M* HCl, add a few drops of aerosol solution, and saturate with H_2S to precipitate Sb_2S_3. Centrifuge and wash the precipitate as in the previous step.

Step 4. Repeat Step 3, but use no Sn or Te carrier.

Step 5. Dissolve the precipitate in 4 ml of concd HCl, boil off the H_2S, add 2 ml of Te^{4+} carrier, and boil for 1-2 min. Add 2 ml more of concd HCl, bring to boiling, saturate with H_2S, and filter on a 15-ml medium fritted glass funnel into a 40-ml short-taper centrifuge tube. Wash the original tube with 2 ml of concd HCl and filter into the original filtrate. Discard the precipitate. Boil the combined filtrate, add 2 ml of Te^{4+} carrier, boil for 1-2 min, saturate with H_2S, and filter into a 40-ml short-taper centrifuge tube, discarding the precipitate.

Step 6. Boil off the H_2S, evaporate the solution to about half of its original volume (it will now be approximately 6*M* in HCl), and dilute with H_2O to make the solution 0.9*M* in HCl. Add 6 ml of H_2O for every 1 ml of solution. Measure volumes accurately and do the dilution carefully. The 0.9*M* value is critical, since the distribution coefficient for Mo rises steeply both above and below 0.9*M* HCl concentration (Note 1).

Step 7. Prepare a Dowex 1-X10 anion resin (100-200 mesh) column (1.1 cm × 5.5 cm) with a glass wool plug both above and below the resin bed. Prewash the column with about 10 ml of 0.9*M* HCl. Place the solution from Step 6 on the column and permit it to flow through. Discard the eluate. Wash the column with 250 ml of 0.9*M* HCl, discarding the washings. Elute the Sb with 20 ml of 20% $NaKC_4H_4O_6$ which has been made basic with 12 drops (about 1 ml) of concd NH_4OH. Collect the eluate in a 40-ml short-taper centrifuge tube.

Step 8. Add concd HCl (about 2 ml) until a precipitate just forms. Dissolve the precipitate by adding concd HCl dropwise, and then add 2 ml of the acid in excess. Saturate with H_2S, centrifuge, and discard the supernate.

Step 9. Dissolve the precipitate in 5-10 ml of concd HCl and boil off the H_2S. Make the solution 3-5*M* in HCl and filter through a 60-ml fine sintered glass crucible into a 40-ml short-taper centrifuge tube.

Step 10. Add sufficient $CrCl_2$ solution (Oxsorbent) to completely precipitate Sb as the metal. Start filtering through a weighed No. 40 Whatman filter circle, 7/8" diameter, within 1 min or less, using a ground-off Hirsch funnel and a filter chimney. Wash the metal with 5-ml portions of H_2O and absolute methanol. Dry at 100° for 15 min. Cool, weigh, and mount (Note 2).

Notes

1. As an alternative to Step 6, after the H_2S is boiled off, the solution may be evaporated *nearly to dryness* on a steam bath, but the material must not be left on the steam bath dry or at elevated temperatures or the Sb may volatilize. Then add a few drops of H_2O until a white precipitate forms, dilute to 10 ml with 0.9*M* HCl, and proceed with Step 7.

2. The Sb is ordinarily not counted until four days after the column step (Step 7), to allow 9.3-hr ^{127}Te to grow into equilibrium with 93-hr ^{127}Sb.

ANTIMONY-127

E. A. Bryant

1. Introduction

This simplified procedure permits a relatively rapid analysis for ^{127}Sb. It was developed primarily for samples containing large amounts of zirconium, niobium, uranium, and hydrofluoric and perchloric acids. The basis for the simplification of the chemistry is the use of a Ge(Li) detector to measure ^{127}Sb and ^{125}Sb (spike) γ-rays in an imperfectly purified sample. Major interference in the measurements is caused by the ^{132}I daughter of ^{132}Te.

The chemical separation consists of a series of Sb_2S_3 and TeI_2 (by-product) precipitations. Exchange with Sb(V) carrier is effected in the presence of aqueous bromine at elevated temperatures. Recovery is measured by means of the ^{125}Sb tracer-carrier; yields are high.

2. Reagents

^{125}Sb tracer-carrier: sufficient activity (source: ORNL) for measurement on the available detector + 10 mg SB(V)/ml, added as $SbCl_5$ in dilute HCl.
Mo(VI) carrier: 10 mg Mo/ml, added as $(NH_4)_6Mo_7O_{24}.4H_2O$
Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_3 in 12 *M* HCl
Te(VI) carrier: 10 mg Te/ml, added as $Na_2H_4TeO_6$ in 3 *M* HCl
HCl: concd
HI: concd
H_3BO_3: saturated aqueous solution
H_2S: gas
Br_2-H_2O: saturated solution

3. Procedure

Step 1. Pipet 1.00 ml of ^{125}Sb tracer-carrier solution into a 40-ml glass centrifuge tube. Add 10 ml of saturated H_3BO_3 and 1 ml of Br_2-H_2O. then pipet the sample into the tube. Stir the solution and place the tube on a steam bath for a minimum of 2, but less than 4, hr. (Prolonged standing results in precipitation of Nb_2O_5 which carries down antimony.)

Step 2. Dilute by a factor of two with H_2O and saturate with H_2S. (If an orange precipitate of Sb_2S_3 does not form. it will be necessary to dilute the solution further and to use more H_3BO_3 to remove fluoride ion still in solution.) Warm the mixture and set it aside for 20 min. Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate in 5 ml of concd HCl and boil for 30 sec. Add 2 drops each of Te(IV) and Mo (VI) carriers and boil for 20 sec. Dilute to 20 ml with H_2O and saturate with H_2S. Warm. set aside for 20 min. centrifuge, and discard supernate.

Step 4. Add 5 ml of concd HCl to the precipitate. warm, and stir. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate of MoS_3 and TeS_2. Boil the supernate for 30 sec.

Step 5. Add 5 ml of H_2O and 2 ml of HI and boil for 30 sec. Add 2 drops of Te(IV) carrier. boil. centrifuge. transfer the supernate to a clean centrifuge tube, and discard the TeI_2 precipitate. Add 2 drops of Te(VI) carrier and bring the solution to a boil. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the TeI_2 precipitate.

Step 6. Dilute to 20 ml with H_2O. saturate with H_2S. and warm gently. Centrifuge and discard the supernate. Dissolve the precipitate in 3 ml of concd HCl and centrifuge; discard any insoluble residue.

Step. 6 Pour the solution into a convenient container for counting (e.g., a Packard 25-ml polyethylene vial). Take a preliminary measurement of the activity to determine whether there has been adequate decontamination. The number of counts in the 228 keV ^{132}Te full energy peak should be *no more* than 50 times larger than the counts in the 473 keV ^{127}Sb full energy peak. If this ratio is exceeded, repeat Steps 5 and 6. When adequate decontamination has been attained, measure the ^{125}Sb activity by means of its 176, 428, 464, and 635 keV γ rays and that of ^{127}Sb by means of its 473, 685, and 783 γ rays.

November 1970

ANTIMONY II

B. R. Erdal

1. Introduction

This rapid procedure for the separation of antimony from fission products is based on an article by A. E. Greendale and D. L. Love, Anal. Chem., 35, 632 (1963). The main decontamination process is the formation of stibine, SbH_3, and the collection of this volatile compound in a bromine water solution. A tellurium(IV) sulfide scavenge is then performed and the antimony is reduced to the elemental state for counting and chemical yield purposes.

The procedure requires about 15 minutes per sample and gives chemical yields of 40-60%. Decontamination factors of at least 10^5 from ^{235}U thermal-neutron fission products are obtained.

2. Reagents

Sb carrier: 10 mg Sb/ml, added as $SbCl_3$ in 6*M* HCl. The solution is standardized by precipitation of Sb metal with about 1.6*M* $CrCl_2$

Te(VI) carrier: 10 mg Te/ml, added as $Na_2H_4TeO_6$ in 6*M* HCl

HCl: concd; 6*M*

Br_2

NH_4OH: concd

Drierite ($CaSO_4$)

N_2: gas

Zn: dust

$NH_2OH{\cdot}HCl$: solid

Ethanol: absolute

$CrCl_2$: ~1.6 *M* aqueous solution (Fisher Scientific Co.)

3. Procedure

Step 1. Assemble the separation apparatus as shown in Fig. 1. Fill the U-tube with Drierite ($CaSO_4$) and cover each side with glass wool. Place 10 ml of 6*M* HCl and 10 drops of Br_2 in each of the traps. Add 20 g of Zn dust to the round-bottomed flask and bring the water bath to a boil. Flush the entire system well with N_2.

Step 2. Pipet 3.0 ml of standard Sb carrier into the reservoir of the apparatus, add the sample, and make the solution up to a volume of about 5 ml with 6*M* HCl. Drop the solution onto the Zn in one batch, collect the gas (SbH_3 and H_2) for 10-15 sec, and then open the vent.

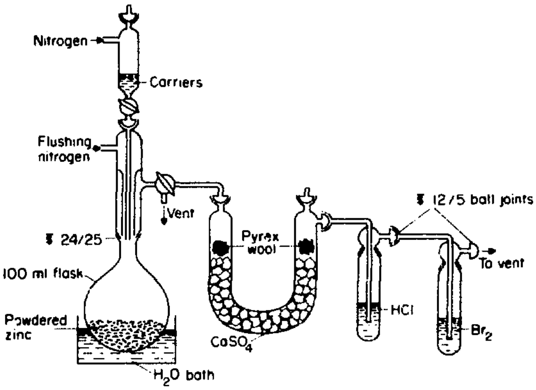

Fig. 2.

Step 3. Transfer the Br_2-HCl solutions (Note) to a 40-ml glass centrifuge tube, add 10 mg of Te(VI) carrier, heat in a steam bath for a few minutes, add 100 mg of $NH_2OH{\cdot}HCl$, and saturate with H_2S. Digest in a steam bath until the precipitate has coagulated and filter through a glass frit of medium porosity into a clean centrifuge tube. Discard the precipitate.

Step 4. Add about 4 ml of concd NH_4OH (the resulting solution should be about 2*M* in HCl), saturate with H_2S, and digest in a steam bath for a few minutes. Filter the Sb_2S_3 precipitate onto a glass frit of medium porosity. Wash the Sb_2S_3 with H_2O, discontinue suction, and discard the filtrate. Dissolve the Sb_2S_3 in 10 ml of concd HCl, start suction, and collect the filtrate in a clean centrifuge tube.

Step 5. Heat the filtrate in a steam bath to expel H_2S, add 10 ml of absolute ethanol, mix, and then add 5 ml of about 1.6*M* $CrCl_2$. Swirl for 15 sec and filter the metal precipitate onto a tared Gelman VF-6 filter paper (0.45 μm pore size). Wash the precipitate with a 50/50 mixture of 6*M* HCl and ethanol, then with H_2O, and finally with ethanol alone. Dry under suction for a few minutes, weigh, and mount.

Note

The first Br_2-HCl trap generally contains about 90% of the Sb.

THE SEPARATION OF ARGON-37 FROM IRRADIATED CALCIUM OXIDE

J. W. Barnes, J. Balagna, R. J. Prestwood,
and B. P. Bayhurst

1. Introduction

This procedure describes the separation of Argon-37 from a calcium oxide pellet which has been irradiated with high energy (2.5-14.5 MeV) neutrons.

$$^{40}_{20}\text{Ca} + {}^{1}_{0}n \rightarrow {}^{37}_{18}\text{Ar} + {}^{4}_{2}\text{He}$$

In a system which has been previously evacuated, the CaO pellet is treated with an excess of dilute HCl in the presence of added Ar carrier. The resulting solution is distilled to bring about complete mixing of ^{37}Ar with carrier, and the Ar is then cryopumped into a thin-windowed (1 mil Be) gas sample container fabricated from stainless steel and sealed with a bellows valve. The 2.62 keV x-ray from ^{37}Cl, formed from ^{37}Ar by electron capture, is counted on a lithium-drifted silicon crystal.

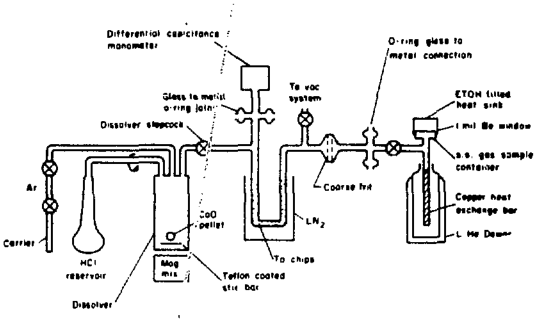

Fig. 1. Dissolver apparatus

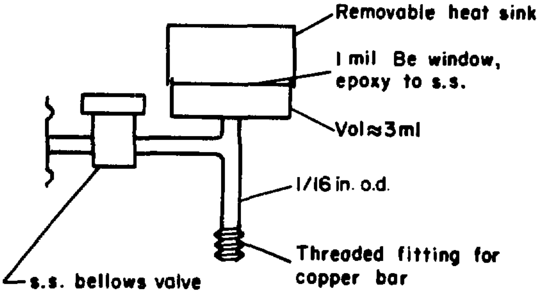

Fig. 2. Stainless steel sample container.

2. Reagents

Ar carrier: high purity gas
HCl: 4*M*
Ta turnings

3. Procedure

Step 1. Add the CaO pellet (about 90-100 mg), which has been compressed in a hydraulic press at high temperatures and pressures before irradiation to the dissolver of the apparatus (Figure 1). On another vacuum line fill the two sections of the Ar carrier tube with the gas to a pressure of 250 Torr and connect the tube to the apparatus as shown in Figure 1 (Note 1). Add about 2.5 ml of 4*M*HCl to the HCl reservoir and evacuate the system in the following manner. Start the pumping at room temperature with a mechanical pump and when the pressure has dropped to 0.2-0.5 Torr, connect the system to a diffusion pump. When the pressure reaches 20-50 mTorr, freeze the HCl solution with liquid nitrogen. Open the bellows valve to the stainless steel sample container (Figure 2). Continue pumping until the pressure is about 2 x 10^{-5} Torr (1-2 hr). Close the stopcock to the pumping system and follow the pressure rise with the differential capacitance manometer. If the pressure rise within 5 min is less than 2 mTorr proceed with Step 2. If the rise is greater than 2 mTorr, continue the evacuation process until the pressure rise is satisfactory. Open the stopcock to the pumping system.

Step 2. Close the dissolver stopcock, open the one to the first half of the Ar carrier, melt the HCl solution with an electric heat gun, and pour the solution onto the CaO pellet. Stir for 10 min with a magnetic stirrer to obtain a clear solution (Note 2).

Step 3. Chill the HCl reservoir by means of liquid nitrogen, apply heat (electric heat gun) intermittently to the dissolver (stirring is maintained) until the solution distills into the reservoir and only solid $CaCl_2$ remains. (The Ar is not condensed by the liquid nitrogen, but the distillation permits complete mixing between carrier gas and the ^{37}Ar released from the CaO pellet.) Place a Dewar filled with liquid nitrogen around the U-tube filled with the Ta turnings (glass beads would probably work as well). Melt the solid plug of HCl solution (heat gun) and refreeze in the bottom of the reservoir in order to eliminate plugging at the upper portion by frozen HCl solution.

Step 4. Close the stopcock to the pumping system and cool the copper heat exchange bar with liquid nitrogen. Slowly open the dissolver stopcock and record the pressure indicated by the differential capacitance manometer (Note 3). Replace the liquid nitrogen around the copper bar with liquid helium and record the pressure decrease at 2-min intervals for 8 min, and then at 1-min intervals until the pressure drops to zero or remains constant (10-12 min). Shut the dissolver stopcock and the bellows valve and remove the liquid helium container for refilling for later use. Be certain that the stopcock to the pumping system remains closed.

Step 5. Open the stopcock to the second half of the Ar carrier, remove the liquid nitrogen from around the HCl reservoir, and melt the HCl ice (heat gun). Pour the solution onto the $CaCl_2$ in the dissolver and stir for about 10 min.

Step 6. Repeat Step 3.

Step 7. Cool the copper heat exchange bar with liquid nitrogen and then replace the nitrogen with liquid helium. Slowly open the dissolver stopcock and record the pressure shown on the differential capacitance manometer. After the copper bar has been cooled with liquid helium for 1.5-2 min, open the bellows valve. Record the pressure decrease at 2-min intervals for 8 min and then at 1-min intervals until the pressure drops to zero or remains constant. Close the bellows valve, the dissolver stopcock, and the top Ar carrier stopcock. Observe the pressure in the manometer for another 5 min to make certain that the bellows valve is sealed tightly. Open the stopcock to the pumping system and check the manometer for possible zero drift. Remove the liquid nitrogen container from the U-tube containing the Ta turnings, warm the turnings with an electric heat gun, and pump for about 10 min. Disconnect the sample container and count the 2.62 keV x-ray from ^{37}Cl on a lithium-drifted silicon crystal.

Notes

1. The quantity of carrier gas should be held constant from run to run to eliminate errors due to self-absorption of the gas.

2. The ^{37}Ar will not be released quantitatively from the CaO pellet if solution in HCl is not complete.

3. The manometer reading will verify whether approximately half of the Ar carrier gas has been introduced. P-V calibrations of the apparatus should have been carried out previously.

ARSENIC

R. J. Prestwood and B. J. Dropesky

1. Introduction

In the separation of radioarsenic from fission products, the sulfide is first precipitated in acid medium. The chief contaminants of this precipitate are germanium, tellurium, molybdenum, and cadmium. Fuming of the sulfide with a mixture of nitric, hydrochloric, and perchloric acids removes germanium, which volatilizes as the tetrachloride; arsenic is oxidized to arsenic acid. The arsenic is then converted to the triiodide by treatment with hydroiodic acid and extracted into benzene; tellurium, molybdenum, and cadmium remain in the aqueous phase. The extraction is an excellent decontamination step. After washing, the benzene solution is treated with dilute sulfuric acid, and arsenic is extracted into the aqueous phase. After appropriate repetition of the extraction process, the arsenic is precipitated as the sulfide. The latter is dissolved and arsenic is finally reduced by chromous chloride to the metal, in which form it is weighed and counted. The chemical yield approximates 90%.

2. Reagents

As carrier: 10 mg As/ml, added as $Na_3AsO_4 \cdot 12H_2O$ in H_2O, standardized
HCl: 2*M*; 6*M*; concd
HNO_3: concd
H_2SO_4: 1*M*
$HClO_4$: 70 to 72%
HI: 47%
NaI: solid
$CrCl_2$ solution (Oxsorbent)
H_2S: gas
Aerosol: 0.1% aqueous solution
Benzene
Ethanol: absolute

3. Preparation and Standardization of Carrier

Prepare an aqueous solution containing 56.6 g of $Na_3AsO_4 \cdot 12H_2O$ per liter. Pipet exactly 5 ml of the carrier solution into a 40-ml conical centrifuge tube, add 10 ml of 6*M* HCl, and heat. To the hot solution add 10-15 ml of $CrCl_2$ solution (Oxsorbent) and stir vigorously for 2 min while maintaining the solution near its boiling point. Filter the metallic arsenic precipitate into a weighed 30-ml sintered glass crucible of medium porosity. Wash the precipitate three times with 5-ml portions of H_2O and once with 5 ml of absolute ethanol. Dry at 110° for 15 min. Cool and weigh. Four standardizations are carried out.

4. Procedure

Step 1. Pipet the sample into a 40-ml conical centrifuge tube which contains exactly 2 ml of standard As carrier. Add 10 ml of concd HCl and about 20 mg of solid NaI. Pass H_2S into the solution which is maintained at room temperature. Centrifuge the sulfide precipitate and discard the supernate.

Step 2. To the As_2S_3 precipitate add 0.5 ml each of concd HNO_3 and HCl, and 1 ml of concd $HClO_4$. Heat the solution gently and then to fumes of $HClO_4$ over a burner, and continue heating until all free sulfur has been oxidized. Permit the solution to cool.

Step 3. Transfer the dissolved As (now in the +5 state) with 10 ml of 3*M* HCl into a 125-ml separatory funnel. Add 5 ml of 47% HI and 30 ml of C_6H_6. Shake the mixture thoroughly and then permit it to stand for 1 min (Note 1). Drain the aqueous phase and discard.

Step 4. Wash the C_6H_6 phase containing AsI_3 with 5 ml of 3*M* HCl and 2 ml of 47% HI. Drain and discard the wash solution.

Step 5. Add 10 ml of 1*M* H_2SO_4 to the C_6H_6 phase and shake for 1 min. Permit the mixture to stand for 1 to 2 min, then drain the aqueous phase into a clean 125-ml separatory funnel, and discard the C_6H_6 layer.

Step 6. To the aqueous phase add 10 ml of 6*M* HCl, 8 ml of 47% HI, and 30 ml of C_6H_6. Shake the mixture thoroughly and drain and discard the aqueous phase.

Step 7. Repeat Steps 4, 5, 6, and 4.

Step 8. Add 15 ml of 1*M* H_2SO_4 to the C_6H_6 solution and shake for 1 min. Let the mixture stand for 1 to 2 min and then drain the aqueous phase into a clean 40-ml centrifuge tube.

Step 9. Add 10 ml of concd HCl and saturate the solution with H_2S. Centrifuge the As_2S_3 precipitate and discard the supernate.

Step 10. Repeat Step 2.

Step 11. Add 10ml of 6*M* HCl and heat to boiling. Add 5 ml of $CrCl_2$ solution (Oxsorbent) and stir continuously for 1 min, while keeping the solution hot. Again add 5 ml of $CrCl_2$ and stir continuously for 1 min. Wash down the walls of the tube with a few drops of aerosol solution.

Step 12. Filter the elementary arsenic onto a tared No. 42 Whatman filter circle, 1" diameter, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with several 5-ml portions of H_2O and then with absolute methanol. Dry at 110° for 10 min, cool, weigh, and mount (Note 2).

Notes

1. Because of the toxicity of benzene vapor, it is advisable to perform extractions with this solvent in a fume hood.

2. Beta-counting of the 38.7-hr ^{77}As formed in fission is begun immediately. If a half-life of less than 38.7 hr is obtained it is likely that some normal As was present and the (n,γ) reaction on it gave ^{76}As (26.5 hr). The thermal neutron capture cross section for As is quite high and ^{76}As is a prevalent contaminant.

barium, beryllium, bismuth

BARIUM

W. G. Warren

The procedure for the separation and determination of barium is a modification of one described by L. E. Glendenin, CC-971 (September 15, 1943).

1. Introduction

Barium may be separated from fission-product material by the specific precipitation in the cold as $BaCl_2 \cdot H_2O$ by means of a concentrated hydrochloric acid-ethyl ether mixture. The procedure for the determination of barium as outlined below consists of the isolation of $BaCl_2 \cdot H_2O$, followed by conversion to the chromate, $BaCrO_4$. Three precipitations of the chloride are carried out, the first and second being followed by ferric hydroxide scavenging steps. The final precipitation of barium as the chromate is preceded by a lanthanum hydroxide scavenging step to remove lanthanum and other fission products which form insoluble hydroxides and which were not removed by iron hydroxide scavenging. The chemical yield is about 70%.

2. Reagents

Ba carrier: 10 mg Ba/ml. $Ba(NO_3)_2$ solution. standardized
Fe carrier: 10 mg Fe/ml. added as aqueous $FeCl_3 \cdot 6H_2O$
La carrier: 10 mg La/ml. added as aqueous $La(NO_3)_3 \cdot 6H_2O$
HCl-ethyl ether mixture: 5 parts (by volume) of concd HCl to 1 part of ethyl ether
NH_4OH: 1*M*; 6*M*
HCl: 6*M*
$\left.\begin{array}{l} HC_2H_3O_2\text{: } 6M \\ NH_4C_2H_3O_2\text{: } 3M \end{array}\right\}$ as one solution
Na_2CrO_4: 1.5*M*
Phenolphthalein indicator solution
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 19.0 g of $Ba(NO_3)_2$ in H_2O and dilute to 1 liter. Pipet 5.0 ml of carrier solution into a 250-ml beaker and dilute to approximately 100 ml. Add 10 ml each of 6*M* $H_2C_3O_2$ and 3*M* $NH_4C_2H_3O_2$. Place on a hot plate and bring to a boil. Add 5 ml of 1.5*M* Na_2CrO_4 dropwise with stirring, boil for 1 min with stirring, cool to room temperature, and filter the Ba_2CrO_4 into a fine sintered glass crucible which has been washed with water and ethanol, dried at 110° for 15 min, and weighed. Wash the precipitate three times with 5-ml portions of H_2O and three times with 5-ml portions of ethanol. Dry at 110°, cool, and weigh. Four standardizations of the carrier solution are performed. The spread in results is about 0.5%.

4. Procedure

Step 1. To the sample in a 40-ml centrifuge tube, add 2 ml of standardized Ba carrier (combined volume not to exceed 5 ml). Evaporate to reduce volume, if necessary. Place the tube in an ice bath and add 30 ml of cold HCl-ether reagent (Note 1). Stir for 1 min or until a precipitate of $BaCl_2 \cdot H_2O$ is formed. Centrifuge and discard the supernate (Note 2).

Step 2. Dissolve the precipitate in 4 ml of H_2O and add 1 drop of phenolphthalein solution and 3 drops of iron carrier. Neutralize with 6*M* NH_4OH and add 12 drops in excess. Centrifuge and pour the supernate into a clean centrifuge tube.

Step 3. Add 30 ml of HCl-ether mixture to the supernate and proceed as in Steps 1 and 2, but do not add additional Ba carrier.

Step 4. Repeat the precipitation of $BaCl_2 \cdot H_2O$ with HCl-ether reagent. Dissolve the precipitate in 10 ml of H_2O, and add 1 drop of phenolphthalein solution and 10 drops of La carrier. Neutralize with 6*M* NH_4OH and add 10 drops in excess. Bring the mixture to a boil, centrifuge, and pour the supernate into a clean centrifuge tube.

Step 5. Neutralize the supernate with 6*M* HCl, and then add 10 ml of the 6*M* $HC_2H_3O_2$-3*M* $NH_4C_2H_3O_2$ solution. Heat to boiling and dropwise add 2 ml of 1.5*M* Na_2CrO_4. Boil for 1 min with constant stirring, centrifuge, and discard the supernate. Wash the precipitate by stirring with

20 ml of H_2O, centrifuge, and discard the supernate. Slurry the precipitate with 20 ml of H_2O and filter the $BaCrO_4$ on a previously washed, dried, and weighed filter paper, using a filter chimney and ground-off Hirsch funnel. Wash the precipitate three times with 5-ml portions of H_2O and three times with 5-ml portions of ethanol. Dry at 110°, cool, weigh, and mount (Note 3).

Notes

1. For a maximum yield of $BaCl_2:H_2O$ the solution must be cooled to about 5°.

2. If sulfuric acid, hydrofluoric acid, or oxalate ion is present in the sample, or if the volume of sample plus carrier exceeds 5 ml, the following preliminary treatment is carried out before $BaCl_2 \cdot H_2O$ is precipitated. To the mixture of sample and carrier in a 40-ml centrifuge tube add 2 to 4 drops of concd H_2SO_4 to precipitate $BaSO_4$. Wash the precipitate by stirring with 10 ml of H_2O, centrifuge, and discard the supernate. Add 5 ml of saturated K_2CO_3 solution and boil for 2 min, adding H_2O if necessary. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H_2O as above. Add 1 ml of concd HCl, heat to boiling, and then add 1 ml of 6*M* HCl, maintaining the solution hot. Add 3 ml of H_2O and cool in an ice bath. Proceed with the *precipitation of $BaCl_2 \cdot H_2O$.*

3. The $BaCrO_4$ precipitates are set aside for 134 hr before counting is begun. This permits ^{140}Ba and ^{140}La daughter activities to come to equilibrium. If results are desired earlier, a computer program for the IBM 7094 allows early consecutive counts to give the answer, taking into account the growth and different absorption corrections for ^{140}Ba and ^{140}La.

BERYLLIUM

R. J. Prestwood

1. Introduction

This procedure is suitable for the determination of radioberyllium in fission-product solutions containing macro quantities of other metal ions and is much shorter and more effective than the procedure it supersedes, which consisted mostly of by-product scavenges to effect decontamination. This procedure consists of the extraction into carbon tetrachloride of the Be acetylacetone complex from a solution of EDTA at a pH of 7.7 (Note 1), followed by an anion column separation, a NaOH scavenge, fluoride scavenges, and mounting as $BaBeF_4$. The chemical yield is approximately 90%. Beryllium run on 10^{14} fissions 4 days old gave less than 1 β count/min. Another sample consisting of a mixture of ^7Be, 10^{14} old fission products, and 2×10^{14} fresh fission products in 100 ml of 4*M* HCl, resulted in pure ^7Be.

2. Reagents

Be carrier: 2.5 mg Be/ml, added as $Be(NO_3)_2 \cdot 3H_2O$
Zr, La, and Sc carriers: 10 mg metal/ml, added as nitrate or chloride
Te carrier: 10 mg Te/ml, added as Na_2TeO_4 in H_2O
HCl: concd, 6*M*
HNO_3: concd
HF: concd
NH_4OH: concd
NaOH: 10*M*
$BaCl_2$: 1.0*M*
EDTA: 0.2*M* solution of the disodium salt
Dowex AG 1-X8 anion column: 50-100 mesh, 8 mm x 4 cm, pretreated with concd HCl
Methyl red indicator solution: 0.1% in ethanol
Acetylacetone (3,4-pentanedione): solution made by shaking 15 ml with 100 ml H_2O
Wash solution: the wash solution for the extraction is made up as follows:
  15 ml acetylacetone
  100 ml 0.2*M* EDTA
  300 ml H_2O
  NH_4OH added to pH 7.7. Keep in tightly closed polyethylene bottle.
CCl_4
pH meter

3. Procedure

Step 1. Add *in order* into a suitable size beaker 2 ml Be carrier, the sample to be analyzed, an equal volume of EDTA or 10 ml EDTA, whichever is larger, and 10 ml of acetylacetone solution (see Reagents for preparation). Mix thoroughly. Add concd NH_4OH until the pH equals 7.7 ± 0.1. (Use the pH meter to get an accurate pH reading.) Transfer the solution to an appropriate size separatory funnel. A water rinse may be used on the beaker since it does not change the pH.

Step 2. Add 8 ml CCl_4 and shake 1 min. Transfer CCl_4 layer to 60-ml separatory funnel. Extract two more times with 8 ml CCl_4, each being added to the same 60-ml separatory funnel. Discard the H_2O layer. To the 24 ml of CCl_4 add 20 ml of "wash solution" (see Reagents). Shake 1 min and let stand a couple of minutes. Transfer the CCl_4 to a clean separatory funnel.

Step 3. Add 10 ml 6*M* HCl to the CCl_4 and shake ~30 sec. Drain the CCl_4 into a clean 60-ml separatory funnel and then the 10 ml of 6*M* HCl containing the Be is drained into a 125-ml erlenmeyer flask. Add 5 ml 6*M* HCl to the CCl_4 in the separatory funnel, shake 30 sec and discard the CCl_4. Drain the 5 ml of 6*M* HCl into the 125-ml erlenmeyer containing the first 10-ml portion of 6*M* HCl.

Step 4. Add 1 drop each of Zr and Te, then boil the 6*M* HCl down almost to dryness, adding a few drops of concd HNO_3 if the solution starts to turn dark because of the organic material present. Add ~2 ml of concd HCl and boil down again almost to dryness. Cool. Add 2-3 ml concd HCl and swirl to dissolve the contents of the erlenmeyer. Pass through ~2 inches depth of Dowex AG 1-X8, 50-100 mesh prepared as described in Note 3 on page 74. Wash the erlenmeyer with 2 ml portions of concd HCl and pass through the column. Collect all effluents in a 40-ml centrifuge cone. Heat in a steam bath carefully with stirring to drive off some of the excess HCl gas. Add 5 ml 0.2*M* EDTA and 10 ml H_2O. Add excess NH_4OH and put in an ice bath for ~1/2 h or until all the Be has precipitated as $Be(OH)_2$. Centrifuge and discard the supernate if it is clear. If not, replace in the ice bath and centrifuge again.

Step 5. Dissolve the $Be(OH)_2$ in 10 drops concd HCl and add 1 drop Zr. Make the volume ~15 ml with H_2O and add 3-4 ml 10*M* NaOH. Mix thoroughly and centrifuge the $Zr(OH)_4$. Transfer the supernate to a clean polyethylene tube and discard the $Zr(OH)_4$.

Step 6. To the supernate add 2 drops methyl red and concd HCl until the solution is acid. Precipitate $Be(OH)_2$ by adding NH_4OH. Centrifuge and discard the supernate. Dissolve the $Be(OH)_2$ with 10 drops concd HCl and dilute to 15 ml with H_2O. Add 4 drops La carrier and 25 drops of concd HF. Mix thoroughly and centrifuge, then transfer the supernate to a clean polyethylene tube.

Step 7. Add NH_4OH until the solution is neutral. Add 1 more drop and 4 drops La. Centrifuge and pour supernate into a clean polyethylene tube. Add 5 ml concd HCl and 10 drops Sc. Heat for 5 min on the steam bath, let stand a couple of minutes, centrifuge, transfer the supernate to a clean polyethylene tube, and discard the ScF_3.

Step 8. Put sample in steam bath until hot and add 1.5 ml of 1*M* $BaCl_2$. Digest in the steam bath for 2 min, let stand a few minutes, then centrifuge. Discard the supernate, wash precipitate with 15 ml H_2O, centrifuge, and discard the wash. Transfer the precipitate with H_2O to the Millipore filter system. (See Note 2). Filter the sample, wash with water, allow to remain on the filter assembly with suction applied for about 20 min, then disassemble and dry at 110° for 5 min.

Notes

1. The extraction is very specific for Be and the only activities observed after this step were ^{132}Te-^{132}I and ^{95}Zr-^{95}Nb. The anion column removes both Te and Zr.

2. The Millipore filter system consists of the 25 mm, 0.8μm pore size, designation AAWP 025 00 Millipore filter, clamped on top of a Whatman No. 42 filter paper mounted on a regular Millipore sintered glass filter and suction flask. After filtering, the chimney is left clamped in place and air is sucked through until the precipitate and papers are dry. This prevents the Millipore filter paper from sticking to the chimney when it is removed. By using the Whatman filter as a backing, the two filters may be removed as a unit and dried and weighed together. A Millipore filter with a precipitate on it is difficult to handle, hence the double papers. A pair of similar filters are treated the same as the sample for use as a tare in the balance. After weighing, the Millipore filter is treated with 4 or 5 drops of 6% rubber cement in benzene, separated from the Whatman filter, dried, and mounted for counting.

BERYLLIUM

B. P. Bayhurst and R. J. Prestwood

1. Introduction

This procedure is suitable for the determination of radioberyllium in fission-product solutions containing macroquantities of other metal ions. An initial precipitation of hydroxides by means of aqueous ammonia in the presence of the disodium salt of EDTA (ethylenediaminetetraacetic acid) serves to remove macroamounts of iron and aluminum. Other hydroxides are then precipitated with sodium hydroxide in the presence of zirconium and iron carriers. This is followed by hydroxide and fluoride scavenging steps performed in the presence of fluoride ion, the latter keeping beryllium in solution as the fluoroberyllate ion, BeF_4^{2-}. Further decontamination is accomplished by an anion exchange step and by acid sulfide scavenging. The beryllium is finally precipitated as $BaBeF_4$, in which form it is counted.

The chemical yield is 50-60% and quadruplicate analyses can be carried out in about 8 hr.

2. Reagents

Be carrier: 2.5 mg Be/ml, added as $Be(NO_3)_2 \cdot 3H_2O$
Zr, Fe, La, Sc, and Pd carriers: 10 mg metal/ml, added as nitrate or chloride
Te carrier: 10 mg Te/ml, added as Na_2TeO_4 in H_2O
HCl: concd; gas
HF: concd
H_2SO_4: concd
H_3BO_3: saturated solution
H_2S: gas
NH_4OH: concd
NaOH: 10*M*
$NH_2OH \cdot HCl$: solid
$BaCl_2$: 1.0*M*
EDTA: 0.2*M* solution of the disodium salt
Dowex A 1-X8 anion column: 50-100 mesh; 8 mm × 4 cm; pretreated with concd HCl
Methyl red indicator solution: 0.1% in ethanol

3. Procedure

Step 1. To 2.0 ml of Be carrier add the sample and an equal volume of 0.2*M* EDTA or 10 ml EDTA, whichever is larger. Add 5 ml saturated H_3BO_3 and bring almost to a boil. Neutralize the solution with NH_4OH and add a few ml excess. Allow to stand overnight. Centrifuge in a 40-ml cone. Discard the supernate.

Step 2. Thoroughly wash the precipitate twice with H_2O. Add 2 ml of concd H_2SO_4 and boil over a burner until strong SO_3 fumes appear. Cool and dilute to 10 ml with H_2O. Add 100 mg of $NH_2OH \cdot HCl$, warm, and then add 1 drop each of Zr and Fe carriers. Neutralize with 10*M* NaOH and then add 2 ml in excess. Heat on a steam bath to coagulate $Fe(OH)_3$ and $Zr(OH)_4$. Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate.

Step 3. Add 1 drop each of La and Sc carriers. Mix thoroughly, heat on a steam bath for a few minutes, centrifuge, and transfer the supernate to a 40-ml conical *polyethylene* centrifuge tube. Discard the precipitate.

Step 4. To the solution, add 2 drops of methyl red indicator solution, make barely acid with concd HCl, and then add 10 drops of the acid in excess. Make the solution basic with an excess of concd NH_4OH, centrifuge, and discard the supernate. Wash the precipitate well with H_2O to remove residual sulfate ion and discard the washings.

Step 5. Add 1 ml of concd HCl and 5 drops of La carrier. Dilute to 20 ml with H_2O and add 1 ml of concd HF. Mix thoroughly, centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate.

Step 6. To the solution, add 2 drops of methyl red indicator and then concd NH_4OH dropwise to the endpoint and add 1.5 ml of concd NH_4OH. Add 1 drop each of Fe and La carriers and mix thoroughly. Place on a steam bath for a few minutes, centrifuge, and transfer the supernate to a clean polyethylene centrifuge tube.

Step 7. Add 6 ml of concd HCl and 4 drops of Sc carrier and place on a steam bath for a few minutes. Centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate.

Step 8. Add 1-2 ml of 1.0*M* $BaCl_2$ and place on a steam bath for a few minutes. Centrifuge and discard the supernate.

Step 9. Slurry the $BaBeF_4$ precipitate in 3 ml of concd HCl, add 3 ml of saturated H_3BO_3, and dilute to 20 ml with H_2O. Place on a steam bath until the precipitate has dissolved completely. Stir continuously while adding 10 drops of concd H_2SO_4. Let stand for 5 min, centrifuge, and transfer the supernate to a clean 40-ml *glass* centrifuge tube.

Step 10. Add an excess of concd NH_4OH to precipitate $Be(OH)_2$. Centrifuge and discard the supernate. Wash the precipitate thoroughly with H_2O (see Note) and discard the washings. Add 10 drops of concd HCl and dissolve the precipitate. Add 4 drops of Te(VI) carrier and saturate the solution with HCl gas.

Step 11. Transfer the solution to the Dowex A 1-X8 anion exchange column. Rinse the centrifuge tube twice with 1-ml portions of concd HCl and add the rinsings to the column. Collect all effluents in a clean glass centrifuge tube. Add two 2-ml portions of concd HCl to the column and collect the effluent with the others.

Step 12. Boil until the total volume is reduced to about 1 ml. Dilute to 20 ml with H_2O and add 2 drops of Pd carrier. Place on a steam bath and bubble in H_2S until the precipitate which forms is completely coagulated. Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate.

Step 13. Add 2 drops of Pd carrier, place on a steam bath, and bubble in H_2S until the precipitate which forms is completely coagulated. Centrifuge, transfer the supernate to a clean glass centrifuge tube, and discard the precipitate.

Step 14. Add an excess of concd NH_4OH to precipitate $Be(OH)_2$. Centrifuge and discard the supernate.

Step 15. Dissolve the precipitate in 1 ml of concd HCl and boil vigorously to expel H_2S. Add 1 drop each of Fe and La carriers. Dilute with H_2O to 20 ml. Add sufficient 10*M* NaOH to precipitate $Fe(OH)_3$ and $La(OH)_3$ and then 2 ml in excess. Centrifuge, transfer the supernate to a clean *polyethylene* centrifuge tube, and discard the precipitate.

Step 16. Repeat Steps 3 through 8.

Step 17. Slurry the $BaBeF_4$ precipitate with 0.5 ml of 1.0*M* $BaCl_2$ and 10 ml of H_2O. Transfer the precipitate onto a weighed 1″ diameter, 0.8 micron Millipore filter and pad combination using a ground-off Hirsch funnel and standard chimney setup. Wash the precipitate with H_2O and apply a vacuum until the precipitate is practically dry. Complete the drying process in an oven at 110°, cool, and weigh. Mount on standard Al plates with two-sided Scotch tape and cover with Mylar.

Note

It is necessary to remove all the excess NH_4OH and NH_4^+ ion at this point, otherwise the large amounts of NH_4Cl which are formed will plug up the anion exchange column in the next step.

SEPARATION OF RADIOBERYLLIUM FROM PLUTONIUM

D. C. Hoffman and T. T. Shull

1. Introduction

Radioberyllium can be separated from plutonium by (1) precipitation of lanthanum fluoride, which carries plutonium, or (2) carrying plutonium on lanthanum hydroxide, precipitated by means of excess sodium hydroxide solution. In either case, beryllium remains in solution.

2. Procedure A

Step 1. To an aliquot of sample, add 10 mg of Be carrier and precipitate LaF_3 as described in Steps 1 and 2 of the standard Pu procedure (Note). Centrifuge.

Step 2. The supernate is analyzed for Be after removal of fluoride by fuming with $HClO_4$. The analysis for Pu is carried out on the fluoride precipitate in the usual manner.

3. Procedure B

Step 1. To an aliquot of sample, add 10 mg of Be carrier, ^{236}Pu tracer, and 2 to 5 drops of La carrier (10 mg La/ml). To the resulting solution add dilute NaOH solution until precipitation is complete and the supernate is distinctly alkaline (i.e., the Be is in solution as beryllate). Centrifuge.

Step 2. Be is determined in the supernate by the Tracerlab method. The $La(OH)_3$ precipitate is dissolved in either dilute HCl or HNO_3 and the solution made 2 to 4*M* in acid concentration. Pu is then determined by the usual procedure.

Note

If the sample is contained in a relatively large volume of solution, it is advisable to perform an initial $La(OH)_3$ precipitation with NH_3 gas. The precipitate is dissolved in dilute HCl or HNO_3 and the solution made 2 to 4*M* in acid. The analysis for Pu is then performed on the fluoride precipitate.

BISMUTH

R. J. Prestwood

1. Introduction

In the separation of radiobismuth (RaE) from other activities the essential steps consist of (a) precipitation of bismuth as the oxychloride, (b) extraction of bismuth triiodide into hexone, (c) silver chloride scavenging, and (d) precipitation of bismuth sulfide from 1.5*M* HCl. The bismuth is finally weighed and mounted as the oxychloride. The chemical yield is about 65% and four samples can be analyzed in about 5 hr.

2. Reagents

Bi carrier: 10 mg Bi/ml, added as $Bi(NO_3)_3 \cdot 5H_2O$ in 1*M* HCl, standardized
Rh carrier: 10 mg Rh/ml, added as $RhCl_3 \cdot 4H_2O$ in 0.01*M* HCl
Ru carrier: 10 mg Ru/ml, added as $RuCl_3$ in 0.01*M* HCl
Ag carrier: 10 mg Ag/ml, added as $AgNO_3$ in H_2O
Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_3 in dil HCl
HCl: 1*M*; 3*M*; 6*M*; concd
$HClO_4$: concd
NH_4OH: concd
$N_2H_4 \cdot H_2SO_4$: solid
NaI: solid
$NaNO_2$: solid
H_2S: gas
Saturated aqueous SO_2
Hexone (4-methyl-2-pentanone)
Methanol: anhydrous

3. Preparation and Standardization of Carrier

Dissolve 23.21 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 1*M* HCl, make up to 1 liter with the acid, and filter. Pipet 10.0 ml of the solution to a 250-ml erlenmeyer flask, add 200 ml of boiling H_2O, and digest overnight on a steam bath. Filter into a weighed 15-ml sintered glass crucible of medium porosity. Wash the BiOCl precipitate with H_2O and then with methanol. Dry at 110° for 15 min, cool, and weigh. Four standardizations gave a total spread of 0.2% (Note 1).

4. Procedure

Step 1. To 2.0 ml of Bi and 1 ml of Te(IV) carriers in a 125-ml erlenmeyer flask, add an aliquot of the sample. Place on a hot plate and evaporate to dryness. Add 5 ml of concd HCl and again evaporate to dryness. (Evaporation is necessary to insure Te exchange and also to remove NO_3^-, which inhibits reduction of Te to metal.) Add 15 ml of 3*M* HCl and about 100 mg of $N_2H_4 \cdot H_2SO_4$. Heat to boiling on a hot plate and add saturated aqueous SO_2 periodically while the solution is boiling until all the Te is precipitated as metal and the solution has no blue tinge. (This may take as long as 10 min, with SO_2-water being added at about 2-min intervals.) Filter and collect the filtrate in a 40-ml conical centrifuge tube. Rinse the erlenmeyer flask with hot 3*M* HCl containing SO_2-water and pass the solution through the filter into the centrifuge tube.

Step. 2. To the filtrate add concd NH_4OH to precipitate $Bi(OH)_3$. Centrifuge and discard the supernate (Note 2).

Step 3. To the precipitate add 10 drops of 6*M* HCl, 5 drops of Rh carrier, and stir to dissolve. Wash the sides of the centrifuge tube with 2 to 4 ml of H_2O and heat on a steam bath. (The solution at this point should be clear.) Add 30 ml of boiling H_2O and digest for 5 min. Centrifuge the BiOCl precipitate and discard the supernate.

Step 4. To the precipitate add 2 ml of concd $HClO_4$ and 5 drops of Ru carrier, and with vigorous stirring heat to fumes. Fume until all the RuO_4 has been volatilized and then allow the solution to cool.

Step 5. Add 10 drops of Ag carrier, dilute to 20 ml with H_2O, and then add 2 ml of 6*M* HCl with vigorous stirring. Centrifuge and transfer the supernate to a clean centrifuge tube containing 5 ml of concd NH_4OH. Centrifuge and discard the supernate.

Step 6. Add 5 ml of 6*M* HCl to the $Bi(OH)_3$ precipitate and transfer the solution to a 60-ml separatory funnel. Wash the centrifuge tube with 10 ml of 6*M* HCl and add the washings to the separatory funnel. Add 15 ml of hexone and shake vigorously. Drain the H_2O layer into a clean separatory funnel. Add 10 ml of hexone, 1-2 g of solid NaI, shake, and discard the H_2O layer. Add 10 ml of 6*M* HCl containing approximately 1 g of NaI to the hexone layer. Shake and discard the H_2O layer. To the hexone phase add 10 ml of 6*M* HCl and approximately 0.5 g of solid $NaNO_2$ and swirl. Place the stopper in the separatory funnel and shake vigorously. (At this point the aqueous layer is essentially colorless and the hexone phase may be slightly yellow.) Drain the H_2O layer into a clean 40-ml centrifuge tube containing 5 ml of concd NH_4OH. Centrifuge and discard the supernate.

Step 7. To the $Bi(OH)_3$ precipitate add 10 ml of 3*M* HCl and 10 ml of H_2O. Place on a steam bath and saturate with H_2S for at least 2 min. Centrifuge and discard the supernate. Dissolve the Bi_2S_3 precipitate by boiling in 5 ml of 6*M* HCl.

Step 8. Precipitate $Bi(OH)_3$ as in Step 2.

Step 9. Repeat Steps 3, 4, and 5.

Step 10. Transfer the $Bi(OH)_3$ precipitate with 15 ml of 6*M* HCl to a 60-ml separatory funnel. Add 10 ml of hexone, 1 to 2 g of solid NaI, shake, and discard the H_2O layer. Add 10 ml of 6*M* HCl containing approximately 1 g of NaI to the hexone layer. Shake and discard the H_2O layer. To the hexone phase add 10 ml of 6*M* HCl and approximately 0.5 g of solid $NaNO_2$ and swirl. Place the stopper in the separatory funnel and shake vigorously. Drain the H_2O layer into a clean 40-ml centrifuge tube containing 5 ml of concd NH_4OH. Centrifuge and discard the supernate.

Step 11. Repeat Step 7.

Step 12. Repeat Step 2 and then Step 3, the latter in the absence of Rh holdback carrier.

Step 13. Filter the BiOCl on to a weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate with H_2O and then with methanol. Dry at 110° for 5 min, cool for 20 min, weigh, and mount for counting.

Notes

1. The weight of $Bi(NO_3)_3 \cdot 5H_2O$ employed in the standardization corresponded (by calculation) to 10.0 mg of Bi/ml, whereas the actual standardization as BiOCl showed 10.1 mg Bi/ml.

2. If large quantities of Pb activities are present in the sample, they may be removed in the following manner at this stage of the procedure. To the $Bi(OH)_3$ precipitate add 5 drops of Pb carrier, 2 ml of 12*M* NaOH, and boil with vigorous stirring. Add 20 ml of H_2O and continue boiling for 3-5 min. Centrifuge and discard the supernate which contains the Pb as plumbite. This procedure has proved extremely effective for the removal of Pb.

cadmium, calcium, cerium, cesium, chlorine, chromium, cobalt, curium

CADMIUM

B. P. Bayhurst and R. J. Prestwood

1. Introduction

This procedure is designed for the rapid separation of cadmium from fission products. Decontamination steps include scavenging with cadmium sulfide, acid sulfide, and iron hydroxide. The cadmium, in $4M$ HCl, is then placed on an anion exchange resin (Dowex AG 1-X8) and eluted with $1.5M$ H_2SO_4. Finally, the cadmium is converted to the elemental form by electroplating. The chemical yield is about 80%.

2. Reagents

Cd carrier: 10 mg Cd/ml, added as $Cd(NO_3)_2 \cdot 4H_2O$ in very dilute HCl, standardized
Ag carrier: 10 mg Ag/ml, added as $AgNO_3$ in very dilute HNO_3
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
Pd carrier: 10 mg Pd/ml, added as $PdCl_2$ in H_2O
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
HCl: concd; $6M$; $3M$; $0.1M$
H_2SO_4: $1.5M$
NH_4OH: concd
NaOH: $10M$
H_2S: gas
Dowex AG 1-X8, 50-100 mesh anion exchange resin, slurry in $6M$ HCl
Methyl red indicator solution

3. Preparation and Standardization of Carrier

Dissolve 27.4 g of $Cd(NO_3)_2 \cdot 4H_2O$ in H_2O, make the solution slightly acidic with HCl, and dilute to 1 liter with H_2O. Pipet exactly 5.0 ml of the above carrier solution into a 40-ml conical centrifuge tube and evaporate to dryness. Dissolve the residue in 20 ml of H_2O, add 2 ml of $3M$ NH_4Cl and 2 ml of $1.5M$ $(NH_4)_2HPO_4$, and bring the solution to a boil. Permit the mixture to come to room temperature and filter through a 60-ml sintered glass crucible of medium porosity. Wash the precipitate with water and then with 95% ethanol. Dry for 15 min at 110°, cool, and weigh as $CdNH_4PO_4 \cdot H_2O$.

4. Procedure

Step 1. Add the sample to 2 ml of Cd carrier in a 40-ml conical centrifuge tube. Add sufficient $6M$ HCl to make the solution $0.1M$ with respect to this acid. Bubble in H_2S for about 3 min, centrifuge, and discard the supernate.

Step 2. To the precipitate add 2 ml of concd HCl and boil to expel H_2S. Dilute to 20 ml with H_2O, add 2 drops of Fe carrier, and make basic by the dropwise addition of concd NH_4OH. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. Add 2 drops of La carrier, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 3. Add 1 ml of Ag carrier and then concd H_2SO_4 dropwise until the solution is acid to methyl red indicator. Add 10 drops of $6M$ HCl and place on a steam bath for about 3 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 4. Saturate the supernate with H_2S, centrifuge, and discard the supernate.

Step 5. Dissolve the CdS precipitate in a few drops of concd HCl, boil briefly, and add 10 ml $3M$ HCl and 3 drops of Pd carrier. While the solution is being heated on a steam bath, saturate it with H_2S. Centrifuge, filter the supernate through a No. 41 H Whatman filter paper into a 125-ml erlenmeyer flask, and discard the precipitate.

Step 6. Boil the solution to expel H_2S and then place it on top of a Dowex AG 1-X8, 50-100 mesh anion exchange resin column (0.8 cm × 5 cm resin bed). Wash the flask with 2 ml of $3M$ HCl and add the washings to the column. Wash the column with 10-15 ml of $0.1M$ HCl. Discard all eluates. Add 10 ml of $1.5M$ H_2SO_4 to the column and, when this has passed through, add 20 ml of H_2O. Collect the eluates in a clean centrifuge tube.

Step 7. Make the solution basic with $10M$ NaOH, centrifuge, discard the supernate, and proceed with the electroplating of Cd metal.

ELECTROPLATING OF CADMIUM

1. Introduction

The procedure for electroplating of cadmium following its separation from fission products has two major advantages in the isolation and counting of cadmium in elemental form rather than as the usual compound such as $CdNH_4PO_4 \cdot H_2O$: (a) superior stability and reproducibility of the final product as the metal, and (b) an approximate 40% increase in counting efficiency.

2. Procedures

Following separation of cadmium from fission products, the step preceding electroplating should be the precipitation of $Cd(OH)_2$ with NaOH. The precipitate is thoroughly washed twice with H_2O before performing the following procedure.

Step 1. To the precipitate in a 40-ml conical centrifuge tube add 5 ml of 2*M* NaCN and stir until solution is effected, heating if necessary. Transfer the solution to a plating cell (see the Uranium-235 Procedure for details of the plating assembly), the cathode of which is a weighed polished Pt disk of 1" diameter. Wash the centrifuge tube with 5 ml of 2*M* NaCN and transfer the washings to the plating cell.

Step 2. Plate the cadmium onto the Pt disk at 25 ma at room temperature for 1 hr 10 min, the amperage being maintained constant by means of a variable resistance in series with the plating cell. Upon completion of the plating remove the cell, discard the electrolyte, wash the cell with distilled H_2O, and disassemble it. Wash the cadmium-plated Pt disk thoroughly with absolute ethanol, allow to dry at room temperature, weigh, and mount.

CALCIUM

W. H. Burgus

This procedure is an adaptation of one previously reported by E. P. Steinberg in *Radiochemical Studies: The Fission Products*, Book 1, McGraw-Hill, New York, 1951, p. 482.

1. Introduction

Calcium is first separated from most of the fission products by appropriate ferric hydroxide, acid sulfide, and ammonium sulfide scavenging steps, followed by separation of calcium, strontium, and barium as oxalates. The oxalates are then dissolved and strontium and barium are removed quantitatively by precipitation of their nitrates from fuming nitric acid. The 40-hr ^{140}La, which has grown in from 12.5-day ^{140}Ba during the interval between the ferric hydroxide scavenging step and the last separation of barium and strontium from calcium, is separated by means of lanthanum hydroxide scavenger. Calcium is finally precipitated as calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, and counted in this form. The chemical yield approximates 30%, and the time for a single analysis is about 1¾hr.

2. Reagents

Ca carrier: 10 mg Ca/ml, added as $Ca(NO_3)_2 \cdot 4H_2O$ in very dilute HNO_3, standardized
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
Pd carrier: 10 mg Pd/ml, added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl
Cu carrier: 10 mg Cu/ml, added as $CuCl_2 \cdot 2H_2O$ in H_2O
Ni carrier: 10 mg Ni/ml, added as $Ni(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3
Co carrier: 10 mg Co/ml, added as $Co(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3
Sr carrier: 10 mg Sr/ml, added as $Sr(NO_3)_2 \cdot 4H_2O$ in very dilute HNO_3
Ba carrier: 10 mg Ba/ml, added as $Ba(NO_3)_2$ in H_2O
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
HCl: 6*M*
HNO_3: concd; white fuming
NH_4OH: concd
$(NH_4)_2CO_3$: saturated aqueous solution
$(NH_4)_2C_2O_4$: 4% aqueous solution
$NaBrO_3$: 1*M*
H_2S: gas
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 59.0 of $Ca(NO_3)_2 \cdot 4H_2O$ in H_2O, add 1 ml of HNO_3, and dilute to 1 liter with H_2O.

Pipet a 2-ml aliquot of the above carrier solution into a 100-ml beaker, dilute to 50 ml, heat to boiling, precipitate $CaC_2O_4 \cdot H_2O$ by the addition of a slight excess of 4% $(NH_4)_2C_2O_4$ solution. Filter into a tared sintered glass 15-ml Gooch crucible (fine porosity). Wash three times with 10-ml portions of hot H_2O and once with ethanol. Suck dry for several minutes. Dry to constant weight in an oven at no more than 100°.

Four standardizations are performed. The results should agree within 0.5%.

4. Procedure

Step 1. To the sample in a 40-ml centrifuge tube, add sufficient H_2O to bring the volume to 15 to 20 ml, then add 2 ml of standard Ca carrier. If no appreciable quantity of U is present, proceed immediately to Step 2. If U is present, heat the solution to boiling and precipitate ammonium diuranate by the dropwise addition of concd NH_4OH. Centrifuge and discard the precipitate, transferring the supernate to a 40-ml centrifuge tube.

Step 2. Acidify the solution with concd HNO_3, add 6 drops of Fe carrier, heat to boiling, and precipitate $Fe(OH)_3$ by the dropwise addition of concd NH_4OH. Centrifuge and discard the precipitate, transferring the supernate to a 40-ml centrifuge tube.

Step 3. Repeat Step 2 twice.

Step 4. Make the supernate, after the $Fe(OH)_3$ scavenging operation, 0.1*M* in HCl, and add 4 drops of Pd and 8 drops of Cu carriers. Heat to boiling and pass in H_2S for 4-5 min. Filter the acid sulfide scavenging precipitate on a No. 40 Whatman paper and discard it, catching the filtrate in a 40-ml centrifuge tube.

Step 5. Add 4 drops each of Ni and Co carriers to the filtrate and heat to boiling. Add concd NH_4OH until the solution is basic to litmus, then add an additional 0.5 ml of NH_4OH. Pass in H_2S for 3 min and filter the ammonium sulfide scavenging precipitate on a No. 40 Whatman paper and discard it, catching the filtrate in a 40-ml centrifuge tube.

Step 6. Add 3 ml of 4% $(NH_4)_2C_2O_4$ solution to the filtrate from Step 5. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of H_2O.

Step 7. Dissolve the precipitate in 5 ml of H_2O and 1 ml of concd HNO_3. Add 1 ml each of Ba and Sr scavengers. Precipitate $Ba(NO_3)_2$ and $Sr(NO_3)_2$ by the addition of 30 ml of white fuming HNO_3. Cool in an ice bath for several minutes. Centrifuge and discard the precipitate, transferring the supernate to a 125-ml erlenmeyer flask.

Step 8. Boil down the Ca-containing supernate to a volume of 1-2 ml. Add 5 ml of H_2O, 1 ml each of Ba and Sr carriers, and 30 ml of fuming HNO_3 to precipitate $Ba(NO_3)_2$ and $Ca(NO_3)_2$. Cool and transfer the mixture to a 40-ml centrifuge tube. Centrifuge, transfer the supernate to a 125-ml erlenmeyer flask, and discard the precipitate.

Step 9. Repeat Step 8.

Step 10. Boil down the supernate to 2-3 ml and add 30 ml of H_2O. Transfer to a 40-ml centrifuge tube and make ammoniacal with concd NH_4OH. Add 2 ml of 4% $(NH_4)_2C_2O_4$ solution to insure complete precipitation of $CaC_2O_4 \cdot H_2O$. Centrifuge and discard the supernate.

Step 11. Dissolve the $CaC_2O_4 \cdot H_2O$ in 2 ml of concd HNO_3 and 2 ml of 1*M* $NaBrO_3$ (Note 1). Boil down to about 1 ml. Add 30 ml of H_2O, make strongly ammoniacal, and add 4 ml of saturated $(NH_4)_2CO_3$ solution. Centrifuge the $CaCO_3$ and discard the supernate.

Step 12. Dissolve the $CaCO_3$ in 1-2 ml of concd HNO_3. Dilute to 30 ml, and add 1 ml of La carrier. Precipitate $La(OH)_3$ by the addition of concd NH_4OH. Centrifuge, transfer the supernate to a 40-ml centrifuge tube, and discard the precipitate.

Step 13. Heat the supernate to boiling and precipitate $CaC_2O_4 \cdot H_2O$ by the dropwise addition of 3 ml of 4% $(NH_4)_2C_2O_4$. Filter the $CaC_2O_4 \cdot H_2O$ on a tared Whatman No. 42 circle, using a ground-off Hirsch funnel and a filter chimney. Wash three times with 10-ml portions of hot H_2O and then with ethanol. Suck dry. Dry in oven at 100° for 5 min. Weigh, mount, and count (Note 2).

Notes

1. $NaBrO_3$ is used to destroy oxalate and thus avoid precipitation of lanthanum oxalate when the La carrier is added (Step 12).

2. No special precautions need be taken in counting. If short-lived isotopes are present, the decay curve must be resolved. If 150-day ^{45}Ca is to be counted, the chemistry employed for separation of Ca is carried out after the decay of the short-lived isotopes.

A. THE DISSOLUTION OF BULK GRAPHITE CONTAINING URANIUM AND NIOBIUM CARBIDES, AND

B. THE DISSOLUTION OF ACTIVATED CHARCOAL

J. W. Barnes

Introduction

The procedures described are designed for dissolving graphitic carbon containing fission products.

Bulk graphite containing both uranium carbide (abbreviated UC) and niobium carbide (NbC) (the UC can be present in beads which are coated with pyrolytic graphite) is brought into solution by wet ashing with 70% $HClO_4$ in the presence of a small amount of CrO_3. Two points in the dissolution of the bulk graphite merit special mention. When heat is not removed with sufficient rapidity from the graphite, the dissolving process may accelerate to an uncontrollable rate and an explosion may occur. This condition results when the gases evolved interfere with heat exchange between the solid and the acid. The explosion hazard may arise early in the dissolving process either from the presence of a few remaining chunks of graphite which have not yet disintegrated to powder form or from the use of too large a sample relative to the quantity of acid. Danger of explosion may also arise late in the dissolving process if one permits the acid to become so depleted that the mixture approaches dryness.

The second point to note is the possible loss of significant quantities of fission products which may be entrained in droplets of solution carried away by the carbon dioxide liberated in the dissolving process. This possibility is avoided through the use of a device for separating the droplets from the carbon dioxide and returning them to solution.

Activated charcoal is first partially ignited in oxygen and then dissolved in 90% HNO_3 and 70% $HClO_4$. The ignition is performed because wet ashing of activated charcoal without such treatment is hazardous and may result in violent explosions. It is even more hazardous if carried out in the absence of 90% HNO_3.

Part A: The Dissolution of Bulk Graphite Containing UC and NbC

1. Reagents

$HClO_4$: 70%
HNO_3: 90% (yellow fuming)
HF: concd
HCl: 6*M*
HCl-HF solution: 4*M* in HCl and 0.3*M* in HF
CrO_3 solution: aqueous, 0.5 g/ml
Activated charcoal

2. Remarks on Equipment

The apparatus used is depicted in Fig. 1. The dissolving flask is made of Vycor, which is resistant to thermal shock and much less reactive with aqueous HF than Pyrex. The baffles stop and return gas-carried liquid to the dissolving flask. The activated charcoal trap collects any volatile radioactive iodine species.

3. Procedure

Step 1. Place a 1/2" slice of fuel element (~6 g) in a Vycor flask equipped with a magnetic stirrer bar. Add 1 ml of CrO_3 and 150 ml of 70% $HClO_4$ (Note). Connect flask to condenser apparatus. The condenser trap should contain about 40 ml of 6*M* HCl, that is, enough to cover

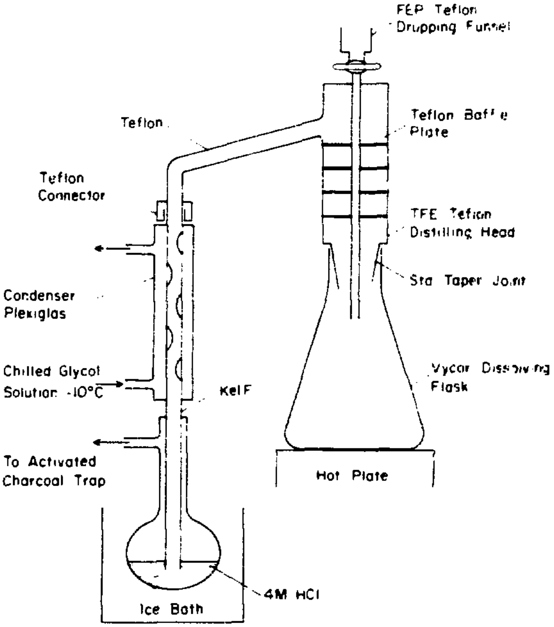

Fig. 1.

the outlet tube. Boil for approximately 1 hour. Cool to about 100° and add 10 ml 90% HNO_3 slowly through the dropping funnel.

Step 2. Bring the solution again to a boil and continue boiling. The sample should be a reddish color in approximately 2 hours from the time of the addition of HNO_3. There will probably be black specks of Zr or Nb carbide present at this point. Boil 2 more hours after the reddish color appears.

Step 3. Cool to near room temperature, disconnect flask from the condenser, and add about half of the 6*M* HCl from the condensation trap. Reconnect flask to the condenser and start warming and stirring. Add about 5 ml concd HF through the dropping funnel. If the reaction appears to be too vigorous, resulting in possible loss of sample, it may be necessary to cool the flask. As the reaction permits continue stirring and warming the solution, adding HF as needed to dissolve the black particles.

Step 4. When the solution is clear with a white precipitate in the bottom of the flask, cool the solution and decant the clear supernate into a 500 or 1000 ml polyethylene volumetric flask. If a polyethylene volumetric flask is not available, the cool solution may be made up to volume in a Pyrex volumetric flask, then transferred to a polyethylene bottle for storage.

Step 5. Try to dissolve the white solid in the bottom of the flask with H_2O, adding a little HF and warming if necessary. If all the white solid does not dissolve, it may be necessary to repeat the procedure.

Step 6. Add the distillate in the cold trap to the volumetric flask. Rinse the cold trap and the dissolving flask with 10-15 ml of HCl-HF solution and add the rinse to the volumetric flask. Mix the contents of the volumetric flask and make up to volume, finally mixing thoroughly. The solution is now ready for fission product analysis.

Part B: The Dissolution of Activated Charcoal

1. Reagents

$HClO_4$: 70%
HNO_3: 90% (yellow fuming)
HCl: 4*M*
O_2 gas: pure, tank

2. Procedure

Step 1. In a fume hood, place 20-50 g of sample in a 1500-ml Vycor beaker and cover the beaker with a Pyrex watch glass which has a hole in the center for the admission of a glass tube of 5-6 mm o.d. connected to an O_2 tank. By means of an appropriate heat source, heat the bottom of the beaker to raise the temperature of the sample to about 600°. Pass O_2 *slowly* over the sample and continue heating for 2 hours. (Too rapid an O_2 flow will tend to blow solid oxide products from the beaker. It is not necessary that combustion be complete.)

Step 2. Add 50 ml of 90% HNO_3 and 100 ml of 70% $HClO_4$. Boil on a hot plate while permitting an additional 50 ml of HNO_3 to drip from a dropping funnel into the mixture through the hole in the watch glass. Continue boiling for 20 min after a clear solution is obtained. (The total time of Step 2 is 1-1.5 hours. There may be a few chunks of unreacted sample present at the end of that time.) Cool the solution. At this point some salts may precipitate out.

Step 3. Add 20 ml of 4*M* HCl to complex Fe(III) and enough H_2O to bring the volume to about 40 ml. Filter into a 500-ml volumetric flask and make up to volume with H_2O. The solution can now be analyzed for fission products.

Note

It would not be necessary to add the CrO_3 initially if it were possible to add the fuming HNO_3 in the beginning. When the HNO_3 is added initially with the $HClO_4$, the reaction proceeds smoothly at first, but when the greenish fumes characteristic of chlorine are replaced by the white fumes of $HClO_4$, enough pressure is generated in the system to blow the sample into the condenser, or blow the equipment apart.

CERIUM

D. P. Ames

The procedure for the determination of cerium in fission-product material is based on a method described by N. E. Ballou, CN-2815 (June 30, 1945).

1. Introduction

In the analysis for radiocerium, exchange between carrier and fission-product cerium is effected by a Ce (III)-Ce (IV) oxidation-reduction cycle. Cerium (III) and other rare earths are separated from other fission products by precipitation as fluorides with hydrofluoric acid. Cerium is then oxidized to the +4 state and separated from other rare earths by precipitation as the iodate, $Ce(IO_3)_4$. Cerium is converted to the +3 state and zirconium, plutonium (IV), and thorium activities are removed by zirconium iodate scavenging. Precipitation of $Ce(OH)_3$ separates cerium from alkaline earth activities. Cerium is finally precipitated as the oxalate and ignited to the oxide CeO_2, in which form it is weighed and counted. The chemical yield approximates 75%. Quadruplicate analyses can be performed in about 7 hr.

2. Reagents

Ce carrier: 10 mg Ce/ml, added as $Ce(NO_3)_3 \cdot 6H_2O$ in H_2O, standardized
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
HCl: 6*M*; concd
HNO_3: concd
HF: concd
H_3BO_3: saturated aqueous solution
HIO_3: 0.35*M*
NH_4OH: concd
$NaBrO_3$: saturated aqueous solution
$(NH_4)_2C_2O_4$: saturated aqueous solution
H_2O_2: 30%

3. Preparation and Standardization of Carrier

Dissolve 31.0 g of $Ce(NO_3)_3 \cdot 6H_2O$ in H_2O and dilute to 1 liter. (To obtain cerium that is free from other rare earths it may be necessary to purify by two $Ce(IO_3)_4$ precipitations as in Steps 4 and 5 of *Procedure.*)

Pipet 5 ml of the cerium carrier solution into a 100-ml beaker and dilute to about 20 ml with H_2O. Warm on a steam bath and add about 50 ml of saturated $(NH_4)_2C_2O_4$ solution. Continue heating on the steam bath until the precipitate has coagulated. Cool in an ice bath for 15 min and filter through a filter funnel, using a No. 42 Whatman filter paper (11 cm). Ignite in a porcelain crucible at 800° for 30 min, cool, and weigh as CeO_2.

Four standardizations, with results agreeing within 0.5%, are carried out.

4. Procedure

Step 1. To a 40-ml centrifuge tube, add 2 ml of Ce carrier and 5 ml of concd HNO_3, and pipet in the sample for analysis. Add 1 ml of saturated $NaBrO_3$ solution and heat on a steam bath for 10 min (Note 1).

Step 2. Remove the tube from the steam bath and add 30% H_2O_2 dropwise with vigorous stirring (Note 2) until the solution has a light reddish-brown color. Heat on the steam bath until the Br_2 color disappears, adding a drop or two of H_2O_2 if necessary.

Step 3. Add 2 ml of La carrier and 2.5 ml of Zr holdback carrier and transfer the solution to a 50-ml Lusteroid tube. Add 3 ml of concd HF to precipitate CeF_3 and LaF_3. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5*M* HF, centrifuge, and discard the supernate.

Step 4. To the precipitate add 1 to 2 ml of saturated H_3BO_3 solution and suspend the precipitate by stirring. Then add 4 ml of concd HNO_3 and stir vigorously until a clear solution is formed. Transfer to a 40-ml glass centrifuge tube and add 4 ml of concd HNO_3 and 1 ml of saturated $NaBrO_3$ solution. Heat on a steam bath for about 10 min.

Step 5. Add 20 ml of 0.35*M* HIO_3 and stir vigorously. Cool for 5-10 min in an ice bath. Centrifuge and discard the supernate, retaining the $Ce(IO_3)_4$ precipitate (Note 3).

Step 6. Suspend the precipitate in a solution made up by the addition of 8 ml of H_2O, 3 ml of concd HNO_3, and 3 ml of 0.35*M* HIO_3. Centrifuge and discard the supernate. Repeat this washing step twice, suspending the precipitate each time.

Step 7. Add 1 ml of La carrier to the precipitate. Add 4 ml of concd HNO_3 and a drop or two of concd HCl and slurry the $Ce(IO_3)_4$ by stirring vigorously. Add 0.2 ml of 30% H_2O_2 and stir until dissolution of $Ce(IO_3)_4$ is complete. Add 1 ml of saturated $NaBrO_3$ and 4 ml of concd HNO_3. Reoxidize Ce (III) to Ce (IV) as in Step 4.

Step 8. Repeat Step 5.

Step 9. Repeat Step 6, washing the precipitate three times. (All other rare earths have now been removed from the cerium.)

Step 10. Add 1 ml of Zr carrier to the precipitate from Step 9 and dissolve the precipitate as in Step 7, using 8 ml of concd HNO_3, 0.2 ml of concd HCl, and 0.2-0.3 ml of 30% H_2O_2. Add 20 ml of 0.35*M* HIO_3 to the clear solution to precipitate $Zr(IO_3)_4$ (Note 4). Centrifuge and transfer the supernate to a 50-ml Lusteroid tube, discarding the $Zr(IO_3)_4$ precipitate.

Step 11. Add 5 ml of concd HF to precipitate CeF_3. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of 5*M* HF. Centrifuge and discard the supernate.

Step 12. Dissolve the CeF_3 by making a slurry in 1 ml of saturated H_3BO_3 and adding 2 ml of concd HNO_3. Transfer to a 40-ml centrifuge tube. Heat on a steam bath for 5 min to insure complete dissolution.

Step 13. Dilute to 10 ml with H_2O and make strongly basic with concd NH_4OH to precipitate $Ce(OH)_3$. Centrifuge and discard the supernate. Wash the precipitate with 10 ml of H_2O. Centrifuge and discard the supernate.

Step 14. Dissolve the $Ce(OH)_3$ in 1 to 2 ml of 6*M* HCl. Heat on the steam bath to ensure complete dissolution.

Step 15. Add 25 ml of saturated $(NH_4)_2C_2O_4$ to precipitate $Ce_2(C_2O_4)_3$. Allow the precipitate to coagulate before removing the tube from the steam bath (3-5 min).

Step 16. Cool the precipitate for 15 min in an ice bath. Filter on a No. 42 Whatman filter circle, ½″ diameter, using a Hirsch funnel.

Step 17. Transfer the precipitate to a porcelain crucible and ignite at 800° for 30 min. Cool for 30 min and weigh as CeO_2 (Note 5).

Step 18. Mount on an Al plate in a centered depression, 5/16″ in diameter and 1/32″ deep. Count (Note 6).

Notes

1. In a strongly acid (HNO_3) medium, BrO_3^- ion oxidizes Ce (III) to Ce (IV).

2. Ce (IV) is reduced by H_2O_2 in acid medium. The oxidation-reduction cycle performed in Steps 1 and 2 promotes exchange between radiocerium and carrier.

3. If the concentration of HNO_3 is low, $La(IO_3)_3$ will also precipitate at this stage.

4. The $Zr(IO_3)_4$ scavenging step removes any Th and Pu isotopes which may be present, as well as active Zr.

5. CeO_2 should be white. If it is not white at this stage, decontamination from other rare earths is not complete.

6. If it is desired to obtain the mass 144 chain, count the samples immediately through 217 mg Al/cm^2 to cut out the 32.5-day ^{141}Ce and the 290-day ^{144}Ce betas. This gives only the activity from the 17.5-min ^{144}Pr. To eliminate 33-hr ^{143}Ce, one should allow 20 days from the end of bombardment before beginning the analysis. If it is desired to determine ^{141}Ce, it is best to count with no added absorber and use a least squares separation of the ^{141}Ce and ^{144}Ce-^{144}Pr activities.

CERIUM-144

J. W. Barnes

1. Introduction

The procedure described below has been successfully employed for the analysis of cerium-144. The major steps include: (a) an oxidation-reduction cycle in the presence of cerium carrier to insure exchange; (b) two by-product extractions from nitric acid solution with dibutyl phosphate (DBP) in carbon tetrachloride to remove contaminants such as zirconium, neptunium, thorium, plutonium, and uranium; (c) a cerium (III) fluoride precipitation; (d) the extraction of cerium (IV) into hexone; and (e) the final conversion of cerium to the dioxide. The chemical yield is 50-60%, and eight samples can be analyzed in 6-8 hr.

2. Reagents

Ce carrier: 12 mg Ce/ml, added as $(NH_4)_2Ce(NO_3)_6$ in 3*M* HNO_3, standardized
HNO_3: concd; 9*M*
HF: concd
H_3BO_3: saturated aqueous solution
NH_4OH: concd
$NaBrO_3$: 2*M*
$(NH_4)_2C_2O_4$: saturated aqueous solution
H_2O_2: 30%
Dibutyl phosphate (DBP): 5% in carbon tetrachloride (The DBP employed was obtained from the Victor Chemical Works, Chicago Heights, Ill.)
Hexone (4-methyl-2-pentanone)
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 47.8 g of $(NH_4)_2Ce(NO_3)_6$ in 190 ml of concd HNO_3 and dilute to 1 liter.

Pipet 5 ml of the cerium carrier solution into a 100-ml beaker and dilute to about 20 ml with H_2O. Warm on a steam bath and add about 50 ml of saturated $(NH_4)_2C_2O_4$ solution. Continue heating on the steam bath until the precipitate has coagulated. Cool in an ice bath for 15 min and filter through a filter funnel, using a No. 42 Whatman filter paper (11 cm). Ignite in a porcelain crucible at 800° for 30 min, cool, and weigh as CeO_2.

Four standardizations, with results agreeing within 0.5%, are carried out.

4. Procedure

Step 1. To 2 ml of Ce carrier in a 40-ml conical centrifuge tube, add the sample, then 3-5 drops of 2*M* $NaBrO_3$ and heat on a steam bath for 10 min. Dilute to 30 ml and add sufficient concd NH_4OH to precipitate $CeO_2 \cdot XH_2O$. Centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of concd HNO_3 and add 3-5 drops of 30% H_2O_2 and 7-8 ml of H_2O.

Step 2. Transfer the solution to a 60-ml pear-shaped separatory funnel and shake with about 25 ml of 5% DBP in carbon tetrachloride solution. Permit the layers to separate and drain off the organic (lower) layer. If the original sample contains uranium or plutonium, transfer the organic layer to the appropriate waste bottle. If these elements are absent, discard the organic layer.

Step 3. Repeat the extraction with another 25-ml portion of the 5% DBP, again appropriately disposing of the organic layer.

Step 4. Transfer the aqueous layer into a 40-ml conical centrifuge tube. Dilute to about 20 ml with H_2O, add 3-4 ml of concd HF, and stir well to permit the precipitate to coagulate. Centrifuge and discard the supernate. Wash the precipitate with about 20 ml of H_2O and discard the washings.

Step 5. Stir the precipitate with 1 ml each of concd H_3BO_3 and concd HNO_3, heating if necessary to obtain dissolution. Dilute to 20-30 ml with H_2O and add an excess of concd NH_4OH. Centrifuge and discard the supernate.

Step 6. Pretreat 50 ml of hexone with a mixture of 50 ml of 9*M* HNO_3 and 2 ml of 2*M* $NaBrO_3$ by shaking for about 1 min and discarding the aqueous layer. Dissolve the precipitate from Step 5 in 10 ml of 9*M* HNO_3 and add 2 ml of $2M$ $NaBrO_3$. Transfer to a 125-ml pear-shaped separatory funnel, add 50 ml of hexone and shake for about half a minute. Discard the aqueous layer. Wash the organic layer twice with 5 ml of $9M$ HNO_3 containing 2-3 drops of $2M$ $NaBrO_3$ and discard the washings. Back extract the cerium by shaking the hexone solution with 5 ml of H_2O containing a few drops of 30% H_2O_2. Discard the hexone layer.

Step 7. Add concd NH_4OH to the aqueous layer until an orange precipitate barely persists. Add concd HNO_3 dropwise until the precipitate dissolves, then add 10-15 ml of saturated $(NH_4)_2C_2O_4$. Stir briefly, cool, centrifuge, and discard the supernate. Transfer the precipitate by means of a stream of ethanol onto a No. 42 Whatman filter circle, 1" diameter, using a Hirsch funnel. Transfer the precipitate to a porcelain crucible and ignite at 800° for 30 min. Cool, weigh as CeO_2, mount, and β-count through a 217 mg cm^{2} Al absorber (Note).

Note

The procedure probably can be used for ^{143}Ce, although it has not been thoroughly checked out for this isotope.

CESIUM I

P. B. Elkin

This procedure is similar to one reported by L. E. Glendenin and C. M. Nelson. CN-1312 (May 15. 1945).

1. Introduction

In the separation of cesium from other fission-product activity, a preliminary precipitation of the element as the silicotungstate is carried out. This step gives a decontamination factor of 100 to 200, and is a specific separation of cesium from ammonium ion, rubidium, and the other alkali metals which may interfere in the determination of cesium as the perchlorate. The silicotungstate is dissolved in alkali and $CsClO_4$ precipitated from perchloric acid medium with absolute ethanol. The initial perchlorate precipitation is followed by two ferric hydroxide scavengings and two additional perchlorate precipitations. Cesium is finally filtered as the perchlorate, which is dried, weighed, and mounted for counting. The chemical yield is 60-70% and the time required for analysis in quadruplicate is about 8 hr.

2. Reagents

Cs carrier: 10 mg Cs/ml, added as CsCl in H_2O, standardized

Fe carrier: 10 mg Fe/ml, added as $Fe(NO_3)_3 \cdot 9H_2O$ in very dilute HNO_3

HCl: 6*M*; concd

HNO_3: concd

$HClO_4$: 70%

NaOH: 6*M*; pellets

NH_4OH: 6*M*

Silicotungstic acid: solid

Ethanol: absolute

Phenolphthalein indicator solution: 1% in 90% ethanol

3. Preparation and Standardization of Carrier

Dissolve 12.7 g of CsCl in H_2O and dilute to 1 liter with H_2O.

Pipet 5 ml of the above carrier solution into a 125-ml erlenmeyer flask and add 1 ml of concd HNO_3 and 5 ml of $HClO_4$. Boil until dense, white fumes appear, cool to room temperature, and add 15 ml of absolute ethanol. Cool for 15 min in an ice bath. Filter on a weighed sintered glass 15-ml Gooch crucible (fine porosity) and wash three times with 3-ml portions of absolute ethanol. Dry at 110° for 15 min, cool, and weigh as $CsClO_4$.

Four standardizations, with results agreeing within 0.5%, are run.

4. Procedure

Step 1. To 5 ml of carrier solution in a 40-ml short-taper centrifuge tube, add an aliquot of sample and make up to a volume of 40 ml, the final solution being 6*M* in HCl. (If the active solution contains HNO_3, evaporate (with carrier) to dryness and take up with 40 ml of 6*M* HCl.)

Step 2. Add about 2 g of silicotungstic acid dissolved in 2 ml of H_2O and let stand for at least 1 hr (preferably overnight). Centrifuge, discard the supernate, and wash the precipitate twice with 10-ml portions of 6*M* HCl.

Step 3. Dissolve the Cs precipitate by boiling with 2 ml of H_2O and adding 2 pellets of NaOH (about 0.24 g). Add H_2O, if necessary, to prevent boiling to dryness. Pour into 20 ml of hot 6*M* HCl in a 125-ml erlenmeyer flask and boil. Add 0.5 ml of concd HNO_3 and continue to boil. Add 10 ml of $HClO_4$ and boil until white fumes appear. Cool, and add 10 ml of H_2O, heat almost to boiling, and centrifuge in a 40-ml tube (Note 1).

Step 4. Pour the supernate into a 50-ml erlenmeyer flask, add 1 ml of concd HNO_3, and boil until white fumes appear. Cool to room temperature and transfer to a 40-ml centrifuge tube using 30 ml of absolute ethanol to aid in the transfer. Cool in an ice bath. Stir, let stand for 15 min, and centrifuge. *Immediately pour the supernate into the sink drain with running water.* Wash the precipitate twice with 10-ml portions of absolute ethanol (Note 2).

Step 5. Dissolve the precipitate in 10 ml of H_2O, heat to boiling, add 0.5 ml of Fe carrier, 2 drops of phenolphthalein indicator, and 6*M* NH_4OH dropwise until the solution is basic.

Centrifuge and transfer the supernate to a 40-ml centrifuge tube.

Step 6. Add 0.5 ml Fe carrier and again precipitate Fe$(OH)_3$. Centrifuge and pour supernate into a 50-ml erlenmeyer flask.

Step 7. Boil and remove NH_3 by adding 2 drops of 6*M* NaOH.

Step 8. Add 0.5 ml of concd HNO_3 and 5 ml of $HClO_4$. Boil until white fumes appear. Cool and transfer to a 40-ml centrifuge tube using 15 ml of absolute ethanol. Cool in an ice bath. Let stand for 15 min, centrifuge, dispose of the supernate as before (Step 4), and wash the precipitate twice with 10-ml portions of anhydrous ethanol.

Step 9. Dissolve the precipitate in 2 ml of H_2O, heating if necessary, and transfer to a 50-ml erlenmeyer flask. Wash centrifuge tube with 2 ml of H_2O and transfer washings to the 50-ml erlenmeyer flask. Heat to boiling to remove ethanol (1 min). Repeat Step 8, making sure to remove $HClO_4$ thoroughly by washing *twice* with ethanol.

Step 10. Slurry precipitate in 5 ml of absolute ethanol and filter on weighed filter paper circle, using a ground-off Hirsch funnel and filter chimney. Use absolute ethanol to complete transfer and to wash down sides of filter chimney. Dry at 110° for 15 min. Cool for 10 min, weigh, and mount. Count immediately (Note 3).

Notes

1. It is necessary to heat at this stage to insure rapid and complete dissolution of $CsClO_4$. Silica and tungstic oxide (WO_3) remain behind.

2. The $CsClO_4$ must be washed *thoroughly* with absolute ethanol to remove $NaClO_4$ which has coprecipitated.

3. If 13.7-day ^{136}Cs is to be determined in the presence of 33-year ^{137}Cs, gamma-counting with a scintillation counter is advantageous, since there are two gammas per disintegration for ^{136}Cs and only one for ^{137}Cs. A 400-mg Al cm^2 absorber will stop most of the betas which are emitted by both isotopes of Cs. The most practicable way of resolving the two components, ^{136}Cs and ^{137}Cs, is by a least squares determination.

CESIUM II

B. E. Cushing

1. Introduction

The procedure outlined below is based on the method of analysis described by Yamagata and Yamagata, *Analyst*, **85**, 282 (1960). Cesium is first precipitated as the silicotungstate. Dissolution of this precipitate is followed by a ferric hydroxide scavenge, and then the cesium is precipitated as the dipicrylaminate. This salt is dissolved in 4-methyl-2-pentanone and the cesium extracted by means of $2M$ hydrochloric acid. Cesium is finally precipitated as the perchlorate, in which form it is weighed and counted. The chemical yield approximates 70% and eight analyses can be performed in about 8 hr.

2. Reagents

Cs carrier: 10 mg Cs/ml, added as CsCl in H_2O, standardized
Fe carrier: 10 mg Fe/ml, added as $Fe(NO_3)_3 \cdot 9H_2O$ in very dilute HNO_3
$HClO_4$: $3M$; concd
HCl: $2M$; $6M$; concd
HNO_3: concd
NaOH: pellets
Silicotungstic acid: 1 g/ml H_2O
Sodium dipicrylaminate solution: Stir 25 g of dipicrylamine* with 500 ml of H_2O and add $6M$ NaOH until solution is complete. Allow the solution to stand for several hours and filter.
Ethanol: absolute
4-methyl-2-pentanone
Thymol blue indicator solution: Mix 100 mg of thymol blue with 2 ml of $0.1M$ NaOH and dilute to 100 ml with H_2O.

3. Preparation and Standardization of Carrier

Make up an aqueous solution containing 12.7 g of CsCl per liter. Pipet 5 ml of the solution into a 125-ml erlenmeyer flask and add 1 ml of concd HNO_3 and 5 ml of concd $HClO_4$. Boil until dense white fumes appear, cool to room temperature, and add 15 ml of absolute ethanol. Cool for 15 min in an ice bath. Filter on a weighed sintered glass 15-ml Gooch crucible (fine porosity) and wash three times with 3-ml portions of absolute ethanol. Dry at 110° for 15 min, cool, and weigh as $CsClO_4$.

Four standardizations gave results agreeing within 0.5%.

4. Procedure

Step 1. To the sample in a 40-ml centrifuge tube add 2 ml of Cs carrier and make the solution $6M$ in HCl by the addition of the concentrated acid. Add 2 ml of silicotungstic acid solution, stir, and let the mixture stand for 5-10 min. Centrifuge, discard the supernate, and wash the precipitate with 10 ml of $6M$ HCl.

Step 2. Add 2 ml of H_2O to the precipitate, heat to boiling, and then add 3 pellets of NaOH to dissolve the precipitate.

Step 3. Pour the alkaline solution into 20 ml of hot $3M$ $HClO_4$ in a 125-ml erlenmeyer flask. Boil over a burner until the volume is reduced to about 10 ml. Transfer to a 40-ml centrifuge tube and again heat to boiling. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate which consists of silica and tungsten(VI) oxide.

Step 4. Add 5 drops of Fe carrier, heat, and precipitate $Fe(OH)_3$ by adding NaOH pellets singly. Add a few drops of thymol blue indicator and continue to add NaOH until the solution turns blue. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

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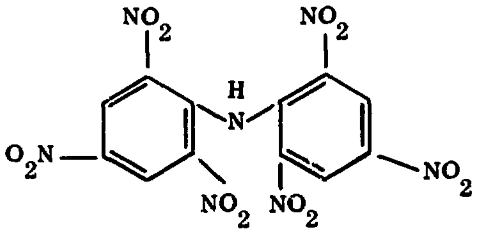
*Dipicrylamine:



Step 5. Cool the solution in an ice-water bath and add 10 ml of sodium dipicrylaminate solution with constant stirring. Continue to stir for 15 min and then place the tube in a refrigerator for at least 30 min.

Step 6. Filter through a fine sintered glass crucible. Wash the precipitate with 10 ml of ice cold water and dry in an oven at 110°.

Step 7. Dissolve the dry precipitate in about 20 ml of 4-methyl-2-pentanone, place the solution in a 60-ml separatory funnel, and add 20 ml of 2*M* HCl. Shake the funnel vigorously for 1 min and permit the aqueous layer to run into a 125-ml erlenmeyer flask. Extract the 4-methyl-2-pentanone solution two more times with 20-ml portions of 2*M* HCl and combine the aqueous extracts.

Step 8. To the aqueous extracts add 1 ml of concd HNO_3 and evaporate the solution to approximately 10 ml. Add 5 ml of concd $HClO_4$ and boil until dense white fumes are evolved.

Step 9. Cool and transfer to a 40-ml centrifuge tube using 20 ml of absolute ethanol to effect complete transfer. Cool in an ice bath, let stand for 15 min, and centrifuge. Wash the precipitate twice with 10-ml portions of absolute ethanol.

Step 10. Slurry the precipitate in 5 ml of absolute ethanol and filter onto a weighed No. 42 Whatman filter paper circle (1"), using a ground-off Hirsch funnel and filter chimney. Use absolute ethanol to complete the transfer of the $CsClO_4$ precipitate. Wash the precipitate several times with 5-ml portions of the alcohol. Dry at 110° for 15 min, cool for 10 min, weigh and mount. Count immediately.

chlorine, chromium, cobalt, curium

CHLORINE

W. H. Burgus

1. Introduction

In the determination of chlorine in the presence of fission products, considerable decontamination is achieved by ferric hydroxide scavenging and by precipitation of silver iodide from ammoniacal medium. Precipitation of silver chloride in the presence of Versene[*] is then performed, primarily to remove chlorine from alkaline earth metal ions but also to separate this element from many other activities. After additional decontamination, silver chloride is formed and the chlorine removed as hydrogen chloride by treatment with concentrated sulfuric acid. Chlorine is finally precipitated as the mercury (I) compound, in which form it is counted. The chemical yield is about 75% and a single analysis can be performed in 2½ hr.

2. Reagents

Cl^- ion carrier: 10 mg Cl^-/ml, NaCl used as primary standard
I^- ion carrier: 10 mg I^-/ml, added as KI in H_2O
Fe carrier: 10 mg Fe/ml, added as $Fe(NO_3)_3 \cdot 6H_2O$ in very dilute HNO_3
HNO_3: concd
HCHO: 37% aqueous solution
NH_4OH: concd
KOH: 10*M*
$AgNO_3$: 0.1*M*
$Hg_2(NO_3)_2$: 0.1*M* solution in dilute HNO_3
KNO_2: solid
Versene: disodium salt (analytical reagent grade, Bersworth Chemical Co.), 8% aqueous solution
CCl_4
C_2H_5OH: absolute

3. Procedure

Step 1. To the solution containing radioactive chlorine and fission products in a 40-ml conical centrifuge tube, add 1.0 ml of standard NaCl carrier. Then add 4-6 drops of Fe carrier and precipitate $Fe(OH)_3$ by the addition of a slight excess of concd NH_4OH. Centrifuge, transfer the supernate containing Cl^- ion to a clean centrifuge tube, and discard the precipitate (Note 1).

Step 2. To the supernate add 5 ml of concd NH_4OH and 4 drops of KI carrier solution. Precipitate AgI by the addition of a slight excess of 0.1*M* $AgNO_3$ solution. Coagulate the precipitate by heating, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 3. To the supernate again add 4 drops of KI carrier and remove a AgI by-product precipitate as in the previous step. However, this time filter the supernate through No. 40 Whatman filter paper (9 cm) in a 2", 60° funnel to ensure complete removal of AgI.

Step 4. To the filtrate add 5 ml of 8% Versene solution and slowly acidify with concd HNO_3 to precipitate AgCl. Boil to coagulate the precipitate, centrifuge, and wash the AgCl with 30-40 ml of H_2O containing 2 drops of concd HNO_3. Discard the supernate and washings.

Step 5. Dissolve the AgCl precipitate in 3 ml of concd NH_4OH, add 5 ml of an 8% Versene solution, dilute to 30 ml, and reprecipitate AgCl by the addition of concd HNO_3. Boil to coagulate the AgCl and wash as in the previous step.

Step 6. Dissolve the AgCl in 40 drops of concd NH_4OH, add 15 ml of H_2O, 10 drops of 10*M* KOH, and 10 drops of 37% HCHO. Heat to boiling to coagulate the metallic Ag precipitate. Add 4 drops of 0.1*M* $AgNO_3$ and again remove a Ag precipitate. Filter both Ag precipitates together through No. 40 Whatman filter paper in a 2", 60° funnel, collecting the filtrate in a 125-ml erlenmeyer flask.

Step 7. Acidify the filtrate with concd HNO_3, add an additional 2 ml of the acid, and heat to boiling (Note 2). Cool and add 4 drops of KI carrier solution. Transfer to a 125-ml separatory funnel, add 50 ml of CCl_4 and a few crystals of KNO_2. Extract I_2 into the CCl_4 layer

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[*] Versene (Bersworth Chemical Co.) is the disodium salt of ethylenediaminetetraacetic acid. Versene forms very stable soluble chelates with a large number of metallic ions

and discard. Add three separate additional 10 ml portions of CCl_4, extract I_2, and discard the CCl_4 layer after each extraction.

Step 8. To the remaining aqueous layer add 2-3 cc of concd HNO_3, transfer to a 40-ml centrifuge tube, and heat to boiling to remove excess NO_2^- ion. Add 4 drops of Fe carrier and precipitate $Fe(OH)_3$ with concd NH_4OH. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 9. Again add 4 drops of Fe carrier and remove a $Fe(OH)_3$ scavenger precipitate as in the previous step.

Step 10. To the Cl^--containing supernate add 0.1*M* $AgNO_3$ to precipitate AgCl. Centrifuge and wash the precipitate as in Step 4.

Step 11. Dissolve the AgCl precipitate in 2 ml of concd NH_4OH. Wash with several milliliters of H_2O into a special distilling flask (see *germanium procedure*). Bubble air through the solution to remove most of the NH_4OH. Cautiously add 6 ml of concd H_2SO_4 (Note 3) and heat until all the HCl has distilled over into a 50-ml beaker containing 20 ml of H_2O.

Step 12. Precipitate Hg_2Cl_2 from the solution of HCl distillate (after adding 1-2 ml of concd HNO_3) by the dropwise addition of 0.1*M* $Hg_2(NO_3)_2$ solution. Wash the precipitate with H_2O after filtering on a tared No. 42 Whatman filter circle, 7/8" diameter, using a ground off Hirsch funnel and a filter chimney. Wash with absolute C_2H_5OH and dry in an oven for 20 minutes at 110°. Cool, weigh, mount, and count (Note 4).

Notes

1. If the radiochlorine is originally in a form other than Cl^- ion or Cl_2, care must be taken to reduce it to one of these forms before beginning the procedure. Otherwise the radiochlorine may be lost as a result of its failure to exchange with Cl^- carrier. The total volume in Step 1 should not exceed 20 ml.

2. Boiling is necessary at this stage to remove most of the volatile HCHO.

3. Addition of concd H_2SO_4 precipitates AgCl. During distillation continue bubbling air through the solution.

4. Hg_2Cl_2 is used as the compound mounted in preference to AgCl because it does not form agglomerates as does AgCl. $PbCl_2$ is too soluble and therefore not suitable. For counting 4×10^5-year ^{36}Cl, a self-absorption curve should be constructed and corrections applied for a 0.72 Mev β^-.

CHROMIUM

W. H. Burgus

1. Introduction

In the analysis for radiochromium, exchange between active chromium and dichromate carrier is promoted by reduction of the latter to the +3 state. Some decontamination of the sample is then effected by acid sulfide scavenging when chromium is in the +3 state. After sulfide scavenging, chromium is oxidized to the +6 state and precipitated as barium chromate, which is then converted to the blue peroxy compound, CrO_5, by treatment with hydrogen peroxide in hydrochloric acid medium, in the presence of ethyl ether. The peroxy compound is extracted into the ether layer (effecting further decontamination), then back-extracted into aqueous ammonia, and barium chromate is again precipitated. After removal of any remaining radiobarium as the sulfate, followed by ferric hydroxide scavenging steps and precipitation of excess sulfate as barium sulfate, chromium is finally precipitated and counted as barium chromate. The chemical yield is 40-50%, and the time for a single analysis is 2-2½ hr.

2. Reagents

Cr carrier: 10 mg Cr/ml. 56.6 g $K_2Cr_2O_7$ per liter, primary standard
Pd carrier: 10 mg Pd/ml, added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl
Cu carrier: 10 mg Cu/ml, added as $CuCl_2 \cdot 2H_2O$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
HCl: concd; dilute (3 ml concd HCl/liter)
H_2SO_4: 3*M*
$HC_2H_3O_2$: 1*M*
NH_4OH: concd
H_2S: gas
H_2O_2: 30%
$Ba(NO_3)_2$: saturated solution
$NaBrO_3$: 1*M*
$NH_4C_2H_3O_2$: 1*M*
Aqueous SO_2 solution: saturated
Ethanol: 95%
Ethyl ether

3. Procedure

Step 1. To the sample in a 40-ml centrifuge tube, add 2 ml of standard Cr carrier. Dilute the solution to 15 ml, add 3 ml of concd HCl, and heat to boiling. Add saturated SO_2 solution dropwise until all of the $Cr_2O_7^{2-}$ has been reduced to Cr^{3+} ion. Boil off the excess SO_2.

Step 2. To the hot solution add concd NH_4OH dropwise to precipitate $Cr(OH)_3$. *Caution*: Do not use a great excess of NH_4OH (Note 1). Centrifuge the $Cr(OH)_3$ and discard the supernate.

Step 3. Dissolve the $Cr(OH)_3$ in 6-8 drops of concd HCl, dilute to 20 ml, heat to boiling, and reprecipitate $Cr(OH)_3$ with concd NH_4OH. Centrifuge and discard the supernate.

Step 4. Dissolve the $Cr(OH)_3$ in 6-8 drops of concd HCl, dilute to 20 ml, and add 4 drops each of Pd and Cu carriers. Heat to boiling and pass in H_2S for 5 min. Filter and discard the sulfide scavenger precipitate, retaining the Cr^{3+}-containing filtrate in a 40-ml centrifuge tube.

Step 5. Precipitate $Cr(OH)_3$ from the filtrate (Step 2), centrifuge, and discard the supernate.

Step 6. Dissolve the $Cr(OH)_3$ in 8 drops of concd HCl, boil out remaining H_2S, and dilute to 20 ml. Add 4 drops each of Pd and Cu carriers and remove another sulfide scavenging precipitate as before (Step 4). Filter and collect the filtrate in a 40-ml centrifuge tube.

Step 7. Repeat Step 5.

Step 8. Redissolve the $Cr(OH)_3$ from Step 7 in 8 drops of concd HCl, heat to boiling to remove H_2S, and reprecipitate $Cr(OH)_3$ with concd NH_4OH. Centrifuge and discard the supernate.

Step 9. Dissolve the $Cr(OH)_3$ in *only* 4-6 drops of concd HCl (Note 2). Add 15 ml of H_2O and about 6 ml of 1*M* $NaBrO_3$. Transfer quantitatively to a 125-ml erlenmeyer flask and heat over a flame until all the Cr^{3+} ion is oxidized to $Cr_2O_7^{2-}$. If the oxidation does not appear to be complete, additional $NaBrO_3$ should be added (Note 3).

Step 10. Add 3-4 ml of saturated $Ba(NO_3)_2$ solution and 3-4 ml of 1*M* $NH_4C_2H_3O_2$. This will result in the precipitation of $BaCrO_4$. If precipitation appears to be incomplete, one drop of concd NH_4OH should be added. Transfer to 40-ml centrifuge tube, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O, centrifuge, and discard the washings.

Step 11. Dissolve the $BaCrO_4$ in about 6 drops of concd HCl and 10 ml of H_2O. (Heating may be required.) Dilute to about 30 ml and reprecipitate $BaCrO_4$ with 1*M* $NH_4C_2H_3O_2$ as before (Step 10). Centrifuge, wash the precipitate with 30 ml of water, centrifuge, and discard the washings.

Step 12. Dissolve the $BaCrO_4$ in 10 ml of H_2O and 5 drops of concd HCl. Cool to 0-5° in an ice bath. Transfer to a 125-ml separatory funnel to which 90-100 ml of cold (below 5°) ethyl ether has been added. Add 3 drops of cold (below 5°) 30% H_2O_2 and *immediately* extract the blue peroxy compound CrO_5 into cold ether (Note 4). Discard the aqueous layer.

Step 13. Wash the ether layer four times with 10-ml portions of cold (about 5°) H_2O containing 3 ml of concd HCl per liter. Discard the washings.

Step 14. Back-extract into H_2O by shaking the ether with about 15 ml of H_2O containing 3 or 4 drops of concd NH_4OH. Transfer the aqueous layer to a 40-ml centrifuge tube.

Step 15. Add 2-3 ml of saturated $Ba(NO_3)_2$ solution to precipitate $BaCrO_4$. Centrifuge and wash with 30 ml of H_2O, discarding the supernate and washings.

Step 16. Dissolve the $BaCrO_4$ in 15 ml of H_2O and 8 drops of concd HCl. Heat to boiling and add 3 drops of 3*M* H_2SO_4. Centrifuge and discard the $BaSO_4$ precipitate. Transfer the supernate to a 40-ml centrifuge tube.

Step 17. Add 6 drops of Fe carrier to the supernate containing the $Cr_2O_7^{2-}$ ion and precipitate $Fe(OH)_3$ with concd NH_4OH. Centrifuge and discard the $Fe(OH)_3$, transferring the supernate to a 40-ml centrifuge tube. Acidify the supernate with HNO_3.

Step 18. Repeat Step 17 and heat the supernate to boiling.

Step 19. Add about 3 ml of saturated $Ba(NO_3)_2$ solution to remove SO_4^{2-} ion. Centrifuge the $BaSO_4$, discard the precipitate, and transfer the supernate to a 40-ml centrifuge tube.

Step 20. Precipitate $BaCrO_4$ from the supernate by the addition of concd NH_4OH. Dissolve in 6-8 drops of concd HCl and reprecipitate from 20 ml of solution by adding 3-4 ml of 1*M* $NH_4C_2H_3O_2$. Centrifuge and discard the supernate.

Step 21. Dissolve the $BaCrO_4$ in 5 drops of concd HCl. Dilute to 30 ml and add 1 ml of 1*M* $HC_2H_3O_2$. Heat to boiling and add 2 ml of 1*M* $NH_4C_2H_3O_2$ dropwise to precipitate $BaCrO_4$. Filter on a tared No. 42 Whatman circle (7/8" diameter), using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate three times with 15- to 20-ml portions of hot H_2O and then with ethanol. Dry for 10 min at 110°. Weigh, mount, and count immediately.

Notes

1. It is important to avoid the use of a large excess of concd NH_4OH to precipitate $Cr(OH)_3$, inasmuch as some of the latter will complex with NH_3 and go into solution.

2. The Cl^- and H^+ ion concentrations must be kept low to avoid reduction of the $Cr_2O_7^{2-}$ which is formed by oxidation of Cr^{3+} ion with BrO_3^-.

3. It is possible, visually, to determine whether oxidation of Cr^{3+} ion to $Cr_2O_7^{2-}$ is complete.

4. The formation and ether extraction of the blue peroxy compound CrO_5 must be carried out in the cold, otherwise the $Cr_2O_7^{2-}$ will merely oxidize the H_2O_2. Only a transient blue color is then observed.

COBALT

W. H. Burgus

1. Introduction

Cobalt is separated from most fission products and specifically from nickel by precipitation as potassium hexanitrocobaltate (III), $K_3Co(NO_2)_6$, from an acetic acid medium. The nitrate ion, in this acid medium, is not only the complexing agent but also serves to oxidize cobalt (II) to the +3 state. The second precipitation of cobalt as the hexanitro complex is followed by appropriate scavenging steps, and cobalt is then extracted as the blue $Co(SCN)_4^{2-}$ complex into an amyl alcohol-ethyl ether mixture, the extraction giving additional decontamination. The cobalt is back-extracted into an ammonia water solution and precipitated as the sulfide. The sulfide is then dissolved and cobalt is plated from strongly ammonical solution and counted as the metal. Some decontamination occurs during the plating process. The chemical yield is 70-75%. About 2 hr are required for the decontamination of a single sample, and 2½-3 hr for the plating process.

2. Reagents

Co carrier: 10 mg Co/ml, added as $Co(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3, standardized
Ni carrier: 10 mg Ni/ml, added as $Ni(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3
Pd carrier: 10 mg Pd/ml, added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl
Cu carrier: 10 mg Cu/ml, added as $CuCl_2 \cdot 2H_2O$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
HCl: concd
HNO_3: concd
H_2SO_4: concd
$HC_2H_3O_2$: 6*M*; 3*M*
KOH: 10*M*
NH_4OH: concd
NH_4SCN: solid; 1 g/2 ml H_2O
$(NH_4)_2SO_4$: solid
KNO_2: solid
H_2S: gas
Amyl alcohol-ethyl ether mixture: equal parts by volume
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 49.3 g of $Co(NO_3)_2 \cdot 6H_2O$ in H_2O, add 1 ml HNO_3, and dilute to 1 liter with H_2O.

Pipet 5.0 ml of the above carrier solution into a 125-ml erlenmeyer flask and add 5 ml of H_2O and 3 ml of concd H_2SO_4. Carefully boil down to copious SO_3 fumes to remove NO_3^- ion. Cool, dilute to 8-10 ml with H_2O, and allow the solution to come to room temperature. Cautiously neutralize with concd NH_4OH, then add 1 ml in excess and allow to cool to room temperature. Transfer the solution quantitatively to plating cell* and dilute to 15 ml with H_2O. Add about 2 g of solid $(NH_4)_2SO_4$, introduce rotating anode, and stir until the $(NH_4)_2SO_4$ has dissolved. Plate out Co with continuous stirring. The current is initially kept at 0.10 amp at about 3 v. During the first half hour of plating the current is gradually increased to 0.20 amp, which current is maintained for the remainder of the plating process. (The optimum plating time is at least 3 hr.) The cell is dismantled, the plate removed and washed several times with distilled H_2O and once with ethanol. It is then air-dried and weighed.

Four standardizations, with results agreeing within about 0.2%, are usually made.

4. Procedure

Step 1. To the sample in a 40-ml centrifuge tube, add sufficient H_2O to bring the volume to 20 ml. Add 3 ml of standard Co carrier and 1 ml of Ni carrier. Precipitate Co and Ni hydroxides by the addition of 10*M* KOH (Note 1). Centrifuge and wash the hydroxides with 15 ml of H_2O, discarding the supernate and washings.

Step 2. Dissolve the precipitate by warming

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*Plating cells: 5-mil Pt square cathode (preweighed), mounted on brass plate and held in position by ⅞" i.d. glass cylinder, with gasket between platinum and glass cylinder; rotating Pt anode; dc source; resistance in series with current source and cell. (One plating cell each per sample and standard.)

with 3 ml of 6*M* $HC_2H_3O_2$.Dilute to 25 ml with H_2O and cool to room temperature.

Step 3. Precipitate $K_3Co(NO_2)_6$ by addition of reagent made by saturating 6 ml of 3*M* $HC_2H_3O_2$ with KNO_2. Allow about 3 min for complete precipitation. Centrifuge, discard the supernate, wash the precipitate once with 30 ml of H_2O, and discard the washings.

Step 4. Dissolve the $K_3Co(NO_2)_6$ by the addition of several milliliters of concd HCl. Boil off the decomposition products. Add 1 ml of Ni carrier and dilute to 25 ml with H_2O.

Step 5. Precipitate Co and Ni hydroxides with 10*M* KOH as in Step 1. Dissolve the hydroxides as in Step 2.

Step 6. Repeat Step 3.

Step 7. Dissolve the $K_3Co(NO_2)_6$ in 4-5 ml of concd HCl, boiling almost to dryness. Add 2 drops of Pd and 4 drops of Cu carriers. Dilute to 20 ml with H_2O and make about 0.1*M* in HCl. Heat to boiling and pass in H_2S for 5 min. Filter onto No. 40 Whatman filter paper, catching the filtrate in a 125-ml erlenmeyer flask and discarding the sulfide scavenging precipitate.

Step 8. Boil out H_2S from the filtrate. Add 2 drops Pd and 4 drops of Cu carriers and dilute to 20 ml with H_2O. Make 0.1*M* in HCl, heat to boiling, and pass in H_2S for 5 min. Again remove sulfides by filtration (Step 7).

Step 9. Boil out H_2S from filtrate. This will require concentration almost to dryness (Note 2). Dilute to 25 ml with H_2O and transfer quantitatively to 40-ml centrifuge tube. Add 4 drops of Fe carrier and precipitate $Fe(OH)_3$ by addition of concd NH_4OH, adding about 0.5 ml of NH_4OH in excess. Centrifuge and discard $Fe(OH)_3$ scavenge, retaining the supernate.

Step 10. Acidify the supernate with HCl. Add 4 drops of Fe carrier and remove $Fe(OH)_3$ again by the addition of concd NH_4OH (0.5 ml excess). Centrifuge and discard the precipitate.

Step 11. Repeat Step 10.

Step 12. Acidify the supernate from Step 10 with concd HCl, adding 1 ml in excess. Transfer to 125-ml separatory funnel. Add 15 g of NH_4SCN and shake until all the solid has dissolved. Extract the Co-SCN complex into 50 ml of amyl alcohol-ethyl ether mixture. Wash the organic layer twice with 10-ml portions of NH_4SCN solution. Discard washings.

Step 13. Back-extract the Co into 20 ml of H_2O to which 4 to 6 ml of concd NH_4OH has been added. Discard the organic layer and transfer the aqueous layer to a 40-ml centrifuge tube.

Step 14. Precipitate CoS from solution by passing in H_2S for 1 min. Centrifuge and discard the supernate.

Step 15. Transfer the CoS precipitate with 5-10 ml of H_2O to a 125-ml erlenmeyer flask. Add 10 ml of concd HNO_3. Boil nearly to dryness (1-2 ml). Add 3 ml of concd H_2SO_4 and heat to SO_3 fumes. Cool and slowly add 5-10 ml of H_2O. Cool again. Neutralize with concd NH_4OH and add 1 ml in excess. Add 2 g of $(NH_4)_2SO_4$, transfer to plating cell and electroplate Co on a weighed Pt foil. (For a circular foil about ⅞" diameter begin plating at 3-4 v and 0.10 amp. After the first half hour increase current to 0.20 amp. Plate for 2½-3 hr.) After plating, wash with distilled water and then with ethanol. Dry at room temperature, weigh, and count. The counting procedure is dependent on the isotope involved.

Notes

1. The purpose of the initial precipitation by means of KOH is to remove the Co from the strongly acid solution. For as complete a precipitation of $K_3Co(NO_2)_6$ as possible, mineral acids and oxidizing agents must be absent.

2. The H_2S is removed by boiling to prevent precipitation of Co as CoS when the $Fe(OH)_3$ scavenging step is made.

CURIUM-242

J. W. Barnes

1. Introduction

In this procedure, curium is sufficiently decontaminated from other activities so that a pulse analysis of the final product gives the ratio of the unknown quantity of ^{242}Cm present to the known quantity of added ^{244}Cm tracer. The procedure has the advantage over one which utilizes an HCl-cation column in that an equally effective separation of curium from rare earth activities can be obtained with less time and effort. This procedure does not separate americium and curium from other trivalent actinides.

In the analysis, the first major step is the adsorption of some of the impurities on an anion column from concentrated hydrochloric acid. The curium is then adsorbed on an anion column as a thiocyanate complex from 5*M* ammonium thiocyanate at pH 1.5. This step gives effective decontamination from alkali and alkaline earth metal activities. The rare earths are poorly adsorbed, and any that are fixed on the column are eluted by washing with ammonium thiocyanate solutions. The curium is finally removed from the column by elution with a more dilute ammonium thiocyanate solution and is collected on a platinum disk. After drying and ignition at red heat, the sample is pulse analyzed.

2. Reagents

Y carrier: 10 mg Y/ml, added as $Y(NO_3)_3 \cdot 6H_2O$ in H_2O
^{244}Cm standard solution: 100-1000 c/min/ml
$HClO_4$: concd
HCl: concd; 3*M*
HNO_3: concd
NH_4OH: 3*M*
NH_4CNS: 5*M*; 1*M*, in a 3:1 ethanol to H_2O mixture
Solution "A": a mixture containing 2-3 drops of concd HNO_3 to 15 ml of concd HCl
Ethanol: 95%
Hydrion paper: pH range 1.2-2.4
Dowex DI-X8, 100-200 mesh anion resin
Dowex DI-X2, 200-400 mesh anion resin

3. Procedure

Step 1. To the ^{244}Cm tracer (Note 1) in a 50-ml erlenmeyer flask, add an aliquot of the sample, 3 drops of Y carrier, and 0.5-0.7 ml of concd $HClO_4$. Boil to dryness and allow to cool.

Step 2. Prepare a column 6 mm by 7-8 cm of Dowex anion resin DI-X8, 100-200 mesh, and pretreat with 3-5 ml of Solution "A". Dissolve the dry residue from Step 1 in 1-2 ml of Solution "A" (do not heat, even though all the solid does not dissolve) and pass the resulting solution through the resin column and ignore any precipitate. Rinse the erlenmeyer flask with 1 ml of Solution "A" and pass the rinsings through the column. Collect the effluent and the wash in a 50-ml erlenmeyer flask, add 0.5 ml of concd $HClO_4$, and fume to dryness. Cool.

Step 3. Prepare a column 3.5 mm by 7-8 cm of Dowex anion resin DI-X2, 200-400 mesh, and wash the column with 2 ml of 5*M* NH_4CNS. Add 2 ml of 5*M* NH_4CNS to the dry residue in the erlenmeyer flask and swirl to obtain solution. With the use of Hydrion paper (pH range 1.2-2.4) and 3*M* NH_4OH and 3*M* HCl, adjust the pH to about 1.5. Add the solution to the anion column and push it through at the rate of 1 drop every 7-15 sec. Rinse the top of the column with 2 ml of 5*M* NH_4CNS which has been adjusted to pH 1.5 with 3*M* HCl and push this solution through at the same rate. Make up a 1*M* NH_4CNS solution in a 3:1 ethanol to H_2O mixture and adjust the pH to 1.5 with 3*M* HCl. Wash the column with 3 ml of this solution and collect the washings in a clean 40-ml conical centrifuge tube. (This wash is kept as a precaution in case Cm happens to be eluted at this stage.) Dilute the 1*M* NH_4CNS solution with an equal volume of H_2O and add 1 drop of concd HCl for each 4 ml of the resulting solution. Pass 1 ml of the final solution through the column and collect the eluate in a clean 40-ml conical centrifuge tube.

Step 4. Transfer this eluate, which contains the Cm activity, to a Pt disk (1¾" diameter) on a brass ring on a hot plate. Turn up the heat, gently at first, and evaporate the liquid on the Pt disk to dryness. When the disk is dry, adjust the hot plate to its maximum heat and volatilize the NH_4CNS. Finally, heat the disk to redness in a Fisher burner flame. Place the disk in the pulse analyzer and count (Note 2).

Notes

1. The quantity of ^{244}Cm tracer employed is 3-5 times that of the estimated ^{242}Cm content of the aliquot.

2. If the pulse analysis curve is unsatisfactory because of too much β-γ activity, the material on the Pt disk must be further purified. This is accomplished in the following manner. Warm the disk under a heat lamp with several small portions (each approximately 0.5 ml) of Solution "A". Pass the resulting solution through a Dowex DI-X8 column as in Step 2. Complete Step 2 and the rest of the procedure. If experience with gamma readings on the final eluate from Step 3 indicates that further purification is necessary, do not dry the eluate. To the eluate add sufficient solid NH_4CNS to make the solution 4-5*M* in the salt. Pour the solution onto a clean Dowex DI-X2 column as in Step 3 and repeat this step.

germanium, gold

GERMANIUM

R. J. Prestwood

1. Introduction

In the separation of radiogermanium from other fission products, acid sulfide, lanthanum fluoride, and barium sulfate scavengings are performed in the presence of fluoride ion which keeps germanium in solution as the GeF_6^{2-} ion. The fluo complex is then decomposed and germanium distilled as the tetrachloride in a specially designed multiple still. Germanium is finally precipitated and mounted as the sulfide GeS_2. The chemical yield is 80-90% and the analysis of samples in quadruplicate requires about 4 hr.

2. Reagents

Ge(IV) carrier: 10.00 mg Ge/ml, see *Preparation of Carrier*
As carrier: 10 mg As/ml, added as $Na_3AsO_4 \cdot 12H_2O$ in H_2O
Ba carrier: 10 mg Ba/ml, added as $Ba(NO_3)_2$ in H_2O
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Cu carrier: 10 mg Cu/ml, added as $Cu(NO_3)_2 \cdot 6H_2O$ in H_2O
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
HCl: 4.5-5.5*M*; concd
HI: 47% aqueous solution
H_2SO_4: concd
HF: concd
H_3BO_3: saturated solution
NH_4OH: concd
H_2S: gas
CH_3OH: anhydrous

3. Preparation of Carrier

Fuse 14.4092 g of CP GeO_2 with 30.0 g of Na_2CO_3. Dissolve the melt in H_2O and dilute to 1 liter. Permit to stand for 24 hr and filter. The solution contains 10.00 mg Ge/ml and is used as a primary standard.

4. Procedure

Step 1. To the sample in a 125-ml erlenmeyer flask add the following: 2 ml of standard Ge carrier; 1 ml of As carrier; 1 ml of Ba carrier; 1 ml of Cu carrier; 1 ml of La carrier; 2 ml of 47% HI solution; and 1 ml of concd HF. Make the solution neutral by the addition of concd NH_4OH, add 10-20 drops of concd H_2SO_4, place on a steam bath, and saturate with H_2S for a few minutes.

Step 2. Filter into a clean 125-ml erlenmeyer flask through No. 40 Whatman filter paper in a 2″, 60° funnel. Wash the precipitate with a small quantity of water. Discard the precipitate.

Step 3. To the filtrate add 10 drops of La carrier and 1 ml of Cu carrier and saturate with H_2S on a steam bath. Filter as in Step 2 and wash the precipitate.

Step 4. To the filtrate add 1 ml of Cu carrier and saturate with H_2S in the cold. Filter as in Step 2 and wash the precipitate.

Step 5. Repeat Step 4.

Step 6. To the filtrate add 10 ml of concd HCl and 10 ml of saturated H_3BO_3, and saturate with H_2S. Transfer to 40-ml conical centrifuge tube, centrifuge the GeS_2 precipitate, and discard the supernate (Note 1).

Step 7. Dissolve the GeS_2 in 1 ml of concd NH_4OH and dilute to 15-20 ml with H_2O. Add 4 drops of Zr carrier, centrifuge, and discard the precipitate. Make the supernate 3*M* with HCl, saturate with H_2S, centrifuge, and discard the supernate.

Step 8. Slurry the GeS_2 with 4.5-5.5*M* HCl (Note 2) and transfer the solution to the special still (see figure). The total volume of acid used should be about 15 ml.

Step 9. Distill the $GeCl_4$ on an oil bath at 120° into a 50-ml beaker containing 5 ml of 4.5-5.5*M* HCl saturated at room temperature with H_2S and placed in an ice bath (Note 3). $GeCl_4$ begins to distill over after 15-20 min and then the distillation must be maintained for 10-15 min more to ensure completion. Almost 100% yield is obtained.

Step 10. Transfer the distillate to another special still and repeat the distillation.

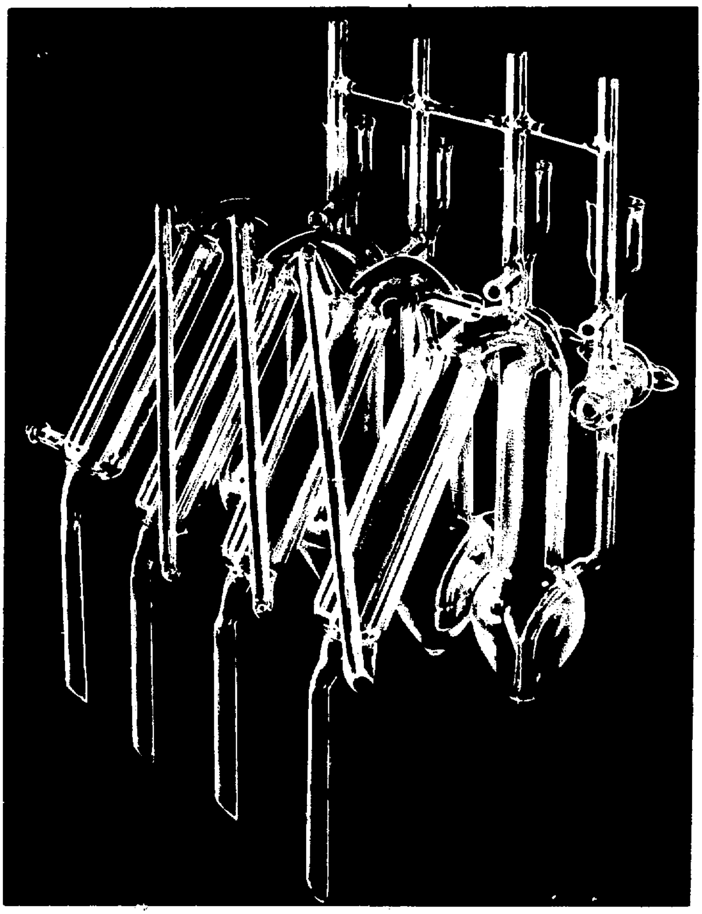
Step 11. Saturate the receiver with H_2S and filter the precipitate onto a weighed No. 42 Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with anhydrous CH_3OH and dry in an oven at 110-120° for 10 min. Cool, weigh as GeS_2, and mount.

Notes

1. A water-clear supernate is not ordinarily obtained upon centrifugation of the GeS_2 unless the mixture is permitted to stand for several hours. Since it is not practicable to wait so long and since the losses are insignificant, do not hesitate to discard a slightly turbid supernate from a GeS_2 precipitation.

2. The concentration of HCl must not exceed that of the constant boiling mixture or $GeCl_4$ will escape during the distillation unless the delivery tube is below the surface of the receiving liquid. If the HCl concentration in the still is less than that required for the constant boiling mixture, only water and no $GeCl_4$ is distilled. As soon as the composition of the still reaches that of the constant boiling mixture, all the $GeCl_4$ comes over rapidly. At higher HCl concentrations the $GeCl_4$ is immediately swept out with HCl gas.

3. The H_2S is present in the receiver to show (by the formation of white GeS_2) when $GeCl_4$ begins to distill.



Special distilling flask.

GOLD

G. A. Cowan

1. Introduction

Gold is separated from most fission-product activities by reduction to the metal by means of hydrogen iodide in hydrochloric acid solution in the presence of sulfosalicylic acid. The latter serves to complex strongly and therefore holds back many of the ions found in fission-product solutions. The precipitated gold is further decontaminated by dissolution in aqua regia, followed by silver chloride and ferric hydroxide scavenging precipitations. Last traces of contaminating activities are removed by extraction of gold (III) chloride from 1*M* HCl into ethyl acetate. The tripositive gold is finally converted by hydrogen iodide reduction to the metallic state in which form it is counted. The chemical yield is approximately 75% and one sample can be analyzed in about 3 hr.

2. Reagents

Au carrier: 10 mg Au/ml, added as $AuCl_3$ in about 0.1*M* HCl, used as a primary standard
Ag carrier: 10 mg Ag/ml, added as $AgNO_3$ in H_2O
Te carrier: 10 mg Te/ml, added as $H_2TeO_4 \cdot 2H_2O$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in 1*M* HCl
HCl: 1*M*; 2*M*; concd
HNO_3: concd
HI: concd
NaOH: concd
Sulfosalicylic acid: 5% in H_2O
Ethyl acetate: CP

3. Preparation and Standardization of Carrier Solution

Dissolve 10.0 g of pure Au metal in a minimum quantity of aqua regia. Evaporate the solution nearly to dryness in the presence of excess HCl and dilute to 1 liter with 0.1*M* HCl. The solution is used without further standardization.

4. Procedure

Step 1. To the sample (Note 1) contained in 20 ml of 1*M* HCl in a 40-ml conical centrifuge tube, add 2 ml of 5% sulfosalicylic acid solution, 2.00 ml of Au carrier, 1 drop of Te^{6+} holdback carrier (Note 2), and 1.5 ml of concd HI. Heat on a steam bath for 10-15 min. Centrifuge and discard the supernate.

Step 2. Wash out chloride ion by filling the centrifuge tube with H_2O and decanting. Repeat. Digest the Au precipitate with 1 ml of concd HNO_3, boiling for 1 min in the hood. Centrifuge and discard the supernate.

Step 3. Fill the tube with H_2O and decant. Dissolve the precipitate in 2 ml of concd HCl and 3 or 4 drops of concd HNO_3. Boil off all the HNO_3.

Step 4. Dilute to 20 ml with 1*M* HCl and repeat Steps 1 to 3 twice.

Step 5. Dilute the solution to 20 ml with 1*M* HCl and add 3 drops of Ag carrier. Centrifuge and transfer the supernate to another 40-ml centrifuge tube, discarding the AgCl precipitate.

Step 6. Add 4 drops of Fe carrier and then a slight excess of concd NaOH. Without delay, centrifuge and transfer the supernate to a clean 40-ml centrifuge tube, discarding the $Fe(OH)_3$ precipitate. Immediately reacidify the supernate with concd HCl (Note 3).

Step 7. Add 1.5 ml of concd HI and reprecipitate metallic Au as before (Step 1). Dissolve the precipitate in a minimum amount of aqua regia.

Step 8. Wash the solution into a 125-ml separatory funnel with about 40 ml of 1*M* HCl. Extract with 25 ml of ethyl acetate. Wash the ethyl acetate layer twice with 5-ml portions of 2*M* HCl.

Step 9. Transfer the ethyl acetate extract to a 125-ml erlenmeyer flask and remove the ethyl acetate on a steam bath. Add 25 ml of 1*M* HCl and 1.5 ml of concd HI. Heat on steam bath for 10-15 min to precipitate metallic Au.

Step 10. Filter the Au on a weighed No. 41 H Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with 1*M* HCl, and then with acetone. Dry for 15 min at 110°. Cool, weigh, and mount (Note 4).

Notes

1. If any oxidizing acids are present in the original sample, they must be removed prior to reduction with HI.

2. Te^{4+} carrier is added since reduction to the +4 state by HI promotes exchange with active species.

3. Although Au (III) is amphoteric, considerable Au is lost by precipitation of the hydrous oxide if the solution is kept strongly alkaline for an hour or more after the $Fe(OH)_3$ scavenging step.

4. This procedure has been used for the determination of 2.69-day ^{198}Au. Counting is carried out in a proportional counter and is begun immediately upon completion of the chemistry.

indium, iron

INDIUM

G. A. Cowan

1. Introduction

In its determination in fission products, indium is first separated rapidly from cadmium so that a separation time from its parent activity is accurately known. The separation is accomplished by precipitation of indium hydroxide by means of ammonium hydroxide; cadmium remains in solution as an ammonia complex. The hydroxide is then dissolved and acid-insoluble sulfides are precipitated from a buffered solution (pH 3-4) in the presence of sulfosalicylic acid. Indium is leached from the mixture of sulfides with cold 1*M* HCl and is then precipitated as the hydroxide and converted to the bromide by means of 4.5*M* hydrogen bromide. The bromide is extracted into ethyl ether and indium is finally precipitated and weighed as the 8-hydroxyquinoline (oxine) derivative.* The chemical yield is about 50% and one sample can be run in about 4 hr.

2. Reagents

In carrier: 10 mg In/ml, added as $InCl_3$ in 1.5*M* HCl, standardized

Sb carrier: 10 mg Sb/ml, added as $SbCl_3$ in 1*M* HCl

Cd carrier: 10 mg Cd/ml, added as $CdCl_2$ in 1*M* HCl

HCl: 1*M*; 1.5*M*

HBr: 4.5*M*

NH_4OH: concd

H_2S: gas

Buffer solution: (1*M* $HC_2H_3O_2$ - 2*M* $NaC_2H_3O_2$)

Sulfosalicylic acid: 5% in H_2O

8-hydroxyquinoline: 5% in 2*M* $HC_2H_3O_2$

Ethyl ether: saturated with 4.5*M* HBr

3. Preparation and Standardization of Carrier

Dissolve 10.0 g of pure In metal in a minimum of HCl and dilute to 1 liter with 1.5*M* HCl.

Pipet 2.00 ml of the above solution into a 100-ml beaker, and add 20 ml of H_2O, 5 ml of $HC_2H_3O_2$ - $NaC_2H_3O_2$ buffer solution, and 2 ml of 8-hydroxyquinoline solution. Permit the precipitate to settle and add 8-hydroxyquinoline solution dropwise to the supernate until no further precipitation occurs. Filter the precipitate on a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate thoroughly with H_2O and dry at 110° for ½ hr. Cool and weigh as $In(C_9H_6NO)_3$ (20.99% In).

Three standardizations, with results agreeing within 0.5%, are run.

4. Procedure

Step 1. To 5-20 ml of sample in a 40-ml conical centrifuge tube, add 2.00 ml of In carrier, 2 drops of Cd holdback carrier, and an excess of concd NH_4OH. Centrifuge the precipitate and discard the supernate.

Step 2. Dissolve the precipitate in 20 ml of 1*M* HCl and repeat Step 1 twice.

Step 3. Dissolve the precipitate in 10 ml of 1*M* HCl and add 2 ml of 5% sulfosalicylic acid, 5 ml of $HC_2H_3O_2$ - $NaC_2H_3O_2$ buffer solution, and 1 drop of Sb carrier. Saturate the solution with H_2S, keeping the solution cold. Centrifuge and discard the supernate.

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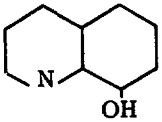
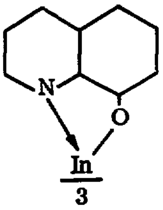
*When 8-hydroxyquinoline (oxine)



is used as a precipitant, the hydrogen of the hydroxyl group is replaced by one equivalent of metal ion. Thus indium forms the following compound:



This compound is insoluble in aqueous medium but soluble in the usual organic solvents.

Step 4. Wash the precipitate with 5 ml of diluted (1:10) buffer solution, centrifuge, and discard the supernate.

Step 5. Add 5 ml of 1*M* HCl and digest just at boiling for 1 min. Centrifuge and transfer the supernate to a clean 40-ml centrifuge tube. Discard the precipitate.

Step 6. Dilute the solution to 10 ml with H_2O and repeat Steps 3 through 5 three times.

Step 7. To the solution containing $InCl_3$ in 1*M* HCl, add an excess of concd NH_4OH and centrifuge. Discard the supernate.

Step 8. Dissolve the precipitate in 25 ml of 4.5*M* HBr, transfer the solution to a 125-ml separatory funnel, and extract $InBr_3$ into 50 ml of ethyl ether which is saturated with 4.5*M* HBr. Discard the aqueous layer and wash the ether layer twice with 10-ml portions of 4.5*M* HBr.

Step 9. Draw off the ether into a 250-ml erlenmeyer flask. Evaporate the ether on a steam bath and take the residue up in 20 ml of 1*M* HCl. Add 5 ml of buffer solution and 2 ml of 8-hydroxyquinoline reagent. Test for completeness of precipitation by the addition of another drop of reagent to the clear supernate. Filter on a weighed No. 41H Whatman filter circle, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate thoroughly with water and dry at 110° for ½ hr. Cool, weigh, and mount. Count immediately in a proportional counter (Note).

Note

This procedure has been used for the determination of 4.5-hr ^{115}In, daughter product of 58-hr ^{115}Cd.

IRIDIUM

J. S. Gilmore

1. Introduction

In this procedure for the analysis of radioactive iridium in dirt samples, the major steps include: (a) fuming with concd $HClO_4$, a process which converts the iridium to polynuclear cationic species in which the element is in at least the +4 oxidation state, (b) adsorption of the complexed iridium on a cation exchange resin, followed by elution with 4.5*M*HCl; (c) conversion of the element to anionic chloro complexes and passage of the latter in 0.05*M*HCl through a cation column (the two exchange resin steps essentially remove all contaminants except the other platinum metals and molybdenum and tellurium); (d) extraction of molybdenum from solution in 7*M* HCl into diisopropyl ether; (e) separation of tellurium by reduction to the elemental state with sulfur dioxide; (f) distillation of ruthenium as RuO_4 from fuming $HClO_4$; (g) oxidation of iridium to the tetrapositive state by means of HNO_3 and extraction into TBP (tributyl phosphate) in *n*-hexane, leaving rhodium(III) behind; (h) reduction of iridium to the +3 state and extraction of dipositive palladium and platinum as iodide complexes into TBP-*n*-hexane; and (i) oxidation of iridium to the +4 condition and precipitation as Cs_2IrCl_6, the form in which it is mounted for counting. Chemical yields of about 50% are obtained.

The following literature references proved helpful in the development of the procedure: F. H. Faye and W. R. Inman, Anal. Chem., 35, 985 (1963); and A. F. Marks and F. E. Beamish, *ibid* 30, 1464 (1958).

2. Reagents

Ir Carrier: yields 10 mg of Cs_2IrCl_6/ml. Weigh out 3.596 g of K_2IrCl_6 (previously dried to constant weight at 110°) and dissolve in 500 ml of 2*M* HCl.
Mo carrier: 10 mg Mo/ml, added as $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in 6*M* HCl
Te carrier: 10 mg Te/ml, added as Na_2TeO_3 in dilute HCl
Rh carrier: 10 mg Rh/ml, added as Na_3RhCl_6 in 1*M* HCl
HCl: 0.05*M*; 1*M*; 4.5*M*; 6*M*; concd
1*M* HCl - 0.1*M* HF
HNO_3: concd
$HClO_4$: concd
NaOH: 6*M*
KI: 4% aqueous solution
CsCl reagent: 4 g in 60 ml of 6*M* HCl
KCl: solid
TBP reagent: 50% by volume in *n*-hexane
n-Hexane
Diisopropyl ether
SO_2: gas
Ethanol: absolute
Dowex AG 50W-X8 cation exchange resin, 100-200 mesh

3. Procedure

Step 1. To the sample of pulverized dirt (1-25 g) in a Teflon beaker add 3 ml of Ir carrier and dissolve the material in a mixture of concd HNO_3, $HClO_4$, and HF. Fume down to a low volume of $HClO_4$ and to the cooled mixture add sufficient H_2O to make the solution 2*M* in $HClO_4$.

Step 2. Prepare a cation exchange resin bed, 8 mm x 10 cm, in a polycarbonate column fitted with a plug of Teflon turnings to support the resin. Wash the resin successively with 4.5*M* HCl, H_2O, and 1*M* $HClO_4$ and transfer the solution from Step 1 to the top of the column. Permit the solution to pass through, wash the column with 60 ml of 1*M* HCl-0.1*M* HF, and then with 10 ml of 1*M* HCl. Discard the eluate. Add 40 ml of warm 4.5*M* HCl to the resin column and collect the eluate in a 150-ml beaker.

Step 3. Add 3 drops of Mo and 1 ml of Te carriers and heat on a hot plate for 10 min. Transfer the solution to a 125-ml separatory funnel with sufficient HCl to make the final solution about 7*M* in acid. Extract twice with 50 ml of diisopropyl ether, discard the organic (upper) phase, and transfer the aqueous layer to a 150-ml beaker. Evaporate to a small volume on a hot plate (with the aid of an air jet), add 2-3 drops of concd HNO_3, and then evaporate to dryness on a steam bath.

Step 4. Prepare a cation resin bed, 8 mm x 15 cm, in a glass column. Wash the resin with 4.5*M* HCl and then with 0.05*M* HCl. Transfer the residue from Step 3 to the resin with 15 ml of 0.05*M* HCl and collect the eluate in a 125-ml erlenmeyer flask. Wash the resin with 5 ml of 0.05*M* HCl and combine the eluate with the previous one.

Step 5. Add 10 ml of concd HCl and 1 ml of Te carrier to the combined eluates and saturate the hot solution with SO_2. Filter off the Te precipitate and collect the filtrate in a 125-ml erlenmeyer flask. Boil to expel SO_2.

Step 6. Add 5 ml of concd $HClO_4$ and 2 ml of concd HNO_3 and evaporate to dense fumes of $HClO_4$. (RuO_4 volatilizes.)

Step 7. Dilute the solution to 2*M* in $HClO_4$ and repeat Step 2.

Step 8. Add 2 drops of Rh carrier and about 40 mg of KCl. Heat to effect solution and then evaporate to dryness in a steam bath. Add 3 ml of concd HCl and 3 drops of concd HNO_3, and evaporate to dryness again. Repeat the last evaporation process. (Ir is converted to $IrCl_6^{2-}$.) Dissolve the residue in 10 ml of 6*M* HCl and transfer the solution to a 60-ml separatory funnel, using an additional 10 ml of 6*M* HCl. Add 20 ml of TBP reagent, shake for 1 min, and transfer the organic (upper) layer to a 40-ml glass centrifuge tube. Add 2 drops of concd HNO_3 to the aqueous phase, repeat the extraction with TBP, combine the organic phases and discard the aqueous. Centrifuge and remove the trace of aqueous layer with a transfer pipet. To the combined organic phases add 2 ml of 6*M* HCl, let the mixture settle, and remove and discard the aqueous layer.

Step 9. Transfer the organic layer to a 125-ml separatory funnel, add 1 ml of 4% KI, shake, and allow to stand for 10 min. Add 20 ml of 6*M* HCl, shake well, and discard the organic phase. Add 20 ml of TBP reagent, shake, and discard the organic phase. Wash the aqueous phase with two 30-ml portions of *n*-hexane and discard the washes.

Step 10. Repeat Step 8 omitting the addition of Rh carrier and KCl.

Step 11. Transfer the organic layer to a 125-ml separatory funnel. Back-extract the Ir with two 40-ml water washes and discard the organic phase. Wash the aqueous phase twice with 30-ml portions of *n*-hexane and discard the washes. Transfer the aqueous phase to a 150-ml beaker, add 5 ml of concd HCl and a few drops of concd HNO_3, and evaporate to near dryness on a hot plate, using an air jet. Then evaporate to dryness in a steam bath.

Step 12. Prepare and wash a cation resin column as in Step 4. Transfer the residue from Step 11 to the column with 10 ml of 0.05*M* HCl and collect the eluate in a 40-ml Vycor centrifuge tube. Wash the column with 10 ml of 0.05*M* HCl and combine the eluate with the previous one. Stir well and transfer one-half of the solution to a second 40-ml Vycor tube. To each tube add 10 ml of concd HCl and 1 ml of CsCl reagent and heat for 2 hr in a steam bath, adding HCl as needed to prevent evaporation to less than 10 ml. Occasionally add 1 drop of concd HNO_3. Centrifuge and discard the supernates. Wash each precipitate with 10 ml of 6*M* HCl, twice with ethanol, and discard the washes. With the use of ethanol as the transfer agent, filter one of the precipitates onto a No. 42 Whatman filter circle, 14-mm diameter, using a ground-off Hirsch funnel-filter chimney setup. Dry the precipitate at 110° for 10 min, weigh, mount, and count on an L x-ray counter. Carefully evaporate the last traces of ethanol from the second precipitate, dry it in centrifuge tube at 110° for 15 min, transfer to a previously weighed Teflon vial for NaI-well counting, and weigh (Note).

Note

1. The isotope of mass 190 is determined from the part of the gamma spectrum with energy greater than 1.4 MeV. Mass 192 is calculated from the region 0.32 to 1.4 MeV by subtracting the contribution from ^{190}Ir. Similarly ^{193}Ir and ^{189}Ir are derived from the L and K x-rays respectively by subtracting the other three isotopes.

IRON

J. S. Gilmore

1. Introduction

In the separation of radioiron from fission products, high-order decontamination is obtained by the precipitation of iron (II) sulfide from an ammoniacal medium containing tartrate as a complexing ion. Further decontamination is effected by acid sulfide scavenging, followed by extraction of iron (III) into isopropyl ether from hydrochloric acid solution. Iron is finally electroplated from solution. The chemical yield is about 50%.

2. Reagents

Fe carrier· 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in $1M$ HCl, standardized
Sb (III) carrier: 100 mg Sb/ml, added as $SbCl_3$ in $3M$ HCl
Sn (II) carrier: 100 mg Sn/ml, added as $SnCl_2$ in $3M$ HCl
Te (IV) carrier: 10 mg Te/ml, added as $TeCl_4$ in $3M$ HCl
Tl (III) carrier: 10 mg Tl/ml, added as $TlCl_3$ in H_2O
I^- carrier: 100 mg I^-/ml, added as KI in H_2O
HCl: $0.2M$; $8M$; concd
HNO_3: concd
Tartaric acid: saturated aqueous solution
NH_4OH: concd
$(NH_4)_2S$: aqueous solution, light
$(NH_4)_2CO_3$ reagent: 392.5 g of $(NH_4)_2CO_3$ in 175 ml of concd NH_4OH, diluted to 1 liter
$NH_4H_2PO_4$ reagent: 230 g $NH_4H_2PO_4$ per liter
Br_2: liquid
Aerosol: 0.1% aqueous solution
Isopropyl ether (alcohol-free)
Ethanol: 95%

3. Preparation and Standardization of Carrier

Weigh out 48.4 g of $FeCl_3 \cdot 6H_2O$ and make up to 1 liter in $1M$ HCl. Pipet 5.0 ml into the electroplating cell and add concd NH_4OH dropwise until $Fe(OH)_3$ begins to precipitate. Add 1 ml of $NH_4H_2PO_4$ reagent and 10 ml of $(NH_4)_2CO_3$ reagent. Plate onto a weighed 1″ Pt disk at 2 amp and 70° for 90 min. Wash the plate with H_2O and with 95% ethanol. Dry in an oven at 100° for 5 min, cool, and weigh.

Four standardizations, with results agreeing within 1%, are performed.

4. Procedure

Step 1. To the sample in a 40-ml conical centrifuge tube, add 4.0 ml of standard Fe carrier. Make the solution ammoniacal with concd NH_4OH and add 5 ml of $(NH_4)_2S$ solution. Centrifuge and discard the supernate.

Step 2. Dissolve the FeS precipitate in 3 or 4 drops of concd HCl and boil the solution to drive off H_2S. Add 1 ml of Te (IV) carrier, 1 drop each of Sn (II) and Sb (III) carriers, and 20 ml of $0.2M$ HCl. Add 1 drop of aerosol solution and saturate with H_2S. Filter into a clean 40-ml centrifuge tube and discard the precipitate.

Step 3. To the filtrate add 1-2 ml of saturated tartaric acid and 5 ml of $(NH_4)_2S$ solution. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate in 3 or 4 drops of concd HCl and oxidize the Fe^{2+} ion with 1 or 2 drops of concd HNO_3. Evaporate the solution to dryness; add 3 or 4 drops of concd HCl, and again evaporate to dryness. Transfer the $FeCl_3$ with the aid of 10 ml of $8M$ HCl to a 125-ml separatory funnel. Add 30 ml of isopropyl ether, shake for 1 min, and discard the aqueous phase. Add 10 ml of H_2O to the ether phase and shake for 1 min. Transfer the aqueous phase to a 40-ml centrifuge tube and discard the ether layer.

Step 5. To the aqueous phase add 1 ml of saturated tartaric acid and 5 ml of $(NH_4)_2S$ solution. Centrifuge and discard the supernate.

Step 6. To the FeS precipitate add 3 or 4 drops of concd HCl and boil to remove H_2S. Add 1 drop of Sb (III) carrier and 3 or 4 drops of liquid Br_2. Boil off excess Br_2, and add 1 ml of Tl (III) carrier and 1 ml of I^- carrier (Note 1). Make the solution up to a volume of 20 ml with $0.2M$ HCl, add 1 drop of aerosol solution, and saturate with H_2S. Filter into a 40-ml centrifuge tube and discard the precipitate.

Step 7. Repeat Steps 3 through 5.

Step 8. Dissolve the FeS precipitate in 1 ml of concd HCl. Boil, add 1 ml of Te (IV) carrier, and boil again (Note 2). Dilute the solution to 20 ml with 0.2*M* HCl. Add 1 drop each of Sn (II) and Sb (III) carriers, 1 drop of aerosol solution, and saturate with H_2S. Filter into a 40-ml centrifuge tube and discard the precipitate.

Step 9. Repeat Steps 3 through 6.

Step 10. Repeat Steps 3 and 4.

Step 11. Filter the aqueous layer into a clean 40-ml centrifuge tube and precipitate $Fe(OH)_3$ with concd NH_4OH. Centrifuge and discard the supernate.

Step 12. To the precipitate add 1 ml of $NH_4H_2PO_4$ reagent, 10 ml of $(NH_4)_2CO_3$ reagent, and warm to dissolve the $Fe(OH)_3$. Transfer the solution to a plating cell.

Step 13. Plate on a 1" Pt disk for 1 hr at 2 amp and 70°. Wash the plate with H_2O and with 95% ethanol. Dry in oven at 100° for 5 min. Cool, weigh, and beta-count.

Notes

1. To promote exchange between radioantimony and carrier, Sb (III) is first oxidized to Sb (V) by Br_2 and the pentapositive antimony is then reduced by I^- ion. In the next operation H_2S reduces Tl (III) to Tl (I) which is then precipitated as the iodide.

2. When the solution containing Te carrier is boiled with concd HCl, any Te (VI) present is reduced to the +4 state. This operation promotes exchange.

lanthanides, lead

THE LANTHANIDES

K. Wolfsberg

1. Introduction

After the radiochemical purification of the lanthanides (rare earths) as a group, the separation of individual lanthanides is accomplished on a cation column of low cross linkage and fine particle size at room temperature by eluting with α-hydroxyisobutyric acid. The separation of a number of lanthanides--Y (which behaves as higher lanthanide), Eu, Sm, Pm, Nd, Pr, Ce, and La--is best achieved in a reasonable length of time by continuously changing the pH of the eluent.

A chemical yield determination of the mounted oxide samples may be performed after counting by dissolving the samples and titrating with EDTA.

2. Reagents

$HClO_4$: concd
HCl: concd
HNO_3: concd
H_3BO_3: saturated
$H_2C_2O_4$: saturated; 0.5%
HF: concd
H_3PO_4: concd
H_2SO_4: concd
H_2O_2: 30%
$NH_2OH \cdot HCl$: 5*M* aqueous solution
Ethanol: 95%
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
Te carrier: 10 mg Te/ml, added as Na_2TeO_3 in H_2O
Ba carrier: 10 mg Ba/ml, added as $Ba(NO_3)_2$ in H_2O
α-hydroxyisobutyric acid: 0.394*M* solutions adjusted to pH 3.40, pH 4.20 and other pH values for specific applications. The commercially available solid acid comes in the form of the monohydrate.
Dowex Ag 50W-X4 or AG 50W-X8 cation resin, 200-325 wet graded (minus 400 mesh dry), NH_4^+ form
Dowex AG 1-X8 anion resin, 50-100 mesh
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, and Y carriers: 5 mg of oxide/ml, standardized, 99% pure
^{145}Pm tracer: (produced by $^{144}Sm(n,\gamma)^{145}Sm \rightarrow ^{145}Pm$), standardized
0.01*M* EDTA: 3.743 g disodium (ethylene dinitrilo) tetraacetate (direct from bottle) per liter
0.10*M* La^{3+} in 1*M* HCl: prepared from La_2O_3
NH_4Cl: 25% w/v in H_2O
ph 10 buffer: 61.5 g of NH_4Cl dissolved in 400 ml of NH_4OH
Arsenazo indicator 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthylene disulfonic acid trisodium salt: 0.05% in H_2O
Phenolphthalein: 1% in 50% ethanol
8-Quinolinol reagent I: a solution of 0.5 g of 8-quinolinol (8-hydroxyquinoline) and about 100 mg of phenolphthalein in 100 ml of ethanol
8-Quinolinol reagent II: a mixture of 10 ml of quinolinol reagent I and 5 ml of concd NH_4OH diluted to 200 ml with H_2O
Filter aid: for preparation, disintegrate ten 18.5 cm circles of No. 42 Whatman filter paper in water in a blender, dilute to 2 liters with H_2O, and add 1 ml of concd HCl
HCl rinse solution for anion resin column: 10 ml of concd HCl and 1 drop of concd HNO_3, freshly prepared

3. Preparation and Standardization of Carriers

Dissolve 5 g of the desired lanthanide oxide in about 50 ml 6*M* HCl. Heat or add a few drops of concd HNO_3 if dissolution is difficult. Filter and dilute to 1 liter, adjusting the HCl concentration to 2 or 3*M*. Any pure soluble cerium(III) salt may be used for cerium carrier.

For the light lanthanides (La-Tb) and Y, pipet three 10-ml portions of the carrier into 250-ml beakers. Evaporate the solutions almost to dryness under a heat lamp. Add about 40 ml of water and bring the solution almost to boiling on a hot plate. Then add about 25 ml of saturated $H_2C_2O_4$ dropwise while stirring the solution. Digest the precipitate hot for 15 min and then let the mixture stand overnight at room temperature. Filter the oxalate on No. 42 Whatman filter paper, washing with 0.5% oxalic acid. Ignite the oxalate for 1 hr at 950° in previously tared porcelain crucibles. Cool and weigh. The three weights should agree to 0.5%. Two milliliters of carrier should correspond to not more than 11 mg of oxide to avoid the spreading of one lanthanide element into the next during elution.

For the heavy lanthanides, pipet carrier solution and evaporate as above. After diluting to about 30 ml with H_2O, add 10 ml of quinolinol reagent I. Add about 1.5 ml of filter aid and make basic with concd NH_4OH. Heat on a steam bath for 30 min, adding NH_4OH if necessary to keep the solution basic. Cool to room temperature, filter on No. 42 Whatman filter paper, and wash with quinolinol reagent II. Ignite for 1.5 hr at 950° in a previously tared crucible.

Alternatively, the lanthanides may be standardized by pipetting 5 ml of carrier solution directly into a tared porcelain crucible. Evaporate the solution gently under a heat lamp and then ignite the crucible for 2 hours at 950°. The lanthanide chloride is converted to the oxide.

For standardization by means of EDTA titration, pipet three 2-ml portions of the carrier into 125-ml erlenmeyer flasks and titrate with EDTA solution as described in Section 10. The titrations should agree within 0.5%.

4. Standardization of ^{145}Pm

The solution should contain 800-1200 counts per minute of ^{145}Pm per ml. Pipet 5 ml of the solution and about 20 mg of standardized Nd carrier into each of 4 centrifuge tubes. Dilute to about 20 ml, heat on a steam bath, and add approximately 6 ml of concd NH_4OH. Centrifuge. Dissolve the precipitate in 1 ml of concd HCl, dilute to 20 ml, heat on a steam bath, and add 10 ml of saturated $H_2C_2O_4$. Digest the precipitate, centrifuge, filter, ignite to the oxide, and mount as in Step 10 of Section 11. Count the samples on a sodium iodide scintillation counter for several days. The chemical yield of Nd, which corresponds to that of Pm, may be determined in three of the samples by EDTA titration (Section 10). The activities, corrected for yield, should agree within 1%. The fourth sample is retained for use as a standard each time yield is determined. The assumed yield of this sample may be calculated.

5. α-Hydroxyisobutyric Acid

Dissolve 208 g of α-hydroxyisobutyric acid monohydrate in water and dilute to 4 liters. Filter the solution if it is cloudy. Add concd NH_4OH to obtain solutions of the desired pH.

Different commercial batches of the reagent may give rise to different elution curves for a particular concentration and pH. This is not as serious a problem when performing elutions by continuously changing pH as when performing elutions at a single pH. However, it is advisable to determine whether a new batch of α-hydroxyisobutyric acid gives the desired elution curves. If it does not, the pH values or concentrations of the solutions should be adjusted accordingly.

6. Treatment of Resins

Bio-Rad Laboratories will prepare cation resin according to the following specifications: Dowex AG 50W-X4 or X8 "minus mesh"; the actual range is minus 200 mesh wet (U.S. Std.) on the large end down to 0.27 cm/sec settling rate (nominal 62 to 23 μm). The resin is washed successively with 6*M* HCl, 1*M* NH_4CNS, 6*M* HCl, 1*M* NH_4OH, and H_2O. Dowex AG 1 resins as supplied by Bio-Rad need no further purification. Since there are variations among various batches of resin, they should be evaluated before routine use.

7. Preparation of Cation Exchange Columns

Select a 70-cm length of 8 mm i.d. Pyrex tubing. Draw one end out to a drip tip (i.d., 0.8 to 1.2 mm) and make a slight constriction 8 mm from the other end for a tubing connection.

To load a column place a small plug of glass wool in the tip and fill the column with water. Then add the cation resin slurry from the polyethylene wash bottle, releasing the water. The settling rate of the resin may be increased by using air pressure. Resin should be added to a height of about 65 cm. Care should be taken that no portion of the resin goes dry. Columns prepared in this manner may be stored by sealing both ends with dropper bulbs or by storing the columns in a cylinder of water.

8. Preparation of Anion Columns

A 15-ml centrifuge tube is blown out at the bottom and a 15-cm length of 6 mm i.d. glass tubing is attached. The end of the glass tubing is drawn to a 1 mm i.d. drip tip. The glass tubing part of the column is loaded with anion resin in the same manner that the cation resins were loaded. These columns may also be stored as long as the resin is kept wet. Prior to use, two 5-ml portions of HCl rinse solution are passed through the column.

9. Gradient Elution Equipment

A schematic diagram of the gradient elution equipment is shown in Fig. 1. Several columns may be operated from one setup by delivering the eluent from the low pH flask through "Y" connecting tubes; 500-ml flasks are used for 1 or 2 columns and 1000-ml flasks for 3 or 4 columns.

Elution is begun with the levels of the two solutions at the same height. One-half of the volume that is removed from the flask containing the low pH solution is continuously replaced by high pH solution by gravitational leveling. Thus the pH of the eluent changes continuously from that of the low pH solution at the beginning of elution to that of the high pH solution at the end of elution.

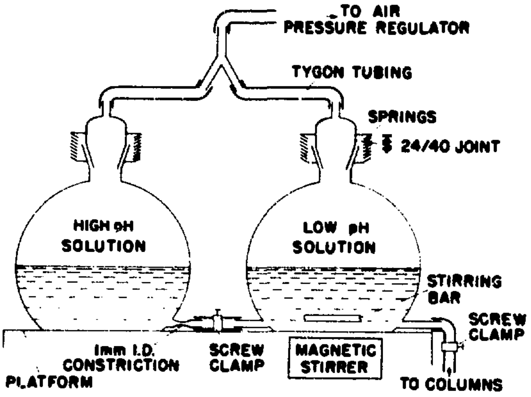


Fig. 1. Gradient elution equipment.

10. EDTA Titrations

Dilute the sample to about 30 ml in a 125-ml erlenmeyer flask and add an excess of 0.01*M* EDTA from a 10-ml buret (0.6-0.7 ml for each milligram of rare earth oxide and about 0.9 ml for each milligram of yttrium oxide). Add about 4 ml of 25% NH_4Cl and a drop of phenolphthalein. Then add pH 10 buffer until the solution turns pink (the pH will be between 8 and 9). Bring the solution almost to boiling. The pink color is destroyed. Add 1 or 2 drops of arsenazo indicator and back titrate with 0.01*M* La^{3+} solution from another 10-ml buret while the solution is still hot. The end-point is reached when the solution turns from salmon to violet or red-violet on the addition of approximately 1/2 drop. More EDTA may be added and another back titration performed.

The relative strengths of the EDTA and La^{3+} solution titrants are obtained by starting the back titration from a solution of about 6 ml La^{3+} solution and an excess of EDTA. The volume of La used in any titration is multiplied by the EDTA/La^{3+} solution ratio and this number is then subtracted from the volume of EDTA delivered to obtain the net volume of EDTA delivered to obtain the net volume of EDTA.

The chemical yield of a sample is the net volume of EDTA required to titrate the sample divided by the net volume required to titrate 2 ml of carrier. For thickness corrections, the weight of the sample can be calculated from the titration of the sample, the titration of 2 ml of carrier, and the gravimetric standardization of the carrier (Section 3).

If accurate standardization of the EDTA solution is desired, the solution may be standardized against zinc (using Eriochrome Black T as an indicator) or against a rare earth oxide which has been ignited at 950° (Note 1).

11. Procedure

In this procedure all precipitates are digested on a steam bath. They may be centrifuged while the solutions are still hot.

Step 1. Into a polycarbonate centrifuge tube, pipet 2 ml of desired carrier and the active sample. If large volumes are involved, pipet into a glass vessel and reduce the volume by boiling or by evaporation under a heat lamp (Note 2). Add H_2O to bring the volume to about 15 ml, then add 2-5 ml of concd HF, digest on a steam bath for 15 min and centrifuge. Wash the precipitate with about 20 ml of H_2O containing a few drops of concd HF. Centrifuge and discard the supernate (Note 3).

Step 2. Slurry the precipitate with 2 ml of saturated H_3BO_3 and add 2 ml of concd HNO_3 10 ml of H_2O, and 2 drops of Zr carrier. Heat to dissolve any precipitate. Add 2-5 ml of concd HF, heat on a steam bath for a few minutes, and centrifuge (Note 3). Wash the precipitate with H_2O containing a few drops of HF. Centrifuge and discard the supernate.

Step 3. Slurry the precipitate with 2 ml of saturated H_3BO_3, add 2 ml of concd HNO_3 and heat on a steam bath if necessary to dissolve the precipitate. Add 15 ml of H_2O.

Step 4. Add 8 ml of concd NH_4OH, heat for 1 min on a steam bath, digest and then centrifuge. Discard the supernate. (The anion resin column may be prepared at this time.) Wash the precipitate with 15 ml of H_2O to which a few drops of concd NH_4OH had been added. Centrifuge and discard the supernate.

Step 5. Dissolve the hydroxide precipitate in 6 ml of concd HCl and 1 drop of concd HNO_3 and add 2 drops each of Zr and Te carriers. Heat the sample for only 30 sec on a steam bath (to promote Te exchange but not to reduce the HCl concentration). Pass the solution through an anion resin column and collect the eluate in a 125-ml erlenmeyer flask. Rinse the column with one 4- and one 6-ml HCl rinse solution (see 2. Reagents) and collect the rinsings in the flask.

Step 6. Boil out excess HCl by heating the flask over a flame and reduce the volume to 4-5 ml. Transfer the solution to a long tapered centrifuge tube with 15 ml of H_2O. Add 8 ml of concd NH_4OH and 3 drops of 5*M*

$NH_2OH \cdot HCl$. Heat on a steam bath for about 1 min, digest, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of H_2O containing a few drops of NH_4OH.

Step 7. Dissolve the precipitate in 6 drops of concd HCl and dilute the solution to about 30 ml with H_2O. Add about 30 drops (transfer pipet) of minus 400 mesh cation resin slurry in H_2O. Stir or shake for about 5 min and centrifuge for 5 min, letting the centrifuge stop without the use of the brake (Note 4). (The centrifuged resin has a volume of about 1 ml.) Discard the supernate.

Step 8. Slurry the resin with about 1 ml of H_2O and, by means of a transfer pipet, transfer it to the top of a previously prepared cation resin column. Allow the resin to settle and remove the H_2O. Rinse the centrifuge tube with 1-2 ml of H_2O, add the rinsings to the column, allow to settle, and remove the H_2O. (A small piece of glass wool may be put in the top of the column.)

Step 9. Connect the column to a delivery tube from the gradient elution equipment. For the analysis of Y, Eu, Sm, Pm, Pr, Ce, and La, the initial pH of the eluent (0.394*M* α-hydroxyisobutyric acid) is 3.40 and the pH is changed at an average rate approximately 0.025 pH unit per hour. For the operation of one column, this condition is met by starting with 144 ml of 0.394*M* α-hydroxyisobutyric acid, pH 3.40, in the first flask and with 144 ml of eluent, pH 4.20, in the second flask. If several columns are operated from one set of flasks, the volumes of eluents are increased proportionally. A small additional volume of low pH solution is added to the first flask to compensate for the difference of volumes between the delivery tubing and the stirring bar. The rate of elution is controlled by the air pressure applied to the reservoirs. Collect the eluate in 15-min fractions using a fraction collector (Notes 5, 6, and 7).

Step 10A. For the light lanthanides and Y, add a few drops of saturated $H_2C_2O_4$ to each fraction to precipitate and locate the individual lanthanides. Pm is located by measuring the activity in the tubes between Sm and Nd. Combine the individual lanthanide fractions in centrifuge tubes. To the Pm fraction add 2 ml of Nd carrier. Add 5 ml of saturated oxalic acid to the centrifuge tubes and digest the oxalates for 15 min on a steam bath. Centrifuge, suspend the oxalates in about 5 ml of H_2O, and filter on a 2.5 cm circle of No. 42 Whatman paper using a filter chimney assembly. Ignite the oxalates in a Coors 00 crucible for approximately 1 hr at 950°. Oxalates may be mounted directly without weighing if chemical yield is to be determined by EDTA titration (Note 8).

Step 10B. For the heavy lanthanides, add about 0.5 ml of 8-quinolinol reagent I to each fraction. Add concd NH_4OH to make each fraction basic (red) and combine the fractions containing an individual element in a 250-ml beaker. (At least 10 ml of reagent I should have been used in those tubes containing the element.) Add about 1.5 ml of filter aid and digest the mixture on a steam bath for 15 to 30 min. Cool to room temperature and filter on a 2.5 cm circle of No. 42 Whatman paper using a filter chimney assembly. Wash with 8-quinolinol reagent II. Ignite the quinolate for 1.5 hr at 950° (Note 8).

Step 10C. If a given light lanthanide is to be cycled through a second cation exchange column when a separation of 10^5 from other lanthanides is required, the oxalate may be dissolved and destroyed by heating it in a centrifuge tube with about 1 ml of concd HNO_3 containing about 100 mg of $KClO_3$. For heavy lanthanides, the 8-quinolate is ignited and dissolved in about 2 ml of concd HCl and 0.5 ml of concd HNO_3. Then one performs Step 6 for the hydroxide precipitation prior to the cation column step. This is usually done for Eu, Gd, Tb, Lu, and Tm, and, when large amounts of Am are present, also for Nd.

Step 11. After the crucibles have cooled, add 2 drops of ethanol to each sample and grind up the oxides with the fire-polished end of a stirring rod. Suspend each sample in several milliliters of ethanol and filter onto a circle of No. 42 paper using a 4/0 ground-off Hirsch funnel and an 11 mm i.d. glass chimney. Dry the sample for 15 min at 110° and mount it on an aluminum plate, covering with No. 850 type 2PTA polyester film tape (Note 9).

If chemical yield is to be determined by weight of the oxide, the circle of paper on which the sample is mounted should be washed, dried, and tared prior to the mounting operation. The papers and samples should be cooled for 20 min before weighing.

Step 12. After counting of a sample is completed, yield determination by EDTA titration may be performed. Remove the sample, filter paper, and tape cover from the counting plate by cutting around the outside of the filter paper with a sharp blade. Place this sandwich in a 125-ml erlenmeyer flask. Add 10 ml of H_2O and 2 ml of concd HCl. Bring to boiling and place the flask on a hot plate set to maintain the temperature just below boiling for about 20 min. The filter paper may disintegrate, but this does not interfere. Titrate the sample in the manner described in Section 10.

CeO_2 does not dissolve with the HCl treatment described above. After the sample sandwich is placed in the flask, add about 2 ml of concd H_2SO_4 and heat the mixture to SO_3 fumes over a flame. Then cautiously add a mixture of 2 parts of concd H_2SO_4 and 1 part of 30% H_2O_2 dropwise to destroy the charred paper and tape. Fume the clear solution down to about 0.25 ml. Dilute to 30 ml, add 0.1-0.2 g of ascorbic acid, and proceed with the EDTA titration as described in Section 10.

Notes

1. The following references may be consulted for general familiarization with EDTA titrations:

G. Schwarzenbach, *Complexometric Titrations*, Interscience Publishers, New York (1955).

H. Flaschka, H. T. Barnard, Jr., and W. C. Broad, Chemist Analyst 46, 106 (1958)

A review of EDTA methods for the lanthanides is given in:

H. Flaschka, H. T. Barnard, Jr., and W. C. Broad, Chemist Analyst 47, 78 (1959).

This procedure was adapted from:

J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, Anal. Chem. 30, 1111 (1958).

2. If Ce is to be determined, steps must be performed to promote exchange between radiocerium and carrier. (See Steps 1 and 2 of the cerium procedure.)

3. If the sample contains large amounts of elements such as Al which form amphoteric hydroxides, treatment of the lanthanide fluoride precipitate with an excess of 6*M* NaOH will precipitate lanthanide hydroxides and dissolve the amphoteric elements. If the amount of fluoride precipitate in Step 1 seems to be too great for the quantity of carrier added, it may be washed with about 10 ml of 6*M* NaOH and then with H_2O before carrying out Step 2. The same treatment may be used after Step 2. Precipitation of hydroxides with 6*M* NaOH may precede or follow Step 3 or may precede the precipitation with NH_4OH in Step 6. In these instances, the precipitate is washed first with 10 ml of 6*M* NaOH and then with H_2O.

4. The 200-400 mesh resin may be centrifuged more easily than the finer resin that is used in the column, and it also settles faster when added to the column. The resin is suspended in water.

5. Under the conditions in Step 9, the lanthanides elute in the following manner.

Element	Time that element starts eluting off column
Y	3.1 hr
Gd	6.5
Eu	8.2
Sm	10.5
Pm	13.2
Nd	16.5
Pr	19.5
Ce	22.5
La	28.0

Those lanthanides which are present in 6-9 mg quantities have elution widths of less than 2 hr. Carrier-free lanthanides elute more sharply. Europium, therefore, is not contaminated with Gd, which is present carrier-free. Decontamination factors for a particular lanthanide from other lanthanides vary from 3×10^{-5} to 2×10^{-6}.

6. For special applications, it may be more convenient to elute with an eluent at a single pH. For Dowex AG 50W-X8, the following values of pH are used to obtain overnight separations: Pr, 3.98; Nd, 3.82; Eu, 3.51; Er-Ho, 3.21; Tm, 3.11; and Lu, 3.05.

7. Some elements elute very closely to each other. Such cases are Sc-Lu-Yb and Am-Nd-Pr. When contamination from a neighboring element is possible, one or two fractions toward that element should be discarded. It is recommended that about 10 mg of Pr be added to spread the peak of that element.

8. For the preparation of a sample as a mass separator source, separation of the desired lanthanide is done without addition of carrier of that element. Ten milligrams of a lighter lanthanide carrier is usually added for an hydroxide precipitation prior to the cation column separation. The activity peaks are located by gross γ counting. About 3 mg of the appropriate carrier is then added to the α-hydroxyisobutyrate solution containing the activity of interest and the element is precipitated and ignited as in Step 10.

After the sample has been ignited, transfer the oxide into a long tapered centrifuge tube. Add 2 ml of concd HCl and 3-5 drops of concd HNO_3. Heat gently on a steam bath for 15 min or until the oxide has dissolved and the solution is clear. (A few additional drops of HNO_3 may be necessary to effect solution of the oxide.) Place the centrifuge tube in an oil bath and evaporate to a volume of a drop or two using an air jet. Transfer the drops in 20-λ portions to the appropriate end of a quartz vial containing quartz wool which has been previously weighed. Dry for about 8 min under a heat lamp after each transfer. Rinse the centrifuge tube with 1 drop of concd HCl and transfer the rinse to the quartz vial. Heat the vial at 600° for 20 min, cool for 20 min, and weigh.

9. The thickness of Scotch polyester film tape (No. 850 type 2PTA) is uniform along the length of a roll and among most of the rolls produced from the same batch, the variation being about 1.5%. However, there may be a large variation between batches. The tape of two batches examined had thicknesses of 4.9 and 6.3 mg cm^{-2}. This variation does not pose a serious problem since a large number of rolls of tape can be obtained from a single batch.

ADDENDUM I TO THE LANTHANIDE PROCEDURE

1. Alternative Group Purification

The steps described below are alternatives for Steps 1 through 7 of Section 11 of the Lanthanide Procedure. The number of manipulations and the time required are decreased by use of this new process of group purification.

The lanthanides are extracted from a dilute nitric acid solution into *n*-heptane containing di-2-ethylhexyl orthophosphoric acid (HDEHP), and the resulting organic phase is scrubbed with dilute nitric acid. Under these conditions, the distribution coefficient, K(o/a), is greater than 96 for the lanthanides and less than 0.02 for contaminants in oxidation states of +1 and +2. The lanthanides are back-extracted into a more concentrated nitric acid, and the aqueous phase is scrubbed with a solution of HDEHP in trichloroethylene. The distribution ratio, K(o/a), for this extraction is less than 0.02 for the lanthanides and greater than 97 for contaminants in higher oxidation states. Radioactivities of Cs, Ba, Ce, Nd, Eu, Y, Zr, Nb, Th, and Pu isotopes were used in obtaining the distribution ratios.

2. Special Reagents

HNO_3: 0.05*M*; 4*M*

0.5*M* HDEHP: a solution of di-2-ethylhexyl orthophosphoric acid (mol wt 322.4) in *n*-heptane

0.1*M* HDEHP: a solution of the acid in trichloroethylene. (The HDEHP used is assayed at greater than 94% pure by the supplier, the Victor Chemical Division of the Stauffer Chemical Co. If highly purified HDEHP is used, some loss of the lighter lanthanides may occur since K(o/a) for extraction from the more dilute nitric acid may be significantly lower.)

3. Procedure

Step 1. To the active solution in a 125-ml erlenmeyer flask, add 10 mg of carrier of each lanthanide to be determined. For locating purposes, about 0.3 mg each of carriers of the other lanthanides may be added. If Pm is to be determined, add ^{145}Pm tracer. The maximum quantity of carrier that can be used is 60 mg.

Step 2. Add 3 ml of concd $HClO_4$, boil the solution to thick fumes of $HClO_4$, and then boil for another minute. (This step may be omitted if the active solution does not contain species which may prevent exchange of lanthanide activities with the carriers. This is true if the active solution in its history prior to analysis has been boiled to fumes of $HClO_4$ and then diluted with dilute HNO_3 or HCl.) Transfer the solution to a 40-ml centrifuge tube. Wash the flask with a small amount of H_2O, and add washings to the centrifuge tube.

Step 3. If the sample does not contain $HClO_4$, evaporate it to dryness under a heat lamp or by boiling gently over a burner; then proceed to Step 4. If the sample does contain $HClO_4$, dilute the solution to 20 ml and add 6-8 ml of concd NH_4OH. Heat for 2 min on a steam bath, centrifuge, and discard the supernate. Wash the precipitate with two 20-ml portions of water. Dissolve the precipitate in 1-2 ml concd HNO_3 and wash down the sides of the tube with a small volume of water. Evaporate the sample to dryness under a heat lamp or by boiling gently over a burner.

Step 4. Dissolve the residue in 10 ml of 0.05*M* HNO_3. Transfer the solution to a 60-ml separatory funnel, add 10 ml of 0.5*M* HDEHP in *n*-heptane, and shake. (Shakings are carried out for 1 min if manual and 2 min if done on a Burrell shaker.) Discard the aqueous (lower) layer.

Step 5. Scrub the organic phase with two 10-ml portions of 0.05*M* HNO_3 and discard the lower phase after each scrubbing.

Step 6. Back-extract the lanthanides by shaking the organic phase with two 5-ml portions of 4*M* HNO_3. Drain the aqueous (lower) phase after each extraction into the same clean 60-ml separatory funnel. If either Y or Tb is to be determined, use four, rather than two, 5-ml portions of 4*M* HNO_3. Discard the organic phase.

Step 7. Scrub the combined aqueous extracts with two 10-ml portions of 0.1*M* HDEHP in trichloroethylene. Discard the lower phase after each scrubbing.

Step 8. Scrub the aqueous solution once with 10 ml of *n*-heptane to remove most of the dissolved HDEHP. Drain the HNO_3 solution (lower phase) into a 40-ml centrifuge tube and discard the heptane.

Step 9. Add 6-8 ml of concd NH_4OH, centrifuge, and discard the supernate. Wash the precipitate with H_2O and discard the washings.

Step 10. Continue with the separation of the individual lanthanides as in Steps 8, 9, 10, and 11 of the Lanthanide Procedure. Addendum II gives methods for mounting and yield determination as alternatives for Steps 10 and 11 of the Lanthanide Procedure.

Note

Y can be separated from the lighter lanthanides by a slight modification of the procedure given above. Instead of scrubbing with 0.05*M* HNO_3 in Step 5, scrub with four 10-ml portions of 0.75*M* HNO_3. By this operation, more than 99.9% of the Nd (and lanthanides of lower atomic number) and about 93% of the Eu are removed into the aqueous scrubs. Eighty-eight percent of Y is retained in the organic phase. In most cases, the remaining Eu contamination is small relative to the Y activity, and the Y product from Step 10 can be mounted directly as the oxalate or oxide and counted. To do this, dissolve the $Y(OH)_3$ from Step 9 in about 4 drops of concd HCl, add 20 ml of H_2O, and proceed as in Step 10 of the Lanthanide Procedure or as in Alternative Step 10 of Addendum II.

ADDENDUM II TO THE LANTHANIDE PROCEDURE

Alternative Procedures for Mounting and Determination of Chemical Yield

Given below are alternatives for Steps 10 and 11 of Section 11 of the Lanthanide Procedure. If the chemical yield is to be determined by EDTA titration, the time required to prepare a sample for mounting can be shortened by mounting the oxalate rather than the oxide. The oxalate is dissolved for determination of yield. The weight of the oxalate itself cannot be used for the yield determinations.

Alternative Step 10. Combine the fractions making up the activity of each lanthanide in a centrifuge tube. Thus, there will be a tube for Nd activity, one for Eu activity, etc. To the tube containing the Pm activity add 2 ml of Nd carrier. To each of the tubes add 5 ml of saturated $H_2C_2O_4$ and digest the oxalate precipitates for 15 min on a steam bath. Centrifuge and discard the supernates. Suspend each precipitate in 5 ml of H_2O, break up the lumps, and filter onto a circle of No. 42 Whatman filter paper, 1" diameter, using a ground-off Hirsch funnel and filter chimney set-up. Wash each oxalate with three successive 5-ml portions each of H_2O, then ethanol, and finally ether. Dry the sample for 10 min at 110° and mount on an Al plate, covering with Scotch polyester film tape (No. 850 type 2 PTA).

Alternative Step 11. After counting has been completed, the chemical yield is determined by EDTA titration. Remove the sample, filter paper, and tape cover by cutting around the outside of the filter paper with a sharp blade. Place the sandwich in the titration vessel, and add 10 ml of H_2O and 2 ml of concd HCl. Pipet in an excess of EDTA solution. Heat the solution on a hot plate for about 20 min and adjust the pH to 8 or 9 as described in Section 10 of the Lanthanide Procedure. Back titrate the excess EDTA with La^{3+} solution (See Note).

Note

The titration may also be performed with an automatic photoelectric titrator. If done in this manner, Eriochrome Black T is used as the indicator, the wave length is set at 650 mμ, and 0.0125*M* EDTA and 0.025*M* La^{3+} solutions are employed.

ADDENDUM III TO THE LANTHANIDE PROCEDURE

W. G. Warren

Special Considerations for the Analysis of the Heavy Lanthanides

1. The $HClO_4$ fuming and the $Zr_3(PO_4)_4$ scavenging precipitation of Step 1 of the *Procedure* and the $BaSO_4$ scavenge of Step 4 may be omitted.

2. If the sample contains large amounts of Al and other elements which form amphoteric hydroxides, the *Procedure* is followed through the volume reduction of Step 7. The solution is then transferred to a plastic tube and Step 7 is completed. The hydroxide precipitate is washed with 6*M* NaOH and H_2O, the residue is dissolved in a few drops of concd HCl, and the hydroxides are reprecipitated as in Step 7. If the mass of the precipitate now seems appropriate for the amount of lanthanide carriers present, proceed to Step 8; if not, the precipitate is dissolved in 4 ml of concd HNO_3 and Step 2 is performed. The fluoride precipitate is dissolved in 2 ml of saturated H_3BO_3 and 2 ml of concd HNO_3, the solution is diluted to 15 ml, and the hydroxides are reprecipitated with concd NH_4OH. Then proceed to Step 8.

3. With 0.5*M* α-hydroxyisobutyric acid as eluent, the following pH values are appropriate for the nongradient elution of the given elements: Eu, 3.50 ± 0.02; Tb, 3.30 ± 0.02; Er, Tm, Yb, and Lu, 3.00 ± 0.02. *(See also Note 5 of the Procedure.)*

4. For locating and precipitating fractions containing the elements holmium through lutetium, a solution of 3% (W/V) cupferron in 6*M* NH_4OH is used instead of saturated oxalic acid as in Step 9 of the *Procedure*. No more than a few drops of the cupferron reagent should be used because these lanthanides are soluble in an excess of the reagent.

May 1968

LEAD

J. S. Gilmore

1. Introduction

In the determination of radiolead (RaD), four decontamination cycles, each consisting of the precipitation of (a) lead nitrate, (b) lead chloride, (c) iron(III) hydroxide, and (d) lead sulfide, are carried out. Lead is finally precipitated and mounted as the chromate. The chemical yield is 60-70% and eight samples can be run in about a day.

2. Reagents

Pb carrier: 20 mg Pb/ml, added as $Pb(NO_3)_2$ in $0.01M$ HNO_3, standardized
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in $1M$ HCl
HCl: concd
HNO_3: concd; fuming (sp gr 1.5)
$HC_2H_3O_2$: $6M$
NH_4OH: $1M$; concd
NaOH: $12M$
$NH_4C_2H_3O_2$: $6M$
Na_2CrO_4: $1.5M$
NH_4Cl: solid
H_2S: gas
Ethanol: 95%
Bromphenol blue indicator solution

3. Preparation and Standardization of Carrier

Weigh out 32.0 g of $Pb(NO_3)_2$ and make up to 1 liter in H_2O. Pipet 5.0 ml of the solution into a 250-ml beaker, add 3 ml of $6M$ $NH_4C_2H_3O_2$ and 2 ml of $6M$ $HC_2H_3O_2$, and dilute to 30 ml with H_2O. Heat to boiling and add 5 ml of $1.5M$ Na_2CrO_4 dropwise. Digest on a steam bath for 30 min and filter onto a weighed 15-ml sintered glass crucible. Wash the precipitate with H_2O until the washings have no dichromate color, and then wash with 95% ethanol. Dry in an oven at 115° for 30 min. Cool and weigh.

Four standardizations gave results agreeing within 0.2%.

4. Procedure

Step 1. Pipet 2.0 ml of Pb carrier into a 40-ml conical centrifuge tube, add an aliquot of sample, 1 ml of concd HNO_3, and evaporate nearly to dryness.

Step 2. Dissolve the residue in a minimum amount of H_2O, add 30 ml of fuming HNO_3 (sp gr 1.5), and cool in an ice bath. Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate in 1 ml of H_2O, and add 1 ml of concd HNO_3, 25 ml of 95% ethanol, and 4 drops of concd HCl. Chill in an ice bath. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate in 20 ml of H_2O, add approximately 2 g of solid NH_4Cl, 4 drops of Fe carrier, and heat to boiling. Add 2 drops of bromphenol blue indicator solution and neutralize to a basic endpoint with $1M$ NH_4OH. Centrifuge while hot and transfer the supernate to a clean centrifuge tube, discarding the precipitate.

Step 5. Saturate the supernate with H_2S. Centrifuge and discard the supernate.

Step 6. Dissolve the precipitate in 2 ml of concd HCl and evaporate to dryness. Add 1 ml of concd HNO_3 and evaporate nearly to dryness.

Step 7. Repeat Steps 2 and 3.

Step 8. Add 20 ml of H_2O to the precipitate, 4 drops of Fe carrier, and heat to boiling. Add $12M$ NaOH dropwise until the $Pb(OH)_2$ precipitate dissolves, leaving only the $Fe(OH)_3$ precipitate. Then add 5 drops of $12M$ NaOH in excess, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 9. Repeat Steps 5 and 6.

Step 10. Repeat Steps 2, 3, 4, 5, and 6.

Step 11. Repeat Steps 2, 3, 8, and 5.

Step 12. Dissolve the precipitate in 2 ml of concd HCl and evaporate nearly to dryness. Add 2 ml of $6M$ $HC_2H_3O_2$ and 3 ml of $6M$ $NH_4C_2H_3O_2$, dilute to 20 ml with H_2O, heat to boiling, and add 3 ml of $1.5M$ Na_2CrO_4, keeping the solution at the boiling point. Filter onto a No. 42 Whatman filter circle, $\frac{7}{8}''$ diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Wash the $PbCrO_4$ precipitate with H_2O and then with 95% ethanol. Dry the precipitate in an oven for 10 min at 115°. Cool, weigh, and mount for counting.

SEPARATION OF LEAD FROM URANIUM AND THE TRANSURANIC ELEMENTS

J. S. Gilmore

1. Introduction

Radiolead is separated conveniently from uranium and the transuranic elements by precipitation as lead sulfide from an acidic solution. The procedure below is applicable to the removal of any element which forms a sulfide insoluble in 1*M* hydrochloric acid.

2. Procedure

Step 1. To an aliquot of the sample in a centrifuge tube, add 30 mg of Pb carrier and the appropriate uranium and transuranic element tracers. Evaporate nearly to dryness. (The sample usually contains $HClO_4$.) Add sufficient dilute HCl to dissolve any solid residue and make the solution about 1*M* in acid concentration. Heat and saturate the solution with H_2S. Centrifuge and transfer the supernate to an erlenmeyer flask. Boil the supernate to remove H_2S, add 5 ml of concd HNO_3, and evaporate to fumes of $HClO_4$. Retain the solution for analysis for uranium and the transuranic elements.

Step 2. Dissolve the PbS precipitate in 2 ml of concd HCl by boiling. Convert the lead to $Pb(NO_3)_2$ by evaporating to a small volume in the presence of concd HNO_3. To determine Pb, carry out the standard Pb procedure from Step 2 onward.

magnesium, manganese, molybdenum

MAGNESIUM

R. J. Prestwood and B. P. Bayhurst

1. Introduction

This procedure has been employed in a search for ^{28}Mg in fission. After common decontamination steps, the magnesium is finally isolated as $MgNH_4PO_4 \cdot 6H_2O$. A sample containing 3×10^{14} fissions 3 days old gave a final precipitate with no detectable contaminants.

2. Reagents

Mg carrier: 10 mg Mg/ml, added as a solution of $Mg(NO_3)_2 \cdot 6H_2O$. The carrier is standardized as $MgNH_4PO_4 \cdot 6H_2O$.
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in 1*M* HCl
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in 1*M* HNO_3
Sc carrier: 10 mg Sc/ml, added as $ScCl_3$ in 1*M* HCl
Zr carrier: 10 mg Zr/ml, added as $ZrOCl_2 \cdot 8H_2O$ in 1*M* HCl
Cd carrier: 10 mg Cd/ml, added as $Cd(NO_3)_2 \cdot 4H_2O$ in 1*M* HNO_3
Co carrier: 10 mg Co/ml, added as $Co(NO_3)_2 \cdot 6H_2O$ in 1*M* HNO_3
Ba carrier: 1*M* $BaCl_2$
Sr carrier: 10 mg Sr/ml, added as $Sr(NO_3)_2 \cdot 4H_2O$ in H_2O
Te(VI) carrier: 10 mg Te/ml, added as $Na_2H_4TeO_6$ in 0.3*M* HCl
Pd carrier: 10 mg Pd/ml, added as $PdCl_2 \cdot 2H_2O$ in 1*M* HCl
HCl: concd; 6*M*
H_2SO_4: concd
NH_4OH: concd; 0.1*M*
NaOH: 10*M*
$NH_2OH \cdot HCl$: solid
NH_4Cl: 3*M*
$(NH_4)_2HPO_4$: 1.5*M*
H_2S: gas
Ethanol: absolute
Dowex AG 50-X4, 100-200 mesh cation resin; slurry in H_20
Dowex AG 1-X8, 50-100 mesh anion resin; slurry in 6*M* HCl

3. Procedure

Step 1. Add the sample (Note) to 1 ml of Mg carrier in a 40-ml conical centrifuge tube and precipitate $Mg(OH)_2$ by the dropwise addition of an excess of 10*M* NaOH. Centrifuge and discard the supernate. Dissolve the precipitate in a minimum of concd HCl, add about 100 mg of $NH_2OH \cdot HCl$, and warm on a steam bath for 3-5 min. Add 5 ml of 3*M* NH_4Cl and dilute to 20 ml with H_2O.

Step 2. Add 2 drops each of Fe, La, Sc, and Zr carriers and then an excess of concd NH_4OH dropwise. Centrifuge and transfer the supernate to a clean centrifuge tube, discarding the precipitate.

Step 3. Add 2 drops each of Fe and La carriers, centrifuge, transfer the supernate to a clean centrifuge tube and discard the precipitate.

Step 4. To the supernate add 10 drops of Cd carrier, 2 drops of Co carrier, bubble in H_2S for about 2 min, centrifuge, and transfer the supernate to a clean centrifuge tube, discarding the precipitate.

Step 5. Repeat the CdS-CoS precipitation. Centrifuge and filter the supernate through a Whatman No. 541 filter paper into a clean centrifuge tube, discarding the precipitate. Boil to remove H_2S.

Step 6. Add 2 drops of Ba carrier, 10 drops of Sr carrier, a volume of absolute ethanol equal to the total volume of solution, and 4 drops of concd H_2SO_4. Let the solution stand for 10 min, then centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. To the supernate add 2 drops of Ba carrier and 10 drops of Sr carrier. let stand for 10 min, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 7. To the supernate add an excess of 10*M* NaOH dropwise to precipitate $Mg(OH)_2$. Centrifuge and discard the supernate.

Step 8. To the precipitate add 5 ml of concd HCl, and 4 drops of Te(VI) carrier and boil the solution down to a volume of 1 ml. Dilute to 15 ml with H_2O, add 2 drops of Pd carrier, and bubble in H_2S for about 2 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 9. Add 2 drops each of Cd and Pd carriers and bubble in H_2S for about 2 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 10. Repeat Step 7.

Step 11. To the precipitate add 3 ml of concd HCl and boil for 1 min. Dilute with H_2O to 20 ml, add 3 ml of 1.5*M* $(NH_4)_2HPO_4$, and then an excess of concd NH_4OH dropwise to precipitate $MgNH_4PO_4 \cdot 6H_2O$. Centrifuge and discard the supernate. Wash the precipitate with H_2O containing a few drops of NH_4OH and discard the washings.

Step 12. Dissolve the precipitate in 1-2 drops of concd HCl and dilute to 10 ml with H_2O. Place the solution on a Dowex AG 50-X4, 100-200 mesh cation resin column (8 mm diameter and 4 cm long), add two 5-ml portions of H_2O to the column, and discard the eluates.

Step 13. Place the cation column on top of a Dowex AG 1-X8, 50-100 mesh anion resin column (8 mm diameter and 4 cm long) so that the eluate from the cation column can drip onto the anion column. To the cation column add two 5-ml portions of 6*M* HCl and permit the eluates to flow into the anion column. Collect the eluate from the anion column in a clean centrifuge tube.

Step 14. Repeat Steps 2 through 11.

Step 15. Dissolve the precipitate in a few drops of concd HCl and dilute the solution to 20 ml with H_2O. Centrifuge and transfer the supernate to a clean centrifuge tube. To the supernate add 3 ml of 1.5*M* $(NH_4)_2HPO_4$ and heat on a steam bath for 2 min. Add concd NH_4OH dropwise until $MgNH_4PO_4 \cdot 6H_2O$ precipitates. Filter the precipitate onto a weighed No. 42 Whatman filter paper, wash the precipitate with 0.1*M* NH_4OH and then with absolute ethanol. Dry in an oven at 110°, cool, weigh, and mount.

Note

If the original sample contains large amounts of salts, it should be treated in the following manner. Insoluble hydroxides are precipitated from a buffered NH_4^+-NH_4OH solution; most of the magnesium is left in the supernate and is recovered by precipitation with NaOH. The precipitate from the NH_4OH treatment is dissolved and reprecipitated until no detectable magnesium is found in the supernate after addition of NaOH. All $Mg(OH)_2$ precipitates are dissolved in concentrated HCl and combined. The solution is then treated with $NH_2OH \cdot HCl$ as described in Step 1 before proceeding to Step 2.

MANGANESE

B. P. Bayhurst and R. J. Prestwood

1. Introduction

In this procedure for the separation of manganese from fission-product solutions, manganese is finally precipitated as $MnNH_4PO_4 \cdot H_2O$ after standard decontamination steps. No detectable contamination was found in the manganese separated from 2.5×10^{14} fissions one hour old.

2. Reagents

Mn carrier: 10 mg Mn/ml, added as $MnCl_2$ in H_2O, standardized
W carrier: 10 mg W/ml, added as $Na_2WO_4 \cdot 2H_2O$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $FeCl_3$ in 1*M* HCl
Pd carrier: 10 mg Pd/ml, added as $PdCl_2 \cdot 2H_2O$ in 1*M* HCl
Zr carrier: 10 mg Zr/ml, added as $ZrOCl_2 \cdot 8H_2O$ in 1*M* HCl
HCl: concd; 6*M*
HNO_3: concd
$HC_2H_3O_2$: glacial
NH_4OH: concd
NaOH: 10*M*
H_2S: gas
$NaBrO_3$: saturated solution
$(NH_4)_2S$: 20% solution
$(NH_4)_2HPO_4$: 1.5*M*
Aerosol: 0.1% in H_2O
Dowex AG 50-X4, 100-200 mesh cation resin, slurry in H_2O
Dowex AG 1-X8, 50-100 mesh anion resin, slurry in 6*M* HCl
Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 22.9 g of $MnCl_2$ in H_2O and dilute the solution to 1 liter. Pipet exactly 2 ml of the solution into a 40-ml conical centrifuge tube, add 5 drops of concd HCl, 3 ml of 1.5*M* $(NH_4)_2HPO_4$, and make basic with concd NH_4OH. Heat to boiling, let stand for 10 min, and filter the precipitate into a weighed sintered glass crucible. Wash the precipitate first with 0.1*M* NH_4OH and then with ethanol. Dry at 110°, cool, and weigh as $MnNH_4PO_4 \cdot H_2O$.

Four standardizations using the above procedure gave results with a total spread of 1%.

4. Procedure

Step 1. Add the sample to 2 ml of Mn carrier in a 40-ml conical centrifuge tube and adjust the volume to about 20 ml with concd HNO_3.

Step 2. Add 5 drops of W carrier and heat on a steam bath for 5-10 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and repeat the W scavenge.

Step 3. To the supernate from the second W scavenge add 3 ml of saturated $NaBrO_3$ and heat on a steam bath. (MnO_2 begins to precipitate and the solution fizzes.) Carefully add another 3 ml of $NaBrO_3$ and heat on a steam bath until the total time of heating is about 10 min. Cool the solution, add water to fill the tube, and centrifuge. Discard the supernate, wash the precipitate twice with H_2O, and discard the washings.

Step 4. To the precipitate add 2 drops of Fe carrier and 6 ml of concd HCl and boil over a burner until the volume of solution is about 3 ml. Dilute to 20 ml with H_2O, add concd NH_4OH dropwise until $Fe(OH)_3$ precipitates, and then add 1-2 drops in excess. Heat on a steam bath for about 2 min and centrifuge. Transfer the supernate to a clean centrifuge tube and repeat the Fe scavenge. Centrifuge and transfer the supernate to a clean centrifuge tube.

Step 5. Add 2 ml of 20% $(NH_4)_2S$, heat for 1-2 min on a steam bath, and centrifuge. Discard the supernate. The precipitate is MnS.

Step 6. To the precipitate add 5 ml of glacial $HC_2H_3O_2$ and boil over a flame. Add 5 drops of Pd carrier, dilute to 20 ml with H_2O, place on a steam bath, and bubble in H_2S. Centrifuge and transfer the supernate to a clean centrifuge tube. To the supernate add 5 drops of Pd carrier, repeat the sulfide scavenge, and transfer the supernate to a clean centrifuge tube.

Step 7. To the supernate add 3 ml of 1.5M $(NH_4)_2HPO_4$ and about 5 drops of concd HCl and boil. Add 2 drops of Zr carrier, centrifuge, and transfer the supernate to a clean tube. Add 2 drops of Zr carrier to the supernate, centrifuge, and transfer into a clean tube.

Step 8. To the supernate add concd NH_4OH dropwise until $MnNH_4PO_4 \cdot H_2O$ precipitates and then heat on a steam bath for 3-5 min. Centrifuge and discard the supernate. Wash the precipitate with a full tube of H_2O, centrifuge, and discard the washings.

Step 9. Dissolve the precipitate in 2-3 drops of concd HCl, dilute to 5-7 ml with H_2O, and place on a Dowex AG 50-X4, 100-200 mesh cation resin column (6 mm diameter and 3 cm long). Rinse the centrifuge tube with H_2O and add the rinsings to the resin. Wash the resin with several 2-3 ml portions of H_2O and discard all washings. To the cation resin column add 6-9 ml of 6M HCl, after placing the column on top of a Dowex AG 1-X8, 50-100 mesh anion resin column (8 mm diameter and 4-5 cm long) so that the eluate from the cation column drips into the anion column. To the eluate from the anion column, which contains the Mn and is collected in a clean centrifuge tube, add 10M NaOH dropwise to precipitate $Mn(OH)_2$. Centrifuge and discard the supernate.

Step 10. To the precipitate, add 10 ml of concd HNO_3, bring to a boil over a flame, and boil until the solution has lost any color. Repeat the W scavenge (Step 2).

Step 11. Repeat Step 3.

Step 12. Repeat the Fe scavenge (Step 4).

Step 13. Repeat the MnS precipitation (Step 5).

Step 14. Repeat the PdS scavenge (Step 6)

Step 15. Repeat the $Zr_3(PO_4)_4$ precipitation (Step 7).

Step 16. To the supernate add concd NH_4OH dropwise until $MnNH_4PO_4 \cdot H_2O$ precipitates and then heat on a steam bath for 3-5 min. Centrifuge, discard the supernate, and dissolve the precipitate in 4-5 drops of concd HCl. Dilute to 20 ml with H_2O, add a few drops of aerosol, and centrifuge. Transfer the supernate to a clean centrifuge tube and reprecipitate $MnNH_4PO_4 \cdot H_2O$. Filter onto a weighed No. 42 Whatman ⅞″ filter circle, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate first with 0.1M NH_4OH and then with ethanol. Dry at 110°, cool, weigh, and mount.

MOLYBDENUM I

J. W. Barnes and E. J. Lang

1. Introduction

The separation of molybdenum from fission products is based primarily on its behavior in the +6 oxidation state on an anion exchange resin. Molybdenum(VI) is adsorbed on the resin from hydrochloric acid solutions of concentrations 5 to $9M$. Resin washes with a mixture of dilute hydrochloric and hydrofluoric acids and with $3M$ ammonium hydroxide remove most of the interfering ions. Molybdenum is eluted from the column with $6M$ ammonium acetate, precipitated with α-benzoinoxime, and converted by ignition to MoO_3, in which form it is weighed and counted. The chemical yield is about 75%.

2. Reagents

Mo carrier: 10 mg Mo/ml $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution, standardized
Fe carrier: 10 mg Fe/ml, added as aqueous $FeCl_3\cdot 6H_2O$
Cu carrier: 10 mg Cu/ml, added as aqueous $CuSO_4\cdot 5H_2O$
H_2SO_4: concd
$H_2C_2O_4$: saturated aqueous solution
NH_4Cl: $3M$
$NaBrO_3$: $0.5M$
HNO_3: $1M$; concd
HCl: $6M$; concd
$HClO_4$: concd
HCl-HF: $0.1M$ in HCl and $0.05M$ in HF
NH_4OH: $3M$; concd
$NH_4C_2H_3O_2$: $6M$
α-Benzoinoxime: 2% in ethanol
Br_2-H_2O
Anion resin: Dowex 1-X8 (50 to 100 mesh; stored in $6M$ HCl) (Note 1)
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 18.4 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in H_2O, add 1 ml of $0.5M$ $NaBrO_3$, and dilute to 1 liter with $6M$ HCl. Pipet 5.0 ml of the solution into a Coors 0 porcelain crucible which has been heated previously in a muffle furnace at 550°, cooled, and weighed. Add 0.5 ml of concd HNO_3 and 0.5 ml of concd $HClO_4$. Carefully dry the sample under an infrared lamp, making certain that no spattering occurs. Ignite in the furnace for 1 hr at 550°. Cool and weigh as MoO_3.

4. Procedure

Step 1. Add the sample to 3.0 ml of Mo carrier in a 125-ml erlenmeyer flask. Then add 1 ml of Br_2-H_2O, 4 drops of Cu carrier, and 1 to 5 ml of concd H_2SO_4, depending upon the amount of uranium in the sample (about 2 ml of the acid is sufficient for 1 g of U). Fume to dryness over a burner, add 30 ml of H_2O, and warm to dissolve the residue. While the solution is kept warm, saturate with H_2S. Pour the mixture into a 40-ml conical centrifuge tube, centrifuge, and save the supernate for the recovery of U (Note 2).

Step 2. Wash the precipitate by stirring with 5 ml of $3M$ NH_4Cl and 10 ml of H_2O. Centrifuge and discard the washings. Dissolve the precipitate in 1 ml of concd HCl and a few drops of concd HNO_3. Add 10 ml of H_2O, boil to remove excess H_2S, and then add 3-4 drops of Fe carrier. Precipitate $Fe_2O_3\cdot XH_2O$ by adding 2 to 3 ml of concd NH_4OH. Warm to coagulate the precipitate, centrifuge, transfer the supernate to a 125-ml erlenmeyer flask, and discard the precipitate.

Step 3. Take the supernate to half volume over a burner. Add 1 ml of concd HCl and again take to half volume. Add 1 ml of concd HCl, take the solution almost to dryness, and then add 10 ml of $6M$ HCl and 1 ml of Br_2-H_2O.

Step 4. Heat the solution to boiling, transfer it to the Dowex 1 anion resin column (Note 3), and permit it to run through under gravity. Wash sides of column with 1 to 2 ml of $6M$ HCl, and when the level of acid reaches the top of the resin, add 10 ml of hot HCl-HF solution (Note 4). When the level of the HCl-HF solution reaches the top of the resin, add 5 ml of $3M$ NH_4OH.

Step 5. As soon as the level of the NH_4OH reaches the top of the resin, all effluents collected to this point are placed in the appropriate waste bottle. Add 10 ml of hot $6M$ $NH_4C_2H_3O_2$ to the resin and permit the solution to pass through, catching the Mo eluate in a clean 40-ml centrifuge tube.

Step 6. To the eluate add 2 ml of concd NH_4OH, stir, and then add 4 drops of Fe carrier. Boil for one minute with stirring. Centrifuge.

Step 7. Add the supernate to an ice-cold mixture of 6 ml of concd HNO_3, 1 ml of Br_2-H_2O, and 1 ml of saturated $H_2C_2O_4$ in a 40-ml centrifuge tube. Cool in an ice bath for 5 min, add 10 ml of α-benzoinoxime solution, and stir vigorously. Filter onto No. 41 H Whatman filter paper, completing the transfer with 1*M* HNO_3.

Step 8. Place the filter paper and contents in a porcelain crucible (Coors O), and ignite to MoO_3 at 550° for about 1 hr (Note 5).

Step 9. After ignition, allow the crucible to cool and grind the MoO_3 to a fine consistency with the end of a stirring rod. Add 2 drops of ethanol and slurry; then add an additional 5 ml of ethanol, stir, and filter onto a previously washed, dried, and weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and stainless steel filter chimney. Wash with ethanol, and dry at 110° for about 10 min. Cool, weigh, and mount (Notes 6 and 7).

Notes

1. The anion resin, AG1-X8, 50-100 mesh, obtained from Bio-Rad Laboratories, Richmond, Calif., is stored in 6*M* HCl.

2. This step is used only when the amount of uranium in the sample exceeds about 50 mg or if plutonium or tungsten are present in appreciable amounts. If the amount of uranium is less than 50 mg and if relatively little plutonium is present, add the sample to 3.0 ml of Mo carrier, and then add 1 ml of concd H_2SO_4 and 1 ml of Br_2-H_2O. Fume to dryness, cool, add 10 ml of H_2O and 3 drops of Fe carrier, and precipitate $Fe_2O_3 \cdot XH_2O$ as in Step 2. Then continue the regular procedure.

3. To prepare the resin column for use (a) place a small plug of glass wool in the tip of the column, (b) add enough resin slurry to obtain a bed height of 4 to 5 cm and (c) allow the acid to drain off. (The column is fabricated by fusing a 15-ml conical centrifuge tube to an 8-cm length of 1-cm tubing drawn to a tip.)

4. The HCl-HF wash removes moderate quantities of uranium and plutonium.

5. A stream of air through the muffle furnace aids in the conversion of the Mo(VI)-benzoinoxime complex to MoO_3.

6. The samples are mounted on Al plates with two-sided Scotch tape and covered with Mylar film. Four drops of rubber cement solution (3 ml rubber cement to 50 ml benzene) are used to keep the MoO_3 under the Mylar film.

7. The sample is permitted to stand for 18 hr before counting in order to allow the 6-hr ^{99}Tc daughter to grow into equilibrium. The individual counts are corrected to zero time using a half-life of 66.4 hr, and a correction for self-absorption in the sample is applied.

MOLYBDENUM II

J. S. Gilmore and H. L. Smith

1. Introduction

The procedure described below, devised originally for the rapid determination of ^{101}Mo in the presence of large quantities of foreign material, has proved to be suitable for the removal of molybdenum from 120 g of uranium or 1 g of plutonium or about 20 g of iron. It also gives excellent decontamination from neptunium and fission products.

The chief decontamination step is an extraction into chloroform of the precipitate of Mo(VI) with α-benzoinoxime. This step may be omitted and decontamination effected by extraction of molybdenum from hydrochloric acid solution into hexone (Note 1) if the sample contains less than 10 g of uranium. If the original sample has a volume greater than one liter, the hexone extraction is essential as a volume reducing step.

Additional decontamination steps include adsorption of Mo(VI) from hydrochloric acid solution on an anion exchange resin and an iron hydroxide scavenge. The molybdenum is finally precipitated as the 8-hydroxyquinolate, in which form it is counted.

The chemical yield is 60-70% and duplicate determinations can be performed in about 45 min.

2. Reagents

Mo carrier: 10 mg Mo/ml. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, standardized as described in the preceding Molybdenum Procedure.
Fe carrier: 10 mg Fe/ml, added as $FeCl_3\cdot 6H_2O$
α-Benzoinoxime: 2% in ethanol
8-Hydroxyquinoline: 5% in 2*M* $HC_2H_3O_2$
HCl: concd; 6*M*; 1*M*
HNO_3: concd
$HClO_4$: concd
H_2SO_4: concd
$HC_2H_3O_2$: 6*M*
NaOH: 0.6*M*
HCl-HF: 0.1*M* in HCl and 0.1*M* in HF
$NH_4C_2H_3O_2$: 6*M*
Acetone
Ethanol: 95%
Chloroform
Methyl red indicator solution
Anion resin: Dowex 1-X10 (200 - 400 mesh; stored in 6*M* HCl)

3. Procedure

Step 1. The sample is made 6-7*M* in HCl and 1-2 ml of Mo carrier is added (Note 1). Boil the solution briefly and dilute with ice and water to 750 ml (Note 2). Transfer the solution to a 1-liter pear-shaped separatory funnel and precipitate Mo with 25 ml of α-benzoinoxime reagent.

Step 2. Add 50 ml of chloroform and shake vigorously. Permit the phases to separate and the precipitate to move from the aqueous to the chloroform phase (Note 3). Transfer the chloroform phase to a 250-ml pear-shaped separatory funnel. Extract the aqueous phase with 10 ml of α-benzoinoxime and 30 ml of chloroform and combine the chloroform layer with that separated previously. Discard the aqueous phase.

Step 3. Wash the chloroform layer with a mixture of 80 ml of 1*M* HCl and 20 ml of ethanol and discard the washings. Transfer the chloroform layer to a 125-ml separatory funnel. Add 25 ml of 0.6*M* NaOH and shake vigorously to remove the Mo. Discard the chloroform and transfer the aqueous layer to a 250-ml Vycor or quartz erlenmeyer flask.

Step 4. Boil the solution briefly to expel any chloroform present. Add 10 ml of concd HNO_3 and boil the solution to half its original volume. Add 4 ml of concd $HClO_4$ and 2 ml of concd H_2SO_4 and boil carefully until the exothermic reaction subsides. Then boil until strong fumes of SO_3 are evolved. (This step removes organic material.)

Step 5. Dilute the solution with 20 ml of 6*M* HCl and place on a Dowex 1-X10 (200-400 mesh) resin column (4-ml bed volume). Wash the resin successively with 10 ml of 6*M* HCl, 15 ml of 0.1*M* HCl-HF, and 10 ml of 3*M* NH_4OH.

Step 6. Elute the Mo from the column with

15 ml of 6*M* $NH_4C_2H_3O_2$ solution. To the eluate add 3 ml of concd NH_4OH and 4 drops of Fe carrier. Boil and filter through 11 cm., 41-H Whatman filter paper, using a 2", 60° funnel. Discard the precipitate (Note 4).

Step 7. To the filtrate add methyl red indicator solution, acidify with 6*M* $HC_2H_3O_2$, then add 2 ml in excess, boil, and add 2 ml of 8-hydroxyquinoline reagent (Note 5). Filter onto a 1" Whatman No. 42 filter circle, using a ground-off Hirsch funnel and filter chimney. Discard the filtrate. Wash the precipitate with H_2O, then with acetone.

Step 8. Dry the Mo oxinate for 30 sec at 140°, weigh, mount, and β-count.

Notes

1. A hexone (4-methyl-2-pentanone) extraction may be performed at this point instead of or in addition to the precipitation and extraction of Mo as the α-benzoinoximate. The hexone extraction is advisable if the sample contains less than 10 g of U and is essential as a volume reducing step if the sample has a volume greater than 1 liter. The solution, which is 6-7*M* in HCl, is extracted with an equal volume of hexone which has been pre-equilibrated with 6*M* HCl to remove Mo. The hexone layer is washed with an equal volume of 6*M* HCl which has been pre-equilibrated with hexone, and is then shaken with 20-50% of its volume of H_2O to back-extract the Mo. If the original sample contained more than 100 mg of Fe, proceed with the precipitation of Mo by means of α-benzoinoxime; otherwise, go directly to Step 5 or, if no Fe is present at this point, the H_2O back-extract may be diluted with an equal volume of concd HCl and the solution put directly on a Dowex-1, 40-ml reservoir, anion column. Then proceed with the regular chemistry.

2. Precipitation of Mo with α-benzoinoxime is more nearly complete if the solution is cold.

3. At least 15 min must have elapsed since end of irradiation before any Mo chemistry is performed to avoid possible separation of ^{99}Nb and ^{99}Mo before the Mo has grown in.

4. The $Fe(OH)_3$ scavenge removes Nb, which otherwise contaminates the final sample.

5. The oxine precipitation constitutes the last Tc separation from the Mo. Therefore, the time of the addition of the 8-hydroxquinoline is accurately observed and recorded.

neptunium, nickel, niobium

NEPTUNIUM-239

H. L. Smith

1. Introduction

The procedure for the determination of ^{239}Np affords excellent decontamination from milligram quantities of uranium, the fission products obtained from 10^{13} fissions, and plutonium. The decontamination factor for the latter element is about 10^4.

An initial fuming with sulfuric acid is recommended to ensure exchange between the ^{237}Np tracer employed and ^{239}Np, and also to complex uranium(VI). If the sample is a dissolved uranium foil, nitric acid must be added before the fuming step to convert uranium to the +6 state. Np(IV) and (V) are carried down by lanthanum fluoride precipitations in the presence of zirconium and strontium holdback carriers, the precipitations providing decontamination from the activities of the latter elements as well as from uranium. Lanthanum fluoride scavenging with neptunium in the hexapositive state decontaminates from the lanthanides and partially from plutonium.

2. Reagents

La carrier: 5 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Sr carrier: 10 mg Sr/ml, added as $Sr(NO_3)_2 \cdot 4H_2O$ in H_2O
Zr carrier: 10 mg Zr/ml, added as $ZrOCl_2$ in H_2O
^{237}Np standard solution: 5,000 to 10,000 counts/min/ml in 2 to 4*M* HCl or HNO_3
HCl: 0.1*M*; 1*M*; 2*M*; concd
H_2SO_4: concd
HNO_3: concd
H_3BO_3: saturated solution
HF: 1:1 H_2O and concd HF
HI-HCl: 1 ml 55-57% HI + 9 ml concd HCl (this mixture may be saved if kept refrigerated but should be discarded when it becomes very dark brown)
HF-HNO_3: equal parts by volume of 2*M* solutions
$NH_2OH \cdot HCl$: 5*M* (or saturated)
$KMnO_4$: 10% solution
NH_4OH: concd; dilute
Methyl red indicator solution: 0.5% in 90% ethanol
Dowex 1-X10 anion exchange resin: 100-200 or 200-400 mesh, slurry in H_2O (Note 1)

3. Standardization of Tracer

The usual technique for standardizing α-emitting tracers, which consists of the evaporation of a measured volume of solution on a Pt plate and α-counting it, does not work very well in the case of ^{237}Np. This is because of the relatively low specific activity of ^{237}Np, which is of the order of 800 counts/min/μg, so that stippling produces a rather massive deposit. A preferable technique is the following: Prepare a solution of pure ^{239}Np from pile-irradiated ^{238}U that contains approximately 10^4 counts/min/100μl. Weigh an aliquot of this solution onto a platinum plate, and add another weighed aliquot to 1 ml of tracer. The ^{239}Np can now be used as a β-emitting tracer to determine the absolute amount of ^{237}Np.

Evaporate the ^{239}Np + ^{237}Np sample to dryness with HNO_3, take into solution with 1 ml concd HCl and pass the solution through an anion column as described in Step 11, then elute the Np with 0.1*M* HCl, and electroplate as described in Step 12. α- and β-count the sample, and β-count the pure ^{239}Np aliquot. Using the known specific β activity of the ^{239}Np, calculate the activity of ^{237}Np/ml of solution.

4. Procedure

Step 1. Pipet 1 ml of ^{237}Np standard into a clean 125-ml erlenmeyer flask and then pipet in the sample. Wash down the sides of the flask with a little H_2O, add 10 drops of concd H_2SO_4 (Note 2), and evaporate nearly to dryness on a hot plate. (No harm is done if the solution is permitted to evaporate to hard dryness.)

Step 2. Dissolve the residue by boiling briefly in a minimum of 2*M* HCl. Transfer the solution to a clean 40-ml Pyrex centrifuge tube, wash the flask once with H_2O, and transfer the washings to the tube. The volume of solution should be 5-10 ml. (Ignore any small residue.)

Step 3. Add 5 drops of La carrier and 3 drops of Zr holdback carrier. Add 2 drops of $NH_2OH \cdot HCl$ for each ml of solution, stir and let stand for a few minutes. Add HF dropwise until the yellow color of the solution disappears and the solution becomes cloudy (LaF_3). Centrifuge. Remove and discard the supernate. Wash the precipitate with 1 to 5 ml of HF-HNO_3.

Step 4. Dissolve the precipitate by slurrying with 3 drops of saturated H_3BO_3 and adding 3 drops of concd

HCl. (Ignore any small residue.) Add 3 ml of 2*M* HCl and precipitate $La(OH)_3$ by adding about 1 ml of concd NH_4OH. Centrifuge and discard the supernate. Wash the precipitate by boiling it briefly with several ml of H_2O.

Step 5. Dissolve the precipitate in about 5 ml of 2*M* HCl. Reprecipitate LaF_3 by adding 10 drops of $NH_2OH{\cdot}HCl$ and 10 drops of HF; centrifuge and discard the supernate. Wash the precipitate with 1 ml of $HF\text{-}HNO_3$. If the precipitate volume is greater than 0.2 ml, repeat the hydroxide and fluoride precipitations until the volume of LaF_3 precipitate does not exceed 0.2 ml.

Step 6. Dissolve the fluoride precipitate in 1 drop each of saturated H_3BO_3 and concd HNO_3. Add 10 drops of $KMnO_4$ and allow to stand for 5 min. Add 2 drops of HF and allow the solution to stand for a few minutes. Centrifuge and transfer the supernate to a clean centrifuge tube. Wash the precipitate with 0.5-1 ml of $HF\text{-}HNO_3$, centrifuge, and add the supernate to the previous one. Discard the precipitate.

Step 7. Add 2 drops of La carrier to the solution, stir, centrifuge, and transfer the supernate to a clean centrifuge tube. Wash the precipitate with 0.5-1 ml $HF\text{-}HNO_3$, add the washings to the previous supernate, and discard the precipitate.

Step 8. Add 5 drops of $NH_2OH{\cdot}HCl$ and 2 drops of Zr carrier, and let stand for a few minutes. Add 2 drops of La carrier, stir well, centrifuge, and discard the supernate. Wash the precipitate with 1 ml $HF\text{-}HNO_3$, centrifuge, and discard the supernate.

Step 9. Repeat Steps 6 and 7.

Step 10. Add 5 drops of $NH_2OH{\cdot}HCl$ and 2 drops of Sr holdback carrier, and let stand for a few minutes. Add 2 drops La carrier, stir well, centrifuge, and discard the supernate. Wash the precipitate with 1 ml $HF\text{-}HNO_3$, centrifuge, and discard the supernate.

Step 11. Dissolve the precipitate with 1 drop of saturated H_3BO_3 and 10 drops of concd HCl. Pass the solution through a Dowex 1-X10 anion exchange column, 3 cm x 3 mm, and wash the column with 1 ml of concd HCl. The Np is now in the +4 oxidation state and is adsorbed on the column. If necessary, remove Pu from the column with HI-HCl (Note 3). Elute the Np with 0.5 ml of 0.1*M* HCl. If a Pu removal step has been done, the solution should be taken to dryness before electroplating; otherwise, the elution can be received directly into the electroplating cell, 1 cm diameter.

Step 12. Adjust the acidity so as to obtain 1-2 ml of a solution that is about 6*M* in HCl. Add 1 drop methyl red indicator and make basic with concd NH_4OH, and then barely acidic with 1*M* HCl. Electroplate for 20 min at 0.5 amp. Make basic with dilute NH_4OH for the last minute of plating. (On several occasions an explosion occurred when concd NH_4OH was used for this neutralization.) Decant the plating solution, and rinse the cell with H_2O and alcohol. Dismantle the cell and ignite the plate to red heat in a burner. Mount with double-sided Scotch tape in the center of an Al plate, α-count to determine the chemical yield, and β-count on three successive days.

Notes

1. The resin is supplied by the Bio-Rad Laboratories, Richmond, Calif., who purify and grade the resins manufactured by the Dow Chemical Co.

2. If the sample has been obtained from more than the equivalent of 50 mg of soil, do not add any H_2SO_4 since $CaSO_4$ will precipitate and carry Np to some extent. Probably repeated fuming with HNO_3 will promote exchange.

3. The procedure should remove 95% of the Pu initially present in the sample. If, at this point, there remains enough Pu to interfere with the determination of the Np yield, that is, more than 1% of the Np tracer, Pu may be removed more efficiently in the following way: Allow 1 ml of HI-HCl solution to drip through the column with no added pressure. Wash the column with several ml of concd HCl and discard the effluent, which contains the Pu in the +3 state, and proceed with the rest of Step 11. One elution step such as the one just described removes 99.5% of the Pu.

NICKEL

W. H. Burgus

1. Introduction

Nickel is separated from fission products by precipitation with dimethylglyoxime (DMG)* from an ammoniacal medium in the presence of a large quantity of citrate ion. Three precipitations in the presence of cobalt as a holdback carrier are carried out. After appropriate scavenging steps, the nickel is again precipitated with dimethylglyoxime and the nickel-dimethylglyoxime complex is extracted into chloroform. The nickel is then back-extracted into dilute hydrochloric acid solution and is finally plated out of strongly ammoniacal solution. The chemical yield is approximately 75%. About 2½ hr are required for the decontamination of a single sample, and 2 hr for plating.

2. Reagents

Ni carrier: 10 mg Ni/ml, added as $Ni(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3, standardized
Co carrier: 10 mg Co/ml, added as $Co(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3
Pd carrier: 10 mg Pd/ml, added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl
Cu carrier: 10 mg Cu/ml, added as $CuCl_2 \cdot 2H_2O$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
HCl: concd; 6*M*
HNO_3: concd
H_2SO_4: concd
NH_4OH: concd
$(NH_4)_2SO_4$: solid
Sodium citrate: 10% in H_2O
H_2S: gas
Dimethylglyoxime reagent (DMG): 1% in ethanol
Chloroform
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 49.5 g of $Ni(NO_3)_2 \cdot 6H_2O$ in H_2O, add 1 ml of HNO_3, and dilute to 1 liter with H_2O.

Pipet 5.0 ml of the carrier solution into a 125-ml erlenmeyer flask, add 3 ml of concd H_2SO_4, boil down to SO_3 fumes to remove NO_3^- ion, and cool to room temperature. Dilute to 8-10 ml with H_2O, and cautiously neutralize with concd NH_4OH, adding 1 ml in excess. Add 1 g of $(NH_4)_2SO_4$, quantitatively transfer to plating cell, and plate for 3 hr at 0.10 amp and about 3 v. Add a drop of concd NH_4OH about every 30 min. When the plating has been completed, wash the cathode several times with distilled H_2O and once with ethanol. Air-dry and weigh.

Four standardizations are carried out with results agreeing within about 0.2%.

4. Procedure

Step 1. To 5-10 ml of the sample in a 40-ml centrifuge tube, add 2 ml of the standard Ni carrier, 10 drops of Co holdback carrier, and 10 ml of 10% Na-citrate solution. Make ammoniacal

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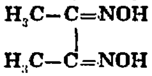
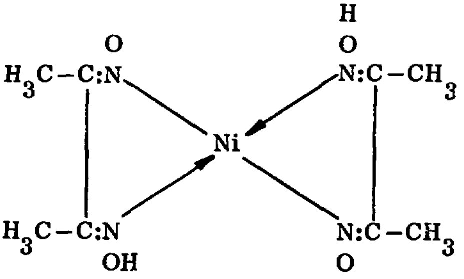
*When dimethylglyoxime (diacetyldioxime)



$$\begin{array}{l} H_3C-C{=}NOH \\ \quad\;\;\;| \\ H_3C-C{=}NOH \end{array}$$

is used as a precipitant, one of the two hydroxyl hydrogens is replaced by an equivalent of the metal ion precipitated. Thus with Ni^{2+}, the following bright red inner complex is formed



The precipitation of nickel is carried out in an ammoniacal medium containing citrate or tartrate ion. The presence of citrate or tartrate is essential in order to complex ions which give insoluble hydroxides and which, therefore, would be coprecipitated with nickel. Palladium, which is partially precipitated from ammoniacal solution, is removed by precipitation of the sulfide from acid medium. The presence of large amounts of oxidizing agents, e.g., hydrogen peroxide, nitrates, and halogens, may prevent the precipitation of nickel.

by addition of concd NH_4OH. (A color change to deep blue-violet indicates that sufficient NH_4OH has been added.) Dilute to 25 ml with H_2O. Precipitate Ni by the addition of 15 ml of 1% alcoholic DMG reagent. Centrifuge and wash precipitate with 30 ml of H_2O containing a drop of concd NH_4OH. Discard the supernate and washings.

Step 2. Dissolve the Ni-DMG precipitate in 2 ml of concd HCl and dilute to 15 ml with H_2O. (Disregard any DMG which precipitates at this stage.) Add 10 ml of 10% Na-citrate, 2 drops of Co carrier, and 5 ml of DMG reagent. Precipitate Ni-DMG by addition of concd NH_4OH. Centrifuge and wash as before (Step 1).

Step 3. Repeat Step 2.

Step 4. Dissolve the Ni-DMG precipitate in 10 ml of concd HNO_3, and transfer to 125-ml erlenmeyer flask. Boil to dryness and heat to destroy *all* organic matter (Note 1). Dissolve NiO (black) in a few milliliters of concd HCl by heating. The solution process is aided by the addition of a drop or two of concd HNO_3. Boil until $NiCl_2$ precipitates and then dilute to 20 ml with H_2O. (Be certain that the heating is continued for sufficient time to remove HNO_3.)

Step 5. Add 3 drops of concd HCl and 4 drops each of Cu and Pd carriers. Heat to boiling and pass in H_2S for 5 min. Filter sulfide scavenger precipitate and discard.

Step 6. Boil out H_2S, add 2 drops of concd HCl, 4 drops each of Cu and Pd carriers, dilute to 20 ml with H_2O, heat and remove another sulfide scavenger precipitate with H_2S. Boil out H_2S from the filtrate and transfer to a 40-ml centrifuge tube.

Step 7. Dilute to 20 ml with H_2O. Add 8 drops of Fe carrier and precipitate $Fe(OH)_3$ from hot solution by the addition of concd NH_4OH (1 ml in excess). Centrifuge and discard $Fe(OH)_3$ scavenger precipitate.

Step 8. Acidify the supernate with HCl or HNO_3. Add 8 drops of Fe carrier and remove a second $Fe(OH)_3$ scavenge. Transfer the supernate to a 100-ml beaker.

Step 9. To the supernate from the $Fe(OH)_3$ scavenge, add 10 ml of 10% Na-citrate and 1 drop of Co carrier. Add 15 ml of DMG solution and transfer to a 600-ml separatory funnel. Add 500 ml of $CHCl_3$ and extract Ni-DMG (Note 2).

Step 10. Wash $CHCl_3$ layer twice with 50-ml portions of H_2O containing 1 drop of concd NH_4OH. Discard washings.

Step 11. Back-extract Ni into 20 ml of 6*M* HCl. Transfer water layer to a 125-ml erlenmeyer flask (Note 3), and boil nearly to dryness. Add 4-5 ml of concd HNO_3. Boil nearly to dryness. Add about 3 ml of concd H_2SO_4 and heat to SO_3 fumes (Note 4). Cool to room temperature.

Step 12. Add 8 ml of H_2O and cautiously neutralize with concd NH_4OH (1 ml in excess). Add 1 gm of $(NH_4)_2SO_4$, dilute to 20 ml with H_2O, and transfer to plating cell. Plate Ni on a weighed Pt foil. (For a circular foil of 7/8" diameter, plate for 2 hr at 0.10 amp. Add a drop of concd NH_4OH about every 30 min.) After plating, wash with H_2O and then with ethanol. Air-dry, weigh, and count (Note 5).

Notes

1. When boiling down with concd HNO_3, be certain to take to dryness, and then heat a little longer. All citrate and decomposition products of DMG must be removed, otherwise it is impossible to precipitate $Fe(OH)_3$ in Step 7.

2. Freshly precipitated Ni-DMG ordinarily extracts rapidly into $CHCl_3$. If it does not do so, add an additional 50 ml of $CHCl_3$ and shake the separatory funnel vigorously. The $CHCl_3$ and H_2O layers do not separate quickly, and at least 5 min should be allowed for the emulsion to break and for separation to occur.

3. The complete disappearance of the yellow-orange color of Ni-DMG in the $CHCl_3$ layer indicates that back-extraction is complete.

4. For successful plating, all organic material and nitrates must be removed.

5. If 36-hr ^{57}Ni is being counted, mount the sample and cover with 1-mil Dural in order to absorb the radiations of 2×10^5-year ^{59}Ni and of 300-year ^{63}Ni.

NIOBIUM

J. S. Gilmore

1. Introduction

In the separation of niobium from other fission activities, zirconium is removed as barium fluozirconate; any +4 uranium present, as well as rare-earth activities, are carried down as the fluorides at this stage. Niobium is then converted to its cupferron derivative which is extracted into chloroform. This step gives an effective separation from +6 uranium. The cupferron complex is destroyed and the niobium precipitated as the hydrous oxide, $Nb_2O_5 \cdot XH_2O$, by means of ammonia water; molybdenum remains in solution as a molybdate. The oxide is dissolved in sulfuric acid and decontamination from tin and antimony is effected by means of a sulfide precipitation. Further decontamination is obtained by additional precipitations of the oxide, extractions of the cupferron derivative, and acid sulfide scavengings. Niobium is finally precipitated as the cupferrate and ignited to the oxide, in which form it is weighed and counted. The chemical yield is 40-50% and duplicate samples can be analyzed in about 4 hr. If the sample solution contains large quantities of uranium the chemical yields are likely to be low; at present there is no explanation for this.

2. Reagents

Nb carrier: 10 mg Nb/ml, added as Nb (V) in oxalic acid solution, standardized
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
Cu carrier: 10 mg Cu/ml, added as $CuCl_2 \cdot 2H_2O$ in H_2O
HCl: 6*M*; concd
HNO_3: 6*M*; concd
H_2SO_4: concd
HF: concd
Tartaric acid: 25% aqueous solution
H_3BO_3: saturated aqueous solution
NH_4OH: 6*M*; concd
$(NH_4)_2C_4H_4O_6$: saturated aqueous solution
$BaCl_2$: 50 mg/ml
$KClO_3$: solid (for standardization)
H_2S: gas
Cupferron reagent: 6% aqueous solution (kept in refrigerator)
Methyl red indicator solution: 0.1% in 90% ethanol
Chloroform

3. Preparation and Standardization of Carrier

(Taken from *Radiochemical Studies*: *The Fission Products*, Book 3, pp. 1524-5)

Dissolve 26.0 g of potassium hexaniobate, $K_8Nb_6O_{19} \cdot 16H_2O$, (Fansteel Metallurgical Corp.) in about 200 ml of H_2O, heat the solution nearly to boiling, and add 15 ml of concd HNO_3 slowly with stirring. Continue heating and stirring for 2-3 min and centrifuge. Wash the precipitate three times, with centrifugation, with 50 ml of hot 2% NH_4NO_3 solution. Add 200 ml of saturated $H_2C_2O_4$, and heat with stirring until Nb_2O_5 dissolves. Cool and dilute with H_2O to 1 liter. Filter the solution if it is not clear.

Pipet exactly 5 ml of the carrier solution into a 100-ml beaker. Add 30 ml of 6*M* HNO_3 and about 1 g of $KClO_3$ and carefully heat the solution to boiling. Boil gently with occasional stirring for about 5 min. Cool the mixture and add about 15 ml concd NH_4OH with stirring to make the pH value 8 to 10. Filter quantitatively on a No. 42 Whatman filter paper through a 2″, 60° funnel, returning the first portion of the filtrate if it is not clear, and wash with hot H_2O. Ignite in a Coors 00 crucible at about 800° for 15-20 min and weigh as Nb_2O_5.

Four standardizations performed as described above gave results agreeing within 0.5%.

4. Procedure

Step 1. To exactly 4 ml of Nb carrier in a 40-ml Lusteroid centrifuge tube, add 3 ml of concd HF, 10 ml of the sample in 4*M* HCl, 1 ml of Zr carrier, and 4 ml of $BaCl_2$ solution (50 mg/ml). Centrifuge the $BaZrF_6$ precipitate, transfer the supernate to a clean 40-ml Lusteroid tube, and discard the precipitate. Repeat the $BaZrF_6$ precipitation three times, the third time transferring the supernate to a 125-ml separatory funnel.

Step 2. To the supernate add 30 ml of a saturated H_3BO_3 to decompose the Nb-fluoride complex and make the solution 1*M* in HCl. Add 4 ml of cold 6% cupferron reagent and let the mixture stand for 1 min. Extract the Nb-cupferron complex into 20 ml of $CHCl_3$ and transfer the $CHCl_3$ layer into a 125-ml erlenmeyer flask.

Step 3. To the aqueous phase, still in the separatory funnel, add 2 ml of cupferron reagent, extract with 10 ml of $CHCl_3$, and combine the extract with the previous one. Wash the aqueous phase with 10 ml of $CHCl_3$ and combine the washings with the previous extracts.

Step 4. Heat the $CHCl_3$-extract with 3 ml of concd H_2SO_4 and about 20 ml of HNO_3 to destroy organic matter.

Step 5. Transfer the solution to a 40-ml conical centrifuge tube and make the solution basic by the addition of concd NH_4OH. Centrifuge and discard the supernate. Dissolve the precipitate ($Nb_2O_5 \cdot XH_2O$) in 3.3 ml of concd H_2SO_4 and dilute the solution to 20 ml with H_2O. Add 1 ml of Cu carrier and saturate the solution with H_2S. Centrifuge and filter into a clean 40-ml conical centrifuge tube, using a 2″, 60° funnel and No. 42 Whatman filter paper.

Step 6. Make the supernate basic by addition of concd NH_4OH to precipitate $Nb_2O_5 \cdot XH_2O$. Centrifuge, discard the supernate, and wash the precipitate with a mixture of 5 ml of 6*M* NH_4OH, 3 ml of 6*M* HNO_3, and 5 ml of H_2O (Note 1). Dissolve the precipitate by warming in 0.5 ml of 25% tartaric acid solution. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard any residue.

Step 7. Add 10 ml of concd HNO_3 to the supernate and heat the mixture on a steam bath for about 15 min. Centrifuge, discard the supernate, and dissolve the $Nb_2O_5 \cdot XH_2O$ precipitate in 1 ml of concd HF and 3 drops of 6*M* HCl.

Step 8. Transfer the solution to a 125-ml separatory funnel, add 10 ml of saturated H_3BO_3, and make the solution 1*M* in HCl. Add 4 ml of cold cupferron reagent and extract the solution with 20 ml of $CHCl_3$. Transfer the $CHCl_3$ layer to a 125-ml erlenmeyer flask.

Step 9. Repeat Steps 3, 4, 5, 6, and 7.

Step 10. Repeat Steps 8, 3, 4, 5, 6, and 7, but dissolve the $Nb_2O_5 \cdot XH_2O$ precipitate formed in Step 7 in 5 ml of saturated $(NH_4)_2C_4H_4O_6$ solution and sufficient concd NH_4OH to make the solution alkaline.

Step 11. Cool the solution in an ice bath and add 4 ml of cupferron reagent. Add 6*M* HCl dropwise to acidify (2 drops past a methyl red end point). Filter the Nb-cupferron complex onto a No. 42 Whatman filter circle, ⅞″ diameter, using the standard ground-off Hirsch funnel and filter chimney equipment. Ignite at 800° for 15-20 min. Cool the Nb_2O_5, mount, and count (Note 2).

Notes

1. The $Nb_2O_5 \cdot XH_2O$ precipitate is washed with NH_4NO_3 solution to prevent peptization.

2. The ignited Nb_2O_5 is mounted on an Al plate, 2½″ × 3¼″, which has a depression ⅝″ in diameter and 1/32″ deep in the center of one side. A dilute solution of Zapon in ethanol is used to spread and fasten the oxide to the plate. The precipitate is covered with rubber hydrochloride. The sample is counted in a beta counter with no absorber. The isotopes counted are 72-min ^{97}Nb, 23.3-hr ^{96}Nb, and 35-day ^{95}Nb.

palladium, phosphorus, plutonium, protactinium

PALLADIUM II

E. J. Lang

1. Introduction

Radiopalladium is separated from fission products by first carrying out the sequence--palladium sulfide precipitation; palladium dimethylglyoximate precipitation; silver chloride and iron(III) hydroxide scavenges--a total of three times. The palladium is then precipitated as the sulfide and converted again to the dimethylglyoxime complex, $Pd(C_4H_7N_2O_2)_2$, in which form it is weighed. The chemical yield is 60-70%.

2. Reagents

Pd carrier: 10 mg Pd/ml, added as $PdCl_2$ in H_2O, standardized
Ag carrier: 10 mg Ag/ml, added as $AgNO_3$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
HCl: 0.4 *M*; 6 *M*; concd
HNO_3: concd
NH_4OH: concd
H_2S: gas
Dimethylglyoxime (DMG) reagent: 1% solution in 95% ethanol
Aerosol: 0.1% in H_2O
Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 16.65 g of $PdCl_2$ in H_2O and dilute the solution to a volume of 1 liter. Pipet 5.0 ml of the carrier solution into a 40-ml concical glass centrifuge tube and make the solution 0.4 *M* in HCl. Add 5 ml of 1% dimethylglyoxime reagent and stir thoroughly. Filter the Pd-DMG precipitate through a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate with small quantities of H_2O and absolute ethanol. Dry at 110° for 15 min, cool, and weigh as $Pd(C_4H_7N_2O_2)_2$.

Four standardizations are carried out. Results are found to agree within 0.5%.

4. Procedure

Step 1. Pipet an aliquot of the sample into a 40-ml conical glass centrifuge tube, add 2.0 ml of Pd carrier, and make the solution 6*M* in HCl.

Step 2. Heat and pass in H_2S to precipitate PdS. Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate by boiling with 0.8 ml of concd HNO_3 and add 0.15 to 0.5 ml of concd HCl.

Step 4. Take the solution to close to dryness by heating over a flame.

Step 5. Add 20 ml of 0.4 *M* HCl and stir. (The solution should be clear. Heating may be necessary to effect complete solution.)

Step 6. Add 5 ml of DMG reagent and 1 drop of aerosol. Centrifuge and discard the supernate.

Step 7. Dissolve the precipitate in 1 ml of concd. HNO_3, boil nearly to dryness, add 2 ml of concd HCl, and boil nearly to dryness. Add 15 ml of H_2O, heat to boiling, and hold at boiling for 1 min.

Step 8. Add 1 drop of concd. HCl and 2 ml of Ag carrier. Heat and stir to coagulate the AgCl precipitate. Centrifuge and transfer the supernate to a clean centrifuge tube.

Step 9. To the supernate, add 1 ml of Fe carrier, make the solution basic with concd NH_4OH, centrifuge, and transfer the supernate to a clean centrifuge tube.

Step 10. Make the supernate 6 *M* in HCl by addition of the concd acid.

Step 11. Repeat Steps 2 through 10 two additional times.

Step 12. Heat the solution and pass in H_2S. Centrifuge and discard the supernate.

Step 13. Dissolve the PdS precipitate in 1 ml of concd. HNO_3 and take the solution almost to dryness by heating over a flame. Add 20 ml of 0.4 *M* HCl, stir, and centrifuge. Transfer the supernate to a clean centrifuge tube.

Step 14. To the supernate, add 5 ml of DMG reagent and 1 drop of aerosol. Centrifuge and discard the supernate. Wash the precipitate by centrifugation first with 30 ml of 0.4 *M* HCl and then with 30 ml of absolute ethanol. With aid of ethanol, transfer the precipitate onto a No. 42 Whatman filter circle, 1" diameter, using a Pyrex filter holder (Millipore Corporation, catalog no. XX1002500). Wash with small portions of H_2O and absolute ethanol. Dry at 110° for 5 min, cool, weigh, and mount. Count the betas from ^{109}Pd and ^{112}Pd.

PHOSPHORUS

N. A. Bonner and H. A. Potratz

1. Introduction

The principal decontamination steps in the determination of radiophosphorus in the presence of fission-product material involve precipitations of the element as zirconium phosphate and ammonium phosphomolybdate. Arsenic is removed by precipitation of the pentasulfide. Lanthanum fluoride scavenging is included. Phosphorus is finally precipitated as $MgNH_4PO_4 \cdot 6H_2O$, in which form it is counted. The chemical yield is 70-80% and the time required for a single analysis is about 7 hr. A sample containing 1.5×10^{15} fissions was decontaminated to less than 3 counts/min measured 2 days after bombardment. A small amount of short-lived contamination (probably 80-min ^{78}As) remains if the sample is counted about 8 hr after the end of bombardment.

2. Reagents

P carrier: 5 mg P/ml, added as $(NH_4)_2HPO_4$ in H_2O, standardized
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
As carrier: 10 mg As/ml, added as $Na_2HAsO_4 \cdot 7H_2O$ in H_2O
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
HCl: 3*M*; concd
HNO_3: 6*M*; concd
HF: concd
Citric acid: 500 g/l of aqueous solution
NH_4OH: 1:20; concd
H_2O_2: 30% (Superoxol)
H_2S: gas
Ammonium molybdate reagent: 200 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 800 ml H_2O, 160 ml concd NH_4OH
Magnesia mixture: 50 g $MgCl_2 \cdot 6H_2O$, 100 g NH_4Cl, 3 to 5 drops concd HCl, 500 ml H_2O
Aerosol solution: 0.1% in H_2O
Ethanol: 50%; 95%

3. Preparation and Standardization of Carrier

Make up a liter of an aqueous solution containing 21.3 g of $(NH_4)_2HPO_4$.

Pipet exactly 5 ml of the above carrier solution into a 100-ml beaker and add 20 ml of magnesia mixture. Make the solution slightly basic by the dropwise addition of concd NH_4OH and permit to stand for 5 min with occasional stirring. Then add 10 ml of concd NH_4OH and allow the mixture to stand for 4 hr, again stirring occasionally. Filter the precipitate onto a weighed 15-ml coarse sintered glass crucible. Wash the precipitate with 1:20 NH_4OH, 50% ethanol, and finally 95% ethanol. Pull air through the filter for approximately 10 min and then allow the precipitate to stand in the balance case for about 30 min. Weigh as $MgNH_4PO_4 \cdot 6H_2O$.

Four standardizations gave results agreeing within 0.5%.

4. Procedure

Step 1. To the sample in a 40-ml Lusteroid centrifuge tube (Note 1), add 20 ml of 6*M* HNO_3 and 1.0 ml of $(NH_4)_2HPO_4$ carrier solution. Heat the solution on a steam bath and add 2 ml of Zr carrier to precipitate zirconium phosphate. Continue heating for 3-5 min. Centrifuge and discard the supernate. Wash the precipitate with H_2O and discard the washings.

Step 2. Dissolve the precipitate in 0.1 ml of concd HF and add 5 ml of H_2O, 10 ml of 6*M* HNO_3, 5 drops of 0.1% aerosol solution, and 5 ml of ammonium molybdate reagent. Heat the mixture on a steam bath for 2-5 min. Centrifuge and discard the supernate. Wash the ammonium phosphomolybdate precipitate with 10 ml of H_2O containing a few drops of aerosol (Note 2).

Step 3. Dissolve the precipitate in 0.5 ml of concd NH_4OH, add 10 ml of H_2O and 4 drops of 30% H_2O_2 (Superoxol), and stir thoroughly. Add 10 ml of concd HCl and 2 ml of Zr carrier (Note 3), and heat on a steam bath for 5 min. Centrifuge and discard the supernate. Wash the precipitate with H_2O and discard the washings.

Step 4. Dissolve the precipitate in 0.2 ml of concd HF and add 10 ml of 3*M* HCl, 0.5 ml of

As carrier and a few drops of aerosol solution. Heat on a steam bath for 15 min while bubbling H_2S through the solution. Centrifuge and transfer the supernate to a clean 40-ml Lusteroid centrifuge tube. Wash the precipitate with 1-2 ml of H_2O containing a few drops of aerosol solution. While the precipitate is being washed, pass H_2S through the original supernate which is being heated on a steam bath. Combine the supernate from the washing with the original supernate. Discard the As_2S_5 precipitate.

Step 5. Add 2 ml of La carrier to the solution from Step 4. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the LaF_3 precipitate.

Step 6. To the supernate, add 4 ml of concd HNO_3 and 5 ml of ammonium molybdate reagent. Heat on a steam bath for 2-5 min, centrifuge, and discard the supernate. Wash the precipitate with 10 ml of H_2O containing a few drops of aerosol and discard the washings.

Step 7. Repeat Steps 3 through 6 twice.

Step 8. Dissolve the ammonium phosphomolybdate precipitate in 1 ml of concd NH_4OH and add 2 ml of citric acid solution (0.5 g/ml). Add 10 ml of magnesia mixture and concd NH_4OH (dropwise) until the solution is barely alkaline, then add 10 drops more. Swirl the solution for about 1 min and if a precipitate does not begin to form, add 5 more drops of concd NH_4OH. After precipitation begins, swirl the mixture for at least 1 min and then add 4 ml of concd NH_4OH. Allow the mixture to stand, with occasional stirring, for at least 10 min. Filter through a 15-ml fine sintered glass funnel and wash the precipitate with a small amount of 1:20 NH_4OH. Dissolve the precipitate in a few drops of concd HCl and a few milliliters of H_2O. Collect the filtrate in a 100-ml beaker.

Step 9. Add 10 ml of magnesia mixture and just enough concd NH_4OH to neutralize the HCl in the mixture. (One drop of NH_4OH in excess should cause the precipitate of $MgNH_4PO_4 \cdot 6H_2O$ to start forming.) Swirl for about 1 min and then add 3 ml of concd NH_4OH. Allow the mixture to stand for at least 10 min. Filter onto a weighed No. 42 Whatman filter circle, ⅞" diameter, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate with small portions of 1:20 NH_4OH, 50% ethanol, and 95% ethanol. Pull air through the filter for 5 min, allow the precipitate to stand in the balance case for about 30 min, weigh, mount, and count (Note 4).

Notes

1. If large amounts of SO_4^{2-} ion are present in the sample, the precipitation of zirconium phosphate is not complete.

2. If the ammonium phosphomolybdate precipitate shows a tendency to peptize, dilute NH_4NO_3 solution should be used for the wash.

3. The reagents should be added in the indicated order. If HCl is added before dilution with H_2O, ammonium phosphomolybdate reprecipitates.

4. 14.1-day ^{32}P is the isotope determined. This has a 1.71 Mev beta and no gamma.

PLUTONIUM

D. C. Hoffman

1. Introduction

The essentially specific procedure for plutonium utilizes the almost-quantitative carrying of Pu (IV) on lanthanum fluoride and the great difference in ability of Pu (III) and Pu (IV) in 12M HCl medium to be adsorbed on a Dowex A-1 anion resin. One cycle of the procedure serves to separate plutonium from other α-emitters, and two cycles usually give complete decontamination from β-emitting fission products.

The initial lanthanum fluoride precipitation, carried out in the presence of hydroxylamine, is an excellent volume-reducing step and also eliminates many elements (notably iron) which may interfere in the subsequent adsorption of plutonium on the resin column. After dissolution of the lanthanum fluoride precipitate in 12M HCl, adsorption on the anion resin column of neptunium, plutonium, and any traces of iron and uranium present is effected while the rare earths, americium and curium, pass through the column. Plutonium is eluted from the column after reduction to Pu (III) with hydriodic acid; neptunium is not reduced to the +3 state and remains quantitatively behind. (A solution containing 15 μg of ^{235}U was run through the procedure, and no fission counts above the usual background of 0.1-0.2 ng (1 ng = 10^{-6} mg) could be detected.)

The plutonium is collected directly from the resin column on 1 7/8" platinum plates which are flamed, α-counted, and, if necessary, pulse analyzed. The plates are usually very clean and may be α-pulse analyzed with a resolution of 1-1.5%.

Samples may be run in quadruplicate and yields are usually determined in one of two ways. ^{236}Pu tracer to the extent of about one-fourth to one-half of the total plutonium α-activity expected may be added to one or two of the original aliquots. On completion of the analysis, the fraction of ^{236}Pu in the sample is determined by pulse analysis, thus permitting the calculation of yield. Yields may also be determined by spiking two of the four samples with a standardized solution of plutonium activity which is at least five times as active as the aliquot to be analyzed. The average of the number of counts per minute in the two unspiked samples is subtracted from the average in the two spiked samples. The resulting value divided by the number of counts per minute in the spike gives the yield. The chemical yield is usually about 97% and for a set of four aliquots analyzed simultaneously is constant to within ±1%. In analysis of solutions of very high ionic strength the yields are somewhat lower (90-97%), probably because under these conditions the lanthanum fluoride carrying step is less efficient. Quadruplicate analyses can be performed in 3 hr.

2. Reagents

La carrier: 5 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O ^{236}Pu standardized tracer solution, in 3M HCl or Pu standardized spike solution, any mixture or Pu isotopes in SM HCl

HCl. concd (12M); 3M

HF: concd

$HF\text{-}HNO_3$: equal volumes of 2M solutions

HNO_3: cond.

H_3BO_3: saturated solution

$NH_2OH \cdot HCl$: 35% by weight in H_2O

Solution I: 0.1 ml concd HNO_3 per 15 ml concd HCl

AGI-X10, 200-400 mesh anion resin (obtained in purified form from Bio-Rad Laboratories, Richmond, Calif.), slurry in H_2O.

HI stock solution: Distill HI (Mallinckrodt analytical reagent grade, 5.5M in HI, 1.5% H_3PO_2 preservative) under nitrogen. The HI cannot be used without distillation since the H_3PO_2 preservation appears to cause the eluted drops to attack the Pt collection disks and make the samples unsuitable for pulse analysis. Commercial preparations of HI without preservative usually contain so much free iodine as to make them unsuitable. Even after storage under nitrogen, distilled HI is slowly oxidized. Oxidation is inhibited by the addition of sufficient hydrazine (up to 20% by volume of 64-84% N_2H_4 in H_2O) to decolorize the HI solution. The final solution is about 4.4M in HI.

HI-HCl eluent; 1 ml of HI stock solution is added to 7 ml of concd HCl to give a solution about 0.44M in HI. The precipitate which results from the hydrazine present is removed by centrifugation and the supernate is saturated with gaseous HCl. The solution is permitted to come to equilibrium at room temperature before use; since the solution is readily oxidized, fresh reagent is required every few days.

3. Procedure

Step 1. Forty-ml long-taper centrifuge tubes are used to hold the samples. Into those tubes which will contain sample on which yield is determined, pipet 1 ml of tracel solution. Pipet sample (3M in HCl) into each centrifuge tube (1 ml aliquots are used if possible, although aliquots as large as 25 ml can be used if necessary). Bring all solutions to the same volume by adding to those which do not contain tracer (or spike) acid of the same concentration as that in the tracer (or spike).

Step 2. To each tube, add 1-2 drops of La carrier per ml of solution and then stir. Add 4-5 drops of $N_2HOH \cdot HCl$ per ml of solution and stir. Add 3 drops of concd HF per ml of solution (Note 1), stir, and let stand for 5 minutes.

Step 3. Centrifuge and discard the supernate.

Step 4. Wash the precipitate with 10 drops of 2*M* HF - 2*M* HNO_3. Stir, centrifuge, and discard the supernate.

Step 5. Dissolve the LaF_3 precipitate by adding 2-3 drops of saturated H_3BO_3 solution, stirring, and then adding 0.5 ml. of concd HCl with stirring. If the solution is clear and colorless, continue adding concd HCl until the volume of solution is 2 ml. Add 1 drop of concd HNO_3 and heat gently. The solution is now ready for Step 6. If the solution, after treatment with concd. HCl, is yellow--even faintly so--dilute to 2 ml with H_2O, and, omitting the addition of La carrier, repeat steps 2 through 5.

Step 6. Transfer the solution to a 3-5 cm x 4 mm Dowex AG-1 resin column which has been washed with about 1 ml. of Solution I (Note 2). (This wash may be driven through the column with air pressure if desired.) By means of air pressure, push the solution containing the sample through the column. Wash the centrifuge tube with two 1-ml portions of Solution I and discard the washes.

Step 7. Wash the sides of the centrifuge tube with 1.5 ml of concd HCl, stir with a stirring rod, and remove the rod. Centrifuge the HCl wash and pass the solution through the resin column under pressure.

Step 8. Add a few crystals of $N_2HOH \cdot HCl$ directly to the top of the resin column. Wash the centrifuge tube with 1 ml of concd HCl, transfer the wash to the top of the column and push it through with pressure. Do not let the column run dry under pressure for air bubbles will be forced into the column and channeling and erratic elution of activity may occur.

Step 9. Transfer about 1 ml of HI-HCl eluent to the top of the column but apply no pressure during elution. The dark band of the eluent may be seen migrating down the column. Start collecting the drops around the edge of a 1 7/8" Pt disk when the band is halfway down the column. After the band reaches the bottom of the column, collect 15 drops of eluent, placing as many of them as possible in the center of the disk. If necessary, the rest are collected on top of the drops already around the edge of the disk.

Step 10. Place the Pt disk on a hot plate (with the setting at about 400) under a heat lamp and allow the drops to evaporate. Heat the disk to red heat in an open flame and then cool. Alpha-count if the original aliquot was spiked, and pulse analyze and α-count if ^{236}Pu tracer was used. (Notes 3 and 4).

NOTES

1. When an appreciable quantity of Fe is present, sufficient HF must be added to not only complex this element (thus decolorizing the solution) but also to precipitate La carrier.

2. The presence of concd HNO_3 in Solution I is necessary to destroy the reducing properties of the original resin and thus avoid premature reduction of Pu (IV) to the tripositive state.

3. If it is desired to fission-count the Pu, plates may be prepared by taking the activity directly from the column. However, if any drops are permitted to run together giving an extreme "bathtub effect " the fission-counting results are invariably too low. To avoid such effects attributable to sample thickness, the samples *should be electroplated using the procedure for Electrode*position of Plutonium for Fission Counting.

4. The Np activity which quantitatively remains on the column after elution of Pu may be removed in the following manner:

(a). By means of pressure run concd HCl containing several drops of HNO_3 per milliliter through the column until the dark color has been removed. Discard the effluent. (During this process the column may separate as a result of bubbling, etc., but can be resettled by means of pressure.)

(b). Wash the resin with concd HCl and pressure, permitting the column to rebed itself.

(c). Elute the Np with 0.1M HCl. If the yield is very low after only one elution with 0.1M HCl, about three cycles of elution alternately with 0.1M HCl and concd HCl usually give yields up to 85%.

ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING

D. C. Hoffman

1. Introduction

The procedure described below is an adaptation of one by R. F. Mitchell, Anal. Chem., 32, No. 3, 326 (1960). The plating setup is the same as that used in the Uranium-235 Procedure.

2. Reagents

HCl: concd; 1*M*
HNO_3: concd
NH_4OH: concd
Ethanol: absolute
NH_4Cl: solid
Methyl red indicator solution

3. Procedure

Step 1. In a graduated centrifuge tube, collect the eluate from Step 9 of the PLUTONIUM procedure. (The same amount of eluate as would normally be collected on the Pt disk for pulse analysis is collected). To the eluate add 2-3 drops of concd HNO_3 and place the tube in an oil bath which is maintained at about 100°. With the aid of an air jet, evaporate the solution to dryness. Add 3 drops of concd HCl and take the resulting solution to dryness. Repeat the HCl treatment four times.

Step 2. After the final evaporation, take the residue up in 0.5 ml of concd HCl and transfer to the electroplating cell. Use a 1" Pt plating disk, a thin-walled chimney, and a plastic gasket. Wash the centrifuge tube with two 0.5-ml portions of distilled H_2O, transferring the washings to the plating cell (vol. ~1.5 ml). Add two small spatulafulls of NH_4Cl may be put in the cell before the sample is added.) Make the solution basic with concd. NH_4OH and then add 1*M* HCl dropwise until the solution is barely acidic.

Step 3. Electroplate at 2 amp and about 6.8 v for 15 min while the solution is stirred with a graphite rod. Just before plating is completed, add 0.5 ml of concd NH_4OH. Immediately turn off the stirrer and the current and pour the plating liquid back into the centrifuge tube. Remove the chimney and wash the Pt disk, first with H_2O and then with ethanol. Flame the plate and count for 1 min on an alpha counter.

Step 4. By means of Duco cement, mount the Pt plate on a standard fission mount.

REMOVAL OF PLUTONIUM-239 FROM RARE EARTHS, CESIUM, AND ZIRCONIUM

B. E. Cushing

1. Introduction

Plutonium(IV) can be quantatively removed from the rare earths, cesium, and zirconium by extraction with triisooctylamine. The separation is not satisfactory if the plutonium is in an oxidation state other than +4. The extraction is carried out in the presence of the appropriate carrier or carriers; for example, if the solution, after removal of plutonium, is to be used for analysis of zirconium, then this element is employed as carrier.

2. Reagents

La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Cs carrier: 10 mg Cs/ml, added as CsCl in H_2O
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
HCl: 5*M*; concd
H_2SO_4: concd
$NaNO_2$: 0.1*M*
Triisooctylamine: 20% by volume in Amsco-95

3. Procedure

All operations are performed in a glove box.

Step 1. Pipet an aliquot of the sample into a 50-ml erlenmeyer flask and add 1 ml each of the desired carriers. Add 10-20 drops of concd H_2SO_4 and heat to fumes of SO_3.

Step 2. Cool the solution and transfer to a 40-ml centrifuge cone with 5-10 ml of 5*M* HCl. Add about 10 drops of 0.1*M* $NaNO_2$ and heat in a boiling water bath for 5 min.

Step 3. Transfer the solution to a 125-ml separatory funnel and rinse the centrifuge cone with a minimum amount of 5*M* HCl, adding the rinsings to the separatory funnel. Add an equal volume of 20% (by volume) triisooctylamine in Amsco-95 and shake well.

Step 4. Allow the phases to separate and draw off the aqueous phase into a clean 40-ml centrifuge tube.

Step 5. To the aqueous extract add 10 drops of 0.1*M* $NaNO_2$ and heat in a boiling water bath for 5 min.

Step 6. Repeat Step 3 (Notes 1 and 2).

Notes

1. The extraction is repeated if necessary. In one experiment it was found that three extractions were sufficient to completely remove 47 mg of plutonium in the sample.

2. The procedure does not remove ^{241}Am activity. Americium activity may be separated from the plutonium-free aqueous solution in the following manner:

(a) Precipitate hydroxides by means of ammonia gas. Centrifuge, discard the supernate, and wash the precipitate with H_2O. Centrifuge and discard the supernate.

(b) Dissolve the precipitate in 1-2 drops of concd HCl and add 1 ml of 5M NH_4CNS buffered at pH 1.2. Put the solution on an AG 1-X8 anion column (100-200 mesh and 1 cm × 6 cm) which has been previously equilibrated with the 5M NH_4CNS solution.

(c) Elute with 10 ml of the cold 5M NH_4CNS solution. This procedure gives a decontamination factor of about 5×10^3 and should be repeated to ensure removal of americium.

HDEHP SEPARATION OF PLUTONIUM FROM SOIL DEBRIS

D. C. Hoffman and F. O. Lawrence

1. Introduction

In this procedure, plutonium is extracted quantitatively into HDEHP (di-2-ethylhexyl phosphoric acid) in *n*-heptane from $4M$ HNO_3 solutions of the fluoride-soluble fractions obtained from soil debris. The method is a convenient one for the isolation of plutonium from large volumes of solutions of high ionic strength, solutions from which the element does not carry well on a fluoride precipitate. The plutonium is predominantly in the (VI) oxidation state in the samples. The element is recovered from the organic phase by reduction to the (III) state and back-extraction with NH_4I-HCl solution. This step accomplishes extensive decontamination since most of the species which extract into HDEHP from $4M$ HNO_3 are not back-extracted by the NH_4I-HCl solution. Further purification of the plutonium can be accomplished by the usual LaF_3 precipitations and elution from an anion resin column with HI-HCl solution as described in the PLUTONIUM procedure.

Plutonium (IV) is also extracted quantatively by HDEHP in *n*-heptane, but it appears that in this oxidation state the element is so tightly held in the organic phase that it is not effectively reduced and back-extracted.

2. Reagents

HDEHP solution: $0.5M$ solution of di-2-ethylhexyl orthophosphoric acid in *n-heptane* (43 ml. ~ 40.25 g. of the acid in 250 ml of solution). The HDEHP used was assayed at > 94% by the supplier, Stauffer Chemical Company, Chicago Heights, Ill.
HCl: $9M$
NH_4I: saturated aqueous solution
NH_4I-HCl solution: 1 volume of the saturated NH_4I solution to 8 of $9M$ HCl
$NH_2OH{\cdot}HCl$: solid

3. Procedure

Step 1. Pre-equilibrate the $0.5M$ HDEHP with an equal volume of $4M$ HNO_3. To an aliquot of the sample (about $4M$ in HNO_3)in either a narrow-necked 40-ml conical centrifuge tube or a 60-ml separatory funnel, add ½ to ⅓ its volume of the pre-equilibrated HDEHP. Shake for 1 min and allow the phases to separate, centrifuging if necessary. Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of $4M$ HNO_3, and discard the wash.

Step 2. To the organic phase, add about 50 mg of solid $NH_2OH{\cdot}HCl$ and then ½ volume of NH_4I-HCl solution. Shake for 2 min and drain the aqueous (bottom) layer into a clean 40-ml centrifuge tube. Discard the organic layer.

Step 3. If the final volume of the aqueous layer is 10 ml or less, dilute with H_2O to about *three times* the volume, and proceed to Step 2 of the PLUTONIUM procedure. If the volume is greater than 10 ml, transfer the solution to a 125-ml erlenmeyer flask and evaporate to the desired volume over a burner. Then proceed to Step 2 of the PLUTONIUM procedure. Be sure to oxidize the Pu (III) by adding 1 drop of concd HNO_3 to the HCl solution and warming just before passing it through the anion resin column.

May 1968

THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION

D. C. Hoffman and F. O. Lawrence

1. Introduction

The basic principle of the separation of plutonium from large volumes of solution is the same as that used in the procedure for HDEHP SEPARATION OF PLUTONIUM FROM SOIL DEBRIS. in which plutonium is extracted quantitatively into HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane from acidic solution. In the procedure described below. the plutonium is extracted into HDEHP-*n*-heptane which has been impregnated on an inert support (a fluorohalocarbon resin). Extraction on such a column is much more convenient than one in which the plutonium-containing solution is extracted with a large volume of HDEHP solution. Moreover. the back-extraction of plutonium from the column is more efficient than from HDEHP solution. With the use of the column. the separation of phases is clean. a situation which is not always true in ordinary liquid-liquid extraction.

2. Reagents

^{236}Pu standardized tracer solution. in 3*M* HCl
HCl: 9*M*; 4*M*
CrO_3: solid
NH_4I: saturated aqueous solution
NH_4I-HCl: 1 volume of saturated NH_4I solution to 8 volumes of 9*M* HCl
$NH_2OH \cdot HCl$: solid
CTFE-2300 (fluorohalocarbon resin) powder: supplied by Allied Chemical Corporation. Morristown. N.J.
HDEHP: di-2-ethylhexyl orthophosphoric acid: crude material assayed at > 94% by the supplier. Stauffer Chemical Company. Chicago Heights. Ill.. purified according to the directions of K. Wolfsberg. Ph.D. Thesis. Washington University. 1959. p.60; University Microfilms (Ann Arbor. Mich.). L.C. Card No. Mic. 59-6946.
n-Heptane

3. Procedure

Step 1. Pipet the tracer Pu and the sample in 4*M* HCl into an erlenmeyer flask and add a few crystals of CrO_3. Heat to boiling and then let cool to room temperature.

Step 2. To the CTFE-2300 (1 g/50 ml of sample solution) (Note) add enough of a mixture of equal volumes of purified HDEHP and *n*-heptane to make a slurry. Allow to equilibrate for 5 min. Stir well and pour the resulting mixture into a glass column (i.d. ~ 1 cm). the tip of which has been plugged with glass wool. Wash the column with 2 ml of 4*M* HCl.

Step 3. Pour the cooled sample-containing mixture onto the column and allow it to pass through either under gravity or with the application of a slight air pressure. Discard the effluent.

Step 4. Wash the (resin) column with 2 ml of 4*M* HCl and then with 2 ml of 9*M* HCl. Discard the washings. Add a few crystals of $NH_2OH \cdot HCl$ to the top of the column.

Step 5. Add 2 ml of NH_4I-HCl solution to the column to elute the Pu. collecting the eluate in a 40-ml graduated glass centrifuge tube.

Step 6. Dilute the eluate to 3*M* in HCl by addition of the appropriate quantity of H_2O. Perform Steps 2 through 10 of the regular PLUTONIUM procedure.

Note

Different batches of CTFE vary somewhat in their properties. so that different ratios of support to sample from that cited may be necessary.

November 1968

THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION. II

F. O. Lawrence and D. C. Hoffman

1. Introduction

In this procedure, DBHQ, (2,5-di-tertiary butylhydroquinone) in 2-ethyl-l-hexanol solution is utilized for the back-extraction of plutonium (IV) from solutions of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The use of DBHQ as a reagent for this purpose was suggested in the May 31, 1968, annual progress report of the Chemical Technology Division of ORNL, ORNL-4272.

Work in our laboratory has shown that treatment with DBHQ reagent followed by contact with 6*M* HCl will back-extract both plutonium-(IV) and (VI) quantatively from HDEHP-*n*-heptane solutions. It should be noted that plutonium (IV), once extracted into HDEHP solutions, is apparently so tightly complexed that previous attempts to back-extract it quantitatively with other reagents, even with those which should reduce the element to the tripositive state, have been unsuccessful. Presumably, in the back-extraction with the DBHQ solution, the plutonium is reduced to the +3 state and then strongly complexed by the DBHQ.

The extraction coefficients (for transfer from aqueous media to HDEHP solutions) for plutonium (IV) are very much higher than for plutonium (VI) and the volume of HDEHP extractant for the former species can be as little as one-fifth the volume of the sample. The procedure can be adapted readily to a mixture of the two plutonium species by increasing the volume of HDEHP extractant to one-third of the sample volume.

To determine the element quantitatively, ^{236}Pu tracer is added and sodium nitrite is used to ensure that all the plutonium is converted to the +4 state to effect complete exchange.

2. Reagents

^{236}Pu standardized tracer solution, in 3 M HCl
HDEHP solution: 0.75 M solution of di-2-ethylhexyl orthosphosphoric acid in *n*-heptane; aource: Eastman Organic Chemicals
DBHQ solution: 0.2M solution of 2,5-di-tertiary butylhydroquinone in 2-ethyl-1-hexanol; Source: Eastman Organic Chemicals.
HCl: 6M; 3M
$NaNO_2$: 10M

3. Procedure

Step 1. Pre-quilibrate the 0.75 *M* HDEHP solution with an equal volume of 3*M* HCl in a separatory funnel. (The size of the funnel should be about twice that of the aliquot of sample that will be used.) Add sufficient 10*M* $NaNO_2$ to an aliquot of the sample and the Pu tracer (in either a narrow-necked conical centrifuge tube or an erlenmeyer flask) to make the final concentration of the salt about 0.2*M* (for example, 1 ml of 10*M* $NaNO_2$ to 50 ml of aliquot of sample). Heat the solution to boiling and then permit it to cool to room temperature. Add the sample to one-third its volume of pre-equilibrated HDEHP, shake for 1 min, and allow the two phases to separate, centrifuging if necessary (Note). Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of 6*M* HCl and discard the wash.

Step 2. To the organic phase, add one-third volume of the 0.2*M* DBHQ solution and shake for about 10 sec. Add one-half volume of 6*M* HCl, shake for about 2 min, and allow 5 min for the separation of the two phases. Drain and save the aqueous (lower) phase and discard the organic layer.

Step 3. If the volume of the aqueous phase is less than 5 ml, add H_2O to make the solution 3*M* in acid and proceed to Step 2 of the PLUTONIUM procedure. If the volume of the aqueous phase is greater than 5 ml, transfer the solution to a 125-ml erlenmeyer flask and evaporate to 2-5 ml over a burner. Transfer the solution to a 40-ml conical centrifuge tube, dilute to make the solution 3*M* in acid by means of water washes from the erlenmeyer flasks, and then continue with Step 2 of the PLUTONIUM procedure.

Note

If very large aliquots (150-200 ml) of sample are used, the volume of HDEHP solution may be increased to one-half volume of that of the sample, and a second back-extraction with 6*M* HCl may be performed.

PROTACTINIUM

H. A. Potratz and N. A. Bonner

1. Introduction

In the determination of protactinium-233 in the presence of fission-product material, lanthanum fluoride scavenging is followed by the carrying of the protactinium on barium fluozirconate. The fluozirconate is converted to an iodate of undetermined composition which is then dissolved in hydrochloric acid and the protactinium is extracted with diisopropyl carbinol; the zirconium remains in the aqueous phase. The protactinium is back-extracted with hydrofluoric acid and mounted carrier-free for counting. Protactinium-231 is used as a tracer to determine chemical yield.

This procedure was tested on a fission-product mixture from 3.2 × 10^{14} fissions 3 days after end of bombardment. Final activity was 8 ± 5 counts/min and the yield was 76%.

2. Reagents

^{231}Pa tracer
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Ba carrier: 30 mg Ba/ml, added as $BaCl_2$ in H_2O
HCl: 6*M*; concd
HNO_3: concd
HF: concd
HIO_3: 1*M*
H_3BO_3: saturated aqueous solution
Diisopropyl carbinol: Eastman's Yellow Label (redistilled)

3. Procedure

Step 1. To the fission-product mixture in about 2*M* HCl in a 50-ml Lusteroid centrifuge tube, add 3 ml of concd HNO_3, 2 ml of Zr carrier, 2 ml of concd HF, and ^{231}Pa tracer in known amount (Note 1).

Step 2. Dilute to 20 ml and add 1-2 ml of La carrier. Centrifuge and transfer the supernate to a clean Lusteroid tube. Wash the precipitate with H_2O and combine the supernate with the previous one, discarding the precipitate.

Step 3. Add 3 ml of Ba carrier and allow the mixture to stand for 2-3 min. Centrifuge and wash the precipitate with H_2O, discarding both the supernate and the washings. Dissolve the $BaZrF_6$ precipitate by treating with 3 ml of saturated H_3BO_3, 1 ml of concd HNO_3, and 2 ml of H_2O.

Step 4. Heat the mixture on a steam bath until the precipitate dissolves completely. Add 15 ml of 1*M* HIO_3 and allow to stand for 5-10 min. Centrifuge (Note 2), wash with H_2O, and discard the supernate.

Step 5. Add 5 ml of concd HCl to the iodate precipitate and heat on the steam bath for about 2 min. Add 2 ml of H_2O and continue heating until the precipitate is entirely dissolved. Transfer the solution to a 125-ml separatory funnel. Complete the transfer with 30 ml of 6*M* HCl. Add 35 ml of redistilled diisopropyl carbinol and shake thoroughly. (If the activity level is high, agitate the mixture with a stream of air.) Draw off and discard the aqueous phase. (This contains most of the Zr.) Wash the carbinol phase with two 25-ml portions of 6*M* HCl and discard the washings. Treat the carbinol phase with two 10-ml portions of a solution made by diluting 3 ml of concd HNO_3 and 0.5 ml of concd HF to 20 ml. Transfer the aqueous extracts to a clean Lusteroid tube and discard the carbinol phase. To the combined aqueous extracts add 2 ml of concd HF and 2 ml of Zr carrier.

Step 6. Repeat Steps 2 through 5, and then Steps 2 through 4.

Step 7. Dissolve the iodate precipitate in 5 ml of concd HCl. Heat and add 2 ml of H_2O. Transfer the solution to a 60-ml separatory funnel. Complete the transfer with 10 ml of 6*M* HCl. Shake the solution with 10 ml of diisopropyl carbinol. Wash the carbinol phase with two 10-ml portions of 6*M* HCl and discard the aqueous phases. Transfer the carbinol phase to a Lusteroid centrifuge cup. Add 0.8 ml of H_2O and 0.2 ml of concd HF and agitate thoroughly. Centrifuge.

Draw off as much of the carbinol phase as possible with a drawn-out dropper tube and discard. Add 5 ml of carbinol, shake, centrifuge, and discard the carbinol phase. Repeat the carbinol wash and draw off. Transfer the aqueous phase by means of a drawn-out dropper onto a Pt disk of 1" diameter. Evaporate under a heat lamp. Alpha-count for ^{231}Pa. Count betas of ^{233}Pa under 10 mg/cm^2 Al absorber.

Notes

1. Only a small amount of ^{231}Pa tracer should be used. The gamma radiation gives about 0.02 counts min on the beta counter for every count per minute on the alpha counter.

2. This precipitate is not a simple zirconium iodate. It may be $BaZr(IO_3)_6$.

rhodium, rubidium, ruthenium

RHODIUM

J. S. Gilmore

1. Introduction

In the determination of radiorhodium the principal decontamination steps include (a) removal of ruthenium as the volatile RuO_4, (b) precipitation of RhI_3, and (c) iron(III) hydroxide and acid sulfide scavenges from solutions containing the extremely stable $[Rh(CN)_6]^{3-}$ complex ion. The rhodium is finally electroplated from sulfuric acid solution after destruction of the complex. The chemical yield is about 60%, and six samples can be analyzed in about one day.

2. Reagents

Rh carrier: 10 mg Rh/ml, standardized

Co carrier: 10 mg Co/ml, added as $CoCl_2 \cdot 6H_2O$ in H_2O

Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in 1*M* HCl

Mo carrier: 10 mg Mo/ml, added as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in H_2O

Ba carrier: 10 mg Ba/ml, added as $BaCl_2 \cdot 2H_2O$ in H_2O

Sb(III) carrier: 10 mg Sb/ml, added as $SbCl_3$ in 1*M* HCl

Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_3 in 1*M* HCl

HCl: 6*M*; concd

HNO_3: concd

H_2SO_4: concd

$HClO_4$: concd

NH_4OH: concd

KCN: 3*M*

$NaNO_2$: 5*M*

Na_2CO_3: 0.5*M*

$Cu(NO_3)_2$ solution: 100 mg Cu/ml

KI: solid

H_2S: gas

Ethanol: 95%

Cation exchange column: 6 mm × 6 cm Dowex 50-X8 (50-100 mesh) pretreated by washing with 3*M* NH_4OH

3. Preparation and Standardization of Carrier

Weigh out 27.34 g of $RhCl_3 \cdot 4H_2O$ and make up to 1 liter in 0.01*M* HCl. Pipet 3.0 ml of the solution into a 125-ml erlenmeyer flask and add 3 ml of concd H_2SO_4, 2 ml of concd $HClO_4$ and 1 ml of concd HNO_3. Heat until SO_3 fumes appear. Transfer the solution with 20 ml of H_2O to the plating cell having a weighed Pt disk as cathode. Electroplate at room temperature and 0.1 amp for 16 hr (Note). Wash the cathode with H_2O and then with 95% ethanol. Dry at 110° for 15 min, cool, and weigh. Four standardizations gave results agreeing within 0.3%.

4. Procedure

Step 1. To a 125-ml erlenmeyer flask add 3 ml of standard Rh carrier and an aliquot of the sample.

Step 2. Add 3 ml of concd H_2SO_4, 2 ml of concd $HClO_4$, 1 ml of concd HNO_3 and heat until SO_3 fumes appear. Cool, add 2 ml of concd $HClO_4$, and evaporate to a volume of 1 ml.

Step 3. Add 3 ml of 6*M* HCl, 1 ml each of Mo and Co carriers, 1 to 2 g of solid KI and boil for 20 min, adding 6*M* HCl as needed to keep the volume of solution approximately constant. Transfer to a 40-ml centrifuge tube, centrifuge, and discard the supernate. Wash the RhI_3 precipitate with 20 ml of warm 6*M* HCl and discard the supernate.

Step 4. To the precipitate add 3 ml of 3*M* KCN and heat until solution occurs. Add 1 ml of Te(IV) carrier, 2 ml of 6*M* HCl, and heat to boiling. While heating, add 5*M* $NaNO_2$ dropwise until I_2 fumes are no longer visible.

Step 5. Dilute to 20 ml with H_2O, add 3 drops of Fe carrier, and then concd NH_4OH until a precipitate barely forms. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

Step 6. Add 2 ml of concd NH_4OH, 1 ml of Ba carrier, 3 ml of 0.5*M* Na_2CO_3 and warm on a steam bath for 5 min. Add 3 drops of Fe carrier, stir, and centrifuge. Transfer the supernate to a clean centrifuge tube and discard the precipitate.

Step 7. Add concd HCl dropwise until the evolution of CO_2 ceases. Add 1 ml of 6*M* HCl, 1 ml each of Te(IV) and Sb(III) carriers, and saturate with H_2S. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 8. Boil the solution for about 30 sec to remove H_2S. Add 7 ml of concd HCl, 2 ml of $Cu(NO_3)_2$ solution, and cool in an ice bath. (The Rh is precipitated, presumably as the compound $Cu_3[Rh(CN)_6]_2$.) Centrifuge and discard the supernate.

Step 9. Dissolve the precipitate in 2 ml of concd NH_4OH and dilute to 10 ml with H_2O. Transfer to the Dowex 50 cation exchange column and allow the solution to pass through under gravity, catching the eluate in a 125-ml erlenmeyer flask. $[Cu(NH_3)_4]^{2+}$ is removed on the column, the $[Rh(CN)_6]^{3-}$ passing through.

Step 10. Evaporate the solution nearly to dryness, add 3 ml of concd H_2SO_4, and concentrate to a volume of 1 ml to remove Rh-cyanide complex.

Step 11. Repeat Steps 3 through 9, but collect the column eluate in a 40-ml centrifuge tube.

Step 12. Repeat Steps 6 through 10.

Step 13. Add 2 ml of concd $HClO_4$, 1 ml of concd HNO_3, and heat until SO_3 fumes are evolved. Transfer to the plating cell with 20 ml of H_2O. Electroplate at room temperature and 0.1 amp for 16 hr on a weighed Pt cathode disk. Wash the cathode with H_2O and then with 95% ethanol. Dry in an oven at 110° for 15 min. Cool, weigh, mount, and β-count.

Note

The components of the plating cell must be extremely clean in order to obtain a smooth, adherent cathode deposit.

ADDENDUM TO THE RHODIUM PROCEDURE

J. S. Gilmore

It has been found convenient to substitute for Step 9 the following method for the removal of Cu from the precipitate, which presumably has the formula $Cu_3[Ru(CN)_6]_2$:

> To the precipitate add 20 ml of H_2O, warm the mixture, and then add sufficient 6*M* NaOH to convert all the copper to the insoluble oxide, leaving the rhodium cyano complex in solution as the sodium salt. When conversion is complete (the precipitate will be black and the solution colorless), centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. Proceed to Step 10.

May 1968

RUBIDIUM

E. J. Lang

1. Introduction

In this procedure for the analysis of radiorubidium in solutions obtained from soil debris, alkali metals are first precipitated as perchlorates in an ethanolic medium. Following $Fe(OH)_3$ scavengings, rubidium is precipitated as the phospho-9-molybdate, a step which serves effectively to decontaminate the element from potassium. Molybdenum is then removed by precipitation as MoS_3 from slightly acidic solution. Rubidium perchlorate is again formed, and the element is separated from cesium by adsorption of the latter on a thallium(I) phospho-12-tungstate (TPT) exchange column. The effluent is treated with aqua regia to oxidize thallium to the +3 state, the solution is evaporated to dryness, and any ammonium ion present is removed by heating the residue. After the thallium is separated by adsorption on an anion exchange resin from a solution 1*M* in HCl, rubidium is finally precipitated as the perchlorate. The chemical yield is 50-60%.

2. Reagents

Rb carrier: 10.0 mg Rb/ml, added as analytical reagent grade RbCl
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in 1*M* HCl
HCl: 1*M*; concd
$HClO_4$: concd
HNO_3: 3*M*; 6*M*; concd
Aqua regia: 3:1 V/V concd HCl: concd HNO_3
NH_4OH: concd
NaOH: 6*M*
H_2S: gas
Ethanol: absolute
9-molybdophosphoric acid solution: 5 g of 12 molybdophosphoric acid, gently heated to ~ 400-450°C. (Color will change through orange to green.) Cool. Leach with ~ 10 ml H_2O. Filter, oxidize greenish solution to yellow solution with bromine water. Make up to ~ 20 ml with 6*M* HNO_3.
TPT exchanger: to 180 ml of a 0.0015*M* $TlNO_3$ solution in 0.4*M* HNO_3, add 50 ml of a solution containing 2% by weight of 12-tungstophosphoric acid ($H_3[PW_{12}O_{40}]$) in 0.4*M* HNO_3. Evaporate the mixture containing precipitated thallium(I) phospho-12-tungstate until the volume is about 10 ml. Add 2.5 g of filter paper pulp and shake thoroughly. (Reference: H. Caron and T. Sugihara, *Anal. Chem.*, **34**, 1082 (1962)).
Anion exchange resin: Dowex AG1-X10, 50-100 mesh, stored in 6*M* HCl

3. Procedure

Step 1. To 2.0 ml of Rb carrier in a 125-ml erlenmeyer flask, add an aliquot of the sample, 5 ml of concd HNO_3, and 8 ml of concd $HClO_4$. Heat until dense $HClO_4$ fumes appear and then cool.

Step 2. Transfer the solution to a clean 40-ml glass centrifuge tube. Wash the erlenmeyer flask with two 10-ml portions of absolute ethanol and add the washings to the centrifuge tube. With vigorous stirring, cool the contents of the tube for about 15 min in an ice bath. Centrifuge and discard the supernate. Add 20 ml of absolute ethanol to the $RbClO_4$ precipitate and, with stirring, cool in an ice bath for 15 min. Centrifuge and discard the supernate. Repeat the ethanol wash.

Step 3. To the precipitate add 20 ml of H_2O and 1 drop of concd HCl and stir to effect solution. Neglect any residue. Add 5 drops of Fe carrier and then concd NH_4OH dropwise until precipitation occurs. Centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate. Repeat the $Fe(OH)_3$ scavenge and transfer the supernate to a clean 125-ml erlenmeyer flask.

Step 4. Evaporate the solution to dryness, add 5 ml of 3*M* HNO_3, and transfer to a clean centrifuge tube. Wash the erlenmeyer flask twice with 10-ml portions of 3*M* HNO_3 and add the washings to the centrifuge tube. Add 10 ml of freshly prepared 9-molybdophosphoric acid solution, heat to boiling, and let the mixture stand until precipitation of rubidium is complete. Centrifuge and discard the supernate. Wash the precipitate with one 10-ml portion of 3*M* HNO_3. Discard the washing.

Step 5. Dissolve the precipitate in a minimum amount of 6M NaOH, heating if necessary. Dilute to 20 ml with H_2O and make barely acidic with 6M HNO_3 and then barely basic with 6M NaOH. Saturate the solution with H_2S, heat to boiling, add 1 drop of concd HNO_3, and heat to coagulate the MoS_3 precipitate. Centrifuge and transfer the supernate to a clean 125-ml erlenmeyer flask.

Step 6. Heat the supernate to dryness. Add 2 ml of 3M HNO_3 to dissolve the residue and transfer the solution to a TPT exchange column, 8 mm x 5 cm, which has previously been prepared by washing with 3M HNO_3 under pressure (6-8 drops per min) until the effluent is clear. Wash the erlenmeyer flask with two 2-ml portions of 3M HNO_3 and add the washings to the column. By means of air pressure force the solution through the column at a rate of 6-8 drops per min. Collect the effluent in a clean 125-ml erlenmeyer flask. Wash the TPT column with a 5-ml portion of 3M HNO_3 and pass the wash through the column. Repeat the washing. Combine all effluents. (Note)

Step 7. Evaporate the solution to dryness, add 5 ml of aqua regia, and take to dryness again. Heat the residue to decompose any ammonium salts present. Cool, add 2 ml of 1M HCl, and put the solution on a Dowex AG1-X10 anion exchange resin column, 8 mm x 5 cm, which has previously been washed with two 5-ml portions of 1M HCl. Rinse the erlenmeyer flask with 2 ml of 1M HCl and add the rinsings to the column. Repeat the washing. Permit the solution and the rinsings to run sequentially through the column under gravity and collect the effluents in a clean 125-ml erlenmeyer flask. (Thallium is adsorbed on the column.)

Step 8. To the solution add 5 ml of concd HNO_3, 8 ml of concd $HClO_4$, and evaporate until dense $HClO_4$ fumes appear. Cool and transfer the solution to a clean centrifuge tube. Wash the erlenmeyer flask with two 10-ml portions of absolute ethanol and add the washings to the centrifuge tube. Cool, with vigorous stirring, in an ice bath for 15 min. Centrifuge and discard the supernate. To the $RbClO_4$ precipitate, add 20 ml of absolute ethanol and, with stirring, repeat the cooling process. Centrifuge and discard the supernate. Repeat the ethanol wash, but this time filter the precipitate onto a weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and stainless steel filter chimney. Dry the precipitate for 5 min at 110°, cool, weigh, and mount for counting.

Note

Radiochemically pure cesium, which is strongly adsorbed on the TPT column, can be eluted with 0.15M $TlNO_3$.

May 1968

RUTHENIUM

M. A. Melnick

The procedure for the determination of radioruthenium in fission products is a modification of a method developed by L. E. Glendenin, CN-1312 (May 15, 1945).

1. Introduction

Radioruthenium is separated from other fission products by oxidation to the tetroxide, RuO_4, and distillation of this volatile oxide. The oxidation is effected by means of a mixture of perchloric acid and sodium bismuthate in the presence of red fuming nitric acid. The bismuthate serves to convert the halogens to their nonvolatile oxyacids. The ruthenium tetroxide is distilled into sodium hydroxide solution and the ruthenium precipitated as a mixture of oxides, Ru_2O_3 and RuO_2, by reduction with ethanol. These oxides are dissolved in hydrochloric acid and elementary ruthenium is precipitated by means of magnesium metal. The chemical yield is about 70% and duplicate analyses can be performed in approximately 3 hr.

2. Reagents

Ru carrier: 10 mg Ru/ml, added as a mixture of $RuCl_3$ and $RuCl_4$ in 0.1*M* HCl

I carrier: 10 mg I/ml, added as KI in H_2O

HCl: 1*M*; 6*M*; concd

$HClO_4$: 70%

H_3PO_4: 85%

NaOH: 6*M*

$NaBiO_3$: solid

Mg metal: powder

Ethanol: 95%

3. Preparation and Standardization of Carrier

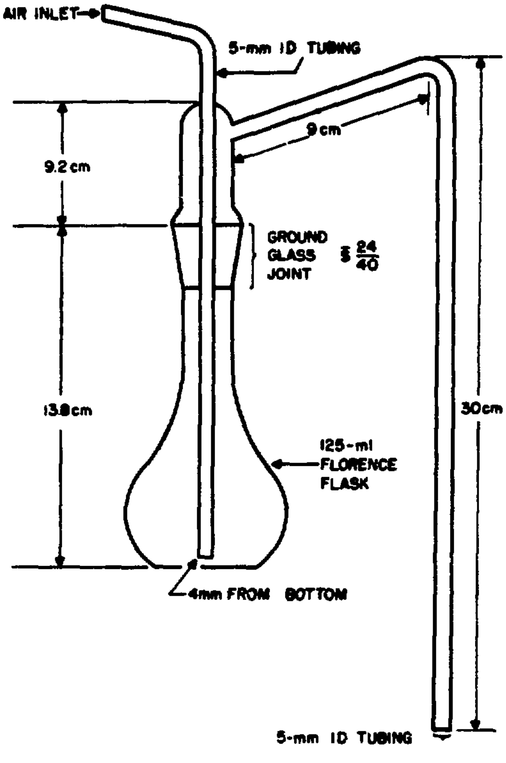
Dissolve 26 g of commercial ruthenium chloride (a mixture of the hydrated trichloride and tetrachloride) in 1 liter of 0.1*M* HCl.

Pipet 5.0 ml of the carrier solution into a 125-ml erlenmeyer flask and add about 0.4 g of powdered Mg metal portionwise, shaking after each addition. Dissolve the excess Mg metal in concd HCl and decant the resulting supernate carefully Add 20 ml of 1*M* HCl and swirl. Filter the Ru metal onto a weighed 60-ml sintered glass crucible of medium porosity. Wash the precipitate twice with 5-ml portions of H_2O and twice with 5-ml portions of 95% ethanol. Dry for 15 min at 110°, cool, and weigh.

Four standardizations are performed with results agreeing within 0.5%.

4. Procedure

Step 1. Pipet an aliquot of the sample into the distillation flask (see diagram); add 2 ml of Ru carrier, 1 ml of I holdback carrier, 6 ml of red fuming HNO_3, 0.4 g of $NaBiO_3$, 1 ml of 85% H_3PO_4 (Note 1), and 10 ml of 70% $HClO_4$. Keep the flask in a hot H_2O bath until the solution is colored light amber.



Ruthenium distilling flask.

Step 2. Heat the distilling flask over a Bunsen burner and catch the first 2 ml of distillation in a 40-ml conical centrifuge tube containing 10 ml of 6*M* NaOH. Discard this portion of the distillate.

Step 3. Place as the receiver a clean 40-ml centrifuge tube which contains 20 ml of 6*M* NaOH and is cooled in an ice bath. Continue the distillation until all the RuO_4 has come over. (At this stage the solution in the distilling flask will be virtually colorless.)

Step 4. To the distillate add 3 ml of 95% ethanol. heat to boiling. and centrifuge the mixture of precipitated ruthenium oxides (Note 2). Discard the supernate.

Step 5. Dissolve the precipitate by heating with 2 ml of 6*M* HCl. Transfer the resulting solution to a 125-ml erlenmeyer flask and add about 0.3 g of Mg powder portionwise. Dissolve unreacted Mg powder in a minimum of concd HCl and carefully decant the supernate. Add 20 ml of H_2O.

Step 6. Filter the Ru metal onto a weighed No. 50 Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate twice with 5-ml portions of H_2O and twice with 5-ml portions of 95% ethanol. Dry at 110° for 15 min, cool, weigh, and mount (Note 3).

Notes

1. The H_3PO_4 is added to the distilling flask to prevent the slight volatilization of molybdenum by $HClO_4$.

2. Technetium is volatilized, probably as Tc_2O_7. However, Tc (VII) is not reduced by ethanol and this element therefore does not contaminate the ruthenium. Moreover, technetium activity is usually absent from most solutions, since 5.9-hr ^{99}Tc (daughter of 67-hr ^{99}Mo) is the longest-lived technetium isotope prominent in fission.

3. The 42-day ^{103}Ru activity can be separated conveniently from 1-year ^{106}Ru since the ^{103}Ru activity is about 43 times as abundant as ^{106}Ru as a result of half-life and fission yield factors. ^{103}Ru also has about three times as many gamma rays as ^{106}Ru. With the use of a scintillation counter and a 2000-mg Al absorber to eliminate the 3.55 Mev beta from ^{106}Ru, ^{103}Ru can be determined. ^{106}Ru may be counted on a beta proportional counter using a 210-mg Al absorber to cut out the 0.68 Mev beta of ^{103}Ru. The 0.55 Mev gamma from ^{103}Ru is counted also and must be corrected for by counting through a series of heavy Al absorbers (1600 to 2500 mg/cm^2) and extrapolating the activity to 210 mg Al.

scandium, silver, sodium, strontium, sulfate

SCANDIUM

J. E. Sattizahn
With modifications by R. J. Prestwood and
B. P. Bayhurst

1. Introduction

The initial step in the procedure for determining radioscandium is the extraction of the element from a solution 10*M* in nitric acid by 0.5*M* HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The scandium is then back-extracted into water as a complex fluoride. After destruction of the complex, scandium is precipitated as the simple fluoride. Other decontamination steps are lanthanum fluoride scavenging while the scandium is complexed and lanthanum hydroxide-ferric hydroxide scavenging. Scandium is finally precipitated as the hydroxide, ignited, and counted as the oxide.

The chemical yield is about 65%, and four samples can be analyzed in about 5 hr.

2. Reagents

Sc carrier: 13 mg Sc/ml, added as $ScCl_3$ in very dilute HCl, standardized
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in very dilute HNO_3
Ce (IV) carrier: 10 mg Ce/ml, added as $Ce(NO_3)_4$
HCl: 6*M*
HNO_3: concd
$HClO_4$: concd
NH_4OH: concd
$NH_2OH \cdot HCl$: solid
H_3BO_3: saturated aqueous solution
NH_4HF_2: mixture of 2 volumes of 6*M* NH_4OH and 1 volume of 27*M* HF
NH_4NO_3: 2% aqueous solution
Methyl red indicator solution: 0.5% in 90% ethanol
Ethanol: absolute
6% rubber cement in benzene
HDEHP: 0.5*M* solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The acid may be obtained from the Victor Chemical Division of the Stauffer Chemical Co., Chicago Heights, Ill. The acid employed was claimed to be 94% pure.

3. Preparation and Standardization of Carrier

Dissolve 20.0 g of Sc_2O_3 in a minimum of concd HCl, add an additional 5 ml of HCl, and make the solution up to a volume of 1 liter with H_2O.

Pipet 5.0 ml of the above carrier solution into a 100-ml beaker and dilute to 20 ml with H_2O. Add 5 ml of concd NH_4OH to precipitate $Sc(OH)_3$. Filter the solution through No. 42 Whatman filter paper (9 cm), using a 2", 60° funnel. Rinse the beaker with 5 ml of 0.1*M* NH_4Cl and filter the washings through the paper containing the $Sc(OH)_3$. Transfer the precipitate to a weighed Coors 00 porcelain crucible and ignite at 900° for 1 hr. Cool and weigh as Sc_2O_3.

Two standardizations gave results agreeing within 0.3%

4. Procedure

Step 1. Add two ml of Sc carrier and then an aliquot of sample to a 60-ml separatory funnel. Make the solution 10*M* in HNO_3, add 5 drops of Ce(IV) carrier [as $Ce(NO_3)_4$], and make the volume approximately 40 ml by the addition of 10*M* HNO_3. Add about 100-200 mg of $NH_2OH \cdot HCl$ to reduce Ce(IV) to Ce(III). (The reduction is evident by the disappearance of the yellow color.) Add 10 ml of HDEHP, stir vigorously for 5 min, and discard the H_2O layer. Wash the heptane layer with 10 ml of 10*M* HNO_3 containing 5 drops of Ce(III) prepared as described above and discard the washings. Transfer the heptane layer to a 40-ml, quartz, tapered centrifuge tube.

Step 2. Add 4 ml of NH_4HF_2 and stir vigorously for 5 min. Add 5 ml of H_2O, stir for 2 min, then add 5 ml of concd $HClO_4$, and heat on a steam bath for 10 min. (ScF_3 precipitates at this point.) Centrifuge and discard both the organic and aqueous supernates. To the ScF_3 precipitate add 1 ml of concd H_2SO_4 and 3 or 4 drops of Ce(IV) carrier and heat to SO_3 fumes. Cool.

Step 3. Dilute to 10 ml with H_2O and heat to dissolve any solid material. Add 100-200 mg of $NH_2OH \cdot HCl$ to reduce Ce(IV), 3 ml of NH_4HF_2, and 2-3 drops of methyl red indicator solution. Add concd NH_4OH until the solution is barely acidic. (CeF_3 precipitates and Sc remains in solution as a fluoro complex.) Add 2 drops of La carrier, centrifuge, and transfer the supernate to a clean 40-ml, polyethylene, tapered centrifuge tube.

Step 4. To the solution, add 4 drops of La carrier, 4 drops of Fe carrier, and 1.5 ml of concd NH_4OH. Dilute to 20 ml with H_2O and heat on a steam bath to coagulate the $La(OH)_3$-$Fe(OH)_3$ precipitate. Centrifuge, transfer the supernate to a clean 40-ml polyethylene centrifuge tube, and discard the precipitate.

Step 5. Add 6 ml of concd $HClO_4$ to the supernate and heat for 5 min on a steam bath. Allow to cool for 10 min, centrifuge, and discard the supernate. (The soluble fluoroscandate is converted to the insoluble ScF_3.)

Step 6. Repeat Steps 3 through 5 twice.

Step 7. Dissolve the ScF_3 precipitate in 2 ml of saturated H_3BO_3 solution and 3 ml of concd HNO_3. Dilute to 20 ml and transfer a clean glass centrifuge tube. Add 10 ml of concd NH_4OH to precipitate $Sc(OH)_3$, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of H_2O and discard the washings. Add 2 ml of concd H_2SO_4 and evaporate to fumes of SO_3. Cool, dilute to 20 ml with H_2O, and add an excess of NH_4OH. Centrifuge and discard supernate.

Step 8. Dissolve the $Sc(OH)_3$ in 1 ml of 6*M* HCl, dilute the solution to 20 ml, and centrifuge. Transfer the supernate to a clean centrifuge tube. Add filter paper pulp and then an excess of concd NH_4OH to precipitate $Sc(OH)_3$. Filter onto a No. 41 H Whatman filter paper (9 cm) and wash the precipitate with H_2O. Ignite at 900° in a Coors 00 porcelain crucible for 20 min. Cool and powder the Sc_2O_3 with the fire-polished tip of a glass stirring rod. Transfer the Sc_2O_3 with ethanol onto a weighed No. 42 Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and a filter chimney. Rinse the centrifuge tube with two 10-ml portions of ethanol and pour through the filter. Dry the Sc_2O_3 at 110° for 10 min, cool, and weigh. Place 5 drops of a 6% solution of rubber cement on the sample and permit it to dry at room temperature. Mount on two-sided Scotch tape on an Al plate and cover with Mylar.

SCANDIUM II

B. P. Bayhurst

1. Introduction

In the analysis of soil samples, it was found that complete exchange between scandium and carrier did not occur when the original procedure for the element was used. Moreover, fluoride precipitations early in the procedure gave compounds which were resistant to further treatment. a fact that caused substantial losses in chemical yield.

This new procedure overcomes the above deficiencies. The major steps are: precipitations with NaOH and NH_4OH: removal of macro-iron and radiozirconium by adsorption on an anion exchange resin from concentrated HCl solution; LaF_3 and $La(OH)_3$-$Fe(OH)_3$ scavenges; and ScF_3 precipitations. The scandium is finally separated as the hydroxide and ignited to the oxide. The chemical yield is 70-80%.

2. Reagents

Sc carrier: 13 mg Sc/ml, added as $ScCl_3$ in very dilute HCl; standardized (see original procedure)
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
La carrier: 10 mg La/ml. added as $La(NO_3)_3 \cdot 6H_2O$ in very dilute HNO_3
Zr carrier: 10 mg Zr/ml. added as $ZrO(NO_3)_2 \cdot 2H_3O$ in 1*M* HNO_3
HCl: concd; 6*M*; gas
H_2SO_4: concd
NaOH: 10*M*
NH_4OH: concd
NH_4HF_2: mixture of 2 volumes of 6*M* NH_4OH and 1 volume of 27*M* HF
Ethanol: absolute
6% rubber cement in benzene
Dowex AG 1-X8. 50-100 mesh. anion exchange resin

3. Procedure

Step 1. Add the sample to 2.0 ml of Sc carrier in an erlenmeyer flask. evaporate to about 2 ml on a hot plate. and transfer with the aid of H_2O (10-20 ml) to a 40-ml glass centrifuge tube. Add an excess of 10*M* NaOH. heat on a steam bath for a few min, centrifuge, and discard the supernate. Dissolve the $Sc(OH)_3$ precipitate in a minimum of 6*M* HCl. dilute to 25 ml with H_2O. and reprecipitate with excess 10 *M* NaOH. Centrifuge and discard the supernate.

Step 2. Dissolve the precipitate in a minimum of 6*M* HCl, dilute with 25 ml with H_2O, and add an excess of concd NH_4OH. Centrifuge and discard the supernate. Repeat the precipitation. centrifuge. and discard the supernate. Wash the precipitate with 30 ml of H_2O. let stand on a steam bath for a few min. centrifuge. and discard the wash.

Step 3. Dissolve the precipitate in 1 ml of concd HCl. add 1 drop of Zr carrier, and saturate with HCl gas. Prepare a Dowex AG 1-X8. 50-100 mesh. anion resin column. 8mm by 3½ in.. and wash with concd HCl. Add the solution to the resin column and collect the eluate in a clean 40-ml glass centrifuge tube. Wash the resin with 25 ml of concd HCl and combine the eluate with the previous one.

Step 4. Evaporate the solution to about 10 ml on a steam bath. Add an excess of concd NH_4OH. centrifuge. and discard the supernate. Add 3 ml of concd H_2SO_4. heat over a burner with stirring until SO_3 fumes appear at the top of the tube. Cool. dilute to about 10 ml with H_2O. and transfer to a clean 40-ml polyethylene centrifuge tube. Reprecipitate $Sc(OH)_3$ with concd NH_4OH. centrifuge. and discard the supernate.

Step 5. Add 3 ml of NH_4HF_2. 1 drop of methyl red indicator, dilute to 10 ml with H_2O. and add concd NH_4OH until the solution is *just* acidic. Add 3 drops of La carrier. place on a steam bath for 2 min. centrifuge. and transfer the supernate to a clean polyethylene centrifuge tube. Discard the precipitate. Add 3 drops of La carrier. centrifuge. transfer the supernate to a clean centrifuge tube. and discard the precipitate.

Step 6. Add 1½ ml of concd NH_4OH. 2 drops each of La and Fe carriers, and heat on a steam bath. Centrifuge. transfer the supernate to a clean centrifuge tube. and discard the precipitate.

Step 7. Add 6 ml of concd HCl, dilute to about 30 ml with H_2O, and keep on a steam bath until ScF_3 precipitates. Centrifuge and discard the supernate.

Step 8. Repeat Steps. 5, 6, and 7 twice.

Step 9. Add 2 ml of 10*M* NaOH, let stand for 5 min on a steam bath, and dilute with 10 ml of H_2O. Place on a steam bath until $Sc(OH)_3$ coagulates, centrifuge, and discard the supernate.

Step 10. Dissolve the precipitate in a minimum of 6*M* HCl, dilute to 20 ml with H_2O, and precipitate $Sc(OH)_3$ with concd NH_4OH. Centrifuge and discard the supernate. Repeat the dissolution, dilution, precipitation, and centrifugation processes.

Step 11. Dissolve the $Sc(OH)_3$ in 1 ml of 6*M* HCl, dilute to 10 ml with H_2O, add filter paper plup, and then an excess of concd NH_4OH to precipitate $Sc(OH)_3$. Filter onto a No. 41 Whatman filter paper (9 cm) and wash the precipitate with H_2O. Ignite at 1000°C in a Coors 00 porcelain crucible for 20 min. Cool and powder the Sc_2O_3 with the fire-polished tip of a glass stirring rod. Transfer the Sc_2O_3 with ethanol onto a tared No. 42 Whatman filter circle, 7/8 in. diameter, using a ground-off Hirsch funnel and a filter chimney. Rinse the crucible with two 5-ml portions of ethanol and pour through the filter. Dry the Sc_2O_3 at 110°C for 10 min, cool, and weigh. Place 5 drops of a 6% solution of rubber cement on the sample and permit it to dry at room temperature. Mount with two-sided Scotch tape on an Al plate and cover with Mylar.

November 1970

SILVER

E. J. Lang

This procedure is a modification of one described by L. E. Glendenin, CN-1312 (May 15, 1945).

1. Introduction

Silver is initially separated from other fission products by the specific precipitation of the chloride from nitric acid solution. The silver is then purified by ferric hydroxide scavenging and silver sulfide precipitation, both of which are performed in ammoniacal solution. After repetition of the scavenging-precipitation cycle, the silver is converted to the oxide and finally to the iodate, $AgIO_3$, in which form it is counted. The chemical yield exceeds 80%. Quadruplicate analyses can be carried out in about 3 hr.

2. Reagents

Ag carrier: primary standard grade, 10 mg Ag/ml, added as $AgNO_3$ in very dilute HNO_3
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
HCl: concd
HNO_3: concd
H_2SO_4: concd
HIO_3: 2*M*
NaOH: 6*M*
NH_4OH: concd
$(NH_4)_2S$: saturated solution
Ethanol: 95%

3. Preparation of Carrier

Dissolve 15.75 g of $AgNO_3$ primary standard grade in a minimum amount of H_2O, add a few drops of HNO_3, and dilute the solution to 1 liter.

4. Procedure

Step 1. (Note 1.) To the sample in a 40-ml conical centrifuge tube, add exactly 2 ml of Ag carrier and 5 ml of concd HNO_3 and dilute the solution to 20 ml with H_2O. Heat to boiling and precipitate AgCl by the addition of 4 drops of concd HCl. Heat until the AgCl has coagulated, cool, centrifuge, and discard the supernate.

Step 2. Dissolve the AgCl in 2 ml of concd NH_4OH, dilute to 20 ml with H_2O, and add 1 ml of Fe carrier. Stir, centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate.

Step 3. To the solution add 1 ml of saturated $(NH_4)_2S$ solution. Stir vigorously, centrifuge (Note 2), and discard the supernate.

Step 4. Dissolve the Ag_2S precipitate by heating with 1 ml of concd HNO_3. Dilute to 20 ml with H_2O and precipitate AgCl by the addition of 4 drops of concd HCl as in Step 1. Centrifuge and discard the supernate.

Step 5. Repeat Steps 2 and 3.

Step 6. Dissolve the Ag_2S by heating with 1 ml of concd HNO_3. Dilute with 20 ml of H_2O, make the solution alkaline with 6*M* NaOH, and then add three drops in excess. Centrifuge the Ag_2O precipitate and discard the supernate. Add 4 drops of concd H_2SO_4 and heat over a burner until a clear solution is obtained. Cool.

Step 7. With stirring, add 20 ml of H_2O and then 1 ml of 2*M* HIO_3. Centrifuge and discard the supernate.

Step 8. Dissolve the $AgIO_3$ in 4 drops of concd NH_4OH and dilute to 20 ml with H_2O. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube.

Step 9. Add 3 drops of concd H_2SO_4 to the solution, stir, and filter the $AgIO_3$ precipitate onto a weighed No. 42 Whatman ⅞" filter circle, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with a large amount of H_2O and then with 5 ml of 95% ethanol. Dry for 10 min at 110°, cool, weigh, and mount (Note 3).

Notes

1. Wait one day after bombardment before

beginning the procedure to allow ^{111}Pd and ^{111m}Pd to decay to ^{111}Ag. The additional silver resulting from this waiting period is only about 0.5% of the total.

2. Although the precipitation of AgCl from acidic solution is specific for Ag^+ among the cations in fission products, it is possible that the precipitate may be contaminated by bromide and iodide. The Ag_2S precipitations are performed to remove any contaminating halogen activities.

3. Beta-counting for 7.4-day ^{111}Ag activity is begun about 16 hr after completion of the chemistry to permit 3.2-hr ^{112}Ag to decay sufficiently so as not to interfere.

ELECTROPLATING OF SILVER

R. J. Prestwood and B. P. Bayhurst

1. Introduction

The procedure for electroplating of silver following its separation from fission products has two major advantages in the isolation and counting of silver in elemental form rather than as the usual compound such as $AgIO_3$: (a) superior stability and reproducibility of the final product as the metal, and (b) an approximate 40% increase in counting efficiency.

2. Procedure

Following separation of silver from fission products, the step preceding electroplating should be the precipitation of Ag_2O with NaOH. The precipitated oxide is washed thoroughly twice with H_2O, and then the following procedure is followed.

Step 1. To the precipitate in a 40-ml conical centrifuge tube add 5 ml of 2*M* NaCN and stir until solution is effected, heating if necessary. Transfer the solution to a plating cell (see the Uranium-235 Procedure for details of the plating assembly), the cathode of which is a weighed polished Pt disk of 1″ diameter. Wash the centrifuge tube with 5 ml of 2*M* NaCN and transfer the washings to the plating cell.

Step 2. Plate the silver on the Pt disk at 15 milliamp at room temperature for 1 hr 10 min, the amperage being maintained constant by means of a variable resistance in series with the plating cell. Upon completion of the plating remove the cell, discard the electrolyte, wash the cell with distilled H_2O, and disassemble it. Wash the Ag-plated Pt disk thoroughly with absolute ethanol, allow to dry at room temperature, weigh, and mount.

SODIUM

B. R. Erdal

1. Introduction

This procedure for the separation of sodium from all other nuclides produced in nuclear reactions is based primarily on an observation by F. Girardi and E. Sabbioni (J. Radioanal. Chem. 1 169, 1968). These investigators found that in concentrated hydrochloric acid only sodium and tantalum, among sixty elements tested, were retained on hydrated antimony(V) oxide, $Sb_2O_5 \cdot xH_2O$ (HAP). The sodium is recovered from the HAP by reduction of the antimony(V) with concentrated hydriodic acid, extraction of antimony(III) into 4-methyl-2-pentanone (hexone) from hydrochloric acid medium, and then passage of the aqueous phase through a Dowex AG 1 anion resin column. The sodium is finally converted to NaCl.

The chemical yield is approximately 75% and duplicate samples can be analyzed in 1-2 hours. A decontamination factor of greater than 10^4 has been found for all ^{235}U thermal-neutron fission products.

2. Reagents

Na carrier: 5 mg Na/ml, added as NaCl in 6*M* HCl, standardized by atomic absorption spectroscopy
K carrier: 5 mg K/ml, added as KCl in 6*M* HCl
Rb carrier: 5 mg Rb/ml, added as RbCl in 6*M* HCl
Cs carrier: 5 mg Cs/ml, added as CsCl in 6*M* HCl
Te carrier: 5 mg Te/ml, added as $K_2TeO_4 \cdot 2\ H_2O$ in 6*M* HCl
Cu carrier: 5 mg Cu/ml, added as $CuCl_2 \cdot 2\ H_2O$ in 6*M* HCl
HCl: concd; 6*M*
HI: concd (47%)
4-methyl-2-pentanone (hexone)
H_2S: gas
HAP: Sb_2O_5, see below for preparation
Anion resin: Dowex AG 1-X8, 100-200 mesh, thoroughly washed with 6*M* HCl
1-Butanol
Butanol-HCl reagent: 1-butanol saturated with HCl gas
Diethyl ether

3. Preparation of HAP

Four hundred and seventy milliliters of $SbCl_5$ are diluted to 2 liters with H_2O and the solution is permitted to hydrolyze overnight with stirring. The resulting hydrated oxide is filtered through a large Buchner funnel containing No. 40 Whatman paper and washed thoroughly first with 6*M* HCl and then with H_2O. The material is dried under reduced pressure for several hours, powdered, and dried in an oven at 270° for about 5 hr. The yellow material is then powdered and sieved. That portion of the oxide having a mesh between 60 and 170 is used in the procedure.

4. Procedure

Step 1. To a 40-ml glass centrifuge tube, add 1 ml of standard Na carrier, an aliquot of the sample, 2 drops each of K, Rb, Cs, Te, and Cu carriers, and dilute to 5 ml with H_2O. (The HCl concentration should be about 1*M*.) Saturate the solution with H_2S, digest, and filter under suction through a glass frit of medium porosity, collecting the filtrate in a 50-ml erlenmeyer flask.

Step 2. Evaporate the solution to dryness and cool. Dissolve the residue in 0.5 ml of H_2O (Note 1), add 10 ml of concd HCl, and transfer the solution to a clean glass centrifuge tube. Add 300 mg of HAP, mix by swirling for about 5 min, centrifuge, and discard the supernate. Wash the HAP three times with 10-ml portions of concd HCl, each time swirling for about 5 min, centrifuge, and discard the supernate.

Step 3. Add 3 ml of concd HI to the HAP and mix until the HAP is well dispersed. Heat for about 2 min on a steam bath, add 1 ml of concd HI, and reheat for about 2 min. Add 6 ml of 6*M* HCl, heat for about 2 min on a steam bath, and transfer the solution to a 60-ml separatory funnel. Add 20 ml of hexone, shake for about 1 min, transfer the aqueous (lower) phase to a clean 60-ml separatory funnel, and discard the organic phase. Extract the aqueous phase with 10 ml of hexone as before and discard the organic phase.

Step 4. Transfer the aqueous phase to a clean 40-ml glass centrifuge tube, add 3 ml of H_2O, and saturate the solution with H_2S. Filter under suction through a glass frit of fine porosity, collecting the filtrate in a 50-ml erlenmeyer flask. Evaporate the solution to dryness, add 1 ml of concd HCl, and again evaporate to dryness. Repeat the addition of HCl and evaporation.

Step 5. Dissolve the residue in a minimum of 6*M* HCl and transfer the solution to the top of a 10 cm x 4 mm Dowex AG 1-X8, 100-200 mesh, anion resin column. Add 10 ml of 6*M* HCl to the column and collect the eluate in a 50-ml erlenmeyer flask. Evaporate the solution to dryness.

Step 6. To the residue, add 0.5 ml of concd HCl, 5 ml of 1-butanol, and about 2 ml of butanol-HCl reagent. Permit the mixture to stand for about 5 min, add 8-10 ml of diethyl ether, and filter through a synthetic filter paper (Note 2). Wash the precipitate on the filter with diethyl ether, dry under suction and mount for counting.

Notes

1. The acidity should be kept as high as possible (~10*M*) in Step 2 to prevent adsorption of Rb on HAP. Some adsorption of that element occurs from solutions 6*M* in HCl.

2. Fluoride Metricel VF-6 filter paper (source: Gelman Instrument Co., P.O. Box 1448, Ann Arbor, MI 48106) wet with methanol has been used for mounting. The paper can be washed with methanol and ether and weighed before use with no problems arising from humidity.

STRONTIUM-90

B. P. Bayhurst

1. Introduction

In the determination of strontium-90, the element is first separated as the nitrate. This is an excellent decontamination step, the major impurity being barium which is removed by a series of barium chromate precipitations. The strontium is then converted to the carbonate, the chemical yield at this stage being about 75%. Yttrium-90 is permitted to grow into equilibrium with the strontium-90; Y carrier is added and separated with the yttrium-90 from the strontium by precipitation as hydroxide. Finally, yttrium is precipitated as oxalate and ignited to oxide, in which form it is counted. The chemical yield of yttrium carrier is about 85%.

2. Reagents

Sr carrier: 10 mg Sr/ml, added as $Sr(NO_3)_2$ in dilute HNO_3
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl
Y carrier: 10 mg Y/ml (for preparation and standardization see Yttrium Procedure)
Ba carrier: 10 mg Ba/ml, added as Ba $(NO_3)_2$ in H_2O
HCl: 1*M*; concd
HNO_3: fuming; concd
$HC_2H_3O_2$: glacial
NH_4OH: concd
Na_2CO_3: saturated aqueous solution
Na_2CrO_4: 10% aqueous solution
$(NH_4)_2C_2O_4$: saturated aqueous solution
$KClO_3$: solid
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 241.5 g of $Sr(NO_3)_2$ in H_2O, add 10 ml of concd HNO_3, and dilute to 1 liter with H_2O.

Into a 40-ml centrifuge tube, pipet 5.0 ml of the carrier solution and add 15 ml of saturated Na_2CO_3 solution. Stir and allow to stand for at least 15 min. Filter the $SrCO_3$ precipitate through a weighed 15-ml fine porosity sintered glass crucible. Wash the precipitate with 10 ml of water and then with 5 ml of 95% ethanol. Dry in oven at 110°.

Four standardizations are carried out, with results agreeing within about 0.5%.

4. Procedure

Step 1. Pipet 2.0 ml of standard Sr carrier into a 40-ml conical centrifuge tube. Add an aliquot of sample and adjust the volume to about 5 ml with H_2O. Add 30 ml of cold (Note 1) fuming HNO_3 and permit the mixture to stand in an ice bath for approximately 10 min. Centrifuge and discard the supernate.

Step 2. Dissolve the $Sr(NO_3)_2$ precipitate in 10 ml of H_2O and add 5 drops of Fe carrier. Make the solution basic by the dropwise addition of concd NH_4OH and then add 10 drops in excess. Stir, centrifuge, and decant the supernate into a clean 40-ml centrifuge tube, and discard the precipitate.

Step 3. Add 2 ml of glacial $HC_2H_3O_2$ to bring the pH of the solution to 3.5-4.0. Then add 2 ml of Ba carrier and 2 ml of 10% Na_2CrO_4 solution and digest for 10-15 min on a steam bath with occasional stirring. Centrifuge, decant the supernate into a clean 40-ml centrifuge tube, and discard the precipitate.

Step 4. Add 5 ml of saturated $(NH_4)_2C_2O_4$ and digest on a steam bath for 5-10 min. Centrifuge and discard the supernate. Wash the precipitate by adding 2 ml of saturated $(NH_4)_2C_2O_4$ and 20 ml of H_2O and stirring. Centrifuge and discard the wash.

Step 5. Add 2 ml of concd HNO_3, 5 ml of H_2O, stir, and then add 30 ml of fuming HNO Allow to stand in ice bath for approximately 10 min. Centrifuge and discard the supernate.

Step 6. Repeat Steps 2 through 4.

Step 7. To the precipitate of SrC_2O_4 add 2 ml of concd HNO_3 and about 200 mg of $KClO_3$. Carefully bring the solution to a boil and then boil vigorously for about 2 min.

Step 8. Adjust the volume to about 15 ml with H_2O and add 5 drops of Fe carrier. Make the solution basic by the dropwise addition of concd NH_4OH and then add 10 drops in excess. Stir, centrifuge, and decant the supernate into a clean 40-ml centrifuge tube, discarding the precipitate.

Step 9. Repeat Step 3, except filter the $BaCrO_4$ precipitate through a 2", 60° funnel on No. 42 Whatman filter paper. Collect the filtrate in a clean 40-ml centrifuge tube.

Step 10. To the filtrate add concd NH_4OH until the solution is barely basic. Then add 5 ml of saturated Na_2CO_3 solution to precipitate $SrCO_3$. Centrifuge and discard the supernate. Wash the precipitate with a mixture of 10 ml of H_2O and 2 ml of saturated Na_2CO_3. Centrifuge and discard the wash. Slurry the precipitate and filter onto a weighed No. 42 Whatman filter circle, 7/8" diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Wash the precipitate with 5 ml of H_2O and 5 ml of 95% ethanol, dry in an oven at 110°, and weigh (Note 2). Transfer the precipitate into a clean 40-ml centrifuge tube and permit ^{90}Y to grow into equilibrium with the ^{90}Sr. (This process requires about 18 days. Note 3.)

Step 11. After equilibrium has been attained, wash down the sides of the tube with 10-15 ml of 1*M* HCl. Add 2 ml of standard Y carrier and stir. Slide the filter circle up the side of the tube with the stirring rod and, while holding the paper, wash with 1*M* HCl and remove it.

Step 12. Add concd NH_4OH dropwise until $Y(OH)_3$ precipitates and then add 5 ml in excess. Centrifuge and save the supernate until the results of analysis for Y have been checked. Record the time (Note 4).

Step 13. Dissolve the $Y(OH)_3$ in a minimum of concd HCl and add 15 ml of H_2O. Add 20 mg of Sr holdback carrier and precipitate $Y(OH)_3$ with excess concd NH_4OH. Centrifuge and discard the supernate.

Step 14. Repeat Step 13.

Step 15. Wash the precipitate with H_2O, dissolve in a minimum of concd HCl, and add 15 ml of H_2O. Again precipitate $Y(OH)_3$ with concd NH_4OH but this time in the absence of Sr carrier.

Step 16. Wash the precipitate and dissolve as in Step 15.

Step 17. Add 5 ml of saturated $(NH_4)_2C_2O_4$ solution and a small amount of HCl, if necessary, to precipitate $Y_2(C_2O_4)_3$. Digest on a steam bath for 5-10 min.

Step 18. Filter the $Y_2(C_2O_4)_3$ precipitate onto a weighed No. 42 Whatman filter circle, 7/8" diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Wash the precipitate with H_2O and place in a porcelain crucible (Coors 000). Ignite at 900° for 30 min. Grind the Y_2O_3 into a powder with a stirring rod and add a few drops of ethanol. Continue grinding until the precipitate is smooth and transfer with 95% ethanol onto a weighed No. 42 Whatman filter circle, 7/8" diameter. Wash down the sides of the filter chimney with ethanol, dry the precipitate in an oven at 110°, cool, weigh, and mount.

Notes

1. By use of refrigerated fuming HNO_3, the time required for cooling in an ice bath is reduced.

2. The $SrCO_3$ formed in this step may be mounted and counted for ^{89}Sr.

3. The 18-day waiting period may be shortened provided a growth correction is made for the time interval between the centrifugation operations in Step 8 and Step 12.

4. The time at which ^{90}Y is separated from ^{90}Sr is recorded as t_0 and all Y counts are corrected to this time.

QUANTITATIVE CHEMICAL RECOVERY OF SPALLATION-PRODUCED ELEMENTS. MOLYBDENUM TARGET

A. SEPARATION OF STRONTIUM

P. M. Grant, M. Kahn,
and H. A. O'Brien, Jr.

Spallation reactions have been induced in molybdenum targets by means of 200-800 MeV protons to produce microcurie amounts of a variety of radio elements. The targets were in the form of 99.90% pure foils, usually 0.51 mm thick, and were irradiated for from 1 to 20 μA-hr of integrated intensity. Following irradiation, a target was permitted to stand for several days to permit the activities to decay to reasonable levels. It was then radiographed and the hot spot cut away from surrounding inactive metal. The radioactive section was cleaned of surface contaminants by immersion in chromic acid cleaning solution for 1-2 min, rinsed with distilled water, dried, and weighed. Typical molybdenum weights ranged from 1-10 g.

A. SEPARATION OF STRONTIUM

1. Introduction

Strontium is quantitatively separated from the irradiated molybdenum by a six-step procedure utilizing precipitation, solvent extraction and ion exchange techniques. The molybdenum metal is first dissolved in 30% H_2O_2 to give a solution of molybdic acid, H_2MoO_4. Following removal of excess H_2O_2, the acid is converted to its ammonium salt and then lead molybdate is precipitated. Extraction of the lead molybdate with 0.12*M* HCl-50% solution of di-2-ethylhexyl orthophosphoric acid (HDEHP) in toluene effectively separates strontium from yttrium; the former is concentrated in the aqueous phase while the yttrium and some other contaminants are extracted into the organic phase. Macroscopic amounts of lead and molybdenum are removed from the aqueous solution, at pH 6.0, through the inorganic exchanger, hydrous zirconium dioxide. Strontium ion is not retained on the exchanger, while many contaminants are held. Yields of strontium, based on radioactivity determinations, are 94 ± 2% and separation is effected from molybdenum, technetium, niobium, zirconium, yttrium, rubidium, selenium, arsenic, zinc, and cobalt.

The long-lived strontium isotopes 82 and 85 are obtained in the irradiation process. If one is interested mainly in strontium activities and the irradiation has not been sufficiently intense to produce milligram quantities of the element, strontium carrier is added at an appropriate place in the procedure.

2. Reagents

HNO_3: 7-8*M* Sr carrier: Added as $Sr(NO_3)_2$ solution

HCl: 0.12*M*

H_2S: gas

H_2O_2: 30% aqueous solution (unstabilized)

NH_4OH: concd; 3.7*M*

0.1*M* NH_4Cl: aqueous solution

$Pb(NO_3)_2$: 5 mg Pb^{2+}ml aqueous solution chromic acid cleaning solution: 35 ml of saturated aqueous $Na_2Cr_2O_7$ in 1 ℓ. of concd H_2SO_4

HDEHP solution: 50% solution by volume of di-2-ethylhexylphosphoric acid (source: Eastman Organic Chemicals) in toluene

Hydrous ZrO_2 ion exchanger: HZO-1 crystals; Source: Bio Rad Laboratories

3. Procedure

Step 1. To the Mo sample in a 400-ml beaker, add sufficient 30% H_2O_2 to dissolve the metal with *mild* heating. (Typically, 10-20 ml of the peroxide is required for each gram of Mo.) Heat the yellow molybdic acid solution gently to drive off excess H_2O_2.

Step 2. By a careful combination of evaporation with gentle heating and the addition of concd NH_4OH make the solution about 1*M* in Mo and 3-4*M* in base. (Care has to be exercised in this operation because of the large tendency of Mo to escape from solution by a mass transport mechanism). During the process, the solution changes from its original bright yellow color to almost colorless, and a small amount of yellow-brown precipitate forms. The precipitate, which is thought to be molybdenum (V) or molybdenum (VI) hydroxide (hydrous molybdenum oxides) or a mixture of the two, carries with it a large amount of Zr and Y activities. Place the mixture of precipitate and solution into a large centrifuge tube, centrifuge, transfer the supernate to a clean centrifuge tube, and set aside the precipitate.

Step 3. To the supernate, add 1 ml of $Pb(NO_3)_2$ solution (5 mg of Pb^{2+}). A white precipitate of $PbMoO_4$ forms immediately. Stir the suspension, heat on a steam bath for 1-2 hr, centrifuge, decant the supernate and set it aside. Wash the $PbMoO_4$ precipitate several times with a 0.1*M* NH_4Cl solution which had been made slightly basic by the addition of NH_4OH. After each wash, centrifuge and set aside the supernate.

Step 4. Add 10 ml of 0.12*M*HCl and 10 ml of HDEHP solution to the precipitate. Stopper the centrifuge tube and equilibrate the mixture on a Burrell wrist-action shaker for 1-2 hr. (The $PbMoO_4$ should be completely dissolved after this time.) Transfer to a 60-ml separatory funnel and draw off the lower (aqueous) layer into a 250-ml beaker. Set aside the organic (upper) layer.

Step 5. Make the aqueous phase basic with 0.5 ml of 3.7*M* NH_4OH. A white precipitate (probably $Pb(OH)_2$) forms. Bubble H_2S through the suspension for about a half-hour. The white precipitate is converted to PbS (brownish black). Acidify the mixture with 0.5 ml of 7-8*M* HNO_3, heat on a steam bath for 10-15 min, cool to room temperature, and filter into a 250-ml filter flask. Discard the precipitate, which is a mixture of PbS and MoS_3.

Step 6. Heat the filtrate to drive off any excess H_2S and adjust the pH to about 6.0 by the dropwise addition of concd NH_4OH. If necessary, add a few milligrams of Sr carrier in the form of $Sr(NO_3)_2$ solution. (See **Introduction**; milligram quantities of Sr are required to maintain a quantitative recovery of the element.) Pass the solution through a column (0.8 cm in diameter X 4 cm in length) of untreated 100-200 mesh hydrous ZrO_2 exchange crystals (HZO-1) at a rate of about 0.1 ml/min. Collect the Sr-containing eluate.

SULFATE

B. P. Bayhurst

1. Introduction

In this procedure for the separation of sulfate ion from fission-product solutions, sulfate is finally precipitated as the barium salt after appropriate decontamination steps. With the use of the procedure, there was no detectable activity in the barium sulfate separated from a fission-product solution six days old and containing 3×10^{13} fissions. The chemical yield is about 75%.

2. Reagents

SO_4^{2-} carrier: equivalent to 10 mg $BaSO_4$/ml; prepared by diluting 2.4 ml of concd H_2SO_4 to 1 liter and standardized by conversion to $BaSO_4$

Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in 1*M* HCl

Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3

HCl: concd; 6*M*; 3*M*; 0.75*M*

NH_4OH: 1*M*

NaOH: 0.5*M*

$BaCl_2$: 1*M*

K_2CO_3: 50% solution

Benzidine reagent: prepared by dissolving 5 g of benzidine hydrochloride in 40 ml of 1*M* HCl and diluting to 250 ml with 50% ethanol

Acetone

Dowex AG 1-8X, 50-100 mesh anion exchange resin; slurry in H_2O

3. Procedure

Step 1. Add the sample (in dilute acid medium) to 3 ml of SO_4^{2-} carrier in a 40-ml Pyrex centrifuge tube. Then add 2 ml of 1*M* $BaCl_2$, centrifuge, and discard the supernate. Wash the $BaSO_4$ precipitate with H_2O, and discard the washings.

Step 2. With the aid of a minimum amount of H_2O, transfer the precipitate to a 125-ml erlenmeyer flask. Add 10 drops of 50% K_2CO_3 solution and heat to dryness. Add 20 ml of H_2O, boil, and transfer the mixture to a clean centrifuge tube. Centrifuge and transfer the supernate containing the SO_4^{2-} ion to a clean centrifuge tube. (The K_2CO_3 treatment should have converted the $BaSO_4$ completely to $BaCO_3$. The precipitate should be treated with 6*M* HCl and if it does not dissolve completely, the K_2CO_3 treatment should be repeated on the remaining $BaSO_4$. The supernate from the second treatment is then combined with that from the first.)

Step 3. To the supernate (or combined supernates), *carefully* add 3*M* HCl dropwise until the pH of the solution is about 2.5 Add 5 ml of benzidine reagent, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of H_2O and 2 drops of concd HCl, centrifuge, and discard the supernate.

Step 4. Dissolve the benzidine sulfate in 5 ml of 0.5*M* NaOH, add 2 drops each of Fe and Zr carriers, heat, centrifuge, and transfer the supernate to a clean centrifuge tube.

Step 5. Repeat the hydroxide scavenging precipitations twice.

Step 6. To the supernate from the last precipitation, add 5 ml of acetone and transfer the solution onto a Dowex 1-X8, 50-100 mesh, anion resin column (8 mm diameter and 4-5 cm long), which has previously been washed with H_2O and dilute NaOH. Wash the column first with 10 ml of a mixture of equal volumes of acetone and water and then with 10 ml of a mixture of equal volumes of 1*M* NH_4OH and acetone. Discard both washes. To elute the SO_4^{2-} ion from the column, add first 5 ml of 6*M* HCl and then 10 ml of 0.75*M* HCl, collecting the eluate in a clean centrifuge tube.

Step 7. Add 2 ml of 1*M* $BaCl_2$, precipitate $BaSO_4$ as in Step 1, and then repeat Steps 2 and 3.

Step 8. Dissolve the benzidine sulfate precipitate in a mixture of 2 ml of concd HCl and 10 ml of H_2O. (Warming speeds dissolution.) Add 2 ml of 1*M* $BaCl_2$, centrifuge, and discard the supernate. Wash the precipitate with H_2O containing a few drops of $BaCl_2$ solution and HCl. Centrifuge and discard the wash. Slurry the precipitate in H_2O and filter through a weighed Millipore (0.8μ) filter. Wash the precipitate with H_2O and dry in an oven at 100°. Cool, weigh, and mount.

tantalum, tellurium, thallium, thorium, tin, transactinides, tritium, tungsten

TANTALUM

B. P. Bayhurst

1. Introduction

In the separation of tantalum from niobium and other fission products, lanthanum fluoride scavengings are followed by the main decontamination step of extracting the element into hexone from a solution 2.88*M* in HNO_3 and 1.1*M* in HF. The tantalum is then back-extracted by means of a 1.5% hydrogen peroxide solution and precipitated as the hydrous oxide, $Ta_2O_5 \cdot XH_2O$. This is ignited to the anhydrous compound, in which form the tantalum is counted. The chemical yield is 80-90%.

2. Reagents

Ta carrier: 10 mg Ta/ml, prepared by dissolving the pure metal in a minimum of a mixture of concd HNO_3 and HF and diluting to the appropriate volume with H_2O.
La carrier: 10 mg La/ml, added as aqueous $La(NO_3)_3 \cdot 6H_2O$
Nb carrier: 10 mg Nb/ml, added as $K_8Nb_6O_{19} \cdot 16H_2O$ in H_2O
HNO_3-HF solution: 2.88*M* in HNO_3 and 1.1*M* in HF
HNO_3: concd
$KClO_3$: solid
Hexone (4-methyl-2-pentanone)
H_2O_2: 1.5% by volume
Ethanol: 95%

3. Procedure

Step 1. Add the sample to 4.0 ml of Ta carrier in a 40-ml polyethylene centrifuge tube and make the solution 2.88*M* in HNO_3 and 1.1*M* in HF. Add 4 drops of La carrier, stir, and place on a steam bath for 2-3 min. Centrifuge, transfer the supernate to a clean polyethylene tube, and discard the precipitate. Repeat the LaF_3 scavenging twice, the last time transferring the supernate to a small polyethylene tube.

Step 2. To the supernate, add 4-5 drops of Nb holdback carrier and extract the solution with hexone (the volume of hexone should be approximately one-third the volume of the solution). Repeat the extraction twice, combining the hexone layers in a clean polyethylene bottle. To the hexone solution add 4-5 drops of Nb carrier and wash with HNO_3-HF solution, discarding the washings. Again add Nb carrier and repeat the washing step. Wash again with HNO_3-HF solution without Nb carrier present and discard the washings.

Step 3. Extract the Ta from the hexone solution with about one-fourth of its volume of 1.5% H_2O_2. Repeat three times, combining all the extracts in a 125-ml erlenmeyer flask and discarding the hexone layer.

Step 4. Add 5 ml of concd HNO_3 and boil the solution down to a volume of 2-3 ml. Repeat. Add about 200 mg of $KClO_3$ and 5 ml of concd HNO_3, boil down to about 2-3 ml, and transfer the mixture to a 40-ml Pyrex centrifuge tube with the aid of concd HNO_3. Centrifuge and discard the supernate. Wash the precipitate twice with concd HNO_3, each time centrifuging and discarding the supernate.

Step 5. To the precipitate, add a slurry of filter paper pulp, stir, and filter through No. 40 Whatman filter paper (9 cm diameter). Transfer the paper to a Coors 00 porcelain crucible and ignite at 900° for 20 min. Permit the crucible to cool.

Step 6. Add 1-2 ml of ethanol to the Ta_2O_5 in the crucible and with the aid of the polished end of a stirring rod crush the oxide to a fine powder. By means of a stream of ethanol from a polyethylene squeeze bottle, transfer the oxide onto a weighed No. 42 Whatman filter circle, using a ground-off Hirsch funnel and a filter chimney. Filter, wash the precipitate with ethanol, and dry at 110°. Cool, weigh, and mount for counting.

TELLURIUM

E. A. Bryant

1. Introduction

This procedure, for the determination of tellurium in fission products, utilizes the difference in behavior between tellurium (IV) and tellurium (VI) in $6M$ HCl on an anion resin column. Tellurium in the +4 state is adsorbed on AG 1-X4 resin, eluted with $0.2M$ HCl, reduced to the metal, and then oxidized to the +6 state with sodium bismuthate in nitric acid. The bismuthate is removed on an anion column, and the tellurium (VI) is made $6M$ in HCl and passed through another column. This last step effectively removes molybdenum (VI), which stays on the column. The tellurium is finally reduced to the elemental state in which form it is weighed and counted. Chemical yields of about 75% are obtained.

2. Reagents

Te carrier: 8.56 mg Te/ml. 10.7 g $Na_2TeO_4 \cdot 2H_2O$ and 8.7 g Na_2TeO_3 in 1 liter of $4M$ HCl, standardized
HBr: concd
HCl: concd; $6M$; $3M$; $0.2M$
HNO_3: concd; $3M$
SO_2: gas
$NaBiO_3$: solid
Dowex AG 1-X4 anion resin column; slurry in $6M$ HCl
Ethanol: absolute

3. Preparation and Standardization of Carrier

Pipet exactly 5 ml of carrier solution into a 125-ml erlenmeyer flask, add 3 ml of concd HBr, and boil nearly to dryness. Repeat the addition of HBr and again boil the solution nearly to dryness. Add 50 ml of $3M$ HCl, saturate the solution with SO_2, and let it stand for about 20 min. Saturate again with SO_2 and filter the elemental Te onto a weighed, fritted filter funnel of fine porosity. Wash the Te first with H_2O and then with absolute ethanol. Dry in an oven at 110°, cool, and weigh.

4. Procedure

Step 1. Add the sample to 3 ml of carrier in a 125-ml erlenmeyer flask. Add 3 ml of concd HBr and boil nearly to dryness. Repeat the HBr treatment twice more and then dissolve the residue in 5 ml of $6M$ HCl.

Step 2. Transfer the solution to the top of a 0.6- × 5-cm Dowex AG 1-X4 50-100 mesh anion resin column which has previously been washed with $6M$ HCl. When the solution reaches the resin, wash the erlenmeyer flask with 3 ml of $6M$ HCl and transfer the washings to the column. Discard the eluates.

Step 3. Wash the column with three 5-ml batches of $6M$ HCl and discard the eluates.

Step 4. Wash the column with two 5-ml portions of $0.2M$ HCl and collect the eluates in a clean 40-ml conical centrifuge tube.

Step 5. To the combined eluates add 2 ml of concd HCl and saturate the solution with SO_2. Let stand for about 20 min, centrifuge, and discard the supernate. Wash the precipitate with 5 ml of H_2O.

Step 6. To the precipitate add 3 drops of concd HNO_3, warm with stirring, and then add 3 ml of $3M$ HNO_3. Add about 50 mg of $NaBiO_3$, stir for 1 min, and add another 50 mg of the salt. Set aside for 10 min.

Step 7. Transfer to an anion resin column that has been made up as already described, but washed with H_2O rather than with $6M$ HCl prior to use. Wash the centrifuge tube with 1 ml of $3M$ HNO_3 and add the washings to the column. Wash the column with 5 ml of $0.2M$ HCl and then with 5 ml of $6M$ HCl. Collect all eluates in a clean centrifuge tube.

Step 8. Add 8 ml of concd HCl to the combined eluates and pass the solution through another anion resin column which has been washed with $6M$ HCl prior to use. When the solution has passed through, wash the column with 5 ml of $6M$ HCl. Collect the eluates in a clean 125-ml erlenmeyer flask.

Step 9. Add 3 ml of concd HBr and boil to dryness. Repeat the HBr treatment twice.

Step 10. Dissolve the residue in a minimum of 3*M* HCl and transfer the solution to a clean centrifuge tube. Saturate with SO_2, let stand for 10 min, centrifuge, and discard the supernate. Wash the precipitate with water and discard the washings. Slurry the precipitate in absolute ethanol, filter onto a weighed No. 42 Whatman filter paper, dry at 110°, cool, weigh, and mount.

THALLIUM

R. J. Prestwood

1. Introduction

In the determination of radiothallium in the presence of fission products, tellurium and the more noble metals are removed by reduction to the elemental state by means of sulfur dioxide and hydrazine in hydrochloric acid medium. This is followed by a series of thallium (I) iodide and lanthanum hydroxide precipitations. The thallium iodide precipitation serves as an excellent decontaminating step, effectively removing thallium from a large number of activities, including cadmium, chromium, cobalt, nickel, and alkaline earths. Thallium (I) is finally converted to the chromate, in which form it is counted. The chemical yield is about 80%. Quadruplicate analyses can be performed in about 4 hr.

2. Reagents

Tl carrier: 10 mg Tl/ml, added as $TlCl_3$ in dilute HCl, standardized
Te carrier: 10 mg Te/ml, added as Na_2TeO_3 in dilute HCl
La carrier: 10 mg La/ml, added as aqueous $La(NO_3)_3 \cdot 6H_2O$
HCl: 3*M*
HNO_3: 6*M*
NH_4OH: concd
$N_2H_4 \cdot H_2SO_4$: solid
$Na_2CrO_4 \cdot 4H_2O$: 10% in H_2O
SO_2: saturated aqueous solution
NaI: solid
Methanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 11.17 g of Tl_2O_3 in dilute HCl and dilute the solution to a volume of 1 liter with the acid.

Pipet exactly 5 ml of the carrier solution into a 125-ml erlenmeyer flask and add 50 mg of solid $KHSO_3$. Boil off excess SO_2 and make the solution alkaline with concd NH_4OH. Add 5 ml of 10% $Na_2CrO_4 \cdot 4H_2O$ solution to precipitate Tl_2CrO_4. Bring to a boil and permit the precipitate to stand for about 12 hr and filter onto a weighed 30-ml sintered glass crucible of fine porosity. Wash the precipitate with 10 ml of H_2O and then with 10 ml of 95% ethanol. Dry at 110° for ½ hr. Cool and weigh.

Seven standardizations were found to give results having a total spread of less than 0.5%.

4. Procedure

Step 1. To the sample in a 125-ml erlenmeyer flask, add 2 ml of Tl carrier and 1 ml of Te carrier. Evaporate barely to dryness over an open flame. Add 5 ml of concd HCl and again evaporate to dryness. Repeat evaporation once again with 5 ml of HCl. Add 20 ml of 3*M* HCl and approximately 0.5 g of $N_2H_4 \cdot H_2SO_4$, and heat to boiling. Add 1 ml of SO_2-H_2O and continue to boil, making three to four successive additions of SO_2-H_2O. Particular care must be taken to insure complete precipitation of Te metal. When the Te has been completely precipitated the supernate is water-white with no suggestion of a bluish tint. Filter into a 125-ml erlenmeyer flask through a 2", 60° funnel, using No. 40 Whatman filter paper. Wash the original flask and the precipitate with dilute SO_2-H_2O. Discard the precipitate.

Step 2. Add enough H_2O to make the total volume approximately 75 ml and then add about 2 g of solid NaI. Centrifuge in two batches in a 40-ml conical centrifuge tube, discarding the supernate after each centrifugation.

Step 3. To the precipitate add 4 drops of La carrier and 1 ml of 6*M* HNO_3. Heat over open flame until all I_2 color has disappeared. Dilute with H_2O to 20 ml, heat over flame until the solution is rather warm, add 2-3 drops of SO_2-H_2O to insure complete reduction of Tl, and make basic by the dropwise addition of concd NH_4OH. Add 1 ml of NH_4OH in excess. Centrifuge, transfer the supernate to a clean 40-ml centrifuge tube, and discard the precipitate of $La(OH)_3$.

Step 4. To the supernate add approximately 1 g of NaI, centrifuge the precipitated Tl (I), and discard the supernate. To the precipitate add 1 ml of 6*M* HNO_3 and heat over open flame until

I_2 color has disappeared. Transfer to a 125-ml erlenmeyer flask, add 1 ml of Te carrier, and repeat Step 1.

Step 5. Repeat Steps 2 and 3.

Step 6. To the supernate add approximately 1 g of NaI, centrifuge, and discard the supernate.

Step 7. Repeat Step 3.

Step 8. To the supernate add 5 ml of 10% $Na_2CrO_4 \cdot 4H_2O$ solution. Allow to stand 5-10 min to permit the Tl_2CrO_4 precipitate to coagulate. Filter on a weighed No. 42 Whatman filter circle, ⅞" diameter, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with 5 ml of H_2O, and then with two 5-ml portions of absolute methanol. Dry at 110° for 10 min. Cool, weigh, mount, and count.

A RAPID PROCEDURE FOR THE SEPARATION OF CARRIER-FREE THORIUM FROM URANIUM AND FISSION PRODUCTS

C. J. Orth and W. R. Daniels

1. Introduction

This procedure describes the purification of thorium which had been produced by 100-MeV proton irradiation of about 100 mg of ^{238}U. The actual separations were begun at EOB+20 minutes and the procedure required about 45 minutes. The resin columns were operated under pressure so that effluent flow rates were about one drop per one or two seconds from the cation column and one drop per two or three seconds from the anion columns.

The separation of thorium required decontamination from fission products, neptunium, protactinium, and macro uranium.

The first decontamination step in the procedure is the adsorption of thorium on a cation resin column from 3*M* HCl. The element is removed from the column with oxalic acid and is taken up in concentrated HCl following destruction of oxalate. Zirconium is then removed by adsorption on anion resin columns and the thorium is extracted into 0.5*M* HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The latter step gives excellent separation from the lanthanides. Finally, the thorium is back-extracted into aqueous HCl-HF and the solution is evaporated on a Teflon foil.

2. Reagents

HCl: concd; 6*M*; 3*M*
HNO_3: concd
$HClO_4$: concd
$H_2C_2O_4$: 0.5*M*
$NH_2OH \cdot HCl$: solid
n-heptane
HDEHP solution: 0.5*M* solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane
AG 50W-X4 cation resin column, 100-200 mesh, H^+ form, stored as a slurry in H_2O
AG 2-X8 anion resin column, 100-200 mesh, Cl^- form, pre-equilibrated with concd HCl

3. Procedure

Step 1. In a 50-ml erlenmeyer flask, dissolve as much as 150 mg of U foil in 3 ml of concd HCl and 2 ml of concd HNO_3. Add 5 ml of concd $HClO_4$, fume to near dryness, and then add 3 ml of 3*M* HCl.

Step 2. Transfer the solution to the top of a 5 cm x 8 mm AG 50W-X4 (100-200 mesh, H^+ form) cation resin column. Wash off U and other contaminating activities first with 16 ml of 3*M* HCl and then with 4 ml of concd HCl. Elute the Th with 10 ml of 0.5*M* $H_2C_2O_4$ and collect the eluate in a 50-ml erlenmeyer flask.

Step 3. Add 5 ml of concd $HClO_4$ and 2 ml of concd HNO_3 and evaporate to dryness over a burner. Cool and add 3 ml of concd HCl. Transfer the solution to the top of a 5 cm x 8 mm AG 2-X8 anion resin column. Pass the solution containing the Th through two of these columns in succession, following with 3 ml of concd HCl wash. Collect the eluate in a 50-ml erlenmeyer flask containing about 100 mg $NH_2OH \cdot HCl$. (Zr and any remaining U, Np, and Pa activities remain on the anion resin.) Boil the solution down to about 2 ml. (At this point, Ce(IV) has been reduced to the III state.)

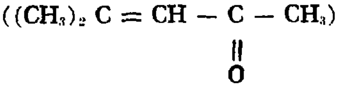
Step 4. Transfer the solution to a 15-ml tapered glass centrifuge tube and add 2 ml of 0.5*M* HDEHP solution in *n*-heptane. Shake for 10 seconds and discard the aqueous (lower) layer which contains lanthanides. Wash the heptane layer successively with 2 ml each of concd, 6*M*, and 2*M* HCl. Each time, shake for 10 seconds and discard the washes. (One can at this stage γ-count the Th in the heptane layer.

Step 5. Add 0.5 ml of concd HF and 1.5 ml of 6*M* HCl to the heptane solution, shake for 10 seconds, and discard the heptane (upper) layer. Contact the aqueous layer with 2 ml of *n*-heptane, shake, and discard the heptane layer. Evaporate the aqueous solution to near dryness on an oil bath, using an air jet to speed up the evaporation process. By means of a finely drawn pipet, place the liquid on a Teflon foil. Rinse the centrifuge tube with a drop of concd HCl and add the rinse to the foil. Evaporate to dryness under a heat lamp.

THORIUM

R. J. Prestwood

1. Introduction

In the separation of thorium from large amounts of fission products (10^{15} fissions or more), four principal decontamination steps are employed: (1) $Th(IO_3)_4$ precipitation gives separation from the rare earths; (2) $Th(C_2O_4)_2$ precipitation effects separation from zirconium; (3) ion exchange from a concentrated (greater than 12*M*) hydrochloric acid solution on AG-1 anion resin results in the adsorption of zirconium, iron, neptunium, plutonium, and uranium, the thorium passing through the column; and (4) extraction of thorium from an aluminum nitrate-nitric acid solution by means of mesityl oxide  $((CH_3)_2 C = CH - \underset{\underset{O}{\|}}{C} - CH_3)$ gives excellent decontamination from the alkali and alkaline earth metal ions (including radium), lanthanum, and cerium. This extraction is ineffective for the separation of thorium from zirconium, plutonium, and uranium, and gives only poor decontamination from neptunium.

Thorium is finally precipitated as the oxalate and ignited to the dioxide, in which form it is mounted and weighed. The yield is 70-80%, and quadruplicate analyses can be carried out in approximately 8 hr.

2. Reagents

Th carrier: 10 mg Th/ml (see preparation and standardization of carrier)
Bi carrier: 10 mg Bi/ml, added as $Bi(NO_3)_3 \cdot 5H_2O$ in dilute HNO_3
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Zr carrier: 10 mg Zr/ml, added as purified $ZrOCl_2 \cdot 8H_2O$ in H_2O
HCl: concd; gas
HNO_3: concd; 6*M*
H_2SO_4: concd
HIO_3: 1*M* (filtered)
$H_2C_2O_4$: saturated solution (filtered)
NH_4OH: concd
H_2S: gas
SO_2: gas
2.4*M* $Al(NO_3)_3$ in 1.2*M* HNO_3 (filtered)
$KClO_3$: solid
Methanol: absolute
Mesityl oxide: Eastman White Label
AG1-X10 anion resin column, 100-200 mesh, stored as a slurry in H_2O.

3. Preparation and Standardization of Carrier

If the purity of the thorium is known, the metal may be weighed out directly as a primary standard. It is dissolved on a steam bath in a small excess of concentrated HNO_3 in a Pt dish, with periodic additions of small amounts of 0.1*M* HF. If thorium nitrate is used as carrier, it is dissolved in about 0.001*M* HNO_3 and filtered. To a 10.0 ml aliquot (four standardizations are usually carried out) of the carrier, 10 drops of concd HCl are added and the solution is boiled over a Fisher burner. Four ml of saturated $H_2C_2O_4$ are then added and the solution is boiled for 2 min. The thorium oxalate precipitate is filtered through No. 42 Whatman filter paper (9 cm) in a 2″, 60° funnel and washed with about 1% $H_2C_2O_4$ solution (the saturated solution is diluted 1 to 10). The precipitate is transferred to a tared porcelain crucible (Coors 000) and is carefully ignited at 900° for 1 hr. The carrier is weighed as ThO_2.

4. Procedure

Step 1. Into a 40-ml short-taper centrifuge tube, pipet 2.0 ml of standard Th carrier; add the fission-product solution and 5 drops of La carrier. Precipitate $Th(OH)_4$ by means of an excess of concd NH_4OH, centrifuge, and discard the supernate.

Step 2. To the precipitate add 8 ml of concd HNO_3, 15 ml of H_2O, and 7 ml of 1*M* HIO_3. Centrifuge the $Th(IO_3)_4$ precipitate and discard the supernate. Wash the precipitate with 15 ml of a solution which is 4*M* in HNO_3 and 0.25*M* in HIO_3. Centrifuge and discard the supernate.

Step 3. To the precipitate add 1 ml of concd HCl and 5 drops of Zr holdback carrier. Heat while stirring over an open flame until the precipitate dissolves and the solution boils. Dilute to 5 ml with H_2O and bubble in SO_2 gas until the solution becomes essentially colorless. Dilute to 10 ml with H_2O and boil until the solution is water-white. Add 4 ml of saturated $H_2C_2O_4$ solution and continue boiling for about 1 min. Centrifuge the oxalate precipitate and discard the supernate.

Step 4. To the precipitate add 1 ml of concd HNO_3 and about 100 mg of solid $KClO_3$. Heat cautiously to boiling to destroy oxalate. Dilute to 15 ml with H_2O and precipitate $Th(OH)_4$ by means of an excess of concd NH_4OH. Centrifuge and discard the supernate.

Step 5. Add 10 drops of concd HCl to the precipitate and bubble in HCl gas through a transfer pipet until the solution is saturated. With the aid of a hypodermic syringe and the same pipet, transfer the solution (which has a volume of approximately 1 ml) onto an AG1-X10 anion resin column. (Before use, the resin column is treated with a wash solution made up by adding 1 drop of concd HNO_3 (Note 1) to 20 ml of concd HCl and saturating with HCl gas at room temperature.) By means of air pressure, force the sample solution through the column in approximately 3 min, but do not allow the meniscus to go below the top of the resin. The effluent is collected in a 40-ml short-taper centrifuge tube. Add 1 ml of the resin wash solution to the original centrifuge tube and transfer the washings by means of the same pipet onto the column. The washings are forced through the column in the same manner as the sample solution, and are collected along with the sample solution. This wash may be repeated if it is necessary to obtain the maximum yield of Th.

Step 6. Dilute the collected sample plus washes to approximately 25 ml with H_2O and make the solution basic with concd NH_4OH. Centrifuge the $Th(OH)_4$ precipitate and discard the supernate.

Step 7. Dissolve the precipitate with 6 drops of $6M$ HNO_3. Use 10 ml of $2.4M$ $Al(NO_3)_3$-$1.4M$ HNO_3 mixture (hereinafter called the extraction mixture) to transfer the sample solution to a 60-ml separatory funnel. Add 10 ml of mesityl oxide to the separatory funnel, shake for 15-20 sec, and discard the water (lower) layer. Wash the mesityl oxide layer twice with 5-ml portions of extraction mixture, discarding each washing. Back-extract the thorium with two 5-ml washes of distilled H_2O, collecting both H_2O layers in a 40-ml short taper centrifuge tube. Dilute to 15 ml and add 8 ml of concd HNO_3 and 7 ml of $1M$ HIO_3 (Note 2). Centrifuge the $Th(IO_3)_4$ precipitate and wash as in Step 2.

Step 8. Repeat Steps 3 through 6.

Step 9. To the $Th(OH)_4$ precipitate, add 5 drops of Bi carrier and 10 drops of concd H_2SO_4. Dilute to 10 ml with H_2O and saturate the solution with H_2S. Filter through a No. 40 Whatman filter paper (9 cm) in a 2", 60° funnel, collecting the filtrate in a 40-ml short-taper centrifuge tube. Wash the precipitate with a small amount of water and combine the wash with the filtrate; discard the precipitate. Make the filtrate basic with concd NH_4OH, centrifuge, and discard the supernate.

Step 10. Repeat Step 7.

Step 11. Repeat Step 3, but do not add Zr holdback carrier and do not centrifuge the oxalate precipitate.

Step 12. Filter the hot solution containing the oxalate precipitate onto a $^{15}\!/_{16}$" No. 42 Whatman filter circle, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with 1% $H_2C_2O_4$ solution. Transfer the filter paper by means of forceps to a Coors 000 porcelain crucible and ignite for 15-20 min at 900°.

Step 13. Transfer the ThO_2 to a *dry* 40-ml long-taper centrifuge tube. (This is readily done by holding the edge of the crucible with forceps and dumping the contents into the centrifuge tube. Little or no ThO_2 adheres to the crucible.) Grind the ThO_2 with a 5-mm fire-polished glass stirring rod; add 1 ml of absolute methanol and continue grinding until the solid is very fine. Add an additional 10 ml of methanol and suspend the solid by vigorous swirling. Transfer onto a tared No. 50 Whatman filter circle ($^{15}\!/_{16}$" diameter) in the regular filter chimney setup. Apply suction until the methanol has passed through the filter circle. Remove the circle, dry in an oven at 115° for 10 min, place in the balance case for 20 min, and weigh. Mount the sample on two-sided Scotch tape which is stuck to an Al plate. Cover the sample with Nylon film (1.5 mg/cm^2).

Notes

1. The purpose of the HNO_3 is to maintain an oxidizing medium on the resin to prevent reduction of Pu.

2. At this point the solution will be slightly colored as a result of oxidation of dissolved mesityl oxide. This, however, does not affect the results.

6. β-Counting of Th

Whenever Th β activities such as isotopes 231, 233, and 234 are counted and ^{232}Th is used as carrier, one is faced with the problem of the growth of β activities from the carrier. Examination of the decay chain of ^{232}Th shows that the amount of β activity depends upon the quantity of ^{228}Th present. In the chain the longest-lived parent of ^{228}Th (half-life 1.9 years) is ^{228}Ra, the half-life of which is 6.7 years. Thus, the amount of ^{228}Th present in ^{232}Th depends upon the time of separation of ^{228}Ra. The β emitters succeeding ^{228}Th grow in essentially with the half-life of ^{224}Ra which is 3.64 days. Therefore, the β activity that one observes from natural Th which has had all of its decay products chemically removed grows in with a 3.64-day half-life. One mg of natural Th in equilibrium with its decay products has 494 disintegrations per minute of β activity. Since one does not usually know the history of the Th used as carrier, the most convenient way to correct for these counts is the following:

> Pipet out as much carrier solution as will give approximately the same weight as a true sample would when carried through the whole separation procedure. Perform Steps 9 through 13 of the procedure. Note the time of the last mesityl oxide wash of Step 10. After the sample is mounted, count it every few hours over a period of several days. It is convenient to use the time of the last mesityl oxide wash as t_0. In this manner, one can correct for the growth of betas from the carrier.

7. Absolute β-Counting of Some Th Isotopes

The relation between counts and disintegrations for thorium isotopes of mass numbers 231, 233, and 234 can be obtained from ^{235}U, ^{237}Np, and ^{238}U, respectively. If a weighed quantity of ^{235}U or ^{238}U is taken, Th carrier added, and a chemical separation of Th made, one can calculate in each case the number of Th disintegrations present. By counting the sample and correcting for decay from time of separation, one has a direct relationship between counts and disintegrations. The self-absorption of the sample can be taken into account by the use of this technique on several different weights of Th carrier with identical specific activity. For example, one adds 100 mg of Th carrier to a weighed amount of either ^{235}U or ^{238}U, mixes the solution thoroughly, takes several aliquots of different sizes, and separates the thorium. In this way, one can plot a curve of sample weight *vs* disintegrations.

In the case of ^{233}Th the situation is different. The decay product of this isotope is ^{233}Pa, which is also the immediate decay product of ^{237}Np. By separating ^{233}Pa from a known weight of ^{237}Np and counting the former, one has a direct relationship for ^{233}Pa of counts *vs* disintegrations. For a sample of ^{233}Th one takes two known aliquots, differing by a factor of about 1,000 in activity. (The ratio of ^{233}Pa to ^{233}Th half-lives is 1693:5.) The weaker aliquot is counted for ^{233}Th immediately upon separation of Pa. The stronger one is permitted to decay until it is all ^{233}Pa and is then counted. From the previous (^{237}Np) calibration one then can find the disintegrations of ^{233}Pa for this sample. The sample is corrected for decay back to the time the weaker sample was counted for ^{233}Th, thus obtaining the number of atoms of the latter when aliquot correction is made.

^{230}Th (IONIUM)

J. W. Barnes and H. A. Potratz

A. Determination in Coral Samples

1. Introduction

The determination of ^{230}Th (ionium) in coral samples involves carrier free separation of the total thorium content by use of TTA [4,4,4, trifluoro - 1 - (2-thienyl) - 1, 3 - butanedione]. Thorium is finally adsorbed on a cation exchange column and eluted with oxalic acid. It is then α-counted and pulse analyzed, with ^{228}Th being employed to determine chemical yield. The chemical yield is 50-70%. Duplicate samples may be run in about 6 hr.

2. Procedure

Step 1. Transfer about 20 g of coral, weighed to the nearest 0.1 g, to a 600-ml beaker. Add ^{228}Th tracer in known amount (5-100 counts/min) and wash down the sides of the beaker with H_2O.

Step 2. With a Speedyvap watch glass in place on top of the beaker, gradually add 75 ml of concd HNO_3, dropwise at first to prevent excessive foaming. Place the covered beaker on a hot plate and allow the solution to boil until the vegetable fibers present in most samples have disintegrated and brown fumes are no longer evolved. Cool to room temperature and cautiously add 70% $HClO_4$. (During this and subsequent steps which involve fuming with $HClO_4$, the operator should wear a face shield and rubber gloves). Evaporate to dense white fumes and continue heating for at least an additional 5 min. Cool to room temperature and dilute to about 200 ml with H_2O.

Step 3. Add concd NH_4OH until the solution is barely acid, and then adjust the pH to 2.0-2.5 with the use of 3*M* NH_4OH and 3*M* $HClO_4$.

Step 4. To a separatory funnel add the solution from Step 3 and 150 ml of 0.5*M* TTA in benzene. Stir for at least 1.5 hr with a vortex stirrer driven at high speed by means of an air motor. Permit the layers to separate, draw off the aqueous layer, and discard (Note 1).

Step 5. Wash the benzene layer, containing the thorium complexed with TTA, for about 30 sec by stirring with 100 ml of H_2O. Discard the washings. Wash again with 50 ml of H_2O and discard the washings.

Step 6. Extract the thorium from the benzene by stirring for 3 min with 100 ml of 3*M* HCl.

Step 7. Transfer the aqueous phase to a beaker and evaporate with an air jet on a steam bath until the volume has been reduced to 20-30 ml. Transfer the solution to a 40-ml centrifuge tube and continue evaporation to a volume of 1-2 ml.

Step 8. Add 1 ml of concd HNO_3 and boil over a flame until brown fumes are no longer evolved. Cool to room temperature, then add 0.3-0.4 ml of 70% $HClO_4$, and boil until white fumes appear. Cool to room temperature and dilute to about 3.5 ml with H_2O.

Step 9. Transfer the solution to the top of an AG50-X4 cation exchange column (Note 2) and rinse the centrifuge tube with 0.5 ml of H_2O, adding the rinsings to the column. (If air bubbles are present in the column, they should be removed by stirring with Pt wire.) Force the solution through the column under 2 pounds of air pressure, and then wash the column with 3-4 ml of 3*M* HCl under the same pressure. Discard the first effluent and the wash.

Step 10. Pour 2 ml of 0.5*M* $H_2C_2O_4$ onto the column and allow the solution to run through under atmospheric pressure. Collect the drops from the column on 1" square (1-3 mil) Pt plates, which are placed just far enough below the column so that drops separate from the tip before hitting the plate. Nine drops of effluent are collected on each of four plates. Dry the plates under a heat lamp; then ignite over an open flame.

Step 11. α-count the individual plates and then pulse analyze those plates which carry the activity (Note 3).

Notes

1. The chemical yield may be increased slightly by taking the aqueous layer through an additional extraction.

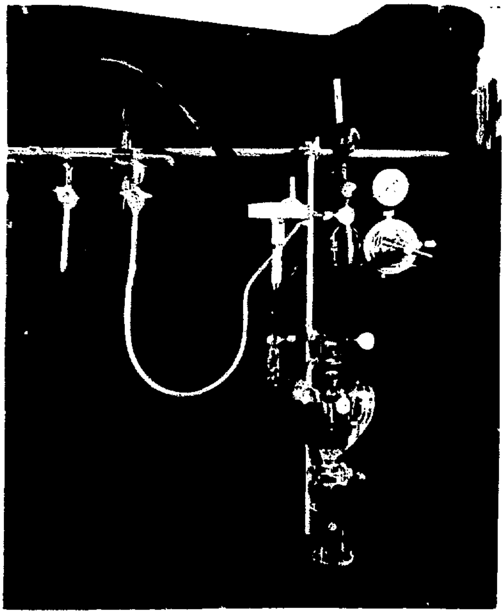
2. The tubes which are used to support the resin columns are shown in the accompanying illustration. They were constructed by blowing out the end of a 15-ml centrifuge tube and sealing on a length of 3-4 mm i.d. tubing. The AG 50-X4 resin was water-graded and the fraction which settled at the rate of 2-5 cm/min was selected for use. This was washed several times with concd HCl and then with H_2O. To support the resin column, a layer of HCl-washed sand about 5 mm thick is placed in the tip of the column tube. A slurry of graded, HCl-washed resin is then added by means of a syringe pipet, the resin slurry being introduced into the tube near the bottom so as to eliminate air bubbles. The amount of slurry added should be sufficient to produce a column 7-9 cm in length after settling. Settling of the resin may be hastened by applying up to 10 pounds of air pressure to the top of the column. To control pressure, the air line is connected to the top of the column through a reducing valve. Slurry liquid is allowed to flow through the column until the liquid level reaches the top of the resin; the stopper is then removed from the top of the column tube. Air must not be permitted to enter the resin column. If air does enter, the resin is reslurried to remove air bubbles. The cation column prepared as described above is washed with 2-3 ml of 3*M* $HClO_4$ and is then ready for use.

3. Pulse analyses were made with a 100-channel analyzer operated at a window setting which placed the ^{228}Th peak in the 83-87 channel region.

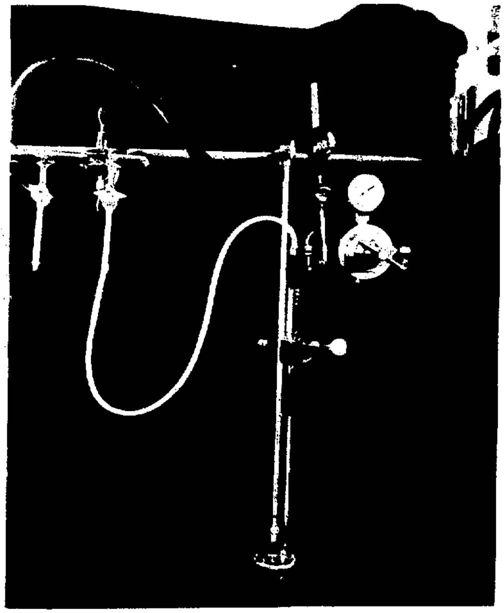
B. Determination in Old Fission-Product Material

1. Introduction

The method described for the determination of ^{230}Th (ionium) in coral samples is not satisfactory for fission-product solutions inasmuch as the plutonium present in the latter comes through the separation procedure and seriously interferes in pulse analyses. To overcome this difficulty, plutonium is removed on an anion exchange column from concentrated hydrochloric acid medium immediately before thorium is adsorbed on the cation column.



Extraction apparatus.



Resin columns.

2. Procedure

Step 1. To an aliquot of the sample in a 150-ml beaker add ^{228}Th tracer in known amount (5-100 counts/min) and then boil until white fumes appear. Dilute to 40 ml with H_2O.

Step 2. Repeat Steps 3 through 7 of Procedure A except cut down amounts of all reagents by a factor of five.

Step 3. Add 0.3-0.4 ml of 70% $HClO_4$ and boil until white fumes appear. Cool to room temperature and dilute to about 4 ml with Solution A. (Solution A consists of concd HNO_3 mixed with concd HCl in the ratio of 0.1 ml HNO_3 to 15 ml of HCl.)

Step 4. Transfer the solution to the top of a 5 cm × 2 mm Dowex AlX2 anion exchange column (Note) and rinse the centrifuge tube with about 0.5 ml of Solution A, adding the rinsings to the column. (Observe the usual precautions to avoid introduction of air bubbles.) Force the solution through the column under 1-2 lb of air pressure and collect the effluent in a 40-ml test tube. Rinse the column with 3 ml of Solution A under the same pressure and collect the effluent in the same test tube. Pu is retained on the column and thorium comes through in the effluent.

Step 5 The effluent is evaporated with an air jet to about 1 ml on a steam bath.

Step 6. Add 1 ml of concd HNO_3 and boil over a flame until brown fumes are no longer evolved. Cool to room temperature and add 1 ml of 70% $HClO_4$. Boil until white fumes appear, then cool to room temperature, and dilute with H_2O to about 3.5 ml.

Step 7. Repeat Steps 9, 10, and 11 of Procedure A.

Note

The anion exchange column is prepared in essentially the same manner as the cation column (see Note 2, Procedure A). The resin used is a 0.5-2 cm/min fraction of Dowex Al-X2. The resin is prepared for use by washing with Solution A.

PREPARATION OF CARRIER-FREE ^{234}Th (UX$_1$) TRACER

G. A. Cowan

1. Introduction

In the separation of ^{234}Th (UX$_1$) from uranium, the latter, originally present in the form of $UO_2(NO_3)_2$, is converted to a soluble uranyl carbonate complex by means of ammonium carbonate solution. Then at pH 8.0-8.5 the cupferrate of UX$_1$ is made and separated from the uranium by extraction into chloroform. The UX$_1$ is back-extracted into dilute nitric acid containing bromine which serves to decompose the UX$_1$ cupferrate. thus allowing extraction of all the organic material and excess bromine into the chloroform phase.

2. Reagents

$UO_2(NO_3)_2$: 1 g U/10 ml, added as U_3O_8 or $UO_2(NO_3)_2 \cdot 6H_2O$ in dilute HNO_3
HNO_3: 3*M*
$(NH_4)_2CO_3$: saturated aqueous solution
Br_2 water: saturated solution
Cupferron: 6% aqueous solution (freshly prepared and kept in refrigerator)
Chloroform: CP
Hydrion paper (short range)

3. Procedure

Step 1. Pipet 10 ml of $UO_2(NO_3)_2$ solution into a 250-ml beaker and treat with saturated $(NH_4)_2CO_3$ solution and H_2O until the yellow precipitate which first forms dissolves. Sufficient $(NH_4)_2CO_3$ is added to make the final pH of the solution 8.0-8.5 (Note).

Step 2. Transfer the solution to a 250-ml separatory funnel, and add 1-2 ml of 6% aqueous cupferron reagent and 10 ml of chloroform. Shake well and transfer the chloroform layer containing the UX$_1$ to a clean separatory funnel. Repeat the chloroform extraction and combine the extracts.

Step 3. Wash the chloroform extracts with 20 ml of H_2O to which has been added 1 ml of cupferron reagent and sufficient $(NH_4)_2CO_3$ solution to make the pH 8.0-8.5. Transfer the chloroform phase to a clean separatory funnel.

Step 4. To the chloroform phase add 10 ml of 3*M* HNO_3 and a few milliliters of saturated Br_2 water and shake. Discard the chloroform phase and wash the aqueous phase twice with chloroform, discarding the washings. Transfer to a 250-ml beaker and boil for a minute to remove the last traces of chloroform. Transfer the solution to a volumetric flask of the appropriate size and make up to volume with H_2O.

Step 4. Pipet aliquots of solution to 1" cover glasses and evaporate to dryness under a heat lamp. Count.

Note

A pH of 8.0-8.5 appears to be the optimum for the preparation and extraction of the UX$_1$ cupferrate, although a pH in the range 7-8.5 is suitable.

TRACER METHODS FOR ANALYSIS OF THORIUM ISOTOPES

J. W. Barnes

1. Introduction

The principal purification step in tracer work with thorium isotopes depends on the fact that the relatively small, highly charged thorium ion is more tightly bound to a cation exchange resin such as Dowex 50-X4 than are the ions of most other elements. Thorium is adsorbed on the resin bed and washed with dilute hydrochloric acid solutions to remove most impurities; it is then eluted from the column in a very narrow band with oxalic acid. Since thorium oxalate is insoluble, macroquantities cannot be eluted from the column in this way. The Dowex 50-X4 resin with 4% divinyl benzene in the original polystyrene bead is more satisfactory for this separation than any of the other cross-linkages. For example, Dowex 50-X2 does not adsorb thorium strongly enough under the experimental conditions to be useful; the higher cross-linkages in Dowex 50-X8 or -X12 do not allow impurities to be removed at a reasonable rate and also cause so much tailing in the elution that the thorium is not concentrated in the small volume desired. In tracer work with thorium, it is well to avoid solutions containing nitrate, fluoride, sulfate, or phosphate, since these cause considerable losses in steps involving anion and cation exchange columns.

In the analysis for any thorium isotope in a solution containing organic matter such as incompletely decomposed filter paper, it is a necessary first step, after addition of a suitable tracer, to boil to dense fumes with perchloric acid. Even though thorium has only the one stable valence state in solution, there is strong evidence for lack of exchange between added tracer and the radioisotope already in the solution when a hydroxide precipitation is performed without the fuming having taken place. Whether this apparent lack of complete exchange results from complexing of thorium by organic molecules that survived the initial solution of the sample in nitric and perchloric acids, or from the existence of thorium in the solution as some polymeric ion, is difficult to determine. Routine fuming of this type of sample improves the precision of the analysis. If the analysis is performed on solutions containing macroquantities of calcium, two precipitations of thorium on a carrier hydroxide such as iron or a rare earth are necessary to remove most of the calcium. Since most of the analyses were done on solutions containing a very large excess of fission products (Section 5), two Dowex 50-X4 columns were used.

Some of the zirconium and probably a few other unknown contaminants are eliminated by adsorbing them from concentrated hydrochloric acid solution on a relatively high cross-linked, strong-base anion exchange resin such as Dowex 1-X8 or -X10. Two of these columns are used, one after the other, if one of the beta-emitting thorium isotopes is being separated. If an alpha-emitting thorium isotope is being purified, one anion column may be sufficient, and if the sample contains fission products several days old and does not have excessive amounts of plutonium and neptunium, two cation columns provide sufficient decontamination.

Tracer amounts of thorium can be separated from uranium in quantities up to about 1 g with one Dowex 50-X4 column. Amounts of uranium up to about 10 g can be adsorbed on a 150- to 200-ml bed of Dowex 1-X8 from concentrated hydrochloric acid, leaving thorium in the effluent. A carrier-free source of ^{231}Th was prepared from 2 kg of oralloy by doing several ether extractions; then finally a cation column was employed to concentrate the activity in 1 or 2 drops of oxalic acid (Section 7).

Section 6 describes the application of the above principles of separation to the specific analysis of thorium in coral or limestone samples, as developed by W. M. Sackett.

2. Reagents

Fe carrier: 10 mg Fe per ml, added as 72.3 g of $Fe(NO_3)_3 \cdot 9H_2O$ per liter of aqueous solution
HF: concd
$HClO_4$: concd
HCl: concd; gas; 6*M*; 3*M*
HNO_3: concd
NH_4OH: concd
$H_2C_2O_4$: 0.5*M* (45 g of $H_2C_2O_4$ in a 1-l bottle and fill with H_2O)

$NaBrO_3$: 0.5M (75.5 g of $NaBrO_3$ in a 1-l bottle and fill with H_2O)

Anion exchange resin AG 1-X8, 100-200 mesh, stored in concd HCl

Cation exchange resin AG 50-X4, 50-100 mesh

Cation exchange resin AG 50-X4, 100-200 mesh

Both of the cation resins are stored in 3M HCl. It may not be necessary to further purify the resins if they are obtained from Bio-Rad Laboratories. However, if the decontamination or chemical yields are not satisfactory, it may be well to treat the resins as follows. Place a quantity of the resin in a large fritted disk funnel of medium or coarse porosity. (In this Laboratory, we use a 12-cm fritted disk funnel sealed to a 30-cm length of glass tubing so that much larger quantities of resin can be handled.) The treatments described below are speeded considerably by draining reagents into a large (2-4 liter) suction flask connected to vacuum to promote complete removal of a reagent before the next one is added. When adding a reagent to the partially dried resin it is helpful to stir it up with a heavy porcelain spatula and then let it settle and flow by gravity awhile to prolong the treatment time before suction is applied and the reagent removed. The reagents used successively for treating the resin are an organic solvent such as acetone or alcohol which removes short-chain organic polymers not firmly anchored in the resin matrix, water to rinse out the organic solvents, and concd HCl containing about 1 ml of 2M $NaBrO_3$ per 100 ml to dissolve extraneous inorganic matter. This solution is removed with water or dilute HCl in an amount equal to 10-20 times the volume of resin being purified. (The resin may be washed with 3M NH_4OH and then with water at this point, but it probably is not necessary.) The resin should now be washed with 5-10 times its own volume of whatever solution it is to be stored in. Undesirable fine particles can be removed by running distilled water upward through the fritted disk to float them over the top, leaving the bulk of the resin in the tube.

3. Special Equipment

Resin Columns: 4 per sample: three 0.6 cm i.d. and 7 cm high, and one 0.35 cm i.d. and 7 cm high. The glass container for the column of resin is most conveniently made by sealing a piece of tubing, either 0.6 cm i.d. by 7 cm or 0.35 cm i.d. by 7 cm, to the bottom of a tapered 15-ml centrifuge tube. If glass wool is to support the resin, the size of the opening in the tip at the bottom of the column is not critical, 0.3-2 mm being satisfactory. A glass wool column plug is made by cutting off a short piece of fibers, wetting and rolling it into a ball, and pushing it to the bottom of the column with a rod. The hole size for a sand support should not be much larger than 0.3-0.5 mm; first put in a layer of coarse sand and then cover it with a layer of finer material to guarantee that the column will not be part of the effluent. The sand should be boiled and leached with HCl, or better, be made of glass. The choice between sand and glass wool as a column support is a matter of personal preference.

Pressure Regulator: The pressure of air used to push solutions through columns is regulated by a diaphragm reducing valve with a scale reading from zero to 100 lb and the first mark at about 4-5 lb. If an ordinary on-off valve is used in place of the diaphragm type, light pressure may be obtained by holding one outlet from the manifold to one's ear and turning the valve until air can barely be felt or heard or by inserting a tee tube between the reducing valve and the manifold and leading a plastic or rubber tube below the surface of a column of water in some conveniently-sized tube such as a liter graduate; the valve is then opened to pass just enough pressure to cause bubbles to rise in the tube.

4. Preparation and Standardization of Tracers and the Calculations Involved in Their Use

In analyses for the beta emitters ^{231}Th and ^{234}Th, the best tracer is ^{230}Th since no daughter products grow into it within a time that could affect the analysis. Since one needs to get good statistics with a single alpha counting to determine chemical yield, it is desirable to use around 10,000 counts/min of ^{230}Th tracer. It is well to have on hand several standards made with the amount of tracer being used in the analysis; then the chemical yield is determined by a ratio of sample-to-standard counted very close together, thus eliminating any small error due to change in response of the alpha counter.

The beta counting efficiencies for ^{231}Th and ^{234}Th are determined by mixing a known amount of ^{230}Th tracer with a known quantity of the appropriate uranium parent, either ^{235}U or ^{238}U. After a perchloric acid fuming to guarantee exchange and to eliminate nitrate that may be present, the solution is diluted to 2 to 3*M* in H^+ ion concentration and an AG 50-X4 column step is performed as in the last step of the fission product decontamination (Step 9 of Section 5), except that a drop or two of 0.5*M* $NaBrO_3$ is added to the initial solution and to the wash to ensure that the uranium will be present as U(VI). U(IV) behaves the same as Th(IV) on this column and will lead to enough deposit on the plate to cause errors in the alpha counting. The directions for obtaining large quantities of ^{231}Th or ^{234}Th for use as tracers are given under Section 7.

The best tracer to use in analysis for ^{230}Th is ^{228}Th, as free from ^{229}Th as possible. Since ^{230}Th and ^{228}Th are both alpha emitters, the final plate is pulse-analyzed to get the ratio of the two. The alpha energy of ^{229}Th (as compared to that of ^{228}Th) is so much closer to that of ^{230}Th that tail corrections are much larger and more subject to error when ^{229}Th is present in the ^{228}Th tracer. This tracer is made by the (d, 2n) reaction on ^{232}Th.

$$_{90}{}^{232}\mathrm{Th}\ (\mathrm{d,2n})\,_{91}{}^{232}\mathrm{Pa} \xrightarrow[1.32\mathrm{d}]{\beta^-}$$

$$> {}_{92}{}^{232}\mathrm{U} \xrightarrow[70\mathrm{y}]{\alpha} > {}_{90}{}^{228}\mathrm{Th}$$

It is possible to standardize a solution of ^{228}Th by allowing it to decay until all its daughters are at equilibrium, then alpha counting it and subtracting the contribution of the rest of the decay chain. It is, however, quicker and more reliable to mix accurately-measured quantities of ^{228}Th and a known ^{230}Th solution, fume with $HClO_4$, and then separate from daughter activities with an AG 50-X4 column as in Step 9 of the regular fission product purification. The resultant plate is pulse-analyzed to get the ratio of ^{228}Th to ^{230}Th which, when multiplied by the alpha count of ^{230}Th, gives the correct alpha-count rate for ^{228}Th. If this tracer is to be used for an appreciable length of time, a decay correction for its 1.9-year half-life will have to be made.

Also, a correction is to be made in pulse analyses involving ^{228}Th. The energy from 4.6% of the alphas of the ^{224}Ra daughter of ^{228}Th coincides with the alpha peak of ^{228}Th. The time of last separation of the daughter is noted. This is the time when the last HCl wash comes off the last AG 50-X4 column. This parent-daughter relationship falls into the classification of transient equilibrium, where the equation of radioactive decay is simplified to

$$N_2(t) = \frac{N_1{}^0\ \lambda_1}{\lambda_2 - \lambda_1}\ (e^{-\lambda_1 t}),$$

where the subscript 2 refers to ^{224}Ra and the subscript 1 refers to ^{228}Th. $N_1{}^0$ is constant for the times involved, so it is convenient to prepare a plot of $N_2/N_1{}^0$ against time using the above equation. The elapsed time from the end of the HCl wash on the last cation exchange column to the midpoint of the pulse analysis is noted on the curve, and the fraction $N_2/N_1{}^0$ is read from the graph, multiplied by 0.046, and subtracted from the counts under the ^{228}Th peak.

To get the counting rate of ^{230}Th in a sample with ^{228}Th tracer, the ratio of the ^{230}Th/^{228}Th peaks is multiplied by the alpha-counting rate of ^{228}Th as obtained above.

5. Procedure for Thorium Isotopes in a Solution of Fission Products

Step 1. Pipet the tracer into an erlenmeyer flask of the proper size: a 50-ml flask for a sample-plus-tracer volume less than 10-15 ml and a 125-ml flask for 12-50 ml. Pipet the sample into the flask, using a clean pipet for each sample so that the solution will not become contaminated with the tracer. Add a few drops of Fe carrier and about 1 ml of concd $HClO_4$. Evaporate to dense white fumes and continue heating for at least 2 min after their first appearance. This evaporation is most rapidly done over a Fisher burner, but if there is no hurry use an air jet, hot plate, or oil bath. Cool and add 10-15 ml of H_2O and transfer to a short-taper 40-ml centrifuge tube. There may be a fine-grained residue of SiO_2 in the flask, but thorium loss at this point is not very great.

Step 2. Add an excess of concd NH_4OH, mix well, centrifuge, and discard the supernate.

Step 3. Dissolve the precipitate from Step 2 in 1 ml of 3*M* HCl and dilute with H_2O to half the volume of the tube. Add concd NH_4OH to precipitate the hydroxide, centrifuge, and discard the supernate.

Step 4. Dissolve the precipitate from Step 3 in about 5 ml of 3*M* HCl. If there is a very heavy precipitate of $Fe(OH)_3$, it may be necessary to add more 3*M* HCl to obtain complete solution. Again ignore a small residue of SiO_2 if it is present. Prepare a column 0.6 cm in diameter and about 7 cm high filled with AG 50-X4, 50-100 mesh resin. Pour the HCl solution onto the top of the resin and allow it to run through by gravity. Wash the column with 10 ml of 3*M* HCl and discard both the wash and the first effluent. Put a 50-ml erlenmeyer flask containing 1 ml each of concd $HClO_4$ and HNO_3 under the column and add 3.5 ml of 0.5*M* $H_2C_2O_4$ to the top and allow this to pass through by gravity.

Step 5. Evaporate the solution from Step 4 to dense white fumes and continue heating for about a minute.

Step 6. Transfer the solution to a 40-ml long-taper centrifuge tube and rinse the contents of the flask into it with 2 ml of concd HCl. Add 2 or 3 drops of 0.5*M* $NaBrO_3$ and saturate with HCl gas while the tube is surrounded by water at room temperature. Prepare a wash solution by adding a few drops of $NaBrO_3$ to concd HCl and saturate it at the same time.

Step 7. Prepare two columns for each sample. The diameter of each column is 0.6 cm and each is filled to a height of about 7 cm with AG 1-X8 or AG 1-X10, 100-200 mesh resin. Add the solution from Step 6 to the top of one of the columns and collect the effluent in a dry centrifuge tube. Rinse the original tube and column with 1.0-1.5 ml of the wash solution prepared in Step 6. Combine this wash with the effluent and pass through the second column. Rinse this in the same manner as the first and collect the combined effluents in a 50-ml erlenmeyer flask. It may be desirable to use very light air pressure to push the solution through these two columns.

Step 8. Evaporate the solution from Step 7 to 2-3 ml and add 1 ml of concd HNO_3 and 0.5 ml of concd $HClO_4$, and continue heating until dense white fumes have been evolved for about a minute. Cool and add 2 ml of water.

Step 9. Prepare a column 0.35 cm by about 7 cm filled with 100-200 mesh AG 50-X4 resin. Pour the solution from Step 8 on the top of the column and force it through with light air pressure (2-3 lb). Wash the column with 4.5 ml of 6*M* HCl and discard this wash and the first effluent. Add 0.3-0.4 ml of 0.5*M* $H_2C_2O_4$ and push down the column with very light air pressure. Make sure that the leading edge of the oxalic acid band does not reach the bottom of the resin and get discarded with the other effluent. Add 0.7 ml of 0.5*M* $H_2C_2O_4$ to the top of the column and collect the sample on a 5-mil Pt plate. If it is for alpha counting only, use a 1¾" to 2" diameter plate. If beta counting is to be performed also, the sample is collected on a 1" diameter plate. The samples are dried under heat lamps and are left there until most of the $H_2C_2O_4$ is sublimed. Then they are heated to red heat in a flame.

6. Thorium Procedure for Coral or Limestone Samples

Step 1. Dissolve 100-125 g of coral (accurately weighed) in 250 ml of concd HNO_3 and make up to 500 ml with H_2O. This gives a solution containing about 0.2 g of coral per milliliter.

Step 2. Add a 50 ml aliquot of the well-mixed solution to a 90-ml centrifuge tube together with 1 ml of ^{234}Th (see Section 7) tracer solution and 1 ml of Fe carrier. Stir and heat in a hot water bath for 1 hr; then cool (Note 1).

Step 3. Add concd NH_4OH slowly with stirring until $Fe(OH)_3$ precipitates and then centrifuge for 5 min (Note 2).

Step 4. Decant and dissolve the precipitate in 5 ml of concd HNO_3, dilute with H_2O, and again precipitate $Fe(OH)_3$ with concd NH_4OH.

Step 5. Centrifuge, decant, and dissolve the precipitate in 5 ml of concd HNO_3, and use H_2O to wash the solution into a Pt dish. Add 10 ml of concd $HClO_4$ and 5 ml of concd HF.

Step 6. Take to fumes of $HClO_4$ three times, washing the sides of the dish with water after each fuming (Note 3).

Step 7. Dilute the $HClO_4$ solution to about 25 ml with H_2O.

Step 8. The first column (4 × 150 mm with a 40-ml reservoir) is filled with an AG 50-X4, 200-400 mesh resin-water mixture and packed to about 120 mm. Wash the resin with 3*M* $HClO_4$ and add the solution from Step 7. Allow the solution to flow at atmospheric pressure or adjust the air pressure to give a flow of one drop about every 30 sec.

Step 9. When the solution reaches the top of the resin, add 3*M* HCl acid in several 1-ml portions, washing down the sides of the column. Continue washing until the ferric chloride color disappears.

Step 10. Elute the Th with 2-3 ml of 0.5*M* $H_2C_2O_4$, catching the effluent in a centrifuge tube. Add to the $H_2C_2O_4$ solution 5 ml of concd HNO_3 and 5 ml of concd $HClO_4$ and take to fumes of $HClO_4$ three times, washing the breaker down with H_2O after each fuming (Note 3).

Step 11. Add the solution, diluted with H_2O to 12 ml, to the second column (2 × 150 mm with a 15-ml reservoir) packed to a length of 120 mm with the same resin and treated as in Step 8. Adjust the flow rate as in Step 8.

Step 12. When the solution reaches the level of the resin, wash with five 1-ml portions of 3*M* HCl, rinsing the sides of the centrifuge tube with each portion.

Step 13. Elute the Th with 0.5*M* $H_2C_2O_4$, collecting the first 10 drops of $H_2C_2O_4$ acid effluent on a Pt plate. (The first few drops, which are HCl, are not collected.) Evaporate to dryness under a heat lamp, and flame.

Step 14. Count ^{234}Th to determine the yield and pulse-analyze the alpha radiation (Notes 4 and 5).

Additional Reagents and Equipment for this section are:

Dowex 50-X4, 200-400 mesh, cation resin
Resin columns — 4 × 150 mm with a 40-ml reservoir
2 × 150 mm with a 15-ml reservoir

Notes

1. The phosphate, chloride, and other impurities in the coral and the high acid concentration seem to take the thorium into a completely exchangeable form.

2. Large quantities of phosphate increase the formation of $Ca_3(PO_4)_2$ which coprecipitates with $Fe(OH)_3$ and leads to a decrease in yield due to the formation of phosphate complexes of thorium.

3. The solution is fumed three times to be sure no fluoride or oxalate remains to interfere in separation.

4. The isotopic thorium composition is calculated from the growth and decay of alpha activity.

5. The yield for this procedure varies from 50 to 90%.

7. Isolation of Thorium Decay Products from Large Quantities of Uranium Parent

^{231}Th is isolated from a solution of oralloy, approximately 93.5% ^{235}U, and ^{234}Th is obtained from normal uranium and the ^{231}Th present allowed to decay. For preparation of tracer using either of these thorium isotopes, the final step is an AG 50-X4 cation exchange column as in the determination of counting efficiency of ^{231}Th or ^{234}Th under Section 4, except that the final oxalic acid effluent is fumed nearly to dryness with 1 ml each of concd HNO_3 and $HClO_4$. If an amount of uranium up to about a gram is sufficient to supply the amount of tracer needed, the AG 50-X4 column can be used as in Section 4. Sources of ^{231}Th or ^{234}Th can be milked from a "cow" of the appropriate uranium isotope adsorbed on an AG 1-X8 column. The uranium is dissolved in concd HCl, and some oxidizing agent such as bromate ion, bromine water, or chlorine gas is used to oxidize the uranium to U(VI). The solution is then saturated with HCl gas at room temperature and adsorbed on an AG 1-X8 column.

For 10 g of uranium, a column about 25 mm in diameter and holding 150 to 200ml of resin bed is satisfactory. The resin is prewashed with concd HCl containing about 0.5 ml of 2*M* $NaBrO_3$ per 100 ml of acid. The uranium solution is passed through the column and then recycled two or three times to get more of it adsorbed. Then the column is washed with about twice the resin bed volume of concd HCl containing a drop or two of the bromate solution. After a suitable growth time for the thorium daughter, the column is treated with concd HCl as above. The solution is evaporated to a small volume, fumed with 1 ml each of concd HNO_3 and $HClO_4$ and treated with an AG 50-X4 column as in Section 4.

A ^{231}Th source reading over 1 r was prepared from 2 kg of oralloy as follows: the uranium metal was dissolved in an excess of concd HNO_3 and this solution was evaporated until the temperature became constant at about 118°. This is the boiling point of $UO_2(NO_3)_2{:}6H_2O$. This solution freezes at about 60°, so it can be cooled to 70 to 80° and the molten hexahydrate poured into a 5-l separatory funnel containing 3-4 l of diethyl ether that is being rapidly stirred with an air-driven stirrer. This must be done in a good hood with explosion-proof fixtures, or out of doors. As long as the molten hexahydrate is added in a slow stream to the ether with good stirring, the operation is perfectly safe and the ether losses are not too large, since the vapor pressure of the ether decreases rapidly as the uranium is dissolved. It is more rapid and easier to add the molten hexahydrate than it is to crystallize it and add the crystals. The final solution in ether from the 2 kg of oralloy should have a volume of about 4 liters. An aqueous layer of about 600 ml is withdrawn. The ether solution is scrubbed with three 3-ml portions of H_2O to insure complete removal of any thorium that might be present. ^{231}Th is allowed to grow for 1 to 2 days and then is removed with three 3-ml portions of H_2O. This aqueous layer is shaken with two 200-ml portions of ether to remove more of the uranium. The residual water layer is first evaporated on a steam bath to remove ether, then fumed with 1 ml each of concd HNO_3 and $HClO_4$ and the AG 50-X4 column used as in Section 4 except that the column dimensions are 0.2 cm × 5 cm. The bulk of the ^{231}Th can be followed down the column with a beta-gamma survey meter and over 80% of it is usually concentrated in 2 or 3 drops. The oxalic acid effluent is placed in small drops on a 10-mil Pt wire about 1.5 in long and the wire gradually heated to red heat by applying a current, controlled by a Variac. In this way the oxalic acid is completely volatilized, leaving a nearly mass-free deposit of ^{231}Th. The ether "cow" of uranium can be kept for several weeks for the preparation of a number of samples.

TIN

D. C. Hoffman, F. O. Lawrence,
and W. R. Daniels

1. Introduction

This procedure for separating tin from fission products is performed about two days after irradiation; this time interval is necessary to allow 2-hr ^{127}Sn to decay to 93-hr ^{127}Sb. When performed after the two-day waiting period, the procedure gives excellent decontamination from fission products.

The sample is first treated with bromine water to convert all the tin to the +4 condition and to promote complete exchange between fission-product tin and Sn(IV) carrier. The oxidation is followed by precipitation of SnS_2 from acid solution and then the tin is dissolved and adsorbed on an anion exchange column from 0.9*M* hydrochloric acid solution; molybdenum, tellurium, and antimony pass through the column. The tin is eluted from the column with 1.8*M* perchloric acid and is again precipitated as the sulfide. The sulfide is dissolved, the tin is complexed by means of hydrofluoric acid, and two acid sulfide scavenges are performed. Following destruction of fluoride ion with boric acid, the tin is again precipitated as the sulfide, dissolved, adsorbed on an anion exchange column, and eluted. After a final SnS_2 precipitation, the tin is dissolved and reduced to the metal by chromous chloride. It is weighed and counted in this form.

The chemical yield is about 70% and four samples can be analyzed in 6-7 hr.

2. Reagents

Sn carrier: 10 mg Sn/ml, added as Sn metal dissolved in 3*M* HCl, standardized
Te^{4+} carrier: 10 mg Te/ml, added as Na_2TeO_3 in 3*M* HCl
Te^{6+} carrier: 10 mg Te/ml, added as Na_2TeO_4 in 3*M* HCl
Mo carrier: 10 mg Mo/ml, added as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 6*M* HCl
Sb carrier: 10 mg Sb/ml, added as $SbCl_3$ in 6*M* HCl
La carrier: 10 mg La/ml, added as aqueous $La(NO_3)_3\cdot 6H_2O$
HCl: 0.9*M*; concd
HF: concd
$HClO_4$: 1.8*M*
H_3BO_3: saturated aqueous solution
H_2S: gas
Br_2-H_2O: saturated solution
$CrCl_2$ solution (Oxsorbent), cold
Anion resin: AG1-X4, 100-200 mesh (treated with 0.9*M* HCl)
Aerosol: 0.1% in H_2O
Ethanol: absolute
Rubber cement: 6% in benzene

3. Preparation and Standardization of Carrier

Accurately weigh ≈2.5 g of Sn metal and dissolve it quantitatively in ≈125 ml of 6*M* HCl using heat and Br_2-H_2O as necessary to complete the dissolution. Dilute to exactly 250 ml, making the solution ≈3*M* in HCl. The concentration of the carrier solution can then be calculated, but if desired, it may be confirmed by precipitation of the Sn as follows: Dilute 1 ml of Sn carrier to 15 ml with H_2O. Add 10 ml of a saturated aqueous solution of phenylarsonic acid, and heat at 110° for 10 min. Cool to room temperature, allow to stand for 15 min, centrifuge, and discard the supernate. Wash with 5 ml absolute ethanol, centrifuge, and discard the supernate. Add 5 ml ethanol and filter through a weighed No. 50 Whatman 1″ filter circle using a ground-off Hirsch funnel and filter chimney setup. Dry for 10 min at 110°, cool, and weigh. Multiply by 0.2288 to obtain weight of Sn metal in precipitate.

4. Procedure

Step 1. To 2.0 ml of the Sn carrier solution in a 40-ml centrifuge tube, add the sample and 0.5 ml of Br_2-H_2O. Heat until the Br_2 is gone and then dilute with H_2O until the solution is 1*M* in HCl. Place in an ice bath and saturate with H_2S. Centrifuge, discard the supernate, and wash the precipitate with 0.9*M* HCl, discarding the washings.

Step 2. Dissolve the precipitate in 1 ml of concd HCl with heat and boil for 3 min to remove H_2S. If the volume is less than 1 ml, make up to this volume with concd HCl. Add 1 drop each of the following carriers: Te^{6+}, Te^{4+}, Sb, and Mo. Then add 0.5 ml of Br_2-H_2O and heat until the Br_2 is gone.

Step 3. Dilute the sample to 12 ml with H_2O. (The solution is now approximately 1*M* in HCl.) Pour the solution onto a column of AG1-X4, 100-200 mesh, anion resin, 5 cm × 9.5 mm, which has been treated with 10 ml of 0.9*M* HCl. After the solution has been permitted to pass through the resin column, wash the column with four 20-ml portions of 0.9*M* HCl. Discard the eluate, including the washings.

Step 4. Elute the tin with 25 ml of 1.8*M* $HClO_4$ and collect the eluate in a 40-ml centrifuge tube. Add 4 drops of Mo carrier and saturate with H_2S. Add 4 drops of aerosol and centrifuge. Discard the supernate, wash the precipitate with 0.9*M* HCl, and discard the washings.

Step 5. Dissolve the precipitate in 2 ml of concd HCl (any MoS_3 present will not dissolve) and boil for 3 min to remove H_2S. Add 1 drop each of the following carriers: Te^{6+}, Te^{4+}, and Sb. Add 0.5 ml each of Br_2-H_2O and concd HF. Dilute the sample to 6 ml with H_2O and boil. Saturate the *hot* solution with H_2S, adding 2 drops of La carrier at the completion of saturation. Add 3-4 drops of aerosol and centrifuge.

Step 6. Transfer the supernate to a clean 40-ml centrifuge tube by means of a transfer pipet and add 1 drop each of Te^{6+}, Te^{4+}, and Mo carriers. Also add 0.5 ml of Br_2-H_2O and boil. Again saturate the *hot* solution with H_2S, adding 2 drops of La carrier at the completion of saturation. Add 3-4 drops of aerosol, centrifuge, and transfer the supernate to a clean 40-ml centrifuge tube as above.

Step 7. Adjust the volume of the supernate to 15 ml by the addition of H_2O. Add 10 ml of saturated H_3BO_3 solution and cool in an ice bath. Bubble in H_2S. Centrifuge, discard the supernate, and wash the precipitate with 0.9*M* HCl.

Step 8. Dissolve the precipitate in 1 ml of concd HCl and boil for 3 min to expel H_2S. Add 1 drop each of Te^{6+}, Te^{4+}, and Sb carriers and 0.5 ml of Br_2-H_2O. Heat until all the Br_2 has been expelled. If a precipitate (MoS_3) is still present, centrifuge, and pipet the supernate into a clean centrifuge tube.

Step 9. Repeat Steps 3 and 4.

Step 10. Dissolve the precipitate in 2 ml of concd HCl with heat and boil the solution for 3 min to remove H_2S. Dilute the solution to about 8 ml with H_2O, cool, and add an equal volume of *cold* $CrCl_2$ solution. To avoid coagulation of the tin, *filter immediately* onto a previously washed, dried, and weighed No. 42 Whatman 1" filter circle, using a ground-off Hirsch funnel and filter chimney. Wash the precipitate first with 0.9*M* HCl, then with H_2O, and finally with absolute ethanol.

Step 11. Dry the precipitate in an oven at 110° for 5-10 min. Cool and weigh. Secure the precipitate with 3 drops of 6% rubber cement in benzene. When the precipitate is again dry, mount it on an Al sample plate using double-sided Scotch tape. Cover the sample with a square of Mylar and count (Note).

Note

Analysis for either or both 26.85-hr ^{121}Sn and 9.625-day ^{125}Sn can be performed. Small amounts of 129.0-day ^{123}Sn and 2.8-year ^{125}Sb (daughter of ^{125}Sn) can also be observed at later times. (The half-life values quoted here are those reported by Lawrence *et al.*[1]) If ^{121}Sn is to be determined, a least-squares analysis of the data is performed with the half-lives fixed. If only ^{125}Sn is to be determined, β-counting is begun about 12 days after bombardment, when the contribution of ^{121}Sn is small, and a correction is applied for the small amount of ^{123}Sn in the sample. A least-squares analysis of the decay data for several samples showed that the contribution of ^{123}Sn was only about 0.7% of the total Sn activity at t_0. (The samples were counted on gas flow, beta-proportional counters having 2" diameter, 4.9 mg/cm² aluminum windows. The proportion of ^{123}Sn activity may, of course, be different for different counting conditions.) For ease in calculation, a graph showing the contribution of ^{123}Sn to the total β count of the sample at various times after irradiation has been constructed from our data (see Fig. 1) for Sn separation from thermal fission products of ^{235}U.

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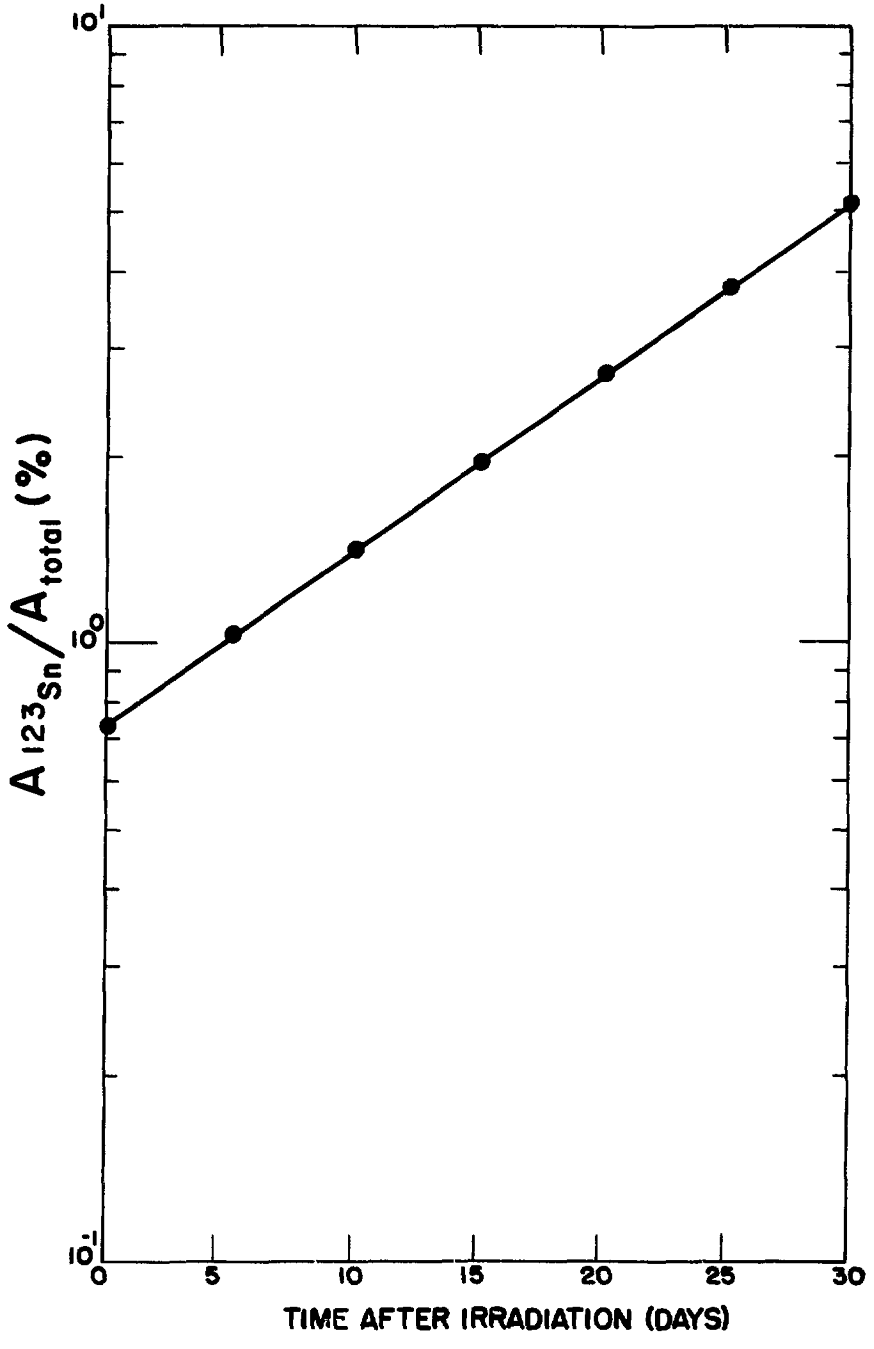

Fig. 1. Contribution of ^{123}Sn to total β count.

TIN II

B. R. Erdal

1. Introduction

This rapid, relatively simple procedure for the separation of tin from fission products is taken from an article by B. R. Erdal and A. C. Wahl, J. Inorg. Nucl. Chem., 30, 1985 (1968). The primary decontamination process makes use of a cyclic solvent extraction system consisting of three steps: (1) the extraction of tin(II) from an aqueous H_2SO_4-KI solution into 4-methyl-2-pentanone (hexone); (2) the oxidation of the tin to the IV state; and (3) the back-extraction of tin(IV) into aqueous H_2SO_4-KI. Following two cycles of the process, an Sb_2S_3 scavenge is performed and then, after SnS_2 precipitation, the tin is reduced to the elemental state, in which form it is counted.

The procedure requires about 15 min per sample and gives chemical yields of 40-60% with a decontamination factor of at least 10^5 for all ^{235}U thermal-neutron fission products.

2. Reagents

Sn carrier: 10 mg Sn/ml, standard solution prepared by dissolving pure Sn metal in concd HCl and making a solution 2*M* in the acid by the addition of *oxygen-free* H_2O
Sb carrier: 4 mg Sb/ml, added as $SbCl_3$ in 12*M* HCl
HCl: concd
NH_4OH: concd
$NH_2OH \cdot HCl$: 1*M* aqueous solution
$NaBrO_3$: 1*M* aqueous solution
H_2SO_4-NaCl solution: 0.6*M* in H_2SO_4 and 0.4*M* in NaCl
KI: 1.2*M* aqueous solution
KI-I_2 solution: 1.2*M* KI-4 mg I_2/ml
$CrCl_2$: ~1.6*M* aqueous solution (Fisher Scientific Co.)
$[(CH_3)_4N]Cl$: 4*M* aqueous solution
4-methyl-2-pentanone (hexone)
Ethanol: 95%
H_2S: gas
N_2: oxygen-free

3. Procedure

Step 1. To 2.0 ml of standard Sn carrier in a 40-ml glass centrifuge tube, add the sample, 4 drops of 1*M* $NaBrO_3$, and then an excess of 1*M* $NH_2OH \cdot HCl$. Dilute to 40 ml with H_2O (the solution should be less than 1*M* in HCl) and saturate with H_2S. Heat to digest the SnS_2 and when the precipitate has coagulated, centrifuge, and discard the supernate.

Step 2. Dissolve the SnS_2 in about 0.6 ml of concd HCl and add 1 ml of 4*M* $[(CH_3)_4N]Cl$ and 17 ml of 95% ethanol to precipitate $[(CH_3)_4N]_2SnCl_6$. Digest on a steam bath for 1 min, centrifuge, and discard the supernate.

Step 3. Dissolve the precipitate in 10 ml of 0.6*M* H_2SO_4-0.4*M* NaCl and add the solution to 10 ml of 1.2*M* KI solution which has been flushed with oxygen-free N_2 in the upper extraction vessel of the extraction apparatus (Fig. 1). With the N_2 flow continuing, start the stirrer, add 2 ml of approximately 1.6*M* $CrCl_2$ solution, and then *immediately* add 2 ml of hexone (Note). Stir for 15 sec, stop the nitrogen flow and the stirrer, and discard the aqueous (lower) phase.

Step 4. To the hexone phase, add 10 ml of 0.6*M* H_2SO_4-0.4*M* NaCl colution and 10 ml of KI-I_2 solution. Stir for 60-90 sec with nitrogen flowing and then stop the

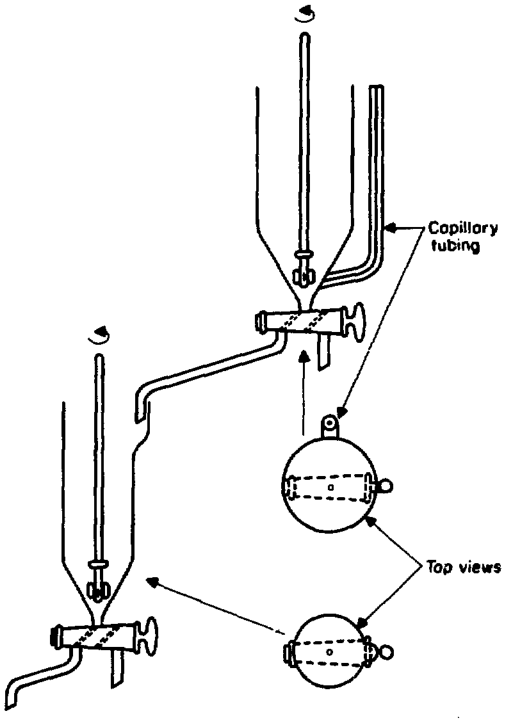

Fig. 1.

nitrogen flow and the stirrer. (Sn(II) is oxidized to Sn(IV) by the I_2 and is extracted into the aqueous phase.)

Step 5. Run the aqueous phase into the lower extraction vessel, add 3 ml of about 1.6*M* $CrCl_2$ solution, and then immediately add 20 ml of hexone. Stir for 15 sec, stop the stirrer, and discard the aqueous phase.

Step 6. Repeat Step 4.

Step 7. Run the aqueous phase into a clean 40-ml glass centrifuge tube containing 10 ml of Sb carrier. Cool the solution by swirling it in a dry ice-isopropanol bath for 45 sec, saturate with a very rapid stream of H_2S for 30 sec, and centrifuge for 45 sec. Filter through a Millipore HA, 0.45μm pore size, filter paper with absorbent pad (Millipore Filter Corp., Bedford, MA), and collect the filtrate in a clean centrifuge tube. Discard the precipitate.

Step 8. Add about 8 ml of concd NH_4OH to the filtrate, saturate with H_2S, and digest on a steam bath until the precipitate coagulates. Centrifuge and discard the supernate.

Step 9. Dissolve the SnS_2 in 2 ml of hot concd HCl, add 40 ml of H_2O previously saturated with H_2S, and digest on a steam bath until the precipitate coagulates. Centrifuge and discard the supernate.

Step 10. Repeat Step 2.

Step 11. Dissolve the $[(CH_3)_4N]_2SnCl_6$ precipitate in 2 ml of hot concd HCl, dilute to 40 ml with H_2O, and saturate with H_2S. Digest the precipitate on a steam bath, centrifuge, and discard the supernate.

Step 12. Dissolve the SnS_2 in 0.5 ml of hot concd HCl, add 8 ml of H_2O, and then add 3 ml of about 1.6*M* $CrCl_2$ to precipitate elemental Sn. Filter through a tared, 10μm pore size, polypropylene filter paper (Gelman Instrument Co., Ann Arbor, MI), wash the precipitate with 95% ethanol, and air dry under suction for about 1.5 min. Weigh and mount.

Note

Unless the hexone is added immediately to extract tin(II), the yield drops substantially since elemental tin begins to form and precipitate.

TRANSACTINIDES

SEPARATION OF ELEMENT 104 FROM FISSION PRODUCTS

R. J. Prestwood and B. P. Bayhurst

1. Introduction

It is expected that the ionic radius of element 104 in its +4 state would be approximately the same as the radius of Zr^{4+} and Hf^{4+} and that element 104 would exhibit similar chemical behavior. It has been shown that hafnium is eluted prior to zirconium from an anion exchange column by means of 9.75*M* hydrochloric acid, and it is assumed in this procedure that element 104 would come off such a column before or with hafnium.

The procedure as outlined below was used to separate element 104 from 25 g of soil containing large amounts of fission products. The soil sample, to which zirconium carrier had been added, was dissolved and made up to 200-220 ml of solution which was 4-10*M* in nitric acid.

2. Reagents

Zr carrier: 17.8 mg Zr/ml, added as $ZrOCl_2$ in 1*M* HCl

Sc carrier: 10 mg Sc/ml, added as $ScCl_3$ in 1*M* HCl

La carrier: 10 mg La/ml, added as aqueous $La(NO_3)_3 \cdot 6H_2O$

Ce(IV) carrier: 10 mg Ce/ml, added as $(NH_4)_2Ce(NO_3)_6$

HCl: 6*M;* concd; gas (tank)

HNO_3: 10*M;* concd

HF: concd; 4*M*

H_2SO_4: concd

H_3BO_3: saturated aqueous solution

NH_4OH: concd

$Ba(NO_3)_2$: saturated aqueous solution

$NH_2OH \cdot HCl$: solid

NH_4HF_2: a mixture of 2 volumes of 6*M* NH_4OH and 1 volume of concd HF

Dowex AG 1-X2 anion resin, 200-400 mesh

HDEHP: 0.5*M* solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The acid may be obtained from the Victor Chemical Division of the Stauffer Chemical Company, Chicago Heights, Ill. The reported purity is 94%.

3. Procedure

Step 1. Transfer the sample, which should be 4-10*M* in HNO_3, to a 250-ml separatory funnel and add 5 drops of Ce(IV) carrier, 200-300 mg $NH_2OH \cdot HCl$, and 25 ml of HDEHP. (The Zr and any Hf and element 104 present are extracted quantitatively into the organic layer.) (Note 1.) Discard the H_2O layer, wash the heptane layer twice with 20-ml portions of 10*M* HNO_3 each containing 5 drops of reduced Ce carrier, and then twice with 20-ml portions of the acid alone. Discard the washings.

Step 2. Transfer the heptane layer to a 40-ml polyethylene bottle, add 10 ml of 4*M* HF, and shake vigorously. (Zr is extracted as a fluorocomplex into the H_2O layer.) Add 3-5 ml of saturated $Ba(NO_3)_2$ solution and shake the mixture for 2 min. Transfer to a 40-ml polyethylene centrifuge tube, centrifuge the $Ba(ZrF_6)$ precipitate, and discard both the aqueous and organic layers.

Step 3. Wash the precipitate with 20 ml of a solution 1*M* each in HF and HNO_3 and 0.01*M* in $Ba(NO_3)_2$ and discard the washings. Dissolve the precipitate in 4 ml of saturated H_3BO_3 plus 4 ml concd HCl plus 10 ml of H_2O. Add 10 drops of concd H_2SO_4 to precipitate $BaSO_4$ and let stand for 10 min. Centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate.

Step 4. To the supernate add 4 drops of La carrier and then add concd NH_4OH dropwise until the solution is basic. (The precipitate formed consists of $Zr(OH)_4$ and $La(OH)_3$ with visible amounts of $Fe(OH)_3$. Centrifuge and discard the supernate.

Step 5. To the precipitate add 3 ml of NH_4HF_2 and 100 mg of $NH_2OH \cdot HCl$. Stir and add concd NH_4OH dropwise until the solution is acidic to methyl red indicator. Dilute to 10-12 ml with H_2O, centrifuge, and transfer the supernate to a clean 40-ml polyethylene centrifuge tube. To the solution add 4 drops of La carrier, 4 drops of Fe carrier, and 2 ml of concd NH_4OH. Dilute to 20 ml with H_2O and heat on a steam bath to coagulate $La(OH)_3$-$Fe(OH)_3$ precipitate. Centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate. Add 6 ml of concd HCl and 2 ml of Sc carrier and heat on a steam bath for 5 min. Centrifuge and transfer supernate to a clean polyethylene tube.

Step 6. Add 3 ml of saturated $Ba(NO_3)_2$ solution to precipitate $BaZrF_6$. Centrifuge, discard the supernate, and repeat Step 3. Transfer the supernate to a clean 40-ml Pyrex centrifuge tube and discard the precipitate.

Step 7. Add an excess of concd NH_4OH to precipitate $Zr(OH)_4$. Centrifuge and discard the supernate. Dissolve the precipitate in 2 ml of saturated H_3BO_3 solution and 3 ml of 6*M* HCl, and dilute to 20 ml. Reprecipitate $Zr(OH)_4$ with excess concd NH_4OH, centrifuge, and discard the supernate. Wash the precipitate with two 20-ml portions of H_2O and discard the washings.

Step 8. Prepare a Dowex AG 1-X2, 200-400 mesh anion resin column (8 mm × 5 cm) and wash it thoroughly with concd HCl. With the aid of concd HCl, remove the top 1-1.5 cm of resin with a transfer pipet and add this portion of the resin to the $Zr(OH)_4$ precipitate. (The precipitate dissolves and the combined volume of resin and solution is about 3 ml.) Bubble HCl into the mixture for 5 min, transfer the solution and resin to the top of the resin column, and apply air pressure to give 1 drop of eluate every 5-6 sec. Collect the eluate in a 125-ml erlenmeyer flask. Add 2 ml of concd HCl to the centrifuge tube which had contained the $Zr(OH)_4$, bubble in HCl for 5 min, and transfer the solution to the top of the resin column. Apply pressure as before and collect the eluate in the same erlenmeyer flask. Add 15 ml of 9.75*M* HCl to the resin column and collect the eluate at the same drop rate in another 125-ml erlenmeyer flask (Note 2).

Step 9. Evaporate the eluate from the addition of the 9.75*M* HCl to about 2 ml, saturate the solution with gaseous HCl, and transfer to the top of a Dowex AG 1-X2, 200-400 mesh anion column (2 mm × 2.5 cm) which has been thoroughly washed with concd HCl. After the liquid has passed through, wash the column with 2 ml of saturated HCl solution. The eluates are collected and saved. To the top of the column add about 5 ml of 9.75*M* HCl (Note 3) and collect each 10 drops of eluate on a separate 2-in Pt plate. Dry the plates under an infrared lamp, flame them if so desired, and count.

Notes

1. At this point various metal nitrates may precipitate as a result of the high HNO_3 concentration. These salts may be disregarded, since they do not affect the extraction of Zr into the organic layer.

2. It has been shown that 15 ml of 9.75*M* HCl will remove 75% of the Hf and only 10^{-5} of the Zr in a sample containing both elements. It is assumed that at least 75% or more of element 104 would have been eluted also. The saturated HCl solution is kept as insurance against element 104 coming through the column immediately.

3. The volume of 9.75*M* needed to elute Hf (and thus any element 104) can be determined with the use of Hf tracer. Normally about 3 ml of the acid is needed.

SEPARATION OF ELEMENT 105 FROM FISSION PRODUCTS

B. P. Bayhurst and R. J. Prestwood

1. Introduction

The major decontamination step in this procedure is an extraction of tantalum and element 105 into hexone from a solution 2.88*M* in HNO_3 and 1.1*M* in HF; niobium is not extracted in this step. The tantalum and element 105 are removed from the hexone by extraction with 1.5% hydrogen peroxide solution. In the final step, niobium carrier, and tantalum and element 105 activities are placed on a Dowex AG 1-X8 anion exchange resin column and then element 105 is eluted with a solution which is 2.0*M* in HCl and 0.01*M* in $H_2C_2O_4$.

2. Reagents

Nb carrier: 10 mg Nb/ml, added as $K_8Nb_6O_{19} \cdot 16H_2O$ in H_2O

HNO_3: fuming; concd
$HClO_4$: concd
HF: concd
H_2SO_4: concd
HCl-$H_2C_2O_4$ solution: 2.0*M* in HCl and 0.01*M* in HF
HCl-$H_2C_2O_4$ solution: 2.0*M* in HCl and 0.01*M* in $H_2C_2O_4$
$H_2C_2O_4$: 0.5*M*
NH_4OH: concd
NH_4NO_3: 1*M*
$KClO_3$: solid
H_2O_2: 1.5% by volume
Hexone (4-methyl - 2-pentanone)
Methyl red indicator solution
Dowex AG 1-X8, 100-200 mesh, anion resin: slurry in 0.5*M* $H_2C_2O_4$

3. Procedure

Step 1. Transfer the sample, which has been previously treated with a mixture of concd HF, fuming HNO_3 and concd $HClO_4$ and brought almost to dryness, to an appropriate extraction vessel. Add a sufficient volume of solution 2.88*M* in HNO_3 and 1.1*M* in HF to dissolve most of the salts in the sample. (A small residue of solid material at this point does not interfere in the procedure.) Extract the solution three times, each with one-third of its volume of hexone, combine the hexone layers, and discard the aqueous layer. Wash the hexone solution three times with one-half of its volume of the HNO_3 - HF solution and discard the washings.

Step 2. Add 1 drop of methyl red indicator solution to the hexone solution and extract with 25-ml portions of 1.5% H_2O_2 until the indicator changes to an orange color. Then extract twice more with 25-ml portions of the H_2O_2 solution. Combine all extracts in an erlenmeyer flask.

Step 3. To the H_2O_2 extract, add 10 drops of Nb carrier, then 20 ml of concd HNO_3, and boil down to about 5 ml to destroy H_2O_2. Add approximately 200 mg of solid $KClO_3$ and 10 ml of concd HNO_3 and boil down to 2-3 ml to precipitate niobium(V) oxide. With the aid of concd HNO_3, transfer the precipitate to a clean 40-ml *quartz* centrifuge tube, centrifuge, and discard the supernate. Wash the precipitate with 15 ml of 2*M* HNO_3 containing 100-200 mg of NH_4NO_3 and discard the washings.

Step 4. Dissolve the precipitate by the dropwise addition of concd HF and transfer the solution to a Pt dish. Wash the centrifuge tube with H_2O and add the washings to the Pt dish. Add 1 ml of concd H_2SO_4 and boil until SO_3 fumes appear. Add 2-3 of concd HF and again boil to SO_3 fumes; repeat.

Step 5. With the aid of a stream of H_2O, transfer the solution from the Pt dish to a clean 40-ml Pyrex centrifuge tube. Add concd NH_4OH dropwise to precipitate $Nb_2O_5 \cdot XH_2O$, and place on a steam bath for about 5 min. Centrifuge and discard the supernate. Wash the precipitate with 1*M* NH_4NO_3 and discard the washings.

Step 6. Dissolve the precipitate in a minimum of 0.5*M* $H_2C_2O_4$ and transfer the solution onto a Dowex AG 1-X8, 100-200 mesh, anion resin column (36 cm × 6 mm), which has been previously washed well with a solution 2*M* in HCl and 0.01*M* in $H_2C_2O_4$. Elute with the HCl - $H_2C_2O_4$ solution at a rate of 0.2 ml per min, employing pressure if necessary. With the volumes of reagents and the column dimensions used in the procedure, element 105 would be expected to come off the column in the first 12 ml of eluate; tantalum is found in the fraction consisting of the 12th to 27th ml of eluate and niobium in the 36th to 69th ml.

ANALYSIS FOR TRITIUM IN WATER SAMPLES

E. A. Bryant and E. J. Lang

1. General Considerations

The preparation of tritiated water samples for analysis by liquid scintillation counting requires more than usual attention to detail to assure results of high quality. This is especially true of samples of low-level activity because of the ever-present possibility of contamination. The equipment must be kept scrupulously clean, and disposable items such as pipets. counting vials. etc.. should not be reused.

Vials should be labeled in a reasonably permanent manner with a unique number and the preparation date. and complete records should be kept on the preparation and counting of each sample. Care is necessary to avoid sample mix-ups in the counter system which will hold a large number of samples. It is strongly recommended that the location of each sample in the counter be entered in a notebook as it is loaded into the counter.

Each sample should be examined before and after counting to detect any abnormality such as cloudiness or phase separation. Counting should be done within 24 hr after preparation of sample.

Samples such as pond or stream water may contain foreign material which would interfere with the counting and should be treated to remove such material.

2. Sample Pretreatment

All water samples should be pretreated to remove organic and inorganic materials which might cause quenching of the scintillating mixture.

Step 1. Pass the sample through the Whatman 541H filter paper to remove suspended solids.

Step 2. Pass 50 ml of the sample through an activated charcoal column. Discard the first 3-4 ml which may contain loose material from the charcoal. The column should be made up in a glass tube 1 cm by 20 cm with a drip tip at the bottom and a glass reservoir of larger diameter fused to the top. Each column should be used only once.

Step 3. Distill the effluent from the column using the apparatus shown in Fig. 1. (Prepare a new apparatus for each sample.) Discard the first and last 2-3 ml of distillate; collect the middle 45 ml and store in a tightly sealed glass bottle.

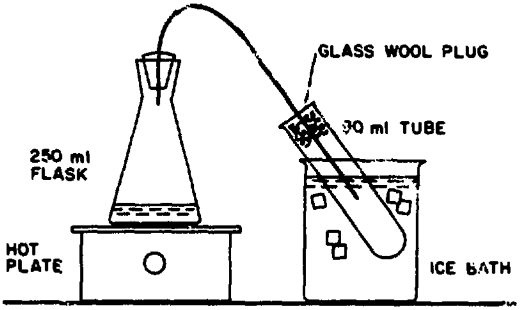

Fig. 1. Distillation apparatus.

3. Sample Preparation and Counting (Note 1)

Step 1. Pipet 16 ml of INSTAGEL (source: Packard Instrument Company, Inc.) into a 25-ml polyethylene counting vial. (For *each* pipetting operation a new. freshly rinsed pipet is used.)

Step 2. Pipet 9 ml of pretreated water into the vial.

Step 3. Cap the vial, shake it vigorously for 1 min. and allow it to stand at room temperature for 15 min. Label the vial with a unique sample number and the date. Use a KUM-KLEEN. or similar. label on cap.

Step 4. Place the sample in the cooler compartment of the counter and record the "counter location" in a notebook. Wait at least 1 hr, but less than 24 hr, before counting the sample. Collect at least two 100-min counts on each low-level sample.

Step 5. Remove the sample from the counter, note its condition in the record, and allow it to warm to room temperature. Add 0.200 ml of H_2O containing a known amount of tritium spike in the range from 100 to 300 dpm. (Higher concentration will be required for high-level samples, but should be avoided if possible.) Remix the sample as in Step 3.

Step 6. Load the sample into the counter again, noting its location in the notebook. Wait at least 1 hr but not more than 24 hr, before counting.

Step 7. Enter counting data in the record as soon as they are available. Cut off the portion of the printer tape containing the data for the sample and fasten it in the record with Scotch tape. Be sure to include GAIN and WINDOW settings in the record.

Note

1. Each group of samples should include a blank not more than 5 days old.

4. WINDOW and GAIN Settings

The directions which follow pertain specifically to the Packard Model 3310 liquid scintillation counting system. However, the general procedure is applicable to other liquid scintillation counting systems.

Step 1. Set the GAIN for WINDOWS 1 and 2 to 75%.

Step 2. Prepare a fresh standard containing 50,000 to 100,000 dpm of tritium. It is important that the standard be fresh so that the pulse-height spectrum will be like those of freshly prepared unknown samples.

Step 3. Place the sample in the counter and wait for at least 1 hr before proceeding with the next step.

Step 4. Set the WINDOW discriminators for channel 1 to 10-1000 and take a 10-min count.

Step 5. Set the GAIN for WINDOWS 1 and 2 to 100% and adjust the upper discriminator of channel 1 downward until the count rate is reduced to 83% of the rate measured in the previous step.

Step 6. Leave the upper discriminator set as in Step 5 and adjust the lower discriminator of channel 1 upward until the count rate is reduced from 83 to 82% of that measured in Step 4. (The lower level discriminator may be adjusted for "balance-point" if desired.)

Step 7. Set the lower level discriminator of channel 2 to the same setting as used for channel 1 (Step 6).

Step 8. Adjust the upper level discriminator of channel 2 down until the count rate is 60% of that measured in Step 4.

Step 9. Check the settings with a second standard.

Step 10. Set the GAIN for WINDOW 3 to 10% and set the lower and upper discriminators to 120 and 1000 respectively. Counts, above background, in this WINDOW will be indicative of sample contamination; a small fraction (<0.1%) of the tritium disintegrations will result in counts in this WINDOW.

November 1970

TUNGSTEN

R. J. Prestwood

1. Introduction

In its separation from fission products, tungsten is initially precipitated as the hydrous oxide ("tungstic acid") $WO_3 \cdot XH_2O$. The tungsten is then further decontaminated by a series of iron hydroxide and acid sulfide scavenging steps. The latter, performed in the presence of tartaric acid which strongly complexes tungsten (VI), removes the troublesome molybdenum activity. Niobium is effectively removed from hydrochloric acid medium by extraction into chloroform with cupferron; this is an excellent decontamination step for other activities also. The tungsten, present as a tartrate complex, is unaffected by cupferron and is finally precipitated from a buffered acetic acid solution as the 8-hydroxyquinoline derivative*, in which form it is weighed and counted. The chemical yield is about 50%, and quadruplicate analyses can be performed in approximately 4 hr.

2. Reagents

W carrier: 10 mg W/ml, added as $Na_2WO_4 \cdot 2H_2O$ in H_2O, standardized
Bi carrier: 10 mg Bi/ml, added as $Bi(NO_3)_3 \cdot 5H_2O$ in very dilute HNO_3
Fe carrier: 10 mg Fe/ml, added as $FeCl_3 \cdot 6H_2O$ in very dilute HNO_3
Mo carrier: 10 mg Mo/ml, added as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in H_2O
Nb carrier: 10 mg Nb/ml, added as Nb_2O_5 in $H_2C_2O_4$ solution
HNO_3: concd
H_2SO_4: concd
$HC_2H_3O_2$: glacial
Tartaric acid: 50% aqueous solution
NH_4OH: concd
Chloroform
Buffer solution: 1*M* in $HC_2H_3O_2$ and 3.6*M* in $NaC_2H_3O_2$
H_2S: gas
Cupferron reagent: 6% aqueous solution (kept in refrigerator)
8-hydroxyquinoline reagent: 5% in 2*M* $HC_2H_3O_2$
Aerosol: 0.1% in H_2O
Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 17.94 g of $Na_2WO_4 \cdot 2H_2O$ in H_2O and make the solution up to a volume of 1 liter.

Pipet exactly 10 ml of the carrier solution into a 125-ml erlenmeyer flask, add 2 ml of glacial $HC_2H_3O_2$ and 8 ml of 6*M* $NH_4C_2H_3O_2$, and heat the solution on a steam bath to about 80°. Add a few drops of aerosol solution and 5 ml of 5% (in 2*M* $HC_2H_3O_2$) 8-hydroxyquinoline reagent. Heat on a steam bath until the 8-hydroxyquinoline derivative coagulates. (The coagulation may be aided by bringing the solution to a boil over an open flame.) Filter the precipitate into a weighed 60-ml sintered glass crucible of medium porosity and wash three times with 5-ml portions of H_2O and once with a 5-ml portion of absolute ethanol. Dry the precipitate at 110° for ½ hr. Cool and weigh.

To determine the quantity of W contained in 1 ml of the standard solution, a known volume of the solution contained in a 125-ml erlenmeyer flask is digested on a steam bath with 6*M* HNO_3 for 12 hr. The $WO_3 \cdot XH_2O$ formed is filtered into a weighed Coors 2 Gooch crucible which is covered with a thin mat of asbestos. The precipitate is ignited at 850° (at 900° WO_3 begins to volatilize) for 1 hr. It is then cooled and weighed as WO_3.

Four standardizations, with results having a total spread of about 1%, are run. In one series of standardizations it was found that 20.0 mg of W gave 54.8 mg of the W-derivative of 8-hydroxyquinoline.

4. Procedure

Step 1. To a 40-ml conical centrifuge tube add 2.0 ml of standard W carrier and an aliquot of the sample. Then add 10 ml of concd HNO_3 and digest on a steam bath for 10 min. Remove, centrifuge, and discard the supernate.

Step 2. To the $WO_3 \cdot XH_2O$ residue add 6 drops of concd NH_4OH and dilute to 15 ml with

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*See the indium procedure for a brief description of the use of 8-hydroxyquinoline (oxine) as a precipitating agent.

H_2O. Add, with swirling, 3 drops of Fe carrier solution (Note 1) and 2 drops of aerosol solution. Centrifuge and decant the supernate into a clean centrifuge tube.

Step 3. To the solution add 10 drops of 50% tartaric acid solution, 10 drops of concd H_2SO_4, and 5 drops each of Bi and Mo carriers. Place on steam bath and bubble in H_2S rather vigorously for at least 2 min (Note 2). (Some time is required for MoS_3 to coagulate. Coagulation is aided by the precipitation of Bi_2S_3.) Filter the hot mixture containing the sulfide precipitates through No. 40 Whatman (9 cm) filter paper in a 2", 60° funnel (Note 3) and collect the filtrate in a clean centrifuge tube. Wash the centrifuge tube and the precipitate with 2-3 ml of water and pour the washings through the filter funnel. To the filtrate add 10 ml of concd HNO_3 and digest on a steam bath for 10 min. Remove, centrifuge, and discard the supernate.

Step 4. Repeat Steps 2 and 3.

Step 5. Dissolve the $WO_3 \cdot XH_2O$ precipitate in 6 drops of concd NH_4OH and add 15 drops of 50% tartaric acid solution. With 10 ml of H_2O transfer the solution to a 60 ml separatory funnel. Add 10 drops of concd HCl, 1 ml of Nb carrier, and 10 ml of chloroform. Shake briefly and add 5 ml of 6% cupferron reagent. Shake for 30 sec and allow to stand for 1-2 min. Drain off chloroform layer and discard. Extract again with 5 ml of chloroform. Drain water layer into clean 40-ml centrifuge tube.

Step 6. Repeat Step 3 but do not add the tartaric acid solution. *Caution*: When the mixture is heated on a steam bath, there is a vigorous evolution of oxides of nitrogen from reaction betwen tartaric acid present in solution and the added nitric acid.

Step 7. To the $WO_3 \cdot XH_2O$ precipitate obtained in Step 6 add 6 drops of concd NH_4OH. Transfer the resulting solution to a 125-ml erlenmeyer flask with the aid of H_2O from a wash bottle. The volume of solution should be about 15 ml. Add 6 drops of glacial $HC_2H_3O_2$ and 10 ml of the buffer solution (see reagents). Heat to boiling and add 1 ml of 5% 8-hydroxyquinoline reagent dropwise. Boil for about 30 sec, let stand for a few minutes, and filter through a tared No. 42 Whatman filter, ⅞" diameter, using a ground-off Hirsch funnel and a filter chimney. (No. 50 Whatman paper is also suitable, but the filtration process is slower.) Dry at 120° for 10 min. Allow to stand for 20 min and weigh. Mount on two-sided Scotch tape on an Al plate and cover with Nylon film. β-count immediately.

Notes

1. The percentage loss of W in this step is almost exactly equal to the number of drops of Fe carrier added.

2. It is necessary at this stage to keep the solution hot in order to keep the formation of sulfur to a minimum in the step where HNO_3 is added to decompose tartrate.

3. Filtration is superior to centrifugation at this stage. "Floaters" are invariably present after centrifugation.

TUNGSTEN II

R. J. Prestwood

1. Introduction

This procedure was developed for the separation of tungsten from fission products in samples obtained from underground nuclear explosions. These samples had large quantities of soil associated with them. and it was found that the original tungsten procedure did not remove niobium adequately.

There are three major differences between this procedure and the original: the chloroform extraction has been eliminated. fuming with concentrated sulfuric acid has been introduced. and the final weighing form of the tungsten is WO_3.

2. Reagents

W carrier: 10 mg W/ml. added as $Na_2WO_4\cdot 2H_2O$ in H_2O; standardized

Fe carrier: 10 mg Fe/ml. added as $FeCl_3\cdot 6H_2O$ in very dilute HNO_3

Mo carrier: 10 mg Mo/ml. added as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in H_2O

Pd carrier: 10 mg Pd/ml. added as $PdCl_2$ in 1*M* HCl

La carrier: 10 mg La/ml. added as $La(NO_3)_3\cdot 6H_2O$ in H_2O

HCl: concd

HNO_3: concd

H_2SO_4: concd

Tartaric acid: 50% aqueous solution

NH_4OH: concd

NaOH: 10*M*

H_2S: gas

Ethanol: absolute

3. Preparation and Standardization of Carrier

Same as in original TUNGSTEN procedure.

4. Procedure

Step 1. To a 40-ml glass centrifuge tube add 2.0 ml of standard W carrier and an aliquot of the sample. Then add 10 ml of concd HNO_3 and digest on a steam bath for 10 min. Centrifuge and discard the supernate. If the original sample is in a large volume of solution (the author has processed as much as 200 ml of sample-containing solution which was 4*M* in HCl), the acidic solution is added to the standard carrier in an erlenmeyer flask and digested on a hot plate for 24 hr. $WO_3\cdot XH_2O$ precipitates and coagulates during the digestion. The mixture is then centrifuged portionwise in a single centrifuge tube. the supernates being discarded.

Step 2. To the precipitate add 3-4 ml of concd H_2SO_4 and. with stirring. fume until SO_3 fumes appear only above the mouth of the centrifuge tube (Note 1). Cool the tube in air until it is safe to cool further with tap water. When cool. carefully add 20 ml of H_2O. stir. and heat on a steam bath for 5-10 min. Centrifuge and discard the supernate.

Step 3. To the precipitate add 10 drops of 10*M* NaOH. dilute to 15 ml with H_2O. and then add 1 drop each of Fe and La carriers. Heat on a steam bath until the precipitate coagulates. Centrifuge. transfer the supernate to a clean centrifuge tube. and discard the precipitate.

Step 4. Repeat the Fe-La scavenge on the supernate. Centrifuge and transfer the supernate to a clean centrifuge tube. discarding the precipitate.

Step 5. To the supernate add 10 drops of tartaric acid. 10 drops of concd H_2SO_4. 1 ml of Fe carrier (Note 2). and 1 drop of Mo and 5 drops of Pd carriers. Place on a steam bath and saturate with H_2S for at least 5 min. Centrifuge. transfer the supernate to a clean centrifuge tube. and discard the precipitate.

Step 6. To the supernate add 5 drops of Pd carrier. place on a steam bath, and saturate with H_2S for 5 min. Centrifuge and filter the supernate through a No. 541 Whatman filter paper into a clean centrifuge tube. Discard the precipitate.

Step 7. To the supernate add 10 ml of concd HNO_3. heat on a steam bath for 10 min. centrifuge. and discard the supernate.

Step 8. Repeat Step 2.

Step 9. Repeat Steps 3 and 4. using concd NH_4OH rather than NaOH.

Step 10. To the supernate add 10 drops of tartaric acid. 10 drops of concd H_2SO_4, and 5 drops of Pd carrier. Saturate with H_2S on a steam bath for 5 min. Centrifuge and filter the supernate through No. 541 Whatman filter paper into a clean centrifuge tube. Discard the precipitate.

Step 11. To the supernate add 10 ml of concd HNO_3, digest for 10 min on a steam bath, centrifuge, and discard the supernate. To the precipitate add 3 ml of concd H_2SO_4 and fume as before (Step 2). Cool, add 20 ml of H_2O. and heat on a steam bath for 10 min. Centrifuge and discard the supernate.

Step 12. Dissolve the precipitate in 1 ml of concd NH_4OH and repeat one Fe-La scavenge. Centrifuge and transfer the supernate to a clean centrifuge tube.

Step 13. To the supernate add 5 ml of paper pulp mixture (Note 3) and 10 ml of concd HCl. Digest for 10 min on a steam bath. Filter the hot mixture onto a Millipore filter (1.2μ or less pore size). Do not wash the precipitate. Transfer the precipitate and filter paper to a Coors 00 crucible and ignite for 5-10 min at 800°. Cool and powder gently with a polished glass rod. Transfer the powdered material with the use of absolute ethanol onto a tared No. 42 Whatman filter circle. Weigh as WO_3.

Notes

1. This treatment seems to ensure subsequent decontamination from Nb.

2. The presence of ferric ion delays the reduction of Mo by H_2S and therefore facilitates its complete precipitation.

3. The pulp mixture is made by adding half a dozen Whatman No. 42 (9 cm) filter papers to 500 ml of H_2O in a Waring blender and macerating for about 5 min. The pulp mixture is transferred to a Pyrex container and made slightly acidic with HCl to inhibit mold formation.

November 1968

THE SEPARATION OF RHENIUM FROM TUNGSTEN

B. P. Bayhurst

1. Introduction

In this procedure for the separation of rhenium activity from radioactive tungsten which has already been decontaminated, the major purification step is the precipitation of Re_2S_7 from a medium which is approximately $5M$ in both hydrochloric and hydrofluoric acid. The chemical yield is about 80%.

2. Reagents

Re carrier: $KReO_4$ in H_2O, corresponding to about 15 mg of $(C_6H_5)_4$ $AsReO_4$/ml; standardized
W carrier: 10 mg W/ml, added as $Na_2WO_4 \cdot 2H_2O$ in H_2O
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
HCl: concd; $6M$
HF: concd
HF-HCl: $5M$ in each
H_2S: gas
NH_4OH: concd
H_2O_2: 30%
NaCl: $5M$
$(C_6H_5)_4$ AsCl: 1% aqueous solution
Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 6.85 g of $KReO_4$ in water and dilute the solution to 1 liter. Pipet 5.0 ml of the solution into a 40-ml glass centrifuge tube, dilute to 20 ml with H_2O, and make the solution $0.5M$ in NaCl. Add 7 ml of 1% $(C_6H_5)_4$ AsCl, bring the solution to a boil, and then permit it to cool overnight in a refrigerator. Filter through a tared fritted glass crucible and wash the precipitate with ice water. Dry in an oven at 110° for 20 min, cool, and weigh as $(C_6H_5)_4AsReO_4$.

Four standardizations agreed with each other within less than 1%.

4. Procedure

Step 1. To about 10 ml of a slightly alkaline solution of the W in a 40-ml glass centrifuge tube, add 2.0 ml of Re carrier, and allow the solution to stand for the desired growth period. Make the solution $6M$ in HCl and heat on a steam bath for 15 min to permit the precipitated $WO_3 \cdot XH_2O$ to coagulate. Centrifuge and transfer the supernate to a clean centrifuge tube.

Step 2. To the supernate, add 2 ml of W holdback carrier, heat on a steam bath for 5-10 min, centrifuge, and transfer the supernate to a clean 40-ml polyethylene centrifuge tube. Discard the precipitate.

Step 3. Make the solution about $5M$ in both HF and HCl. Add 2 ml of W carrier and saturate with H_2S for at least 10 min while heating the solution on a steam bath. Centrifuge and discard the supernate. To the Re_2S_7 precipitate add 30 ml of the HF-HCl mixture, saturate with H_2S, centrifuge, and discard the supernate.

Step 4. To the precipitate add 1 ml of concd NH_4OH and 5-6 drops of 30% H_2O_2. Let the mixture stand on a steam bath, with stirring, until solution is complete. Add 30 ml of the HF-HCl mixture and heat on a steam bath for 5 min.

Step 5. Saturate the solution, still maintained on the steam bath, for at least 5 min with H_2S. Centrifuge and discard the supernate. Wash the precipitate with 20-30 ml of $6M$ HCl and discard the washings.

Step 6. To the precipitate add 1 ml of concd NH_4OH and 5-6 drops of 30% H_2O_2. Heat on a steam bath to dissolve the Re_2S_7, and transfer the solution to a clean 40-ml glass centrifuge tube. Make the solution acidic with HCl and boil over a burner for a few minutes to ensure complete removal of H_2O_2.

Step 7. Add 4 drops of La carrier, make the solution basic with concd NH_4OH, centrifuge, and transfer the supernate to a clean centrifuge tube. Discard the precipitate.

Step 8. To the supernate add 1-2 ml of $5M$ NaCl, 3 ml of 1% $(C_6H_5)_4$ AsCl, and bring the solution to a boil. Cool. filter the $(C_6H_5)_4AsReO$ through a tared No. 42 Whatman filter circle. using a ground-off Hirsch funnel and filter chimney. Wash the precipitate with H_2O and a small amount of absolute ethanol. Dry in an oven at 110° for 5 min. cool. weigh. mount. and count.

November 1968

uranium

URANIUM-235

W. G. Warren

1. Introduction

The procedure described below is a carrier-free method for the determination of ^{235}U, employing ^{232}U as a tracer. Decontamination from neptunium and plutonium is excellent. Removal of plutonium is in part effected by conversion to the tetrapositive state, formation of the cupferron complex, and extraction of the complex into chloroform. Separation of rare earths, partial removal of neptunium, and further decontamination from plutonium is obtained by adsorption of uranium from concentrated hydrochloric acid solution onto a Dowex A2 anion exchange column. Washing of the column with 10*M* and then with 5*M* hydrochloric acid removes any adsorbed plutonium and neptunium, respectively. Uranium is eluted from the column by means of 0.1*M* nitric acid and is then electroplated on platinum. The chemical yield, determined by α-counting the ^{232}U tracer, is 50-90%. The ^{235}U is fission-counted. Four samples can be determined in about 5½ hr with excellent precision.

2. Reagents

^{232}U tracer: amount added is determined by the
  α-counting technique employed
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Fe carrier: 10 mg Fe/ml, added as $Fe(NO_3)_3 \cdot 9H_2O$ in very dilute HNO_3
Dowex A2-X8 anion exchange resin, 400 mesh
HCl: 5*M*; 10*M*; concd
HNO_3: 0.1*M*; 6*M*
NH_4OH: concd
$NH_2OH \cdot HCl$: 5*M*
$(NH_4)_2C_2O_4$ in H_2O: 4%
Aqueous cupferron reagent: 6%
Methyl red indicator solution: 0.1% in 90% ethanol
Methanol: anhydrous
Chloroform
NH_3: gas

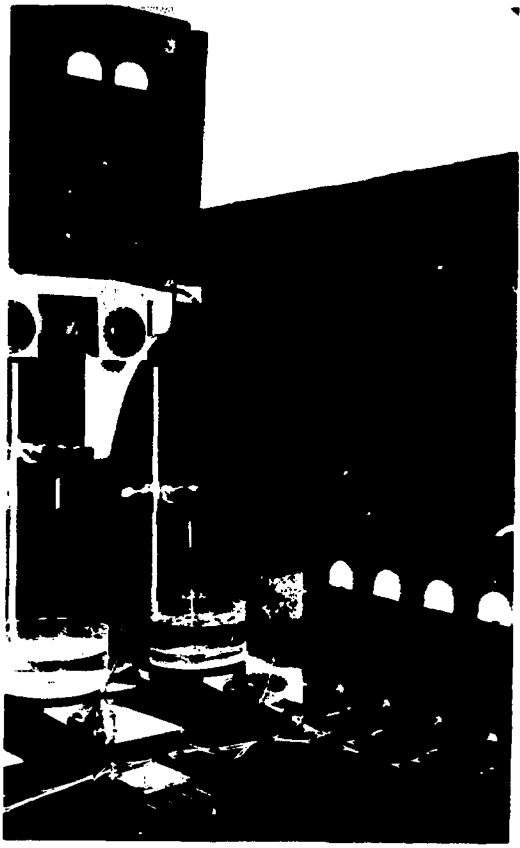
3. Special Equipment

Plating assembly (see photograph): one cell per aliquot of sample

Source of current: Fisher Powerhouse (dc), with variable resistance in series with cell

Cell (see photograph): brass base (3" × 3") for holding Pt cathode; 5-mil Pt circular 1" disk (cathode); gasket to seal cathode and chimney; glass chimney, ⅞" i.d., 4" high with four ears at height of 3"; 1-¼" steel springs for holding chimney to base; rotating Pt anode. The cell is heated for 1 hr at 105° after assembly to ensure formation of seal between glass and Pt.

Water bath for cell (see photograph): Autemp heater; 6" crystallizing dish (for water bath); rubber pad for holding cell.



Plating assembly.

Parts of plating cell.

4. Procedure

Step 1. To an aliquot of sample not exceeding 20 ml (Note 1) in a 40-ml centrifuge tube, add 1 ml of ^{232}U tracer and 3 drops of La carrier, and bubble in NH_3 gas until the precipitate which forms coagulates. Digest for 15 min on a steam bath, centrifuge, and discard the supernate.

Step 2. Dissolve the precipitate in 0.6 ml of concd HCl and dilute to 10 ml with H_2O. Add 5 drops of 5*M* $NH_2OH \cdot HCl$ (Note 2) and 2 drops of Fe carrier (if this element is not already present), and allow to stand for 10 min. Add 4 ml of chloroform, 6 ml of 6% cupferron, and extract the Pu(IV)-cupferron complex by stirring for 2 min. Remove the chloroform layer by means of a transfer pipet and discard. Extract the aqueous phase three additional times with chloroform. To the aqueous layer add 3 drops of La carrier and bubble in NH_3 gas until the precipitate formed coagulates. Digest for 15 min on a steam bath, centrifuge, and discard the supernate.

Step 3. Dissolve the precipitate in 1 ml of concd HCl and transfer the solution with three additional 1-ml HCl rinses to the Dowex A2 resin column, 3mm × 5 cm, which has been previously washed twice with 2.5-ml portions of concd HCl. Force the solution through the column under pressure. Wash the column twice with 2.5-ml portions of 5*M* HCl and discard the washings.

Step 4. Elute the U from the column into the plating cell with two 2.5-ml portions of 0.1*M* HNO_3.

Step 5. Add 5 ml of 4% $(NH_4)_2C_2O_4$, 3 drops of methyl red indicator solution, and make basic by the dropwise addition of concd NH_4OH. Make the solution barely red to the indicator by the dropwise addition of 6*M* HNO_3, and add 3 drops in excess.

Step 6. Plate at 1.1 amp and 8 volts for 1½-hr at 80° in a hot water bath. At the end of the first 10 min, add 3 drops of methyl red solution and make acid with 6*M* HNO_3. Check acidity at two additional 10-min intervals, and at the end of 40 min add 3 drops of concd NH_4OH. At 10-min intervals thereafter check to see that the plating solution is barely basic to the indicator.

Step 7. Remove the cell from the water bath, wash three times with methanol, and dismantle the cell, carefully keeping the Pt disk flat. Flame the disk over a burner, α-count and then mount for fission-counting against standard ^{235}U foils

Notes

1. The aliquot of sample taken must have a ^{235}U content in the range of the ^{235}U standard foils against which it is comparison fission-counted.

2. The $NH_2OH \cdot HCl$ reduces the Pu to the +4 state, in which form it is complexed by the cupferron.

URANIUM-235 II

W. G. Warren

1. Introduction

In this carrier-free method for the determination of ^{235}U, it is unnecessary to obtain complete decontamination from fission products because the uranium is finally fission-counted. The chemical yield is determined by α-counting the ^{232}U used as tracer. The uranium is first adsorbed on an anion exchange resin column from a solution at least 10*M* in HCl. The bulk of the fission products is removed from the uranium by elution with 8*M* HNO_3 and then some decontamination from neptunium and plutonium is accomplished by column washes with 3*M* HCl. The uranium is eluted from the column by means of H_2O and placed on a new anion column. Decontamination from neptunium and plutonium is completed by column washes with 10*M* and 3*M* HCl and the uranium is eluted with H_2O and electroplated onto platinum.

2. Reagents

^{232}U tracer: amount added determined by the α-counting technique employed
HCl: 2*M*; 3*M*; 10*M*; concd
HNO_3: 8*M*
NH_4OH: concd
NH_4Cl: solid
Ethanol: absolute
Methyl red indicator solution: 0.5% solution of the indicator in ethanol
Bio-Rad AG 1-X8 anion-exchange resin, 100-200 mesh, water slurry

3. Procedure

Step 1. To an aliquot of sample not exceeding 50 ml in a 125-ml erlenmeyer flask, add 1 ml of ^{232}U tracer and 20 ml of concd HCl and evaporate the solution to dryness. Repeat twice the addition of HCl and evaporation. Take up the residue in 10-20 ml of concd HCl, heating if necessary to ensure solution.

Step 2. Add the solution to an AG 1-X8 anion exchange resin column (prewashed with concd HCl), 1 cm x 7 cm, and allow it to flow through the column under gravity. (U is adsorbed on the column.) Wash the erlenmeyer flask with 6 ml of concd HCl and pass the wash through the resin column. Discard the effluents.

Step 3. Wash the column twice with 6-ml portions of 8*M* HNO_3 and twice with 6-ml portions of 3*M* HCl. Discard the effluents. Elute the U with two 6-ml portions of H_2O into a clean 125-ml erlenmeyer flask.

Step 4. Evaporate the solution to dryness and take up the residue in 10-20 ml of concd HCl. Place the solution on another AG 1-X8 resin column, 1 cm x 5 cm, and allow it to flow through under gravity. Wash the erlenmeyer flask with 4 ml of concd HCl and pass the wash through the resin column. Discard the effluents.

Step 5. Wash the column twice each with 4 ml of 8*M* HNO_3, 4 ml of 10*M* HCl, and 4 ml of 3*M* HCl. Discard all effluents. Elute the U with two 4-ml portions of H_2O and collect the eluate in an electroplating cell.

Step 6. To the cell add approximately 0.5 g NH_4Cl and 3 drops of methyl red indicator solution. Make the solution basic with concd NH_4OH and then barely acidic with 2*M* HCl. Electroplate the U onto a 1″ Pt disk at 2 amp for 15 min. One minute before completion of the plating, add 1 ml of concd NH_4OH to the cell. Discard the cell solution and rinse the cell with three 5- to 10-ml portions of absolute ethanol. Disassemble the cell, flame the Pt disk, and mount it for counting.

May 1968

URANIUM-235 II

G. W. Knobeloch

1. Introduction

This replaces the May, 1968, URANIUM-235 II procedure because that procedure did not completely remove the plutonium activity from underground bomb debris. In the carrier-free method described below, it is not necessary to obtain complete decontamination from fission products since the uranium is finally fission-counted. The chemical yield is determined by α-counting the ^{232}U used as tracer. The uranium is first adsorbed on an anion exchange resin column from a solution at least 10 *M* in HCl. The bulk of the fission products is removed from the uranium by elution with 8 *M* HNO_3 and then some decontamination from neptunium and plutonium is accomplished by column washes with 3 *M* HCl. The uranium is eluted from the column by water and placed on a fresh anion column. Decontamination from plutonium is completed by elution with an HI-HCl mixture. Then the resin is treated with H_2O_2 to oxidize the uranium to the +6 state, and neptunium is removed with 3 *M* HCl. The uranium is finally eluted with water and electroplated onto platinum.

The procedure as given below is suitable for samples having plutonium activity of less than 10^5 α counts per minute. Footnote 2 tells how the procedure may be modified for decontamination from plutonium of greater activity.

2. Reagents

^{232}U tracer: amount added determined by the α-counting technique employed
HCl: 2 *M*; 3 *M*; concd
HNO_3: 8 *M*
HI-HCl mixture: 1:9 by volume of 47% HI and concd HCl
H_2O_2-HCl reagent: 1 part by volume of 30% H_2O_2 to 40 of 9 *M* HCl
NH_4OH: concd
NH_4Cl: solid
Ethanol: absolute
Methyl red indicator solution: 0.5% in ethanol Bio-Rad AG 1-X8 anion exchange resin, 100-200 mesh, water slurry

3. Procedure

Step 1. To an aliquot of a solution of the sample, not exceeding 50 ml, in a 125-ml erlenmeyer flask, add 1 ml of ^{232}U tracer and 20 ml of concd HCl and evaporate the solution to dryness. Repeat twice the addition of HCl and evaporation. Take up the residue in 10-20 ml of concd HCl, heating if necessary to effect solution.

Step 2. Add the solution to an AG 1-X8 anion exchange resin column (prewashed with concd HCl) (Note 1), and allow it to flow through the column under gravity. (U is adsorbed on the column.) Wash the erlenmeyer flask with concd HCl and pass the wash through the resin column. Discard the effluents.

Step 3. Wash the column twice with 8 *M* HNO_3 (Note 2) and twice with 3 *M* HCl. Discard the effluents. Elute the U with two 6-ml portions of H_2O into a clean 125-ml erlenmeyer flask.

Step 4. Evaporate the solution to dryness and take up the residue in 10-20 ml of concd HCl. Place the solution on another AG 1-X8 resin column and allow it to flow through under gravity. Wash the erlenmeyer flask with concd HCl and pass the wash through the resin column. Discard the effluents.

Step 5. Wash the column as indicated: (a) twice with 8 *M* HNO_3; (b) twice with concd HCl; (c) twice with HI-HCl mixture; (d) once with concd HCl; (e) twice with H_2O_2-HCl reagent; (f) and twice with 3 *M* HCl. Discard all effluents. Elute the U with two 6-ml portions of water into a clean 125-ml erlenmeyer flask.

Step 6. Evaporate the solution containing the U to dryness. Destroy the HI by heating to dryness twice after adding 1-ml portions of concd HNO_3. Convert to the chloride by two successive evaporations to dryness after adding 1 ml of concd HCl.

Step 7. Dissolve the residue in 1 ml of concd HCl. Transfer the solution to an electroplating cell with 5 ml of H_2O. Rinse the erlenmeyer flask with 5 ml of H_2O and add the rinse to the plating cell.

Step 8. To the cell add approximately 0.5 g of NH_4Cl and 3 drops of methyl red indicator solution. Make the solution basic with concd NH_4OH and then barely acidic with 2 *M* HCl. Electroplate the U onto a 1" Pt disk at 2 amp for 15 min. One minute before completion of the plating, add 1 ml of concd NH_4OH to the cell. Discard the cell solution and rinse the cell with three 5- to 10-ml portions of absolute ethanol. Disassemble the cell, flame the Pt disk, and mount it for counting.

Notes

1. Anion resin column size and volume of washes are functions of Pu activity and size of the dirt sample. The following table shows these relationships:

Size of dirt sample, g	Pu limit, c/m	Resin dimensions, cm x cm	Wash volumes, ml
<0.0375	$<10^3$	1 x 5	4
0.0375 - 0.075	10^3–3×10^4	1 x 7	6
0.075 - 1.50	3×10^4–3×10^6	1 x 15	10
1.50 - 4.50	3×10^6 - 10^7	1 x 20	15
>4.5	$>10^7$	1 x 30	25

2. For samples having Pu levels greater than 10^5 cpm, the procedure is modified starting with Step 3 as follows:

Wash the column twice with 8 *M* HNO_3, twice with concd HCl, twice with HI-HCl mixture, once again with concd HCl, and twice with 3 *M* HCl. Discard the effluents. Elute the U with two 6-ml portions of H_2O into a clean 125-ml erlenmeyer flask. Evaporate to dryness and destroy the HI by heating to dryness twice after adding 1-ml portions of concd HNO_3. Convert to the chloride by two successive evaporations to dryness after adding 1 ml of concd HCl. Carry out Steps 4, 5, and 6 as described. Dissolve the residue in 1 ml of concd HCl and place on a third AG 1-X8 resin column. Wash twice with 8 *M* HNO_3, twice with concd HCl, twice with 3 *M* HCl, and elute the U with two 6-ml portions of H_2O into an electroplating cell and plate as in Step 8.

URANIUM-237

W. G. Warren

1. Introduction

In this carrier-free procedure for the determination of ^{237}U, the element is first adsorbed on an anion exchange resin column from a solution at least 10*M* in HCl. The bulk of the fission products is removed from the uranium by elution with 8*M* HNO_3, and the plutonium by elution with a mixture of concentrated HI and HCl. The resin is then treated with hydrogen peroxide to ensure oxidation of uranium to the +6 state and the neptunium is removed from the column by means of 3*M* HCl. The uranium is eluted with H_2O and placed on another anion resin column from concentrated HCl solution. Further decontamination of the element is accomplished by column washings with 8*M* HNO_3, 10*M* HCl, and 3*M* HCl. Following elution of uranium with water, the element is placed on a cation exchange resin column, which is then washed with 0.1*M* HCl, a treatment presumably removing traces of tellurium and iodine. The uranium is eluted with 3*M* HCl and electroplated onto platinum.

The procedure is carried out in the presence of ^{233}U tracer and yield is determined by α-counting this isotope. ^{237}U is determined by β-counting.

2. Reagents

^{233}U tracer: amount added determined by the α-counting technique employed
HCl: 0.1*M*; 2*M*; 3*M*; 10*M*; concd
HNO_3: 8*M*
HI-HCl mixture: 1:9 by volume of 47% HI and concd HCl
NH_4OH: concd
NH_4Cl: solid
Ethanol: absolute
Methyl red indicator solution: 0.5% solution of the indicator in ethanol
H_2O_2 reagent: 0.5 ml of 30% H_2O_2 to 40 ml of 9*M* HCl
Bio-Rad AG 1-X8 anion exchange resin, 100-200 mesh, water slurry
Bio-Rad AG 50W-X8 cation exchange resin, 100-200 mesh, water slurry

3. Procedure

Step 1. To an aliquot of sample not exceeding 50 ml in a 125-ml erlenmeyer flask, add 1 ml of ^{233}U tracer and 20 ml of concd HCl and evaporate the solution to dryness. Repeat twice the addition of HCl and evaporation. Take up the residue in 10-20 ml of concd HCl, heating if necessary to ensure solution.

Step 2. Add the solution to an AG 1-X8 anion exchange resin column (prewashed with concd HCl), 1 cm x 5 cm, and allow it to flow through the column under gravity. (U is adsorbed on the column.) Wash the erlenmeyer flask with 4 ml of concd HCl and pass the wash through the resin column. Discard the effluents.

Step 3. The following sequence of column washes is now carried out: (a) twice with 4-ml portions of 8*M* HNO_3; (b) twice with 4 ml of concd HCl; (c) with 6.5 ml and then 2 ml of HI-HCl mixture; (d) again with 4 ml of concd HCl; (e) twice with 4-ml portions of H_2O_2 reagent (I_2 is removed and the resin column is decolorized); and (f) twice with 4-ml portions of 3*M* HCl. Discard all effluents. Elute the U with two 4-ml portions of H_2O, collecting the eluate in a clean 125-ml erlenmeyer flask.

Step 4. Evaporate the solution to dryness and take up the residue in 10 ml of concd HCl. Place the solution on another AG 1-X8 resin column and allow it to flow through under gravity. Wash the erlenmeyer flask with 4 ml of concd HCl and pass the wash through the resin column. Discard the effluents.

Step 5. Wash the column twice each with 4 ml of 8*M* HNO_3, 4 ml of 10*M* HCl, and 4 ml of 3*M* HCl. Discard all effluents. Elute the U with two 4-ml portions of H_2O, and collect the eluate in a clean 40-ml graduated long-taper glass centrifuge tube. Dilute the eluate to 10 - 15 ml.

Step 6. Place the solution on an AG 50W-X8 cation resin column, 4 mm x 6 cm, and allow it to pass through under slight air pressure. (The optimum flow rate through the column is 1 drop every 6 sec.) Discard the effluent.

Step 7. Wash the column with two 2.5-ml portions of 0.1*M* HCl and discard the washings.

With the use of two 2.5-ml portions of $3M$ HCl elute the U from the resin column into an electroplating cell.

Step 8. To the cell add approximately 0.5 g of NH_4Cl and 3 drops of methyl red indicator solution. Make the solution basic with concd NH_4OH and then barely acidic with $2M$ HCl. Electroplate the U onto a 1" Pt disk at 2 amp for 15 min. One minute before completion of the plating, add 1 ml of concd NH_4OH to the cell. Discard the cell solution and rinse the cell with three 5- to 10-ml portions of absolute ethanol. Disassemble the cell, flame the Pt disk, and mount it for counting.

May 1968

TOTAL URANIUM I

E. J. Lang

1. Introduction

For its determination in material containing fission products, uranium is first converted to uranyl nitrate, $UO_2(NO_3)_2$. The nitrate is then extracted into ether. After removal of the ether, the uranium is finally incorporated into sodium fluoride pellets and determined fluorimetrically.

2. Reagents

U standard: 0.2 μg U/50 λ of solution. Made up by dissolving normal U in HNO_3, the final acid concentration being about 3*M*.

HCl: concd

HNO_3: 3*M*; concd

$Al(NO_3)_3$ reagent: 700 g $Al(NO_3)_3 \cdot 9H_2O$/liter H_2O. Before use, this reagent is treated in the following manner: 35 ml of concd HNO_3 and 100 ml of anhydrous ethyl ether are added to 500 ml of the $Al(NO_3)_3$ solution in a 1-liter separatory funnel. The resulting mixture is shaken for 5 min and then allowed to stand for 5 min. The $Al(NO_3)_3$ layer is then transferred to a clean 1-liter separatory funnel. The extraction is repeated and the $Al(NO_3)_3$ is transferred to the first separatory funnel, which has been cleaned with distilled H_2O. The process is repeated until a total of five extractions has been made.

NaF: solid (Baker and Adamson, meets ACS specifications)

LiF: solid (Baker, CP grade)

NaF flux: a solid mixture of NaF-LiF, containing 2% by weight of LiF.

Ethyl ether: anhydrous (Mallinckrodt, 5 lb cans)

Acetone: reagent grade

3. Procedure

Step 1. Pipet an aliquot (containing about 1 μg of U) of the sample into a 50-ml beaker and evaporate to dryness under a heat lamp. Add 2-3 ml of concd HNO_3 and 1 ml of H_2O and again evaporate to dryness. Repeat the addition of HNO_3 and H_2O and the evaporation twice.

Step 2. To the residue, add 1 ml of H_2O and 5 ml of concd HNO_3. Transfer the solution to the sample holder of the ether extraction apparatus which contains 60 ml of $Al(NO_3)_3$ reagent. Rinse the beaker three times with 2-ml portions of H_2O, adding the washings to the sample holder. Add ether up to the arm of the sample holder, add 8 ml of H_2O and 50 ml of ether to the receiver, and assemble the extraction apparatus. Extract for 1¾ hr. The U is now in the receiving flask.

Step 3. Remove the receiving flask and take off the ether completely by means of a stream of N_2.

Step 4. Transfer the material remaining in the receiver, with three H_2O rinses (5 ml each), to a 50-ml reinforced Pt dish. Evaporate to 1-2 drops under a heat lamp and transfer to a 2-ml volumetric flask by use of a micropipet. Add 3 drops of 3*M* HNO_3 to the dish, swirl, and transfer the rinsings to the volumetric flask. Repeat the HNO_3 rinse.

Step 5. Rinse the sides of the Pt dish with 5 ml of H_2O, add 0.5 ml of concd HNO_3, evaporate the solution to 1-2 drops, and transfer to the 2-ml volumetric flask. Add 3 drops of 3*M* HNO_3 to the dish, swirl, and transfer to the volumetric flask. Repeat the addition of 3*M* HNO_3 and repeat the entire step twice.

Step 6. Make the solution up to volume with 3*M* HNO_3 and shake well. In a porcelain spot plate, place six numbered and tared special Pt dishes (Fig. 1). To each of 9 spots on a paraffin-coated microscope slide, add 1 drop of 3*M* HNO_3. By means of a micropipet coated on the outside with paraffin up to the first bulb, withdraw a 50 λ aliquot from the 2-ml volumetric flask and transfer to a special Pt dish. Rinse the pipet by dipping the tip into one of the drops of 3*M* HNO_3 on the microscope slide and drawing the liquid to above the mark. Add the rinsing to the special Pt dish containing the sample. Dip the pipet tip into the same drop of 3*M* HNO_3 and draw the liquid about half-way up the first bulb. Withdraw the pipet tip from the drop and draw the liquid into the second bulb. Force the liquid back and forth between the two pipet bulbs several times and transfer the liquid to the Pt dish. Fill five other special Pt dishes in the manner described above.

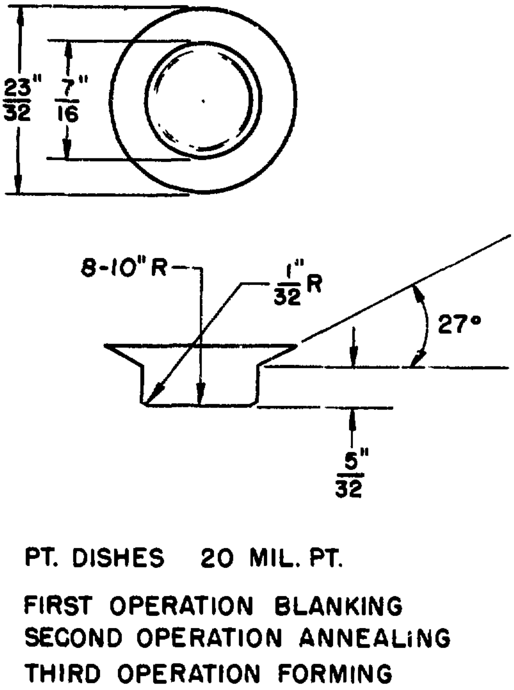


Fig. 1. Specifications for special Pt dishes.

Step 7. Evaporate the solutions in the special Pt dishes under a heat lamp for about 15 min.

Step 8. To each of three of the dishes add 50 λ (0.2 μg) of the U standard in the manner described in Step 6, including the HNO_3 rinsings.

Step 9. Evaporate the contents of all the Pt dishes to dryness under a heat lamp.

Step 10. By means of a pelletizer made of a 10-ml graduated pipet, the ends of which are cut and the tubing fitted with a solid glass plunger, introduce approximately 300 mg of NaF flux into each Pt dish and crush the pellets with a Pt spatula made by flattening one end of a 75-mil Pt rod. On an analytical balance adjust the weight of the flux in each dish to 300 ± 0.2 mg.

Step 11. Fuse the contents of one Pt dish in the fusion apparatus (Fig. 2) for exactly 10 min (Note 1). Ten seconds before the end of the 10-min fusion period, heat a pair of Pt-tipped tweezers in the flame and at the conclusion of fusion remove the dish from the flame with the tweezers. Hold the dish at the end of the iron ring for 20 sec and then replace it in the porcelain spot plate. Repeat the fusion procedure with each Pt dish.

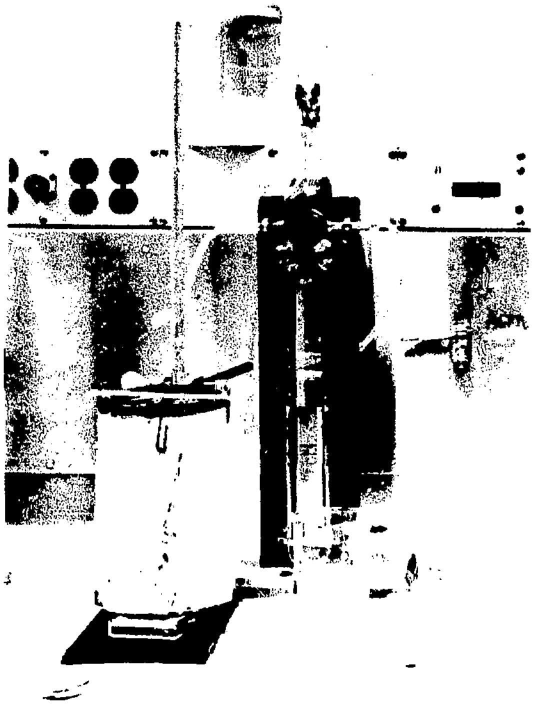


Fig. 2. Fusion apparatus.

Step 12. Allow the Pt dishes to cool for 2-3 hr. Tap out each of the fused fluxes into an individual hole in the porcelain spot plate. The samples are now ready for fluorimetric analysis.

Step 13. Into each of the holes in the sample holder of the D.C. Fluorophotometer (Figs. 3 and 4), place a fused flux, bottom side up, and determine the quantity of fluorescence (Notes 2 and 3).

Step 14. Upon completion of the analysis, the special Pt dishes are cleaned in the following manner. The dishes which had contained *only* aliquots of the sample are placed in a 1-liter erlenmeyer flask along with 200 ml of concd HCl and the solution is refluxed for about 8 hr. The

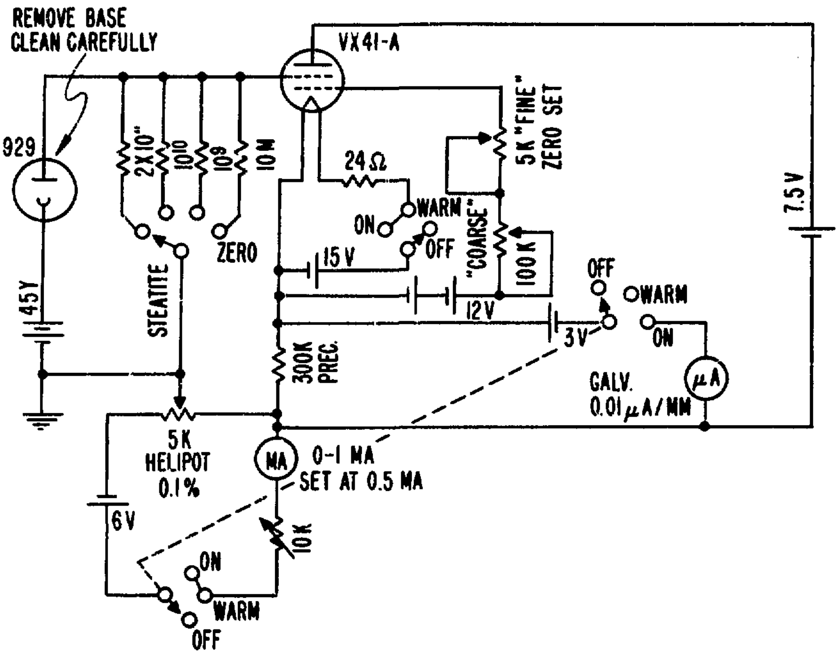


Fig. 3. D.C. Fluorophotometer (schematic).

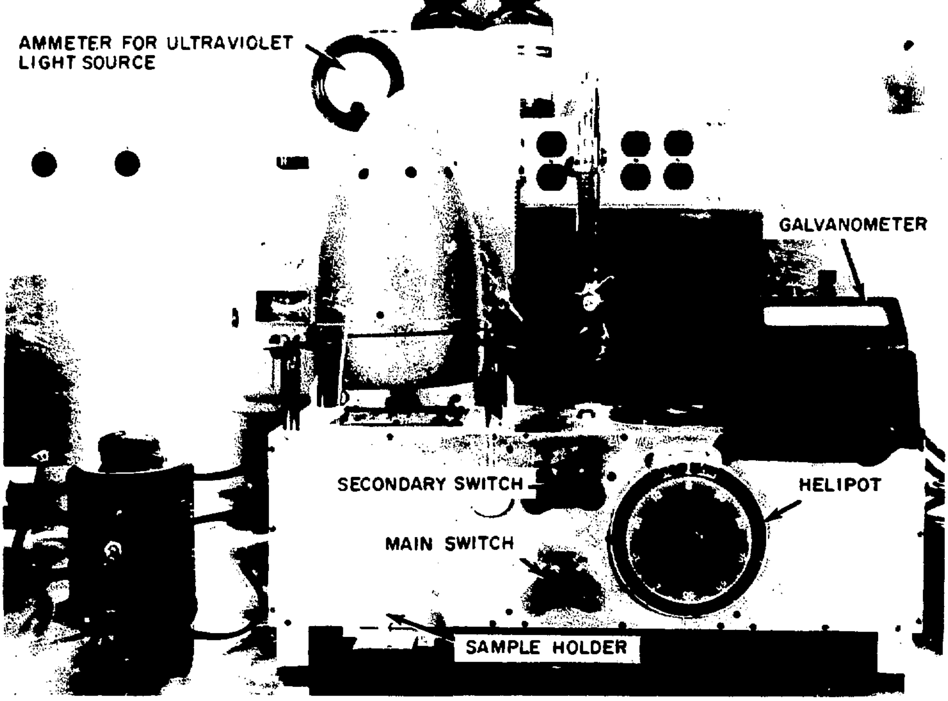


Fig. 4. D.C. Fluorophotometer.

acid is poured off and the flask and dishes are rinsed several times with distilled H_2O. Then 200 ml of concd HNO_3 is added to the flask and this solution is refluxed overnight. The acid is poured off and the flask and dishes are rinsed several times with distilled H_2O. The Pt dishes are then placed on a clean towel by inverting the flask. They are flamed by *gentle* heating in an open flame and while still hot are immersed in distilled water. They are then stored in Petri dishes. The Pt dishes which had contained the standard U are cleaned in a separate flask.

Notes

1. Methane is burned in the Fisher burner of the fusion apparatus, the temperature being controlled by the rate of gas flow. It is important that the temperature be sufficiently high to melt the flux, but not so high as to cause attack of the Pt dish by the flux. The temperature of fusion has been too high and the Pt dish has been attacked when the cooled flux is yellow. The determination of the optimum conditions for fusion is at best an art and the technique must be worked out by each analyst.

2. The D.C. Fluorophotometer (Figs. 3 and 4, designed by R. J. Watts, LASL) is operated in the following manner. The instrument is permitted to warm up for about two hours before use by turning the secondary switch to "zero", the main switch from "off" to "warm", and the ultraviolet light source from "off" to "on". The ultra violet light source and the main switch may also be controlled by means of a No. 1191W Tork clock. The current through the ultraviolet light source should be adjusted to 0.9 amp by use of a Type 216 Powerstat. After the instrument has warmed up, the main switch is turned to "on" and the helipot to "O". The secondary switch is now adjusted to the proper range (1, 2, or 3, depending upon the U concentration of the sample), and the galvanometer is "zeroed" by means of the zero set. A sample is then positioned in the light path by means of the sample holder and the latter is adjusted forward and back until the maximum deflection is obtained on the galvanometer. The helipot is adjusted to "zero" the galvanometer and the helipot reading is taken. The procedure outlined above is repeated for the other samples.

3. Calculation of the average U content in a 50 λ aliquot sample:

A = average of the helipot readings with the 50 λ aliquots containing no added standard U.
B = average of the helipot readings with the 50 λ aliquots containing added standard U.
D = U content, in μg, of the standard in the 50 λ aliquots.

$$\left(\frac{A}{B - A}\right) D = \mu\text{g of U in 50 } \lambda \text{ aliquot sample} + \text{NaF flux.}$$

The value obtained by the above calculation is corrected for the U in the NaF flux, which is determined in the same manner as for the sample. The U value is then adjusted to take into account the chemical yield of the analytical procedure. No correction is necessary for the U in reagents other than NaF, when original aliquots of sample contain about 1 μg of the metal.

TOTAL URANIUM II

W. G. Warren

1. Introduction

This procedure is an adaptation of a procedure developed by the Analytical Chemistry Group of the Chemistry-Metallurgy Division of the Los Alamos Scientific Laboratory. It is appropriate for samples containing 300-500 milligrams of uranium.

Uranium(VI) is reduced to a mixture of uranium(III) and uranium(IV) by means of zinc amalgam in a Jones reductor. All the uranium is then converted to the +4 state by atmospheric oxidation and the uranium(IV) is determined by titration with standard ceric sulfate in the presence of ferroin as indicator. The running of appropriate blanks is essential. The chief interferences in the determination are iron, molybdenum, tungsten, vandium, and nitrate ion. Four samples can be analyzed in about 5 hr.

2. Reagents

H_2SO_4: 5% by volume (5 ml of concd H_2SO_4 to 95 ml of H_2O)

H_2SO_4: concd

Ferric ammonium sulfate: approximately $0.1M$

Ceric sulfate: Standardized. Make up an aqueous solution approximately $0.01M$ and standardize against pure uranium in the following manner. Weigh out to the nearest 0.1 about 1 g of pure U and dissolve the metal in concd HCl, adding a few drops of concd HNO_3 if necessary. Make the solution up to exactly 100 ml by the addition of $2.5M$ HNO_3. Analyze aliquots of the U solution as described under *Procedure*. The solution should be standardized once a month while it is in use.

Jones reductor: For preparation, see any good book on quantitative analysis.

Ferroin indicator: $0.025M$ (in H_2O)

3. Procedure

Step 1. Place the weighed or pipetted sample in a 250-ml beaker. If the sample is in metallic form, bring it into solution with concd HCl and 30% H_2O_2 and proceed to Step 2. If the sample is an oxide, dissolve it in a minimum of concd $HClO_4$, add 100 ml of 5% H_2SO_4, and proceed to Step 3. If the sample is in liquid form, start with Step 2.

Step 2. Add 5 ml of concd H_2SO_4, cover the beaker with a Speedyvap, and take the solution to dryness to remove nitrate and organic matter. Repeat the process three additional times, washing down the Speedyvap and the walls of the beaker each time. If more than trace quantities of nitrate or organic matter are present, a few drops of concd $HClO_4$ are added prior to the second and third evaporation. After the final evaporation add 100 ml of 5% H_2SO_4.

Step 3. Activate a Jones reductor by passing through it 100 ml of 5% H_2SO_4, discarding the effluent. Pass the solution containing the sample through the reductor and collect it in a 500-ml erlenmeyer flask. Pass three 50-ml portions of 5% H_2SO_4 through the reductor, in each case collecting the effluent in the erlenmeyer flask noted above.

Step 4. Aerate the solution in the flask for about 5 min with a stream of air from a glass gas dispersion tube. The bubbles must be active enough to stir the solution. Withdraw the aerating tube and rinse it off, collecting the rinsings in the erlenmeyer flask.

Step 5. Add 3 drops of the ferroin indicator and titrate with standard ceric sulfate until the orange color just begins to fade. At this point add 3 ml of $0.1M$ ferric ammonium sulfate solution to restore the orange color and proceed cautiously with the addition of ceric sulfate until the color of the solution changes to blue-green. This is the endpoint of the titration.

Step 6. Run two blanks and average their titration values.

Step 7. Subtract the average blank titration from the volume of ceric sulfate found in Step 5. Calculate the amount of U in the sample by one of the following formulas:

% U in weighed sample =

$$\frac{\text{ml Ce(SO}_4\text{)}_2 \times \text{N} \times \text{F} \times 100}{g \text{ of sample}}$$

Grams of total U in liquid sample =

$$\text{ml Ce(SO}_4\text{)}_2 \times \text{N} \times \text{F} \times \frac{\text{total vol of sample}}{\text{aliquot vol of sample}}$$

The factor F in these calculations is the milliequivalent weight of the U, with suitable corrections for the isotopic composition:

For depleted U use 0.11900 for F
For normal U use 0.11904
For 93% ^{235}U use 0.11760
For 98% ^{233}U use 0.11650

PURIFICATION OF HIGHLY IRRADIATED URANIUM

K. Wolfsberg

1. Introduction

This procedure describes the purification of uranium which had been irradiated for several weeks (in 1968) in a rabbit in the HFIR (High Flux Isotope Reactor) at Oak Ridge. The experiment was performed to produce ^{237}U, which was to be separated from other uranium isotopes in a mass separator. To facilitate heat transfer during the irradiation process, the uranium (in the form of U_3O_8 highly enriched in ^{236}U) was intimately mixed with the rabbit material, aluminum.

The separation of the uranium requires decontamination from fission products, neptunium isotopes, macro amounts of aluminum, the ^{24}Na formed from the aluminum by the (n, α) reaction, and other induced activities such as ^{51}Cr. The major separation steps include adsorption of the uranium from solution in a large volume of HCl (8-9*M*) onto an anion exchange resin, extraction into ethyl acetate from a HNO_3-$Al(NO_3)_3$ solution, and a second adsorption on an anion exchange resin. The chemical yield is about 90%.

Although the procedure was developed for a specific purpose, it appears to be generally applicable to the analysis for uranium in samples containing highly radioactive contaminants.

2. Reagents

Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_3 in 6*M* HCl
Te(VI) carrier: 10 mg Te/ml, added as $Na_2TeO_4 \cdot 2H_2O$ in 3*M* HCl
HNO_3: concd
HCl: concd; 9*M*; 8*M*
HCl-HNO_3: 9:1 by volume of the concd acids (prepared just before use)
HCl-Br_2: 9*M* HCl, saturated with Br_2
HCl-HI: 9:1 by volume of concd HCl and 47% HI (prepared just before use)
5*M* HCl-0.3*M* HF
0.1*M* HCl-0.06*M* HF
NH_4OH: concd
$Al(NO_3)_3$: saturated aqueous solution (about 2.5*M*)
Ethanol: absolute
Ethyl acetate: 99%
Anion exchange resin: Bio-Rad AG 2-X8, 100-200 mesh

3. Procedure

Step 1. Cut off that section of the rabbit which holds the irradiated sample. (This section will contain about 5 g of Al.) With heating, dissolve the sample plus the cut-off section of the rabbit in a mixture of 190 ml of concd HCl and 10 ml of concd HNO_3. Dissolution takes about 40 min and the volume of liquid is reduced to about 140 ml. Add two 10-ml portions of the HCl-Br_2 mixture (Note 1). Cool and dilute the solution to 300 ml with 9*M* HCl (Note 2) containing 1 drop each of Zr, Te(IV), and Te(VI) carriers. Filter the solution through No. 41 H Whatman filter paper to remove the small quantity of flocculent solid (Al_2O_3?) which generally persists after the dissolution process.

Step 2. Fill a glass column, 8 mm i.d., with anion exchange resin to a height of 3 in. Pre-equilibrate the resin with 8*M* HCl. With the use of air pressure pass the solution from Step 1 through the column at the rate of 10 drops every 7 or 8 sec. (All other column operations in this step and all in Step 6 are carried out at the rate of about 10 drops every 20 sec.) Wash the column first with 5 ml of 8*M* HCl and then with 5 ml of the concd acid, discarding the washings. Elute the U into a 40-ml centrifuge tube with two 5-ml portions of H_2O and then with one 10-ml portion of H_2O (Note 3).

Step 3. Make the solution basic with 4 ml of concd NH_4OH (or 10 ml of 6*M* NH_4OH). Centrifuge and discard the supernate (Note 4). Dissolve the precipitate in 1 ml of concd HNO_3 and add 10 ml of saturated $Al(NO_3)_3$.

Step 4. Transfer the solution to a 40-ml extraction vessel containing 10 ml of ethyl acetate. Stir or shake for 1 min and then discard the lower (aqueous) phase. Scrub the organic phase twice with 10-ml portions of saturated $Al(NO_3)_3$ and discard the washings. Back extract the U with two 10-ml portions of water and collect the extracts in a 40-ml centrifuge tube. Discard the organic phase (Note 5).

Step 5. Make the solution basic with 4 ml of concd NH_4OH. Centrifuge and discard the supernate. Dissolve the precipitate in 10 ml of concd HCl.

Step 6. Prepare another resin column as in Step 2. Since HF will be employed in one of the column steps, plug the tip of the column with polypropylene felt. Pre-equilibrate the resin with concd HCl. Successively, pass the following solutions through column and discard all effluents: (a) the solution from Step 5; (b) two 5-ml portions of concd HCl; (c) two 5-ml portions of HCl-HI; (d) two 5-ml portions of $HCl-HNO_3$ (the column will bubble); (e) five 5-ml portions of 5*M* HCl-0.3*M* HF (after the last addition blow the column dry); and (f) 5 ml of absolute ethanol. Elute the U into a 40-ml centrifuge tube with two 5-ml portions of 0.1*M* HCl-0.06*M* HF (Note 6).

Notes

1. The addition of Br_2 ensures that no reducing substances are present; failure to do this may result in a 5% loss of U in Step 2.

2. Higher HCl concentrations, or higher Al concentrations, can cause the anion exchange resin to become clogged during Step 2.

3. Less than 1% of the U is lost in this step. Further column operations, such as those in Step 6, result in additional losses of U. The column step decontaminates the U from all of the Al, ^{24}Na, and the fission products in the (I), (II), and (III) oxidation states. The γ activity from fresh fission products is reduced to a factor of one-third. At this stage, the main contaminants of the U are Mo, Te, Zr, Nb, Np, and Pu.

4. The supernate contains most of the ^{99}Mo.

5. About 3% of the U is lost in this step. Np and Pu follow U in the extraction. The extraction step separates U from most of the fission products; it is a particularly good step for removal of Te. Zr is retained in the organic phase. The U recovered from this step invariably contains some Al from the $Al(NO_3)_3$ reagent. This fact should be kept in mind if the extraction step is used in some other procedure.

6. Overall decontamination factors from Np and Pu are about 10^3. Most of the Pu (> 99%) and about 1.5% of the Np are eluted in the HCl-HI washes. It has been observed that with six 5*M* HCl-0.3*M* HF washes Np is eluted as follows: 60, 31, 6.2, 1.1, 0.3, and 0.7%. For U, the losses with the same reagent are: 0.01, 0.03, 0.2, 0.7, 1.5, and 2%. A sixth wash is, therefore, not prescribed. If the $HCl-HNO_3$ washes are omitted, a Np decontamination of about 10^4 is obtained with the 5*M* HCl-0.3*M* HF washes. In the first two washes with 5*M* HCl-0.3*M* HF, about 15% of a 25-*mg* sample of U is lost; with a tracer U sample, the loss is about 5%. Any Zr and Nb present are eluted in the 5*M* HCl-0.3*M* HF washes. Any Mo still present remains on the column; Mo has its lowest K_d at about 2*M* HCl. Any Te still present follows the U.

November 1968

yttrium

YTTRIUM

R. J. Prestwood

1. Introduction

In the analysis of radioyttrium in fission products, first yttrium fluoride precipitations are carried out in the presence of zirconium holdback carrier. After dissolution of the fluoride and reprecipitation of yttrium as the hydroxide, separation from europium, samarium, and the lighter lanthanides is effectively accomplished by extraction of the element from 0.75*M* hydrochloric acid solution with 0.5*M* HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. Yttrium is finally precipitated as the hydroxide, ignited, and counted as the oxide.

2. Reagents

Y carrier: 10 mg Y/ml (see *Preparation and Standardization of Carrier*)
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
HCl: 0.75*M*; 1.5*M*; 6*M*
HNO_3: 6*M*
HF: concd; 5*M*
H_3BO_3: saturated aqueous solution
NH_4OH: concd
Ethanol: absolute
6% rubber cement in benzene
$(NH_4)_2C_2O_4$: saturated aqueous solution
HDEHP: 0.5*M* solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane. The acid may be obtained from the Victor Chemical Division of the Stauffer Chemical Company, Chicago Heights, Ill. The reported purity of the acid was 94%.

3. Preparation and Standardization of Carrier

Dissolve 12.7 g of Y_2O_3 in 100 ml of concd HCl and dilute the solution to 1 liter.

To 5.0 ml of the carrier solution in a 40-ml Pyrex centrifuge tube, add 20 ml of H_2O, heat to boiling, and add 20 ml of saturated $(NH_4)_2C_2O_4$ with stirring. Heat for 10 min on a steam bath and then cool in an ice bath for 4 min. Centrifuge the $Y_2(C_2O_4)_3$ and decant the supernate. Take up the precipitate in 10 ml of H_2O and filter through a 2", 60° funnel onto a No. 42 Whatman filter paper (9 cm). Wash the precipitate with H_2O, transfer to a weighed Coors 00 porcelain crucible, and ignite at 900° for 1 hr. Cool and weigh as Y_2O_3.

Four standardizations gave results agreeing within 1%.

4. Procedure

Step 1. To the sample in a 40-ml polyethylene, tapered centrifuge tube, add 4 ml of standard Y carrier and make the solution 2 - 4*M* in HNO_3. Add 2 ml of Zr holdback carrier and make the solution 4*M* in HF. Centrifuge the YF_3 precipitate and discard the supernate. Wash the precipitate with 10 ml of 5*M* HF.

Step 2. Dissolve the YF_3 in 2 ml of saturated H_3BO_3 solution and 2 ml of concd HNO_3, and dilute to 10 ml. Add 2 ml of Zr carrier and enough concd HF to make the solution 4*M* with respect to this acid. Centrifuge the YF_3, decant the supernate, and wash the precipitate with 10 ml of 5*M* HF.

Step 3. Dissolve the precipitate in 2 ml of saturated H_3BO_3 solution and 2 ml of concd HNO_3. Dilute the solution to 10 ml and precipitate $Y(OH)_3$ by the addition of concd NH_4OH. Centrifuge and discard the supernate. Wash the precipitate with 30 ml of H_2O.

Step 4. Dissolve the $Y(OH)_3$ in 2.0 ml of 1.5*M* HCl. Transfer the solution with 8 ml of 0.75*M* HCl to a clean 60-ml separatory funnel. Add 10 ml of HDEHP, shake vigorously for 1 min, and discard the aqueous layer. Wash the heptane layer twice with 10-ml portions of 0.75*M* HCl and discard the washings. Back extract the Y into 10 ml of 6*M* HCl and transfer the aqueous layer to a clean polyethylene centrifuge tube and discard the heptane layer. Add an excess of concd NH_4OH to precipitate $Y(OH)_3$, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the washings.

Step 5. Repeat Step 4 (Note).

Step 6. Dissolve the $Y(OH)_3$ in 1 ml of 6*M* HCl, dilute the solution to 20 ml, centrifuge, and transfer the supernate to a clean polyethylene centrifuge tube. Add paper pulp and then an excess of concd NH_4OH to precipitate $Y(OH)_3$. Filter onto a No. 41 H Whatman filter paper (9 cm), and wash the precipitate with H_2O. Ignite at 900° in a Coors 00 porcelain crucible for 20 min. Cool and powder the Y_2O_3 with the fire-polished tip of a glass stirring rod. Transfer the Y_2O_3 with ethanol onto a weighed No. 42 Whatman filter circle, ⅞″ diameter, contained in a ground-off Hirsch funnel-filter chimney setup. Rinse the crucible twice with ethanol and pour through the filter. Dry the Y_2O_3 at 110° for 10 min, cool, and weigh. Place 5 drops of a 6% solution of rubber cement on the sample and permit it to dry at room temperature. Mount on two-sided Scotch tape on an Al plate and cover with Mylar.

Note

It probably is not necessary to repeat Step 4 if ^{91}Y is being determined. The author has found that repetition of this step is desirable when ^{88}Y is determined in the presence of large amounts of fission products.

THE SEPARATION OF STRONTIUM FROM YTTRIUM

R. J. Prestwood

1. Introduction

It is sometimes necessary to separate a strontium isotope which has grown in from a neutron-deficient yttrium parent. In many instances the yttrium parent is also associated with large quantities of fission-product yttrium, e.g., ^{91}Y. The procedure for the analysis assumes that the yttrium has been separated from all other elements.

2. Reagents

Sr carrier: 50 mg $SrCO_3$/2 ml; standardized
Y carrier: 10 mg Y/ml, added as Y_2O_3 in dilute HCl
HCl: concd
HNO_3: fuming; concd
NH_4OH: concd
$(NH_4)_2CO_3$: 10% aqueous solution
Methyl red indicator solution
Ethanol: absolute

3. Preparation and Standardization of Carrier

Preparation and standardization of the Sr carrier was done as described in the Strontium-90 procedure with two modifications: the carrier solution contained 35.85 g of Sr $(NO_3)_2$ per liter and $(NH_4)_2CO_3$, rather than Na_2CO_3, was employed to precipitate $SrCO_3$.

4. Procedure

Step 1. Following the procedure for the decontamination of Y, the Y_2O_3 from ignition is weighed in a crucible, and transferred to a 40-ml glass centrifuge tube. The crucible is then weighed again to obtain the chemical yield in the original Y separation. Add 1 ml of concd HCl and heat gently to effect solution of the Y_2O_3. Add 2.0 ml of Sr carrier, and permit the solution to stand long enough to allow the desired amount of growth of the Sr isotope to be separated (for example, the growth time suitable for ^{87}Sr is about 16 hr). The time of the last $Y(OH)_3$ precipitation prior to ignition to the oxide marks the start of the Sr growth. The volume of solution should be approximately 15 ml.

Step 2. To the solution add 3 drops of methyl red solution and concd NH_4OH until the solution is just neutral. Then add 3 drops of the base in excess. Swirl and place on a steam bath for 2 min. Centrifuge, pour the supernate into a clean centrifuge tube, and record the time to mark the start of decay of the Sr isotope. Dissolve the $Y(OH)_3$ precipitate in a minimum of concd HCl, dilute with H_2O to 10 ml, add 3 drops of methyl red solution, and then an excess of 3 drops of concd NH_4OH. Centrifuge and add the supernate to the one from the first precipitation of $Y(OH)_3$. The total volume should now be about 25 ml.

Step 3. Add concd HCl until the solution is just acidic and then add 10 drops of Y carrier. Make basic with concd NH_4OH and add 3 drops in excess. Place on a steam bath for 2 min, centrifuge, transfer the supernate to a clean centrifuge tube, and discard the precipitate.

Step 4. Repeat Step 3 twice.

Step 5. To the supernate add 1 ml of concd NH_4OH and 5 ml of 10% $(NH_4)_2CO_3$. Place on a steam bath until $SrCO_3$ precipitates. Centrifuge and discard the supernate.

Step 6. Dissolve the precipitate in 1-3 drops of concd HNO_3 and 1 ml of H_2O. Add 30 ml of ice-cold fuming HNO_3. [$Sr(NO_3)_2$ precipitates immediately.] Centrifuge and discard the supernate.

Step 7. Dissolve the $Sr(NO_3)_2$ in 15 ml of H_2O, add 3 drops of methyl red solution, and repeat the $Y(OH)_3$ scavenge (Step 3) three times. (In the first repetition of Step 3, it is not necessary to make the solution acidic with HCl.)

Step 8. Repeat Step 5.

Step 9. To the $SrCO_3$ precipitate add approximately 5 ml of H_2O and with the aid of a stirring rod suspend the solid. Filter onto a tared No. 42 (1 in.) Whatman filter circle. Wash the precipitate thoroughly with H_2O and then with absolute ethanol. Dry at 110° for 5 min, weigh as $SrCO_3$, and mount.

November 1968

THE SEPARATION OF YTTRIUM FROM ZIRCONIUM

R. J. Prestwood. B. P. Bayhurst. and
W. A. Sedlacek

1. Introduction

This procedure is employed for the separation of an yttrium isotope which has grown in from a neutron-deficient zirconium parent. Usually. the zirconium parent is associated with large amounts of fission-product zirconium. The steps in the separation include precipitation of yttrium fluoride. conversion to the hydroxide, adsorption of the yttrium from nitric acid solution onto a cation exchange resin, and elution with α-HIB (α-hydroxyisobutyric acid). The yttrium is finally precipitated as the oxalate and ignited to the oxide.

2. Reagents

Y carrier: 25.0 mg Y_2O_3/2 ml (See YTTRIUM II procedure for preparation and standardization.)
HNO_3: concd
HF: concd
HCl: concd
H_2SO_4: concd
$H_2C_2O_4$: saturated aqueous solution
NaOH: 10*M*
NH_4OH: concd
Ethanol: absolute
0.5*M* α-HIB (α-hydroxyisobutyric acid); adjusted to pH 3.29 (52.05 g of α-HIB plus about 19 ml conc NH_4OH/liter)
Cation exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh (NH_4^+ form)

3. Procedure

Step 1. Dissolve the decontaminated $Zr(OH)_4$ in 3 ml of concd HCl in a 40-ml polyethylene centrifuge tube. Dilute to 20 ml with H_2O, add 2.0 ml of standard Y carrier, and let the solution stand long enough to permit reasonable growth of the Y isotope to be separated.

Step 2. Add 3-4 ml of concd HF. Centrifuge and save the supernate for possible future use.

Step 3. Add 3 ml of 10 *M* NaOH to the precipitate and, with stirring, let stand on a steam bath for 3 min. Dilute to 20 ml with H_2O. heat for a few minutes, centrifuge, and discard the supernate.

Step 4. Add 3 ml of concd HCl to the $Y(OH)_3$ precipitate and, with the aid of 20 ml of H_2O, transfer the solution to a clean 40-ml glass centrifuge tube. Add an excess of concd NH_4OH. centrifuge, and discard the supernate.

Step 5. Add 3 ml of concd H_2SO_4 to the precipitate and boil until SO_3 fumes appear. Cool well and dilute with 20 ml of H_2O. Warm on a steam bath until solution is complete.

Step 6. Add an excess of concd NH_4OH to precipitate $Y(OH)_3$. Centrifuge and discard the supernate. Wash the precipitate with H_2O and discard the wash.

Step 7. Add 8 drops of concd HNO_3 to the precipitate and dilute to about 25 ml with H_2O. Add the equivalent of 1-1.5 ml of the cation exchange resin, stir for about 1 min, centrifuge. and discard the supernate. With the aid of a small amount of H_2O and a transfer pipet. add the resin to the top of a cation exchange column prepared as described in item 7 on p. 58. The top column is then connected by rubber tubing to a reservoir of 0.5 *M* α-HIB, the pH of which has been adjusted to 3.29. Air pressure is maintained at 4.5 psi and the effluent from the column is collected in 13mm by 100mm glass tubes. The tubes are held in an automatic fraction collector which is set for 18-min change intervals. Under the conditions described, each tube collects about 2.5 ml of effluent. The Y appears in tubes number 35 through 65, approximately. The exact locations of the Y are determined by adding a few drops of saturated $H_2C_2O_4$ which precipitates the oxalate. The contents of the 30 or so Y-contained tubes are combined in two 40-ml glass centrifuge tubes and an excess of $H_2C_2O_4$ is added to precipitate the element quantitatively.

The tubes are then heated to coagulate the precipitate. One of the tubes is centrifuged and the supernate discarded. The contents of the second tube are poured into the first which is again centrifuged, and the supernate is discarded. To the precipitate add 6-8 ml of filter paper pulp (see Note 3. p. 144b) and a few drops of $H_2C_2O_4$. Filter onto a No. 40 Whatman filter paper (9 cm), transfer to a Coors 00 porcelain crucible, and ignite to Y_2O_3 at 1000°C for 10 min. Cool. weigh, mount. and count.

November 1970

THE SEPARATION OF YTTRIUM FROM ZIRCONIUM II

R. J. Prestwood, B. P. Bayhurst,
and W. A. Sedlacek

1. Introduction

In this procedure, separation of yttrium from zirconium is accomplished by a number of precipitations of yttrium fluoride followed by the separation of the element on a cation exchange column. The yttrium is eluted from the column by α-HIB (α-hydroxyisobutyric acid) and finally converted to the oxide.

The procedure, like the previous one, was designed to separate an yttrium isotope which had grown in from a neutron-deficient zirconium parent.

2. Reagents

Y carrier: 10 mg Y/ml, standardized (See YTTRIUM procedure.)
Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
HF: concd
HCl: concd
H_2SO_4: concd
NaOH: 10*M*
NH_4OH: concd
Ethanol: absolute
α-HIB (α-hydroxyisobutyric acid), 0.5*M*, adjusted to pH 3.29 (52.05 g of αHIB + about 19 ml concd NH_4OH/liter)
Cation exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh (NH_4^+ form)

3. Procedure

Step 1. Dissolve the decontaminated $Zr(OH)_4$ in 3 ml of concd HCl in a 40-ml polyethylene centrifuge tube. Dilute to 20 ml with H_2O, add 4.0 ml of standard Y carrier, and let the solution stand long enough to permit reasonable growth of the Y isotope to be separated.

Step 2. Add 3-4 ml of concd HF. Centrifuge and save the supernate for possible future use.

Step 3. To the precipitate add 3 ml of 10*M* NaOH and, with stirring, let stand on a steam bath for 3 min. Dilute to 20 ml with H_2O, heat for a few minutes, centrifuge, and discard the supernate.

Step 4. Dissolve the $Y(OH)_3$ precipitate in 3 ml of concd HCl, add 1 ml of Zr holdback carrier, and dilute to 20 ml with H_2O. Add 3-4 ml of concd HF, centrifuge, and discard the supernate.

Step 5. Repeat Steps 3 and 4, and then perform Step 3 again.

Step 6. Dissolve the precipitate in a few drops of HNO_3, dilute with H_2O, and transfer, with the aid of H_2O, to a glass centrifuge tube. The final volume of solution should be about 30 ml. (If there is indication that the $Y(OH)_3$ has not dissolved completely, add a few drops of HNO_3 and heat.) Precipitate $Y(OH)_3$ with an excess of concd NH_4OH, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the wash.

Step 7. Add 6 drops of concd HNO_3 to the precipitate and dilute to about 25 ml with H_2O. Add the equivalent of 1-1.5 ml of the cation exchange resin, stir for about 1 min, centrifuge, and discard the supernate. With the aid of a small amount of H_2O and a transfer pipet, add the resin to the top of a cation exchange column prepared as described in Item 7 on p. 58. The top of the column is then connected by rubber tubing to a reservoir of 0.5*M* α-HIB, the pH of which has been adjusted to 3.29. Air pressure is maintained at 4.5 psi and the effluent from the column is collected in 13 mm by 100 mm glass tubes. The tubes are held in an automatic fraction collector which is set for 18 min change intervals. Under the conditions described, each tube collects about 2.5 ml of effluent. The Y appears in tubes number 32 through 50, approximately. The exact locations of the element are determined by adding a few drops of saturated $H_2C_2O_4$ which precipitates the oxalate. The contents of the 18 or so Y-containing tubes are combined in two 40-ml glass centrifuge tubes and an excess of $H_2C_2O_4$ is added to precipitate the Y quantitatively. The tubes are then heated to coagulate the precipitate. One of the tubes is centrifuged and the supernate discarded. The contents of the second tube are poured into the first which is again centrifuged, and the supernate is discarded. To the precipitate add 6-8 ml of filter paper pulp (see Note 3, p. 144b) and a few drops of $H_2C_2O_4$. Filter onto a No. 40 Whatman filter paper (9 cm), transfer to a Coors 00 porcelain crucible, and ignite to Y_2O_3 at 1000° for 10 min. Cool, weigh, mount, and count.

YTTRIUM II

R. J. Prestwood

The procedure outlined below is an adaptation of lanthanide separations developed by K. Wolfsberg.

1. Introduction

The determination of radioyttrium in fission products as described here basically involves a separation of the element on a cation exchange resin column. The column step is preceded by two fluoride precipitations. The yttrium is eluted from the column by means of α-HIB (α-hydroxyisobutyric acid) and is finally precipitated as the oxalate and ignited to the oxide.

The analysis gives excellent separation of yttrium from the lanthanides cerium through terbium and erbium through lutetium. Separation from dysprosium and holmium is marginal.

2. Reagents

Y carrier: 12.67 mg Y_2O_3/2 ml; standardized
HNO_3: concd
HF: concd
$H_2C_2O_4$: saturated aqueous solution
NaOH: 10*M*
NH_4OH: concd
0.5*M* α-HIB (α-hydroxyisobutyric acid); adjusted to pH 3.29 (52.05 g of α-HIB + about 19 ml concd NH_4OH/liter)
Cation exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh (NH_4^+ form)

3. Preparation and Standardization of Carrier

Dissolve 12.67 g of Y_2O_3 in a minimum of concd HCl and make the solution up to a volume of 2 liters with H_2O.

Transfer 5.0 ml of the carrier solution to a tared Coors 00 porcelain crucible. Evaporate the solution carefully to dryness and ignite the residue at 1000°C for 1 hr. Cool and weigh as Y_2O_3.

4. Procedure

Step 1. Add 2 ml of standard Y carrier to the sample in a 40-ml polyethylene, tapered centrifuge tube and make the solution 2-4*M* in HNO_3 or HCl and 4*M* in HF. Centrifuge the YF_3 precipitate and discard the supernate.

Step 2. Add 2 ml of 10*M* NaOH to the precipitate, stir, and heat on a steam bath for about 2 min. (See NOTES preceding p. 1 of this volume.) Dilute to 20 ml with H_2O and heat for 2-5 min on a steam bath. (This treatment converts YF_3 quantitatively to $Y(OH)_3$.) Centrifuge and discard the supernate.

Step 3. Dissolve the precipitate in a minimum of HNO_3 and repeat the precipitation of YF_3 and its conversion to hydroxide. Centrifuge and discard the supernate.

Step 4. Dissolve the precipitate in a few drops of HNO_3, dilute with H_2O, and transfer, with the aid of H_2O, to a glass centrifuge tube. The final volume of solution should be about 30 ml. (If there is indication that the $Y(OH)_3$ has not dissolved completely, add a few drops of HNO_3 and heat.) Precipitate $Y(OH)_3$ with an excess of concd NH_4OH, centrifuge, and discard the supernate. Wash the precipitate with 30 ml of H_2O and discard the wash.

Step 5. Add 6 drops of concd HNO_3 to the precipitate and dilute to about 25 ml with H_2O. Add the equivalent of 1-1.5 ml of the cation exchange resin, stir for about 1 min, centrifuge, and discard the supernate. With the aid of a small amount of H_2O and a transfer pipet, add the resin to the top of a cation exchange column prepared as described in Item 7 on p. 58. The top of the column is then connected by rubber tubing to a reservoir of 0.5 *M* α-HIB, the pH of which has been adjusted to 3.29. Air pressure is maintained at 4.5 psi and the effluent from the column is collected in 13mm by 100mm glass tubes. The tubes are held in an automatic fraction collector which is set for 18 min change intervals. Under the conditions described, each tube collects about 2.5 ml of effluent. The Y appears in tubes number 32 through 50 approximately.

The exact locations of the element are determined by adding a few drops of saturated $H_2C_2O_4$ which precipitates the oxalate. The contents of the 18 or so Y-containing tubes are combined in two 40-ml glass centrifuge tubes and an excess of $H_2C_2O_4$ is added to precipitate the Y quantitatively. The tubes are then heated to coagulate the precipitate. One of the tubes is centrifuged and the supernate discarded. The contents of the second tube are poured into the first which is again centrifuged, and the supernate is discarded. To the precipitate add 6-8 ml of filter paper pulp (see Note 3, p. 144b) and a few drops of $H_2C_2O_4$. Filter onto a No. 40 Whatman filter paper (9 cm), transfer to a Coors 00 porcelain crucible, and ignite to Y_2O_3 at 1000°C for 10 min. Cool, weigh, mount, and count.

November 1970

YTTRIUM III

R. J. Prestwood

The procedure is adapted from the "Concentration of Transplutonium Actinides from Nevada Soil Samples", by K. Wolfsberg and W. R. Daniels. LA-1721, 3rd Ed., p. 177.

1. Introduction

The analytical scheme described here is designed for the separation of yttrium from large samples (5-10 g) of Nevada soil. It consists primarily of the extraction of the lanthanides and transplutonium actinides from the bulk of the soil sample into tri-*n*-butyl phosphate (TBP) from a highly salted buffered solution. After this is accomplished, the YTTRIUM II procedure is employed.

2. Special Equipment

1-liter extraction vessel (see E. Fig. 1. p. 178)
Stirring motor and stainless steel centrifugal stirrer
pH meter

3. Reagents (in addition to those given in the YTTRIUM II procedure)

Saturated (about 2.5 *M*) $Al(NO_3)_3$ Dissolve 5 lb of Al $(NO)_3 \cdot 9H_2O$ in 1050 ml of H_2O to produce about 2400 ml of solution. Heating speeds up the solution process.
1.9*M* $Al(NO_3)_3$: 3 parts by volume of saturated $Al(NO_3)_3$ and 1 part of H_2O
10*M* NH_4NO_3-0.2*M* HNO_3: Dissolve 7 lb of NH_4NO_3 in H_2O, add 50 ml of concd HNO_3, and dilute to 4 liters with H_2O
4*M* LiOH: aqueous solution
$Al(NO_3)_3 \cdot 9H_2O$: solid
Tri-*n*-butyl phosphate (TBP)
Fe carrier: 10 mg Fe/ml, added as $Fe(NO_3)_3 \cdot 9H_2O$ in very dilute HNO_3
Y carrier: 12.67 mg Y_2O_3/2 ml; standardized (see YTTRIUM II procedure)

4. Procedure

A typical sample consists of about 5 g of dirt which has been dissolved by the regular dissolving procedure, with a slight modification. The final treatment is dilution to 90-100 ml with water rather than with 4*M* HCl.

The analytical procedure can be carried out either with or without Y carrier.

Step 1. To the solution of the sample (60 to 100 ml) add enough solid Al $(NO_3)_3 \cdot 9H_2O$ and 4*M* LiOH to make the pH approximately 0.9-1 and the $Al(NO_3)_3$ concentration about 1.7 *M* The final volume of solution is usually of the order of 200-300 ml.

Step 2. Transfer the solution to the extraction vessel, add 100 ml of TBP, and stir vigorously for about 5 min. Drain the aqueous (lower) phase. To the TBP phase add 200 ml of 1.9*M* $Al(NO_3)_3$, stir for 2-3 min. and discard the aqueous phase. Repeat the wash with Al $(NO_3)_3$ solution. To the TBP phase add 100 ml of 10*M* NH_4NO_3-0.2*M* HNO_3, stir for 2-3 min. and discard the aqueous phase. Repeat the wash.

Step 3. Add 30 ml of H_2O, stir for about 2 min, and drain the H_2O layer into a clean 40-ml glass centrifuge tube. Repeat three additional times, each time draining the aqueous layer into a clean centrifuge tube. (Ninety percent or more of the yttrium activity is found in the first two tubes.)

If Y carrier is used, make each tube basic with concd NH_4OH, heat on a steam bath to coagulate the $Y(OH)_3$ precipitate, centrifuge, and discard the supernate. Dissolve each precipitate in a few drops of HNO_3 and combine the solutions in a clean 40-ml polyethylene centrifuge tube. Make the solution approximately 4*M* in HNO_3 and 3*M* in HF, centrifuge and discard the supernate. Carry out Step 2 and then Step 5 of the YTTRIUM II procedure.

In the event that no Y carrier was employed, add 3 drops of Fe carrier to each tube. Make the first tube basic with concd NH_4OH, heat on a steam bath for a few min. centrifuge, and discard the supernate. Successively add the contents of tubes 2, 3, and 4 to the first tube, each time repeating the precipitation of $Fe(OH)_3$ with NH_4OH. and discard the supernate. (The lanthanides and actinides are carried on the $Fe(OH)_3$.) Dissolve the $Fe(OH)_3$ in excess concd HCl (2-3 ml) and pass the solution through a 8-mm by 2 in. Dowex AG 1-X8, 50-100 mesh, anion resin column to remove Fe. Wash the column twice with 2- or 3-ml portions of concd HCl and collect the eluates in a 40-ml glass centrifuge tube. Evaporate essentially to dryness and proceed to Step 5 of the YTTRIUM procedure. In the absence of Y carrier, the Y activity in the α-HIB elution is confined to 3 to 4 tubes, starting at about tube 30. The exact location (tube numbers) of the Y activity is found by radiation monitoring (^{91}Y from fission products). Carrier may be added to the combined tubes containing the Y activity to precipitate $Y_2(C_2O_4)_3$, or the α-HIB solution may be further processed.

November 1970

zirconium

ZIRCONIUM-95 and ZIRCONIUM-97

C. W. Stanley, G. P. Ford, and E. J. Lang

This procedure is a modification of one described by D. N. Hume, CN-1312 (May 15, 1945).

1. Introduction

In the procedure described below, exchange between carrier and ^{95}Zr and ^{97}Zr is effected by formation of the fluorozirconate complex ZrF_6^{2-}. Rare-earth and alkaline-earth activities are removed by lanthanum fluoride scavenging, and then zirconium is separated by three barium fluorozirconate precipitations. Zirconium is finally precipitated with mandelic acid from hydrochloric acid medium and ignited to the oxide, ZrO_2, in which form it is weighed and counted. The chemical yield is about 75% and a set of eight analyses can be performed in about 7 hr.

The procedure may be used either to assay for ^{95}Zr or ^{97}Zr separately or to determine them together, depending only on counting and analysis of data. To assay for ^{95}Zr the chemistry is not begun until the 17-hr ^{97}Zr had decayed. On completion of the chemical procedure, the ZrO_2 is counted on the top shelf of a β-proportional counter before too much ^{95}Nb has grown in. To analyze for ^{97}Zr, the ZrO_2 is counted through a 112-mg Al/cm² absorber.

To determine both ^{95}Zr and ^{97}Zr in the sample, the ZrO_2 is counted on the top shelf of the β-proportional counter for sufficient time to resolve the decay curve, which has 17-hr (^{97}Zr), 35-day (^{95}Nb), and 65-day (^{95}Zr) components. The decay curve may be analyzed by least squares.

2. Reagents

Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3, standardized
La carrier: 10 mg La/ml, added as $La(NO_2)_3 \cdot 6H_2O$ in H_2O
Nb hold-back carrier: Solution of potassium niobate, CP, 10 g per 100 ml of solution. Source of the niobate: Fansteel Metallurgical Corporation, North Chicago, Ill.
HCl: 1*M*; concd
HNO_3: 1*M*; concd
H_2SO_4: concd
HF: concd
H_3BO_3: saturated aqueous solution
NH_4OH: concd
$NH_2OH \cdot HCl$: solid
$Ba(NO_3)_2$: 50 mg Ba/ml
Cupferron: 6% aqueous solution (freshly prepared and kept in refrigerator)
Mandelic acid: 16% aqueous solution
Aerosol: 1% aqueous solution
Ethanol: 95%

3. Preparation and Standardization of Carrier

Dissolve 30.0 g of $ZrO(NO_3)_2 \cdot 2H_2O$ in H_2O and add sufficient concd HNO_3 to make the solution 1*M* in HNO_3. Filter and make the filtrate up to 1 liter with 1*M* HNO_3.

Pipet 10.0 ml of the solution into a 100-ml beaker, make the solution 2*M* in HCl, and cool in an ice bath. Add a slight excess of 6% cupferron solution and filter. Wash the precipitate with 1*M* HCl containing a little cupferron. (Keep all solutions and the cupferron derivative of Zr cold.) Transfer the precipitate to a porcelain crucible (Coors 1 or 2) and ignite for 1 hr at 600 to 800°. Cool and weigh as ZrO_2.

4. Procedure

Step 1. Place the sample in a 50-ml Lusteroid tube and add 4 ml of Zr carrier. Adjust to 4-5*M* in HNO_3 and to a volume of about 12 ml (Note 1). Add solid $NH_2OH \cdot HCl$ so that the solution is 2-3% in NH_2OH (Note 2). Add 3 drops of potassium niobate carrier and make the solution 5*M* in HF. Heat for 10 min on a steam bath.

Step 2. Add 10 drops of La carrier and centrifuge for a short time. Add another 10 drops of La carrier on top of the previous precipitate and centrifuge thoroughly. Decant the supernate into another Lusteroid tube and discard the precipitate.

Step 3. Repeat Step 2 twice.

Step 4. After a total of six LaF_3 scavengings, add 1 ml of $Ba(NO_3)_2$ solution per 5 ml of the supernate. Let stand for 1 min and centrifuge. Discard the supernate.

Step 5. To the precipitate add 4 ml of saturated H_3BO_3 (Note 3) and slurry. Add 2 ml of concd HNO_3 and slurry again. Add 10 to 12 ml of H_2O and mix well. If the precipitate does not dissolve completely, centrifuge and decant the supernate into another Lusteroid tube. (This step is made easier by heating the H_3BO_3, the HNO_3, and the H_2O on a steam bath prior to their use.)

Step 6. Precipitate $BaZrF_6$ by the addition of 2 ml of $Ba(NO_3)_2$ solution and 2 ml of concd HF. Centrifuge and dissolve as before (Step 5).

Step 7. Precipitate $BaZrF_6$ as before (Step 6) and dissolve the precipitate in 4 ml of saturated H_3BO_3, 4 ml of concd HCl, and 10 ml of H_2O. Add 3 drops of concd H_2SO_4 diluted with 5 ml of H_2O and let stand for 15 min. Add a drop or two of aerosol solution and centrifuge. Transfer the supernate to a 40-ml glass centrifuge tube and discard the $BaSO_4$ precipitate.

Step 8. To the supernate add concd NH_4OH until the solution is basic. Centrifuge down the $Zr(OH)_4$ and discard the supernate. Dissolve the precipitate in 2 ml of concd HCl, 4 ml of saturated H_3BO_3, and 10 ml of H_2O. Centrifuge and, if a precipitate is formed, transfer the supernate to a 40-ml centrifuge tube, discarding the precipitate. Reprecipitate $Zr(OH)_4$ with concd NH_4OH. Centrifuge and dissolve the precipitate in 15 ml of 8*M* HCl. Heat to boiling, add 10 ml of 16% mandelic acid and again bring to a boil. Wait 2-3 min, centrifuge, and discard the supernate. Dissolve the zirconium mandelate in 20 ml of H_2O and 8 drops of concd NH_4OH. (The dissolution of the precipitate takes 2-3 min and may be hastened by the addition of another drop or two of NH_4OH.) Add 3 ml of concd HCl, heat to boiling, and add 10 ml of 16% mandelic acid. Again bring to a boil, wait 2-3 min, centrifuge and discard the supernate.

Step 9. Slurry the precipitate with 10 ml of ethanol and filter onto a No. 42 Whatman filter circle (1″), using a ground-off Hirsch funnel and stainless steel filter chimney. Transfer the paper and precipitate to a porcelain crucible (Coors 0 or 00 and ignite for 1 hr at 800°. Powder the ZrO_2 with the fire-polished end of a stirring rod. Add 2 drops of ethanol, slurry, and grind again. Add 10 ml of ethanol, stir, and filter onto a previously washed, dried, and tared No. 42 Whatman filter circle, using a ground-off Hirsch funnel and stainless steel filter chimney. Wash the ZrO_2 and chimney with 5 ml of ethanol. Dry at 110° for 10 to 15 min, cool, weigh and mount, and count (Note 4).

Notes

1. With this volume of solution, the chemical yield is good since the loss of Zr with the LaF_3 scavengings is small.

2. NH_2OH reduces Np(VI) and Pu(VI) so that these will be carried on the LaF_3 and thus not interfere in the Zr separation. NH_2OH may decompose on the addition of HF, causing the solution to effervesce.

3. H_3BO_3 removes F^- ion by conversion to BF_4^- and thus aids in the dissolution of $BaZrF_6$ by HNO_3.

4. The samples are mounted on Al plates with two-sided Scotch tape and covered with Mylar film. Four drops of rubber cement solution (6 ml of rubber cement dissolved in 100 ml of benzene) are used to keep the ZrO_2 in place.

ZIRCONIUM II

B. P. Bayhurst, R. J. Prestwood, and W. A. Sedlacek

1. Introduction

The procedure was originally devised for the determination of zirconium in large (up to 300 g) amounts of dissolved soil, and the various steps in the analysis are given below in Part I. Zirconium is first extracted from a nitric acid solution of the sample into HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane and is then removed as $BaZrF_6$. Following other decontamination steps, which include precipitations of zirconium hydroxide and a number of scavengings, the zirconium is finally precipitated as the hydroxide. This material can either be ignited to ZrO_2 or milked for daughter products. The chemical yield is about 65%.

Part II is a shortened version of the procedure which is quite satisfactory for samples that do not contain large amounts of metal ion impurities. The chemical yield is over 80%.

2. Reagents

Zr carrier: ≅20 mg ZrO_2/ml, added as $ZrOCl_2 \cdot 8H_2O$, standardized
Ce(IV) carrier: 10 mg Ce/ml, added as $(NH_4)_2Ce(NO_3)_6$ in H_2O
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
Sc carrier: 10 mg Sc/ml, added as $ScCl_3$ in 1*M* HCl
HNO_3: 10*M*
HCl: concd; 6*M*
H_2SO_4: concd
NH_4OH: concd
NH_4HF_2 solution: 4*M* in NH_4HF_2 and 1*M* in HF
$NH_4H_2PO_4$: 1.5*M* aqueous solution
HDEHP solution: 0.5*M* solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane; supplier Stauffer Chemical Company, Chicago Heights, Illinois; reported purity > 94%
$Ba(NO_3)_2$: saturated aqueous solution
$NH_2OH \cdot HCl$: solid
Methyl red indicator solution
Ethanol: absolute

3. Preparation and Standardization of Carrier

Dissolve 52.31 g of $ZrOCl_2 \cdot 8H_2O$ in H_2O and dilute to 1 liter with 0.1*M* HCl. Pipet 5.0 ml of the carrier solution into an ignited and tared Coors O crucible and carefully evaporate to dryness on a hot plate. Ignite at 900° for 30 min. Cool and weigh as ZrO_2.

4. Procedure

Part I: For Large Amounts of Dissolved Soil

Step 1. Add enough Zr carrier to the dissolved sample which is 4-10*M* in HNO_3 to make a total of 30-40 mg of Zr. [The natural Zr content of soils is usually appreciable (about 100-200 ppm). If the chemical yield of the Zr is needed, other similar soil samples are analyzed for the element.] Transfer the sample to an extraction vessel of appropriate size and add a volume of 0.5*M* HDEHP solution in *n*-heptane equivalent to about one-tenth the sample volume. Extract by vigorous stirring or shaking for about 5 min. Large volumes which are difficult to mix intimately require longer extraction times (20-30 min). Allow the layers to separate and transfer the heptane (upper) layer to a clean extraction vessel. Again extract the aqueous layer with HDEHP, but this time with half the previous volume of the reagent. Combine the heptane layers. Shake the heptane solution with about one-fifth its volume of 10*M* HNO_3, add 1 ml of Ce(IV) carrier, and shake again. Add 100-200 mg of $NH_2OH \cdot HCl$, shake, and discard the wash. Repeat the wash with the HNO_3, Ce(IV) carrier, and $NH_2OH \cdot HCl$. Wash the heptane layer with 10*M* HNO_3, and then with portions of 6*M* HCl until the color of Fe^{3+} ion is no longer visible in the aqueous phase. Discard all washes.

Step 2. Transfer the heptane layer to a polyethylene bottle, add about 3.5 ml of NH_4HF_2 solution, 3 ml of concd HCl, and 10 ml of H_2O. Shake. Add 6 ml of saturated $Ba(NO_3)_2$ solution and shake again. Transfer to a 40-ml polyethylene centrifuge tube and centrifuge. Test the supernate with a few drops of $Ba(NO_3)_2$ solution for completeness of Zr precipitation. If complete, discard; if not, add 3 ml of saturated $Ba(NO_3)_2$ solution, heat, and centrifuge again. Discard supernate.

Step 3. Add 2 ml of concd H_2SO_4 to the $BaZrF_6$ precipitate, stir, and place in a steam bath for a few min. Dilute to 20 ml with H_2O and allow to stand until the $BaSO_4$ precipitates. Centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate.

Step 4. Add 5 ml of 1.5*M* $NH_4H_2PO_4$ to the supernate and heat in a steam bath for a few min. Centrifuge and discard the supernate.

Step 5. Add 4 ml of NH_4HF_2 and 5 drops of La carrier. Stir vigorously, dilute to 15 ml with H_2O, and neutralize to a methyl red endpoint with concd NH_4OH. Centrifuge and transfer the supernate containing the Zr to a clean polyethylene centrifuge tube. Discard the LaF_3 precipitate.

Step 6. Add 4 drops of La carrier, stir, centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate.

Step 7. Add 1 ml of Sc carrier, 6-8 ml of concd HCl, and heat on a steam bath until the ScF_3 coagulates. Centrifuge, transfer the supernate to a clean polyethylene centrifuge tube, and discard the precipitate.

Step 8. Add 6 ml of saturated $Ba(NO_3)_2$ solution, place in a steam bath until $BaZrF_6$ coagulates, centrifuge, and discard the supernate.

Step 9. Repeat Step 3.

Step 10. Add 4 drops of La carrier and an excess of concd NH_4OH. Centrifuge and discard the supernate.

Step 11. Repeat Steps 5 (no La carrier), 6, 7, and 8.

Step 12. Repeat Step 3, but transfer the supernate to a clean 40-ml glass centrifuge tube. Add concd NH_4OH to precipitate $Zr(OH)_4$, centrifuge, and discard the supernate.

Step 13. Dissolve the $Zr(OH)_4$ in concd HCl and reprecipitate with concd NH_4OH. The $Zr(OH)_4$ may be used for milking experiments or may be mounted as in Step 14.

Step 14. Dissolve the $Zr(OH)_4$ in concd HCl, add 5 ml of filter paper pulp mixture (see TUNGSTEN II procedure), make ammoniacal with concd NH_4OH, and filter onto a 9 cm, No. 541 Whatman filter. Transfer to a Coors 00 crucible and ignite at 900° for 5-10 min. Powder with a polished glass stirring rod and, using absolute ethanol, transfer to a tared filter circle. Dry at 110°, weigh as ZrO_2, and count.

Part II. For Samples Containing Small Amounts of Metal Ion Impurities

Step 1. To the dissolved sample in an erlenmeyer flask of suitable size, add 2.0 ml of Zr carrier and make the solution about 4*M* in either HNO_3 or HCl. For each 50 ml of sample solution add 10 ml of 1.5*M* $NH_4H_2PO_4$ solution. Heat until the $Zr_3(PO_4)_4$ coagulates, centrifuge, and discard the supernate. (Note.) Start with Step 5 of Part I and complete that procedure.

Note

This is an excellent decontamination step, expecially for the removal of macro quantities of Fe, Al, Ba, Ca, and Mg.

SEPARATION OF MILLIGRAM QUANTITIES OF ZIRCONIUM METAL FROM TEN GRAMS OF MOLYBDENUM METAL

W. R. Daniels

1. Introduction

The sample is first dissolved in 30% H_2O_2 with gentle warming.* Ten grams of molybdenum metal can be dissolved in about 250 ml of the peroxide in about two hours. The zirconium is then extracted into 0.5*M* HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane, the process giving essentially quantitative separation from molybdenum.

2. Reagents

Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3, standardized. (For standardization, see ZIRCONIUM-95 and ZIRCONIUM-97 procedure, LA-1721, 3rd Ed., pp. 163-164.)
HNO_3: 1*M*; concd
HCl: 6*M*; concd
H_2O_2: 30% aqueous solution; high purity
HDEHP solution: 0.5*M* solution of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane; source of acid, Stauffer Chemical Company, Chicago Heights, Illinois.
NH_4HF_2 solution: 4*M* in NH_4HF_2 and 1*M* in HF
$Ba(NO_3)_2$: saturated aqueous solution
H_3BO_3: saturated aqueous solution
NH_4OH: concd

3. Procedure

Step 1. Place 10 g of Mo sample in an 800-ml beaker and add 10 ml of Zr carrier and 200 ml of 30% H_2O_2. Heat on a hot plate at a low setting until solution is complete (about 2 hr). The reaction is vigorous and cooling may be necessary during the solution process. Occasionally, particularly if there are other impurities in the Mo, a slight residue may remain. It may be removed and dissolved in a minimum of aqua regia. The solution is then combined with the other and the mixture cooled.

Step 2. Transfer the solution to a 250-ml glass separatory funnel, add 20 ml of 0.5*M* HDEHP solution in *n*-heptane, shake vigorously for about one-half minute, and transfer the heptane (upper) layer to a 125-ml separatory funnel. Add another 20 ml of HDEHP solution to the aqueous phase, shake again for one-half minute, and combine the heptane layer with the previous one. Discard the aqueous phase. (Note)

Step 3. Wash the heptane solution by shaking it twice with 40-ml portions of 30% H_2O_2, once with 40 ml of 1*M* HNO_3, and once with 40 ml of 6*M* HCl. Discard the washings.

Step 4. †Transfer the heptane layer to a polyethylene bottle of appropriate size and add 3.5 ml of NH_4HF_2 solution, 3 ml of concd HCl, and 10 ml of H_2O. Shake vigorously for 1 min, add 6 ml of saturated $Ba(NO_3)_2$ solution, and shake again for 1 min. Transfer the mixture to polyethylene centrifuge tubes, centrifuge, and test the supernates with $Ba(NO_3)_2$ solution for completeness of precipitation of $BaZrF_6$. When precipitation is complete, discard the supernates, and dissolve the combined $BaZrF_6$ precipitates in 1 ml of saturated H_3BO_3 and 3 ml of concd HNO_3. Dilute to 15 ml with H_2O, precipitate $Zr(OH)_4$ with concd NH_4OH, centrifuge and discard the supernate. Dissolve the precipitate in a minimum of concd HCl and add sufficient H_2O to make the solution 4*M* in the acid. The solution is now ready for analysis for Zr.

Note

The procedure also separates Zr from Nb quite well.

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*This step is based on U.S. Patent 3,519,385 issued to E. C. Hurst and H. B. Hupf on July 7, 1970, and entitled "A Method for Separating Molybdenum from Technetium."

†The NH_4HF_2 treatment and $BaZrF_6$ precipitation were suggested by R. J. Prestwood and B. P. Bayhurst.

THE SEPARATION OF YTTRIUM FROM ZIRCONIUM

R. J. Prestwood, B. P. Bayhurst, and
W. A. Sedlacek

1. Introduction

This procedure was devised to separate an yttrium isotope which had grown in from a neutron-deficient zirconium parent. Usually, the zirconium parent is associated with large amounts of fission-product zirconium. The separation is effected essentially by repeated precipitation of yttrium fluoride.

2. Reagents

Y carrier: 10 mg Y/ml; standardized (See YTTRIUM procedure.)
Zr carrier: 10 mg Zr/ml; added as $ZrO(NO_3)_2 \cdot 2H_2O$ in 1*M* HNO_3
HF: concd
HCl: concd
H_2SO_4: concd
NaOH: 10*M*
NH_4OH: concd
Ethanol: absolute

3. Procedure

Step 1. Dissolve the decontaminated $Zr(OH)_4$ in 3 ml of concd HCl in a 40-ml polyethylene centrifuge tube. Dilute to 20 ml with H_2O, add 4.0 ml of standard Y carrier, and let the solution stand long enough to permit reasonable growth of the Y isotope to be separated.

Step 2. Add 3-4 ml of concd HF. Centrifuge and save the supernate for possible future use.

Step 3. To the precipitate add 3 ml of 10*M* NaOH and, with stirring, let stand on a steam bath for 3 min. Dilute to 20 ml with H_2O, heat for a few minutes, centrifuge, and discard the supernate.

Step 4. Dissolve the $Y(OH)_3$ precipitate in 3 ml of concd HCl, add 1 ml of Zr holdback carrier, and dilute to 20 ml with H_2O. Add 3-4 ml of concd HF, centrifuge, and discard the supernate.

Step 5. Repeat Steps 3 and 4, and then perform Step 3 again.

Step 6. To the $Y(OH)_3$ precipitate add 3 ml of concd HCl and, with the aid of 20 ml of H_2O, transfer the solution to a clean 40-ml glass centrifuge tube. Add 1 ml of Zr carrier and precipitate $Y(OH)_3$ and $Zr(OH)_4$ by the addition of an excess of concd NH_4OH. Centrifuge and discard the supernate.

Step 7. To the precipitate add 3 ml of concd H_2SO_4 and boil until the SO_3 fumes appear. Cool well and dilute to 20 ml with H_2O. Warm on a steam bath until solution is complete and then transfer to a clean 40-ml polyethylene centrifuge tube.

Step 8. Add 3-4 ml of concd HF, centrifuge, and discard the supernate.

Step 9. Repeat Step 3.

Step 10. Dissolve the $Y(OH)_3$ precipitate in 3 ml of concd HCl and dilute to 20 ml with H_2O. Add 3-4 ml of concd HF, centrifuge, and discard the supernate.

Step 11. Repeat Steps 3 and 10, and then perform Step 3 again.

Step 12. Dissolve the $Y(OH)_3$ in 3 ml of concd HCl, dilute to 20 ml with water, and precipitate the hydroxide with an excess of concd NH_4OH. Centrifuge and discard the supernate.

Step 13. Repeat Step 12.

Step 14. Dissolve the precipitate in 3 ml of concd HCl, dilute to 20 ml with H_2O, and add 5 ml of paper pulp mixture (see TUNGSTEN II procedure). Make the solution basic with concd NH_4OH and filter onto a 9-cm No. 541 Whatman filter paper. Transfer the precipitate and filter paper to a Coors 00 crucible and ignite for 5-10 min at 900°. Cool, powder gently with a polished glass rod, and transfer with the use of absolute ethanol onto a tared No. 42 Whatman filter circle. Weigh as Y_2O_3.

November 1968

COMBINED PROCEDURES

COMBINED PROCEDURES

SEPARATION OF GERMANIUM AND ARSENIC FROM A FISSION-PRODUCT SOLUTION

R. J. Prestwood

1. Introduction

It is sometimes necessary to isolate both radioarsenic and radiogermanium from the same sample. The separation and isolation of these elements is readily accomplished by utilizing the difference in ease of extraction of germanium (IV) and arsenic (III) iodides into chloroform in the presence of hydriodic acid.

2. Reagents

As (V) carrier: see Arsenic procedure
Ge (IV) carrier: see Germanium procedure
HCl: concd
H_2SO_4: 1*M*
$HClO_4$: 4*M*
HI: 47%
Chloroform

3. Procedure

Step 1. To the sample (Note 1) in a 125-ml separatory funnel, add 2.0 ml of As (V) carrier (Note 2) and 2.0 ml of Ge (IV) carrier. (See As and Ge procedures for the preparation of these carriers.) Make the solution 3*M* in HCl in a total volume of 10 to 15 ml. Add 3 to 4 ml of 47% HI and 20 ml of $CHCl_3$ and shake thoroughly. (The As is completely extracted into the $CHCl_3$ and the Ge remains in the aqueous phase.) Drain the $CHCl_3$ layer into a clean separatory funnel. To the aqueous layer add an additional 10 ml of $CHCl_3$ and extract again. Combine the $CHCl_3$ extracts. The $CHCl_3$ extracts containing AsI_3 can be treated as in Step 4 and the following steps of the As procedure or can be shaken with 10 ml of 1*M* H_2SO_4. If treatment with 1*M* H_2SO_4 is carried out, discard the $CHCl_3$ layer and drain the aqueous layer into a 40-ml conical centrifuge tube. Add 10 ml of concd HCl and pass in H_2S. Centrifuge, discard the supernate, and continue from Step 2 of the As procedure. The latter is safer from the standpoint of decontamination.

Step 2. To the original aqueous layer (which contains the Ge) add 20 ml of 47% HI and extract with 20 ml of $CHCl_3$. Drain the $CHCl_3$ layer (which now contains the Ge as GeI_4) into a clean separatory funnel. Extract the aqueous layer again with 10 ml of $CHCl_3$ and combine the extracts.

Step 3. Wash the $CHCl_3$ containing the GeI_4 with 10 ml of 4*M* $HClO_4$. (This removes any AsI_3 which is present, with a loss of 1% or less of GeI_4.) Drain the $CHCl_3$ layer into a clean separatory funnel and discard the aqueous phase. The $CHCl_3$ containing the GeI_4 is now treated as in Steps 6-10 of the Ge procedure.

Notes

1. The original solution must not contain appreciable quantities of NO_3^- ion, otherwise some of the HI which is added will be oxidized to I_2.

2. As (V) carrier is used so that reduction to the tripositive state may promote exchange between active and inactive species.

Alternative Procedure

1. Introduction

Arsenic (III) is separated from germanium (IV) by precipitation as the sulfide in hydrochloric acid medium containing fluoride ion, the latter strongly complexing germanium (IV) as GeF_6^{2-} and preventing its precipitation. Prior to the sulfide precipitation arsenic (V) is reduced to the tripositive state by means of iodide ion.

2. Reagents

As (V) carrier: see Arsenic procedure
Ge (IV) carrier: see Germanium procedure
HCl: 6*M*

HF: concd
H_3BO_3: saturated solution
H_2S: gas
NaI: solid
Aerosol: 0.1% in H_2O

3. Procedure

Step 1. To the fission-product solution in a 40-ml conical centrifuge tube, add 2.0 ml each of As (V) and Ge (IV) carriers. Make the solution 3 to 5*M* in HCl and the volume to 10 to 15 ml. (Nitrate ion should be absent, or present only in small amount.) Add 50-100 mg of NaI and warm the solution gently. Add 10 drops of concd HF and saturate the solution with H_2S until the As_2S_3 precipitate has coagulated (time required is 3-5 min). Centrifuge and pour the supernate through a No. 40 Whatman filter in a 2″, 60° funnel into a clean centrifuge tube. The As_2S_3 precipitate is then treated as described beginning with Step 2 of the Arsenic procedure.

Step 2. To the filtrate containing the germanium, add 5-6 ml of saturated H_3BO_3 and saturate with H_2S. Centrifuge the GeS_2 precipitate and discard the supernate. The GeS_2 is then treated as in Step 6 of the Germanium procedure up through the point at which the germanate solution is made acid with $HClO_4$. Then the regular Germanium procedure is carried out in its entirety (except for the addition of Ge (IV) carrier).

SEPARATION OF RADIOACTIVE SPECIES OF GOLD, ARSENIC, NICKEL, AND SCANDIUM

J-11 Radiochemistry Group

1. Introduction

In the separation of radioactive gold, arsenic, nickel, and scandium, gold is first removed by extraction into ethyl acetate from a solution 1-4*M* in HCl. Arsenic is then precipitated as the sulfide from hydrochloric acid solution. Following this, scandium is thrown down as the hydroxide by means of ammonia water; nickel remains in solution.

2. Procedure

Step 1. To an aliquot of the sample in a 40-ml centrifuge tube, add 20 mg of Au, As, and Ni carriers and 15 mg of Sc carrier. Adjust the solution to an HCl concentration of 1 to 4*M*. Add a volume of ethyl acetate equal to that of the solution and stir with a motor-driven stirrer. By means of a pipet transfer the ethyl acetate phase containing the Au to a 125-ml erlenmeyer flask. Evaporate the ethyl acetate on a steam bath, and for analysis of Au start with Step 1 of the standard gold procedure, except do not add additional Au carrier.

Step 2. To the aqueous phase from Step 1, add 8 ml of concd HCl and pass in H_2S until As_2S_3 precipitation is complete. Heat on a steam bath for 5 min. Centrifuge and transfer the supernate to a clean centrifuge tube. For analysis of As in the sulfide precipitate, proceed from Step 2 of the standard arsenic procedure.

Step 3. Boil the supernate to remove H_2S and add concd NH_4OH dropwise until the solution is basic and $Sc(OH)_3$ completely precipitated. Centrifuge and transfer the supernate to a clean centrifuge tube. For determination of Sc in the hydroxide precipitate, begin with Step 2 of the standard scandium procedure.

Step 4. For analysis of Ni in the supernate, start with Step 1 of the standard nickel procedure, except do not add additional Ni carrier or NH_4OH.

SEPARATION OF RADIOACTIVE SPECIES OF ARSENIC, GERMANIUM, AND GALLIUM

R. J. Prestwood

1. Introduction

In the separation of radioactive arsenic, germanium, and gallium, tripositive arsenic is first removed as the sulfide in the presence of fluoride ion which serves to complex and keep germanium in solution. The fluoro complex is then destroyed and germanium separated as the sulfide. Gallium is finally precipitated by means of oxine (8-hydroxyquinoline).

2. Procedure

Step 1. To an aliquot of the sample (Note 1) in a 125-ml erlenmeyer flask, add 5 mg of Ga carrier as $GaCl_3$ in 0.1*M* HCl (5.0 mg Ga^{3+} is equivalent to 36.0 mg Ga oxinate) and 20 mg each of Ge and As carriers (see standard Ge and As procedures). Add 2 ml of concd HNO_3 and 1 to 2 ml of concd $HClO_4$ and evaporate to copious $HClO_4$ fumes (Note 2).

Step 2. Adjust the volume of solution to about 15 ml with 4*M* HCl. Add 10 drops of concd HF and about 100 mg of solid NaI and bubble in H_2S for several minutes, warming if necessary to coagulate the As_2S_3 precipitate. Transfer to a 40-ml centrifuge tube, centrifuge, and filter through a No. 40 Whatman filter paper, using a 2", 60° funnel, into a clean 125-ml erlenmeyer flask. Wash the precipitate with a small amount of H_2O, collecting the washings in the clean erlenmeyer flask. To determine As in the sulfide precipitate proceed with Steps 9 and 10 of the standard As procedure.

Step 3. To the solution in the erlenmeyer flask, add 5 ml of saturated H_3BO_3 and bubble in H_2S until GeS_2 has been completely precipitated. (If the precipitate is not pure white, all the As has not been removed.) Filter onto a weighed No. 42 Whatman filter circle (7/8" dia), using a ground-off Hirsch funnel-filter chimney setup. Transfer the filtrate to a clean 125-ml erlenmeyer flask. The GeS_2 precipitate is washed with a small amount of H_2O and then with absolute methanol. The precipitate is dried in an oven at 110°, cooled, weighed as GeS_2, mounted, and counted.

Step 4. To the filtrate containing the Ga, add 1 drop of phenolphthalein indicator, just neutralize with NH_4OH, and then add 10 drops of saturated aqueous tartaric acid. Heat to boiling and add dropwise about 1.5 ml of 5% oxine in 2*M* $HC_2H_3O_2$. Transfer to a clean 40-ml centrifuge tube, centrifuge, and discard the supernate. Dissolve the precipitate in about 3*M* HCl by heating. Centrifuge and transfer the supernate to a clean centrifuge tube (Note 3). Neutralize and precipitate the oxinate as above. Filter while hot onto a weighed No. 42 Whatman filter circle. Wash the precipitate with water and then with ether. Dry in oven at 110°, cool, weigh as the oxinate, mount, and count.

Notes

1. This procedure was developed primarily for (n,p) and (n,α) reactions on As. Therefore only Ge and Ga carriers were added. However, the procedure is generally applicable for these three elements.

2. With this treatment, GeO_2 precipitates. However, the Ge is brought back into solution in Step 2.

3. This centrifugation is performed merely to clean up the solution if it is necessary.

SEPARATION OF RADIOACTIVE SPECIES OF THALLIUM, ARSENIC, AND SCANDIUM

J-11 Radiochemistry Group

1. Introduction

In the separation of radioactive thallium, arsenic, and scandium, thallium is first removed as the iodide, after reduction to the +1 state. Arsenic is then precipitated as the sulfide from hydrochloric acid medium, the scandium remaining in solution.

2. Procedure

Step 1. To an aliquot of the sample in a 40-ml centrifuge tube, add 20 mg each of Tl, As, and Sc carriers and dilute the solution to about 30 ml with H_2O. Add a few drops of saturated aqueous SO_2 solution and then about 2 g of solid NaI. Stir well and centrifuge. Transfer the supernate to a 125-ml erlenmeyer flask.

Step 2. Add 1 ml of 6*M* HNO_3 to the TlI precipitate and heat over an open flame until all I_2 color has disappeared. Add 1 ml each of Te carrier and concd $HClO_4$ and evaporate to heavy fumes over an open flame. Add 5 ml of concd HCl and again evaporate to heavy fumes. Add 15 ml of 3*M* HCl and approximately 0.5 g of $N_2H_4 \cdot H_2SO_4$ and heat to boiling. Add 1 ml of saturated aqueous SO_2 and continue to boil while making three or four successive additions of SO_2-H_2O. When the Te has been completely precipitated (the supernate is essentially water-white), filter into a 125-ml erlenmeyer flask through a 2", 60° funnel using No. 40 Whatman filter paper. Wash the centrifuge tube and the precipitate with dilute SO_2-H_2O and discard the precipitate. For the determination of Tl in the filtrate, start with Step 2 of the standard thallium procedure.

Step 3. Evaporate the solution containing the As and Sc to about 20 ml and transfer to a clean centrifuge tube. Add 5 to 10 ml of concd HCl and pass in H_2S until precipitation of As_2S_3 is complete. Centrifuge and transfer the supernate to a clean centrifuge tube. For analysis of As in the precipitate, start with Step 2 of the standard arsenic procedure.

Step 4. Boil the supernate to expel H_2S and excess HCl. Precipitate $Sc(OH)_3$ by making the solution basic by the dropwise addition of concd NH_4OH. Centrifuge and discard the supernate. To determine Sc start with Step 2 of the standard scandium procedure.

SEPARATION OF URANIUM AND PLUTONIUM FROM LARGE SAMPLES OF UNDERGROUND DEBRIS

H. L. Smith and G. W. Knobeloch

1. Introduction

This procedure was devised for the separation of uranium and plutonium from solutions of high ionic strength obtained by dissolving underground debris. In the separation these elements are oxidized to the +6 state and extracted into diethyl ether from a solution saturated with ammonium nitrate and approximately 1*M* in HNO_3. The extraction is an excellent decontamination step since very little else is taken into the ether. The uranium and plutonium are back-extracted into water and the aqueous solution is evaporated to dryness. Then the procedure for the *Preparation of Uranium and Plutonium for Mass Spectrometric Analysis* is performed.

2. Reagents

HNO_3: fuming
$HClO_4$: concd
NH_4NO_3: solid
Diethyl ether: reagent grade

3. Procedure

Step 1. Transfer the sample in HCl and $HClO_4$ to an erlenmeyer flask of suitable size. Add a volume of fuming HNO_3 equivalent to about 10% of the sample volume and heat carefully on a hot plate for several hours, finally boiling to dryness to drive off all the $HClO_4$.

Step 2. Add approximately 50 ml of fuming HNO_3 and evaporate to dryness again. Heat the sides of the flask to expel any residual $HClO_4$.

Step 3. Dissolve the residue in about 40 ml of fuming HNO_3, warming if necessary. Transfer the solution to 40-ml centrifuge tubes and centrifuge out any insoluble residue (Note 1).

Step 4. Transfer the supernate to a 1-liter beaker, dilute with H_2O to make the solution about 2*M* in HNO_3, and add solid NH_4NO_3 until the solution is saturated with that reagent. Transfer to a separatory funnel and extract twice with equal volume portions of diethyl ether (Note 2). Combine the ether phases in a clean separatory funnel.

Step 5. Back-extract with three portions of H_2O, each equivalent in volume to about 10% that of the combined ether phases. Combine the aqueous extracts and go to Step 1 of the procedure for *Preparation of Uranium and Plutonium for Mass Spectrometric Analysis*, p. 171.

Notes

1. If the residue shows no activity, it may be discarded. If, however, it contains a substantial fraction of the total activity in the sample, an attempt should be made to bring the active substances into solution. Heating with 6*M* NaOH, followed by acidification with HNO_3, will usually remove most of the activity from the precipitate.
2. Isopropyl ether is not satisfactory as an extractant.

PREPARATION OF URANIUM AND PLUTONIUM FOR MASS SPECTROMETRIC ANALYSIS

H. L. Smith

1. Introduction

This is a one-column procedure which will separate into successive fractions the lanthanides-actinides in their +3 oxidation state, plutonium, neptunium, and uranium from as much as one gram of dissolved underground debris. The yield of each fraction is at least 70%. The lanthanide-actinide fraction may be processed separately for americium and curium; the uranium and plutonium fractions are treated to destroy any organic matter and are then subjected to mass spectrometric analysis without further purification.

Radiochemical decontamination is unnecessary in preparing heavy elements for mass spectrometric analysis unless the contaminants have interfering masses. The main requirements for a mass spectrometer sample are relative freedom from massive contaminants so that the sample can be evaporated on the filament (a small rhenium strip), and freedom from organic material which produces a peak at every mass position. Iron is the major component of underground debris that is adsorbed from concentrated HCl on a strongly basic anion resin (AG 1-X8 or -X10) along with uranium, plutonium, and neptunium. The iron may be eluted with 8*M* HNO_3, without much loss of the heavy elements.* After the iron is removed, the column is reconverted to the chloride form and the plutonium is reduced to the +3 state and eluted with a mixture of HI-HCl (see the plutonium procedure). This reagent seems to reduce the uranium slowly to the +4 state, in which form it acts similarly to neptunium and would be eluted with 5*M* HCl. In order to elute all the uranium in one place, 9*M* HCl containing a little H_2O_2 is passed through the column; this treatment apparently oxidizes the uranium to the +6 condition but not the neptunium. The neptunium is then removed with 5*M* HCl and the uranium with water.

There are no precipitation steps in the procedure, and all reagents are easily purified by distillation to eliminate contamination by uranium.

2. Reagents

HCl: concd; 5*M* (6*M* HCl distilled in quartz and either saturated with HCl gas or diluted with H_2O)

HNO_3: 8*M* (sp gr approx 1.26) (fuming HNO_3 redistilled in quartz and diluted)

HI-HCl: 1 vol of concd HI to 9 of concd HCl, each reagent distilled in quartz, freshly prepared

H_2O_2-HCl: 1 vol of 30% H_2O_2 to 20 of 9*M* HCl, prepared immediately before use

$HClO_4$: concd

Anion resin column: Dowex AG 1-X8, 100-200 mesh, 8 mm i.d. x 10 cm long, washed with H_2O and then with concd HCl

3. Procedure

Step 1. Boil the sample to dryness in a 125-ml erlenmeyer flask and then slurry with 10 ml of concd HCl. Transfer to a 40-ml glass centrifuge tube, centrifuge, and save the supernate. Wash the precipitate with concd HCl and add to the previous supernate. (The precipitate consists primarily of Na and Mg chlorides.)

Step 2. Pass the solution through the anion resin column and collect the eluate in a clean 125-ml erlenmeyer flask. Wash the original flask with 4 ml of concd HCl and add to the column. Combine the eluate with that previously collected. The combined eluates contain the lanthanides, actinides, Th, Al, and metal ions of +2 charge. Boil to dryness and process for specific element desired.

Step 3. Allow two 4-ml portions of 8*M* HNO_3 to pass through the column with no additional pressure. Continue to pass through 4-ml portions of HNO_3 until the eluate is no longer yellow, but use no more HNO_3 than necessary since loss of U may occur if large volumes are used. Uranium has a K_d of 10 in 8*M* HNO_3. Discard all eluates.

Step 4. Pass two or three 4-ml portions of concd HCl through the column under pressure, until the eluate is no longer yellow. Discard the eluate.

Step 5. Allow first 7 ml and then 3 ml of HI-HCl reagent to pass through the column, collecting the eluate in a Vycor tube. Evaporate the solution to dryness, then treat the residue with a few drops each of fuming HNO_3 and $HClO_4$, take up in a small volume of 2*M* HNO_3 for mass spectrometric analysis. If the U is very much more abundant than the Pu, additional chemistry must be done on the Pu. Proceed as in the Note.

Step 6. Pass 6 ml of concd HCl through the column and discard the eluate.

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*Faris, J. P., and Buchanan, R. F., Anal. Chem., 36, 1157 (1964).

Step 7. Prepare the H_2O_2-HCl reagent and allow two 4-ml portions to pass through the column. Iodine is removed from the column, which becomes decolorized. The process is accompanied by vigorous bubbling.

Step 8. Under gravity, pass through the column two 4-ml portions of 5*M* HCl. The eluate contains most of the Np, which may be combined with the Pu and allowed to decay, if advisable.

Step 9. Elute the U with two 4-ml portions of H_2O, collecting the eluate in a Vycor or quartz tube. Fume to dryness with HNO_3 and $HClO_4$, and take up the residue in a suitable volume of 2*M* HNO_3 for mass spectrometric analysis.

Note

After evaporating the Pu fraction to dryness in Step 5, add a few drops of HNO_3 and evaporate to dryness again. Dissolve the residue in 10 drops of concd HCl and do a scaled-down version of the anion column, using an anion column 3 mm i.d. x 4 cm long. Allow the 10 drops of concd HCl to run through the column; wash tube and column with 5 drops concd HCl. If there is an appreciable amount of Fe on the top of the column, introduce two successive 200 μl portions of 8*M* HNO_3 to elute the Fe, then reconvert the column to the Cl^- form with 1-2 ml of concd HCl. Elute the Pu with HI-HCl reagent, evaporate to dryness, add 3 drops each of fuming HNO_3 and $HClO_4$, and evaporate to dryness again. Dissolve the Pu in a suitable volume of 2*M* HNO_3 for delivery to the mass spectrometer.

ADDENDUM TO THE PROCEDURE ON PREPARATION OF URANIUM AND PLUTONIUM FOR MASS SPECTROMETRIC ANALYSIS

F. O. Lawrence and D. C. Hoffman

For the extraction of plutonium from large volumes of solution (greater than 30 ml) carry out the procedure given in THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION II (p. 94C), omitting the addition of Pu tracer. Then perform Steps 2 through 9 of the PLUTONIUM procedure (p. 91), but collect the final eluate in a 40-ml glass centrifuge tube. Add 3 drops of concd HCl and evaporate to dryness. Repeat twice. Add 3 drops each of fuming HNO_3 and concd $HClO_4$. Evaporate to dryness and take up the residue in a suitable volume of 2*M* HNO_3 for mass spectrometric analysis.

B. PREPARATION OF PLUTONIUM FOR MASS SPECTROMETRIC ANALYSIS

F. O. Lawrence and D. C. Hoffman

For the extraction of plutonium from large volumes of solution (greater than 30 ml), carry out the procedure given in THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION. II (p. 94 C), omitting the addition of Pu tracer. Then perform Steps 2 through 9 of the PLUTONIUM procedure (p. 91), but collect the final eluate in a 40-ml Vycor centrifuge tube. Evaporate the solution to dryness and take up the residue in a suitable volume (10-20 λ) of 0.2*M* HNO_3 for mass spectrometric analysis.

GROUP SEPARATIONS OF THE HEAVY ELEMENTS

AMERICIUM AND CURIUM

H. L. Smith

1. Introduction

The procedures given below are suitable for the isolation of americium and curium from a solution containing uranium, plutonium, thorium, and fission products obtained from underground soil debris. The regular procedure, which is employed for relatively small samples of up to several grams, consists of a LaF_3-$La(OH)_3$ cycle to separate the actinides and lanthanides from massive contaminants, anion exchange steps to remove plutonium, adsorption of the lanthanides and remaining actinides on a cation exchange column, and elution of the latter elements with alcoholic HCl.

The alternative procedure is somewhat more laborious, since a number of extractions are performed, but may be used for larger soil samples. This procedure utilizes, in modified form, the extractions with di-(2-ethylhexyl) orthophosphoric acid (HDEHP) described by Peppard and coworkers (D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, *J. Inorg. Nucl. Chem.*, **4**, 334 (1957); D. F. Peppard, G. W. Mason, and S. W. Moline, ibid., **5**, 141 (1957). Unpurified HDEHP is used directly as obtained from the Stauffer Chemical Company, Chicago Heights, Ill.

2. (a) Reagents for Regular Procedure

^{243}Am tracer: standardized by counting a known volume or known weight of solution

^{244}Cm tracer: standardized by counting a known volume or known weight of solution

La carrier: 5 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O

HCl: 1*M*; 2*M*; 6*M*; concd

HNO_3: concd

HF: concd

H_3BO_3: saturated aqueous solution

HF-HCl wash solution: 1*M* in each component

NH_4OH: concd

Alcoholic HCl solution: 20% by volume of ethanol in concd HCl, saturated with gaseous HCl

Anion exchange resin: AG 1-X10, 100-200 mesh

Cation exchange resin: AG 50-X4, finer than 400 mesh; tested to make certain that it is suitable for the separation of the lanthanides from the actinides

Methyl red indicator solution

(b) Additional Reagents for Alternative Procedure

HCl: 0.05*M*; 5*M*

HDEHP solution: 0.5*M* solution of the unpurified material in heptane

Heptane

Diethyl ether: pre-equilibrated with 6*M* HCl

3. (a) Regular Procedure (Note)

Step 1. To an aliquot of sample in a 125-ml erlenmeyer flask, add amounts of ^{243}Am and ^{244}Cm tracers approximately equal to those of the ^{241}Am and ^{242}Cm expected. Adjust the acid concentration to about 1*M*, adding some HCl if none is present. Allow the sample to stand on a steam bath overnight.

Step 2. Boil the sample to dryness and then add 10 ml of concd HCl and 3 drops of concd HNO_3. Pass the solution through an AG 1-X10 anion resin column, 8 mm x 8 cm, collecting the effluent in a clean 40-ml long-taper glass centrifuge tube. Wash the column with 4-5 ml of concd HCl and combine the effluent with the previous one.

Step 3. Boil the sample to dryness. Take up the residue in 5 ml of 2*M* HCl, add 4 drops of La carrier, and make the solution 2*M* in HF. Allow the mixture to stand for 5 min, then centrifuge, and discard the supernate. Wash the precipitate with 2 ml of HF-HCl solution and discard the washings.

Step 4. Dissolve the precipitate by slurrying with 1-4 drops of saturated H_3BO_3 solution and adding an equal volume of concd HCl. Dilute to 4-5 ml with H_2O and precipitate $La(OH)_3$ by the dropwise addition of concd NH_4OH. Let the mixture stand on a steam bath for 5 min, centrifuge, and discard the supernate. Wash the precipitate with several ml of H_2O, heat on a steam bath, centrifuge, and discard the supernate.

Step 5. Dissolve the precipitate in 5 ml of

2*M* HCl, make the solution 2*M* in HF, let it stand for 5 min, centrifuge, and discard the supernate. Wash the precipitate with HF-HCl wash solution, centrifuge, and discard the supernate. Dissolve the precipitate by slurrying with 1 drop of H_3BO_3 solution, then 10 drops of concd HCl and approximately 0.02 ml of concd HNO_3.

Step 6. Pass the solution through two successive AG 1-X10 *anion* resin columns, 3 mm x 3 cm. Collect the effluent in a clean 40-ml long-taper centrifuge tube. Wash the original centrifuge tube and the resin columns successively with 3 drops of concd HCl and combine the washings with the previous effluent. Discard the resin columns. Evaporate the solution to dryness.

Step 7. Dissolve the residue in 1 drop (50 μl) of concd HCl and transfer the solution to an AG 50-X4 cation resin column, 3 mm x 10 cm, which has previously been washed with alcoholic HCl solution. Pass the solution into the resin column by means of a slight air pressure. Add another drop of concd HCl to the centrifuge tube and transfer to the resin column, again passing the solution into the column. Elute the Am-Cm with alcoholic HCl, collecting fractions of about 0.1 ml each in 0.5-ml beakers or planchets.

Step 8. Dry the fractions and locate the Am-Cm peak by α-counting. Transfer the activities to a plating cell with 6*M* HCl. Add 5 drops of methyl red indicator solution, make basic with concd NH_4OH, and then make barely acidic with 1*M* HCl. Electroplate onto a 1" Pt disk for 20 min at 2 amp. (Details for the electrodeposition of actinide elements at tracer concentrations have been described by R. F. Mitchell, *Anal. Chem.*, **32**, 326 (1960)). The ^{241}Am and ^{242}Cm are related to the ^{243}Am and ^{244}Cm tracers by α-pulse analysis.

(b) Alternative Procedure

Step 1. Same as in regular procedure.

Step 2. Boil the sample to dryness and dissolve the residue in 10 ml of 0.05*M* HCl. Ignore any insoluble residue. Transfer the solution (and any residue) to a 60-ml separatory funnel or 40-ml conical centrifuge tube, add 10 ml of HDEHP solution, and mix the phases thoroughly. Separate the phases and discard the aqueous (lower) layer.

Step 3. If there is a precipitate in the HDEHP phase, filter it through dry filter paper. Wash the HDEHP phase with three 10-ml portions of 0.05*M* HCl and discard the washes. The Am and Cm activities are now in the organic phase.

Step 4. Back-extract the Am and Cm with 10 ml of 5*M* HCl and discard the HDEHP. Wash the HCl phase with 10 ml of heptane and discard the washings.

Step 5. Add sufficient concd HCl to make the solution 6-7*M* in acid. Extract twice with volumes of diethyl ether equal to that of the acid solution. (The ether should have been pre-equilibrated with 6*M* HCl.) Discard the ether washings.

Step 6. Cautiously evaporate the aqueous solution to dryness; at first the evaporation should be carried out on a steam bath in a large enough vessel to prevent loss of sample through any violent ebullition of the ether.

Step 7. Add 4 drops of La carrier and proceed with Steps 5-7 of the regular procedure.

Note

The regular procedure will ordinarily handle the solution obtained from 0.1-0.3 g of soil. If it is necessary to take a larger sample or if the sample contains a large amount of calcium, the alternative procedure should be used. The extractions may be performed in separatory funnels or in centrifuge tubes, mixing the phases with transfer pipets and then centrifuging to separate the phases. The volumes may, of course, be increased as desired for larger amounts of sample.

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GROUP SEPARATIONS OF THE HEAVY ELEMENTS

SEPARATION OF AMERICIUM AND CURIUM FROM TRANSCURIUM ELEMENTS

H. L. Smith

1. Introduction

This procedure is based primarily on information contained in ORNL-3273, *Separation of Transplutonium Elements by Phosphonate Extraction*, by R. D. Baybarz. The separation of americium and curium from the transcurium elements depends upon the preferential adsorption of the latter from dilute hydrochloric acid solution onto a Kel-F column treated with 2-ethylhexylphenylphosphonate [2-EH(ϕP)A].

2. Reagents

$HClO_4$: concd

HCl: 4*M*; 1*M*

2-EH(ϕP)A: 1*M* in *n*-heptane [29 ml of 2-EH(ϕP)A made up to 100 ml with *n*-heptane].

Kel-F: Kel-F 6051 (from Applied Science Laboratories, State College, Pa.). Slurry in *n*-heptane.

Column: 3.5 mm × 5 cm; plugged with glass wool or sand and filled with the Kel-F slurry in heptane; treated prior to use with 5 ml of 2-EH(ϕP)A reagent and 5 ml of 1*M* HCl.

3. Preparation of 2-Ethylhexylphenylphosphonate [2-EH(ϕP)A] from Di-2-Ethylhexylphenylphosphonate

To a 2-liter quartz erlenmeyer flask add 200 g of di-2-ethylhexylphenylphosphonate (source: Victor Chemical Division, Stauffer Chemical Company, Chicago Heights, Ill.), 60 g of NaOH, and 500 ml of H_2O. Add a Teflon stirring bar, cover with a watch glass, and heat on a heater-stirrer such as a Thermo-mix) for about 72 hr. The saponification reaction is complete when the volume of the organic phase has increased by about 50%. Remove the watch glass and maintain the heating to permit the 2-ethylhexanol formed to evaporate; add H_2O, as necessary, to prevent bumping. When all the 2-ethylhexanol has evaporated, the monoester will be dissolved in the sodium hydroxide solution, leaving a single phase. Acidify the solution with HCl, decant the organic (upper) phase into centrifuge cones, and centrifuge to remove any solid contaminant. The compound may be used without further purification.

4. Procedure

Step 1. Evaporate the sample to dryness with concd $HClO_4$.

Step 2. Take up the sample in 100λ of 1*M* HCl and allow the solution to run into the column. Wash the sample tube with 50λ of 1*M* HCl and add the washings to the column (Note 1). Add several ml of 1*M* HCl to the column reservoir.

Step 3. Collect ten 1-FCV (Note 2) increments; these will contain Am and Cm. Cf starts eluting at the 10-FCV point.

Step 4. Remove what remains of the 1*M* HCl in the reservoir and add 4*M* HCl to the column. The next four FCV's of eluate should contain 99% of the Cf.

Notes

1. Am and Cm start eluting immediately.

2. FCV denotes "free column volume," i.e., the liquid in the column. For the size column employed in the procedure, this amounts to 6-8 drops.

A RAPID SEPARATION OF THE TRANSCURIUM ELEMENTS FROM NEVADA SOIL SAMPLES

W. G. Warren and D. C. Hoffman

1. Introduction

This procedure is suitable for the separation of the transcurium elements from solutions of high ionic strength obtained by dissolving Nevada soil samples.

Following an initial concentration of the heavy elements by precipitation as hydroxides, the lanthanides and actinides are extracted into di-(2-ethylhexyl) orthophosphoric acid (HDEHP) from a solution of pH 1.2-2.0. They are then recovered as an aqueous phase after esterification of the HDEHP with decanol. A number of the lighter actinides are removed by adsorption on an anion exchange resin column from 10*M* HCl, this step being preceded and followed by hydroxide precipitations. The lanthanides and the remaining actinides are further purified by adsorption on a cation exchange resin column and subsequent elution with 6*M* HCl. After another hydroxide precipitation, the transcurium actinides are separated from the lanthanides and americium and curium by elution from a cation exchange resin column with an ethanol-hydrochloric acid solution.

2. Reagents

HCl: concd; 10*M*; 6*M*; 0.1*M*
HNO_3: concd; 0.05*M*
La carrier: 10 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O
NH_3: gas
NH_4OH: 6*M*
Ethanol-hydrochloric acid solution (EtOH-HCl): 20% absolute ethanol - 80% concd HCl (by volume) saturated with HCl gas at room temperature.
0.5*M* HDEHP: Dilute 645 g of di-(2-ethylhexyl) orthophosphoric acid (about 94% purity) to 4 liters with heptane.
n-Heptane
Decanol
Anion exchange resin: Bio-Rad AG 1-X8, 100-200 mesh; slurry in H_2O.
Cation exchange resin: Bio-Rad AG 50W-X4, 200-400 mesh; slurry in H_2O.
Cation exchange resin: Bio-Rad AG 50W-X4, minus 400 mesh; slurry in H_2O.

3. Procedure

Step 1. Pass gaseous NH_3 into a solution of the sample in a 40-ml long-taper Pyrex centrifuge tube until precipitation is complete. Centrifuge, wash the hydroxide precipitate with water containing a small amount of NH_4OH. Centrifuge and discard the washings. Repeat the washing process.

Step 2. Dissolve the precipitate in 20-25 drops of concd HNO_3 and adjust the pH to 1.2-2.0 by the dropwise addition of 6*M* NH_4OH. Dilute to about 10 ml with H_2O and add the solution to a 60-ml separatory funnel. Add 10 ml of 0.5*M* HDEHP and shake the mixture gently for about 1 min. Allow the two phases to separate and drain the aqueous (lower) layer into a clean separatory funnel. Add 5 ml of HDEHP to the aqueous phase, shake gently, discard aqueous phase, and combine the two HDEHP phases. Wash the combined HDEHP phases four times with 15-ml portions of 0.05*M* HNO_3, discarding the aqueous phase in each case.

Step 3. Drain the HDEHP phase into a 125-ml erlenmeyer flask and add 7.5 ml of concd HCl and 4 ml of decanol. Boil with magnetic stirring on a hot plate for 15 min to convert the HDEHP to the decanol ester. (Add more HCl, if necessary.) Add the mixture to a 60-ml separatory funnel, allow the two phases to separate, and transfer the HCl layer (top) into a clean separatory funnel. To the ester phase, add about 4 ml of 6*M* HCl. Shake and allow the two layers to separate. Combine the HCl fraction with that previously isolated and discard the ester fraction. Wash the combined HCl fractions with 11.5 ml of heptane, discard the washings, and transfer the HCl fraction to a clean 40-ml long-taper Pyrex centrifuge tube.

Step 4. Add 1 drop of La carrier if necessary and bubble in NH_3 gas until precipitation is complete. Centrifuge and discard the supernate. Wash the precipitate with about 2 ml of H_2O, centrifuge, and discard the washings.

Step 5. Dissolve the hyroxide precipitate in 1 ml of 10*M* HCl and 1 drop of concd HNO_3, and pass the solution through a Bio-Rad AG 1-X8, 100-200 mesh, anion exchange resin bed 2.5 cm long in a column 8 cm × 1 cm o.d. (The column is prepared for use by washing with three separate mixtures of 1 ml of 10*M* HCl containing 1 drop of concd HNO_3). Collect the eluate in a 40-ml long-taper Pyrex centrifuge tube.

Step 6. Dilute the eluate to about 8 ml with H_2O. Bubble in NH_3 gas until precipitation is complete, centrifuge, and discard the supernate. Wash the precipitate with about 2 ml of H_2O, centrifuge, and discard the washings.

Step 7. Dissolve the precipitate in 1 drop of concd HCl, dilute the solution to 12 ml with H_2O, and pass it through a Bio-Rad AG 50W-X4, 200-400 mesh, cation exchange resin column of the same dimensions as the anion column. Wash the centrifuge tube with two 1-ml portions of 0.1*M* HCl and add the washings to the column. Elute with three 1-ml portions of 6*M* HCl, catching the eluates in a clean long-taper centrifuge tube.

Step 8. Bubble NH_3 gas into the combined eluates to precipitate hydroxides. Centrifuge and discard the supernate. Wash the precipitate with 1 ml of water, centrifuge, and discard the washings.

Step 9. To the precipitate, add 1-2 drops of EtOH-HCl solution, and add the resulting solution to the top of a Bio-Rad AG 50W-X4, minus 400 mesh, cation exchange resin column, 12-14 cm × 3 mm i.d., with a tip giving about 120 drops per ml. Add 1 or 2 drops of EtOH-HCl solution to the centrifuge tube, centrifuge, and add the solution to the top of the resin column. Repeat the EtOH-HCl wash of the centrifuge tube. Add 3 ml of EtOH-HCl solution to the resin column and apply sufficient pressure (2-3 psi) to give a drop rate of about 40 sec per drop. Collect dropwise in 1-ml beakers or on platinum plates. Dry these fractions and α count. The transcurium elements elute first, followed by Am and Cm (about 1.9 column volumes after the free column volume; see Fig. 2 or 3, Trans Pu procedure in this section).

After identification of the Am-Cm peak, combine all the previous fractions for the transcurium sample. Evaporate to dryness at about 120° in an oil bath with an air jet. Take up in 1 ml concd HCl and proceed as in Step 2 of the procedure for *Electrodeposition of Plutonium for Fission Counting*.

CONCENTRATION OF TRANSPLUTONIUM ACTINIDES FROM NEVADA SOIL SAMPLES

K. Wolfsberg and W. R. Daniels

1. Introduction

In the procedure below, lanthanides and transplutonium actinides are extracted into tri-n-butylphosphate (TBP) from large volumes of solutions of low acidity which are heavily salted with $Al(NO_3)_3$. Following extraction, the TBP is scrubbed with an NH_4NO_3 solution and the elements are back-extracted into water. To keep the volumes of TBP and water reasonable, a relatively small volume of TBP is repeatedly brought into contact with small volumes of feed solutions. This is done at the expense of about 10% of the yield of product.

The actinides and lanthanides are extracted into di-2-ethylhexyl ortho-phosphoric acid (HDEHP) from a solution of low acidity, and are recovered in an aqueous phase after boiling the HDEHP with decanol. Further decontamination is accomplished by passage of a concentrated hydrochloric acid solution of these elements through an anion exchange resin column.

The actinides are then separated from the lanthanides by elution from a cation exchange resin column with an ethanol-hydrochloric acid (EtOH-HCl) solution. A separation between the transcurium actinides and americium and curium can be made on this column.

The purpose of the procedure is to concentrate the tripositive actinide elements produced in undergorund detonations. One may encounter samples of a range of weights, and it is necessary to use equipment of various sizes to accommodate the different samples. This procedure is written for samples weighing approximately 250 g.

2. Special Equipment

Extraction vessels (Fig. 1): TBP vessel, 25 cm long x 12.5 cm o.d.,; HDEHP vessel, 20 cm long x 9 cm o.d.
Transfer vessels (Fig. 1): TBP vessel, 20 cm long x 9 cm o.d.; HDEHP vessel, 20 cm long x 7 cm o.d.
Stainless steel centrifugal stirrers
Stirring motors
Teflon glands (source: Arthur F. Smith Co., 201 S.W. 12th Avenue, Pompano Beach, FL)
Separatory funnels, with Teflon stopcocks
Bottles: 2 liter; 4 liter; 9 liter
pH meter with combination glass and Ag-AgCl probe (Beckman 39030)
Rotary flash evaporator, with a water-cooled condenser
Vacuum pump
Vinyl tubing
Teflon stopcocks
Solenoid valves
Switches for operating solenoid valves
Dispensing burets, with Teflon stopcocks
Glass columns for anion exchange resin: 8 cm long x 10 mm o.d.
Glass columns for cation exchange resin: 38 cm long x 9 mm o.d., with standard taper joint at top
Glass wool: used as plugs in tips of all columns

3. Special Reagents

$Al(NO_3)_3$: saturated, approximately 2.5*M*, made by dissolving 5 lb of $Al(NO_3)_3 \cdot 9H_2O$ in 1050 ml of H_2O to produce about 2400 ml of solution; 1.9*M*, made by diluting 3 volumes of saturated $Al(NO_3)_3$ with 1 volume of H_2O
NH_4NO_3-HNO_3 reagents: 10*M* in NH_4NO_3 and 0.2*M* in HNO_3, made by dissolving 7 lb of NH_4NO_3 in H_2O, adding 50 ml of concd HNO_3, and diluting to 4 liters with H_2O; 0.65*M* NH_4NO_3-0.05*M* HNO_3, made by making 28 ml concd HNO_3 and 570 ml saturated NH_4NO_3 up to 9 liters with H_2O
LiOH: 4*M*, made by dissolving 671 g of $LiOH \cdot H_2O$ in H_2O and diluting to 4 liters
Buffer solution: pH 1, for standardizing pH meter
HCl: 10*M*
Tri-*n*-butylphosphate (TBP)
HDEHP: 0.5*M*, made by diluting 645 g of di-2-ethylhexyl orthophosphoric acid (about 94% purity) to 4 liters with *n*-heptane
Decanol
HCl-HF: 4*M* in each acid
Te(IV) carrier: 10 mg Te/ml, added as Na_2TeO_3 in 6*M* HCl
Te(VI) carrier: 10 mg Te/ml, added as $Na_2TeO_4 \cdot 2H_2O$ in 3*M* HCl
$NH_2OH \cdot HCl$: solid
n-Heptane
EtOH-HCl: 20% absolute ethanol-80% concd HCl-0.1% $NH_2OH \cdot HCl$, saturated with HCl gas
Anion exchange resin: Bio-Rad AG 1-X10, 100-200 mesh
Cation exchange resin: Bio-Rad AG 50W-X4, (H^+ form), nominal minus 400 mesh, batch selected to give satisfactory separation)

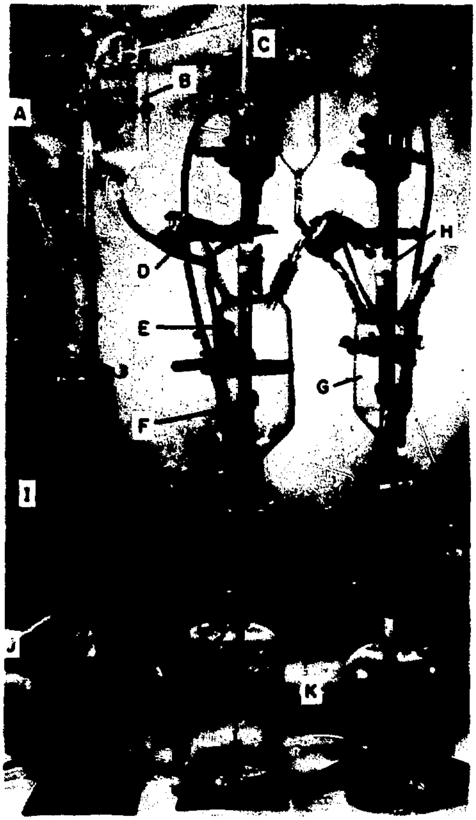

Fig. 1. TBP and HDEHP extraction apparatus, showing: A, lines to $Al(NO_3)_3$, NH_4NO_3, and HNO_3 wash solutions and to H_2O; B, TBP transfer vessel; C, HDEHP transfer vessel; D, typical solenoid valve; E, TBP mixing vessel; F, stainless steel centrifugal stirrer; G, HDEHP mixing vessel; H, Teflon gland; I, air pressure line; J, feed solution vessel; K, vessels for receiving waste solutions or product.

4. Dissolving Procedure (Brief Summary)

The ground-up sample is dissolved in a mixture of concd HNO_3, $HClO_4$, and HF, and boiled to fumes of $HClO_4$ after each addition. The solution is made 4*M* in HNO_3, then 4*M* in HF, and the insoluble fluorides (including the tripositive actinide fluorides) are filtered. The precipitate is washed twice with 4*M* HF-4*M* HNO_3, dissolved in concd $HClO_4$, and diluted to make a solution 1 to 2*M* in $HClO_4$.

5. Procedure

Step 1. To the sample, add enough saturated $Al(NO_3)_3$ and 4*M* LiOH to make the solution 1.7-1.9*M* in $Al(NO_3)_3$ and about 0.1*M* in H^+ (pH 1) This is generally accomplished by pouring the sample into a 9-liter bottle and adding about 4000 ml of saturated $Al(NO_3)_3$ and then 4*M* LiOH slowly from a dispensing buret while stirring the solution vigorously. Stop the addition of LiOH when the indicated pH is 0.9-1.1. Adjust the $Al(NO_3)_3$ concentration up to 1.7-1.9*M* (about three-fourths saturated, Note 1).

Step 2. Pour 1 kg of TBP into the extraction vessel. Then add 500 ml of 1.9*M* $Al(NO_3)_3$ and stir for 2 min. Draw off the preequilibrating $Al(NO_3)_3$ wash (the lower phase) and discard. (Fig. 1 shows the extraction apparatus. In general, solutions are transferred by means of air pressure, pumps, or gravity flow.)

Step 3. Drain 500 ml of feed (the solution from Step 1) from the transfer vessel into the TBP in the extraction vessel. As soon as the addition of feed is begun, start the stirrer and continue stirring for 3 min. After the phases separate, drain off the aqueous phase and discard. Repeat the procedure with successive 500-ml portions of feed; the total number of such contacts is not to exceed about 20 (Note 2).

Step 4. Wash the TBP phase with one 500-ml portion of 1.9*M* $Al(NO_3)_3$, stirring for 2 min, and then with five 500-ml portions of 10*M* NH_4NO_3-0.2*M* HNO_3, stirring for 5 min each time. Discard the washings.

Step 5. Back extract the lanthanides and actinides with three 500-ml portions of H_2O, stirring for 2 min. Collect the aqueous phases in a plastic bottle.

Step 6. Concentrate the back-extracted sample to about 200 ml by boiling in an appropriate glass vessel or by using a rotary flash evaporator with a water-cooled condenser. (The concentration step should be terminated before any material comes out of solution.) Pass the concentrated solution through a filter to remove any remaining TBP.

Step 7. To the concentrated solution, slowly add concd NH_4OH until a pH of 1.5-1.75 is reached. Transfer the solution directly to the HDEHP extraction vessel, add 200 ml of 0.5*M* HDEHP, and stir for about 2 min. After the phases separate, drain the aqueous phase and discard.

Wash the HDEHP phase with three 200-ml portions of 0.65*M* NH_4NO_3-0.05*M* HNO_3 drained from the transfer vessel into the extraction vessel. Discard the washings.

Step 8. Drain the HDEHP phase into a 1-liter erlenmeyer flask, and add 100 ml of decanol, 50 ml of concd HCl, and a magnetic stirring bar. Heat the flask on a stirrer-hot plate, and gently boil the mixture for 15-20 min. If necessary, add additional concd HCl to maintain an aqueous phase.

Step 9. Pour the hot mixture into a separatory funnel. Drain the aqueous phase into a second separatory funnel. Extract the organic phase with 25 ml of 6*M* HCl, and add the aqueous phase to the second separatory funnel. Scrub the combined aqueous phase with about 10 ml of heptane and discard the heptane. Boil the sample in an erlenmeyer flask almost to dryness.

Step 10. Fill a glass column (see Special Equipment) with anion exchange resin and pretreat the resin with about 15-20 ml of 10*M* HCl containing 2 drops of concd HNO_3. Dissolve the sample from Step 9 in 10 ml of concd HCl. Add 1 drop each of concd HNO_3, Te(IV) carrier, and Te(VI) carrier and warm gently. Pass the solution through the resin column (about 1 drop per sec), collecting the eluate in an erlenmeyer flask. Rinse the column twice with 5-ml portions of 10*M* HCl containing 1 drop of concd HNO_3, collecting the eluates in the same flask.

Step 11. Boil the sample to about 2 ml; dilute with H_2O to about 20 ml. Add 4 ml concd HF, centrifuge, and discard the supernate. Wash the precipitate with 20 ml of 4*M* HCl-4*M* HF and discard the wash. Dissolve the precipitate in 1-2 ml each of saturated H_3BO_3 and concd HCl, dilute the solution to 15 ml with H_2O, and make the solution basic with 6*M* NaOH. Centrifuge and discard the supernate. Wash the precipitate with H_2O and discard the washings. Dissolve the precipitate in 1-2 ml of concd HCl, dilute to about 20 ml with H_2O, and add about 100 mg of $NH_2OH{\cdot}HCl$. Warm the solution gently, make basic with concd NH_4OH, and centrifuge. Discard the supernate, wash the precipitate with H_2O, and discard the washings.

Step 12. Dissolve the precipitate in 3-5 drops of concd HCl and dilute to about 30 ml with H_2O. Add the equivalent of 2 ml of centrifuged cation exchange resin in water-slurry form, stir for 1 min and centrifuge. Discard the supernate and wash the resin twice with H_2O.

Step 13. About 1 day prior to the next step, prepare the cation exchange column. Treat the cation exchange resin (a quantity equivalent to a resin volume of 25 ml when centrifuged from a slurry in H_2O) twice with 50 ml of concd HCl and three times with EtOH-HCl solution. This treatment is performed in a Buchner funnel with a medium frit, and the resin is sucked dry between treatments. Slurry the resin with EtOH-HCl, and transfer to a glass column for cation exchange, filling to a height of about 32 cm under 10 psi of air pressure. Pass EtOH-HCl through the column under 10 psi of pressure until the column is ready to be used. Just prior to use, reduce the height of the resin to 30 cm.

Step 14. Slurry the resin from Step 12 in 1-2 ml of H_2O and transfer to the top of the cation exchange column. Complete the transfer with a small H_2O wash. Allow the resin to settle and draw off the H_2O. Start eluting with EtOH-HCl under about 10 psi air pressure, at a flow rate of about 0.1 ± 0.015 ml/min. The elution curve shown in Fig. 2 is reproducible on a volume basis. The free column volume is about 6 ml. The valley between Am-Cm (there is essentially no separation between these elements with the eluent used) and Lu occurs between 32 and 40 ml. The method of collecting fractions (by volume, time, or drop number), counting them, and combining them will vary with the nature and intent of the purification (Note 3).

Step 15. After combining the desired fractions in a centrifuge tube, boil almost to dryness. Add 2 ml of 0.05*M* HNO_3. Heat if necessary to ensure dissolution. Add 2 ml of 0.5*M* HDEHP, stopper the tube, and shake for 2 min. Centrifuge briefly, and withdraw and discard the lower phase. Wash the organic phase with 2 ml of 0.05*M* HNO_3 in a similar manner. Transfer the HDEHP to a 100-ml round-bottomed flask containing several glass beads, add 1 ml of decanol and 1 ml of concd HCl, and boil for 15 min. Add 0.5 ml concd HCl several times to insure the presence of an aqueous phase. Transfer the mixture to a centrifuge tube, centrifuge, and transfer the aqueous phase to a new centrifuge tube. To the HDEHP phase add 1 ml of 6*M* HCl and stir. Centrifuge, draw off the aqueous phase, and combine it with the previous aqueous phase. Scrub the combined aqueous phase with 2 ml of heptane, centrifuge, and transfer the aqueous phase to a quartz or Vycor vessel. Boil the sample to dryness. Add a few drops of concd HNO_3 and concd $HClO_4$ and fume the sample dry again.

At this point, there is generally no visible material present. If there is any residue, a further separation can be performed by the precipitation of the actinides with NaOH in the presence of Fe(III) carrier. The iron is then removed on a small anion exchange resin column by a procedure like that described in Step 10. Another possible

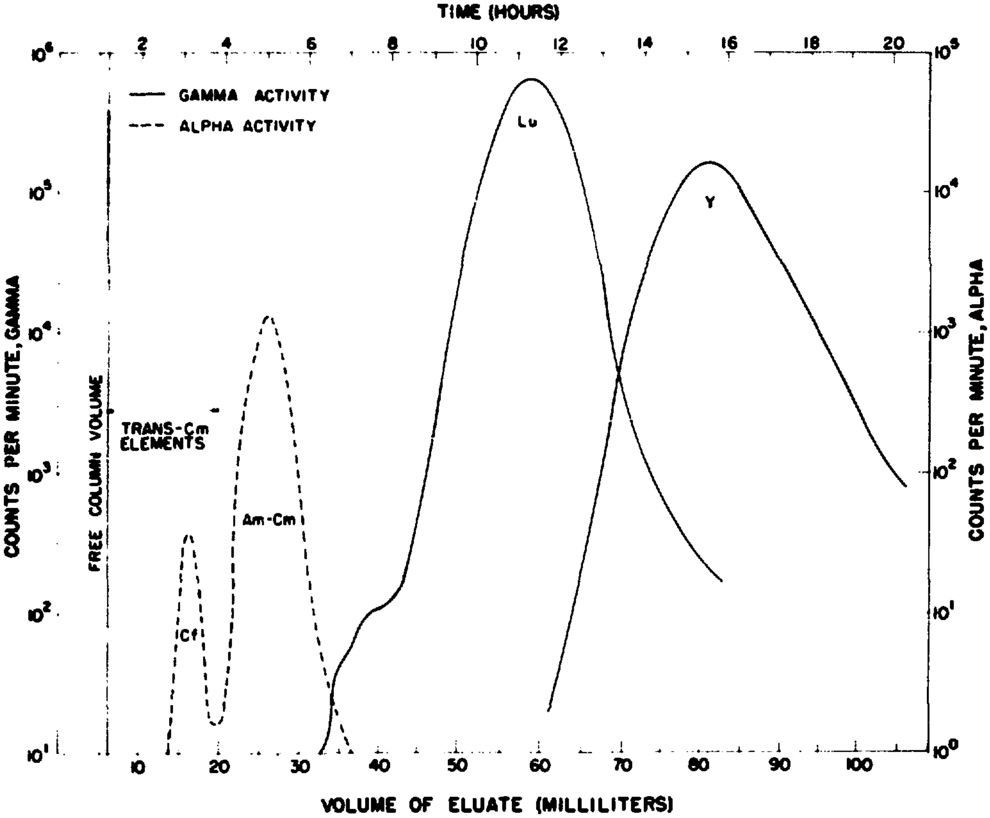

Fig. 2. Elution curve for transplutonium actinides.

purification can be accomplished by adsorbing the actinides on a small Dowex 50 cation exchange column from a solution 0.1*M* in HCl, washing with the same acid, and stripping with 6*M* HCl.

Notes

1. The pH is not necessarily a real indication of the hydrogen-ion concentration in the concentrated solution, but it seems as good a way as any for arriving at a reproducible starting solution of low hydrogen-ion concentration.

2. An oversimplified way to look at this step is to treat each contact as an individual organic-aqueous system with an apparent distribution coefficient, K(o/a), between 20 and 40. With relative volumes of organic phase to aqueous phase of 2 to 1, between 97.5 and 98.8% of the actinides in the extraction vessel will be in the organic phase after each extraction. The following table shows how the over-all yield would drop as a function of the number of extractions.

Number of Extractions	% Extracted	
	K = 40	K = 20
1	99	98
5	96	93
10	94	87
15	91	82
20	88	78

In fact, the distribution coefficient probably changes with the number of contacts. The TBP becomes more viscous, and phase separation times increase with the number of contacts.

A value of 20-40 for the apparent K is probably fairly representative of Y. For Nd, the value is between 10 and 20. In general, the value of K (and recovery) varies in the order: Nd Eu Am Y Tb Cf Fm. This difference might result in about a 10% fractionation of the actinides.

3. The Am(+Cm) fraction from the column is suitable for the determination of Am by gamma counting. Step 15 can be omitted.

SEPARATION OF TRACE AMOUNTS OF TRANSPLUTONIUM ELEMENTS FROM FISSION PRODUCTS

D. C. Hoffman, J. W. Barnes,
H. L. Smith, W. R. Daniels

1. Introduction

The following procedure was devised to separate the transplutonium elements from day-old fission product samples containing 10^{15} to 10^{16} fissions. These elements are carried with yttrium or lanthanum fluoride and hydroxide precipitates which are subsequently dissolved and the HCl solutions passed through several anion resin columns to remove U, Np, Pu, and most of the remaining fission products (in particular, Zr and Te). An ethanol-HCl elution from a cation resin column[1] is used to remove the lanthanides. Final separation of the individual transplutonics is accomplished by elution from a cation resin column with ammonium α-hydroxyisobutyrate.[2]

2. Reagents

Y carrier: 10 mg Y/ml, added as $Y(NO_3)_3 \cdot 6H_2O$ in H_2O

La carrier: 5 mg La/ml, added as $La(NO_3)_3 \cdot 6H_2O$ in H_2O

Zr carrier: 10 mg Zr/ml, added as $ZrO(NO_3)_2$ in 1*M* HNO_3

Te carrier: 10 mg Te/ml, added as Na_2TeO_3 in 1*M* HCl

Sr carrier: 10 mg Sr/ml, added as $Sr(NO_3)_2 \cdot 4H_2O$ in H_2O

NH_4OH: concd

HCl: 0.1*M*; 0.5*M*; 3*M*; concd

10*M* solution I: 0.1 ml concd HNO_3 per 15 ml 10*M* HCl

HF: concd

HF-HNO_3: equal volumes of 2*M* solutions

HF-HCl: solution 0.006*M* in HF and 0.1*M* in HCl

HNO_3: concd

H_3BO_3: saturated solution

Phenolphthalein indicator solution

Ethanol-HCl eluent: 20% ethanol-80% concd HCl (by volume) saturated with HCl gas at room temperature. (If a cold solution is passed through a resin column, bubbles will form, disturbing the resin bed.) This solution should be prepared just prior to use.

Ammonium α-hydroxy isobutyrate eluent: The stock solution of α-hydroxy isobutyric acid is prepared (usually 0.5 or 1*M*), and kept refrigerated to inhibit possible mold formation. The compound may be obtained from Fairmount Chemical Company, Newark, N. J. From the stock solution, small quantities are withdrawn and partially neutralized with ammonium hydroxide to obtain eluent of the desired pH. The pH of the eluent should be chosen so as to elute the activities in a convenient volume, considering the column volume and the speed with which the separation must be made. If 0.5*M* isobutyrate is used, the peak position in FCV (free column volume units) may be estimated directly from Table I and Fig. 1. If stronger or weaker acid is used, the pH corresponding to a given anion activity (as shown in Fig. 2) must be calculated, using the relationship

TABLE I
Separation Factors with Ammonium α-hydroxy isobutyrate
(Cm = 1.0)

Element	Relative Peak Position
Es	0.13
Cf	0.19
Bk	0.37
Cm	1.00
Am	1.39
Lu	0.011
Yb	0.016
Tm	0.022
Er	—
Ho	0.039
Y	0.069
Dy	0.076
Tb	0.14
Gd	0.22
Eu	0.34
Sm	0.7
Pm	1.1
Nd	2.3
Ce	3.4

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[1] Thompson, Harvey, Choppin, and Seaborg, J. Am. Chem. Soc., 76, 6229 (1954).

[2] H. L. Smith and D. C. Hoffman, J. Inorg. and Nuclear Chem., 3, 243 (1956).

$$K_1 = \frac{(H^+)(A^-)}{(HA)} \sim \frac{10^{-pH}(A^-)}{(M_{HA}) - (A^-)}$$

or

$$10^{-pH} \sim \frac{K_1\ [(M_{HA}) - (A^-)]}{(A^-)}$$

where

$K_1 \sim 10^{-3.9}$

(M_{HA}) = molarity of α-hydroxy isobutyric acid

(A^-) = anion activity (isobutyrate) read from Fig. 2.

Anion exchange resin: Bio-Rad AG 1-X10, 100-200 mesh for large columns and 200-400 mesh for the small column (Note 1). The resin is stored as a slurry in H_2O.

Cation exchange resins: Bio-Rad AG 50-X4, 400 mesh or finer. The resin is prepared by washing in succession with H_2O, NH_4OH, H_2O and three times with concd HCl. For the ethanol-HCl columns, the resin is stored as an HCl slurry. For the slurry in H_2O, the resin should be washed an additional three times with H_2O.

Dowex 50 cation resin is used for the butyrate column, from 2-8% DVB (% divinylbenzene which is proportional to cross-linkage), depending on individual preference and what is available. Time required for attainment of equilibrium and volume required for elution increase with percentage DVB of the resin. The data in the accompanying graphs were taken with 4% resin. The resin should be very fine, 400 mesh or finer; or if wet-graded, that fraction which settles at a rate of 0.1-1.5 cm/min. If the resin has not been specially treated by the supplier, it should be washed thoroughly with 6*M* ammonium thiocyanate, 6*M* ammonium hydroxide, water, and hydrochloric acid, then stored as the ammonium form in water. (If no resin can be found that achieves a good separation at room temperature, 12% DVB Dowex 50 may usually be used successfully with a column heated to 80-90°.)

Ion exchange columns: The ion exchange columns are fabricated by fusing a length of glass tubing to a centrifuge cone and drawing out the tip to make 6-cm × 2-mm i.d. glass columns, 14-cm × 2-mm i.d. glass columns, 12-cm × 8-mm i.d. glass columns. The column tip is plugged with glass wool or sand. A slurry of resin is introduced and allowed to settle, and the supernate discarded. The resin is washed by passing several ml of eluent through the column. (Just prior to use, the butyrate column is slurried with the eluent and allowed settle again.) A uniformly deposited bed of resin, free from air bubbles or channels, is essential to a successful elution. The free column volume is approximately equal to half the apparent volume of the resin bed.

4. Procedure

Step 1. To an aliquot of the sample in a 40-ml centrifuge tube, add 2 drops each Zr, Te and Sr carriers and 1 drop of Y carrier. Using phenolphthalein indicator, add NH_4OH to precipitate the $Y(OH)_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5-1.0 ml H_2O.

Step 2. Dissolve the precipitate in a minimum amount of 3*M* HCl and transfer to a polyethylene test tube. Add 2 drops concd HF per ml of solution. (If the solution contains a large amount of Fe or U add HF to decolorize the solution, then 2 drops per ml in addition.) Let the solution stand for 5 min, centrifuge, discard the supernate, and wash the precipitate with 0.5 ml of the 2*M* HF-2*M* HNO_3 solution.

Step 3. Dissolve the fluoride precipitate by adding 1 drop saturated H_3BO_3, stirring, and then adding 2 ml concd HCl. Transfer the solution to a 40-ml glass centrifuge tube. Add 2 drops Sr carrier and then boil the solution briefly. Precipitate the $Y(OH)_3$ with NH_4OH, centrifuge, discard the supernate, and wash the precipitate twice with 0.1-1.0 ml H_2O.

Step 4. Dissolve the precipitate in 3 ml 10*M* HCl. Add 1 drop concd HNO_3. Transfer the solution to a 5-cm × 2-mm AG 1 anion resin column which has been washed with several column volumes of 10*M* solution I. Push through under pressure. After adding 1 drop each of Zr and Te carriers, pass the solution through two additional 10-cm × 8-mm anion columns which have also been treated with 10*M* solution I. Wash the centrifuge tube and then all three columns in succession with two 3-ml portions of 10*M* solu-

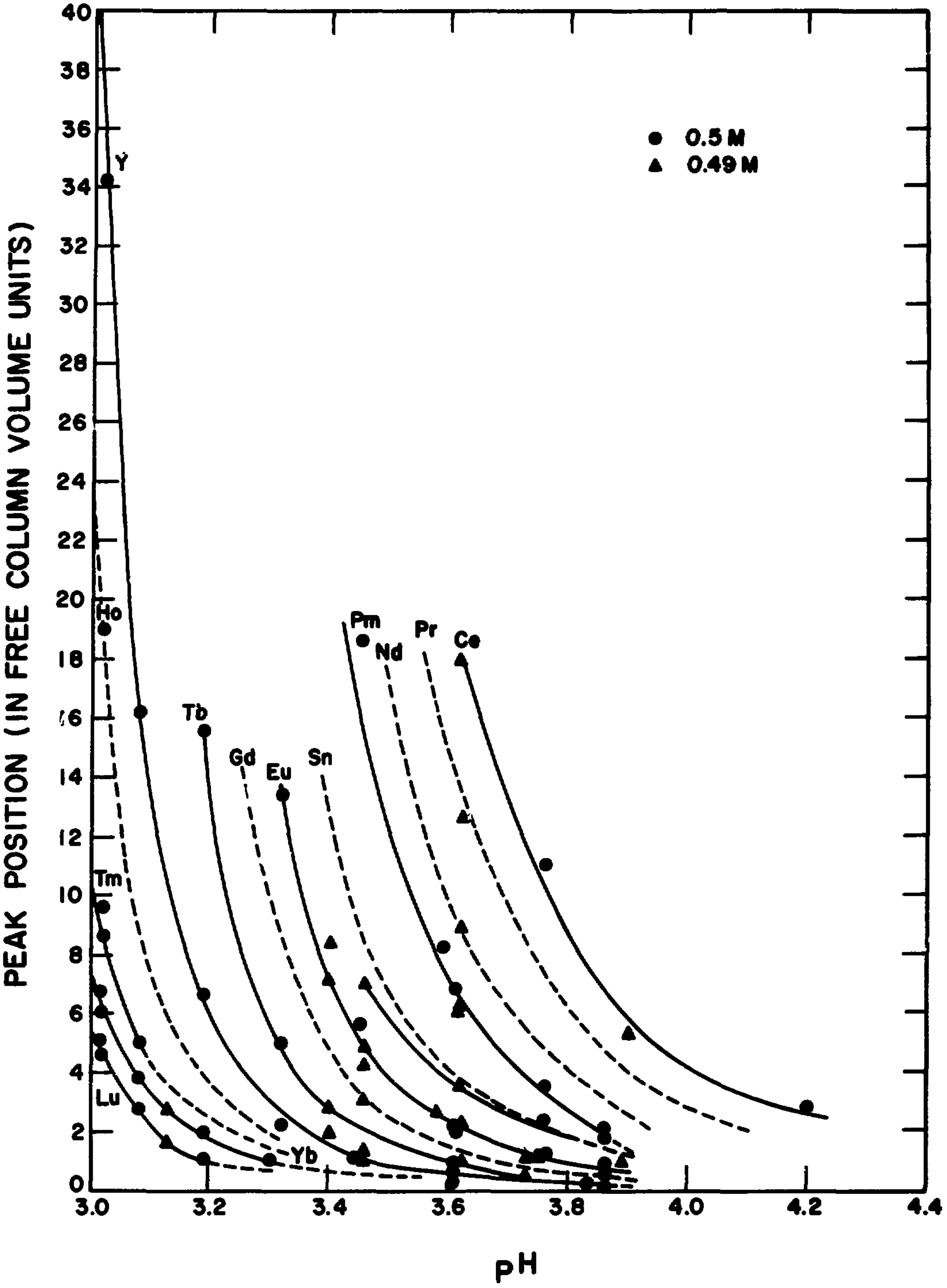

Fig. 1. Lanthanide elution positions *vs* pH with 0.5M α-hydroxy isobutyric acid.

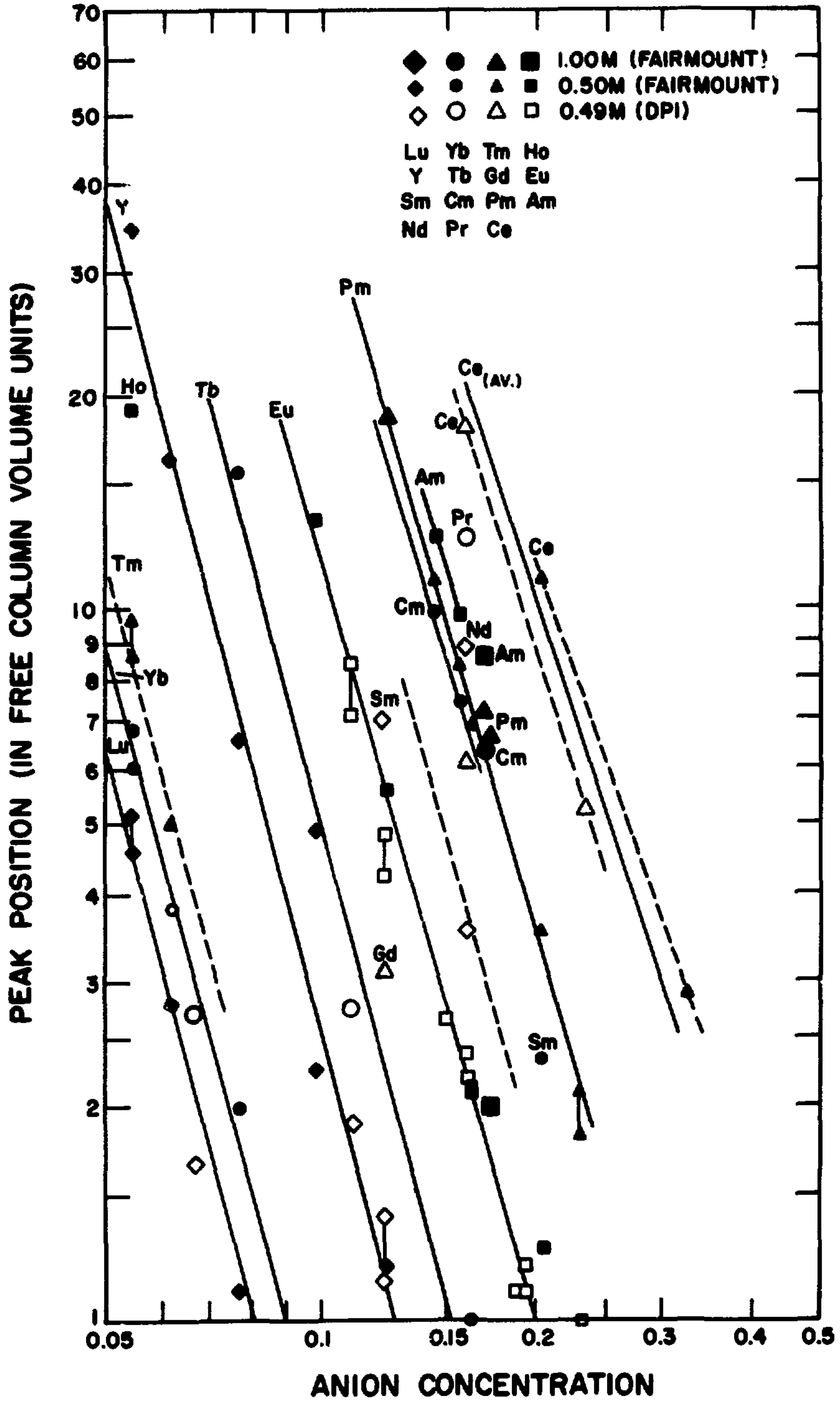

Fig. 2. Lanthanide and actinide elution positions *vs* α-hydroxy isobutyrate anion concentration.

tion I. (The small column contains the Pu, which can be determined by the procedure described under plutonium in this volume.)

Step 5. Add NH_4OH to the combined 10*M* solution I fractions to precipitate $Y(OH)_3$. Centrifuge, discard the supernate, and wash the precipitate twice with 0.5 ml H_2O.

Step 6. Dissolve the precipitate in a minimum amount of 0.1*M* HCl and pass the solution through a 1-cm × 2-mm AG 50 cation resin column which has been previously washed with several column volumes of 0.1*M* HCl. Wash the column with 1 ml of 0.1*M* HCl, then 2 ml of the 0.006*M* HF-0.1*M* HCl solution, and finally 1 ml 0.5*M* HCl (Note 2).

Step 7. Using a transfer pipet and a minimum of H_2O, transfer the cation resin from the 1-cm column to the top of a 12-cm × 2-mm Dowex 50 resin column which has been previously washed with several column volumes of the ethanol-HCl eluent. After the resin has settled, withdraw the excess H_2O and wash out the column above the resin with a small portion of ethanol-HCl. Elute the activity with the 20% ethanol-HCl solution using sufficient pressure to give approximately 1 drop every 45 seconds. Collect the desired fraction (Note 3) in a 40-ml centrifuge tube. (See Fig. 3.)

Step 8. Place the tube containing the sample in an oil or steam bath and evaporate to approximately 0.5 ml, using a stream of air over the solution if rapid evaporation is desired. Add a drop of lanthanum nitrate solution (5 mg La/ml), and transfer the sample to a 3-ml centrifuge cone. The final solution should consist of 1.5 ml of 2-4*M* HCl.

Step 9. Precipitate $La(OH)_3$ with gaseous ammonia or carbonate-free ammonium hydroxide. Centrifuge, discard supernate, and wash the precipitate with 0.5 ml of water.

Step 10. Dissolve the precipitate in a few

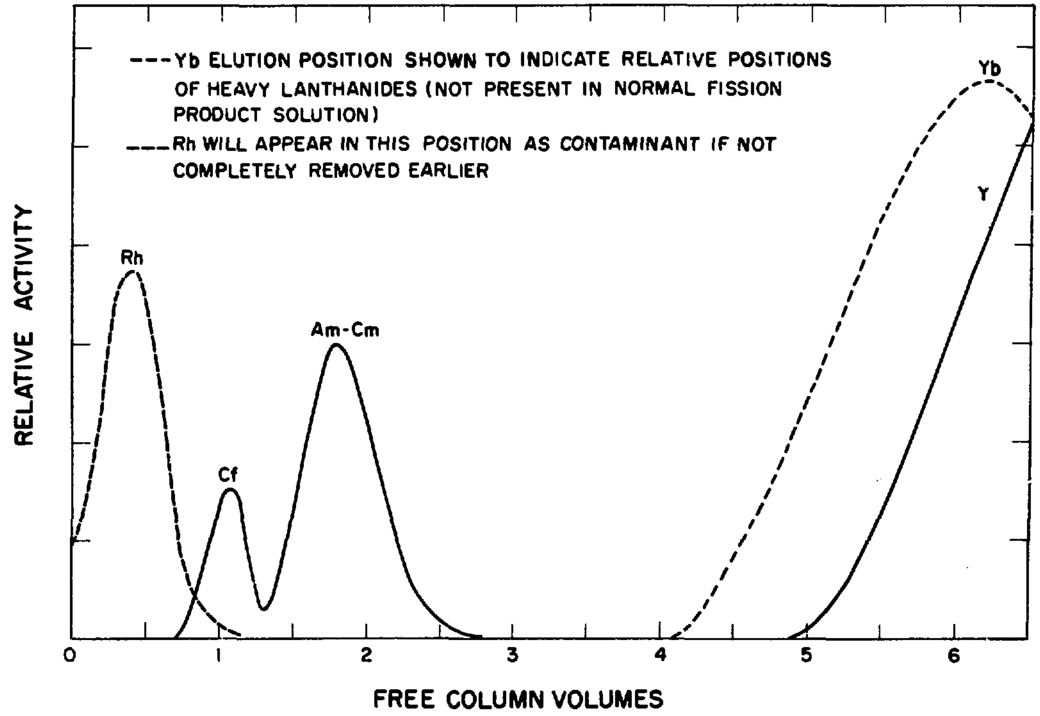

Fig. 3. 20% ethanol-saturated HCl elutions from AG 50-X4 cation resin.

drops of 0.1*M* HCl and equilibrate this solution with a small quantity of resin from the top of the butyrate which is small with respect to the size of the column. Transfer the slurry carefully to the column reservoir and allow to settle. Withdraw the supernate and discard.

Step 11. Introduce carefully several ml of the butyrate. so as not to disturb the active band at the top of the column. Apply slight air pressure, if necessary, to produce a flow rate of a drop every 1-3 min. (Pressure may be applied with a 10-ml syringe fitted with a rubber stopper, or, more conveniently, from a pressure reduction valve attached to a source of compressed air.)

Step 12. Collect the effluent dropwise on platinum plates or in 1-ml beakers. Assay all fractions and combine the drops which comprise a peak. If additional chemistry is necessary, the butyrate may be destroyed by evaporating the solution to dryness, then destroying residual organic matter with nitric and perchloric acids.

Notes

1. Specially purified and graded resins may be obtained from Bio-Rad Laboratories, Richmond, Calif. For some reason, resins vary from batch to batch in their ability to achieve various separations, so it is recommended that several samples of resin be tried before discarding the method.

2. The small cation column was used as an alternative to equilibrating and washing the resin in a test tube and then transferring the resin to the top of the column. It seemed to be more rapid, give better decontamination and necessitate less direct handling of the rather "hot" solution.

3. Essentially no separation of Am and Cm was observed in these ethanol-HCl elutions.

HOT CELL PROCEDURE FOR DISSOLVING LARGE SAMPLES (up to 1 kg) OF UNDERGROUND SHOT DEBRIS

J. W. Barnes

1. Introduction

This procedure is designed for the recovery of zirconium, niobium, the lanthanides, and the actinides from samples, up to 1 kg in size, of debris from underground nuclear explosions. The samples are siliceous and have a wide range of particle size. The initial chemical step in the separation is a leaching with concd hydrofluoric acid at room temperature. This is followed by removal of silica by reaction with hydrogen fluoride at about one-fourth atmosphere of pressure and a temperature near the boiling point of water. The resulting fluoride slurry is centrifuged to separate the insoluble lanthanide and actinide fluorides from zirconium and niobium which are in the form of soluble fluoride complexes. The insoluble fluorides are then treated with fuming nitric and concd perchloric acids and the mixture is evaporated to dryness. The residue is dissolved in dilute nitric acid.

All operations are carried out with the use of manipulators.

2. Reagents

HF: concd; gas
HNO_3: 90% (yellow fuming); 1*M*
$HClO_4$: 70%
LiOH: 3.5*M* aqueous solution

3. Procedure

A. Preliminary Treatment. The sample is distributed in a number of plastic tubes having the dimensions 1 in. x 13 in. To each tube add about 300 ml of H_2O and shake the mixtures for 10 min on a paint shaker equipped with a holding plate for the tubes. Transfer the mixtures to a coarse screened filter (about 1/8 in. mesh). Permit the fines to pass through into a holding vessel. and discard them if they show little activity (Note 1). It is sometimes possible to concentrate the coarse particles further on the filter screen by examination of the individual pieces for relative γ activity.

B. *Chemical Treatment.* The quantities of reagents and sizes of equipment are for high-graded samples (i.e.. those which have undergone preliminary treatment) of 250 g size. Appropriate scale-up or subdivision of sample is made for larger samples.

1. *Leaching with Concd HF.* Transfer the high-graded sample to a 2-liter polypropylene erlenmeyer flask (Note 2). Add 600 ml of concd HF in 50-ml portions over a 15-min interval and shake the mixture for a few min on an ordinary paint shaker after each increment of acid. When the final portion of HF has been added, shake for an additional 30 min.

2. *Removal of SiO_2.* Transfer the fluoride slurry to a polypropylene gas chamber (Fig. 1; Note 3) and bubble gaseous HF vigorously into the slurry at room temperature and under a slight vacuum (water aspirator. see below). After 15 min, begin to heat the water jacket surrounding the chamber, and decrease the pressure to about ¼ atm. While the HF gas flow is main-

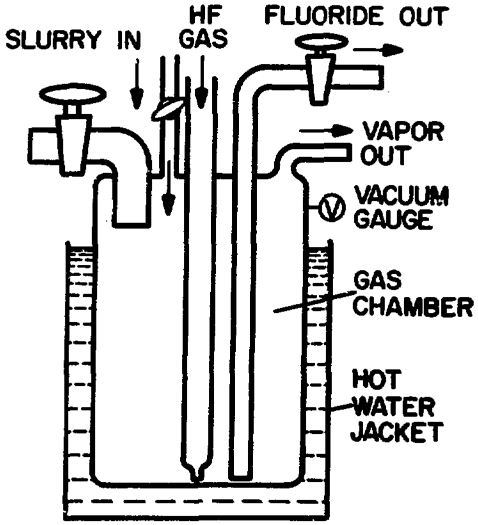

Fig. 1. Gas chamber.

tained. rapidly raise the temperature of the water in the jacket to the boiling point. Permit the vapor effluent from the gas chamber to pass first through an empty polypropylene pot and then into a pot containing 3.5*M* aqueous LiOH. The latter is connected to a water aspirator. The HF treatment is carried out for 1 hr.

3. *Centrifugation.* By air pressure. transfer the thin fluoride slurry into a 1-liter polypropylene centrifuge bottle (Fig. 2). Centrifuge for about 10 min. [A floor model centrifuge was modified by removing the base and cutting about 6 in. off the top. It was equipped with a special head (source: International Equipment Company) for holding four 1-liter bottles.] Pour off the supernate containing the Zr and Nb into a 2-liter Teflon breaker. Wash the precipitate twice with about ¾ liter of H_2O, adding the first wash to the supernate containing the Zr and Nb and discarding the second. The washing is effected by stirring with a high speed plastic stirrer.

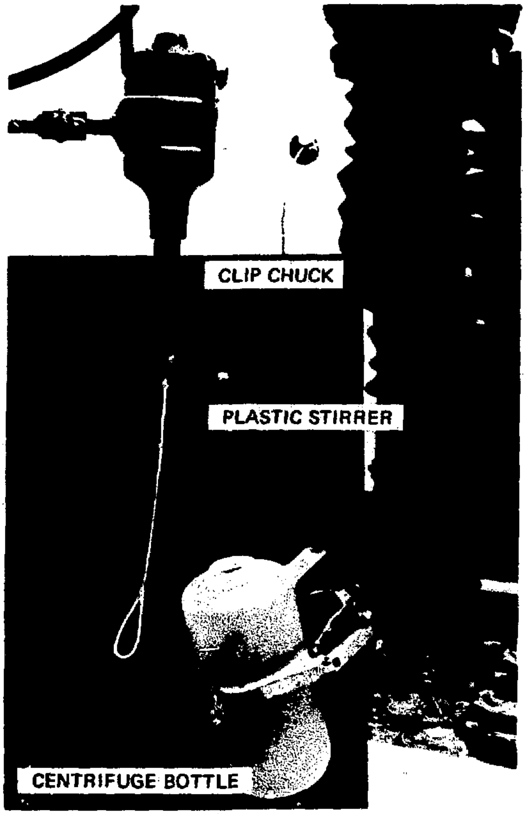

Fig. 2. Centrifuge bottle and stirrer.

4. *Conversion to Solution in HNO_3.* Add 160 ml of 90% HNO_3 and 240 ml of 70 % $HClO_4$ to the precipitate and stir the mixture. Pour the slurry into a 0.6-liter Teflon exaporation bottle (Fig. 3; Note 4). Evaporate the slurry to dryness by heating the bottle on a hot plate. The evaporation may be accelerated by having an Al covering around the bottle and introducing a stream of heated air into the bottle through an opening in the tapered Teflon joint. The evaporation process is complete when droplets of condensate no longer appear in the Kel F connecting tube. Cool the dry solid and separate the evaporation bottle at the tapered joint. Add 700 ml of 1*M* HNO_3 and stir magnetically.

Suitable Teflon vessels do not appear to be available for use with samples greater than 1 kg in size.

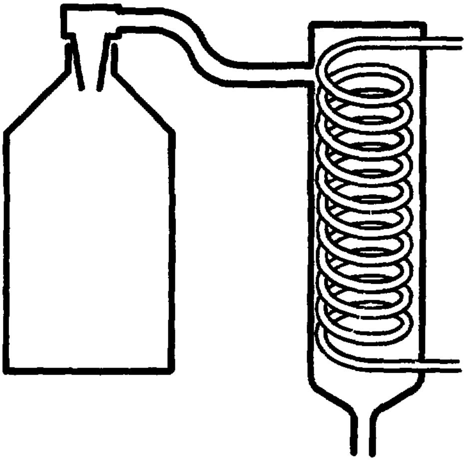

Fig. 3. Teflon evaporation equipment.

Notes

1. If the fines show an appreciable fraction of the activity. they are washed gently with H_2O and are then combined with the high-grade.

2. The concd acids used in the procedure—concd HF, 90% HNO_3, and 70%$HClO_4$—are extremely corrosive. Polypropylene reaction

vessels have been found to be highly suitable for use with these acids at room temperature and with concd HF at elevated temperatures, and much more desirable than vessels constructed from polyethylene. The propylene polymer has a high working temperature limit and greater strength than polyethylene.

3. For specific details regarding the construction and operation of this piece of equipment and the others used in the procedure, see the paper by J. W. Barnes, in the *Proceedings of the 18th Conference on Remote Systems Technology*, 1970, published by the American Nuclear Society.

4. Bottles of various capacities — 0.6 liter to 2 liter — were used depending upon the size of the original sample. The bottles are equipped with a tapered Teflon joint and a Kel F connecting tube to permit ready connection with the Teflon condenser shown.

November 1970

THE DISSOLUTION OF DIRT SAMPLES

G. W. Knobeloch

1. Introduction

The successful dissolution of dirt samples depends basically on repeated evaporations with concd HF to convert silica and silicates to volatile silicon tetrafluoride. The actual steps in the procedure are varied with the size of the sample and the nature of the analysis to be performed on it. The procedure given below is the one utilized for the dissolving of underground dirt samples weighing up to 5 grams.

1. Reagents

HNO_3: fuming
$HClO_4$: concd
HF: concd
HCl: 3*M*
NaOH: 6*M*

3. Procedure

Step 1. Place the dried pulverized sample in a cylindrical Teflon vessel of about 700 ml capacity. Add 25 ml of fuming HNO_3, 100 ml of concd $HClO_4$, and, with care, 50 ml of concd HF. Heat to strong fumes of $HClO_4$ on a hot plate (medium setting). (The solution process may be accelerated by placing an Al jacket around the Teflon container.)

Step 2. Cool, add another 50 ml of concd HF, and again evaporate to strong fumes of $HClO_4$.

Step 3. Repeat Step 2 twice more. (If 10 g of dirt are being dissolved, Step 2 is repeated four times, $HClO_4$ being added as necessary to prevent the sample from becoming dry.)

Step 4. Evaporate until the volume is about 50 ml, cool, and add 100 ml of 3*M* HCl. Warm slightly to dissolve any solids.

Step 5. Divide the solution among four 40-ml Vycor centrifuge tubes. Wash the Teflon vessel with 3*M* HCl and add the washes to the centrifuge tubes. Centrifuge for 2 min at 3500 rpm. During the centrifugation wash the Teflon vessel under a stream of H_2O. Rub the inner surfaces well and flush them with H_2O to remove adhering SiO_2 particles, which may be discarded. The vessel is now ready for re-use in the following step.

Step 6. Transfer the supernate to the clean Teflon vessel, add 50 ml each of concd HF and $HClO_4$ and begin heating on a hot plate (medium setting).

Step 7. Wash the precipitates in the centrifuge tubes with 3*M* HCl, centrifuge, and add the supernates to the Teflon vessel on the hot plate.

Step 8. To each of the precipitates remaining in the centrifuge tubes add 2-3 ml of 6*M* NaOH and boil with stirring over a burner. Cool, acidify with 3*M* HCl, bring to a boil and centrifuge. Combine the supernates with those in the Teflon vessel. If more than a few grains of sand and/or any beta-gamma activity remain, repeat the NaOH-HCl treatment until no sand is left or until it is no longer active. (For *complete* destruction of solids, the sequence of Steps 2-8 is repeated until the sand is entirely dissolved.)

Step 9. Heat the contents of the Teflon vessel to strong fumes of $HClO_4$. Cool, add 50 ml of concd HF, and evaporate the solution until the volume is about 50 ml. Cool.

Step 10. Add 100 ml of 3*M* HCl and warm slightly to dissolve any solid material. Divide the solution among four clean 40-ml Vycor centrifuge tubes and centrifuge at 3500 rpm.

Step 11. Filter the supernate through polypropylene "paper" into a labeled, graduated polyethylene bottle. Wash the Teflon vessel and the centrifuge tubes with 3*M* HCl, centrifuge, and filter the washes into the polyethylene bottle. If any precipitate remains in the centrifuge tubes, add 2-3 ml of 6*M* NaOH and heat over a burner. Cool, neutralize with 3*M* HCl, centrifuge, and decant the supernate through the filter into the polyethylene bottle. Repeat the NaOH-HCl treatment if precipitate still remains in the centrifuge tubes.

Step 12. Add 3*M* HCl to make the "concentration" of the original sample in solution $\leqslant 7.5$ mg, per ml. Heat the final solution overnight in a water bath at about 90°. (For reasons which are not at all clear, this heat treatment gives a sample solution which may be analyzed satisfactorily. Without such treatment, results may be erratic.)

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