Aug. 5, 1969 C. P. RUIZ ETAL 3,459,634

RADIOISOTOPE PROCESSING

Filed Sept. 19, 1966 2 Sheets-Sheet 1

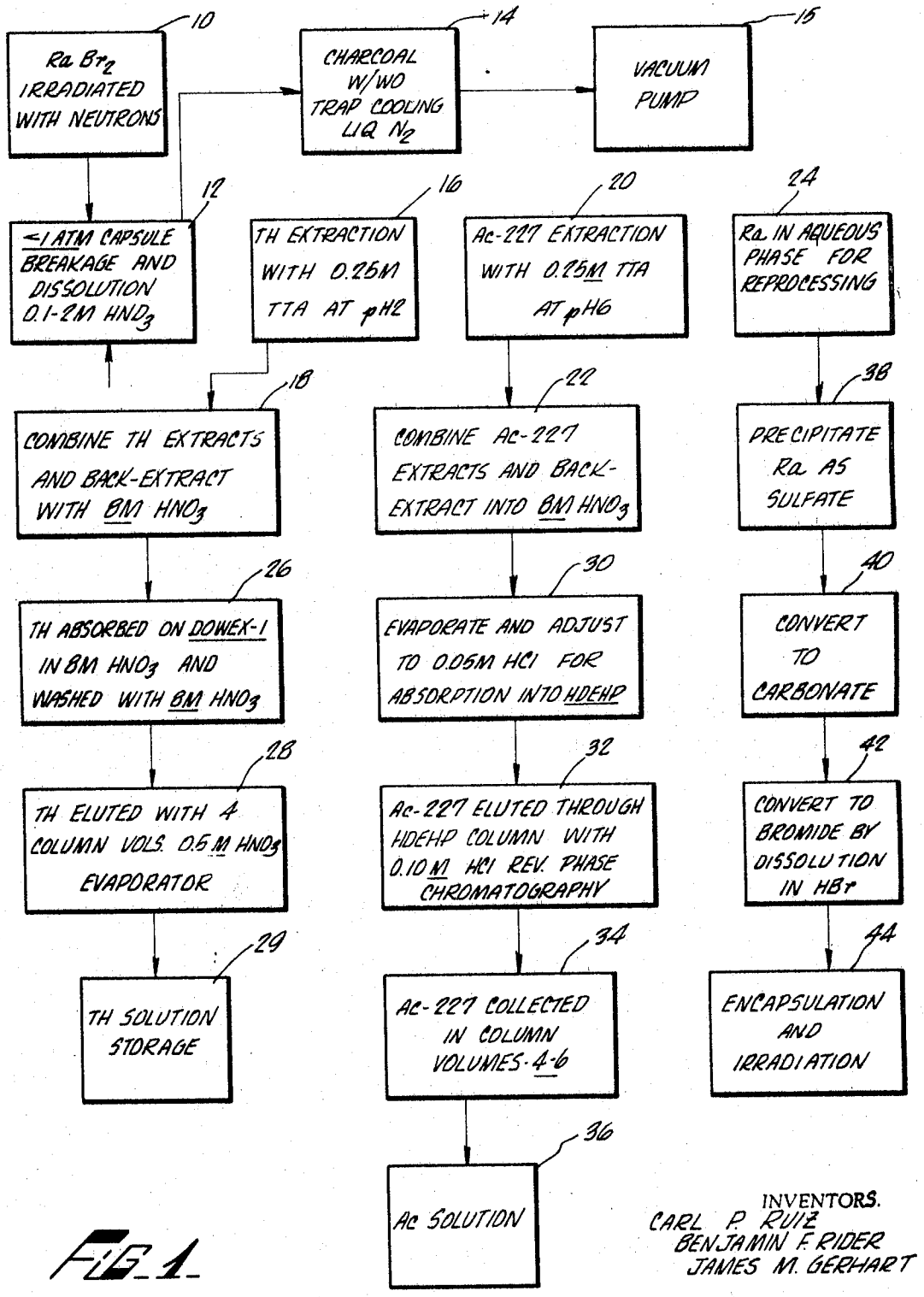


FIG. 1

INVENTORS.
CARL P. RUIZ
BENJAMIN F. RIDER
JAMES M. GERHART

Aug. 5, 1969 C. P. RUIZ ET AL 3,459,634

RADIOISOTOPE PROCESSING

Filed Sept. 19, 1966 2 Sheets-Sheet 2

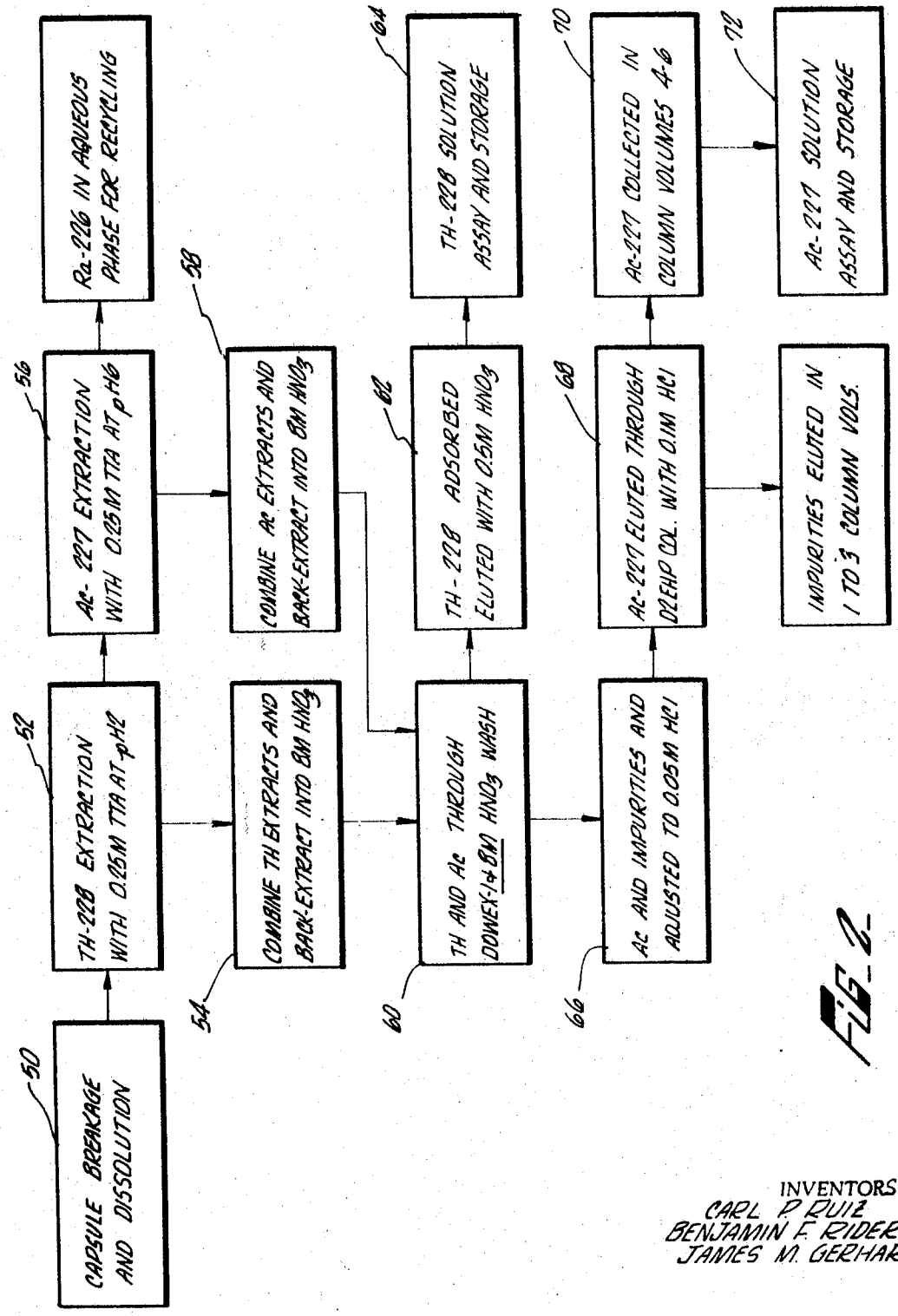


FIG 2

INVENTORS.
CARL P. RUIZ
BENJAMIN F. RIDER
JAMES M. GERHART

United States Patent Office

3,459,634

Patented Aug. 5, 1969

3,459,634

RADIOISOTOPE PROCESSING

Carl P. Ruiz and Benjamin F. Rider, Fremont, and James M. Gerhart, Walnut Creek, Calif., assignors to General Electric Company, New York, N.Y., a corporation of New York

Filed Sept. 19, 1966, Ser. No. 580,476
Int. Cl. G21f 1/02; C01f 1/00, 15/00
U.S. Cl. 176—16 23 Claims

ABSTRACT OF THE DISCLOSURE

A method of preparing and separating actinium-227 and thorium-228 from radium-226 is disclosed. Basically, this system consists of irradiating radium-226 with neutrons for a period sufficient to form a mixture of actinium-227, thorium-228 and radium-226, dissolving the mixture in an aqueous acid solution, extracting thorium-228 with an organic solvent, adjusting the pH of the solution and extracting actinium-227 with an organic solvent, drying the resulting organic solution, dissolving the dried material containing actinium-227 in an aqueous acid solution, adsorbing actinium-227 onto a column containing di-(2-ethylhexyl) phosphoric acid or a homolog thereof, then eluting the purified actinium-227 from the column.

The invention relates to the production and separation of the radioactive isotopes Ac-227 (actinium-227) and Th-228 (thorium-228) from Ra-226 (radium-226).

Existence of the isotopes Ac-227 and Th-228 has been known for many years. However, to date these isotopes have remained the subject of laboratory investigations hampered by troublesome by-products.

This invention provides a practical and economical process for irradiating Ra-226 with neutrons to produce a mixture of Ra-226, Ac-227, and Th-228, which are separated in accordance with the process of this invention to provide industrial amounts of the isotopes Ac-227 and Th-228.

Radioactive isotopes are, at present, most commonly used in space power generators utilizing thermoelectric or thermoionic direct energy conversion or in dynamic systems utilizing Rankine or Brayton cycles. For the system to be satisfactory, the radioisotopes must have a half-life which is compatible with the mission life of the system. The radioisotope fuel must also be in a form capable of operating at high temperatures and for a power density high enough to produce the required heat with a reasonable size source. The radioactive radiation of the isotope must be low enough to prevent radiation damage or interference with other equipment in the system, and minimize exposure of the personnel associated with ground handling or in the spacecraft.

Ra-226 has a half-life of about 1620 years, which is far too long for most space power generator applications. Ac-227, on the other hand, has a half-life of about 21 years, and Th-228 has a half-life of about 2 years, which makes them ideally suited for a number of space power generator applications. Moreover, Ac-227 has a power density five times greater than that of Cm-244 (curium-244), and over one hundred times greater than Sr-90 (strontium-90), which at present are considered the most likely candidates for space power systems requiring relatively long half-life isotopes, i.e., greater than 5 years. Th-228 has a slightly higher power density than Cm-242, and has the advantage of a half-life which is over four times as long. Thus, from a half-life and power density standpoint, Ac-227 and Th-228 are well suited for space power application.

Briefly, the method of this invention includes the steps of irradiating Ra-226 with neutrons and to form Ra-227 which decays spontaneously with a half-life of 41 minutes to Ac-227. The irradiation of the Ra-226 is continued over a sufficient period so that a portion of the newly-formed Ac-227 is also irradiated with neutrons to form Ac-228 which decays with a half-life of about 6 hours to form Th-228.

Thereafter, the mixture of Ra-226, Ac-227, and Th-228 is dissolved in an aqueous acid solvent, and separated by a combination of solvent extraction and chromatographic column separations.

The Ac-227 and Th-228 are recovered separately to provide the radioisotope heat and neutron sources required for space power generator applications, and the Ra-226 is recovered and re-irradiated to produce additional Ac-227 and Th-228.

The invention will be more fully understood from the following detailed description and the accompanying drawings, in which:

FIG. 1 is a flow sheet showing the presently-preferred process of the invention giving high purity products; and

FIG. 2 is a flow sheet showing an alternate process of the invention.

Referring to FIG. 1, a sample of Ra-226 in the form of $RaBr_2$ (radium bromide) was irradiated with neutrons in a nuclear reactor **10**. The $RaBr_2$ was encapsulated in ¼" diameter quartz vials and had a surface-to-mass configuration greater than 1.0 cm.²/gm. to limit the amount of resonance self-shielding. If the surface-to-mass ratio configuration is lower than about 1.0 cm.²/gm., the effective cross section of the Ra-226 for capturing neutrons decreases because of resonance self-shielding.

A relatively high neutron flux was used in irradiating the Ra-226 to minimize the decay losses of Th-228 during irradiation. For example, fluxes of about 10^{14} neutrons/cm.²/sec. were used to obtain satisfactory results. Irradiation of Ra-226 with neutrons produces the following reactions:

$$\begin{array}{ccccc} \text{Ra-226} & \xrightarrow{n,\gamma} & \text{Ra-227} & & \\ & & \downarrow \beta^-(41\text{ mins.}) & & \\ & & \text{Ac-227} & \xrightarrow{n,\gamma} & \text{Ac-228} \\ & & \downarrow \beta^-(21.2\text{ yrs.}) & & \downarrow \beta^-(6.13\text{ hrs.}) \\ & & \text{Th-227} & \text{Th-228} & \xrightarrow{n,\gamma} \text{Th-229} \\ & & \downarrow \alpha\ (18\text{-days}) & \downarrow \alpha\ (1.9\text{ yrs.}) & \end{array}$$

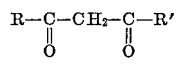
From the above, it can be seen that the Th-228 also captures neutrons to produce Th-229 which is diluent and, therefore, limits the exposure of the Ra-226 to neutrons to avoid excessive conversion of the useful Th-228 to the undesired Th-229.

After irradiation, the quartz capsules with a mixture of Ra-226, Ac-227, and Th-228 were placed in a capsule breakage chamber **12** which contained 2 molar HNO_3 (nitric acid). The chamber was sealed, and the capsules broken remotely so that the Ra, Th, and Ac dissolved in the aqueous nitric acid. A relatively inert gas such as helium, nitrogen, or air was bubbled into the nitric acid solution to sweep radon gas produced by the natural decay of Ra-226 from the chamber and into a charcoal trap **14** cooled with liquid nitrogen, although adequate adsorption on the charcoal trap was also achieved at room temperature operation. A vacuum pump **15** connected to the charcoal trap kept the breakage chamber at sub-

atmospheric pressure, conveniently about ¾ atmospheric pressure.

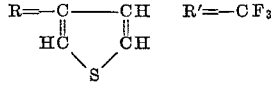
The aqueous acid solution of Ra, Th, and Ac was vigorously mixed in a first mixer or extractor **16** with 0.25 molar TTA (thenoyltrifluoroacetone) dissolved in toluene at pH 2. Other solvents such as the homologues of toluene or their equivalents can be used. Homologues of TTA can also be used. TTA is a chelate which combines with the Ra, Ac, and Th to form compounds soluble in organic solvents. The pH of the TTA in the first mixer **16** is adjusted to about 2 by the addition of sodium hydroxide. At a pH greater than about 1, Th is extractable into TTA, whereas the Ac is extractable at a pH greater than about 4. With an organic-to-aqueous volume ratio of 2, 80% of the Th was extracted into the organic phase in about five minutes at pH 2 with vigorous mixing of the aqueous and organic phases. The yield approached 94% for an extraction time of thirty-five minutes, and there was no extraction of Ac.

Homologues of TTA have the basic formula



in which:

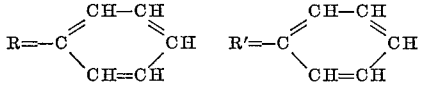
(1) Thenoyltrifluoroacetone (TTA) has:



(2) Acetylacetone has:

$R{=}{-}CH_3 \qquad R'{=}{-}CH_3$

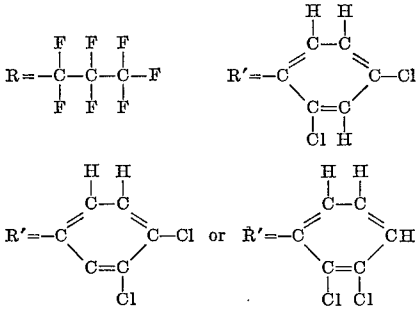
(3) Dibenzoylmethane has:



(4) Trifluoroacetylacetone has:

$R{=}{-}CF_3 \qquad R'{=}{-}CF_3$

(5) Dichlorophenylheptafluorohexanedione has three isomers:



The organic phase with the Th extracted in the first mixer **16** was placed in a first back-extractor **18** and mixed vigorously with 8 molar HNO_3 to back-extract the Th into an aqueous phase. The back-extraction can be performed with acidities greater than about 1 M.

The remaining aqueous phase in the mixer **16** was transferred to a second mixer or extractor **20** and adjusted to pH 6 by the addition of ammonium hydroxide and mixed vigorously with .25 molar TTA in toluene to extract the Ac. The acidity of the solution gradually increased during the extraction according to the following equation:

$$Ac^{+3}+3HTTA \rightarrow Ac(TTA)_3+3H^+$$

Therefore, the pH of the extraction system for the Ac was continually adjusted during the initial few minutes of the extraction by the addition of NH_4OH (ammonium hydroxide), during which time most of the Ac was extracted.

The organic phase with the Ac was transferred from the second extractor **20** to a second back-extractor **22** and mixed vigorously with 8 molar HNO_3 which back-extracted the Ac into the aqueous phase. This back-extraction can be performed with acidities greater than about 0.1 M. Any residual Th is back-extracted with the Ac at this stage.

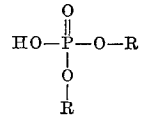
The aqueous phase in the second mixer contained the Ra-226 and was transferred to a storage tank **24** for further processing and recovery, as described in detail below.

The aqueous thorium solution in the first back-extractor was passed through a Dowex 1 x 8, 200–400 mesh anion exchange chromatographic column **26**, 3 mm. in diameter by 5 cm. long and preconditioned with 8 M HNO_3. This column will work with other anion exchange resins of the quaternary amine type having cross linking other than 8%, e.g., 4%, and other mesh sizes, e.g., 100–200 mesh, and can be operated at elevated temperatures up to 70° C. for improved adsorption rates. The Th was adsorbed in such a column at concentrations of HNO_3 greater than about 5 molar. Ac and Ra were not adsorbed at any HNO_3 concentration. After passing the Th extract through the first chromatographic column, it was washed with 8 column volumes of 8 molar HNO_3. 1 column volume is defined as the volume of liquid occupying the void space in 1 bed volume. The Th was then eluted from the first chromatographic column with 4 column volumes of 0.5 molar HNO_3 and collected in an evaporator **28** where the volume of the Th solution is reduced to a convenient size. Thereafter, the Th solution is placed in a storage tank **29** for further use, when desired.

The aqueous phase of the second back-extractor with the dissolved Ac and some residual Th and traces of Ra is evaporated to dryness in a second evaporator **30** and dissolved in a small volume of .05 molar HCl (hydrochloric acid) and passed through a reverse phase chromatographic column **32** which is then eluted with 0.10 molar HCl at a flow rate not exceeding 2 column volumes per minute. The first 3 column volumes eluted from the reverse phase chromatograph contain Th and Ac daughter products as well as some residual Ra-**226**. The Ac-**227** fraction is collected in column volumes 4 through 6 and placed in a third evaporator **34**.

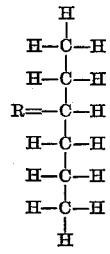
The reverse phase chromatographic column used 20% HDEHP (di(2-ethylhexyl)phosphoric acid) supported on Chromosorb operated at 87° C. This column can be operated at lower temperatures at the expense of reduction in rate of adsorption and desorption. Ra and Ac were adsorbed at HCl concentrations less than .001 molar and 0.05 molar, respectively. The Th was adsorbed strongly at all HCl concentrations. Excellent separation was achieved by eluting the Ra at .005 molar and the Ac at 0.1 molar HCl. Th was subsequently eluted with a mixture of 6 molar HCl plus 1 molar HF (hydrofluoric acid).

Other homologues of HDEHP can be used in place of HDEHP. Homologues of HDEHP have the basic formula:

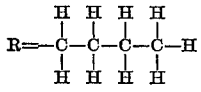


in which:

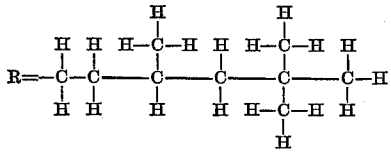
(1) Di(2-ethylhexylphosphoric acid (HDEHP) has:



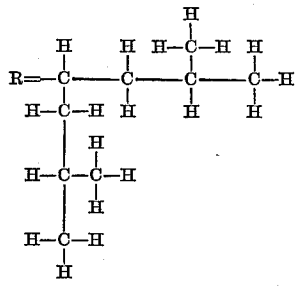
(2) Di-n-butylphosphoric acid has:



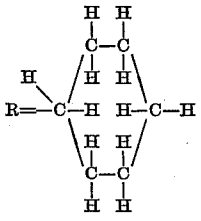
(3) Bis(3,5,5-trimethylhexyl)phosphoric acid has:



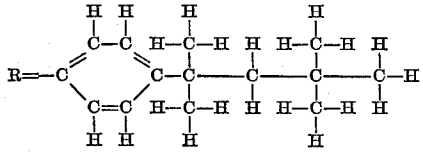
(4) Bis(di-isobutylmethyl)phosphoric acid has:



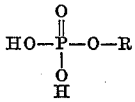
(5) Dicyclohexylphosphoric acid has:



(6) Bis(p-tert-octylphenyl)phosphoric acid has:

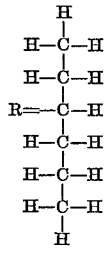


Homologues of H_2EHP (mono(2-ethylhexyl)phosphoric acid) having the basic formula:

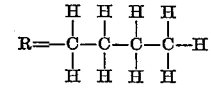


in which:

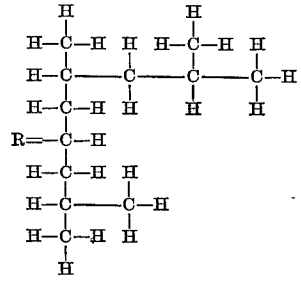
(1) Mono-2-ethylhexylphosphoric acid has:



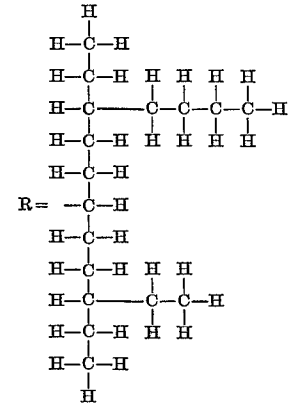
(2) Mono-n-butylphosphoric acid has:



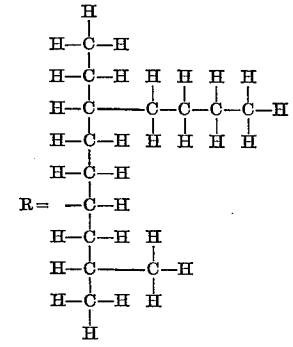
(3) Monododecylphosphoric acid has:



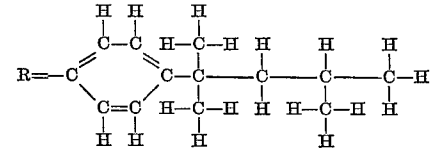
(4) Monoheptadecylphosphoric acid has:



(5) Monotetradecylphosphoric acid has:



(6) Mono(p-octylphenyl)phosphoric acid has:



can also be used in place of HDEHP.

The Ac can be stored in a tank **36** until further use, such as a neutron source when mixed with Be (beryllium). This useful combination is obtained by treating the Ac solution in storage tank **36** with a mixture of HNO_3 and HF at a molarity of greater than 0.1. The product is AcF_3 (actinium fluoride) which is easily converted to elemental Ac for best contact with Be in accordance with the following equation:

$$2AcF_3 + 29Be \xrightarrow{\text{heat}} \underset{\uparrow}{3BeF_2} + AcBe_{13}$$

In the final separation of Ac-227 to yield a high-purity product, i.e., the chromatographic separation from the reverse phase HDEHP column, the Ac-227 is probably combined with the HDEHP in the eluted fraction. This results in the presence of a considerable amount of HDEHP in the final Ac-227 product which thus requires additional purification.

The additional purification is performed by the precipitation of the Ac-227 as the compound AcF_3 from the mixture of HNO_3 and HF. For some applications, the additional purification is not performed, such as when an actinium glass as desired. Instead of treating the eluate with the mixture of HNO_3 and HF, the eluate from the reverse phase HDEHP column is evaporated to produce a residue which has the properties of a glass due to the presence of the phosphate resulting from the decomposition of the HDEHP. The properties of the glass can be modified or adjusted to desired values by treating the eluate from the HDEHP column with additives such as sodium, iron, etc. to obtain a glass having a low enough melting point to obtain a melt, and low leachability.

The Ra in the aqueous phase in the storage tank **24** is precipitated as radium sulfate in a reaction tank **38** and converted to radium carbonate in an autoclave **40** by heating with sodium carbonate solution. The radium carbonate is then dissolved in HBr (hydrobromic acid) in a convertor to form radium bromide which is then encapsulated at **44** and ready for irradiation.

The chemical processing procedure can be used as described above, or it can be varied to meet certain requirements. For example, if high-purity material is not required, the separation process can be stopped after the separate TTA solvent extractions of the Th and Ac from the aqueous nitric acid.

FIG. 2 shows an alternate procedure for preparing Ac-227 and Th-228 in accordance with this invention.

A radium bromide capsule is irradiated with neutrons, broken in a sealed chamber **50** and dissolved in nitric acid as previously described. During the breakage and dissolution, helium gas is bubbled through the solution to sweep radon gas into a cooled charcoal trap like that referred to with respect to FIG. 1.

After about ½ minute helium purge, the solution is adjusted to ph 2 with ammonium hydroxide. 2 volumes of .25 molar TTA in toluene are added to the aqueous phase in a first extractor **52**, and the mixture stirred vigorously for 5 minutes to extract thorium. The TTA phase is separated from the aqueous phase and placed in a first back-extractor **54**. The 5-minute extraction is repeated with another double volume of TTA and the two organic phases are combined in the first back-extractor **54**. The thorium is back-extracted in the aqueous phase in 8 molar HNO_3.

The aqueous phase from the first extractor with dissolved actinium is treated in a second extractor **56** with .25 molar TTA in toluene with the aqueous phase pH adjusted to 6 with ammonium hydroxide to extract the actinium. Two 5-minute extractions are performed as in the first extractor **52** with careful control of the pH by addition of dilute ammonium hydroxide. The two TTA fractions are combined in a second back-extractor **58**, and the actinium is back-extracted into an aqueous phase with 8 molar HNO_3.

The Ac solution from the second back-extractor is passed through a chromatographic column **60** of the conventional type known as a Dowex 1 x 8, 200–400 mesh, 3 mm. by 5 cm. column, preconditioned with 8 molar HNO_3. The Th solution from the first back-extractor is passed through the column after the Ac solution.

The column is washed with 4 more column volumes of 8 molar nitric acid, and the wash solution discarded. The Th-228 is eluted with 4 column volumes of .5 molar HNO_3 and placed in an evaporator **62** where it is evaporated to a small volume and then transferred to a storage tank **64**. The Ac solution which passes through the chromatographic column **60** is placed in a second evaporator **66**, evaporated to dryness, and then dissolved in a small volume of .05 molar HCl, which is then loaded on a preconditioned HDEHP column **68** prepared as described above with reference to FIG. 1, and eluted with 0.10 molar HCl. Column volumes 1 through 3 contain impurities, and are discarded. Ac-227 is collected in column volumes 4 through 6 in an evaporator **70** and then treated as previously described with respect to FIG. 1 and placed in storage tank **72**.

From the foregoing description, it will be apparent that the Th and Ac can also be extracted simultaneously with TTA at pH 6, and thereafter separated in accordance with the column chemistry described with respect to FIG. 2.

We claim:

1. The method of preparing actinium-227 and thorium-228 from radium-226 which comprises the steps of:

(a) irradiating radium-226 with neutrons to form actinium-227;

(b) continuing said neutron irradiation so that some of said actinium-227 forms actinium-228, which decays into thorium-228, whereby a mixture of radium-226, actinium-227 and thorium-228 is produced;

(c) performing a single cycle comprising the steps of:

(1) dissolving said mixture in an aqueous acid solvent;

(2) adjusting the pH of said aqueous acid solution to about 2;

(3) extracting thorium-228 with an organic solvent;

(4) adjusting the pH of said aqueous acid solution to about 6;

(5) extracting actinium-227 with an organic solvent;

(d) after said single cycle evaporating the actinium-227 solution to dryness;

(e) dissolving the dried actinium-227 material in an about 0.05 molar aqueous acid solution;

(f) passing the resulting solution through a column containing a composition selected from the group consisting of di-(2-ethylhexyl) phosphoric acid and its homologs; and

(g) eluting actinium-227 from said column with an about 0.1 molar aqueous acid solution, whereby said actinium-227 is substantially free from thorium-228, radium-226 and impurities.

2. The method according to claim **1** wherein said organic solvent used for said extraction of thorium-228 comprises a compound selected from the group consisting of thenoyltrifluoroacetone and homologs thereof.

3. The method according to claim **2** wherein said organic solvent comprises about 0.25 molar thenoyltrifluoroacetone dissolved in another organic solvent at a pH of about 2.

4. The method according to claim **1** wherein said organic solvent used for said extraction of actinium-227 comprises a compound selected from the group consisting of thenoyltrifluoroacetone and homologs thereof.

5. The method according to claim **4** wherein said organic solvent comprises about 0.25 molar thenoyltrifluoroacetone dissolved in another organic solvent at a pH of about 2.

6. The method according to claim 1 wherein said elution of actinium-227 from said column is performed with about 0.1 molar hydrochloric acid.

7. The method according to claim 6 wherein said elution includes washing the actinium-227 from said column with about six column volumes of 0.1 molar hydrochloric acid and collecting volumes 4 through 6 separately from volumes 1 through 3.

8. The method according to claim 6 which includes treating the eluted actinium-227 with a solution comprising nitric acid and hydrofluoric acid at an acidity greater than about 0.1 molar to form actinium fluoride.

9. The method of claim 8 further including the steps of mixing said actinium fluoride with beryllium, and heating the mixture to drive off beryllium fluoride as a gas, whereby an alloy of actinium and beryllium is formed.

10. The method according to claim 6 wherein subsequent to the elution of actinium-227 from said column, thorium-228 is eluted with a mixture comprising about 6 molar hydrochloric acid and about 1 molar hydrofluoric acid.

11. The method according to claim 1 further including the step of eluting radium-226 from said column with an about 0.005 molar hydrochloric acid solution.

12. The method according to claim 1 wherein the organic solution containing actinium-227 is contacted with an about 8 molar aqueous acid solution to back-extract the actinium-227 into the aqueous phase before said step of evaporating to dryness.

13. The method according to claim 1 wherein the organic solution containing thorium-228 is back-extracted with an about 8 molar aqueous acid solution, to return the thorium-228 to the aqueous phase, then the aqueous solution is concentrated by evaporation.

14. The method according to claim 1 which includes recovering the residual Ra-226 and re-irradiating it with neutrons to form additional Ac-227 and Th-228.

15. The method according to claim 14 which includes precipitating the recovered residual radium as a salt, encapsulating the precipitated radium salt, and irradiating the radium salt with neutrons to form Ac-227 and Th-228.

16. The method according to claim 1 in which the mixture of Ra-226, Ac-227, and Th-228 is dissolved in nitric acid.

17. The method according to claim 16 in which the nitric acid is at least about 0.2 molar.

18. The method according to claim 1 which includes flowing a relatively inert gas past the mixture of Ra-226, Ac-227, and Th-228 to remove radon gas given off from the mixture.

19. The method according to claim 18 which includes the step of passing the relatively inert gas and radon gas through a filter.

20. The method according to claim 19 in which the filter includes charcoal, and including the step of cooling the charcoal below about −100° C.

21. The method according to claim 1 which includes the step of dissolving the mixture of Ra-226, Ac-227, and Th-228 in an aqueous acid solvent in a container at less than atmospheric pressure to prevent the out leakage of radon gas given off by the mixture.

22. The method according to claim 1 in which the surface-to-mass ratio of the Ra-226 is greater than about 1.0 $cm.^2/gm.$

23. The method according to claim 1 which includes the step of adding a base during the extraction of the Ac-227 to keep the pH of the extraction solution at least 6.

References Cited

UNITED STATES PATENTS

2,632,763	3/1953	Hagemann	23—339
2,723,901	11/1955	Hagemann et al.	23—23
2,856,418	10/1958	Calvin	23—339
2,916,349	12/1959	Crandall et al.	23—339

OTHER REFERENCES

MLM–1204, September 1964, p. 19.

MLM–558–Del-1, March 1960, pp. 4, 6–9, 15, 16, 19–21, 33, 34, 43.

MLM–773–Rev., March 1960, pp. 3–6.

MLM–1297, February 1966, pp. 3–11.

MLM–1176, September 1963, pp. 3, 11.

AECD–3084, p. 25, March 1951.

Nuclear Engineering Handbook, November 1958, sec. 11, pp. 91–97, sec. 14, p. 31.

MLM–622–Del-1, 1959, p. 9.

J. Amer. Chem. Soc., vol. 78, November 1956, pp. 5953–5954 by Danon.

J. Amer. Chem. Soc., February 1950, vol. 72, pp. 768–774 by French Hagemann.

J. of Chemical Education, vol. 36, No. 9, September 1959, pp. 462–465 by Choppin.

Can. J. Chem., vol. 37, 1959, pp. 1094–1103, by Cabell.

CARL D. QUARFORTH, Primary Examiner

H. E. BEHREND, Assistant Examiner

U.S. Cl. X.R.

23—339, 341; 75—122; 252—301

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,459,634 August 5, 1969

Carl P. Ruiz et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 29, "The", first occurrence, should read -- This --. Column 2, line 2, cancel "and"; line 53, "(18-day should read -- (18 days) --. Column 5, line 2, "Di(2-ethyl-hexylphosphoric" should read -- Di(2-ethylhexyl)phosphoric -- Column 7, line 10, "$AcBe_{13}$" should read -- $2AcBe_{13}$ --; line 2 "as" should read -- is --; line 56, "ph" should read -- pH --

Signed and sealed this 7th day of July 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents