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HEU AGE DETERMINATION*

by

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ABSTRACT

A technique has been developed to determine the Highly Enriched Uranium (HEU) Age which is defined as the time since the HEU was produced in an enrichment process. The HEU age is determined from the ratios of relevant uranium parents and their daughters viz $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$. Uranium isotopes are quantitatively measured by their characteristic gammas and their daughters by alpha spectroscopy. In some of the samples where HEU is enriched more than 99%, the only mode of HEU age determination is by the measurement of ^{231}Pa since there is negligible quantity of ^{230}Th due to very low atom concentrations of ^{234}U in the sample. In this paper we have presented data and methodology of finding the age of two HEU samples.

INTRODUCTION

The HEU age has become of interest recently because of the dismantlement of nuclear weapons and the possible availability of the HEU to enter the commercial sector as low enriched uranium after dilution. It is desirable to ensure that HEU which is undergoing dilution comes from dismantled weapons rather than from new production. It is also useful from the safeguards perspective to verify that HEU in storage is from dismantled nuclear weapons rather than from new production in countries which have joined the NPT and given up their nuclear weapons.

The HEU age is determined by chemically and quantitatively separating from the dissolved HEU sample the daughter products ^{230}Th and ^{231}Pa in the ^{234}U and ^{235}U decay chains as discussed in reference (1) and outlined schematically in Figure 1. Following the separate chemical separation of thorium and protactinium from the enriched uranium, the alpha activity of the ^{230}Th and ^{231}Pa samples was measured with an alpha spectrometer.

The ratios of the $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$ activity determined the age of the enriched uranium samples. Two different samples of HEU containing different fractions of ^{234}U and ^{235}U were studied.

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CHEMICAL SEPARATION

In an earlier paper the procedure (1,2) called for the use of acid mixtures of acetic acid and hydrochloric acids of various normalities to effect separation of the isotopes of thorium, protactinium and uranium. However since the samples which were analyzed were either pure uranium oxide or metal it was not necessary to use acetic acid in the acid mixture.

Two schematic flow diagrams (Figures 2 and 3) show the chemical separation process for thorium and protactinium which was used to determine the age of HEU sample. Two types of samples were available for the age determination. In one case HEU sample, from Argonne National Laboratory (ANL), was 93% enriched and a second sample from ORNL was more than 99.9% enriched.

DISSOLUTION

An aliquot was prepared which contained a little more than 500 mg of the enriched uranium oxide from the ANL sample. The enriched uranium oxide was weighed and dissolved in about 10 ml of concentrated HNO_3 in a teflon beaker. In the case of the 99.9% enriched sample the sample was in the metal form and it took longer to dissolve in nitric acid. The solution was evaporated to dryness at low heat and concentrated HCl was added to convert to the chloride form. It was evaporated to dryness again and finally a solution in 10N HCl was made in a volumetric flask.

TRACERS

Two tracers were needed for the current investigation to measure the chemical recovery efficiency. Gamma emitting Pa^{233} for quantifying ^{231}Pa and alpha emitting ^{228}Th for quantifying ^{230}Th were used as tracers. Certified ^{228}Th was obtained commercially. About 10 mCi of Pa^{233} was produced by irradiating pure ^{232}Th (natural thorium nitrate) in the BNL High Flux Beam Reactor (HFBR) as shown schematically in Figure 4. Neutron irradiated natural thorium was dissolved in 10N HCl and passed through a 2 ml anion exchange resin polypropylene column. About 20 column volumes of 10N HCl was passed to clean the column free of most thorium leaving behind Pa^{233} in the column. Pa^{233} was eluted with a mixture of 10 column volumes 8N HCL + 0.1N HF the effluent was collected in a teflon beaker. The acid effluent containing Pa^{233} was purified with the anion exchange column again. This was done by evaporating the solution in the teflon beaker to dryness and redissolving the residue in 10N HCl and repeating the procedure described above. This yielded the Pa^{233} tracer solution almost carrier-free. The Pa^{233} solution was stored in a weighed 25 ml polypropylene container.

GAMMA COUNTING

A known aliquot of the solution, representing about 5 mg of uranium oxide, was withdrawn and weighed in a 15 ml polypropylene bottle for gamma counting in a an intrinsic Ge detector. The 15 ml

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bottle geometry was previously calibrated with a NIST traceable mixed gamma standard. The 15 ml bottle was diluted to appropriate volume and gamma counted in the Ge detector for 2000 seconds.

Gamma activities were averaged from two gammas (185 and 143 KeV) for quantifying ^{235}U in the uranium solution. Similarly ^{234}U was quantified from their respective two gamma (530 and 580 Kev) rays.

A known weighed aliquot from the Pa^{233} solution was counted in Ge detector for gamma (310 KeV) quantification of the solution.

SAMPLE ANALYSIS

After the withdrawal of an aliquot of the sample solution in 10N HCl for gamma counting, the remainder of the solution was quantitatively transferred to a teflon beaker. Appropriate weighed amount of tracers ^{228}Th and ^{233}Pa were added to the sample solution. The sample is stirred with a magnetic stirrer gently for homogeneity.

THORIUM SEPARATION

Thorium isotopes were separated as shown schematically in the flow diagram in Figure 2.

A 35 ml teflon column as shown in figure 4 was filled with anion exchange resin (AG 1x4, from Dowex) is prepared using a syringe pump. The column was conditioned with 10N HCl using a piston pump. The sample containing the tracers in 10N HCl was introduced, passed through the column at a flow rate of 5 ml/minute and the effluent was collected in a 200 ml polypropylene bottle. The column was washed with 10N HCl until 200 ml of the effluent was collected in the bottle. The 200 ml bottle was counted in a Ge detector for identification and quantification of the uranium daughters ^{231}Th and ^{234}Th. This was only to trace the intermediate chemical recovery of thorium isotopes.

A fifty ml aliquot of the 200 ml solution was transferred to a teflon beaker and evaporated to dryness. To the dry beaker dilute acid and 100 ugm of neodymium carrier were added and gently heated. A quantitative precipitation using a filter paper was performed as described in the references (3 & 4) for alpha spectroscopy. A typical alpha spectra for the thorium isotopes are shown in Figure 5. ^{230}Th is quantified from the abundance of ^{228}Th.

PROTACTINIUM SEPARATION

Protactinium isotopes were separated as shown schematically in Figure 3.

After the separation of thorium isotopes the ion exchange

resin now contained mostly uranium and protactinium isotopes. The eluant was changed to acid mixture of 8N HCl + 0.1 HF to elute protactinium isotopes. 200 ml of the acid effluent is collected in a teflon beaker. The solution was evaporated to dryness and protactinium was purified twice with a 2 ml anion exchange column.

Since the ^{234}U is present in the HEU in much larger quantity than ^{231}Pa, some ^{234}U finds itself in the final ^{231}Pa sample which poses a difficulty to obtain a well resolved alpha spectra for ^{231}Pa. It was necessary to purify the separated protactinium twice even at the expense of decreasing the chemical recovery to get a reliable alpha activity of ^{231}Pa.

The twice purified protactinium fraction was subjected to alpha spectroscopy as described in the procedure for thorium. The ^{231}Pa alpha spectra which was obtained is shown in Figure 6.

Uranium was eluted from the 35 ml column with 200 ml of 0.1N HCl and stored as waste.

RESULTS

The 93% ^{235}U HEU sample yielded an age of about 26 years using $^{230}Th/^{234}U$ ratio whereas $^{231}Pa/^{235}U$ ratio yielded an age of about 30 years as shown in Table 1. The age of the HEU sample with 99.9% ^{235}U isotopic abundance, was determined to be 30 years as shown in Table 2. In HEU samples containing negligible quantities of ^{234}U and, therefore ^{230}Th, the only way to determine its age is by using the $^{231}Pa/^{235}U$ ratio methodology.

Table 1

93% ANL HEU SAMPLE

(Age of HEU sample using $^{231}Pa/^{235}U$ ratio)

Sample weight (gm)	^{235}U gamma (dpm)	^{231}Pa alpha (dpm)	Age (Years)
0.5041	1900320	969	24
0.5590	2023000	1152	27

(Age of HEU sample using $^{230}Th/^{234}U$ ratio)

Sample weight (gm)	^{234}U gamma (dpm)	^{230}Th alpha (dpm)	Age (Years)
0.501	51948000	23975	30

Table 2

99.9% HEU SAMPLE

(Age of HEU sample using $^{231}Pa/^{235}U$ ratio)

Sample weight (gm)	^{235}U gamma (dpm)	^{231}Pa alpha (dpm)	Age (Years)
0.5347	2245178	1280	28
0.5710	2481516	1638	32

CONCLUSION:

A radiochemical thorium and protactinium separation technique combined with alpha spectroscopy has been developed to measure the ratios of $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$ to determine the age of HEU samples. This technique can be used routinely to determine the HEU age.

REFERENCES

1. Moorthy, A.R. and Kato, W.Y., Heu Age Determination, Proc. of the 35th Annual Meeting of the INMM, Jul 17-20, 1994, Naples, FL., p 768.

2. Kim, J.I. and Born, H.J., Anion Exchange Behavior of Thorium, Protactinium, Uranium, and other Elements in Hydrochloric and Acetic Acid Mixtures, Radiochimica Acta, Band 14, Heft 1, 1970, p.35.

3. Hindman, F.D., Neodymium Floride Mounting for Alpha Spectrometric Determination of Uranium, Plutonium, and Americium, Anal. Chem., 55, 2460-2461, (1983).

4. Sill, C.W. and Williams, R.L., Preparation of Actinides for Alpha Spectrometry without Electrodeposition, Anal. Chem. 53, 415-421 (1981)

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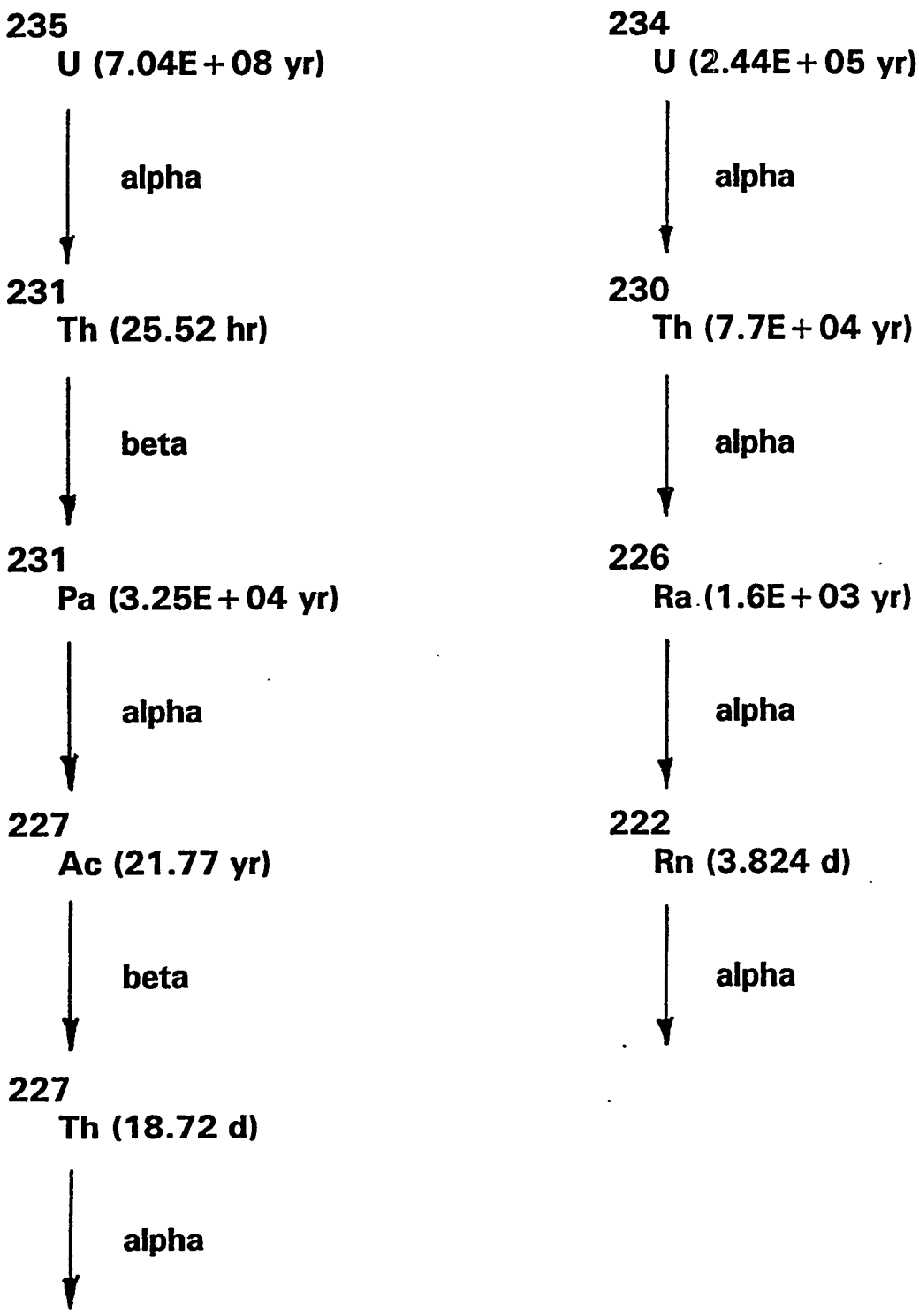
FIGURE 1

DECAY CHAIN OF ^{234}U AND ^{235}U ISOTOPES



Thorium Chemistry Separation

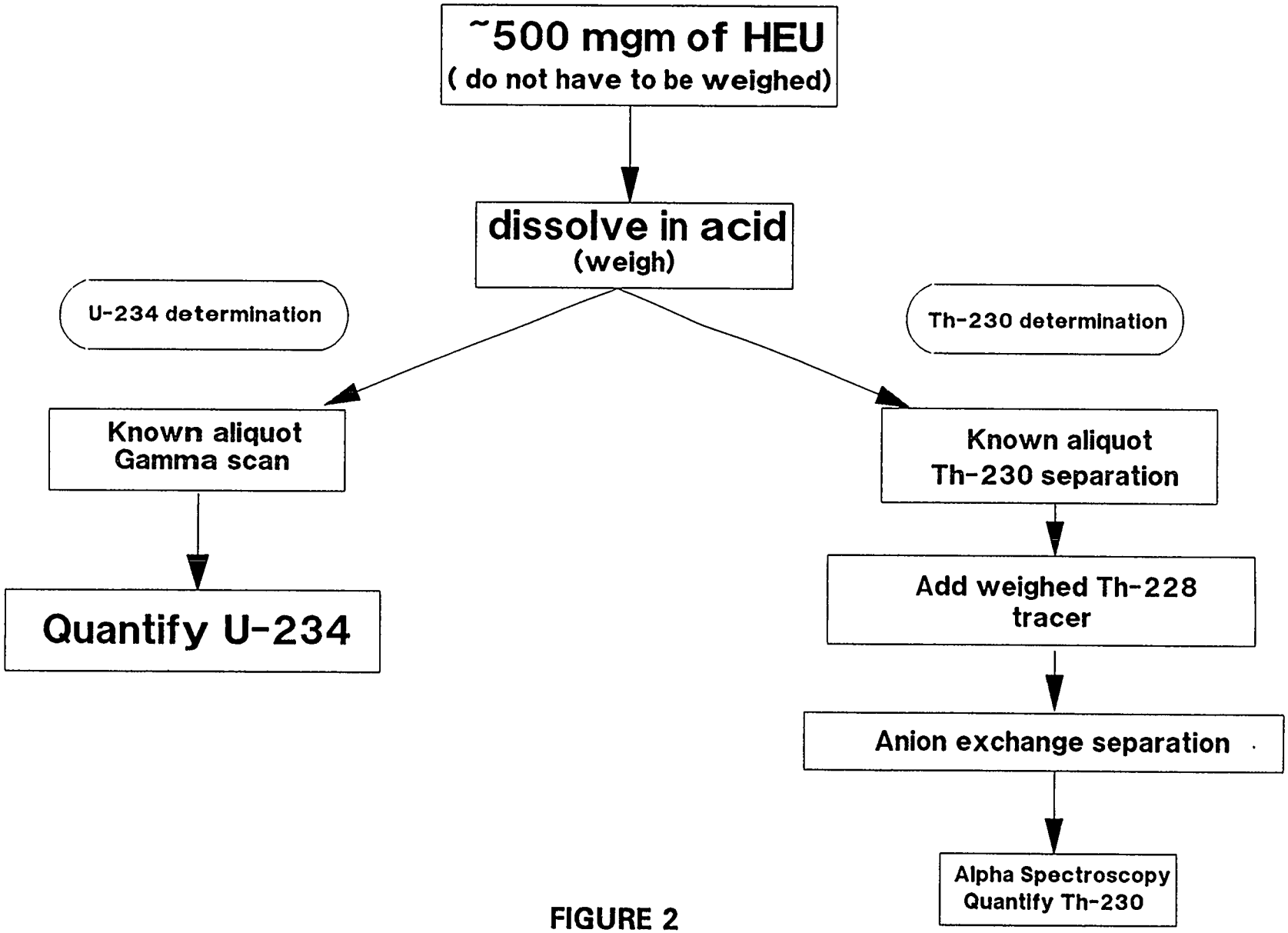


FIGURE 2

heuThflo.drw

Protactinium Chemistry Separation

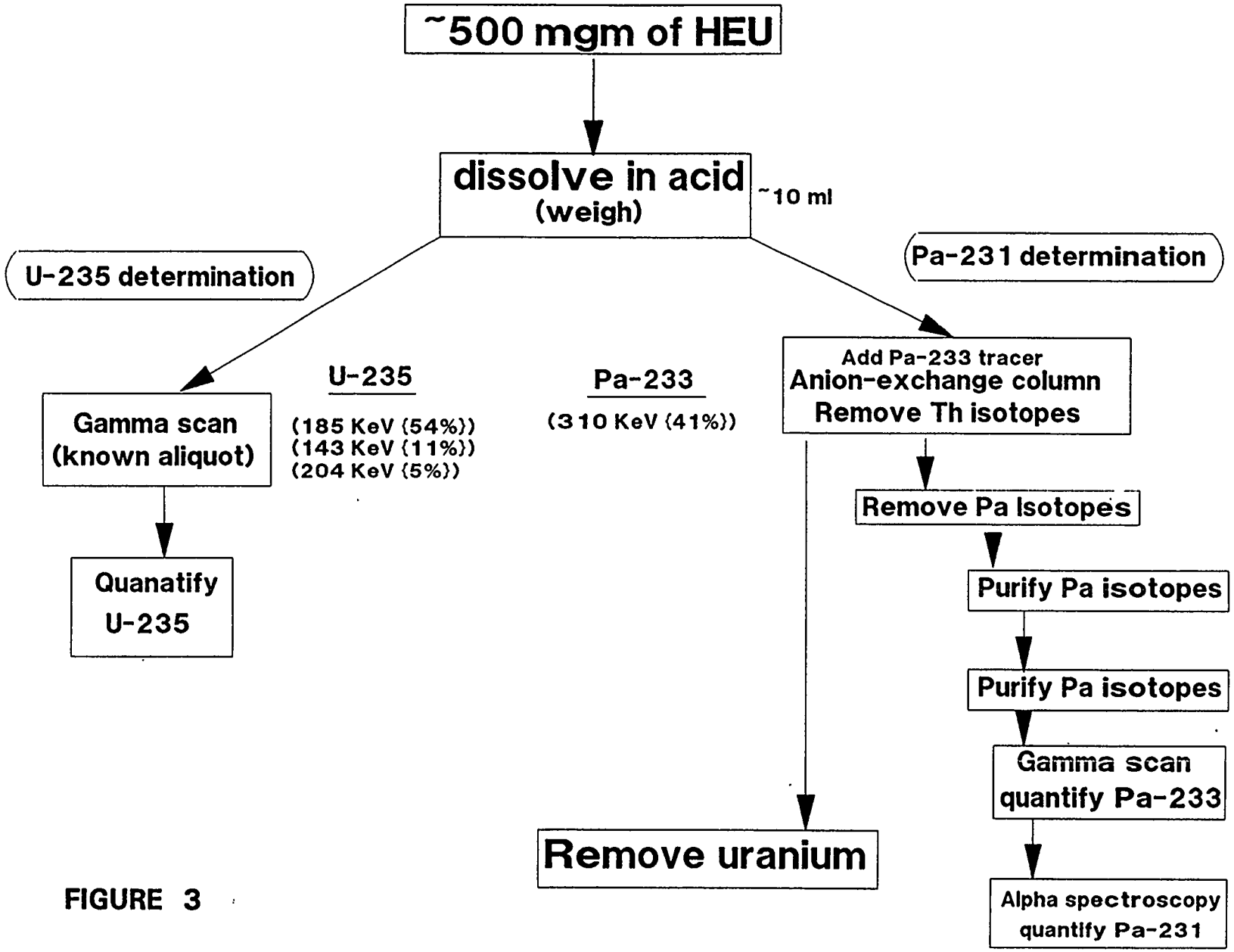
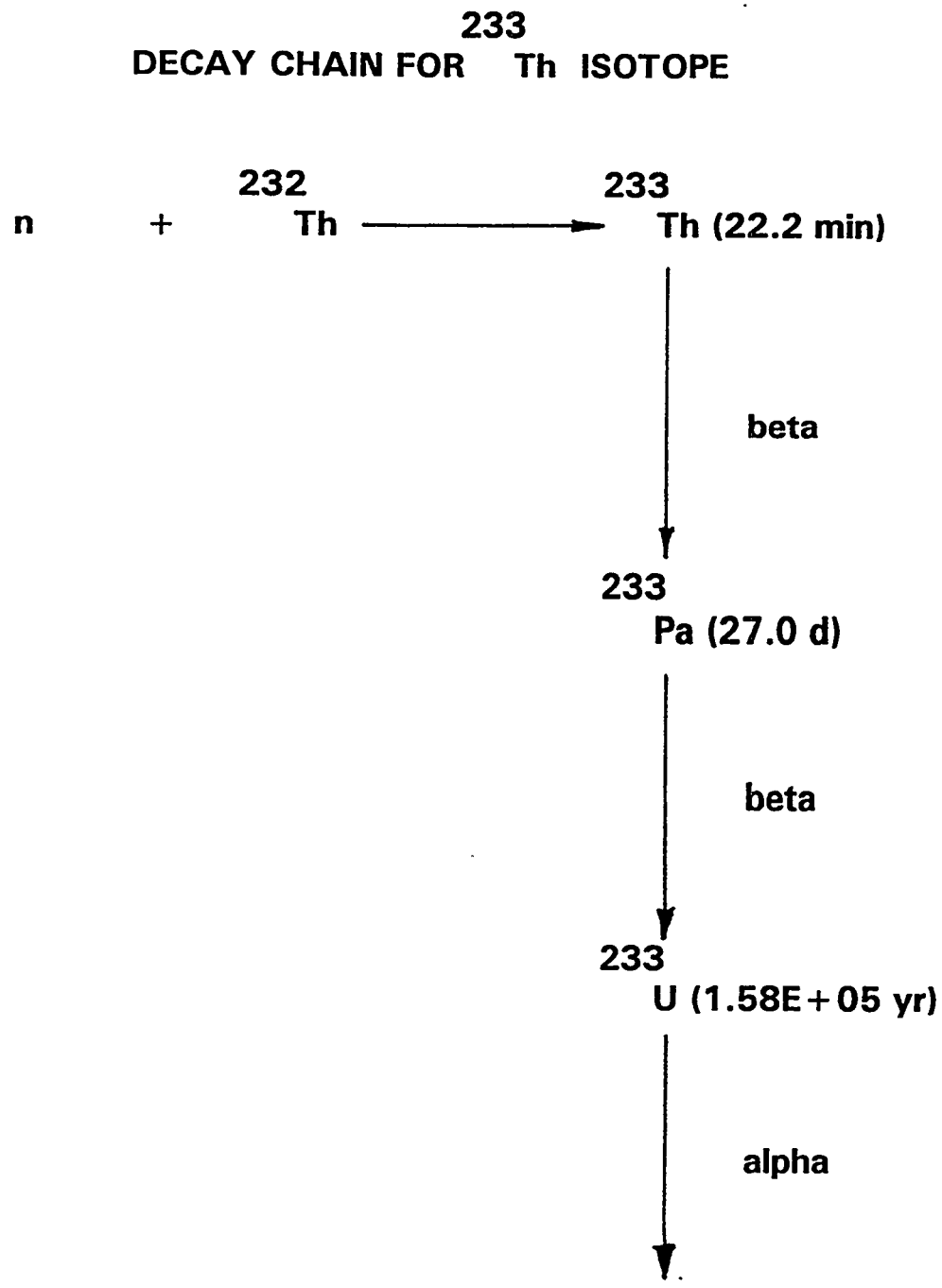


FIGURE 3

heupaflo.drw

FIGURE 4


233
DECAY CHAIN FOR Th ISOTOPE
n + 232 Th → 233 Th (22.2 min)
beta
233 Pa (27.0 d)
beta
233 U (1.58E+05 yr)
alpha

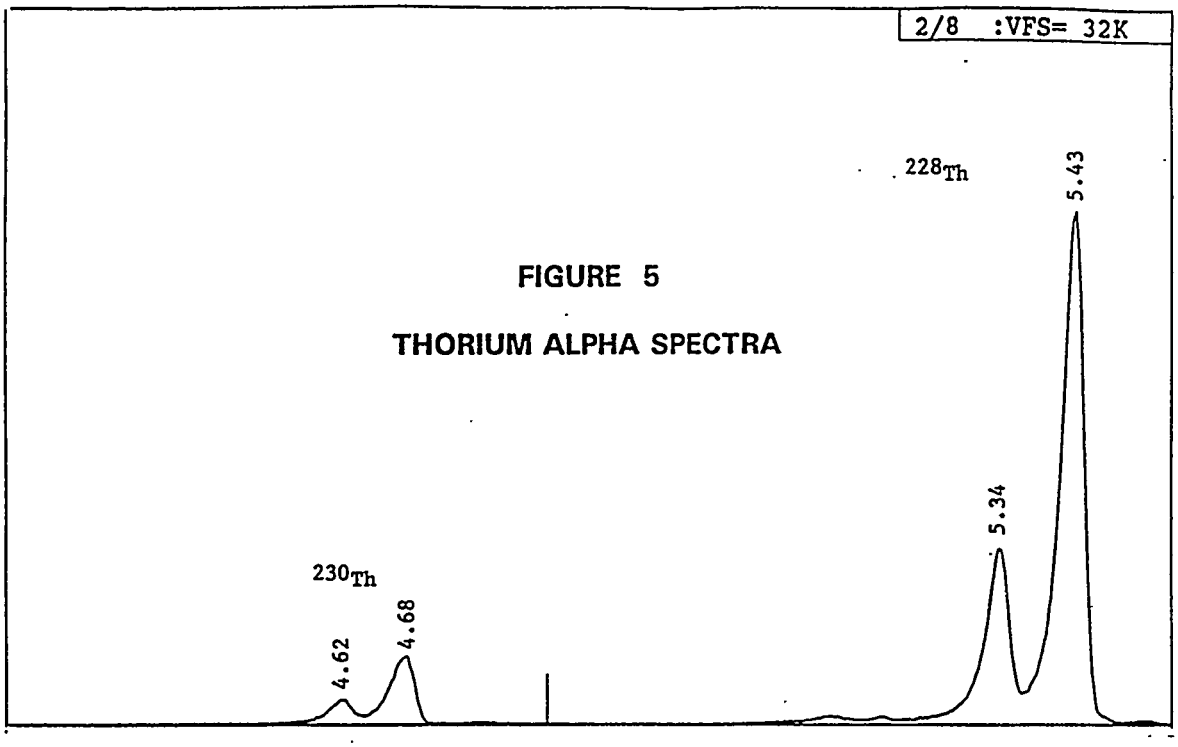


FIGURE 5

THORIUM ALPHA SPECTRA

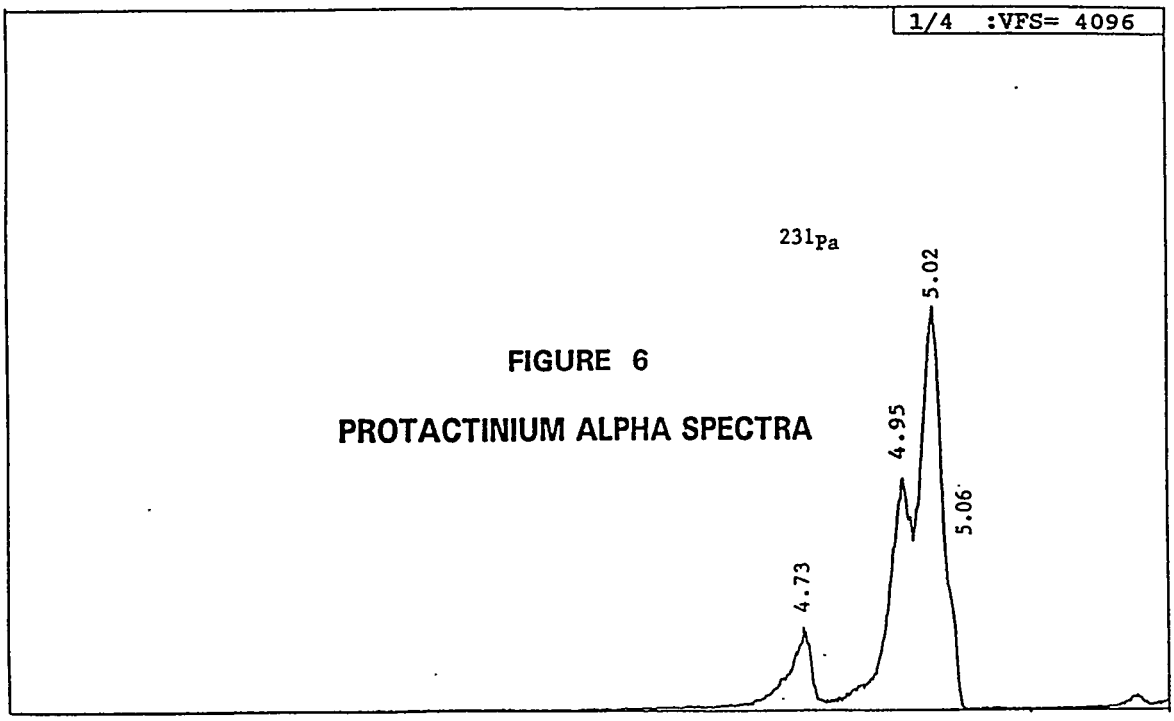


FIGURE 6

PROTACTINIUM ALPHA SPECTRA