Basic Studies on the Production of Enriched Uranium-237 and the Measurement of Its Specific Activity

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Tetsuo HASHIMOTO* and Masanobu SAKANOUE

Radiochemical Laboratory, Department of Chemistry,

Faculty of Science, Kanazawa University

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*Present address : Research Reactor Institute, Kyoto University, Kumatori, Osaka Prefecture

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1. Introduction

The natural uranium consists of three radionuclides having the mass number 234, 235 and 238 and all these nuclides emit alpha particles. By measuring these α-particles, the very small amounts of each nuclide can be determined. And, the activity ratio of $^{234}U/^{238}U$ can be measured easily by alpha spectrometry taking advantage of the energy difference of each α-particle, and the anomalous values of this ratio in natural materials give some interesting problems in the geochemical field[27]. If a suitable tracer of uranium may be employed in the purification procedure of this element and its chemical yield can be known, the absolute content of uranium in the sample will be determined simultaneously with the $^{234}U/^{238}U$ ratio. In this respect, an artificial radionuclide, uranium-237, seems to be the most appropriate nuclide as tracer for this purpose, because it can be easily detected by its beta and gamma rays and it also has a convenient half life, 6.75 days[5].

Since uranium-237 had been discovered first by Japanese investigators (1940)[1], extensive studies have been made on the excitation function of the following reactions for producing this nuclide; (n, 2n)[1]-[10], (r, n)[11]-[17], (p, np)[18], (α, nα) and (d, t) reactions. On the other hand, this nuclide can de found in the waste of the reactor fuel[9] and fallouts after the nuclear explosion[40] as the result of the (n, 2n) reaction.

The effective nuclear reaction has not been yet found for the carrier free production of this nuclide. Therefore, the above-mentioned reactions should be employed, and so uranium-237 produced is always accompanied with the target nuclide, uranium-238. In order to obtain higher specific activity, the higher flux of bombarding particles and/or the longer irradiation time are required. According to E. Akatsu et al.[17], uranium-237 of 0.2 mCi/g could be produced by the photonuclear reaction of uranium-238. They have also suggested that this nuclide having the specific activity of 1 mCi/g would be obtained from longer irradiation. But, such conditions are not available at present in our laboratory.

In the present study, the author aims to obtain uranium-237 of specific activity higher than 0.32 mCi/g. In such a case, the ratio of absolute beta activity to alpha may become about 500 and uranium-237 of such specific activity is required in order to apply this nuclide as tracer for the determination of small amounts of uranium in nature.

If hot atom effects are adapted for the enrichment of uranium-237, such higher specific activity may be realized[19]-[25]. From this point of view, some basic experiments on hot atom effects were carried out along with the examination of the target compound and the collecting agent of recoil atoms. In connection with the hot atom separation, the dynamic method with an ion exchanger[36]-[39] was also studied at first using a few cobalt complexes as targets, and then the method was applied to an uranyl-oxalato complex.

The three methods are proposed to know the specific activity; they are the beta and alpha counting method, the beta counting ratio method and the gamma spectrometric method. The application of the last method makes it possible to determine the specific activity of the sample as low as 3×10^{-3} μCi/g. Such a low specific activity could not ever be determined by any other methods so far.

A purification procedure for the irradiated uranium and a simple method for preparing the counting source by electrodeposition are also reported in this paper.

It has not been achieved to produce uranium-237 having such high specific activity as to be required for the geochemical investigation, but many valuable informations have been obtained for the production of uranium-237 and the measurement of its specific activity.

2. The Methods of the Production of Uranium-237

The nuclide ^{237}U at first was found in the course of experiments for the study of the fission of uranium with fast neutron[1]; ^{238}U (n, 2n)^{237}U reaction took place in this case. Another production of this nuclide is brought about by the irradiation of high energy Bremsstrahlung on ^{238}U; the reaction is expressed as ^{238}U(γ, n)^{237}U. Otherwise, such a thermal neutron reaction as ^{236}U(n, γ)^{237}U may also produce ^{237}U [13], but the difficulty in the preparation of the target nuclide makes this reaction

unavailable. Though other methods
have been also proposed as mentioned
before, the reaction with fast neutron
or Bremsstrahlung was mainly applied
for the production of ^{237}U in this
study.

2.1 The (n, 2n) reaction

The excitation function of the
(n, 2n) reaction for ^{238}U is shown
in Fig. 1 along with that of the (n,
fission) reaction[42]. The threshold
value of this reaction is 6.1 Mev[10]
and the maximum cross section is
given as 1.5 barns at 10 Mev of neutron
energy. Therefore, it can be understood
that the irradiation by fast neutron is
necessary to prepare ^{237}U, and that,
in its turn, the (n, 2n) reaction will
be also utilized as a monitor of very
fast neutron when the produced ^{237}U
is determined.

Fig. 1   Excitation Function of Uranium–238.

2.1.1 Irradiation in reactor

The fission neutron spectrum extends throughout wide energy region from the fast
neutron to the thermal. The occurrence of the (n, 2n) reaction in the reactor can be
confirmed by the existence of large amounts of neptunium-237 as the daughter of
uranium-237 in the waste of the reactor fuel. As to the present experiment, the
irradiation position and its neutron flux in TRIGA-reactor are shown in Fig. 2 and
Table 1, together with the gamma exposure rate in the respective conditions. As the
fast neutron flux in this table was determined by the ^{32}S(n, p)^{32}P reaction in this
case, the flux had the energy above 2 Mev and the values were found to be about one
order less than the thermal neutron flux which was estimated by the gold foil method.
The thermal neutron reacts easily with ^{235}U and the subsequent existence of fission
products in the target makes the chemical purification procedure complicated. By
wrapping the target with cadmium metal, the fission reaction caused by thermal neutron
is greatly diminished.

In convenience to estimate simply the specific activity of ^{237}U produced in various
experiments, a nomograph is made as given in Fig. 3[32]. It consists of five factors,
viz. cross section, neutron flux, decay time, irradiation time and specific activity.
One of them can be estimated easily, if other four values are fixed in this figure. As
the cross section for the fast component of the reactor neutron, the value of 12.5

1. rotary specimen rack. (r.s.r.)
2. central thimble. (c.t.)
3. thermal column. (t.c.)

A: Target resin
B: Bed resin
C: Resin column
D: Lead shield
E: Wooden plate
F: Saran filters

For the irradiation in t.c.

For the irradiation in c.t.

Fig. 2 (A) Irradiation Position; (B) Cross Sectional View of the Dynamic Irradiation Assembly

Table 1   Flux and Exposure Rate in TRIGA–reactor (at power 100 Kw/hr)

Irradiation position	Central thimble (c.t.)	Rotary speci–men rack (r.s.r.)	Thermal column (t.c.)
Thermal neutron flux (n/cm^2 sec)	3.7×10^{12}	4.9×10^{11}	3.0×10^{10}
Fast neutron flux (n/cm^2 sec)	1.6×10^{12}	5.6×10^{10}	1.0×10^8
Gamma exposure rate (r/hr)	4×10^7	1.4×10^6	7×10^3
Cadmium ratio with Au foil	2.5	3.2	30

millibarns may be adopted[10]. So. by using the neutron flux in Table 1 and setting 14 days as a decay time and 10 hours as an iraradiation time, the specific activity obtainable in this condition becomes $1 \sim 20$ μCi/g. When a depleted uranium is employed for the production of ^{237}U, the absolute ratio of β-activity to α will have the value higher than that shown in this nomograph.

2.1.2 Irradiation by cyclotron

In application of this machine, fast neutrons are produced by the bombardment of lithium metal with deuterons and fall between about $10 \sim 15$ Mev (^{7}Li(d, n) 2α; Q= 15.1 Mev). Therefore, as a cross section value, 1 barn may be employed in Fig. 3. If the other variables were fixed at the appropriates in the similar manner as in the preceding case, the specific activity obtainable by the cyclotron (Institute of Physical
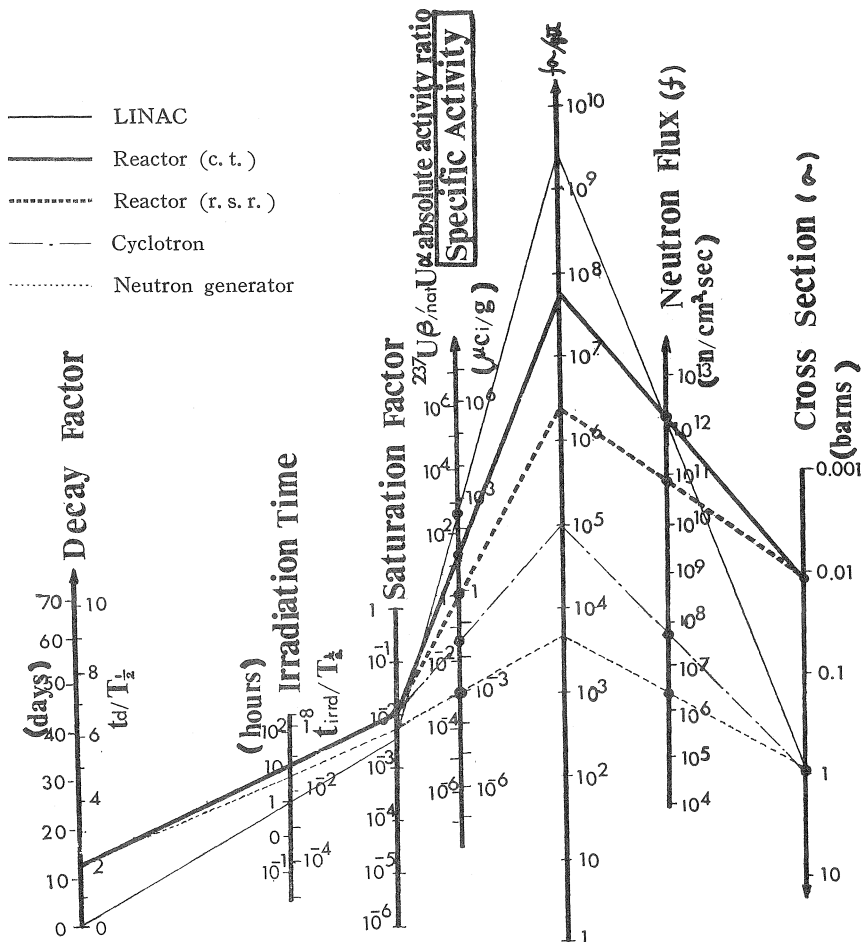
Fig. 3   Nomograph for Estimating the Specific Activity of Uranium-237

and Chemical Research, Tokyo, Japan.) is estimated as about 4×10^{-2} μCi/g.

2.1.3 Irradiation by neutron generator

Fast neutrons having the average energy of about 14 Mev are obtained by the T(d, n)He reaction in this machine. So, this neutron can be used for the (n, 2n) reaction with uranium target. The specific activity is estimated as about 10^{-3} μCi/g from Fig. 3 in the same way as the preceding two cases.

The application of the neutron from cyclotron or neutron generator will be suitable to enrich ^{237}U by hot atom effects, because the gamma exposure rate is considerably low during the irradiation. However, on the other hand, the flux of neutron produced by these machines is too low to obtain such high specific activity as to be required.

2.2 The (γ, n) reaction

Uranium-237 can be also produced by the photo-nuclear reaction, ^{238}U(γ, n)^{237}U. In this experiment, uranium dioxide was irradiated for two hours with a 20 Mev

Bremsstrahlung from a linear electron accelerator at Japan Atomic Energy Research Institute. The same machine has been employed by Akatsu et al.[17] and the value of 0.2 mCi/g has been reported as the specific activity obtained by the irradiation of one hour. By using this value as the specific activity and 1 barn as the cross section[15], it is found, from the nomograph in Fig. 3, that the flux of this irradiation source corresponds to about $10^{12} n/cm^2$ sec as neutron flux. When the decay time is taken as 14 days, the specific activity, 0.1 mCi/g, can be estimated in present experimental conditions.

3. Experimental

3.1 Chemical purification of uranium from the irradiated target and the preparation of the counting source

3.1.1 Chemical purification of uranium from the target

The alpha and beta radioactivity measurement of uranium must be carried out after the complete chemical separation from its daughters. Futhermore, the complete removal of fission products and the trans-uranium elements is also necessary in the treatment of the irradiated uranium. Hence, the author established the chemical purification scheme for the irradiated sample as follows. In the case of an organic compound, the target was subjected at first to the decomposition with perchloric acid. Otherwise, all uranium targets were dissolved into the 7:93 nitric acid. And then the solution was treated by the next procedure.

It consists of two main parts; the solvent extraction with ethyl acetate and the anion exchange process with 8 N HCl and 8 N HCl-0.3 N HF solution as shown in Fig. 4[26][27]. In each step of this scheme, the fission products, the daughter of uranium (^{234}Th) and neptunium can be excluded one by one from uranium. Finally, the purified uranium can be obtained by the elution with 0.1 N HCl solution. The radiochemical purity of uranium in this solution was examined by means of γ-spectrometry or β-decay curve. Based on the results of these radioactive measurements, this procedure was found to be satisfactory to obtain purified uranium in all cases. Furthermore, if necessary, the purified uranium solution was converted into the 7:93 nitric acid solution and the electrodeposition of uranium was carried out.

3.1.2 The simple quantitative electrodeposition of uranium

A thin and uniformly deposited counting source is required for the measurement of β and α-activity. The electrodeposition seems to be the most suitable method for such a requirement and various methods have been proposed for the complete electrodeposition of uranium[28]-[30]. However, these methods are rather troublesome in regard to the following points; the pH control of the feed solution and the temperature adjustment during the electrodeposition. So, the author aimed to develop a more simple method of electrodeposition of uranium.

Sample solution
$(7{:}93\ HNO_3\ 5ml + Al(NO_3)_3 9H_2O)$

Ethyl acetate 10 ml

Aq.   (Solvent extraction)   Org.

$1\ N\ HNO_3 + Al(NO_3)_3$

soln. 5 ml

Aq.   (Washing)   Org.

Ethyl acetate 20 ml

Aq.   Org.

H_2O

Aq.   (Back extraction)   Org.

Evap. up to dryness

Dissolve in 8 N HCl

Ion exchanger

Dowex 1×8

200~400 mesh

Washing

(1) 8 N HCl : for the removal of UX_1 (Th)

(2) 8 N HCl—0.3 N HF : for the removal of Np

0.1 N HCl : for the elution of uranium

Evap. up to nearly dryness

Dissolve in 7:93 HNO_3

Electrodeposition

Fig. 4 The Analytical Scheme for the Chemical Purification of Uranium

In this experiment, all the apparatus were the same ones described in the other literature[45] from our laboratory, except that a rotary spiral platinum (about 60 rev/min) and a stainless steel plate ($\phi = 3.5$ cm) were used this time as an anode and a cathode, respectively. About 120 μg of uranium was used and the electrodeposition behaviour of this element could be easily known by using [237]U as tracer. At the end of the electrolysis, the solution was withdrawn and the cathode plate was rinsed with pure alcohol to wash the plate. This plate was dried under an infrared lamp and the deposition yield was determined directly by counting its β-activity. Otherwise, the γ-activities of the feed and the final solution were used to determine the deposition

yield.

The following factors affecting the deposition yield were examined; the time, the current during electrolysis and the concentration of buffered solutions (ammonium acetate or formate). From the results shown in Fig. 5, it was found that the following condition was recommended for the most simple and quantitative mothod : The electrolyte was made by mixing 0.5 ml of nitric acid (7 : 93) containing uranium sample, 4.5 ml of 0.25 M ammonium formate buffered solution and 10 ml of pure ethyl alcohol. The time and the current were chosen as two hours and 400 mA, respectively. The pH value of the electrolyte varied from 3.8 to 8.6 during the electrodeposition.
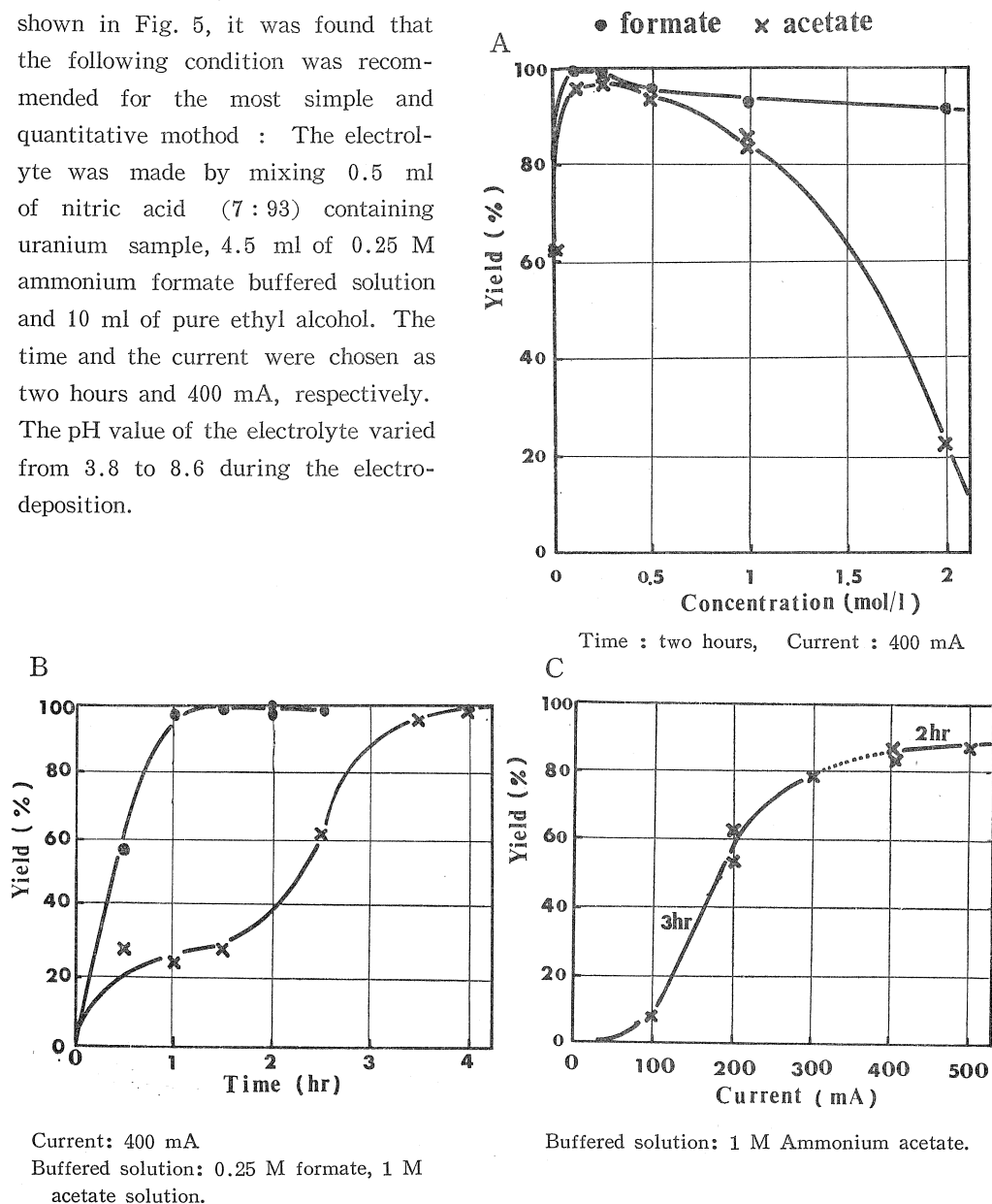
● **formate   ✕ acetate**

A

Time : two hours,   Current : 400 mA

B

Current: 400 mA
Buffered solution: 0.25 M formate, 1 M
  acetate solution.

C

Buffered solution: 1 M Ammonium acetate.

Fig. 5   The Electrodeposition of Uranium
The composition of electrolyte:
Uranium(about 120 μg): 0.5 ml of 7:93 nitric acid solution
Buffered solution: 4.5 ml of ammonium formate or acetate solution.
Pure alcohol: 10 ml of ethyl alcohol.

3.2 Measurement of the specific activity

3.2.1 Beta and alpha counting method

If the sample had high specific activity, the ratio of uranium-237 to -238 could be readily determined by measuring the β and α-activity respectively. In order to prevent the self-absorption of α-particles, it was desirable to prepare the counting source by the electrodeposition method which was described just above. Each activity was measured with GM-counter (coupled with the end window type GM-tube of $2''\phi$) and ZnS scintillation counter respectively. From the ratio of β-activity to α, the true specific activity can be calculated by making the corrections in regard to the decay factor and the counting geometry. This method could be applied successfully for evaluating the specific activity of the sample produced by (γ, n) reaction in LINAC or (n, 2n) one in the reactor.

However, this method cannot be applied to the samples of low specific activity for the following reasons. The first is the difficulty in the preparation of a thin film source with such a large amount of uranium as to be sufficient for the precise β-counting. The second is that the counting error increases with the decrease of the specific activity and, futhermore, this error is influenced largely by the growth of daughter nuclides of uranium (UX_1, UX_2 and UZ).

3.2.2 The beta counting ratio method

The daughters of uranium-238 grow up in the chemically purified uranium sample, while uranium-237 decays into neptunium-237 which is an α-emitter of a long half life. Thus, the total β-activity of such a uranium sample varies with time as the sum of the growth and the decay of such activities. Therefore, each β-decay or growth curve has the characteristic feature corresponding to its own specific activity. This relationship will be utilized for the determination of the specific activity.

The decay of ^{237}U itself and the growth of the UX_1 from the radiochemically purified ^{238}U are shown respectively as the lowest curve and the uppermost one in Fig. 6. Between these two curves, the other curves are drawn as the composite curves with the known counting ratio of the decaying ^{237}U to the growing UX_1. In order to assign the $^{237}U/^{238}U$ specific activity to each curve, the growth curves of three samples (T, N and M) are plotted experimentally in this figure. These three samples were prepared by evaporating each uranium solution of a known specific activity in a porcelain counting pan, respectively, and the gross β-activity of each sample was measured by means of the GM-counter. The β-activity at the time one hour after the chemical purification was taken as the initial activity and this value was normalized to unity in the figure. From this data, if the counting is carried out in the same condition, the true value of the specific activity for each curve can be assigned without knowing the counting efficiency for each nuclide. The values obtained in this way are shown on the right ordinate.
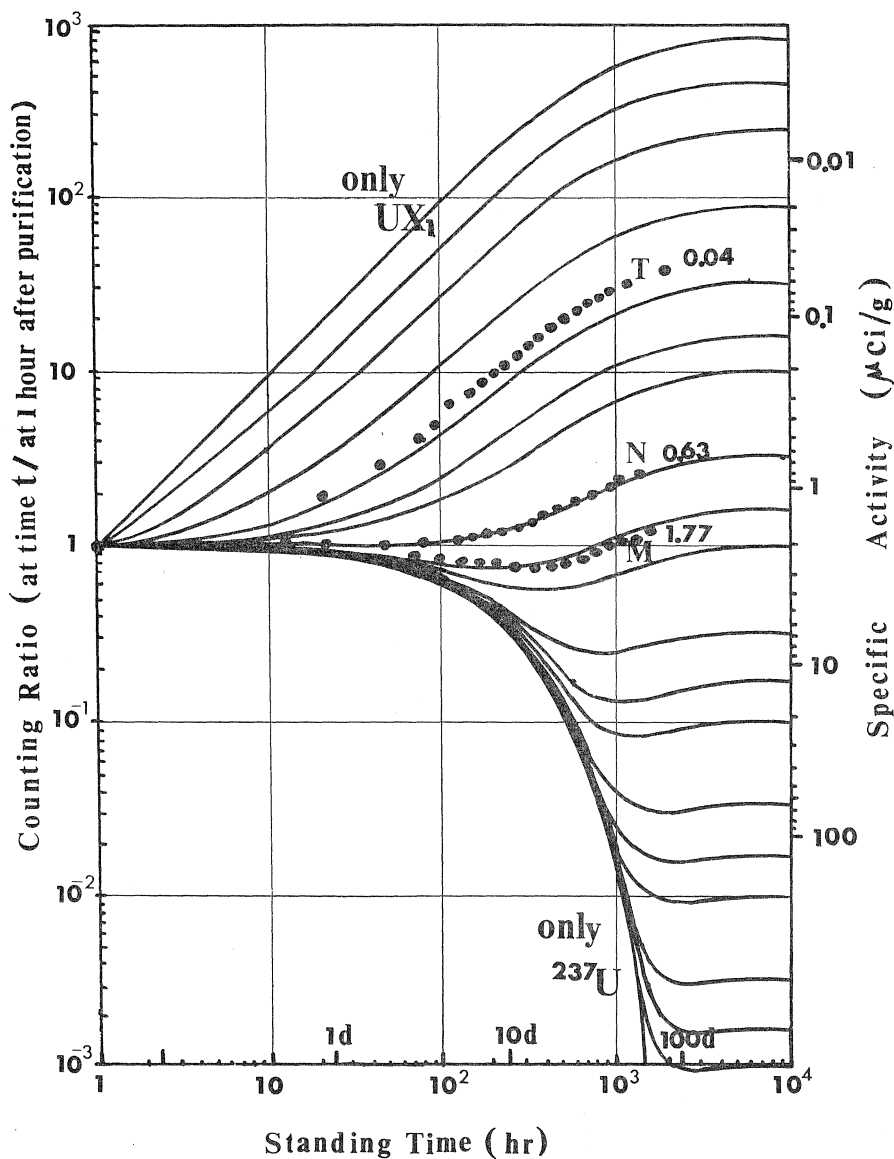
Fig. 6   The Theoretical Composite Beta Decay or Growth Curve for ²³⁷U and UX.

By the use of this relationship, the specific activity of uranium can be known readily for the irradiated sample as follows.   The ratio of the gross β-activity at a definite time to that at the time just one hour after the purification is put on the left ordinate and the time after the purification is put on the abscissa, and then one point can be obtained in this figure.   From the curve passing close to this point, the specific activity of this sample is estimated from the end of the corresponding curve on the right ordinate.   As it needs not to consider the self-absorption of β-ray to a large

extent, the preparation of the counting source is relatively easy when the meas-
urements are done by this method.   This method can be applied successfully for the
samples within the specific activity range of 10~0.05 μCi/g.

But it appears as a drawback in this method that the specific activity cannot be
known rapidly just after the purification, because a long standing time is required to
determine the corresponding grow-up curve.

3 2.3 Gamma spectrometric method

The determination of a low specific activity is usually accompanied with a large
counting error.   The sample of such low specific activity is produced in the cases of a
very low flux and/or a short irradiation.   In order to estimate such a low specific
activity, the most convenient method is proposed. As shown in Fig. 7, the gamma
spectrum of the purified natural uranium consists almost of the peak due to ^{235}U
(main peak 185 Kev)[31][43].   On the other hand, main peaks of ^{237}U appear at the
energy of 60, 103 and 208 kev. By the use of the characteristics of the respective
γ-spectra, the specific activity of the sample may be known from the composite
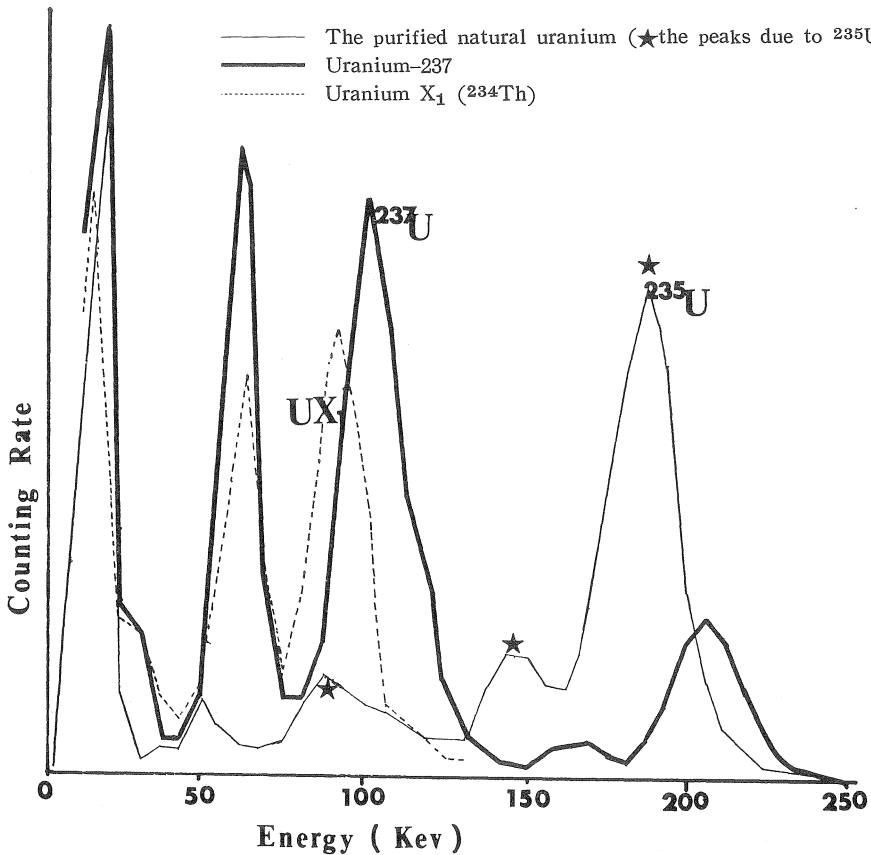

Fig. 7 Gamma Spectra

r-spectra. For this purpose, various samples of konwn specific activity are prepared and then the r-spectra (P, Q, R, S and T) are recorded as given in Fig. 8 by using a scintillation detector (NaI (Tl), well type) and a multichannel pulse height analyser (Kobe Kogyo AN-100). To simplify the subsequent treatment, each spectrum was devided into three energy regions; they are (I) 70~125 Kev, (II) 125~230 Kev and (II)′ 160~195 Kev. One of the main peak of ^{237}U is included in the (I) region and that of ^{235}U in the (II)′ region. The total activity of each region was calculated from the spectrum and their ratios ($(I/II)_{1h}$, $(I/II)_{41h}$ and $(II'/II)_{1h}$) were plotted as
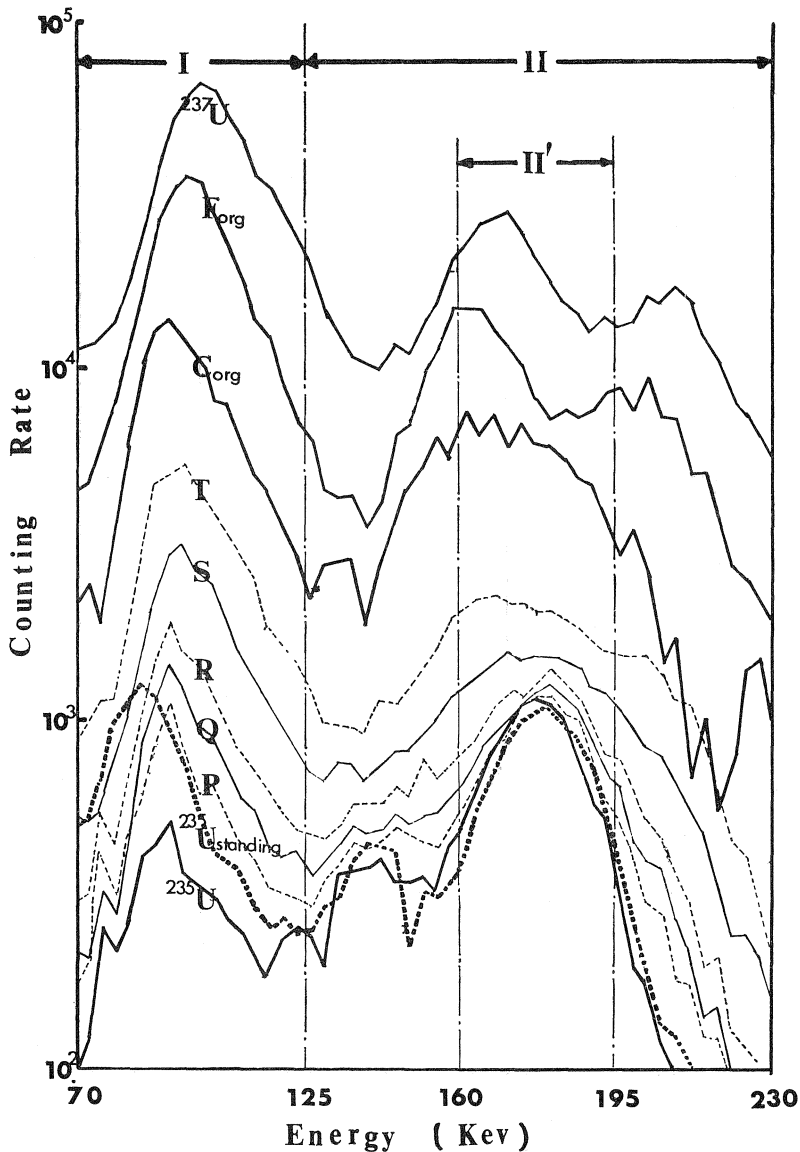

Fig. 8 Gamma Spectra of Various Samples Obtained from Experiments.

the function of each specific activity as shown in Fig. 9. The curve concerning the
(I/II) ratio, at one hour after the purification, has the most sharp slop. As the
standing time goes by, the daughters of uranium grow up in the region (I) (c.f.
"^{235}U-stand-ing" in Fig. 8) and so the slope of the curve becomes gentle as shown
in the curve at 41 hours. Apparently, the former curve of the sharp slope gives more
accurate specific activity and may be applied to the practical determination. As the
specific activity of the order of $0.1 \sim 0.003$ μCi/g can be estimated rapidly by this
method, it was applied to the low level samples prepared by cyclotron (indicated as
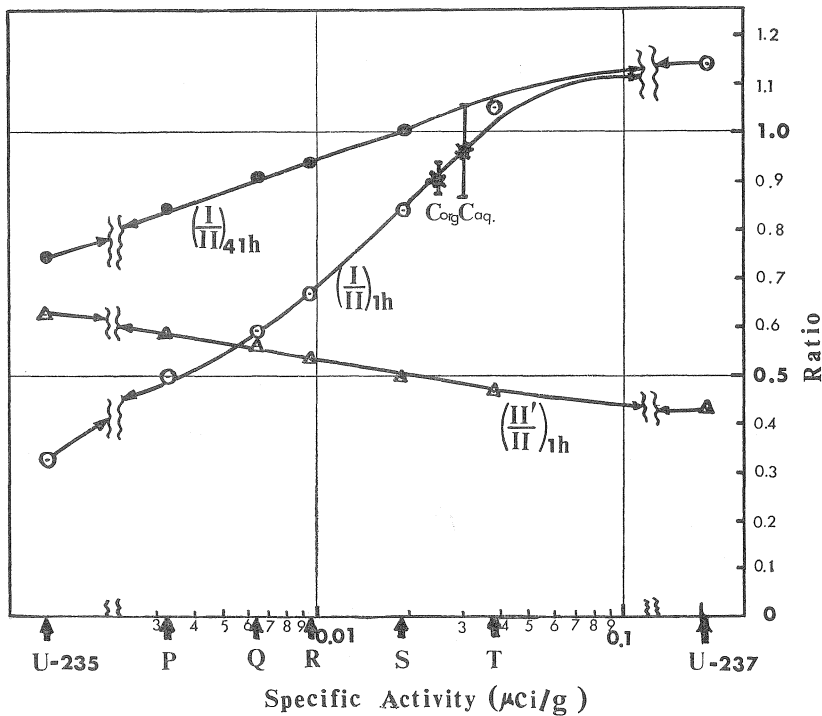C_{org} and C_{ap} in Fig. 9) or neutron generator.

Fig. 9   The Relation Between the Counting Ratio from γ–Spectrum
and the Specific Activity

3.3 Irradiation experiment of the uranium target

3.3.1 Preparation of the target compound suitable for the hot atom separation

An organometallic compound is frequently used in the investigation of hot atom
effects, because the recoil atom can be easily distinguished by the simple procedure
from the nonactivated atom. In such cases, the irradiated compound is generally
dissolved in organic solvent and then the separation of the recoil atoms is tried with

aqueous phase. Therefore, it is favourable for this purpose that the organometallic compound has no hydrolytic property. For this reason, the uranyl dibenzoyl methane seems to be suitable for the study of hot atom effects for uranium[21][25] and this compound was chosen as a target material in this experiment. The compound was prepared from dibenzoyl methane and uranyl ion solution according to the literatures [33]-[35]. If this crystalline compound is contaminated with free uranyl ions, it will cause a decrease in the specific activity of the separated uranium sample. Therefore, the recrystallized compound was furthermore subjected to the removal of such uranyl ions by the following method. The compound was dissolved in ethyl acetate and this solution was shaken with pure water in order to extract uranyl ions into water phase. And then, uranyl dibenzoyl methane was recrystallized again from this ethyl acetate solution.

3.3.2 The preliminary studies on the separation of hot atom from the target material

When the uranyl dibenzoyl methane is irradiated with neutron, recoil uranyl atoms will go out from their bonds with dibenzoyl methane and become free ionic state. Some studies were carried out to collect these species effectively.

K.P.Martinov et al. proposed the coprecipitation procedure with barium carbonate emulsion as the best collecting agent[25]. When this procedure is applied to uranyl dibenzoyl methane-acetone solution, it is supposed that the decrease of the separable yield may be unavoidable owing to the existence of organic material which must be thoroughly washed out from the precipitate. In fact, despite the repeated experiments, the satisfactory results have not been obtained as shown in Table 2. Therefore, some other methods were examined to separate hot atom species from the target material. And these experiments were generally carried out by using uranium-237 as tracer and uranyl ions in the solution were regarded as the recoil atoms. Futhermore, to check the coprecipitation of the organo-uranyl compound with various collecting agents, the

Table 2　Examination of Collecting Agents by Tracer Technique

Solvet for dis-solution of target (U–DBM)	Collecting agents	Collecting *U–DBM only	agent/Solvent *UO_2^2 ions only	activity ratio *U–DBM+*UO_2^2 (activity ratio 1)
Acetone	$BaCO_3$ emulsion 0.5 ml	0.01	1.8	0.02
Acetone	$AlPO_4$ emulsion 0.5 ml	0.21	55	0.22
Ethyl acetate	Water (stripping)	0.005	—	0.91
Diisobutyl Ketone	Water (stripping)	0.007	—	1.3

*U : uranium–237 as tracer

U–DBM : uranyl dibenzoyl methane

uranyl dibenzoyl methane labelled with ^{237}U was prepared and used in the experiment.

The solvents and the collecting agents shown in Table 2 were examined for this purpose and the results obtained are also listed in the same table. From these results, the extraction of uranyl ions from ethyl acetate solution into water found to be the most effective and convenient method. So, this method was employed hereafter for the hot atom separation.

3.3.3 The results obtained by various static irradiations and the discussion

3.3.3.1 The (n, 2n) reaction

The (n, 2n) reaction for the production of ^{237}U is mainly used for the study of the hot atom effects. This reaction can be caused by the irradiation in the nuclear reactor, the cyclotron or the neutron generator (see Fig. 3). According to Martinov et al.[25], the enrichment factor of 10^3 and the separation yield of 8 % have been reported for the irradiation experiment of the same uranyl compound with the generator neutron (10^{11} n/sec). In the present experiments, as shown in Table 3, the specific activity of ^{237}U produced by the reactor had the value higher than that produced by the other two machines. This difference may be attributed mainly to the fast neutron flux in these different irradiation conditions. The studies on hot atom effects were carried out by irradiating uranyl dibenzoyl methane with fast neutron from the reactor and the cyclotron. As seen from the results in Table 3, the only slight enrichments were observed in these experiments as compared with the result of the preceding literature[25]. This fact will be attributed to the following two factors; the increase of annealing effects due to the long standing time after the irradiation at room temperature and/or the deficiency of fast neutron flux (refer to Fig. 3). In regard to the annealing, about 10 days had passed from the end of the irradiation to the beginning of the hot atom separation owing to the transportation of the sample to our laboratory. Therefore, the earlier separation after the irradiation and the higher neutron flux are desired to produce the higher specific activity.

3.3.3.2 The (γ, n) reaction

All the uranium-237 used as the tracer in the preceding experiments were produced by this photo-nuclear reaction, because the sample having the highest specific activity could be obtained by its powerful irradiation condition. On the other hand, it is difficult to expect the high enrichment by the hot atom effects, because the intense radiolysis of the target may take place during the irradiation. But, it must be mentioned that the most fission products were collected in the boric acid fraction when the mixture of uranium dioxide and boric acid was irradiated with Bremsstrahlung from LINAC[17]. Furthermore, it is supposed that some slight enrichments of ^{237}U may also occur in the same fraction as the result of hot atom effects.

In the present experiment, the mixture (1:10 at weight ratio) of uranium dioxide and boric acid powder under 200 mesh was pressed into the pellet form and irradiated

for two hours with a 20 Mev Bremsstrahlung from a linear electron accelerator. After about 10 days passed by owing to the transportation of the sample, the pellet was dissolved with the following solution of each about 20 ml successively; (1) hot water, (2) hot water, (3) 1 N nitric acid and (4) concentrated nitric acid. The former two solutions are employed to dissolve the boric acid component out of the mixture. Each fraction was treated chemically as mentioned before in order to determine the specific activity of ^{237}U and the relative yield was also estimated for each fraction.

From the results shown in Table 3, it can be concluded that the slight enrichment of the ^{237}U is observed in the boric acid fraction; the total yield of the boric acid fractions is 1.5 % and the specific activity in the fraction (1) has the maximum value in our experiments. This result suggests that, at present, this method seems to be the best one for the production of the ^{237}U having the high specific activity to be used as tracer.

When the organometallic compound was used as the target materials in this study, the irradiated uranyl dibenzoyl methane was apparently suffered from the strong radiolysis and partially carbonized. So, it is expected that the higher enrichment effects will not be able to obtain in such system.

Table 3 Yield and Specific Activity Obtained in Various Static Method

Irrad. form	Irrad. machine	Fraction	Specific activity (μCi/g)	Enrichment factor	Separation yield (%)
UO$_2$ – H$_3$BO$_3$ pellet	LINAC	1. Hot water	182.8	2.2	1.4
		2. Hot water	106.5	1.3	0.1
		3. 1N HNO$_3$	90.1	1.1	1.8
		4. Conc. HNO$_3$	81.9	Unity	96.7
U–DBM	LINAC	Aq. (Water)	166.9	1.3	12.2
		Org. (Ethylacetate)	125.7	Unity	87.8
U–DBM	Reactor (r.s.r.)	Aqueous	2.4	2.4	2.1
		Organic	1.0	Unity	97.9
U–DBM	Cyclotron	Aqueous	3.0×10^{-2}	1.2	9.1
		Organic	2.5×10^{-2}	Unity	90.9
U$_3$O$_8$	Neutron generator	Conc. HNO$_3$	10^{-3}	—	100

Specific activity was determined in 10~15 days after each irradiation.

3.4 Basic studies on the dynamic method (by some cobalt complexes)

3.4.1 Preparation of the sample

The complex salts, $K_3[Co(C_2O_4)_3]$, $Na_3[Co(NO_2)_6]$ and $K_3[Co(CN)_6]$, were prepared by the method described in "Inorganic Synthesis"[46] and they were purified by the repeated crystallization. Anion exchange resins, Dowex 1x8 of 120~150 mesh and 40~50 mesh in dry condition, were chosen as the sample resin.

After the resin was conditioned finally by acetic acid solution, it was converted into the complex ion form by treating with an excess amount of about 0.1 normal solution of the complex salts and washed thoroughly with pure water. The resin was then treated by nitric acid solution of a known pH, which is to be used as an eluent of the separable species. The resin of the compex ion form was prepared just before the irradiation.

3.4.2 Irradiation and separation

In static irradiation, about 2 ml of the sample resin was taken into a polyethylene vial with about 0.5 ml of the digesting liquid mentioned above and irradiated batchwise in the rotary specimen rack or in the thermal column (with lead shield) of the TRIGA-reactor. The neutron flux and the exposure rate at each position are given in Table 1. After the irradiation for 20 min or 2 hr in the respective position, it was transferred into a glass column and then the nitric acid of a definite pH was passed through the resin as an eluent of the enriched cobalt species at a flow rate of about 2~4 ml/min. The effluent was sampled in seven 25 ml portions by a fraction collector.

In the dynamic method, during irradiation in the thermal column or in the central thimble, the separation of the recoiling species was realized as reported before[37][38]. The irradiation assemblies used in these experiments are shown in Fig. 2 (B). The volume of the resin loaded with complex ion is 10 ml and 2 ml for the respective irradiation positions, while the volume of the bed resin was fixed to be 1 ml throughout the experiments. The irradiation was done for two hours of the reactor operation. Futhermore, the eluent was passed at a constant flow rate of 4 ml/min for more one hour and a half after the shutdown of the reactor. The effluent was collected in each fraction by a fraction collector as in the case of the static method.

It should be reported here that in the case of the oxalato-complex (green coloured), a pink coloured anionic species of relatively high specific activity was observed in the bed resin part. This species was supposed to be an intermediate between the parent species and the completely aquated one and might have the form of $[Co(C_2O_4)_2]^-$[41]. This compound was eluted by 0.02 N nitric acid. Likewise, in the nitro-complex (yellowish brown), a yellow coloured anionic species of a relatively low specific activity became to appear in the bed and it was eluted in the later portions of effluents when the nitric acid of more than 0.01 N was used as the eluent. The form of this species has not been identified yet.

3.4.3 Measurements

The activity of each aliquot of the effluents and that of the resin were counted with a well type NaI (Tl) scintillation counter. The measurements of the specific activity on static runs were made for the most enriched first two or three fractions in the eluents. In order to determine the nonactive cobalt in these eluents, the following method was employed; the activation analysis utilizing $^{60m}Co(T_{\frac{1}{2}}=10.5$ min) with the aid of a multichannel analyzer or the colourimetry with nitroso-R salt.

3.4.4 Results

The results obtained are shown in Tables 4 and 5. The interpretation of the experimental results and some theoretical discussions will appear in the other paper by the cooperation of the author with T.Matsuura[39].

Table 4 Separable Yield and Specific Activity of Enriched Fraction for Various pH of Eluent and Irradiation Conditions (The value of specific activity are shown in the brackets)

Resin* Form	pH of eluent	Yield (%) and specific activity (μCi/mg)		
		Static method at r.s.r.(irrad. for 20 min)	Static method at t.c. (irrad. for 2 hr)	Dynamic method at t.c. (irrad. for 2 hr)
$[Co(C_2O_4)_3]^{3-}$	6**	70.7 [1.5]	50.4 [0.3]	86.6 [1.4]
	6**(40~50 mesh)	43.4 [1.0]	36.0 [0.2]	55.0 [0.5]
	4.0	76.7 [1.8]	51.5 [0.4]	74.6 [1.5]
$[Co(NO_2)_6]^{3-}$	6**	7.9,7.6 [0.5]	7.3 [0.1]	3.8 [0.5]
	3.0	8.5 [0.8]	10.3 [0.1]	13.9 [0.4]
	2.5	16.9 [0.7]	10.7 [0.1]	47.7 [0.2]
	2.0	52.1 [0.6]	49.9 [0.1]	97.7,90.2 [0.2]
	2.0(40~50 mesh)	34.5 [0.8]	34.4 [0.1]	61.0 [0.1]
$[Co(CN)_6]^{3-}$	6**	0.8 —	3.1 —	5.2 —
	3.0	6.1,5.2 [400]	6.8 [200]	5.9 [120]
	2.0	7.4,7.0 [150]	7.7 [100]	8.6 [50]
	2.0(40~50mesh)	6.5,5.9 [100]	9.6 [20]	9.9 [20]
	1.0	11.0 [70]	10.4 [20]	16.5 [0.2]
	0****	46.8 [0.2]	46.9 [0.05]	89.9 [0.01]

    * The mesh size of resin is 120~150 mesh except otherwise noted.

    ** Pure water.

    *** 1 N HNO$_3$

Table 5 Separable Yield and Specific Activity of Enriched Fraction by the Dynamic Method
in the Central Thimble
(The mesh size of resin is 120~150 mesh; the irradiation time is 2 hr, except otherwise noted)

Resin form	pH of eluent	Yield (%)	Specific activity (μCi/mg)
$[Co(C_2O_4)_3]^{3-}$	6*	17.0	1.4
	6*,**	7.1	1.4
	6*,** $\left(\begin{array}{l}\text{irrad. for} \\ \text{40 min}\end{array}\right)$	8.0	1.2
$[Co(NO_2)_6]^{3-}$	2.0	98.3	2.0
$[Co(CN)_6]^{3-}$	2.0	16.3	80

   * See Table 4
   ** Flow rate is 2 ml/min.

3.5 Preliminary experiment for the production of uranium-237 by the dynamic method

In order to obtain enriched uranium-237, the application of the dynamic method seems to be favourable as in the case of cobalt complexes. For this purpose, uranyl oxalato complex was chosen as a complex-resin sample and prepared as follows.

Ammonium diuranate was precipitated in uranyl nitrate solution by adding dropwise aqueous ammonia. Then, the precipitate was dissolved in a saturated oxalic acid solution and the solution was passed through the anion exchange resin column (acetate form, Dowex 1X8, 120~150 mesh). After the yellow uranyl oxalate was completely adsorbed on the resin, this column was washed with distilled water sufficiently. The resin was put in a polyethylene column or vial and was subjected to the irradiation at central thimble in TRIGA-reactor, using the assembly shown in Fig. 2 (B). The further procedures were the same as in the cobalt complexes.

The following results were obtained by this experiment. In these cases, each effluent was condensed by evaporation and then the chemical purification for uranium was carried out and finally the radioactivity of each fraction was measured.

Dynamic method
    Resin fraction (retention) : 20.7 μCi/g
    Bed resin fraction   : 21.5 μCi/g
    Eluted fraction   : No [237]U activity (mainly composed of fission products)

Static method (with the use of ion exchange resin)
    Resin fraction (retention) : 21.3 μCi/g
    Eluted fraction   : No [237]U activity (mainly composed of fission products)

From these results, a slight enrichment of ^{237}U seems to appear in the bed resin fraction. This enrichment is probably derived from hot atom effects. These facts give some possibility of the enrichment by the application of the dynamic method to such system. In the oxalate system, the recoil uranium ions may be rapidly recombined with carbonate ions which are reily produced by the radiolysis of oxalate as in the case of trioxalatocobaltate complex[39]. Therefore, in order to enrich more ^{237}U in bed resin or eluted fraction, other system must be applied to the dynamic method.

4. Consideration

Throughout these experiments, the maximum specific activity of 180 μCi/g was obtained in the boric acid fraction separated from the pellet which had been irradiated with a Bremsstrahlung. However, even this ^{237}U sample cannot be applied to the determination of uranium for the geochemical purpose because of its relatively low specific activity.

Here, the authors propose one of the methods for the enrichment of ^{237}U. From the present experiments, it was found that the application of the organometallic compound was advantageous to obtain the high enrichment factor. On the other hand, the application of the dynamic method led to enhance the separable yield in the cases of the cobalt complexes. If the organometallic compound is used in the dynamic method, the two favourable factors for the preparation of the enriched ^{237}U may be realized simultaneously. As the organometallic compound has generally the nonpolar property, it cannot be adsorbed on ion exchange resin, but it can be easily dissolved in organic solvent. So, the best method for this purpose seems to be the application of the reversed phase partition chromatography which has been been used recently in the field of analytical chemistry[44].

For the preparation of the solvent-column, ethyl acetate solution of uranyl dibenzoyl methane may be supported with the conventional supporter such as Kel-F. And, this supporter will be subjected to the dynamic method instead of the resin of the complex-form which is used in the present study. If uranium-237 atoms or ions in recoil state were produced in this supporter column by neutron irradiation, it will be eluted out immediately by the contact with the flowing water. Thus, the ^{237}U atoms or ions will be successively separated from the parent compound and the enriched ^{237}U will be obtained. For such experiments, this paper may present an important information and many valuable data.

Acknowledgements

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