몇가지 알파입자 방출 핵종의 전해석출 및 알파
스펙트럼 측정에 의한 그의 동위원소 정량

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(1983. 2. 14 접수)

Electrodeposition of some Alpha-Emitting Nuclides and its Isotope Determination by Alpha Spectrometry

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(Received February 14, 1983)

요 약. 몇가지의 알파입자를 방출하는 핵종, 즉 악티늄족 원소들, ^{207}Bi 및 ^{210}Po을 전해석출하는 장치를 만들었다. 스텐레스 원판으로된 환원전극에 이 동위원소들을 석출했으며(석출부분 직경=18 mm), 산화전극으로는 백금선을 썼다. 전해질로 염화암모늄을 쓰고, 초기 pH=4, 염소이온농도 =0.6M 이하, 용액부피=15m*l* 로 하여 1.5암페어(전류밀도=0.59A/cm²)의 전류를 100 분간 흘려주어 98.3 % 의 석출 회수율과 ±0.7 %의 재현도를 얻었다. 석출된 시료의 알파스펙트럼을 측정한 결과 에너지 분리도로서 $^{210}Po=18.3keV, ^{234}U=21.8KeV$ 및 $^{239}Pu=36.0keV$인 반치전폭 (full width at half maximum)을 얻었다. 국산 천연우라늄(충북·괴산) 시료를 전해석출하여 그의 알파스펙트 럼을 구한 결과 $^{238}U: ^{234}U=1:6.1×10^{-5}$을 얻었으며 $1.8×10^{13}$ neutrons/cm² · sec 인 중성자속으로 144일 동안 쪼여준 ^{238}U 시료를 전해석출하여 그의 알파스펙트럼을 구한 결과 $^{238}U: ^{239}Pu: ^{241}Am=$ $100:0.0263:5.20×10^{-5}$을 얻었다. 조사시료중의 ^{238}U 에 대한 본실험의 정량결과는 고체형광측정법 및 질량스펙트럼법에 의한 결과들과 상대오차 1.6 % 이내에서 일치하였으며, ^{239}Pu 의 경우는 음이 온교환분리-알파스펙트럼 측정 및 삼불화테노일아세톤(thenoyltrifluoroacetone)을 쓴 용매추출-알파 스펙트럼 측정에 의한 정량결과들과 상대오차 ±4.0 % 이내에서 일치하였다.

ABSTRACT. An apparatus was made for the electrodeposition of alpha emitting actinide nucli-des, ^{207}Bi and ^{210}Po. The electrodeposition was made on a polished stainless steel plate cathode. The anode was made of platinum wire and to stir the solution. With the ammonium chloride as electrolyte, initial pH=4, chloride concentration=0.6M and solution volume=15m*l*, a current of 1.5 ampere(current density=0.59A/cm²) was flowed for 100 minutes for the quantitative recovery of electrodeposition and on average recovery of 98.3 % was obtained within ±0.7 % uncertainty. Alpha spectrometry of the electrodeposited sample showed alpha peaks from ^{210}Po, ^{234}U and ^{239}Pu having energy resolution (FWHM) of 18.3, 21.8 and 36.0 keV respectively. The electrodeposi-tion and alpha spectrometry for a natural uranium sample of domestic origin gave $^{238}U: ^{234}U=1:$ $6.1×10^{-5}$ and for a neutron-irradiated uranium sample did $^{238}U: ^{239}Pu: ^{241}Am=100:0.0263:$ $5.20×10^{-5}$. The result of ^{238}U determination in the irradiated sample by electrodeposition-alpha spectrometry was in accord within ±1.6% of relative error with the results of solid fluorimetry

and mass spectrometry. For ^{239}Pu the result of electrodeposition-alpha spectrometry was in accord within ±4.0 % of relative error with the results of anion exchange separation and the thenoyl-trifluoroacetone(TTA) extraction both followed by alpha spectrometries.

INTRODUCTION

For the alpha spectrometric determination of some nuclides it is necessary for the deposited sample to be as thin as possible and electrodeposition can be a good measure for such a purpose. Mitchell electrodeposited actinides on platinum[1]; but the possibility of contamination of platinum makes his procedure somewhat inapplicable. Donnan and Dukes[2] electrodeposited actinides using natural uranium as carrier. Talbitie elctrodeposited actinides from sulfate medium[3], but this unnecessarily delays deposition time and he did not describe the details of the apparatus and conditions. Puphal and Olsen[4] used chloride-oxalate mixed electrolyte, flowing a current of 4A for the electrodeposition. But at this current overheating results and oxalate can precipitate with tervalent metal ions accompanying coprecipitation of the actinides.

Kametani and Kawakami[5] used molybdenum as carrier in electrodepositing natural uranium. Some authors used electrodeposition for determining α-emitting nuclides from environmental or marine samples[6~9] and others electrodeposited protactinium to determine its isotopes[10]. But all of these authors did not show the detailed description of the apparatus and procedure.

For such reasons we consider that a study of both the electrodeposition and α-spectrometry for the determination of α-emitting nuclides is necessary.

EXPERIMENTAL

The Cell. The cell and electrodes were made as shown in *Fig.* 1. The electrodeposition was made at the s.s. plate cathode put inside the

brass bottom, around which a cooling water coil was surrounded by welding. The bottom of the teflon cell bod ywas joined to the s.s. plate using an O-ring to keep the solution leak-tight for the electrolysis. The anode was a rotating platinum electrode in a disk shape. At the upper part of the anode stirrer a brass cylinder was made to enclose the stirrer rod. A spring cushioned carbon bar linked to power supply contacted the rotating surface of the brass cylinder for the electrical connection between the power supply and the anode. To protect the solution from contamination by metal particulates of other dusts, a glass cover was made on the anode stem to cover the teflon cap. But the cover was made somewhat larger in diameter
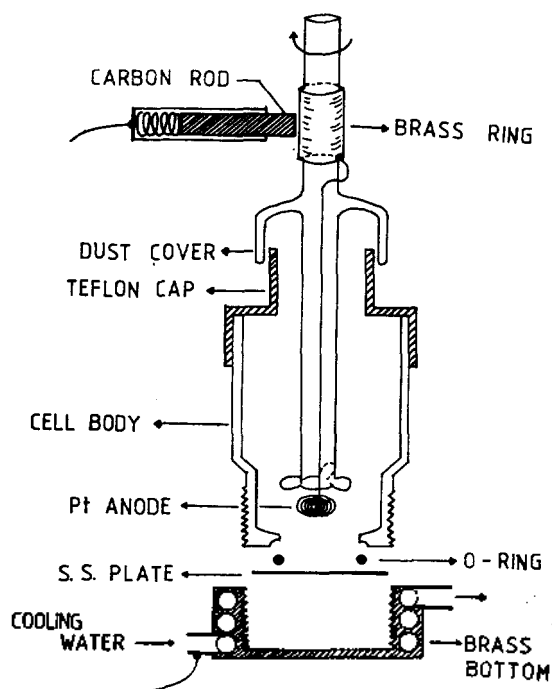

Fig. 1. Apparatus for the electrodeposition of α-emitting nuclides.

than the cap for its free rotation.

Reagents. (1) Diethylene triamine pentaacetic acid, penta sodium salt(DTPA-Na salt)-A chemical purpose reagent by Eastman-Kodak Co. was diluted (1 : 1) with water to give $0.41M$.

(2) 118mg/ml Na$_2$SO$_4$, Saturated hydroxylamine hydrochloride, $3M$ and sat'ed NH$_4$Cl, 0.05% methyl red (in ethanol), etc., were all of G. R. grade.

(3) Reference α-sources ^{210}Po, ^{239}Pu and ^{241}Am(Radioisotope Products Laboratories, USA), each of 0.1μCi, were used.

Instruments. (1) Direct current supply-One which could supply 0 to 3A with precision of $\pm1\mu$A at 0~105V was made.

(2) Fluorimetry for uranium-A Jarrell-Ash 26-000 fluorimeter was used to determine uranium.

(3) α-gross counting-A ZnS(Ag) Coated PM tube was used for detecting α-particles. The counting was made by Eberline MS-2 scaler.

(4) α-spectrometry-A surface barrier detector with 50mm^2 of active area was used to detect α-particles with different energies, with the sample chamber air-evacuated by pumping. The pulse height spectra of α-particles were acquired and analyzed by 8192 channel Canberra Series 8000 analyzer.

PROCEDURE

First, polish the s.s. plate to mirror with three zero (000) roll type or CW 1500 sand paper and clean it. Put it inside the brass bottom. Set an o-ring in the groove of the bottom of body. Then tighten the body and the bottom together. Wash the inside of the cell and take a sample of about <100μg or <0.1 μCi. Add 0.5ml of the Na$_2$SO$_4$ solution, 4 drops of 1 : 1 DTPA-Na salt and one dr. of sat'ed

hydroxylamine hydrochloride. Add a proper volume ($\leq$3ml) of $3M$ NH$_4$Cl with care for the [Cl$^-$] not to exceed $1M$. Add 7ml of distilled water, one dr. of methyl red, then 1 : 1 NH$_4$OH until the solution becomes yellow. Again, add $1M$ HCl till the solution turn to be red for thirty seconds. Add 3 dr. of 1 : 5 HF. Finally, add an appropriate volume of distilled water to make the total volume 15ml.

Set the cell with the electrodes 4mm apart, stir the solution and circulate cooling water. Flow 1.5A for 100 minutes. If the voltage between the electrodes become greater than 15V during electrodeposition, add an appropriate volume of sat'ed NH$_4$Cl ($\leq$1ml) and make sure that the voltage does not drop below 7.5V.

Two minutes before the end of electrodeposition, with the stirrer off and the current on, add 2ml of 1 : 1 NH$_4$OH to make the solution alkaline.

On completing electrodeposition, take out the plate and wash it with 1 : 99 NH$_4$OH-EtOH. Roast the plate on a hot plate at about 700-800°C or a propane flame for 5 minutes.

RESULTS AND DISCUSSION

Conditions for Quantitative Electrodeposition. More than 2A of current resulted in overheating in continued electrodeposition, whereas 1A took too long a time for the complete deposition; the optimum current taken was 1.5A.

Bisulfate was added to the solution for the appropriate nuclides to exist in a more suitable form for deposition. Excessive amount of bisulfate delayed the deposition and so 59mg of Na$_2$SO$_4$, amounting to 50mg of NaHSO$_4$, was added.

DTPA-Na salt somewhat delayed the deposition but contributed to selective deposition of

the nuclides and to an even, well-agglutinated deposit. A solution excessively alkaline caused metal hydrolysis leading to an obstruction of the deposition, whereas a solution excessively acid brought about corrosion of the cathode and deposit; the pH was set at 4.

When the $[Cl^-]$ was more than $1M$, corrosion also took place at the cathode and deposit and it was made not to exceed $0.6M$. With the solution composition as above and 1.5A for electrodeposition, the initial voltage was 7.5V (or resitance of solution$=\dfrac{V}{I}=\dfrac{7.5}{1.5}=5\Omega$). But as reaction proceeded, because of the consumption of the electrolyte by Cl_2 gas evolution at the anode, the voltage increased continuously with the resultant overheating of the cell and the apparatus. So, when the voltage exceeded more than 15V, an appropriate volume of sat'ed NH_4Cl ($\leq 1ml$) was added ensuring that the voltage does not decrease below 7.5V. Two or more of such additions were necessary during the electrodeposition.

With $[Cl^-]=0.6M$ and a current of 1.5A, 100μg of depleted U_3O_8 were deposited as a function of time. By determining the residual uranium in solution by solid fluorimetry[11] and counting the total activity of the plates, the percentage recoveries of uranium were obtained and the results are shown in *Fig.* 2. As can be seen from this, more than 90 minutes were required to exceed 98 % recoveries and 100 minutes were taken for the quantitative recoveries by electrodeposition. Four electrodepositions of 100μg U_3O_8 wth the same electrolysis conditions resulted in 98.3% average recovery within ±0.7% uncertainty. Our electrolysis conditions are much similar to those of Puphal and Olsen's[4] and it can be said that all actinide elements, along with [207]Bi and [210]Po, are electrodeposited in same percentage recoveries as uranium.
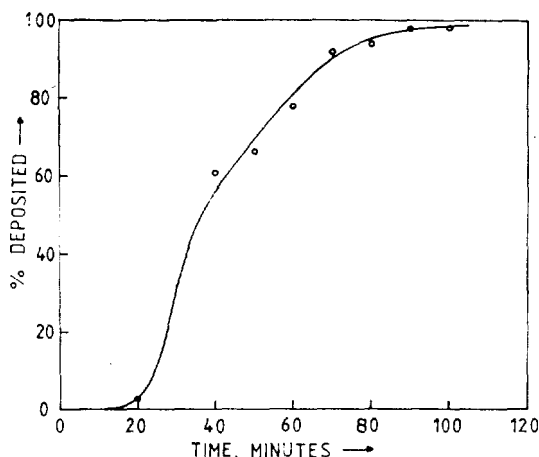

Fig. 2. Percentage recovery of uranium by electrodeposition as a function of time.
Sample=100μg of depleted U_3O_8; Current=1.5A; $Cl^-=0.6M$; Voltage=7.5—20V,

Electrodeposition of Known Samples.

A 0.911 nCi of [233]U standard solution was taken to be electrodeposited and the resulting plate was counted at a distance of 15mm from the surface barrier detector; from the count rate (C), detection efficiency $(f=\dfrac{C}{D}$, $D=$disintegration rate) was found to be 0.0106.

Also, an NBS-certified U-500 standard with the isotope composition of [234]U(0.5181%), [235]U (49.696%) and [238]U (49.711%) was taken in an amount of 11.8μg U_3O_8 and then electrodeposited. The α-spectrum of the resulting plate was taken for 3000 seconds(*Fig.*3). According to this result, we can see the two peaks of [234]U (total count=599) and one peak of [210]Po (count=551).

If we let the number of radioactive nuclides $=N$ and the half life$=t_{1/2}$, [14]

$$N=\dfrac{t_{\frac{1}{2}}}{0.693}\cdot D=\dfrac{t_{\frac{1}{2}}}{0.693}\cdot \dfrac{C}{f} \qquad (1)$$

From the data of *Fig.*3 and Eq. (1), isotope ratio [234]U : [210] Po of U-500 is found to be 1 : 5.17×10^{-8} or [238]U : [210]Po$=1 : 5.39\times10^{-10}$. So,
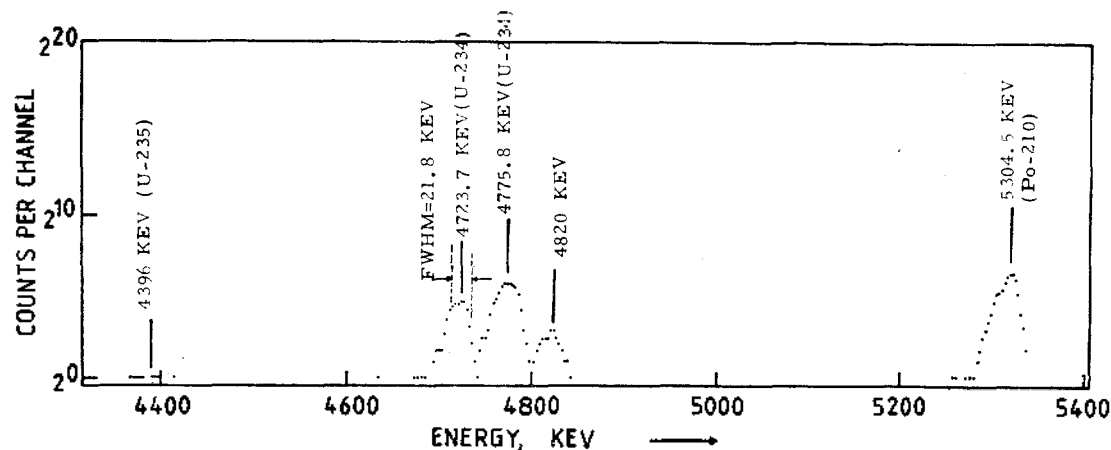
Fig. 3 Alpha energy spectrum of an electroplated sample of U–500(^{238}U : ^{235}U : ^{234}U=49.696 : 49.711 : 0.518). Counting time=3,000 sec.

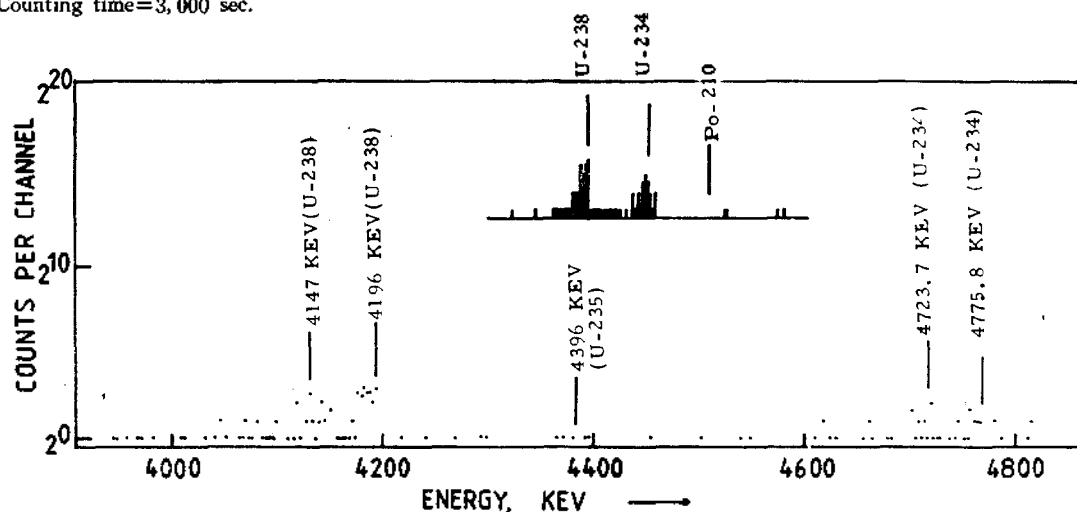*Fig.* 4. Alpha energy spectrum of depleted uranium (^{238}U : ^{235}U=1 : 0.00240) counting time=6,000 sec.

compared to the natural uranium, whose isotope ratio[13] ^{238}U:^{210}Po=1:8.36×10^{-12}, it can be said that U–500 standard sample is much enriched in ^{210}Po as ^{235}U is.

100μg(U_3O_8) of depleted uranium (^{238}U:^{235}U =1 : 0.00240) was taken to be electrodeposited with subsequent α–spectrometry for 6,000 sec. of counting as shown in *Fig.* 4. *Fig.*4 shows some counts of ^{238}U(count=113) and ^{234}U(count =38). Comparing this result with that of U–500, peaks of ^{210}Po in *Fig.* 3 disappear in *Fig.*4, This indicates that the depleted uranium sample is completely void of ^{210}Po. From the

above results and Eq. (1), ^{238}U and ^{234}U in depleted uranium is found to be 1:1.8x10^{-5}. The literature value[12] of ^{238}U : ^{234}U for natural uranium is 1 : 5.4x10^{-5} and we can say that the depleted uranium sample is reduced in ^{234}U amount by 33% of that in natural uranium. In other words, the depleted uranium sample is reduced in both ^{234}U and ^{235}U amount by equal proportions(33% of those in natural uranium).

Electrodeposition of Natural Uranium. An aliquot of a magnesium diuranate sample, obtained from ores of domestic origin(Goe-San, Choong-Buk), was taken to be electrodeposited
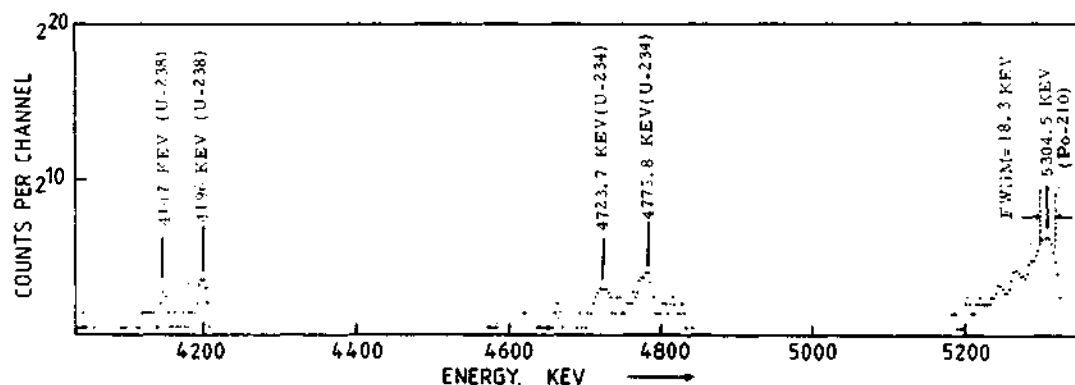
Fig. 5. Alpha energy spectrum of natual uranium sample from Goe-San Mine (Korea), counting time=10, 000sec.

Table 1. Isotope ratios of some uranium samples. ( )=Reference values.

Sample Isotope Ratio	Natural Uranium (Goe-San, Korea)	Depleted Uranium	Enriched Uranium (U-500)
$^{235}U/^{238}U$	$(0.0073)^a$	$(0.00240)^b$	$(1.00)^c$
$^{234}U/^{238}U$	6.1×10^{-5} $(5.4\times10^{-5})^a$	1.8×10^{-5}	$(0.0104)^c$
$^{210}Po/^{238}U$	$(8.36\times10^{-22})^d$	not detected	5.39×10^{-10}

a Cf. Ref. (12). *b*Determined by Mass Spectrometry. *c*Certified by NBS. *d*Cf. Ref. (13)

and the α-spectrometry with 10, 000 sec counting was made of the resulted plate (*Fig.* 5). This result shows peaks of ^{238}U (count=133), ^{234}U (count=149) and ^{210}Po. From these results and Eq. (1) ^{238}U : ^{234}U of the sample was 1:6.1× 10^{-5}(Reference value[12]=1 : 5.4×10^{-5}). The peak of ^{210}Po appears to be overlapped with other peaks of trace radionuclides.

The results of the natural, enriched and depleted uranium samples are compared in *Table* 1. The peak around 4820 KeV in *Fig.* 3 and *Fig.* 5 could not be identified.

Electrodeposition of Neutron-Irradiated Uranium. An aliquot of a uranium sample whi-

ch was irradiated with a flux of $1.8\times10^{13}n/cm^2$. sec for 144 days was taken to be electrodeposited and an α-spectrometry was taken of the resultant plate for 10, 000 seconds (*Figs.* 6B and 7). As shown in this result, peaks of ^{238}U, ^{239}Pu and ^{241}Am are well separated, whereas the simply deposited sample (*Fig.* 6A) shows the impossibility of peak separation. ^{238}U, ^{239}Pu and ^{241}Am of *Fig.* 6B and 7 had counts of 255, 12, 100 and 135 respectively: from these and Eq. (1) the calculated values of concentrations were 2.39 g/l, 0.620 mg/l and 1.24 μg/l, respectively (or ^{238}U:^{239}Pu:^{241}Am=100 : 0.0263:5.20×10^{-5}). Whereas, the results for ^{238}U was 2.46g/l and 2.48g/l by solid fluorimetry[11] and mass spectrometry, with the resultant average of 2.44g/l and relative error of 1.6% between the results of the electrodeposition-α spectrometry and those of the other two methods. The ^{239}Pu concentrations determined by anion exchange separation and TTA-solvent extraction both followed by α-spectrometry were 0.576 and 0.582mg/l and the result of electrodeposition-α-spectrometry was in accord within ±4.0% relative error with those of the other two methods (*Table* 2).
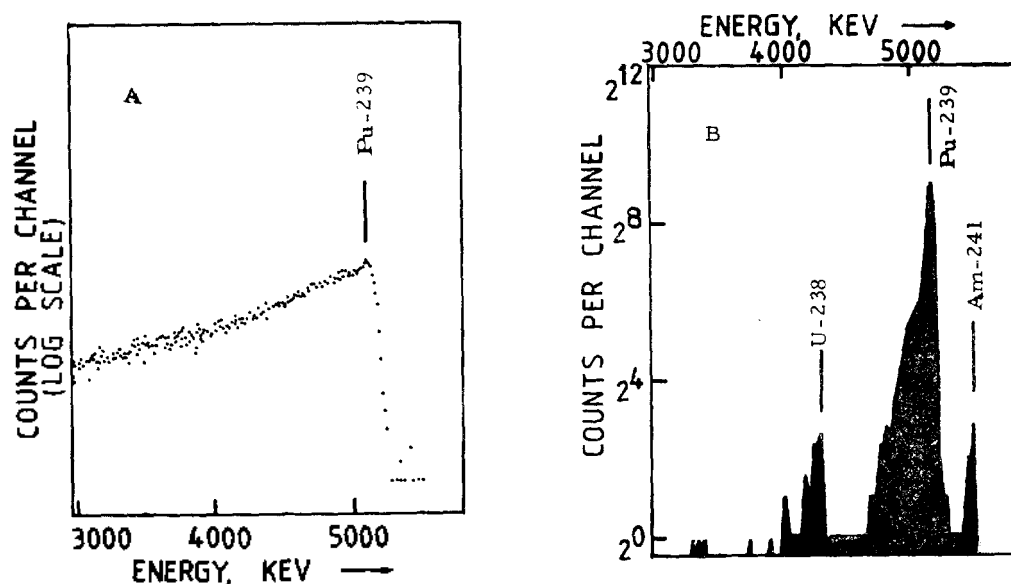
Fig. 6. Alpha energy spectrum of neutron-irradiated uranium sample. Irradiattion Time=144 Days Neutron Flux=1.8×10¹³ N/cm² · sec. A: Obtained from a Simply Deposited Planchette.
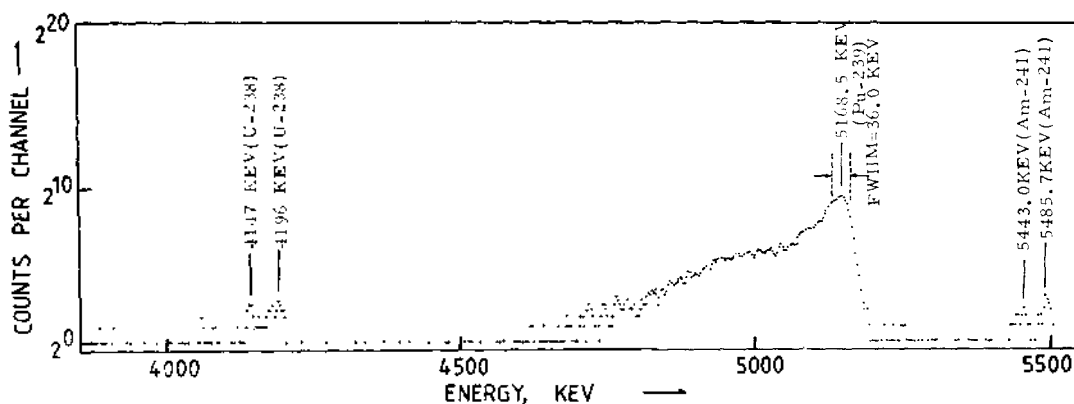B: Obtained from a Electrodeposited Sample. Counting Time=10,000 sec.

Fig. 7 Expanded View of *Fig.* 6B.

Table 2. Amounts some isotopes in irradiated uranium. Neutron flux=1.8×10¹³n/cm² · sec, Irrad. time=144 days.

Method Isotope	Electrodeposition-ᵃSpectrometry	Others		Average
²³⁸U	2.39g/l	2.46g/lᵃ	2.48g/lᵇ	2.44±0.04g/l (Rel. error=1.6%)
²³⁹Pu	0.620mg/l	0.576mg/lᶜ	0.582mg/lᵈ	0.592±0.024mg/l (Rel. error=4.0%)
²⁴¹Am	1.24μg/l			

ᵃBy solid fluorimetry. ᵇBy mass spectrometry. ᶜBy anion exchange separation-α spectrometry. ᵈBy TTA solvent extraction-α spectrometry.

ACKNOWLEGEMENT

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