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ULTRA PURE PLUTONIUM-237. PRODUCTION AND CHARACTERISTICS

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The ^{237}Pu was obtained in the reaction ^{235}U (^{4}He, 2n) at the high-current heavy ion accelerator U-200. ^{235}U of the 99,99% isotopic purity was used as a target. The dependences of ^{236}Pu, ^{237}Pu, ^{238}Pu yields on the energy of the ion beams were studied. Plutonium was isolated from the irradiated target by using the anion-exchange chromatography. An additional isotopic enrichment of the ^{237}Pu was carried out with an electromagnetic mass-separator YASNAPP-2. The preparation obtained with ^{236}Pu/^{237}Pu/^{238}Pu ratio equal to $2.10^{-7}/1/\leq 3.10^{-7}$ (Bq/Bq) is the purest one among the preparations reported to date by different Laboratories. The preparation with the above purity is practically harmless for the volunteer's organism at the metabolism study *in vivo*.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions and at the Laboratory of Nuclear Problems, JINR.

Ультрачистый плутоний-237. Получение и характеристики

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Плутоний-237 получен в реакции ^{235}U (^{4}He, 2n) при облучении мишени из высокообогащенного ^{235}U (99,99%) на высокоточном ускорителе У-200. Исследована зависимость выхода ^{236}Pu, ^{237}Pu, ^{238}Pu от энергии ^{4}He. Выделение плутония из облученной мишени проводилось с использованием анионообменной хроматографии. Дополнительное изотопное обогащение ^{237}Pu проводилось на электромагнитном масс-сепараторе ЯСНАПП-2. Полученный препарат плутония-237 с отношением активностей ^{236}Pu/^{237}Pu/^{238}Pu = $2 \cdot 10^{-7}/1/3 \cdot 10^{-7}$ (Bq/Bq) является существенно более чистым по сравнению с аналогичными препаратами, произведенными в других лабораториях. Препарат указанной чистоты является практически безопасным для организма человека при проведении исследований метаболизма плутония in vivo.

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The considerable interest to the problem of the production of ^{237}Pu is based on the fact that it is the only Pu isotope which answers the medical requirements to the metabolism research *in vivo*. A ^{237}Pu preparation used for injection to human body must be substantially free from alpha-emitting plutonium isotopes. Some works have reported on the methods of preparing ^{237}Pu in the following reactions: ^{235}U, (^{4}He, 2n) [1—4], ^{238}U (^{4}He, 4n) [5], ^{235}U (^{3}He, n) and ^{238}U (^{3}He, 4n) [6,7]. The purest ^{237}Pu preparation was obtained by Pelevin et al. [4] at irradiating an enriched ^{235}U (99,99%) target with alpha-particles of 24 MeV at the cyclotron U 200 of FLNR. The ratios of the Pu isotopes activity (Bq/Bq) in this preparation were $1.7 \cdot 10^{-5}$ ($^{236}Pu/^{237}Pu$) and $1.1 \cdot 10^{-4}$ ($^{238}Pu/^{237}Pu$). That was a high, but insufficient purity. The calculated committed effective doses (mSv/kBq) for Pu isotopes are: 182 (^{236}Pu), 0.001 (^{237}Pu), 504 (^{238}Pu) [8], i.e. 1 kBq of the above preparation has about 0.060 mSv, from which ^{237}Pu gives only 1.5%.

The main goal of this work was the elaboration of the method of producing a radiochemically and isotopically ultra pure ^{237}Pu preparation. A simple calculation shows that the ratios of the activities of ^{236}Pu and ^{238}Pu to that of the ^{237}Pu must be less than 10^{-6} for the effective dose of the Pu preparation to be formed in the main by the ^{237}Pu. To achieve this goal the optimal irradiation conditions were determined and an additional enrichment of ^{237}Pu with a mass-separator was used. The initial ^{237}Pu preparation was produced in ^{235}U (^{4}He, 2n) reaction with an enriched ^{235}Pu (99,993%) target at the cyclotron U-200.

Experimental

Target preparation and irradiation. The isotopically enriched ^{235}U(99,993%) as an oxide was converted to a nitrate form. The uranyl nitrate was spread on the aluminium target block with the cylindrical surface, which was then heated to convert the uranium to the oxide form. The thickness of the uranium targets was 1.0 (eight targets) and 5.0 mg.cm^{-2}. The ^{235}U targets were irradiated in the inner channel of the cyclotron U-200 at the ^{4}He-ions energy from 22.0 up to 26.5 MeV.

Isolation of Pu from the target. After cooling for 3 days, the irradiated uranium targets on aluminium backings were dissolved from the backings with the 12 M nitric acid. Plutonium was then reduced to Pu(IV) with a sodium nitrite and the preliminary separation of Pu(IV) from uranium

was carried out by the lanthanium fluorid method. The sediment was dissolved with the 7.5 M HNO_3 – 0.1 M $NaNO_2$ solution and the solution containing Pu(IV) was introduced into the anion exchange column filled with the Dowex 1 × 8 200/400 mesh resin. The residual uranium, the activation and the fission products were eluted from the columns with a large volume of 7.5 M HNO_3 – 0.1 M $NaNO_2$ solution and then with 9.0 M HCl. The plutonium fraction was obtained from the column by elution with the 9.0 M HCl – 0.1 M NH_4I solution. The solution was then evaporated to dryness and burnt on a hot-plate untill the decomposition of ammonium iodide. After that the sediment was dissolved with a small volume of the 7.5 HNO_3 – 0.1 M $KBrO_3$ solution, which was introduced into a microcolumn filled with the Dowex 1×8 200/400 mesh resin. The potassium bromate eluted with 9.0 M HCl and plutonium was then eluted with a small volume (2—3 drops) of 2.0 M HCl solution. This solution was used to prepare the sources for the alpha-spectrometric analysis and for the production of mass-separator targets.

Separation of Pu isotopes was carried out with the electromagnetic mass-separator ISOL-Fasility YASNAPP-2 of LNP [9]. The high temperature ion source with surface ionization was used. The ionizer is a hollow tungsten ampoule (the external diameter is 5 mm, the walls are 1 mm thick, mass is 6 g) heated by the electron bombardment. The ions are extracted through a hole (0.15—0.20 mm in diameter) at the end of the ampoule. The parallel monoenergetic ion beam enters the analysing magnet, where it is mass-separated and focussed vertically and horizontally. the dimensions of the ion beam cross section in the focal plane of the collector chamber are 1 mm vertically and 2 mm horizontally. The cathode power of the ionizer is generally 550—650 W. The mylar foils (11 mm wide and 50 mm long) were used as collectors. The ^{235}U and the ^{238}U isotopes were used as tracers.

Alpha and X-ray spectrometry of the Pu preparation were carried out before and after the mass separation.

Before separation. The aliquots from the Pu fraction obtained from the elution of plutonium by the ion exchange were tested by using a Ge(Li) detector of 80 cm^3 (full width at the half maximum intensity (FWHM) = 3.0 keV at 1.33 MeV) and using a Si(Au) surface barrier detector of 300 mm^2 with the resolution of about 35 keV. The activity of ^{237}Pu has been calculated from the Np – $K_{\alpha 1}$ X-ray peak intensity, the ratios of the activities (Bq/Bq) ^{236}Pu to ^{237}Pu and of ^{238}Pu to ^{237}Pu

were calculated from the alpha peak intensities. The value of a total alpha-branching of $4{,}2 \cdot 10^{-3}$% was used [10]. The sources for the alpha spectrometry were obtained by the electrodeposition.

After separation. The mylar foils after the separation (in analogy with the above described) were analyzed by the X-ray spectrometry to determine the full activity of ^{237}Pu. Then the foils were placed into special shielding cassettes the bottom of which had a 1 mm wide transverse slot. The cassettes were equipped with a device which allowed one to move them above the slot. Inside the cassette the foil length was scanned by Ge(Li) detector at a step of 1 mm between the observable «spots» of separated ^{235}U and ^{238}U. Basing on the results of scanning the location of the ^{237}Pu activity maximum was defined ($\approx$ 2 mm over the foil length) which was cut out. The obtained samples of ^{237}Pu were thoroughly investigated using X-ray, gamma and alpha spectrometry. Low background Ge-detector of (FWHM = 1.2 keV at 122 keV), Ge(Li)-detector of 40 cm^3 (FWHM = 3 keV at 1.33 MeV) and Si(Au) detectors with the resolution of 35 keV (300 mm^2) and 12 keV (7 mm^2) were used.

Results and Discussion

As indicated above the aim of this work is the elaboration of the methods of producing the ^{237}Pu preparation with the ratio ^{236}Pu/^{237}Pu/^{238}Pu = $\leq 10^{-6}$/1/ $\leq 10^{-6}$ (Bq/Bq). Besides, this method is to produce high activity ultra pure ^{237}Pu (at least 100 kBq) to attract practical interest. As was shown in the preliminary experiments, the average efficiency of separating ^{237}Pu from ^{236}Pu and from ^{238}Pu with the YASNAPP-2 mass-separator would be about $8—10 \cdot 10^2$ and $2—4 \cdot 10^2$ correspondingly. The separation yield of ^{237}Pu varied from 20 to 40%.

With the account of the above requirements and the mass-separator possibilities, the conditions of the uranium target irradiation are to ensure the production of the ^{237}Pu preparation with a high yield and with the ratios ^{23}Pu/^{237}Pu and ^{238}Pu/^{237}Pu of about 10^{-4} (Bq/Bq).

Table 1. The results of target irradiation

Target	Energy of ion MeV	^{237}Pu kBq	$^{236}Pu/^{237}Pu$ Bq/Bq	$^{238}Pu/^{237}Pu$ Bq/Bq
U—1	22.0	5.0	10^{-5}	$8.5 \cdot 10^{-4}$
U—2	22.4	11.0	10^{-5}	$6.0 \cdot 10^{-4}$
U—3	23.5	9.0	$1.0 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
U—4	24.0	27.5	$1.6 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
U—5	24.5	32.5	$2.0 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
U—6	25.2	37.5	$3.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
U—7	25.8	35.0	$2.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
U—8	26.5	38.0	$7.5 \cdot 10^{-3}$	$3.0 \cdot 10^{-4}$

The experimental results given in Table 1 show the activity of ^{237}Pu and the above ratios in the uranium targets. The total charge of the ions for each target was of about $2.0 \cdot 10^5$ μC.

As can be seen for the 1 mg·cm^{-2} uranium targets the maximum activity of ^{237}Pu was observed at the ^{4}He-ions energy from 24.0 to 26.5 MeV (targets U4—U8). As was indicated above we used a target block with a cylindrical surface. In this case the calculation of the ^{237}Pu yield per 1 mg of the ^{235}U is difficult since the exact data about the change of the incident angle of the beam to the targets surface are absent.

The targets U1—U8 were irradiated, however, in identical conditions and, thus, the results obtained for the targets U4—U8 indicate that ≈24.0 MeV is the lower end-point energy for producing the high activity ^{237}Pu. The ratios of the activities (Bq/Bq) of the ^{236}Pu and ^{238}Pu to ^{237}Pu, which satisfied the above requirements were observed in the energy range of 23.5—25.2 MeV. With the account of these results, the energy range 24.5—25.0 MeV was chosen for the production of the ^{237}Pu for the mass-separation.

The ^{235}U (99.993%) target 5 mg·cm^{-2} was irradiated with ^{4}He-ions with the initial energy of 25 MeV at the ion-beam current of about 30 μA during 70 hours. The activity of the ^{237}Pu in the solution after the first anion-exchange column was about 1.5 MBq and the ratio of

Table 2. Energy and relative intensity of α-line ^{237}Pu-preparation

			Count	Intensity (%%) (Stat ERR)		
		^{237}Pu				
1	1.	5654.6	2729	7.8	0.2	18.3 ± 5
	2.	5614.6	2619	7.5	0.2	
	3.	5562.8	1031	2.9	0.1	
	4.	5354.7	2012	5.7	0.2	
	5.	5334.0	15825	45.1	0.6	64.1 ± 1.1
	6.	5300.9	4764	13.6	0.3	
	7.	5256.7	949	2.7	0.1	
	8.	5150.8	3784	10.8	0.2	
	9.	5086.3	287	0.8	0.1	97%
2*	10.	5370.0	260	0.7		
	11.	5220.0	243	0.7		
	12.	5205.0	213	0.6		
	13.	5190.0	136	0.4		
	14.	5173.0	119	0.3		
	15.	5018.0	78	0.2		3%
3		Pu—238 + Pu237?				
		5498.6	328			
		5448.3	67			1.1%
4		Pu—236				
		5767.6	109			
		5718.1	29			0.4%

2* — Estimated value

Pu isotopes was $1.6 \cdot 10^{-4}$ (^{236}Pu/^{237}Pu) and $1.3 \cdot 10^{-4}$ (^{238}Pu/^{237}Pu). After the final anion-exchange column the solution with the activity of 1.2 MBq was obtained.

Two sources with the activity of about 500 kBq each were prepared for the mass-separation. Subsequently two mylar foils were obtained after the separation. The activity of each foil was about 200 kBq, i.e. the separation yield of ^{237}Pu was $\approx 40\%$. The foils were scanned by the X-ray spectrometry as was described in the experimental part and sam-

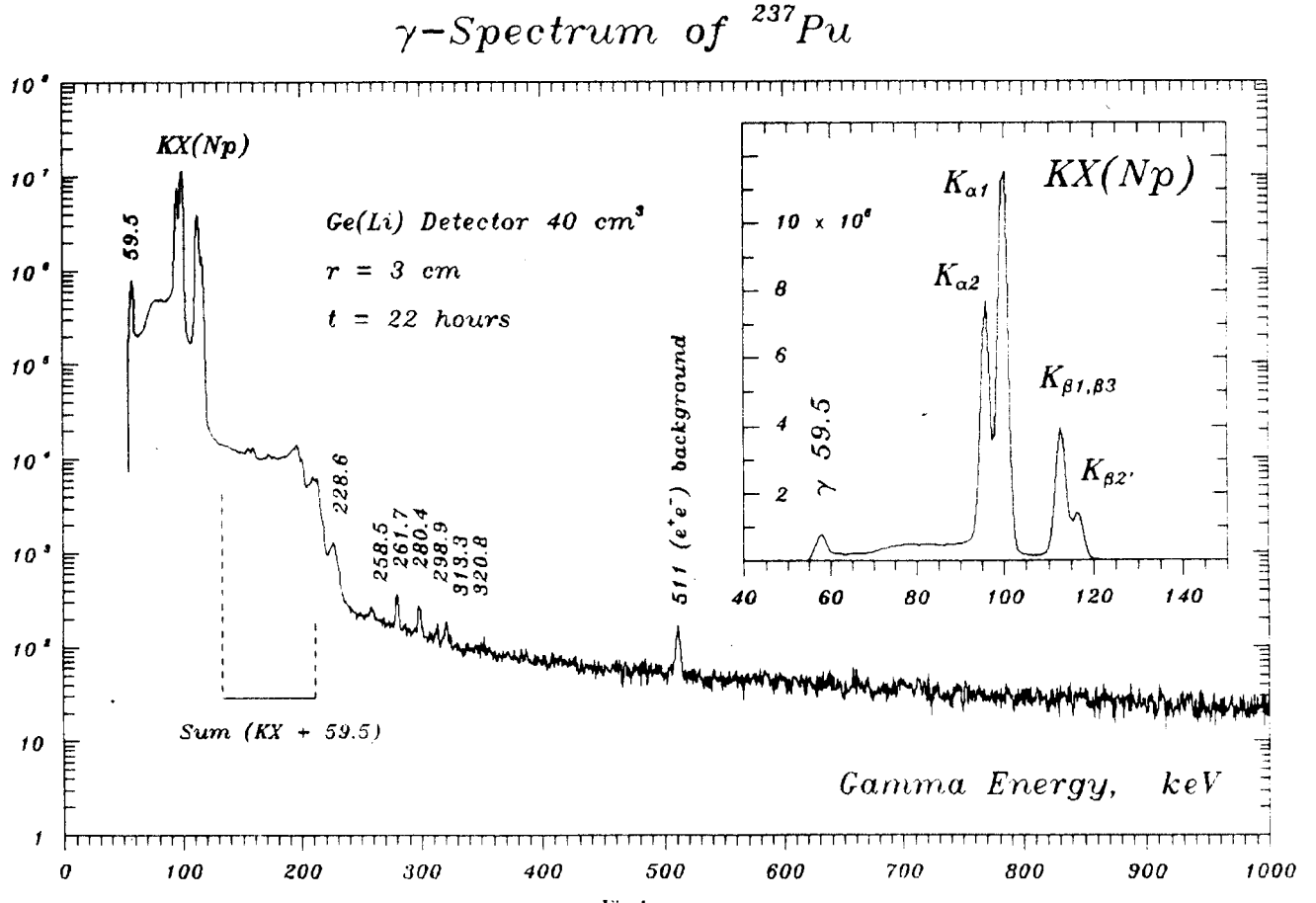
γ-Spectrum of ^{237}Pu
KX(Np)
59.5
Ge(Li) Detector 40 cm³
r = 3 cm
t = 22 hours
228.6
258.5
261.7
280.4
298.9
313.3
320.8
511 (e⁺e⁻) background
Sum (KX + 59.5)
Gamma Energy, keV
KX(Np)
Kα1
Kα2
Kβ1,β3
Kβ2'
γ 59.5
10 x 10⁶

Fig.1

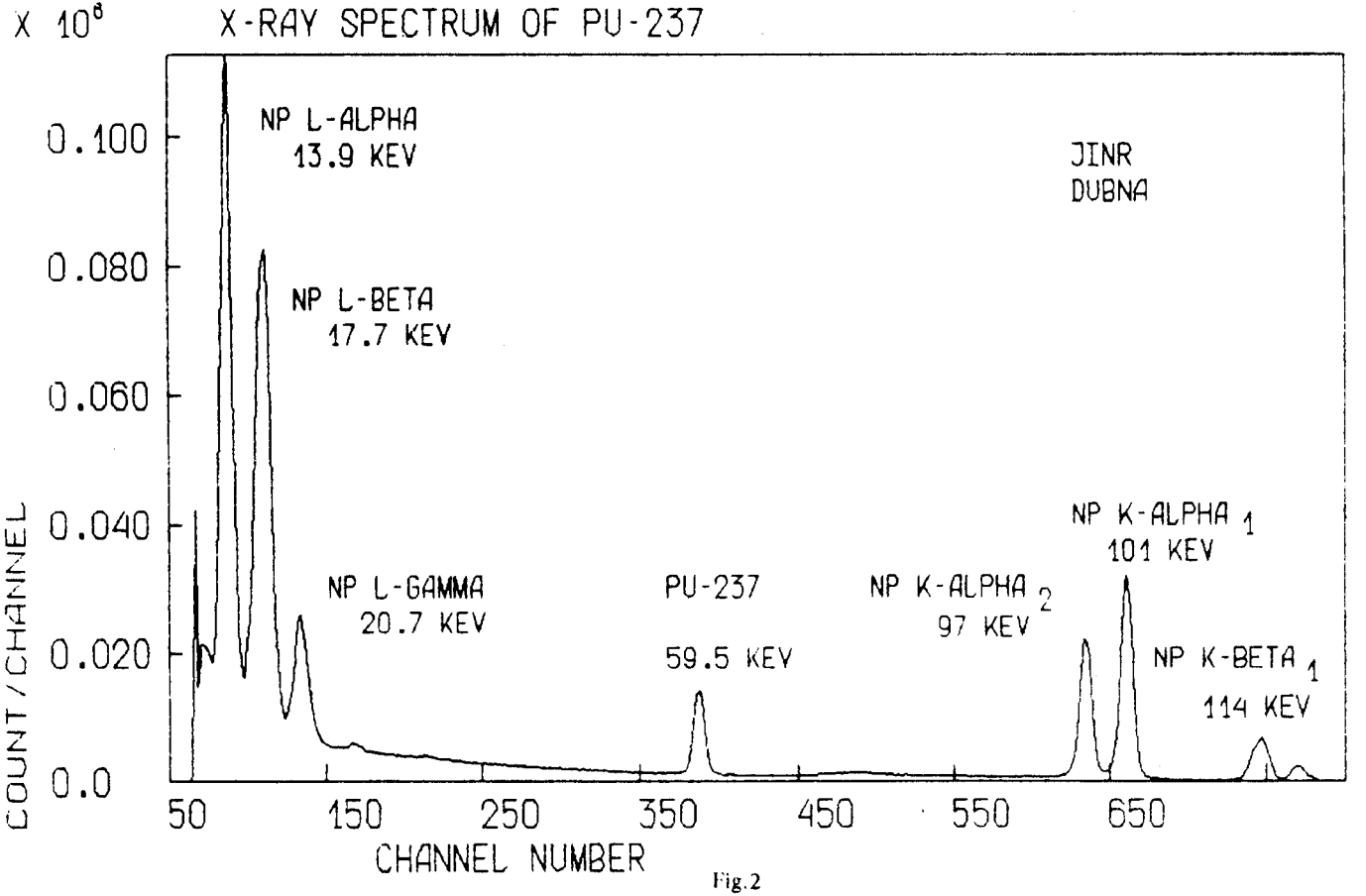
X 10⁶
X-RAY SPECTRUM OF PU-237
NP L-ALPHA
13.9 KEV
NP L-BETA
17.7 KEV
NP L-GAMMA
20.7 KEV
PU-237
59.5 KEV
NP K-ALPHA 2
97 KEV
NP K-ALPHA 1
101 KEV
NP K-BETA 1
114 KEV
JINR
DUBNA
COUNT / CHANNEL
0.100
0.080
0.060
0.040
0.020
0.0
50
150
250
350
450
550
650
CHANNEL NUMBER

Fig.2

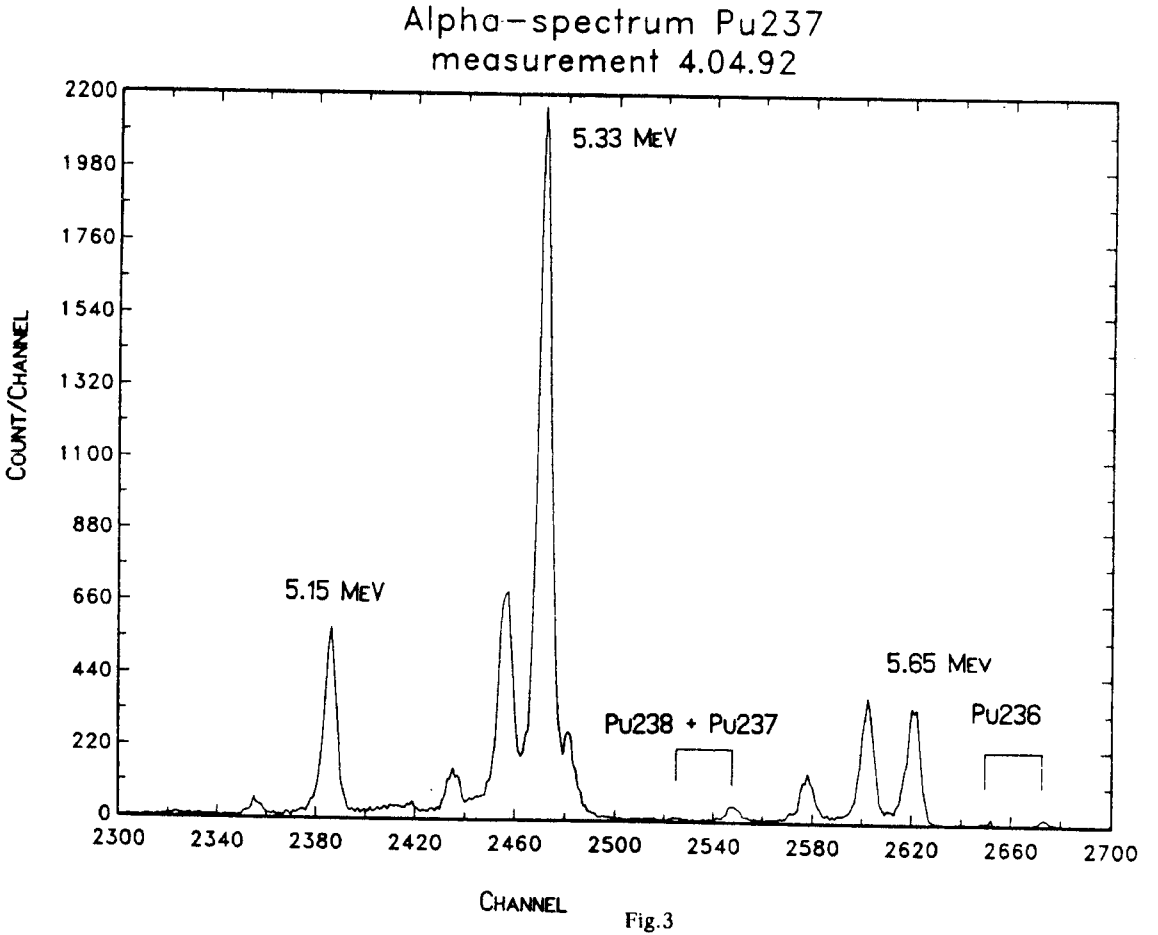
Alpha-spectrum Pu237
measurement 4.04.92
5.33 MeV
5.15 MeV
Pu238 + Pu237
5.65 MeV
Pu236
COUNT/CHANNEL
CHANNEL
2200
1980
1760
1540
1320
1100
880
660
440
220
0
2300
2340
2380
2420
2460
2500
2540
2580
2620
2660
2700

Fig.3

ples of ^{237}Pu (pieces of the foils, 2 mm long) were obtained. The activity of each sample was about 150 kBq. These samples were carefully tested by using Ge, Ge(Li) and Si(Au) detectors. The X-ray and gamma spectrum of ^{237}Pu preparation are given in Figs.1,2. The ratio of Pu isotopes was $2 \cdot 10^{-7}$ ($^{236}Pu/^{237}Pu$) and $3 \cdot 10^{-7}$ ($^{238}Pu/^{237}Pu$).

It should be noted that the determination of the ratios of the plutonium isotope activities was carried out by direct measurements of the alpha-spectra. At using a low background Si(Au) detector of 300 mm^2 with a resolution of 35 keV the measurement time to obtain the statistics necessary for the calculation of isotopic ratio ($\sim n \cdot 10^3$ counts) was from 1 to 4 hr. The analysis of the alpha spectra of the ultra pure ^{237}Pu showed that the number of alpha lines and especially of their relative intensities differ essentially from the data reported before [11]. For more correct determination, the sample of the ultra pure ^{237}Pu with an activity of 140 kBq was tested using a low background Si(Au) detector of 7 mm^2 with a resolution of 12 keV. The resulting spectrum obtained at the 70 hr measurement is given in Fig.3. The value of the energy and the relative intensity normalized over the sum of all the ^{237}Pu alpha lines is given in Table 2. This ^{237}Pu sample was remeasured 45 days later. The absolute intensities of all the alpha line given in Table 2 for the ^{237}Pu were decreased approximately twofold, the relative intensities remained constant.

Conclusion

A techniques for producing radiochemically and isotopically ultra pure ^{237}Pu was developed. The optimal conditions for irradiating the ^{235}U (99,993%) targets at the cyclotron U-200 and for the subsequent separation of the Pu isotopes by the electromagnetic mass-separator YASNAPP-2 were determined.

The ^{237}Pu preparation obtained with $^{236}Pu/^{237}Pu/^{238}Pu$ ratio equal to $2 \cdot 10^{-7}/1/\leq 3 \cdot 10^{-7}$ (Bq/Bq) is the purest one among the preparations reported to date by different Laboratories. The effective dose of this preparations is only 0.0012 mSv/kBq, which is practically equal to that of the monoisotopic ^{237}Pu. The preparation with the above ratio of the alpha-active Pu isotopes is practically harmless for the volunteer's organism at the metabolism study.

This ^{237}Pu preparation (about ~100 kBq) was passed over to the Harwell Biochemical Research Department (Harwell Laboratory, UK) for a metabolism study.

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References

1. Todt R., Logan R. — J. Appl. Radiat. Isot., 1968, v.19, p.141.
2. Jenkins I.L., Wain A.G. — Int. J. Appl. Radiat. Isot., 1971, v.22, p.429.
3. Ahmad I., Hines J., Gindler J.E. — Phys. Rev., 1983, v.27C, p.2239.
4. Pelevin L.A., Gedeonov A.D., Shuvalov B.I. — Radiochimia, 1988, №6, p.806.
5. Hata K. et al. — Int. J. Appl. Radiat. Isot., 1976, v.27, p.713.
6. Aaltonen J. et al. — Proc. Int. Conf. Actinides-89, Nauka, Moscow, 1989, p.40.
7. Aaltonen J. et al. — Radioanal. Chem., 1981, v.64, p.73.
8. Recommendations of the Int. Com. Radiol. Protect., ICRP Publication 60, Pergamon Press, 1990.
9. Kalinnikov V.G. et al. — JINR, D13-90-183, Dubna, 1990.
10. Ellis Y.A., Emery J.F., Toth K.S. — Phys. Rev., 1979, v.20, p.799.
11. Radionuclide Transformations, ICRP Publication 38, Pergamon Press, p.1159, 1980.

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