

## Production of $^{225}\text{Ac}$ and $^{223}\text{Ra}$ by Irradiation of Th with Accelerated Protons

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**Abstract**—The possibility of producing  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  by irradiation of natural  $^{232}\text{Th}$  with medium-energy protons was examined. Thorium foils were irradiated with 90-, 110-, and 135-MeV protons at the accelerator of the Institute for Nuclear Research, Russian Academy of Sciences, in Troitsk (Moscow oblast). The cumulative production cross sections for  $^{225}\text{Ac}$  were  $6.7 \pm 0.9$ ,  $9.8 \pm 1.9$ , and  $13.9 \pm 1.5$  mb, and for  $^{227}\text{Th}$  ( $^{223}\text{Ra}$  precursor),  $43 \pm 5$ ,  $37 \pm 6$ , and  $35 \pm 4$  mb, respectively. Based on the experimental data and theoretical calculations, the possible yields of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  in irradiation of thick thorium targets at various accelerators were determined. An efficient procedure was suggested for isolating the products from the irradiated targets:  $^{225}\text{Ac}$ , by liquid extraction and extraction chromatography, and  $^{223}\text{Ra}$ , by sublimation from a thorium–lanthanum melt followed by thermochromatographic separation in metallic titanium columns and extraction-chromatographic isolation of radium. The procedure allows production of large (units of curies) amounts of radiochemically pure  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$ , which is promising for wide use of these radionuclides in nuclear medicine.

**Keywords:** actinium-225, radium-223, proton irradiation, extraction, chromatography, sublimation

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Actinium-225 ( $T_{1/2} = 10.0$  days) is one of the most promising  $\alpha$ -emitting radionuclides for therapy of various tumor diseases [1, 2]. It is also promising to use this radionuclide in generators as a source of the daughter short-lived  $^{213}\text{Bi}$  ( $T_{1/2} = 46$  min).

Various methods for  $^{225}\text{Ac}$  production are known [3]. Usually this radionuclide is isolated from products of  $^{233}\text{U}$  decay following the scheme  $^{233}\text{U}$  ( $T_{1/2} = 1.6 \times 10^5$  years)  $\rightarrow$   $^{229}\text{Th}$  ( $T_{1/2} = 7340$  years)  $\rightarrow$   $^{225}\text{Ra}$  ( $T_{1/2} = 14.8$  days)  $\rightarrow$   $^{225}\text{Ac}$  [4, 5]. Difficult availability of the starting  $^{233}\text{U}$  restricts the possibility of producing large amounts of  $^{225}\text{Ac}$ .  $^{229}\text{Th}$ , from which  $^{225}\text{Ac}$  is directly isolated, can also be produced from  $^{230}\text{Th}$  ( $T_{1/2} = 75400$  years) by irradiation with fast neutrons or  $\gamma$ -quanta [6]. The starting  $^{230}\text{Th}$  is a member of the  $^{238}\text{U}$  radioactive series, and its content is about 20 g per ton of uranium, i.e., this material is also difficultly available.

Another route is production of  $^{225}\text{Ac}$  from  $^{226}\text{Ra}$

targets by their irradiation with fast or thermal neutrons [7, 8],  $\gamma$ -quanta [9], or accelerated protons or other charged particles [10, 11]. The starting  $^{226}\text{Ra}$  is also difficultly available. In addition, radium targets of relatively large mass are dangerous in handling, which gives rise to serious problems in their wide application, especially in cases when radium regeneration from the irradiated targets is required.

Another radionuclide promising for medicine is  $^{223}\text{Ra}$  ( $T_{1/2} = 11.4$  days). It is directly used for therapy of bone tumor diseases [12]. It can also serve as a source of  $^{211}\text{Pb}$  ( $T_{1/2} = 36$  min) in generators [13]. The common route to small amounts of  $^{223}\text{Ra}$  is its isolation from  $^{235}\text{U}$  decay products. Large amounts of  $^{223}\text{Ra}$  can be produced by irradiation of  $^{226}\text{Ra}$  in a nuclear reactor, followed by chemical isolation of the formed  $^{227}\text{Ac}$  ( $T_{1/2} = 21.8$  years) decaying into  $^{227}\text{Th}$  ( $T_{1/2} = 18.7$  days) and then into  $^{223}\text{Ra}$ . As already noted, irradiation and processing of a radium target involve serious problems.

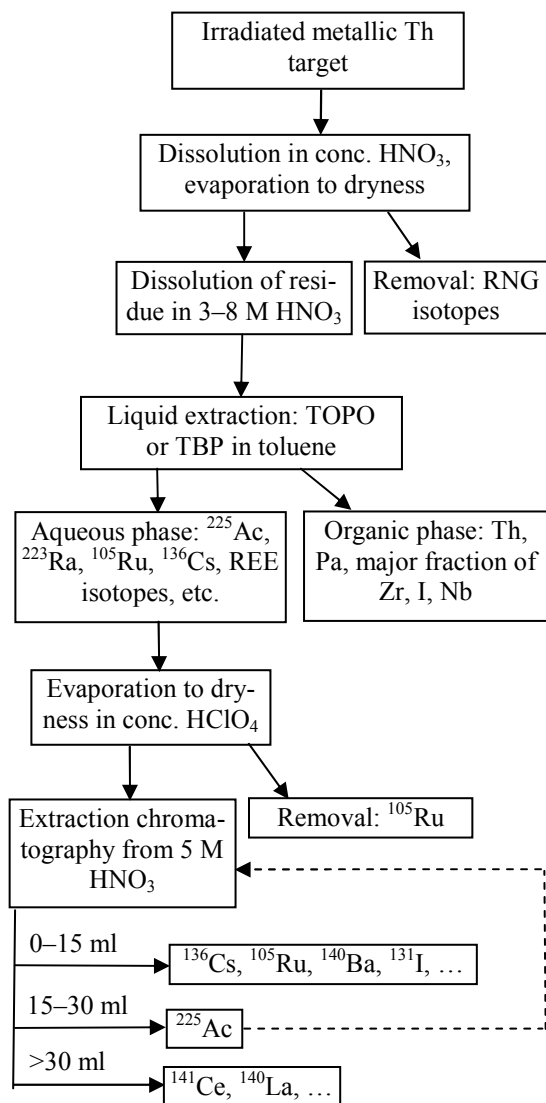


Fig. 1. Scheme of  $^{225}\text{Ac}$  isolation from irradiated thorium target.

We believe that the most promising route of production of  $^{225}\text{Ac}$ ,  $^{223}\text{Ra}$ , and some other important radionuclides is irradiation of natural  $^{232}\text{Th}$  targets with medium-energy protons, followed by product isolation. In the early 1960s, Lefort et al. experimentally measured the production cross sections of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  from  $^{232}\text{Th}$  at a proton energy of 150 MeV [14], and Gauvin measured the  $^{225}\text{Ac}$  production cross sections at proton energies in the range 43–115 MeV [15]. Also,  $^{232}\text{Th}$  was irradiated with the aim of  $^{225}\text{Ac}$  production with 660-MeV protons at an accelerator in Dubna [16] and with 600-MeV protons at an accelerator in CERN [17]. The possibility of producing  $^{225}\text{Ac}$  from thorium by its irradiation with protons of the en-

ergy lower than 40 MeV was noted recently [18], but no experimental data confirming this assumption were presented. On the whole, only limited information is available on optimization of production of various radionuclides from a thorium target and on radiochemical procedures for isolation of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  from irradiated Th and on their purification to remove other radionuclides. Up to now,  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  were not actually produced by this procedure.

The major goal of this study was measuring the  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  production cross sections in reactions of Th with 90–135-MeV protons with the aim to optimize the conditions for production of large amounts of these radionuclides on the proton beam of the Moscow Meson Factory [Institute for Nuclear Research (INR), Russian Academy of Sciences, Troitsk]. In the course of our study, we developed efficient radiochemical procedures for isolating Ac and Ra in the radiochemically pure state. It can be expected that wide use of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  in medicine will allow in the future cardinal solution of the problem of treating many tumor diseases.

## EXPERIMENTAL

**Th irradiation.** In irradiation experiments we used  $10 \times 10 \text{ mm}^2$  pieces of 5- $\mu\text{m}$ -thick Th metal foil. The foils were irradiated with a beam of accelerated protons of energy 128, 143, and 158 MeV at the linear accelerator of the Institute for Nuclear Research, Russian Academy of Sciences [19], at a beam current of approximately 5  $\mu\text{A}$ . In the course of irradiation, thorium foils wrapped in aluminum foil were intensely cooled with a water flow. To decrease the proton energy to 90, 110, and 135 MeV, graphite absorbers were arranged before the target. The accuracy in the proton energy determination was approximately  $\pm 2.5 \text{ MeV}$ . The uncertainty was determined by the accelerator parameters and by proton scattering as a result of their absorption by graphite and cooling water. The proton flux was monitored with Al and Cu foils by production of  $^{22}\text{Na}$  and  $^{62}\text{Zn}$ , respectively, whose production cross sections are known [20].

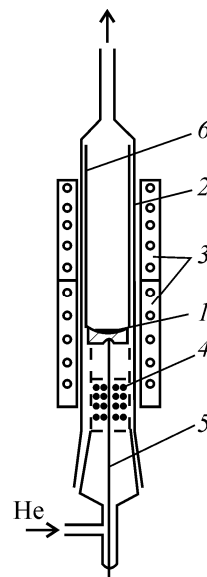
The foils after irradiation were withdrawn and subjected to  $\gamma$ -ray spectrometric analysis using a spectrometer equipped with a HPGe detector with a beryllium window (Canberra GR 3818).

**$^{225}\text{Ac}$  isolation.** Actinium was isolated by the scheme shown in Fig. 1. The procedure consisted of the steps of liquid extraction and extraction chroma-

tography. Irradiated Th metal foils were dissolved in concentrated  $\text{HNO}_3$ , the solution was evaporated to dryness, the residue was dissolved in 3–8 M  $\text{HNO}_3$ , and Th was extracted with two portions of 1–5 M TBP or 0.1–0.5 M TOPO solution in toluene [21]. After the Th extraction, the aqueous phase was evaporated to dryness, concentrated  $\text{HClO}_4$  was added, and the solution was evaporated to dryness to remove Ru isotopes. For further purification, the residue was dissolved in 5 M  $\text{HNO}_3$  and subjected to extraction chromatography in 5 M  $\text{HNO}_3$  in a column (volume 2.5 ml) packed with a sorbent based on octylphenyl- $N,N$ -diisobutylcarbamoylmethylphosphine oxide (TRU-resin<sup>®</sup>, Eichrom Technologies, Inc.) [11, 22]. After washing the column with 15 ml of 5 M  $\text{HNO}_3$ , Ac was eluted with the next 15 ml of 5 M  $\text{HNO}_3$ , and the solution was collected. For complete purification of Ac, the extraction chromatography was performed twice. The radiochemical purity of  $^{225}\text{Ac}$  was determined by  $\gamma$ - and  $\alpha$ -ray spectrometry with a semiconductor PIPS detector (Canberra).

**$^{223}\text{Ra}$  isolation.** Chemical isolation of Ra from irradiated metallic Th was performed by a gas-chemical method. For this purpose, a piece of irradiated thorium foil (3 mg) together with metallic La (280 mg) was placed in a crucible of metallic Zr. Addition of La ( $T_m = 918^\circ\text{C}$ ) leads to formation of a melt with Th (for Th,  $T_m = 1755^\circ\text{C}$ ), and in the liquid metal diffusion and, correspondingly, release of the sublimed microelements are considerably faster than in solid Th. The crucible was heated for 1 h in succession at 970, 1040, 1130, 1190, 1270 $^\circ\text{C}$  in a stream of helium purified with a titanium getter (the heating temperature was determined with an accuracy of  $\pm 15^\circ\text{C}$ ). Radium and other radionuclides were deposited at the furnace outlet on tantalum collectors in the form of foils which were replaced when changing the heating temperature.

In another experiment (Fig. 2), an irradiated thorium sample with metallic La was heated for 1 h at  $1200 \pm 15^\circ\text{C}$ , and the released products were transferred with a helium stream into a thermochromatographic column (quartz tube lined with titanium foil from the inside); the sublimed elements were deposited on the Ti surface in different temperature zones. After the heating completion, the titanium foil serving as collector for sublimed products was cut into pieces (corresponding to temperature zones), and the  $\gamma$ -ray spectrum of each piece of the collector was measured. After that, the piece of the collector with the deposited Ra, Ba, and Sr was subjected to further purification by



**Fig. 2.** Installation for gas-chemical isolation of Ra: (1) irradiated Th in melt with metallic La in zirconium crucible, (2) quartz tube lined with niobium, (3) tubular resistance furnaces, (4) titanium getter for purification of helium being fed, (5) Pt/Rh thermocouple, and (6) titanium foil serving as collector for Ra and other sublimed products.

extraction chromatography. The elements were washed off from the surface of the titanium foil-collector with 7 M  $\text{HNO}_3$ , and the resulting solutions were passed through an extraction-chromatographic column packed with the sorbent containing 4,4'(5')-di-*tert*-butylcyclohexano-18-crown-6 (Sr-resin<sup>®</sup>, Eichrom Technologies, Inc.). Radium was eluted with a 7 M  $\text{HNO}_3$  solution. Under these conditions, Ra is washed out, whereas Ba and Sr remain on the column.

The radiochemical purity of  $^{223}\text{Ra}$  was determined by  $\gamma$ - and  $\alpha$ -ray spectrometry. To prepare specimens for  $\alpha$ -ray spectrometry, a known aliquot of the solution was applied dropwise onto stainless steel disks.

By this procedure, we prepared radiochemically pure Ac and Ra samples. Figure 3 shows the  $\gamma$ -ray spectra of the irradiated thorium target and of chemically isolated Ac and Ra fractions.

## RESULTS AND DISCUSSION

**$^{225}\text{Ac}$  production cross sections and yields.** In proton irradiation of Th,  $^{225}\text{Ac}$  is produced along several pathways. According to theoretical calculations, the major pathways are the nuclear reaction  $^{232}\text{Th}(p,p7n)^{225}\text{Th}$  followed by  $\beta^+$ -decay into  $^{225}\text{Ac}$  with 10% probability and direct production by the reaction

**Table 1.** Contribution of various nuclear reactions (%) to the  $^{225}\text{Ac}$  yield in irradiation of Th with protons of various energies (calculation by ALICE-IPPE model, irradiation for 6 ч, cooling for 15 days)

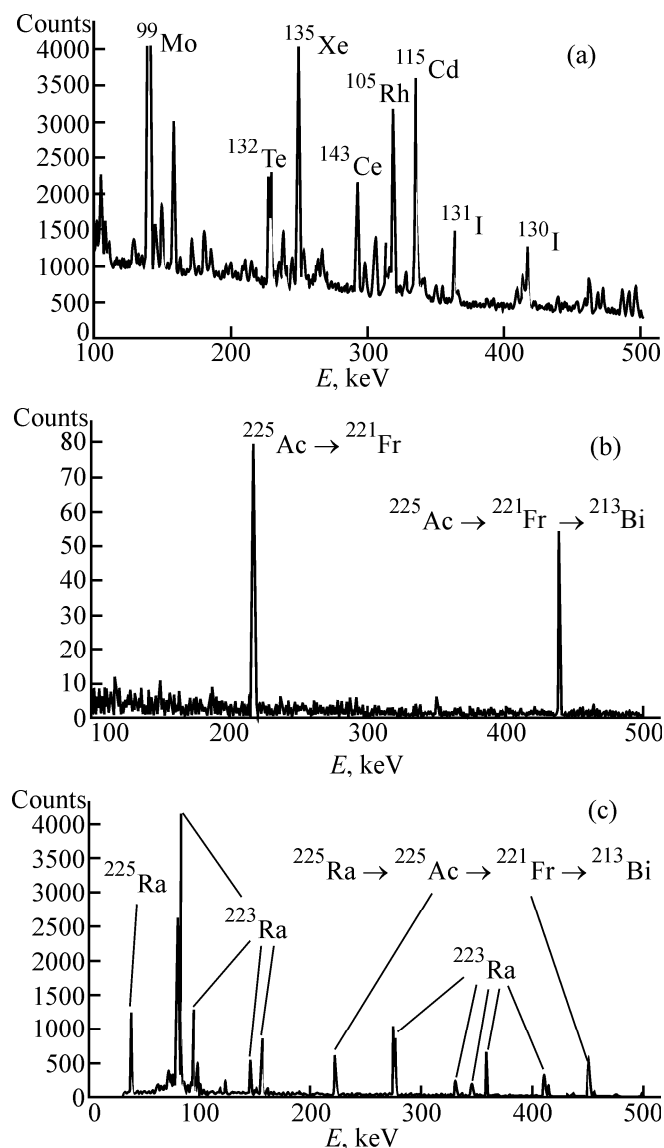
Proton energy, MeV	$(p,4n)^{229}\text{Pa} \rightarrow ^{225}\text{Ac}$ (0.25%)	$(p,p7n)^{225}\text{Th} \rightarrow ^{225}\text{Ac}$ (10%)	$(p,2p6n)^{225}\text{Ac}$	$(p,3p5n)^{225}\text{Ra} \rightarrow ^{225}\text{Ac}$ (100%)
90	0.8	52.7	45.8	0.7
110	0.4	25.5	73.8	0.3
135	0.2	13.1	86.5	0.2

$^{232}\text{Th}(p,2p6n)^{225}\text{Ac}$  (Table 1). Thus, the experimentally measured production cross sections are cumulative, and they cannot be accurate, because the production cross sections of the parent  $^{225}\text{Th}$ ,  $^{225}\text{Ra}$ ,  $^{229}\text{Pa}$ , and

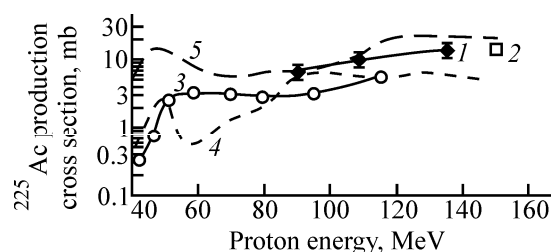
$^{225}\text{Ra}$  were not determined sufficiently reliably. Nevertheless, these cumulative cross sections allow estimation of  $^{225}\text{Ac}$  yields in irradiation of targets in different ranges of proton energy.

The  $^{225}\text{Ac}$  production cross sections that we calculated from  $\gamma$ -ray spectrometric data are plotted in Fig. 4 in comparison with the theoretical values obtained using different models: ALICE (ALICE-IPPE version) and cascade evaporation (CEF). For the proton energies of 90, 110, and 135 MeV, the experimental cross sections were  $6.7 \pm 0.9$ ,  $9.8 \pm 1.9$ , and  $13.9 \pm 1.5$  mb, respectively. Figure 4 also shows the experimental data obtained previously [14, 15]. Our experimental data lie between the theoretical data calculated by different models and better agree with the previous experimental data reported in [14], rather than in [15].

Figure 5 shows the  $^{225}\text{Ac}$  yields that we calculated for a thorium target in relation to its thickness and initial (“inlet”) energy of protons incident on the thick target (the energy of protons leaving the target was taken equal to 40 MeV; below this energy, the  $^{225}\text{Ac}$  yield is extremely low). Figure 5 shows the experimental yield curve plotted on the basis of compilation of our data with those reported in [14] (at relatively high energies) and [15] (at lower energies). The yield curve plotted on the basis of theoretical cross section calculations (ALICE-IPPE model) is also given. The values from [15] are in poor agreement with the results of



**Fig. 3.**  $\gamma$ -Ray spectra: (a) irradiated thorium target (2 days after irradiation completion), (b) Ac fraction isolated from irradiated Th, and (c) Ra fraction isolated from irradiated Th.



**Fig. 4.** Cumulative production cross sections of  $^{225}\text{Ac}$ : (1) experimental data of this study, (2) experimental data of [15], (3) experimental data of [14], (4) theoretical calculation by the cascade evaporation model, and (5) theoretical calculation by the ALICE-IPPE model.

**Table 2.** Parameters of proton accelerators, yields of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$ , and amounts of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  that can be produced by 10-day irradiation at a cooling time of 10 days for  $^{225}\text{Ac}$  and 16 days for  $^{223}\text{Ra}$ . Without parentheses, estimation from available experimental data and by their extrapolation; in parentheses, estimation by theoretical calculations using ALICE-IPPE model

Accelerator	Proton energy, MeV		Beam current, $\mu\text{A}$	Yield, <sup>a</sup> $\mu\text{Ci } \mu\text{A}^{-1} \text{h}^{-1}$		Amount produced, <sup>b</sup> Ci	
	initial	incident on target		$^{225}\text{Ac}$	$^{223}\text{Ra}$	$^{225}\text{Ac}$	$^{223}\text{Ra}$
INR (Russia)	158	145	120	0.11 (0.18)	0.40 (0.79)	2.6 (4.1)	9.2 (18.4)
Brookhaven (USA)	200	185	80	0.20 (0.32)	0.54 (1.07)	3.1 (4.9)	8.3 (16.6)
Los Alamos (USA)	100	90	180	0.02 (0.04)	0.17 (0.35)	0.7 (1.3)	6.1 (12.1)
TRIUMF (Canada)	120	110	60	0.04 (0.06)	0.26 (0.52)	0.5 (0.7)	3.0 (6.0)
Arronax (France)	70	65	180	0.005 (0.02)	0.06 (0.12)	0.2 (0.7)	2.2 (4.3)

<sup>a</sup> Without taking into account the loss in gaps between targets and in the course of chemical processing.

<sup>b</sup> Taking into account loss (for explanation, see text).

theoretical calculations for low proton energies and, apparently, require additional experimental verification. As can be seen, it is more appropriate to produce  $^{225}\text{Ac}$  at proton energies exceeding 100 MeV.

On the basis of the available experimental and theoretical data (Table 2), we calculated the amounts of  $^{225}\text{Ac}$  that can be produced in one 10-day irradiation run at various accelerators: in INR, Brookhaven National Laboratory (USA), Los Alamos National Laboratory (USA), TRIUMF (Canada), and Arronax (France). The real beam current attainable at these installations on thorium targets, taking into account the possibilities of their cooling, is given. The proton energy decreases on passing through inlet windows, cooling water layer, and target shell, so the energy of protons incident on the target ("inlet" energy) is usually lower by 5–15 MeV than the initial accelerated proton energy. Some installations use multilayer targets for better cooling, and certain energy loss is observed in water gaps between the target layers and in the shells (this loss was taken equal to 10%). The chemical yield was taken equal to 90%. The target was kept after irradiation for 10 days in the case of  $^{225}\text{Ac}$  and 16 days in the case of  $^{223}\text{Ra}$  (the best time for accumulation from  $^{227}\text{Th}$ ).

As can be seen, the Ac yield monotonically increases with an increase in the proton energy, and efficient production is possible by irradiation of a metallic Th target with accelerated protons of the energy exceeding 100 MeV.

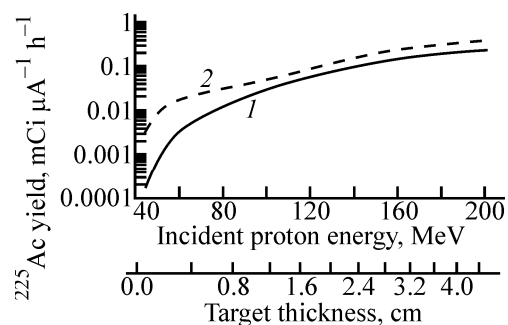
#### $^{227}\text{Th}$ production cross sections and $^{223}\text{Ra}$ yields.

Theoretical calculations show that the major pathway of  $^{223}\text{Ra}$  formation is via  $\alpha$ -decay of  $^{227}\text{Th}$  ( $T_{1/2} = 18.7$  days) produced by the ( $p,p5n$ ) reaction and via

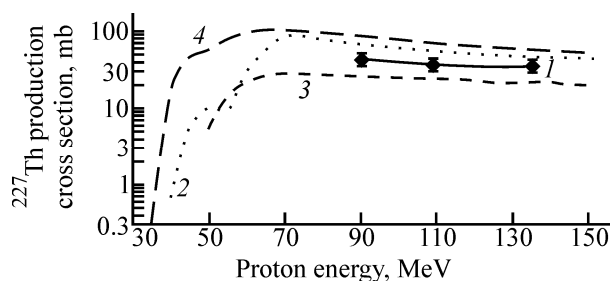
$\beta^+$ -decay of  $^{227}\text{Pa}$  produced by the ( $p,6n$ ) reaction. The contributions of the direct  $^{223}\text{Ra}$  production and its production via  $^{223}\text{Fr}$  and  $^{223}\text{Rn}$  are insignificant (<1%).

The experimental cumulative production cross-sections of  $^{227}\text{Th}$ , determined in this study for proton energies of 90, 110, and 135 MeV, are  $43 \pm 5$ ,  $37 \pm 6$ , and  $35 \pm 4$  mb, respectively. In Fig. 6, these data are given in comparison with the results of calculations by two versions of ALICE code and by the CEF model. The theoretical and experimental values are in reasonable agreement.

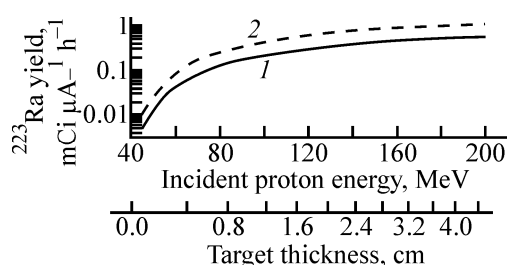
Figure 7 shows the calculated  $^{223}\text{Ra}$  yields in irradiation of a thorium target (irradiation for 10 days, cooling for 16 days, an optimal time for the decay of  $^{227}\text{Th}$  into  $^{223}\text{Ra}$ ). The possibilities of  $^{223}\text{Ra}$  production at various existing accelerators are compared in



**Fig. 5.** Yield of  $^{225}\text{Ac}$  in a thorium target as a function of its thickness and incident proton energy (energy of protons leaving the target 40 MeV, irradiation time 10 days, cooling time 10 days). (1) Calculation based on a compilation of the experimental data of this study and of [14, 15] and on extrapolation to higher energies using theoretical cross section calculations by the ALICE-IPPE model; (2) theoretical calculation by the ALICE-IPPE model.



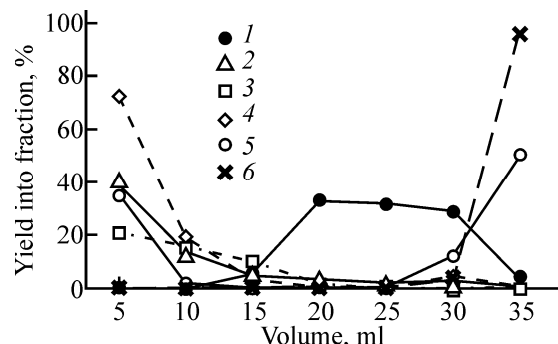
**Fig. 6.** Cumulative production cross sections of  $^{227}\text{Th}$ : (1) experimental data obtained in this study, (2) theoretical calculation by the cascade evaporation model (CEF), (3) theoretical calculation by the ALICE model, and (4) theoretical calculation by the ALICE-IPPE model.



**Fig. 7.** Yield of  $^{223}\text{Ra}$  in a thick thorium target as a function of the target thickness and incident proton energy (energy of protons leaving the target 40 MeV, irradiation time 10 days, cooling time 16 days). (1) Calculation based on experimental data of this study, extrapolated to higher and lower energy on the basis of theoretical calculations by the ALICE-IPPE model, and (2) theoretical calculation by the ALICE-IPPE model.

Table 2. It is appropriate to produce  $^{223}\text{Ra}$ , like  $^{225}\text{Ac}$ , at accelerators with the energy exceeding 100 MeV and high beam current.

**Chemical isolation of Ac.** The  $\gamma$ -ray spectrometric analysis revealed the presence of more than 80 radioactive isotopes of various elements in products of Th irradiation. Along with the desired  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$ , other radionuclides are formed by fusion and spallation reactions and by the subsequent decay of the products of these reactions:  $^{224}\text{Ra}$  ( $T_{1/2} = 3.7$  days),  $^{225}\text{Ra}$  (14.8 days),  $^{226}\text{Ac}$  (29 h),  $^{227}\text{Ac}$  (21.8 years),  $^{227}\text{Th}$  (18.7 days),  $^{228}\text{Th}$  (1.9 years),  $^{231}\text{Th}$  (25.5 h),  $^{228}\text{Pa}$  (22 h),  $^{229}\text{Pa}$  (1.4 days),  $^{230}\text{Pa}$  (17.4 days),  $^{232}\text{Pa}$  (1.3 days),  $^{233}\text{Pa}$  (27 days), and  $^{230}\text{U}$  (20.8 days). It is important that irradiation of metallic Th is not accompanied by formation of significant amounts of  $^{222}\text{Rn}$  (3.8 days), giving rise to serious technical problems in the isolation of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  from radium sources. Also, some fission products were detected in amounts comparable (in activity) with those of the de-



**Fig. 8.** Extraction-chromatographic separation of Ac from other elements using a sorbent based on isobutylcarbamoyl phosphine oxide: (1)  $^{224}\text{Ac}$ , (2)  $^{105}\text{Ru}$ , (3)  $^{131}\text{I}$ , (4)  $^{136}\text{Cs}$ , (5)  $^{140}\text{Ba/La}$ , and (6)  $^{141}\text{Ce}$ .

sired radionuclides:  $^{111}\text{Ag}$  (7.5 days),  $^{103}\text{Ru}$  (39.3 days),  $^{106}\text{Ru}$  (372 days),  $^{131}\text{I}$  (8.0 days),  $^{126}\text{Sb}$  (12.4 days),  $^{127}\text{Sb}$  (3.9 days),  $^{125}\text{Sn}$  (9.6 days),  $^{123}\text{Sn}$  (129 days),  $^{124}\text{Sb}$  (60.3 days),  $^{127}\text{Xe}$  (36.4 days),  $^{115m}\text{Cd}$  (44.6 days),  $^{129m}\text{Te}$  (33.6 days),  $^{136}\text{Cs}$  13.2 days),  $^{95}\text{Zr}$  (64.0 days),  $^{95}\text{Nb}$  (35.0 days),  $^{93}\text{Y}$  (10 h),  $^{140}\text{Ba}$  (12.8 days),  $^{99}\text{Mo}$  (66 h),  $^{141}\text{Ce}$  (32.5 days),  $^{148m}\text{Pm}$  (41.3 days),  $^{147}\text{Nd}$  (11.0 days), etc. (several hundreds of peaks in the  $\gamma$ -ray spectra). The relative activity of  $^{225}\text{Ac}$  in the mixture formed was as low as  $\sim 1\%$ , and that of  $^{223}\text{Ra}$ , several percents.

Thus, isolation of radiochemically pure  $^{225}\text{Ac}$  from a complex mixture of radionuclides is a complex problem. The process for  $^{225}\text{Ac}$  isolation from solution consisted of extraction and extraction-chromatographic steps. In liquid extraction, macroamounts of Th, and also Pa, Zr ( $>90\%$ ), I ( $>75\%$ ), and Nb (35–40%) pass to the organic phase, whereas the other elements, including Ac and Ra, remain in the aqueous phase.

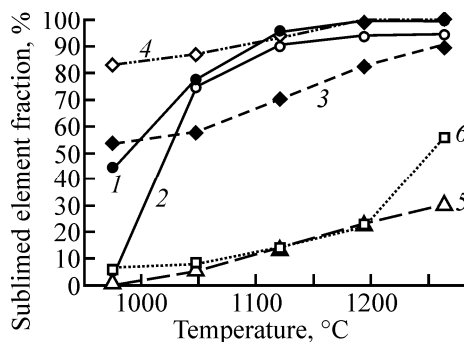
The results of extraction-chromatographic separation of a number of elements in the carrier-free state are shown in Fig. 8. Washing of the column with 15 ml of 5 M  $\text{HNO}_3$  eliminates such interfering radionuclides as  $^{136}\text{Cs}$ ,  $^{105}\text{Ru}$ ,  $^{140}\text{Ba}$ , and  $^{131}\text{I}$ . The Ac fraction was eluted in the next 15 ml of the acid, whereas such interfering radionuclides as  $^{141}\text{Ce}$  and  $^{140}\text{La}$  remained on the column. We found that  $^{225}\text{Ac}$  was fully purified when the extraction chromatography was performed twice. Figure 3b shows the  $\gamma$ -ray spectrum of the isolated Ac fraction. The purity of the product obtained by irradiation of Th with 110-MeV protons and purified using the above-described chemical procedure is characterized by the following parameters: chemical yield of  $^{225}\text{Ac}$  no less than 90%; radionuclidic purity of

the product (18 days after irradiation completion), determined by  $\alpha$ - and  $\gamma$ -ray spectrometry:  $^{226}\text{Ac}$  ( $T_{1/2} = 29$  h) 0.1%,  $^{227}\text{Ac}$  ( $T_{1/2} = 21.8$  years)  $\leq 0.1\%$ , other radionuclides  $< 0.1\%$ .

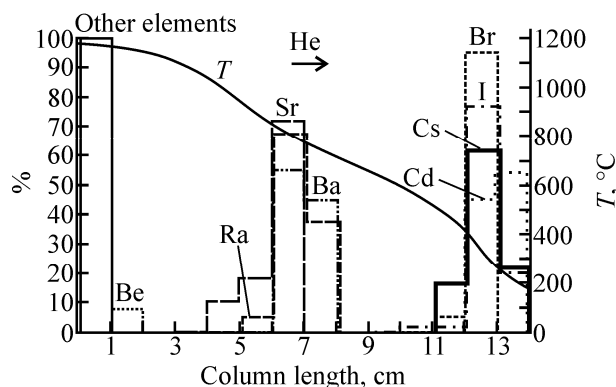
**Chemical isolation of Ra.** Radium-223 was isolated by a gas-chemical method used previously for isolating certain actinide, lanthanide, and alkaline-earth elements in the carrier-free form [23, 24]. The method is based on the fact that Ra in the metallic state is considerably more volatile than Th and a number of other interfering elements (Ac, Pa, La, Pm, Ce, Nd, Be, Cr, Zr, Mo, Nb, Tc, Sn, Ag, Ru, Rh). The addition of metallic La is extremely important. Thorium placed in a zirconium crucible together with metallic La dissolved in liquid La in the course of heating, which ensured fast diffusion of the microelements being isolated in the liquid metal and high degree of sublimation of Ra isotopes. The presence of metallic La also stabilizes the metallic state of nonvolatile elements (actinides, lanthanides, and also Sn) which could sublime at the experiment temperature in the form of volatile lower oxides from vessels made of Ti and Zr [25]. Lanthanum also binds into nonvolatile compounds Sb and Te, which under other conditions readily sublime at approximately  $1200^\circ\text{C}$  [26]. Special experiments showed that without metallic La the Ra sublimation yield decreased and some other interfering elements sublime, which makes the subsequent thermochromatographic separation less efficient.

Heating of the irradiated metallic Th in the presence of La for 2 h at  $1200^\circ\text{C}$  ensured release of more than 99% of radium isotopes ( $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ ,  $^{225}\text{Ra}$ ), of Sr and Ba isotopes, and also of I, Br, Cd, and Cs, which are highly volatile in the elementary state. The elements that exhibit low volatility in the elementary state (Ac, Th, Pa, U, Ru, Sn, Zr, Nb, Y, Mo, Ce, Pm, Nd), and also Sb and Te did not sublime and fully remained in the crucible. Figure 9 shows the temperature dependence of the release of various elements from a melt with La (the points characterize stepwise heating of the same sample at successively increasing temperatures, for 1 h at each temperature). The relatively low degree of the release of I can be accounted for by low rate of diffusion of large iodide ion in a Th–La melt.

Figure 10 shows the distribution of the isolated elements in the titanium thermochromatographic column. The deposition temperature of Ra, Ba, and Sr (maximum of the thermochromatographic peak) under these conditions was  $800 \pm 30$ ; that of Be,  $\geq 1170$ ; that of



**Fig. 9.** Temperature dependence of the release of Ra and some other elements from a melt of Th with La (stepwise heating of the same sample at successively increasing temperatures, for 1 h at each temperature): (1)  $^{223}\text{Ra}$ , (2)  $^{140}\text{Ba}$ , (3)  $^{136}\text{Cs}$ , (4)  $^{22}\text{Na}$ , (5)  $^7\text{Be}$ , and (6)  $^{131}\text{I}$ .



**Fig. 10.** Thermochromatogram of radioelements in a titanium column, sublimed in a helium stream from Th dissolved in La. Other elements: Th, Ac, Pa, La, Pm, Ce, Nd, Cr, Zr, Mo, Nb, Tc, Te, Sn, and Sb.

Cs, I, and Br,  $350 \pm 50$ ; and that of Cd,  $220 \pm 30^\circ\text{C}$ . Apparently, Ra, Ba, Sr, Be, Cs, and Cd are transported along the thermochromatographic column in the elementary state, whereas I and Br form compounds with Ti. As can be seen, by depositing the sublimed elements on the Ti collector in the temperature range  $1100\text{--}600^\circ\text{C}$  (the range is refined depending on the isolation conditions), it is possible to obtain a fraction of Ra containing only Ba and Sr impurities.

The subsequent extraction-chromatographic purification of this fraction allows us to obtain a fraction of pure Ra containing  $^{223}\text{Ra}$  with impurities of  $^{225}\text{Ra}$  and  $^{224}\text{Ra}$  (Fig. 3c).

Thus, we have developed an efficient procedure for isolating  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  from metallic Th irradiated with medium-energy accelerated protons. The procedure involves liquid extraction and extraction chroma-

tography for the isolation of  $^{225}\text{Ac}$  and gas-chemical isolation and extraction chromatography for  $^{223}\text{Ra}$ . The results obtained are the basis for a process [27] for production of large amounts (several curies) of  $^{225}\text{Ac}$  and  $^{223}\text{Ra}$  by isolation from thick metallic Th targets irradiated on a high-flux proton beam, which is important for wide use in nuclear medicine.

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