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Yu.T.Chuburkov, V.P.Perelygin, I.Zvára, Z.Szeglowski,
S.P.Shtanko, G.V.Buklanov, Yu.P.Kharitonov, A.G.Belov,
T.P.Drobina, V.N.Bugrov, B.Bisplinghoff*, R.Brandt*

A NOVEL APPROACH TO THE PROBLEM
OF HIGHLY-SENSITIVE REGULAR ANALYSES
FOR MAN-MADE PLUTONIUM IN ENVIRONMENT
AND HUMAN BODY

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*Kernchemie, F.B.14, Philipps-Universität, Marburg, Germany

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Introduction

Recent thorough studies have confirmed expectation that the Earth crust and its surface layers contain only negligible quantities of natural plutonium. For instance, in granites and hot spring water (Salton Sea) investigated in Refs.1-3, plutonium content does not exceed $6 \cdot 10^{-16}$ g/g. Only in uranium ores (pitchblende), due to peculiar physical and geochemical reasons, the content of Pu reaches $10^{-14} - 10^{-12}$ g/g. The observation of Meir et al.[4] of relatively large Pu concentrations in some rather young volcano lavas could not be confirmed [2].

Element plutonium was first obtained artificially in nuclear interactions in 1941 [5]. During the last half a century, it has been produced on industrial scale and widely used for military and peaceful purposes - weapon production, nuclear propulsion of military and civil ships, research and power reactors, etc.

Today, as a result of numerous weapon tests and accidents at reactors and chemical processing plants, some man-made plutonium is widely distributed over the Earth surface. The mean concentration of the main isotope ^{239}Pu in soils is estimated to be at a level of 10^{-13} g/g. However, it may be larger in some selected places near nuclear establishments. For example, Barth et al.[3] found up to 10^{-11} g/g of Pu in some German river sediments.

Unfortunately, so far the chemical behavior of plutonium in biological cycle, including human body, has been poorly investigated. There are contradictory points of view of plutonium hazard to health. They range from total absence of any hazard, based on sophisticated assumption that plutonium cannot be deposited in human body tissues, to high radiotoxicity producing lethal dose at a plutonium amount of $10^{-6} - 10^{-7}$ g in human body. Such disagreement of opinions and estimates has an objective reason in difficulties of measuring very low concentration of Pu.

In the experiments mentioned above, plutonium concentration was determined with the help of a very sensitive α -spectrometric equipment. Nevertheless, determination in the range of $10^{-12} - 10^{-16}$ g/g required chemical separation of plutonium from specimens weighing up to kilograms, because of the low specific α -activity of ^{239}Pu , which in only 0.25 Bq per 10^{-10} g of Pu. That is why the systematic study of plutonium content in environment at the level of sensitivity less than 10^{-12} g/g, and especially in the tissues of animals and in human body — at the level less than 10^{-10} g/g, even with the help of most-sensitive α -spectrometric devices seems to be very difficult.

The chemical behavior of uranium, which has a clark concentration of 10^{-6} g/g in the Earth crust, is well-known. It has been found that uranium concentration in ocean water, plants, and animal organisms varies only within one order of magnitude around 10^{-7} g/g; i.e., uranium does not concentrate neither in plants, nor in living organisms. This can be explained by the solubility U(VI) compounds in water. But the chemical behavior of plutonium differs significantly from uranium; most probably in living organisms plutonium exists in Pu(IV) state, and contrary to U(VI), can be accumulated in some tissues; see, e.g., Refs.6-8. It is important to note, that if the level of plutonium content in potable water is 10^{-15} g/g, during 10 years up to 10^{-8} g of Pu could be accumulated in a human body.

In the near future, the concentration of man-made plutonium in geo- and bio-

spheres will perhaps increase while there is still no possibility to perform systematic monitoring at the level of sensitivity of 10^{-12} g/g. Thus, the problem of developing appropriate high-sensitive determination techniques for plutonium is very urgent and important.

In principle, one can achieve a sensitivity of ^{239}Pu determination as high as 10^{-15} g/g by using radiochemical isolation of Pu plus thermal neutron-activation with counting induced fission events, because the fission cross-section of ^{239}Pu is very high: $\sigma_f = 7.4 \cdot 10^{-22}$ cm². But such an approach meets the problem of possible minor uranium impurities left in the Pu fraction as natural uranium contains 0.7% of ^{235}U , which has also a very high induced fission cross-section, $\sigma_f = 5.8 \cdot 10^{-22}$ cm².

Deep chemical decontamination of the Pu fraction from uranium is certainly possible. But there is no real way to check the chemical separation procedure with the traditional method of radioactive tracers, especially in routine analyses, because the separation coefficient must be very high, up to 10^6 .

In Refs.9,10, it was first proposed to make use of photofission of heavy nuclei with energetic gamma-rays to solve the difficulties with controlling the Pu — U separation. In natural uranium, the abundance of ^{238}U is 140 times higher than that of ^{235}U , while, contrary to the thermal neutron cross sections, the photofission cross sections for the two isotopes are nearly equal [11]. It means that the photofission of ^{238}U can be used to look for ^{235}U in the Pu fraction.

Earlier it was demonstrated [9,10] that the sensitivity of the new method is sufficiently high. In this paper, we present data of analyses made at JINR, Dubna of about one hundred samples of soils, water, river sediments, plants, and human gallstones for Pu content at the level of sensitivity up to 10^{-13} g/g. In addition, some samples were analysed also at Marburg Philipps University using a different chemical procedure followed by high-sensitivity alpha-spectrometry.

Experimental

1. Preliminary treatment of samples; administration of a tracer for Pu chemical yield determination

Weighted probes for analysis were taken from representative samples of materials. The soils and sediments were dried. For water analysis, a measured volume was evaporated, and the dried residue weighted. The plants and gall-stones were dried and weighted. To all the dried samples a nitric acid solution containing α -active ^{236}Pu [12] in an amount of 0.3 Bq was added.

The organic matter was destroyed by boiling with 8M HNO_3 in the presence of KBO_3 ; the final solution was evaporated. The dried residue was heated in air during 2-3 hours at 550°C.

2. Leaching of plutonium

Contrary to uranium, the man-made plutonium is not incorporated in the silicate matrices of the obtained solid remnants, which were not melted. So complete solution of the silicates seems unreasonable. In order to leach plutonium, the specimens were treated with boiling concentrated HNO_3 containing some H_2O_2 . The solution was then separated with a centrifuge, evaporated, and the residue was dissolved in 6 ml of 3M HNO_3 in the presence of NaNO_2 .

3. Separation of plutonium from uranium and thorium

We used the method described in [13]. The nitric acid solution was filtered through a chromatographic 2column filled with a polysorb resin, which had been saturated with trioctylmethylammonium nitrate. The column was washed to eliminate uranium and thorium, and plutonium was eluted with 6 ml of 0.3% solution of ammonium oxalate in 0.5M HNO_3 .

4. Plating of the Pu fraction

The plutonium fraction must be deposited as a layer with a thickness less than the range of fission fragments. To achieve this, the above eluate was evaporated and heated in order to completely destroy ammonium oxalate, and the remnant was dissolved in isobutyl alcohol. The solution was loaded in an electroplating cell (see Fig.1). For the cathode - the backing of the final sample - a chemically inert stainless steel was used, which contained in the surface "working layer" (about 10 mg/cm^2 - the fission fragment range) no more than 10^{-15} g of ^{235}U per cm^2 . The anode was of platinum metal. The deposition time at a voltage of $\sim 600 \text{ V}$ was 40 min. In order to avoid the adsorption of microquantities of plutonium on glass and teflon surfaces, all the cell elements were preliminarily boiled in nitric acid 2solution of a lanthanoid element.

5. Registration of induced fission events; bombardment conditions

The fission fragments due to fission of heavy nuclei with thermal neutrons and hard gamma-rays were registered by solid state track detectors (SSTD) [14]. A PETP (lavsan) foil was used as a detector; it contained less than 10^{-10} g/g of natural uranium, which corresponds to less than 10^{-15} g/cm^2 of ^{235}U in the surface working layer. For quantitative determination of plutonium a "thin" standard sample of natural uranium was made, containing $3.29 \cdot 10^{14}$ atoms of U per cm^2 . All the irradiations of plutonium preparations both with thermal neutrons and gamma-rays, were performed together with the uranium standard. In every irradiation, fresh lavsan foils were always used.

The bombardments with thermal neutrons were conducted at the JINR pulsed nuclear reactor IBR-30 of Frank Laboratory of Neutron Physics, and with bremsstrahlung gamma-rays ($E_\gamma \leq 25 \text{ MeV}$) - at the microtron MT-25 of Flerov Laboratory of Nuclear Reactions. The chosen thermal neutron fluences of $\approx 10^{15} \text{ /eV.cm}^2$ (cadmium ratio was about 10^2) produced $(1-2) \cdot 10^6$ fission fragment tracks with the calibrated U standard, and correspondingly, some 100 tracks with 10^{-13} g of ^{239}Pu to yield about $\pm 10\%$ counting error bars. The background from induced fission events both in the stainless steel backing and the lavsan track detector was negligible.

6. Analytical procedure at Marburg

The analysis typically started with a (100-200)g sample. About 0.3 Bq of ^{242}Pu tracer of high isotopic purity, (supplied by the US National Bureau of Standards, Washington, DC) were added. The sample was refluxed with 500 ml of conc. HNO_3 for 5 h and then centrifuged. The solution was dried to near-dryness and the residue was dissolved in 250 ml of 2M HNO_3 ; any precipitates were centrifuged off. In order to oxidize Pu^{3+} to Pu^{4+} , 10 ml of NaNO_2 solution were added, and the solution was heated for a short time to 80° C . Then Pu^{4+} was extracted four times with 250 ml

0.5 M thenoyltrifluoroacetone in xylene. The organic phase was washed twice with 100 ml of 2 M HNO_3 . Plutonium was back-extracted three times with 10 M HNO_3 . This aqueous phase was evaporated to near-dryness and converted into a 6 M HCl solution. Then Fe^{3+} was removed by extraction with ether. The remaining aqueous phase contained only small amount of salts, which could be separated by adsorbing Pu onto conventional anion-exchange columns. Plutonium was then eluted from the column with III/HCl-mixture (1:7) or with 3 M HCl only. Finally, the sample was prepared for alpha-counting by an electrodeposition technique. Plutonium was deposited on a Pt-plate, using Pt-anode and NH_4Cl solution at $\text{pH}=5$, typically in 45 min at 12 V. At the end, conc. ammonia was added, and the sample was washed with water and ethanol. The Pt-foil was flamed gently to convert hydroxides to oxides. The entire chemical procedure is described in Ref.3.

Results and Discussion

The Dubna results of ^{239}Pu content determination in different materials and of ^{235}U impurity measurement in the same samples are presented in Table 1. The data of the interlaboratory comparison experiments are shown in Table 2. The agreement is satisfactory.

In a number of samples, plutonium concentration could be measured at Dubna also by α -activity (6 h counting, surface barrier Si-detectors). As one can see from Table 1, unlike the traditional α -spectrometric technique, the sensitivity of the new track method reaches 10^{-13}g/g with as little as 1-3 g of the tested material. In the same time, relatively high plutonium concentrations, $\geq 10^{-12}\text{g/g}$, which are still at the limit of sensitivity for α -spectrometry, especially for the routine analyses, were measured with the new method with sufficiently high precision. The sensitivity of Pu determination could be hopefully increased up to 10^{-15}g/g by applying inorganic SSNTDs - synthetic mica and quartz glass, which contain $10^{-14}-10^{-15}\text{g/g}$ of uranium and can register fission fragment tracks even at the thermal neutron fluences as high as 10^{20}cm^{-2} .

It is clearly seen from Table 1, that plutonium, in spite of the stability of Pu(IV), which must be absorbed by sediments, is still present in water in dangerous concentration. Thus the problem of determining plutonium in animal and human body tissues and studying the dynamics of its accumulation becomes very challenging.

That is why the next aim of our investigations is the plutonium determination sensitivity to 10^{-14}g/g and in the near future — to 10^{-15}g/g . Such methodical development could be done at the Joint Institute for Nuclear Research.

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Table 1. Concentration of ^{239}Pu in various natural materials and ^{235}U in chemically separated plutonium fractions

Place of sampling: code	Mass of material g	Concentration of ^{239}Pu by SSTD g/g	Amount of ^{235}U g	Concentration of $^{239,240}\text{Pu}$ by α -spectrometry g/g
Kiev region				
soil ^a :				
B3-43	1.9	$(4.0 \pm 0.4) \cdot 10^{-13}$	$< 10^{-13}$	---
B3-14	2.1	$(6.0 \pm 0.5) \cdot 10^{-12}$	10^{-13}	---
Potable-water ^b	10 l	$\sim n \cdot 10^{-16}$ g/l	---	---
Cheliabinsk region, soil ^a :				
244TD	2.05	$(2.0 \pm 0.2) \cdot 10^{-13}$	10^{-14}	---
19MA ₂ F	2.03	$(6.0 \pm 0.5) \cdot 10^{-11}$	10^{-12}	$(5.2 \pm 1.3) \cdot 10^{-11}$
Bielorussia ^b				
Water of river and drill holes				
	10 l	$\sim < n \cdot 10^{-15}$ g/l	$\sim 10^{-14}$	---
Plants	20	$(1 \div 3) \cdot 10^{-15}$	$\sim 10^{-14}$	---
Human gall-stones ^c				
"	2.40	$(2.3 \pm 0.2) \cdot 10^{-13}$	$\sim 10^{-14}$	---
"	2.48	$(1.2 \pm 0.1) \cdot 10^{-13}$	$\sim 10^{-14}$	---
"	2.51	$(2.1 \pm 0.2) \cdot 10^{-13}$	$\sim 10^{-14}$	---

The typical number of samples being investigated was 30-40 for different kind of material, but only the next results are presented:

- a --- soils with minimum and maximum plutonium concentrations;
- b --- for waters - the mean Pu concentration, for plants - the measured intervals of concentrations.
- c --- results of single determinations.

Table 2. Interlaboratory comparison; concentration of Pu in g/g.

	Sample 1	Sample 2
Marburg		
by α -spectrometry ($^{239,240}\text{Pu}$)	$(8 \pm 2) \cdot 10^{-11}$	$(5 \pm 1) \cdot 10^{-12}$
Dubna		
by α -spectrometry ($^{239,240}\text{Pu}$)	$(13 \pm 4) \cdot 10^{-11}$	$(4.7 \pm 1.5) \cdot 10^{-12}$
Dubna		
by SSTD (^{239}Pu)	$(12 \pm 2) \cdot 10^{-11}$	$(5.7 \pm 1.2) \cdot 10^{-12}$

The samples were supplied by Marburg.

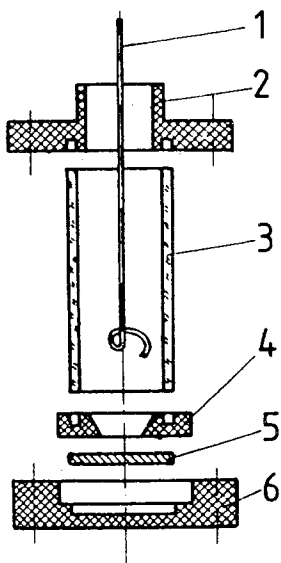


Fig. 1. Schematic of electroplating cell for Pu deposition.

1. Platinum wire
2. Upper teflon lid
3. Glass cylinder
4. Teflon washer
5. Stainless steel cathode
6. Bottom metallic lid

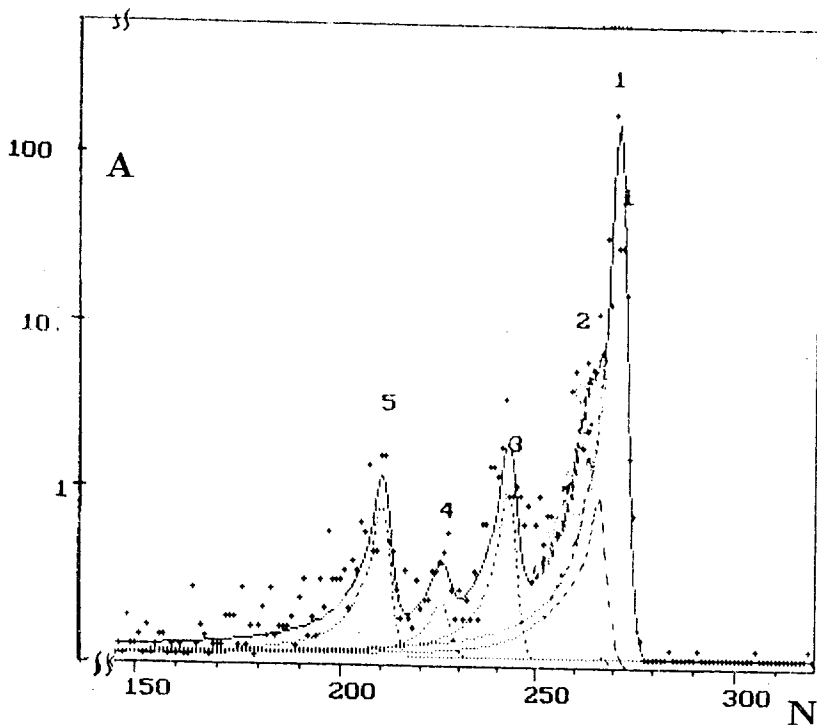


Fig. 2. Alpha-spectrum of a plutonium fraction isolated in Dubna
(see Table 2, sample 2).

A - alpha counts in arbitrary units;

N - channel number:

1,2 - ^{236}Pu (5.77, 5.72 MeV);

3,8 - ^{238}Pu (5.55 MeV);

4 - ^{237}Pu (5.65, 5.35 MeV);

5 - $^{239,240}\text{Pu}$ (5.16, 5.14, 5.17, 5.72 MeV).

Lines 1-4 are attributed to the ^{236}Pu tracer.

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Новый подход к проблеме серийных высокочувствительных анализов на содержание техногенного плутония в окружающей среде и организме человека

Предложен метод определения субпикограммовых количеств плутония в почвах, илах, воде, растениях и живых организмах. Плутоний химически был выделен из проб исследуемых веществ. Для контроля выхода применялся альфа-активный ^{236}Pu . Подложки с нанесенной плутониевой фракцией помещали в контакт с трековыми твердотельными детекторами (ТТД)-фольгами из полиэтилентерефталата, облучали их и уран содержащий эталон тепловыми нейтронами, флюенсом около 10^{15} см^{-2} . После надлежащего химического травления и сканирования было определено содержание ^{239}Pu в материалах по трекам осколков деления. Контроль за возможными примесями урана во фракции плутония осуществлялся облучением Pu -фракции и эталона с новыми ТТД высоким флюенсом γ -квантов с энергией $\leq 25 \text{ МэВ}$ (тормозное излучение микротрона). Удалось обеспечить определение нижнего предела примесей ^{235}U на уровне $< 10^{-13} \text{ г}$ благодаря примерно равному сечению фотоделения всех изотопов U и Pu . Предложенный метод обеспечивает определение содержания ^{239}Pu с чувствительностью на уровне 10^{-13} г/г в серийных анализах. В работе выполнено более ста определений содержания ^{239}Pu в пробах указанных выше сред из Украины, Белоруссии, региона Урала и Германии. Видится принципиальная возможность достичь чувствительности на уровне $10^{-14} - 10^{-15} \text{ г/г}$.

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A Novel Approach to the Problem of Highly-Sensitive Regular Analyses for Man-Made Plutonium in Environment and Human Body

A method of determining subpicogram quantities of plutonium in soil, mud, water, plant and animal tissues is proposed. Plutonium is chemically isolated from the samples, while the α -active ^{236}Pu is used to control yield. The plutonium fraction deposited on some backing as well as an uranium containing standard are put in contact with solid state track detectors (SSTD) — foils of polyethyleneterephthalate, and irradiated by thermal neutrons of approximately 10^{15} cm^{-2} fluence. After an appropriate chemical etching, the content of ^{239}Pu in the samples is determined by scanning fission fragment tracks in the SSTD. To control possible uranium impurities in the plutonium fraction, the latter and the standard (in contact with a fresh SSTD) are bombarded by a high fluence of γ -quanta with energies $\leq 25 \text{ MeV}$ (microtron bremsstrahlung). We have succeeded in determining the lower limit of ^{235}U impurities at a level of $< 10^{-13} \text{ g}$, due to similar photofission cross section of all Pu isotopes. The proposed method provides the determination of ^{239}Pu content in routine analyses with a sensitivity at a level of 10^{-13} g/g . More than one hundred assays for ^{239}Pu content in specimens of above indicated media from Ukraine, Belorussia, Ural region and Germany have been performed. In future, one will hopefully reach a sensitivity of $10^{-14} - 10^{-15} \text{ g/g}$.

The investigation has been performed at the Flerov Laboratory of Nuclear Reaction, JINR.

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