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«МЕЖДУНАРОДНЫЙ ГОСУДАРСТВЕННЫЙ
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На № _____ от _____

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zu Drs.	2848

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Anhörung zu Leukämie in der Elbmarsch

Sehr geehrte Damen und Herren,

im Auftrag der Auftraggeber (vertreten durch Dr. Pflugbeil) übersende ich Ihnen den Report der von mir durchgeführten Untersuchungen von Bodenproben aus Deutschland.

Mit freundlichen Grüssen

Prof. V.P. Mironov

Übersetzung von S.Bajda

CONCENTRATION OF ISOTOPES OF URANIUM, THORIUM AND PLUTONIUM IN SAMPLES OF SOIL FROM GERMANY

Task: I received a number of soil samples from Germany and was commissioned to determine specific activity of isotopes of uranium, thorium and plutonium in the samples.

Methods: We have applied the complex scheme of radiochemical analysis (see fig. 1), that allows to determine isotopes of Pu, U and Th simultaneously by using of just one sample. This procedure was necessary to conduct at least double analysis of the same sample. The masses of samples were small (in limits from 0,4 up to 20 g). The majority of samples represented a mineral part of soil with the various content of black particles ("microspheres") Sample "H" (less than 0,5 g mass) basically consisted of such black particles of various sizes. Sample "humus" with the major content of organic matter was probably a homogenized layer of sod (ignition coefficient is more than 30).

Before annealing, samples were grinded using an agate mortar. Thus there was an additional homogenization. Annealing was carried out up to 6 hours at temperature 600±50° . As long-term practice has shown, there is the complete removal of compounds of carbon and phosphorus.

At the request of the customer, the complete dissolution of sample in a mixture of concentrated HNO_3 and HF at 90°C was carried out.

During concentration and purification procedures, aiming to get rid of macro- and trace contaminants, uncontrollable losses of isotope to be determined are possible. Therefore the chemical yield of the analyzed radionuclide is always less than 100 %. For the quantitative determination of chemical yield, the indicator of a chemical yield (tracer) should be added at a stage of complete dissolution of sample. Usually it is an isotope of chemical element to be determined. In our case it is such isotopes of U, Th and Pu, which are not present in the analyzed sample, and have the energy of α-particles distinguishable from energy of α-particles of the radionuclides to be determined. We have carried out the analysis of several samples without addition of the chemical yield indicator and we have shown that there are no isotopes of ^{242}Pu, ^{232}U and ^{229}Th in the analyzed samples.

The scheme of analysis

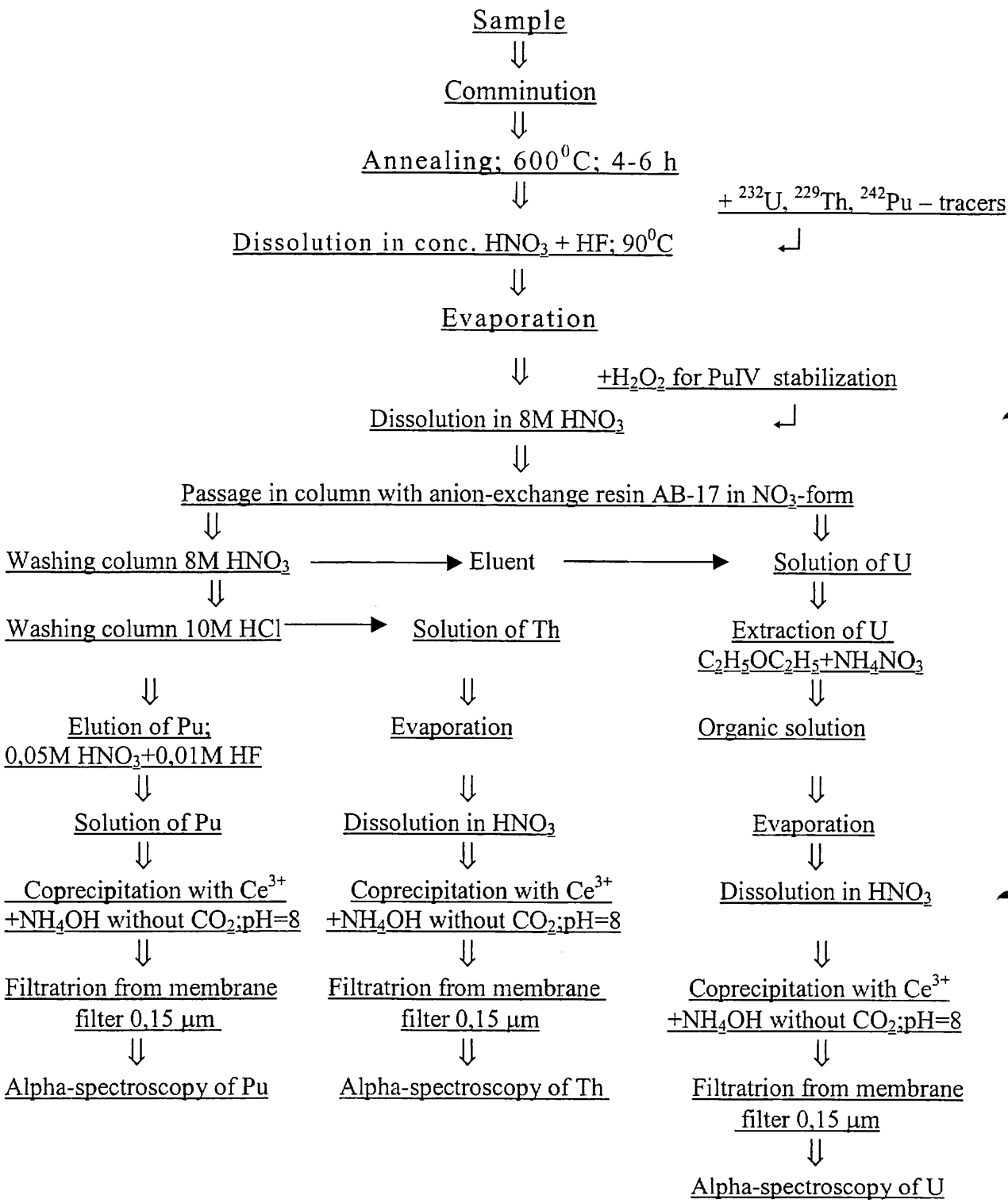

Fig. 1

Scheme of sample preparation for Alpha-spectroscopy

The energies of α-particles (MeV) of these radionuclides differ essentially from energies of α-particles of the radionuclides to be determined, therefore we used these isotopes as indicators of chemical yield (see fig. 2,3,4).

U-238	U-235	U-236	U-234	U-233	U-232
					5,320 (68,6)
					5,264 (31,2)
				4,824 (84,4)	
				4,78 (13)	
			4,776 (72,4)		
			4,724 (27,4)		
	4,598 (5)				
	4,556 (4,2)				
		4,494 (74)			
		4,445 (26)			
	4,396 (55)				
	4,370 (6)				
	4,364 (11)				
	4,325 (4,6)				
	4,217 (5,7)				
4,196 (77)					
4,147 (23)					

Fig. 2

Energies of α-particles (MeV) from uranium isotopes

Pu-242	Pu-239	Pu-240	Pu-238	Pu-236
				5,77 (69)
				5,72 (31)
			5,499 (72)	
			5,456 (28)	
		5,168 (73,5)		
	5,155 (73,3)			
	5,143 (15,1)			
		5,123 (26,4)		
	5,105 (11,5)			
4,901 (78)				
4,856 (22)				

Fig. 3

Energies of α-particles (MeV) from plutonium isotopes

Th-232	Th-230	Th-229	Th-228
			5,340 (27)
			5,423 (73)
		4,845 (56)	
		4,814 (9)	
		4,968 (6)	
		4,901 (10)	
	4,688 (76)		
	4,621 (23)		
4,010 (77)			
3,953 (23)			

Fig. 4

Energies of α-particles (MeV) from thorium isotopes

A fixed amount of chemical yield indicator is added at a stage of samples dissolution. After carrying out of this operation, chemical forms of tracers and determined isotopes become identical and their behavior at the further stages of the analysis will be identical. The chemical yield may be calculated on the last stage of analysis by taking α-spectrometry measurements of the amount of the indicator on an accounting target.

Evaluations were made on the basis of the following empirical formula:

$$A_x = A_{tr} \cdot (I_x/I_{tr})/M$$

Where A_x A_{tr} - specific activity of radionuclide to be determined and tracer;

I_x and I_{tr} – instrumental counts of radionuclide to be determined and tracer;

M - mass of the sample.

The chemical yield was usually more than 70 % at the analysis of the given samples.

The ion-exchange method was utilized for separation and radiochemical purification of Pu and Th. Anion-exchange separation of plutonium from the nitrate solutions is widely applied in many methods of plutonium determination in environmental samples.

Distribution number of Pu (IV) from the nitrate solutions on the strong-base anion exchanger AB-17 (such as Dauex-1) makes 3500, for Th (IV) it is 300. In 7-8 HNO_3 these elements exist as the negative charged complexes of $[Me(NO_3)_5]$ - or $[Me(NO_3)_6]^{2-}$ type. Uranium exist here as cation UO_2^{2+} and practically is not detained by anion exchanger. More than 80 % of uranium is washed away with the first portions of eluate from anion exchanger.

Purification of uranium from macro- and trace contaminants was carried out by using the approved method of diethylketone extraction.

Elution of Th from the column was carried out with 10 HCl, Pu – with solution of 0,05M HNO_3 + 0,01M HF.

Manufacturing of thin layer targets for α-spectrometric measurements was carried out by coprecipitation of allocated U, Th and Pu with microgram amounts of cerium oxyhydroxide. The precipitate obtained was filtered off under vacuum through a membrane filter.

For the measurement, the alpha-spectrometer Canberra 7401/VR with PIPS detector was used, with an active area of the detector of 450 mm^2. Registration efficiency of α-particles in the field of energy from 3 eV up to 10 eV makes 30 %. The detection sensitivity is 0,001 Bq. The energy resolution is 18 kev.

The energy calibration of alpha-spectrometer and background measurements (0,0003 counts per second) were regularly carried out.

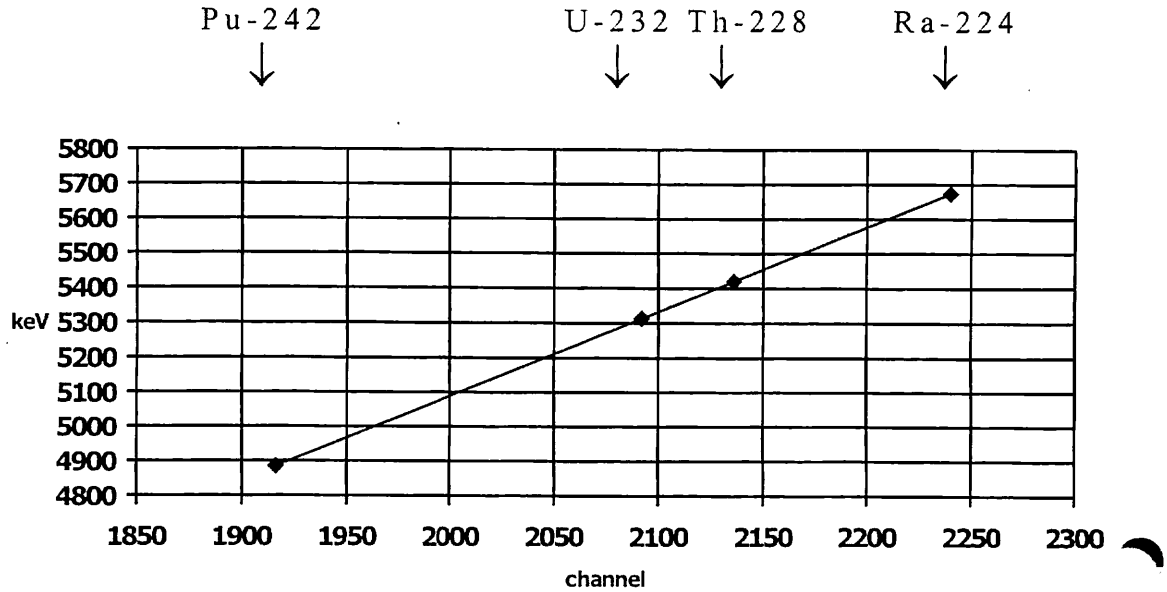

Fig. 5

The calibration of the alpha-spectrometer on isotopic sources

The counting time was from 5 hours till 3 days depending on the activity of the targets (the statistical error of the counting is in limits from 10 % up to 30 %). The minimal error conforms to the highest counting rate and, inversely, the maximum error conforms to the least counting rate.

Results:

The results of analysis are presented in the table 1.

Table 1. The results of determination of U, Th, Pu specific activity

Isotope	Sample code	
	A-1/7+C-1/6, Bq/kg	D-2/6+G-2/7, Bq/kg
U-238	28±9	21±8
U-236	-	-
U-235	<0,5	<0,3
U-234	12±3	12±3
Th-232	38±14	11±3
Th-230	650±60	64±12
Th-228	25±7	9,6±1,9
Pu-239+240	2,7±0.9	7,7±1.5
Pu-238	<0,5	<0,3

Isotope	Sample code		
	I-W-Sch, Bq/kg	E-2/5, Bq/kg	Humus, Bq/kg
U-238	190±20	13±3	50±14
U-236	85±23	12±3	31±9
U-235	95±25	13±3	30±9
U-234	230±20	15±4	45±12
U-233	90±15	12±3	20±6
Th-232	210±20	40±12	82±20
Th-230	310±30	45±14	58±15
Th-228	210±20	45±14	80±20
Pu-239+240	36±9	11±3	10±3
Pu-238	11±3	3,2±1,2	4,8±1,4

Isotope	Sample code			
	H, Bq/kg	B-1/5, Bq/kg	J-1/4, Bq/kg	F-2/4, Bq/kg
U-238	1200±160	64±15	60±15	42±19
U-236	1100±300	52±14	56±15	47±12
U-235	830±230	38±10	50±12	58±15
U-234	980±200	60±15	55±15	40±10
Th-232	1100±200	80±20	140±30	62±12

Th-230	1600±300	78±20	160±30	140±25
Th-228	2000±350	50±13	110±20	90±19
Pu-239+240	60±15	4,5±0,9	6,2±1,3	8,2±1,7
Pu-238	25±8	2,2±0,5	2,4±0,5	4,0±1,2

From the experimental data which are presented in the table it is obvious, that specific activity of the radionuclides differs more than a factor of 100 from sample to sample.

The maximal specific activity of uranium-238 found was 1200 Bq/kg, for plutonium-239+240 it was 60 Bq/kg, and for thorium-232 it was 1100 Bq/kg. In some samples the high content of thorium-230 is revealed. Sample «H» consisted of practically only of black particles («spheres»).

For better visualization of origin determination of radionuclides, results of analyses are grouped in the tables in element order (Pu, Th, U).

Table 2.

Sample code	Pu-239+240, Bq/kg	Pu-238, Bq/kg	Pu-238/Pu-239+240, Bq/Bq
I-W-Sch	36	11	0,31
E-2/5	11	3,2	0,29
Humus	10	4,8	0,48
D-2/6+G-2/7	7,7	<0,3	<0,04
A-1/7+C-1/6	2,7	<0,5	<0,2
H	60	25	0,42
B-1/5	4,5	2,2	0,49
J-1/4	6,2	2,4	0,39
F-2/4	8,2	4,0	0,49

Discussion of results

The basic sources of plutonium in the environment are as follows:

1. Nuclear weapon tests ("bomb-originated" or "global" plutonium).

The isotope ratio $^{238}Pu/^{239+240}Pu$ for "bomb-originated" plutonium in the year 1964 averaged 0,02 Bq/Bq. This ratio remained constant till 1965, but in the spring of 1966 it has increased up to 0,042. This presumably can be explained by the fact of ^{238}Pu input in the atmosphere as the result of combustion of space system SNAP-9A.

2. The accidents at nuclear reactors and factories on reprocessing of nuclear fuel (Chernobyl, Sellafield-Windscale, etc.).

In these cases levels of local contamination by plutonium-239/240 can exceed 50000 Bq/m^2 ("reactor-originated" plutonium), while levels of "global" plutonium contamination for the middle latitudes of northern hemisphere is in the level of 60 Bq/m^2. At normal operation of nuclear reactors, emissions of plutonium were not noticed. In the case of the accident at the Chernobyl NPP the isotope ratio $^{238}Pu/^{239+240}Pu$ for "reactor-originated" plutonium is ~ 0,5. The isotope ratio $^{238}Pu/^{239+240}Pu$ more than 0,06 indicates the presence of "reactor-originated" plutonium.

Table 3.

Sample code	Th-232, Bq/kg	Th-228, Bq/kg	U-233, Bq/kg	$^{232}Th/^{228}Th$, Bq/Bq
I-W-Sch	210	210	90	1,0
Humus	82	80	20	1,0
E-2/5	40	45	12	0,89
A-1/7+C/1/6	38	25	-	1,5
D-2/6+G-2/7	11	9,6	-	1,1
H	1100	2000		0,55
B-1/5	80	50		1,6
J-1/4	140	110		1,3
F-2/4	62	90		0,69

Natural thorium consists practically of one isotope ^{232}Th ($T_{1/2}$ = 1,4 · 10^{10} y). Its daughter isotope ^{228}Th ($T_{1/2}$ = 1,91 years) is of insignificant amount (~ 10^{-8} % in mass.) and is in secular equilibrium with mother isotope ($^{232}Th/^{228}Th \approx 1$).

$$^{232}Th \xrightarrow[1{,}41\cdot10^{10}\ y]{\alpha} {}^{228}Ra \xrightarrow[5{,}76\ y]{\beta^-} {}^{228}Ac \xrightarrow[6{,}13\ h]{\beta^-} {}^{228}Th$$

Thorium is a source for production of a secondary nuclear fuel (^{233}U). It can be produced with the following basic nuclear reaction.

$$^{232}Th\ (n,\gamma)^{233}Th \xrightarrow[22.3\ min]{\beta^-} {}^{233}Pa \xrightarrow[27\ d]{\beta^-} {}^{233}U$$

It is known, that during the period since 1967 to 1988 in Germany experimental reactor AVR with a capacity of 15 MW on thorium fuel was exploited. Fuel elements had a spherical form. Thorium was used in a mixture with highly enriched uranium. The total amount of such fuel «microspheres» made approximately 100000 what is equal to 1360 kg of fuel. On the basis of AVR reactor, THTR reactor with a capacity of 300 MW, which was working in Germany since 1983 to 1989 on bulk uranium - thorium fuel, has been developed. Fuel producing has been put on an industrial basis. There is no information about emergencies on such enterprises, and at normal exploitation the probability of thorium and uranium emissions into the environment is very low.

Thus, the presence of ^{233}U in soil samples indicates that thorium-232 was irradiated with thermal neutrons (with a cross section of 7,3 barns).

Table 4.

Sample code	^{238}U Bq/kg	^{236}U Bq/kg	^{235}U Bq/kg	^{234}U Bq/kg	$^{234}U/^{238}U$ Bq/Bq	$^{235}U/^{238}U$ %mass	$^{236}U/^{238}U$ %mass
I-W-Sch	190	85	95	230	1,2	7,8	0,34
Humus	50	31	30	45	0,9	9,4	0,48
A-1/7+C-1/6	28	-	<0,5	12	0,43	<0,3	
D-2/6+G-2/7	21	-	<0,3	12	0,57	<0,2	
E-2/5	13	12	13	15	1,2	16	0,71
H	1200	1100	830	980	0,82	11	0,70
B-1/5	64	52	38	60	0,94	9,3	0,62
J-1/4	60	56	50	55	0,92	13	0,72
F-2/4	42	47	58	40	0,95	22	0,86

Isotope ratios $^{235}U/^{238}U$ and $^{236}U/^{238}U$ specify the origin of uranium (natural or technogenic). In natural uranium the ^{235}U content makes 0,725 % mass of ^{238}U.

In light-water nuclear reactors of common NPPs U-235 enrichment is equal to 4 %. During the work of nuclear reactor, uranium-236 is formed on ^{235}U (n, γ) ^{236}U nuclear reaction. Note, that in natural uranium U-236 is practically absent ($^{236}U/^{238}U \sim 10^{-10}$ g/g). Detection of uranium-236 during an isotope analysis indicates that we are dealing with uranium which was irradiated in a reactor ("reactor-originated" uranium).

An isotope ratio $^{235}U/^{238}U$ less than 0,3 % mass corresponds to the depleted uranium which was used in the past in battle operations.

Thus, on the basis of the received experimental data it is possible to conclude, that only technogenic uranium presents in analyzed samples (reactor-originated and depleted).

The high content of thorium-230, which is present at U–238 radioactive row, is strange. Only in the "humus" sample the isotope ratio $^{230}Th/^{238}U$ corresponds to equilibrium state.