

SELECTIVE RADIOCHEMICAL SEPARATIONS USING SR.SPEC

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Sr.Spec material has been used for the analysis of radioactive strontium nuclides in environmental, biological and nuclear samples and for the simultaneous determination of ^{210}Pb and ^{210}Po nuclides in environmental, biological and industrial samples.

A list of the recent publications on the application of Sr.Spec at the IAEA's Laboratories at Seibersdorf and at the Technical University Budapest has been prepared (Table 1). Although major part of the list covers progress reports and conference papers, but two articles for periodicals are also included and the length of the list expresses the wide-spread use of the Sr.Spec.

1. Radiostrontium analysis in environmental, biological and nuclear samples

Strontium nitrate is extracted by the 4,4'-(5')-bis(tert-butylcyclohexano)-18-crown-6 molecule based on its relatively high selectivity towards strontium complexes from 3M or more concentrated nitric acid solutions. Strontium is stripped from the column with distilled water. The theoretical background, the retention mechanism has been studied exhaustively by Mr. Horwitz and his colleagues.

Depending on the composition of the sample to be analyzed there are different interferences in any separation procedure. Special attention has to be paid to those elements which are better retained by the crown ether than strontium itself, as Pb, Pu(IV), to those which show comparable retention properties as Ba or Hg, as well as to those which are represented at higher activity concentrations in the sample than the strontium nuclides e.g. K (^{40}K) in most of the natural materials (soil, plant etc.). To obtain a pure strontium fraction from different materials a simple separation procedure has been developed and applied under test conditions and using a great variety of standard reference materials. The purity of the strontium fraction has been checked by different analytical techniques (tracer studies with alpha, beta and gamma counting techniques, gamma spectrometry, ICP-AES).

The basic separation scheme is shown in Figure 1. It consists of the following parts; sample dissolution, strontium preconcentration by co-precipitation with calcium-magnesium oxalate, chromatographic separation of strontium using Sr.Spec, strontium oxalate precipitation to determine the chemical yield by gravimetry, beta counting of the strontium nuclides by liquid scintillation counting technique.

This separation procedure was appropriate for most of the samples to be analyzed, but in certain cases some modifications had to be included into the procedure e.g. a repeated chromatographic separation (primary coolant), addition of calcium to

samples of low calcium content (radioactive waste), determination of the total (non-radioactive) strontium content of the sample to correct the chemical recovery (grass, bone). The gamma spectrometric analysis of the final strontium source to check its purity is always recommended. There is a special way of purity control in LSC; the measurement of ^{90}Y while it grows into the ^{90}Sr parent nuclide.

1.1. ^{90}Sr analysis in environmental and biological samples

For most of the environmental and biological samples potassium can be regarded as the critical component - due to the relatively high activity of ^{40}K and the high energy of the emitted beta particles interfering with those of ^{90}Sr and ^{89}Sr . The removal of the bulk potassium is easily accomplished by the oxalate precipitation. Traces of potassium are removed by the chromatographic separation and the final oxalate precipitation for strontium source preparation.

Results of ^{90}Sr analysis in standard reference materials are shown in Table 2. Measured activity concentrations for soil, milk, grass and animal bone samples agree well with the reference values. Results for samples containing relatively high amounts of strontium (comparable with 10 mg of strontium carrier) were corrected for the total strontium content.

Improving our original method a detection limit of about 1 Bq ^{90}Sr /kg ash can be achieved. The chemical recoveries vary between 60 and 80%.

The presence of ^{89}Sr in environmental samples has to be checked under accidental conditions. ^{89}Sr can be distinguished from ^{90}Sr and ^{90}Y by means of beta spectrometry and repeated counting.

1.2. Radiostrontium analysis in nuclear samples

In fissile materials a great variety of strontium nuclides are produced (Figure 2) either by direct fission or from the decomposition of the precursor fission products (rubidium and krypton nuclides). In the reactor core strontium nuclides are also produced by neutron activation from different isotopes. On the other side strontium nuclides decay to yttrium nuclides. As a result of fuel failures and of surface contamination on fuel claddings radiostrontium nuclides appear in the primary coolant of nuclear reactors. Based on their relative amounts conclusions can be drawn on the fuel element failures. Regarding the half lives of the strontium nuclides, ^{89}Sr , ^{90}Sr , ^{91}Sr and ^{92}Sr can be detected in the coolant. The latter two nuclides emit gamma radiations, while ^{89}Sr and ^{90}Sr are well-known pure beta emitters.

To analyze the radiostrontium nuclides in the coolant samples were chromatographically separated from 3M nitric acid solutions with the Sr.Spec crown ether. (The preconcentration step was omitted.) ^{91}Sr and ^{92}Sr were analyzed by gamma spectrometry in the freshly separated strontium oxalate source that might have contained some contamination (^{140}Ba , $^{110\text{m}}\text{Ag}$). After some day-long cooling time the separation procedure was repeated and ^{90}Sr and ^{89}Sr were analyzed by LSC.

Some of the results are shown in Table 3.

Waste samples of the nuclear reactors are usually stored for many years. Among the radiostrontium nuclides only the long-lived ^{90}Sr is of special interest concerning environmental contamination. Evaporation concentrates were analyzed by the original procedure with minor modification. Because of the low alkali earth metal content calcium was added to the samples to co-precipitate strontium with calcium oxalate. The final strontium sources were always analyzed by gamma spectrometry and in some cases the chromatographic separation was repeated to reach a higher decontamination factor for the contaminants (mostly $^{110\text{m}}\text{Ag}$ or ^{60}Co).

Some results are shown in the Table 4.

2. ^{210}Pb and ^{210}Po analysis in environmental, biological and industrial samples

It is known from the publications of Mr. Horwitz that Sr.Spec shows extremely high selectivity for lead in a wide nitric acid concentration range. (Eventually, it should have received the Pb.Spec name, but it refers now to another product of the EiChrom Co.) Although, according to Mr. Horwitz, polonium has a high distribution coefficient on Sr.Spec from dilute nitric acid, concentrated acid solutions are preferred for the separations following an acid dissolution procedure of solid samples. According to our column chromatographic experiments polonium was not well retained from 1M nitric acid.

Distribution coefficients for lead, bismuth and polonium were determined from HCl solutions of different concentrations in batch experiments (Figure 3). Lead is well retained by the Sr.Spec from moderately concentrated HCl solutions. The high distribution coefficient (>400) in 0.5-2M HCl indicates a strong but reduced Pb retention compared to nitric acid of same concentration, thus allowing the easier stripping of lead from the column. In 6M HCl lead is not retained, so this solution can be used as a proper stripping agent of lead. The higher the the HCl concentration is the better polonium is retained. From about 2M HCl the distribution coefficient of polonium is above 100 allowing its separation from bismuth. Polonium can be stripped easily from the column with 6M HNO_3 .

A simple radiochemical procedure has been developed to analyze ^{210}Pb and ^{210}Po simultaneously (Figure 4).

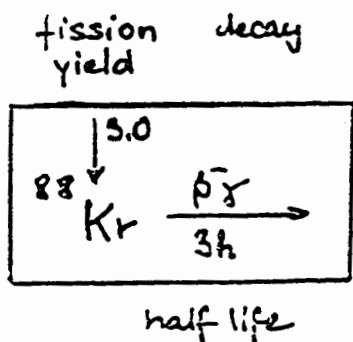
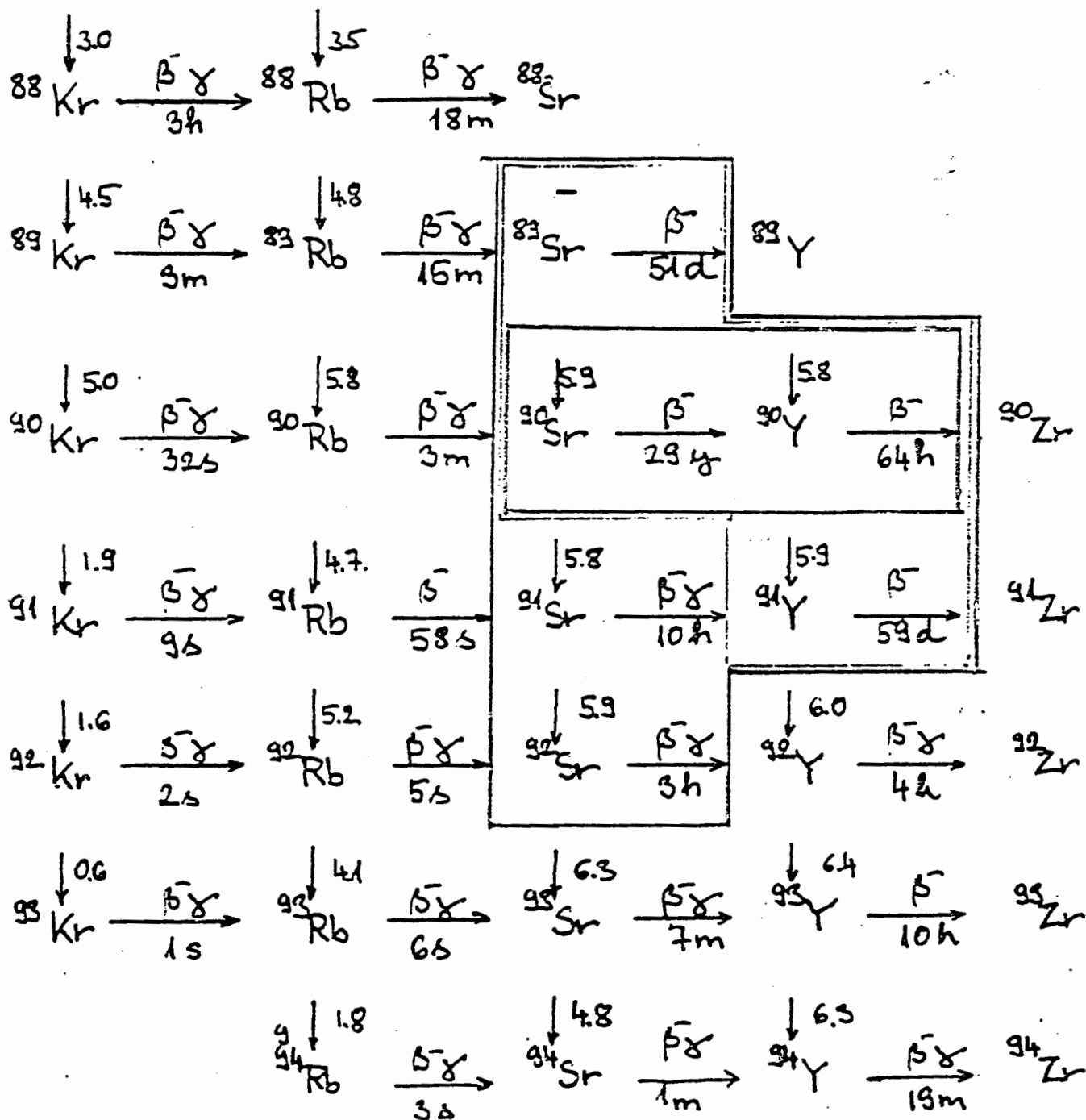
The procedure consists of sample dissolution, lead and polonium separation using the Sr.Spec without any preconcentration. Polonium is stripped with 6M nitric acid while lead with 6M hydrochloric acid. A polonium source is prepared by spontaneous deposition onto a silver disc. The activity concentration of ^{210}Po is determined by isotope dilution alpha spectrometry. Lead is precipitated as oxalate, the chemical recovery is determined by gravimetry. The activity concentration of ^{210}Pb is calculated from the liquid scintillation spectrum.

The chromatographic behaviour of several other elements has been studied by ICP-AES. The elemental composition of the fractions are given in % in Table 5. ICP measurements confirmed the conclusions that lead and polonium are recovered from the column in relatively pure form and by high recoveries. Unfortunately, only a limited number of elements of the periodic table have been studied in detail.

To test the total analytical procedure reference materials of known ^{210}Pb and ^{210}Po concentrations and of different compositions have been analyzed. Samples under studies included sediments, phosphate ore, seaweed and cockle flesh. It has to be mentioned that there is a lack of certified reference materials for ^{210}Pb and ^{210}Po , so materials of recommended and information values have been used, too. (Table 6)

Regarding the good reproducibilities, the agreement of the measured ^{210}Pb and ^{210}Po concentrations with each other and the certified value, the method can be used for the accurate and sensitive determination of both nuclides.

Production and decay scheme of radiostrontium nuclides



Separation scheme of lead and polonium using Sr.Spec

Dry sample weight: 0.1 - 50 g

Addition of 30 mg Pb carrier

Addition of ^{208}Po tracer

SAMPLE DISSOLUTION

evaporation with mineral acids:

65% HNO_3 , 32% HCl

optionally: 40% HF , 32% $\text{HCl} + \text{H}_3\text{BO}_3$

dissolution in 30-50 ml 2M HCl

filtration

CHROMATOGRAPHIC SEPARATION ON SR.SPEC COLUMN

column preparation: 3g Sr.Spec

column conditioning with 100 ml 2M HCl

loading

elution with 100 ml 2M HCl , 25 ml 6M HNO_3

STRIPPING OF PO

60 ml 6M HNO_3

PO SOURCE PREPARATION FOR ALPHA SPECTROMETRY

evaporation

dissolution in 0.1M HCl

spontaneous deposition onto Ag disc

ALPHA SPECTROMETRY

yield determination based on ^{208}Po

^{210}Po

STRIPPING OF PB

60 ml 6M HCl

PB SOURCE PREPARATION FOR LSC

evaporation

evaporation with 3*2 ml 65% HNO_3

Pb-oxalate precipitation

gravimetric yield determination

sample dissolution with 1ml 6M HNO_3

mixing with 15 ml Insta gel*

LSC

^{210}Pb

Separation scheme of strontium from soil samples

5 to 10g soil ash addition of 10 mg Sr carrier

SAMPLE
DISSOLUTION

destruction of soil with
mineral acids:
conc. HNO_3 , 40% HF , H_3BO_3

evaporation, dissolution
in 200ml of 0.5M HNO_3 ,
addition of 5 to 10g oxalic
acid, pH adjustment with NH_3

POTASSIUM
REMOVAL

calcium-magnesium-strontium
oxalate precipitation
at pH 5-6

centrifuging,
washing with 2x70ml of water,
oxalate destruction with
conc. HNO_3 , solubilization
in 2 fcv 3M HNO_3

REMOVAL OF
OTHER
ELEMENTS

strontium separation with
Sr.Spec chromatographic
column

scrubbing elution
of non retained
elements with 22
fcv of 3M HNO_3

stripping elution of
Sr with 6 fcv of dis-
tilled water, boiling,
addition of 200 mg oxalic acid

CHEMICAL YIELD
DETERMINATION

strontium oxalate precipi-
tation
at pH 9 - 10

Sr determination
by gravimetry, dis-
solution with 2 ml of
1M HNO_3 , addition of
15 ml of Instagel

RADIOSTRONTIUM
DETERMINATION

LSC

^{89}Sr ^{90}Sr

PUBLICATIONS ON THE APPLICATION OF SR.SPEC
AT THE INSTITUTE OF NUCLEAR TECHNIQUES, TU BUDAPEST

Separation of strontium

1. N. Vajda, A. Ghods-Esphahani, E. Cooper, P.R. Danesi:
Determination of Radiostrontium in Soil Samples Using a Crown Ether
J. Radioanal. Nucl. Chem. 162(2)pp. 307-323 (1992)
2. N. Vajda, A. Ghods-Esphahani, E. Cooper, P.R. Danesi, D. Bódizs, Zs. Molnár:
Determination of Radiostrontium Using a Crown Ether
Proc. of 3rd Int. Conference on " Nuclear and Radiochemistry"
Sept. 7-11 (1992), Vienna
3. N. Vajda, P.R. Danesi, J. LaRosa, V. Valkovic, R. Zeisler, E. Gjerci, A. Nouredine
Comparative Evaluation of Rapid Analytical Methods for the Determination of ^{90}Sr
International Symposium on Environmental Impact of Radioactive Releases
8-12 May 1995, Vienna
4. J. LaRosa, P.R. Danesi, A. Fajgelj, M. Makarewicz, N. Vajda, P. Stegnar
Analytical Approach to the Measurement of Radionuclides in Environmental Contamination of a Former Nuclear Weapons Testing Area
International Symposium on Environmental Impact of Radioactive Releases
8-12 May 1995, Vienna
5. Vajda N.
Atomreaktorok fűtőelemeinek ellenőrzése új analitikai módszerek segítségével
(Fuel Failure Detection in Nuclear Reactors Using Novel Analytical Techniques)
Thesis of PhD. 1994.
6. Transzuran és stroncium izotópok elemzése primerkörü hűhordozóban hibás fűtőelemek kimutatása érdekében
(Analysis of Transuranium and Strontium Nuclides in Primary Coolant for the Purpose of Fuel Failure Detection)
Progress Report 1992. (Research Contract with Paks NPP and the Hungarian National Committee for Technical Development)
Progress Report 1993. (Research Contract with Paks NPP)
Progress Report 1994. (Research Contract with Paks NPP)
7. ^{90}Sr meghatározása atomerőművi folyékony hulladékokban
(Determination of ^{90}Sr in the Liquid Waste of Nuclear Power Plant Paks)
Progress Report 1993. (Research Contract with Paks NPP)
8. Inventory of Relevant Radioisotopes-Non-Destructive Determination by Correlation with Key Nuclides
Intermediate Progress Report of the Hungarian Participant 1994. (CEC PECO project)

Separation of lead and polonium

1. Vajda N., Kis-Benedek Gy., Bódizs D., Vodicska M.
 ^{210}Pb radiokémiai meghatározása koronaéter segítségével
(Radiochemical Determination of ^{210}Pb Using a Crown Ether)
Izotóptechnika, Diagnosztika 37. évf. 1. szám 25-30.1994.
2. N. Vajda, J. LaRosa, R. Zeisler, P. Danesi, Gy. Kis-Benedek
A Novel Technique for the Simultaneous Determination of ^{210}Pb and ^{210}Po
Using a Crown Ether
J. Environmental Radioactivity (in press)
3. Pathways of Radionuclides Emitted by Non-Nuclear Industries
Intermediate Progress Report of the Hungarian Participant 1994. (CEC Pathways Project)

Figure 3

Fig. : Distribution ratios of Pb, Bi and Po in HCl solutions

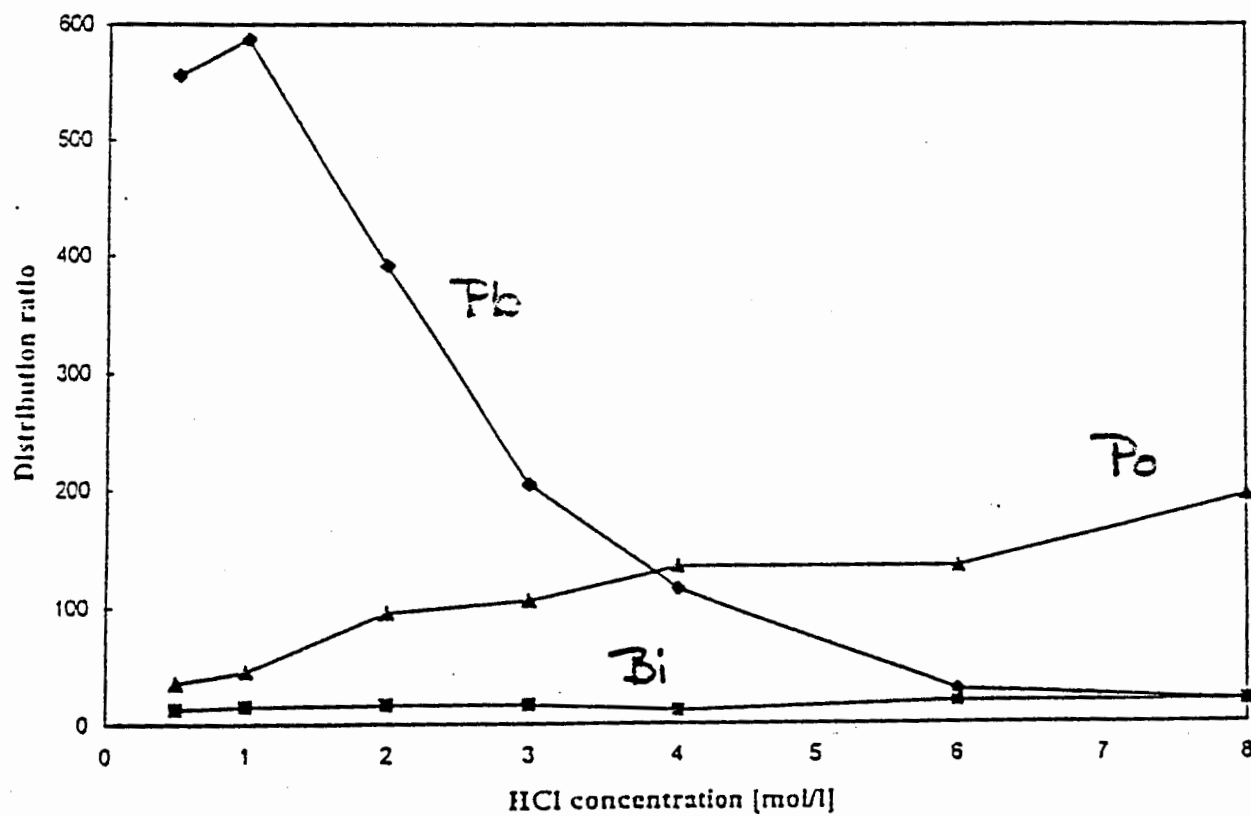


Table 2

TABLE: ^{90}Sr determination in different standard reference materials

Sample	Sr extraction by crown ether				Y extraction by TBP				Reference value	
	Sample weight ash	Average recovery (%)	^{90}Sr Activity concentration* [Bq/kg dry]	Uncertainty [Bq/kg dry]	Sample weight ash	Average recovery (%)	^{90}Sr Activity concentration* [Bq/kg dry]	Uncertainty [Bq/kg dry]	Activity reference value [Bq/kg dry]	^{90}Sr concentration confidence interval [Bq/kg dry]
Soil-6 soil	10	75	28.53	2.0	10	43	26.44*	7.6	30.34	24.20-31.67
IAEA-321 milk	10	79	3.13	0.21	5	75	3.09	1.2	3.3	3.16-3.44
IAEA-373 grass	1-2	70	1387**	64	1-2	45	1282	64	1320	1276-1363
A-12 animal bone	10	52	47.4**	4.3	10	50	39.7	4.0	54.8	46.3-59.2

* result is corrected for Th content of the sample

** result is corrected for Sr content of the sample

Table 3

Activity concentrations of the primary coolant of Paks NPP [Bq/l]

Sampling	^{131}I	^{134}I	^{89}Sr	^{90}Sr	^{91}Sr	^{92}Sr	Remarks
Reactor unit 1							
15.05.1992. 17:1	1550	1620	78	<LD	<LD	<LD	before shutdown
16.05.1992. 6:50	1120	1440	2940	34	1400	490	during shutdown
Reactor unit 2							
31.07.1992. 22:0	<LD	25700	350	12	<LD	<LD	before shutdown
01.08.1992. 7:20	<LD	8300	2750	38	1940	695	during shutdown
Reactor unit 3							
03.07.1992. 13:0	36000	1200000	3005	100	495	<LD	before shutdown
03.07.1992. 18:0	28700	270000	67300	1700	99200	53000	during shutdown
Reactor unit 4							
27.03.1992. 21:4	21000	86000	1040	25	93	<LD	before shutdown
28.03.1992. 4:45	450000	250000	9380	400	11300	4420	during shutdown

Table 4

Activity concentrations in evaporation concentrates of Paks NPP [Bq/l]

Radionuclide	Container code: 01TW30B003		
	surface layer	middle layer	bottom layer
⁹⁰ Sr	41	49	114
¹³⁷ Cs	1.10E+06	1.10E+06	6.50E+05
¹³⁴ Cs	6.40E+05	6.60E+05	3.50E+05
^{110m} Ag	6.30E+04	7.20E+04	8.20E+05
⁶⁰ Co	7.20E+04	6.60E+05	3.50E+05
⁵⁴ Mn	2.80E+04	3.10E+04	2.90E+04
¹²² Sb	7.60E+04	7.40E+04	3.90E+04

Table 5

Table : Elution behaviour of selected elements on Sr.Spec column
 % of the elements in the given fractions determined by ICP-AES
 load: 0.5 g NBS 4354 sediment + 15 mg Pb + 0.07 Bq ^{208}Po

element	effluent 10ml 2M HCl	eluate 25ml 2M HCl	eluate 25ml 2M HCl	eluate 25ml 2M HCl	Po strip 25ml 6M HNO ₃	Po strip 25ml 6M HNO ₃	Po strip 25ml 6M HNO ₃	Pb strip 25ml 6M HCl	Pb strip 25ml 6M HCl	Pb strip 25ml 6M HCl
Pb	0	0	0	0	0	0	0	98	2	0
Zn	61	36	0	0	1	1	0	0	0	0
P	70	30	0	0	0	0	0	0	0	0
Co	75	25	0	0	0	0	0	0	0	0
Fe	72	28	0	0	0	0	0	0	0	0
Cr	76	24	0	0	0	0	0	0	0	0
Mg	74	26	0	0	0	0	0	0	0	0
Ca	73	26	0	0	0	0	0	0	0	0
Cu	71	24	0	1	0	0	1	0	0	0
Tl	76	24	0	0	0	0	0	2	0	0
Zr	74	26	0	0	0	0	0	0	0	0
Y	75	25	0	0	0	0	0	0	0	0
Eu	73	24	0	0	0	0	0	0	3	0
Ce	75	25	0	0	0	0	0	0	0	0
Al	76	24	0	0	0	0	0	0	0	0
Sr	0	99	1	0	0	0	0	0	0	0
Ba	0	73	26	0	0	0	0	0	0	0

