FSUE «RADON»
Moscow

Development and approbation of a method for preconcentration and separation of Sr and Pu(IV) with using an extraction chromatography on Sr Resin

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Sorption material:

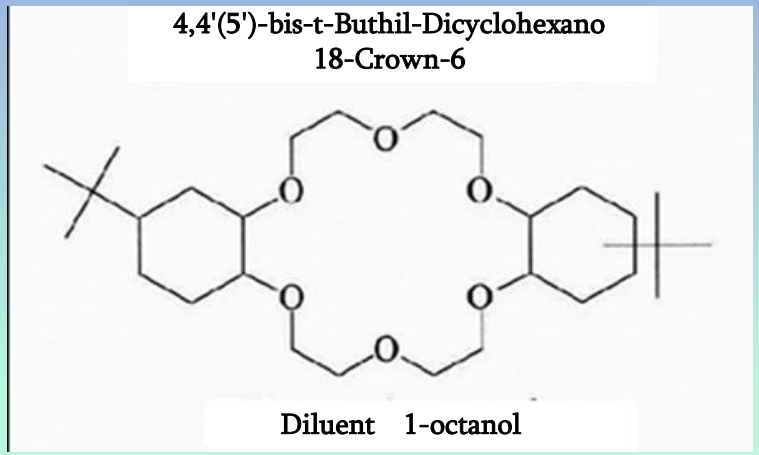
❖ Impregnated sorbent Sr Resin (Eichrom Ind. Inc., Darien, USA)

Support - the granulated macroporous inert synthetic polymer Amberchrom-CG 71: (polymethacrylate)

Specific surface ≈ 500 m^2/g

Particle sizes 50-100 μm,

Stationary phase – 1M solution of 4,4'(5')-bis-t-Buthil-Dicyclohexano 18-Crown-6 in Isodecanol



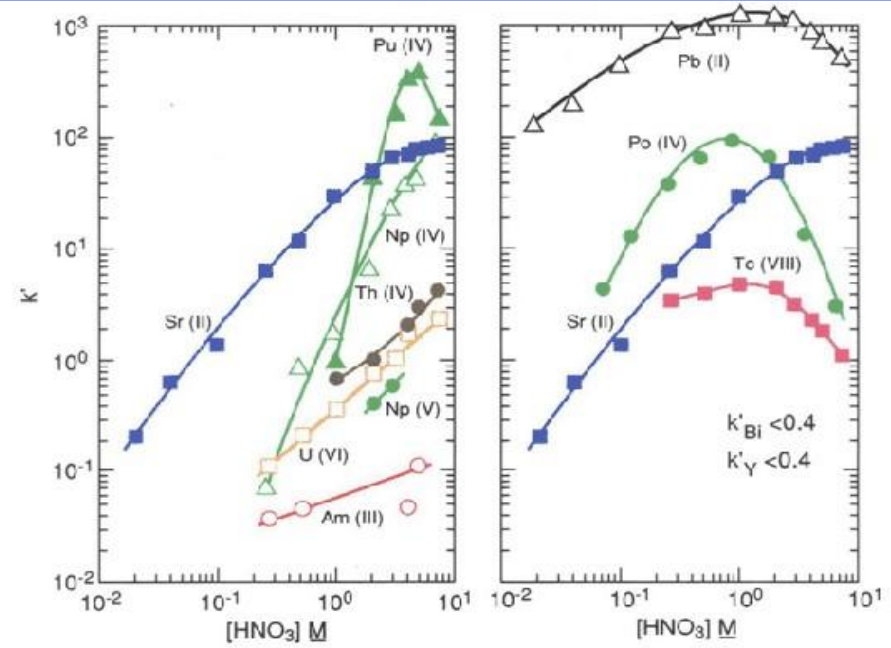
Research problems:

❖ Investigation of sorption of naturally occurring actinides and their daughter products, Pu(IV) and Sr^{2+} on an impregnated sorbent Sr Resin

❖Choice of conditions for sorption preconcentration of plutonium and strontium from nitric acid solutions and their subsequent chromatographic separation

❖Method approbation with samples of environmental objects – soils and bottom sediments. Verification by means of IAEA RM

Sorption of actinides and fission products on impregnated sorbent Sr Resin



Acid dependency of K_d for various ions

Sorbent – Sr Resin

t = 23°C

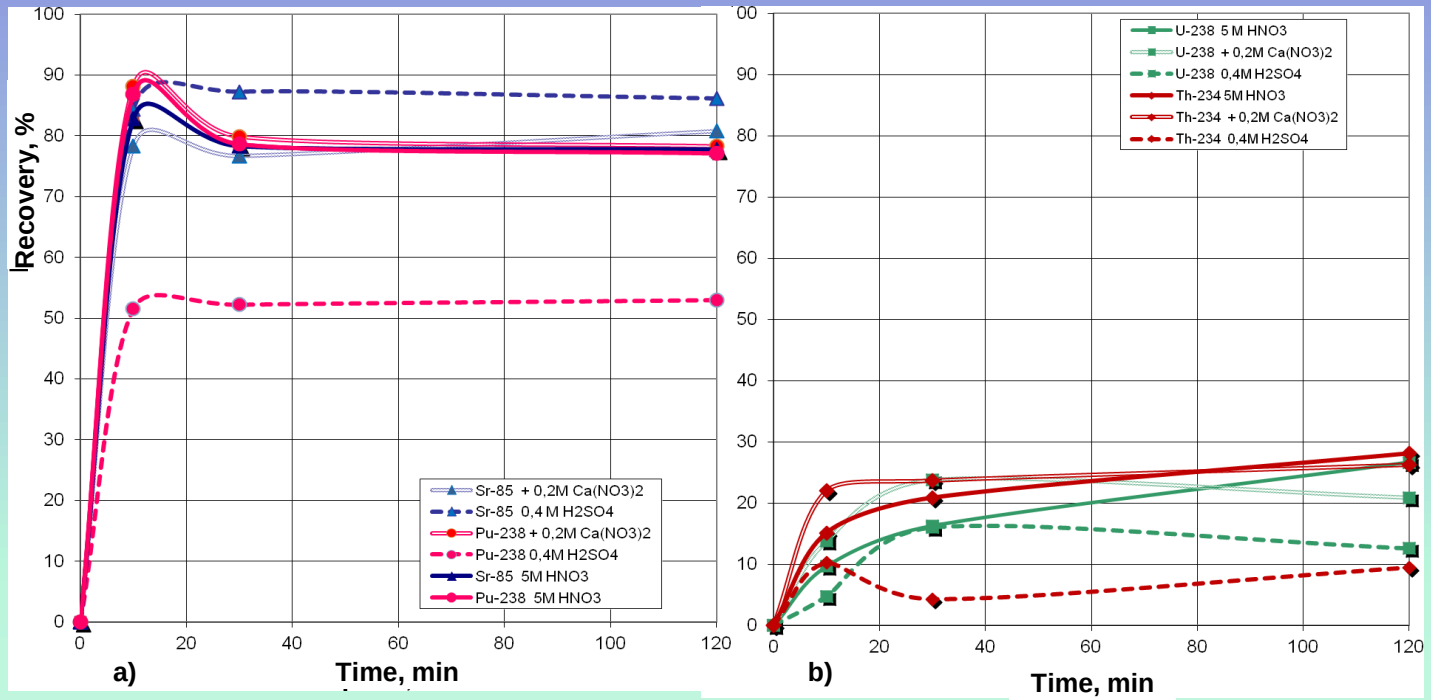
Stationary phase – DCH-18-C-6

In 4-6 M HNO_3 a K_d for Pu(IV) varies at level about 300-400, that is explained by formation of outer-sphere complexes of structure like $Pu(NO3)_6^{2-} \cdot 2H_3O^+$ + 2 DCH-18-C-6.

At the same time K_d value for uranium and thorium is much lower, about 2-5.

Such Sr resin properties do possible the combined retention of Pu and Sr from sample matrix nitric acid solution with subsequent purification and separation by column chromatography.

Investigation of sorption of actinides and Sr on Sr Resin by using model solutions



At an initial stage of experiments the kinetics of sorption of Sr and Pu(IV), and also matrix elements – U and Th on Sr Resin from model solutions on the basis of 5M HNO_3 was investigated

Sorption for various ions on Sr Resin from model solutions on the basis of 5M HNO_3;
V: $m = 50$, $t = 23°C$, a) ○ - Pu(IV) , Δ - Sr, b) □ – U (VI), ◊ - Th(IV)

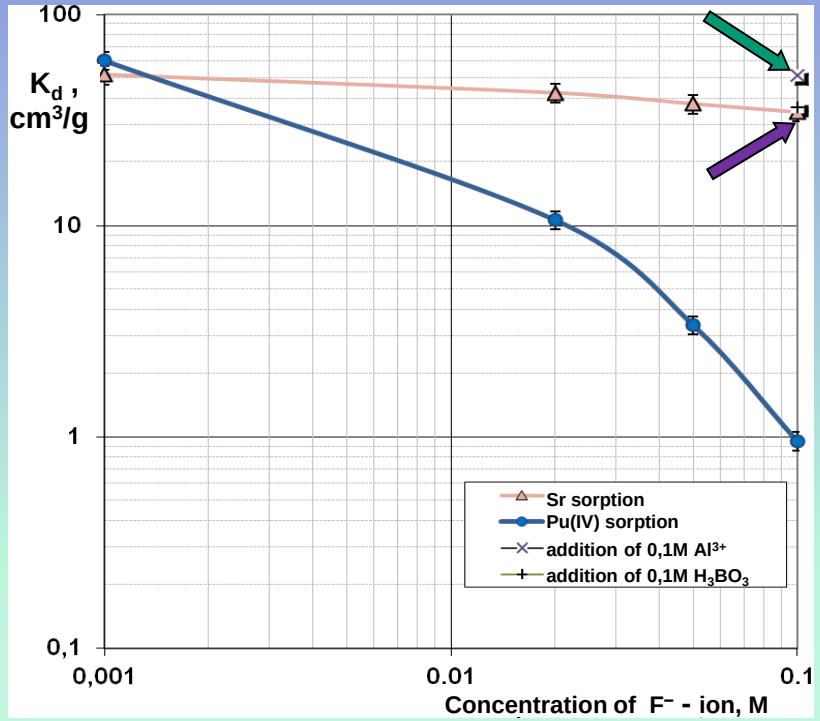
Composition of liquid phase	K_d, cm^3/g			
	Sr^{2+}	Pu(IV)	U(VI)	Th(IV)
5M HNO_3	80	77	8,4	10
5M HNO_3 + 0,2M Ca^{2+}	96	83	6,1	8,2
5M HNO_3 + 0,4M SO_4^{2-}	142	26	3,3	2,4

Investigation of sorption of actinides and Sr on Sr Resin by using model solutions

Effect of F^-- ion concentration on Pu(IV) (□) и Sr (◊) retention by Sr Resin
(for procedures of extraction of plutonium from solid matrixes hydrofluoric acid is often used)

Liquid phase:
7 M HNO_3 + 1M Ca^{2+} solution

Effect of Al^{3+} (x) and H_3BO_3 (+)
(both 0,1M concentration)
on recomplexation of F^-- ions



As a complexing eluent for plutonium a solution of oxalic acid was chosen

Determination of conditions for selective elution of plutonium

HNO_3 concentration	5 M	3 M	3 M	3 M
$H_2C_2O_4$ addition	0,1 M	0,1 M	0,15 M	0,2 M
Sr sorption, K_d	120 ± 5	129 ± 6	125 ± 5	126 ± 5
Pu(IV) sorpion , K_d	50 ± 3	3,0 ± 0,4	2,2 ± 0,3	2,5 ± 0,3

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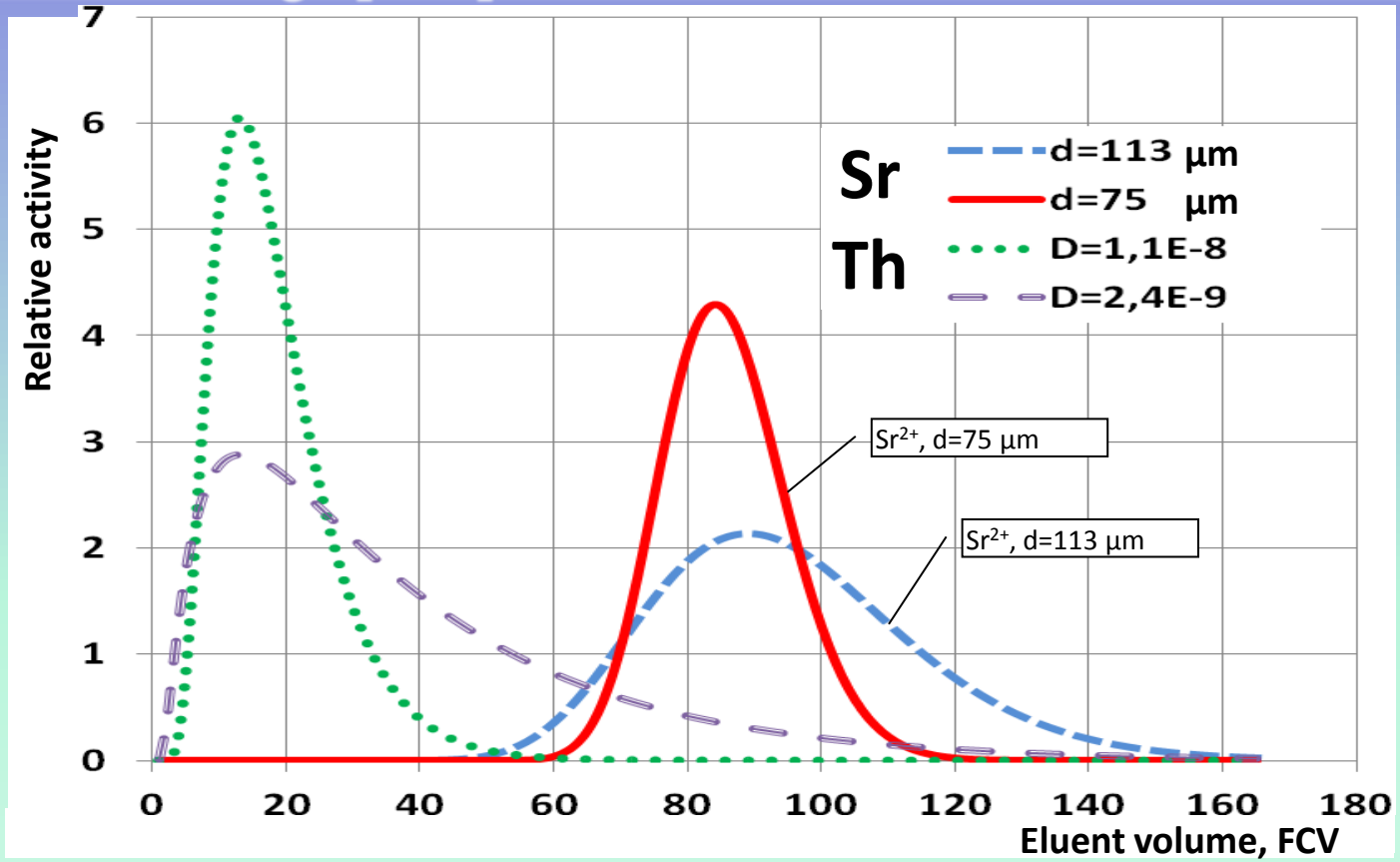
Column preconcentration of Pu(IV) and Strontium, and their chromatographic purification from macro- and microimpurities

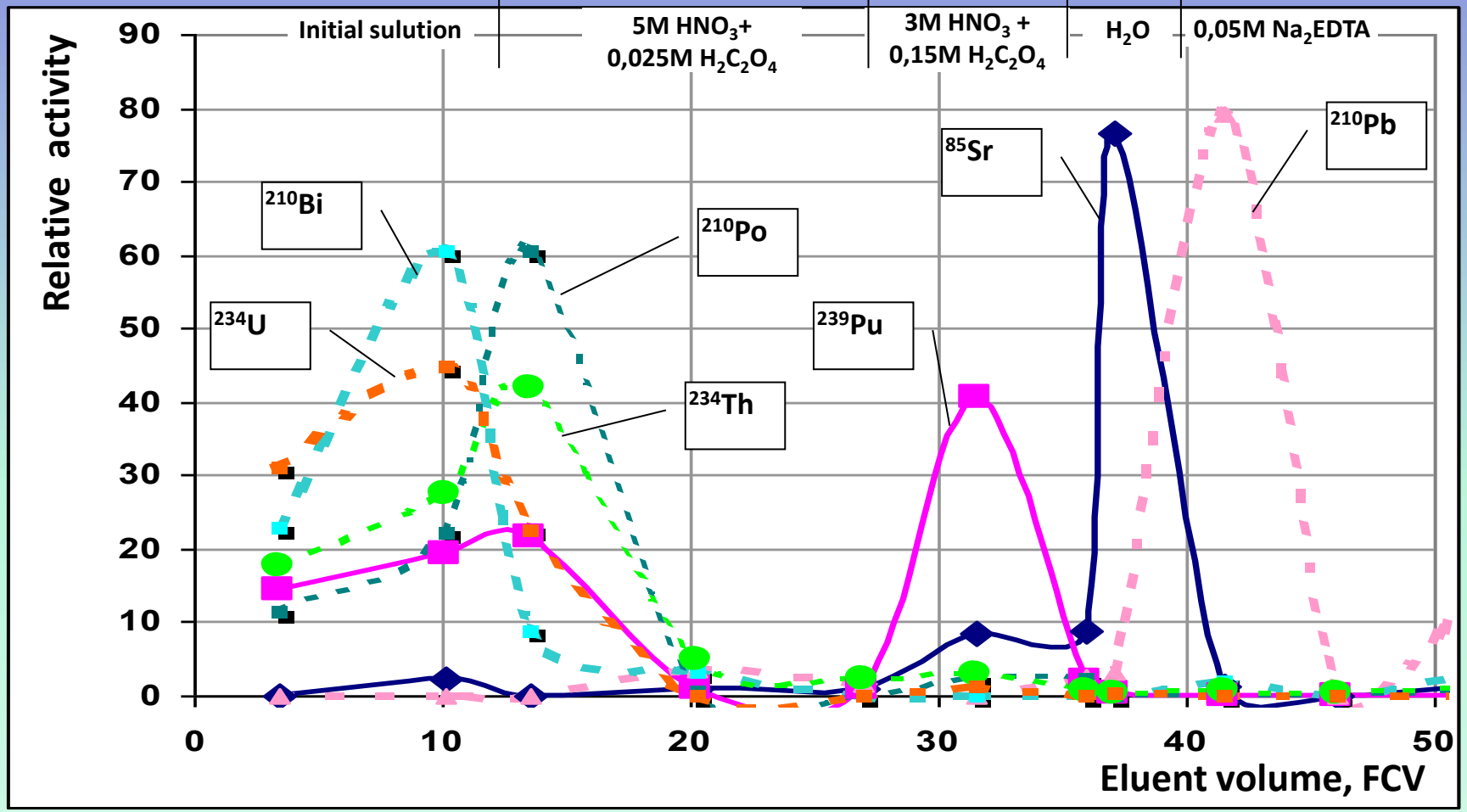


Calculated breakthrough curves (Glueckauf model)

Calculated breakthrough curves of Sr on a column with Sr Resin, column dimensions - 70x7 mm,
distribution coefficient – 72 cm^3/g,
linear speed of a stream – 0,026 cm/sec.
(flow rate – 0,7 cm^3/cm^2 min),
Diameter of resin grains: 75 µm and 113 µm

Accounting estimation of an elution curve of thorium for K_d = 10 cm^3/g at different diffusion coefficients for a complex with DCH-18-C-6 in a stationary organic phase

Column preconcentration of Pu(IV) and Strontium, and their chromatographic purification from macro- and microimpurities



Elution of various radionuclides at complex extraction-chromatographic procedure for Sr and Pu separation. Material Sr-Resin.
Initial solution – tracers in 0,5M Ca^{2+} + 5M HNO_3

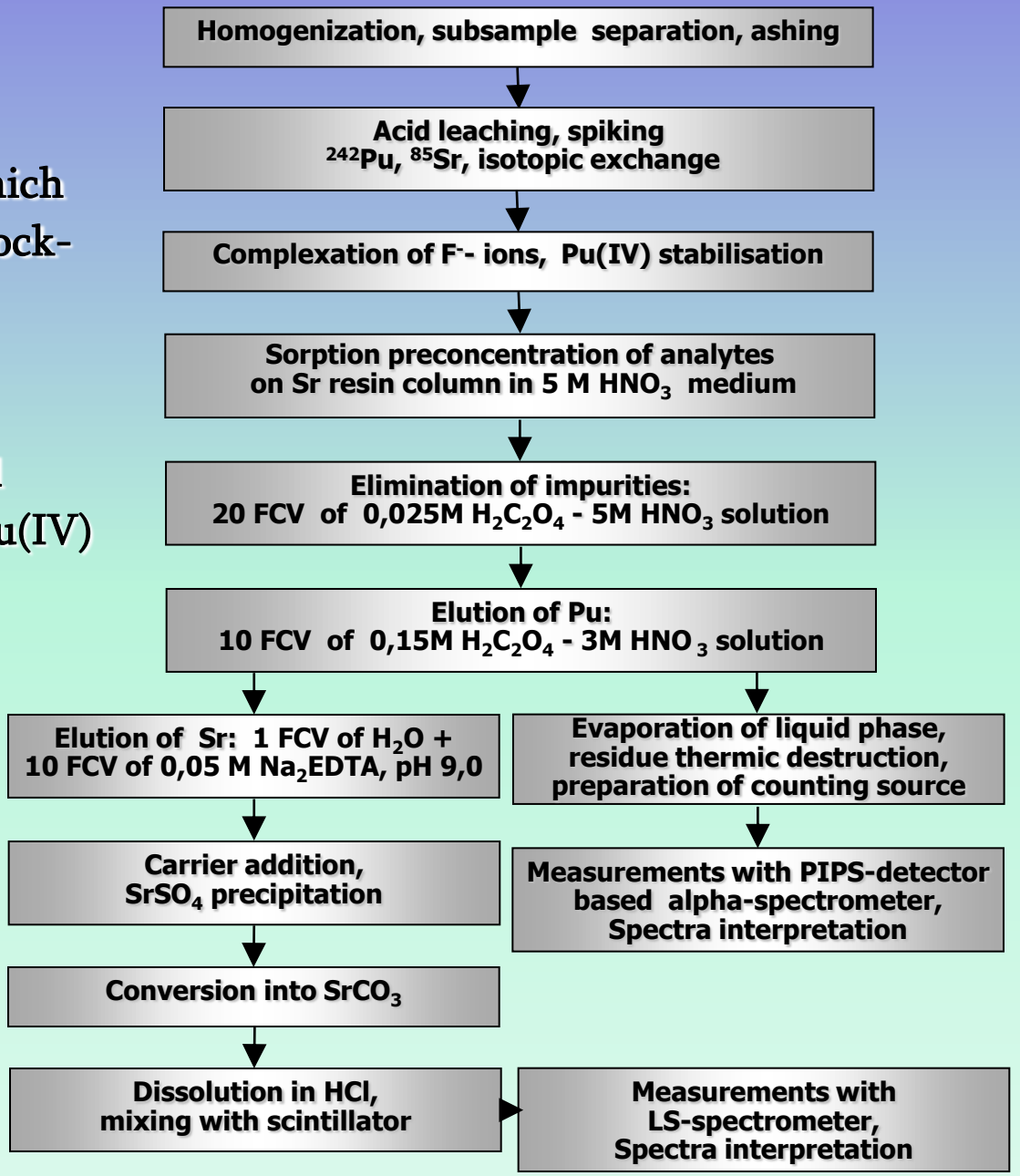
Separation of Sr and Pb in eluate fraction - precipitation of $SrSO_4$ at pH 5,1

Practical application :

On the basis of the analysis of experimental data the technique which includes stages presented on the block-diagram is offered.

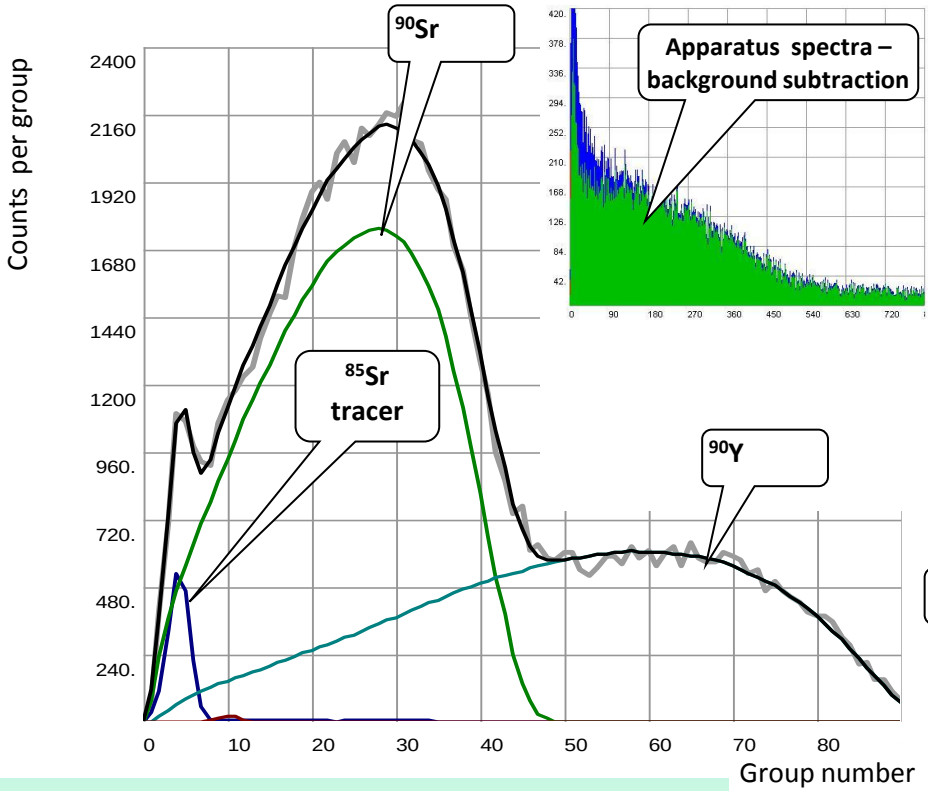
Key analytical procedure is chromatographic concentration and subsequent separation of Sr and Pu(IV) on a column with Sr Resin

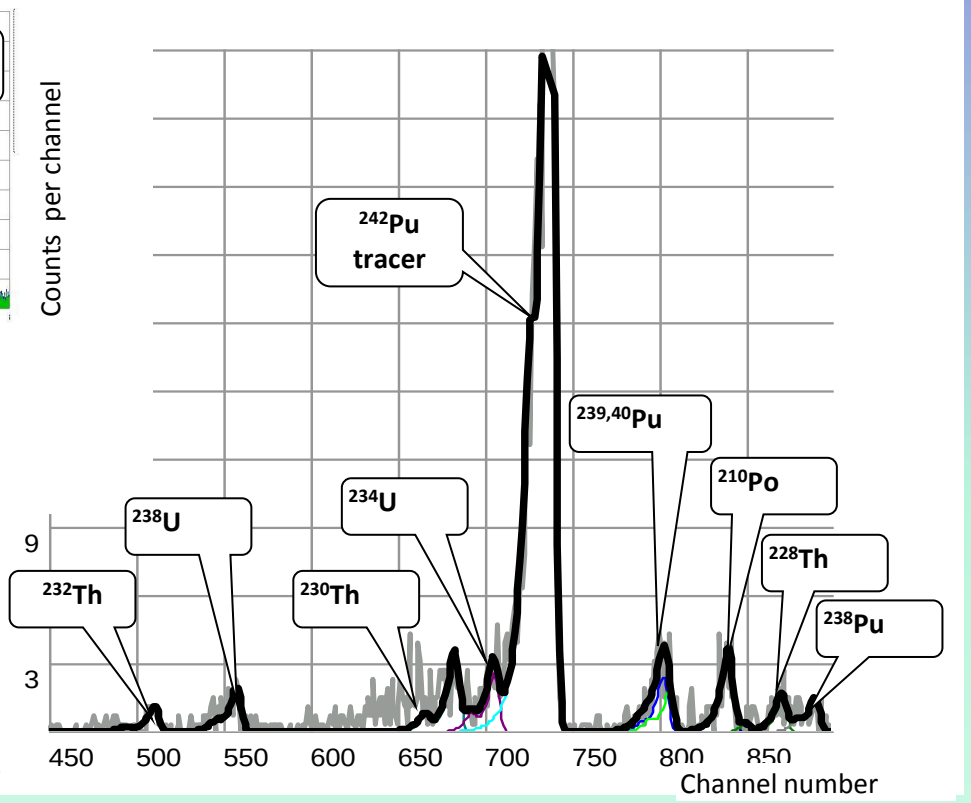
The technique proposed was verified by complex analysis of IAEA Reference Materials with certified contents of various natural and artificial radionuclides



Practical application

The comparative analysis of the certified samples (IAEA RM)





LS-spectrum of strontium fraction and alpha-spectrum of plutonium fraction , separated from RM IAEA-375 matrix by using the submitted method

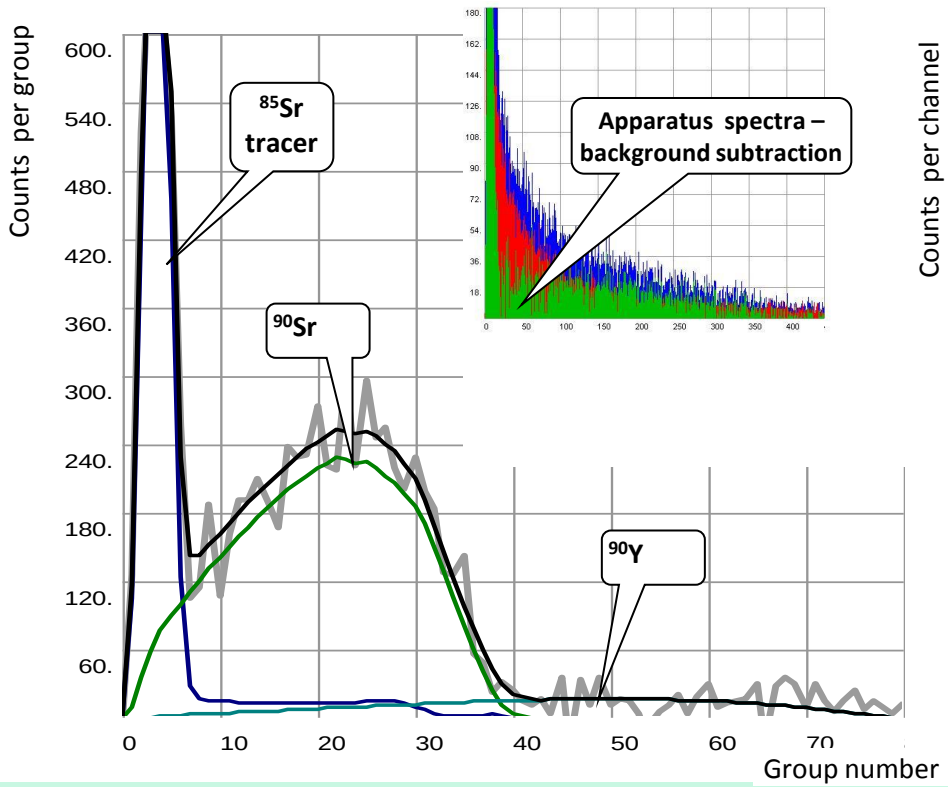
Results: determined activity /certified value (confidence limits) Bq/kg:

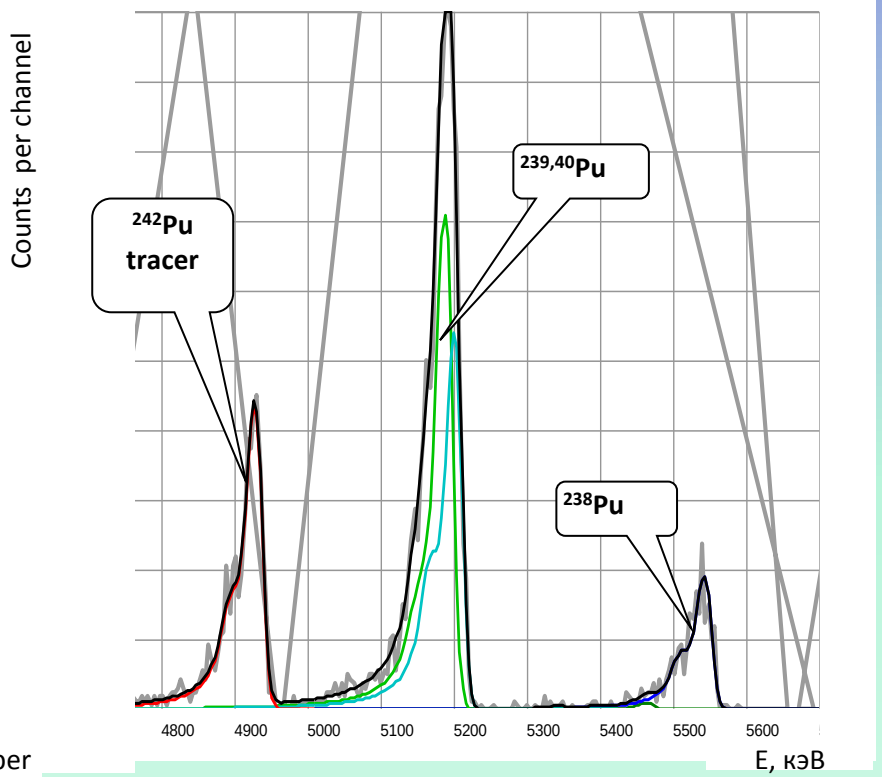
^{239,40}Pu – **0,42 ± 0,11** / 0,3 (0,26 – 0,34)

^{90}Sr – **63,1 ± 30,1** / 108 (101 – 114)

Practical application :

The comparative analysis of the certified samples (IAEA RM)





LS-spectrum of strontium fraction and alpha-spectrum of plutonium fraction , separated from RM IAEA-135 matrix by using the submitted method

Results: determined activity /certified value (confidence limits) Bq/kg:

^{239,40}Pu – **51,1 ± 7,8** / 64,5 (58 - 74)

^{90}Sr – **236 ± 21** / 213 (205 - 225,8)

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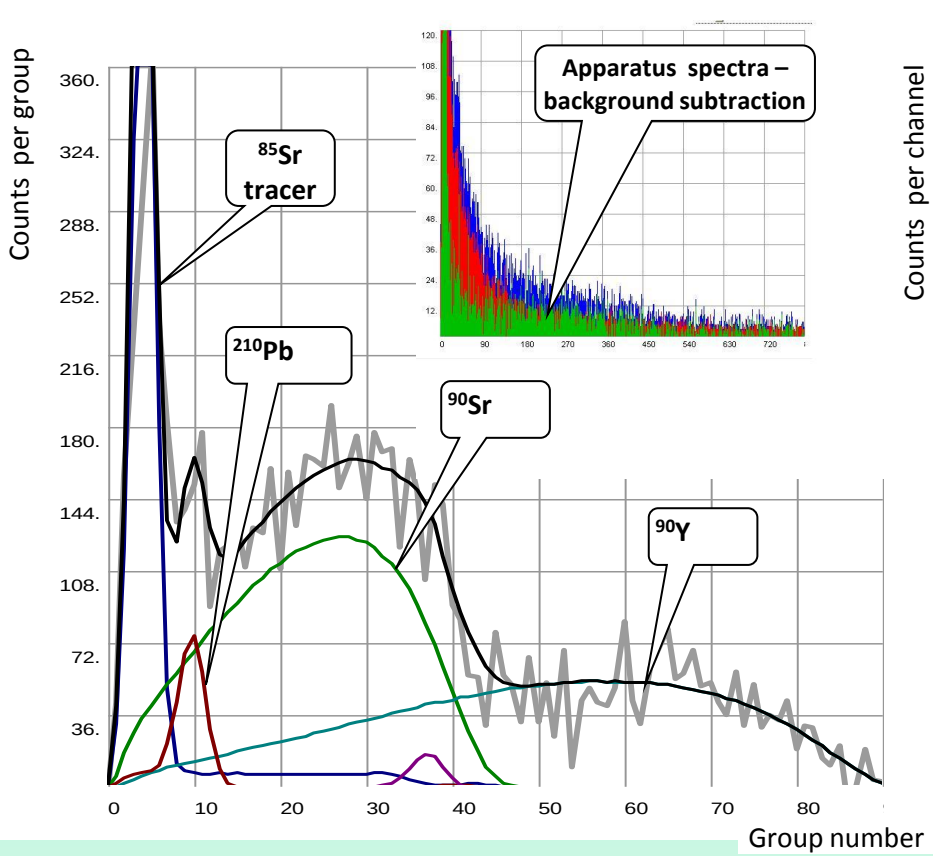
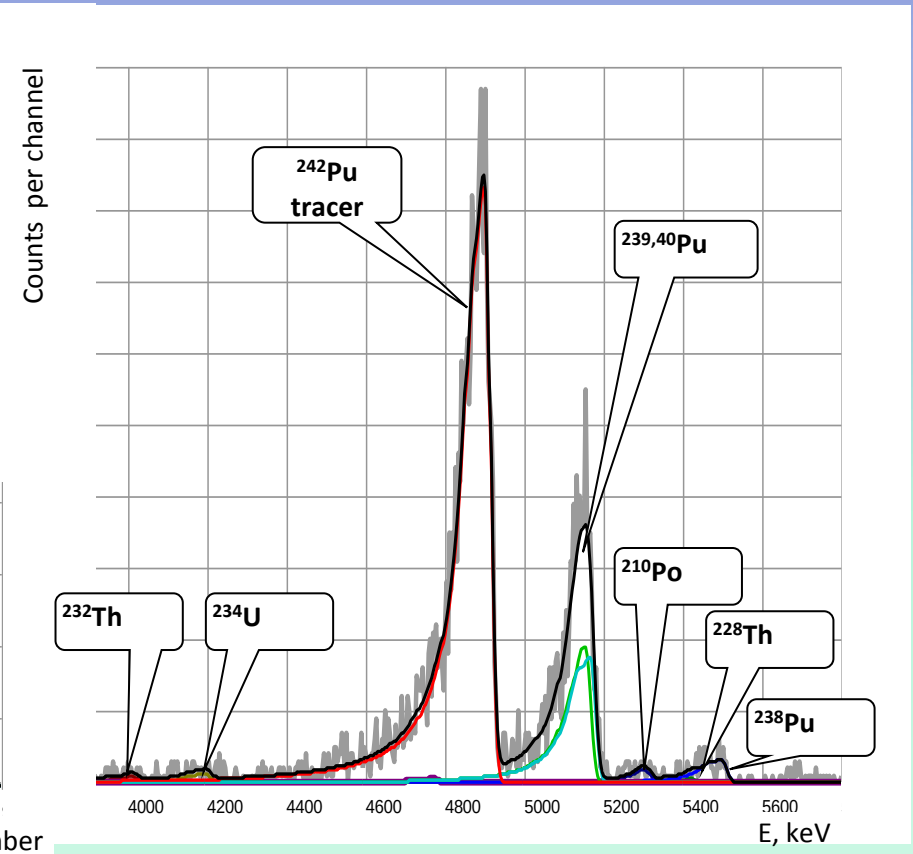
Practical application

The comparative analysis of the certified samples (IAEA RM)





LS-spectrum of strontium fraction and alpha-spectrum of plutonium fraction , separated from RM IAEA-300 matrix by using the submitted method

Results: determined activity /certified value (confidence limits) Bq/kg:

^{239,40}Pu – **3,02 ± 0,33** / 3,55 (3,44-3,65)

^{90}Sr – **9,8 ± 1,3** / 10,8

Conclusion

1. Sorption properties of Sr^{2+}, Pu (IV), uranium and thorium in nitric acid medium on Sr Resin in presence of complexing anions - fluorides, oxalates, sulfates, and also Ca^{2+} have been studied. The submitted results show that Ca^{2+} in concentration up to 0,2 mol/l has no significant impact on sorption of trace quantities of the studied elements. Addition of SO_4^{2-} leads to decreasing extraction of all actinides and to increasing extraction of Sr^{2+}.
2. Calculations for displacement of Sr and Th by 3M HNO_3 from Sr Resin column are carried out (Glueckauf model). The breakthrough curves obtained for Sr are in good agreement with published data. It is necessary to use resin with a size of grain not more than 100 μm in chromatography process.
3. By applying model 5M HNO_3 based solutions, elution curves for ^{85}Sr, ^{239}Pu and impurity radionuclides have been obtained experimentally. By passing 20 FCV of 0,025M $H_2C_2O_4$ - 5M HNO_3 solution, acceptable quality of purification of Sr and Pu fractions from matrix elements and interfering radionuclides is attained.
4. For selective elution of plutonium after its combined retention on column with Sr^{2+}, oxalates can be used. Concentration of 0,15M $H_2C_2O_4$ in 3M HNO_3 is optimum. In these conditions K_d value for Pu(IV) decreases up to 2,2.
5. The chromatographic method for sequential separation of plutonium and strontium from one sample aliquote by means of Sr Resin column has been developed. The submitted method was approved by comparative analysis of certified materials IAEA RM (soil, bottom sedimens).