Absorption of alkaline earth elements and rare earth elements in system Sr-resin – mineral acids.

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Main purposes of radiochemistry department at LNP JINR

- **Preparative radiochemistry (synthesis of radioactive sources for spectroscopy)**
- **The chemical support by preparation samples for low background measurements**
- **Radiochemical science research**

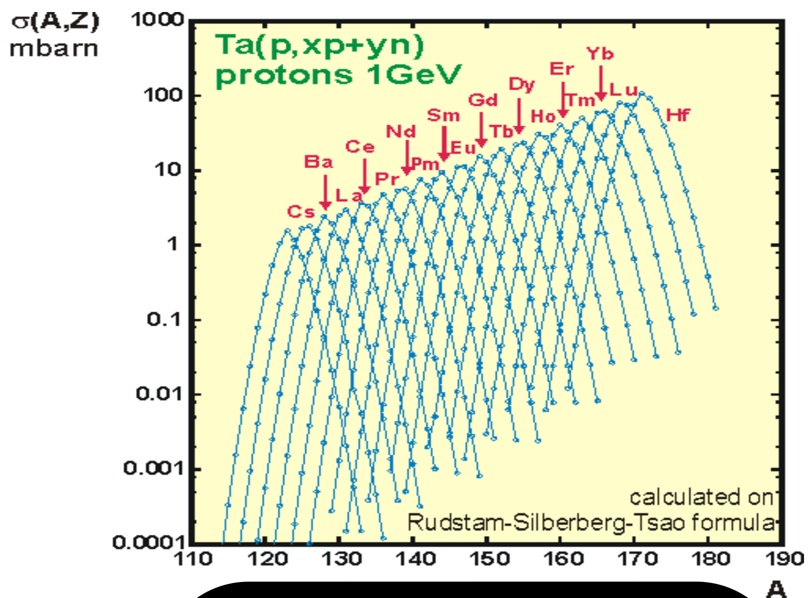
Available irradiation facilities

- Phasotron LNP (E_p=65-660 MeV, I=6 μA)

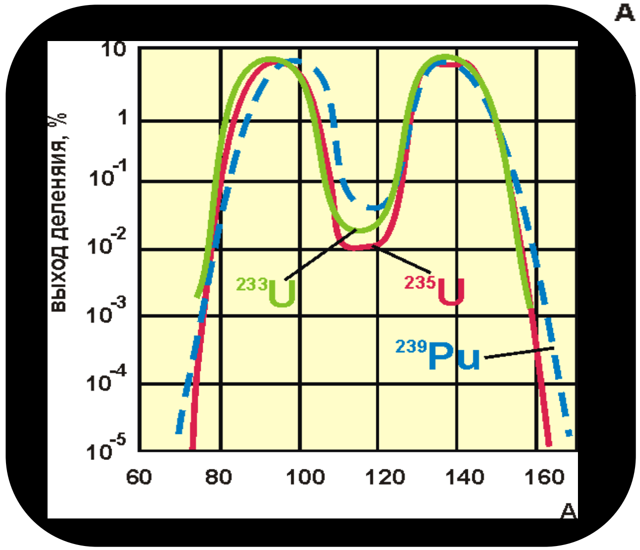
- U-200 of Laboratory of Nuclear Reaction (LNR) (E_α=36 MeV, I=70 μA)
- Microtron LNR (E_β=25 MeV, I=30 μA)
- Ractor IBR-2 ($2 \cdot 10^{12}$ n/s · cm^2)

Production of radionuclides

Spallation



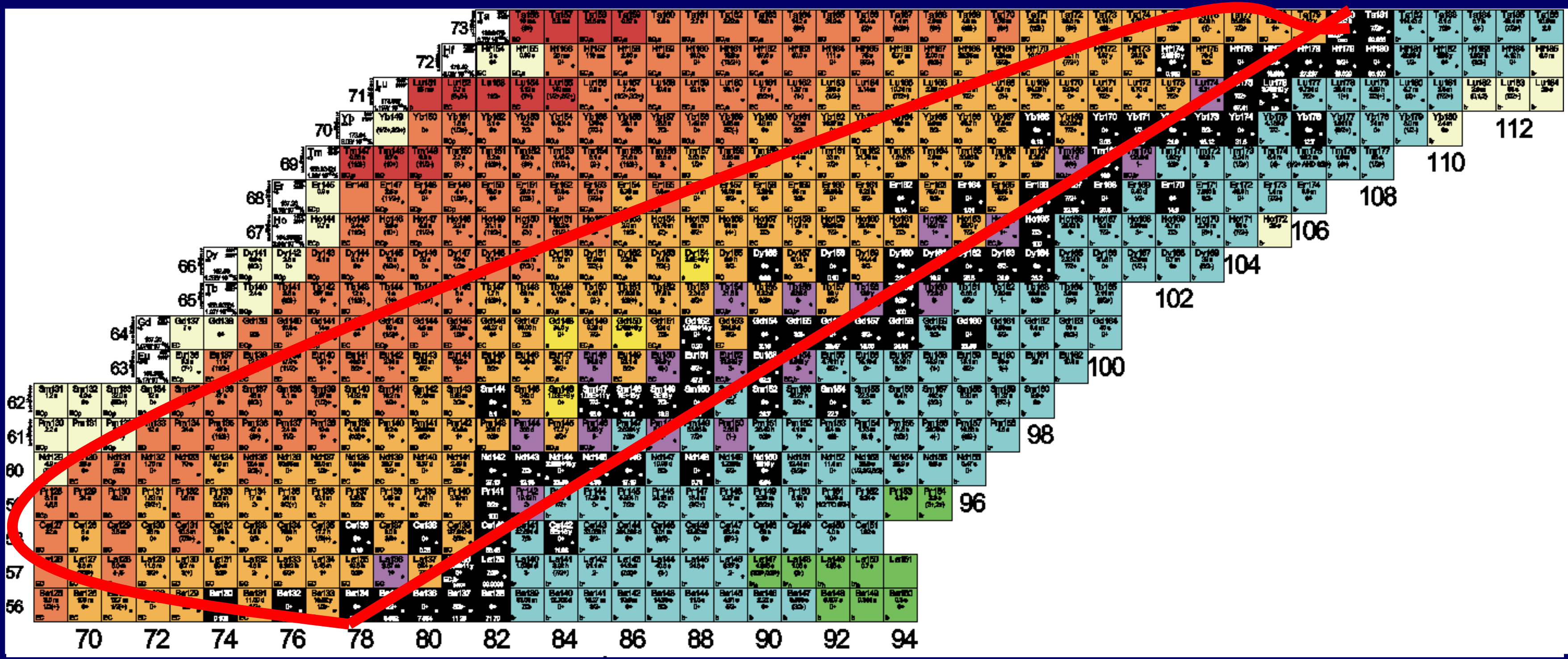
Fission



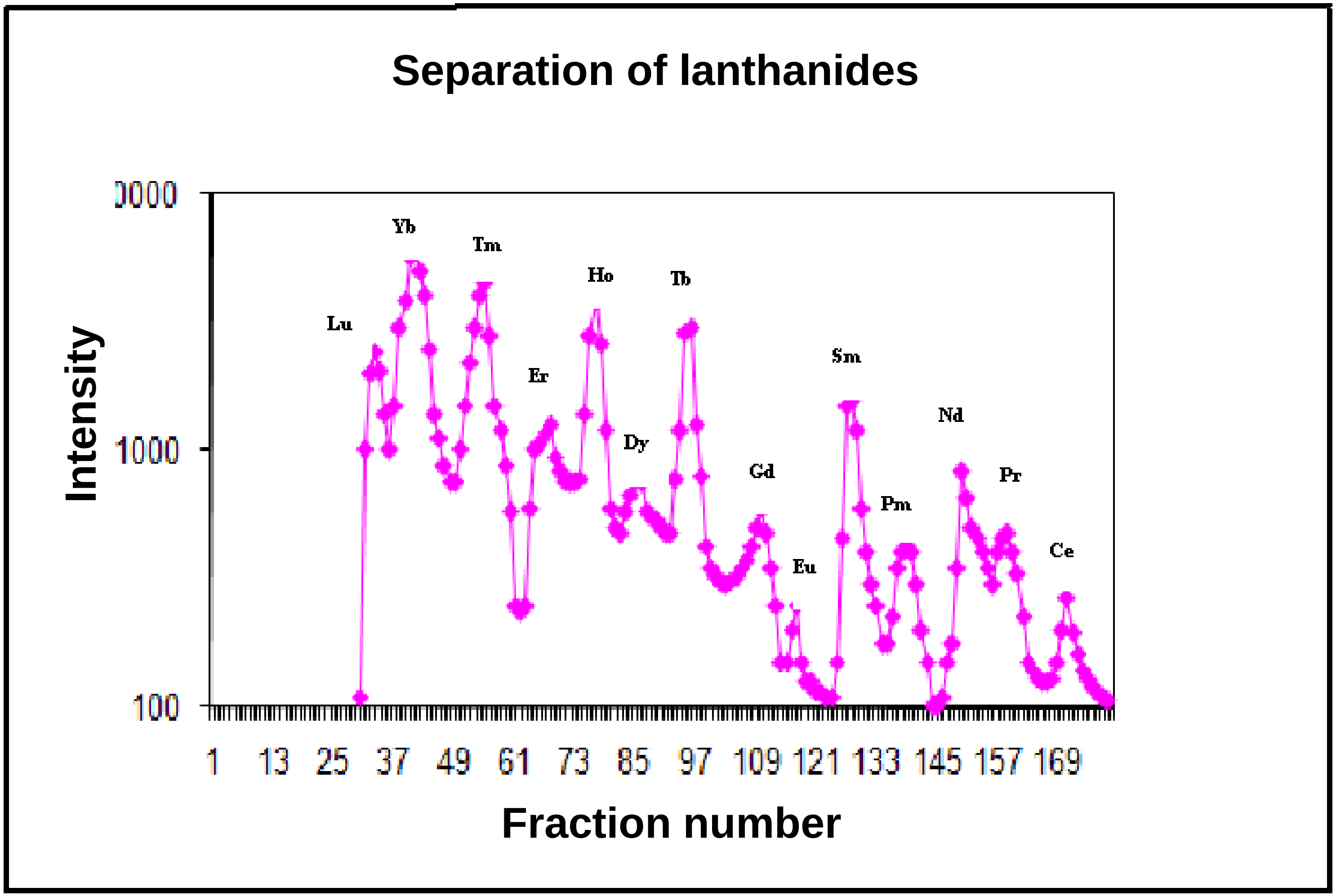
Spallation

Reaction of spallation

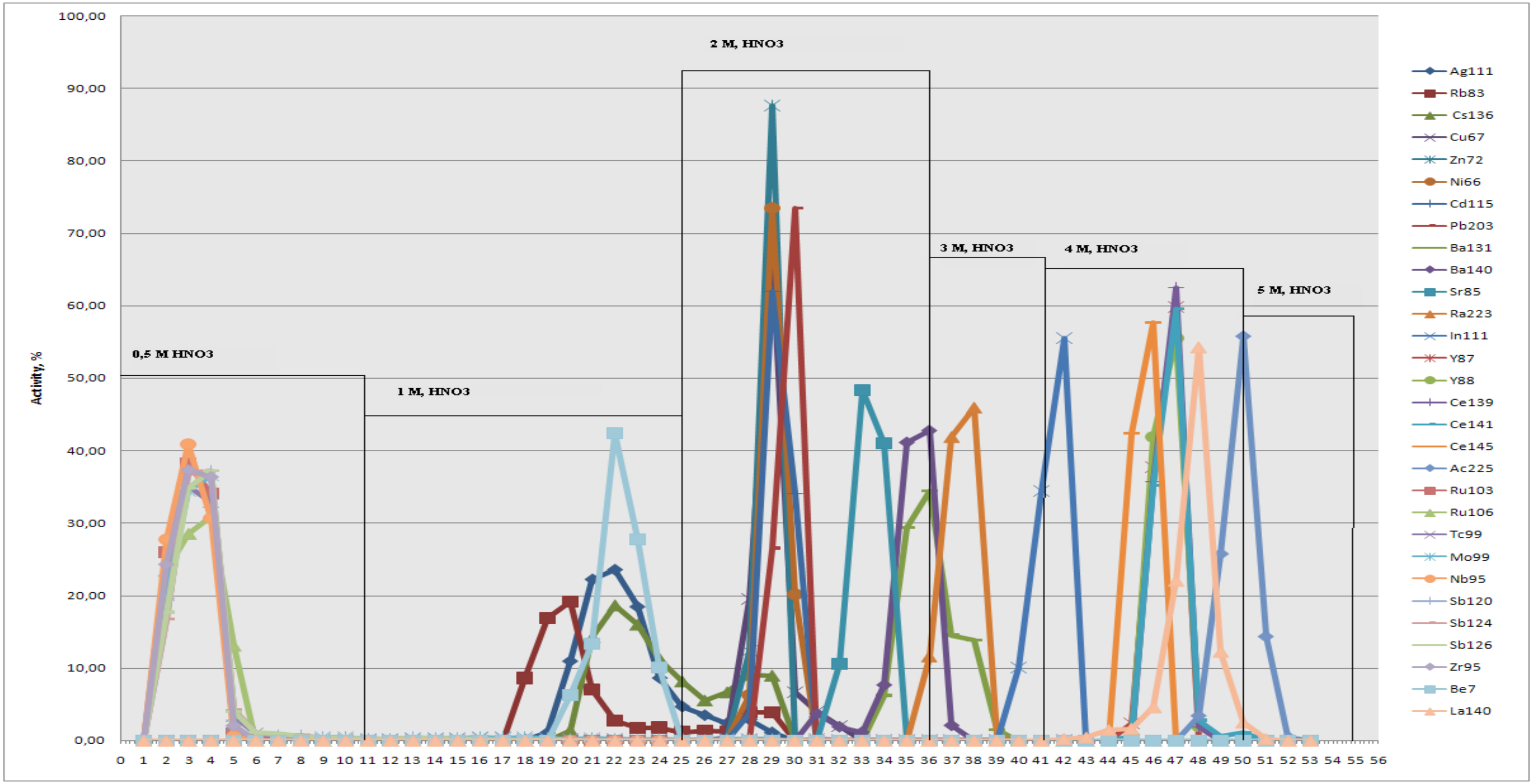
(p,xp yn), x<y, Ep>100MeV



Chromatogram of separation rare earth elements (REE) from tantalum target



Separation of products of nuclear reaction in thorium target on cation exchanger



Chemical support for sources preparartion for low background mesaurements

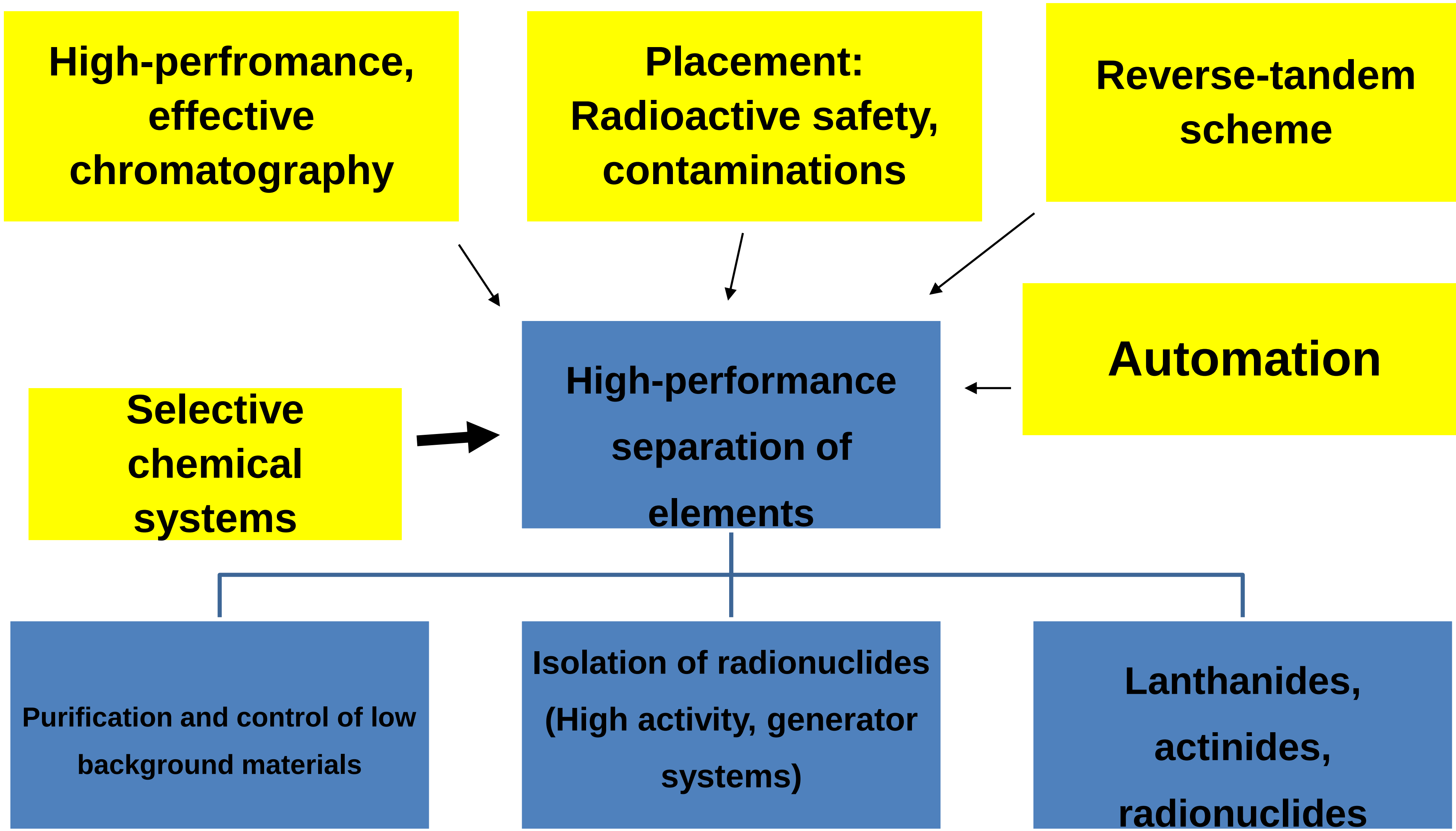
- Evaluation of double beta decay (problem of neutrino mass): approximate order of half-life such radionuclides is 10^{20}-10^{26} a.
- Search for dark matter particles and others rare events

Example – purification of Se (0.5 kg)

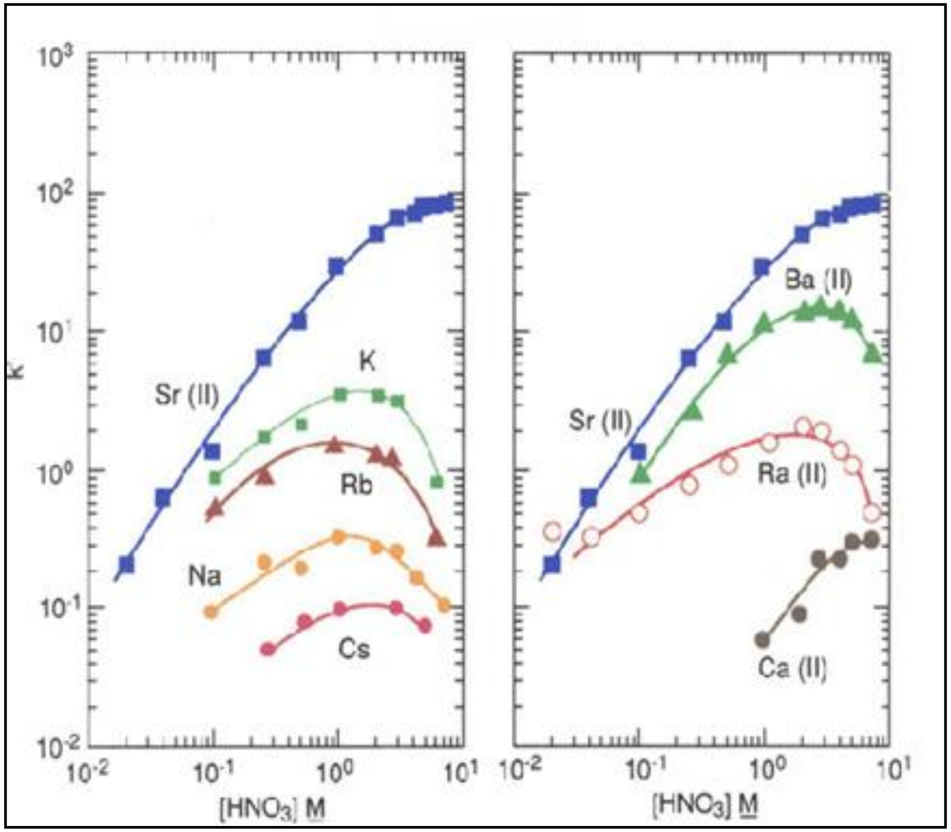
Contamination with radionuclides	^{40}K	^{232}Th	^{238}U	^{226}Ra	^{228}Ra
Content before purification Mbq/kg	59±11	6,2±1,3	<48	10±1	12±2
Content aftre purification MBq/kg	<38	<2,6	<22	<5,8	<3

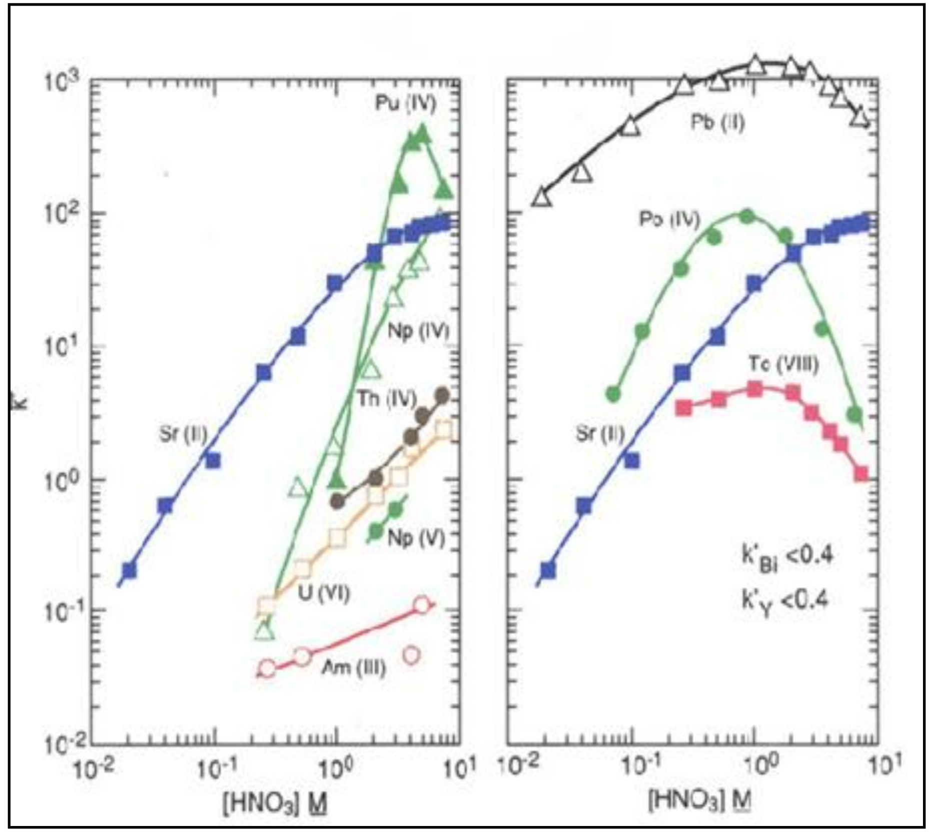
Product ^{83}Sr: Specific activity S= 5×10^{18} Bq/кg

High-pefromance separation of elements



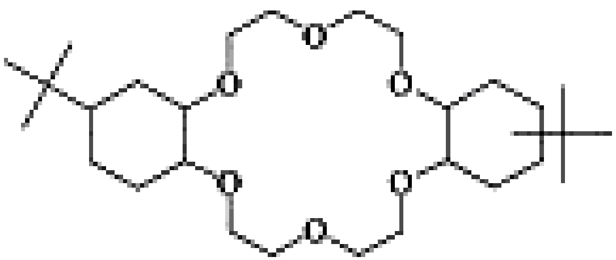
Dependence of distribution coefficients for several elements from concentrations of NHO_3 at T=23-25°C on Sr-resin (Triskem International)

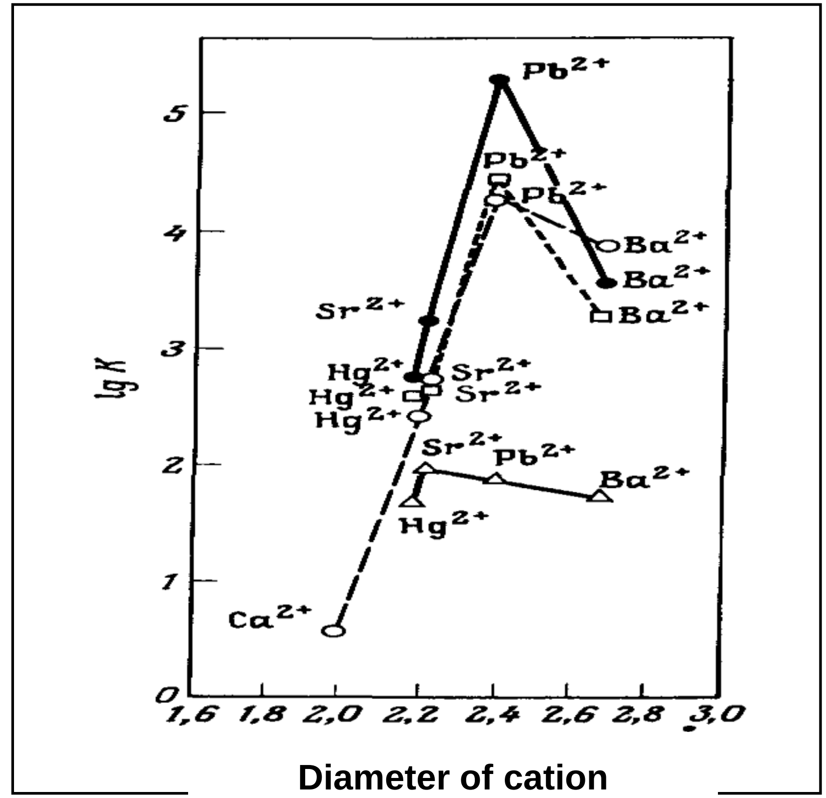




Crown-ethers

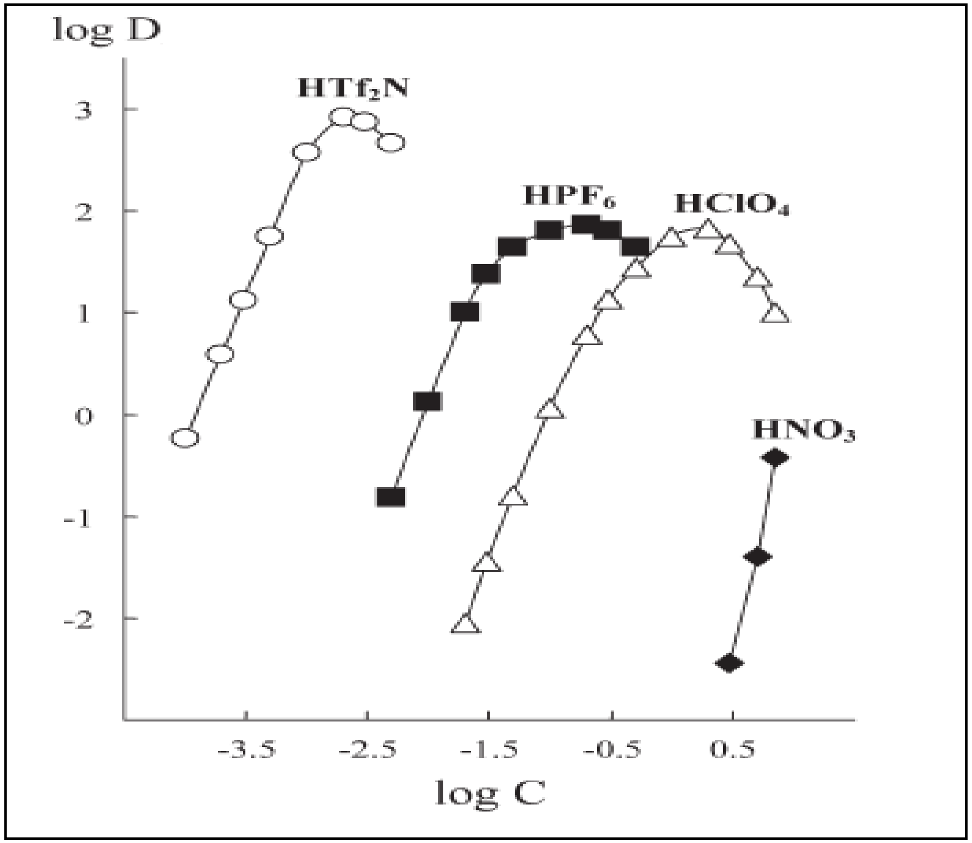
The «Chemical base» of Sr-resin





Dependence of lgK (constant of complex formation) from diameter of cation (reaction M2+ + L = ML2+, H_2O, 25°C). ∆ 15-Crown-5; ○ 18-Crown-6; ● Dicyclohexil-18-Crown-6, Isomer A (cis-sin-cis); □ Dicyclohexil-18-Crown-6, isomer B (cis-anti-cis).

Influence of acids concentrations of HTf_2N, HPF_6, $HClO_4$ и HNO_3 in aquous phase on distribution coefficients of Eu in equilibrium with extracting agent 0,005 M N,N'-dimethyl-N,N'-diphenyl-3-oxopentadiamide in 1,2 - dichlorethan



Turanov A. N., Karandashev V. K. and Baulin V. E. Effect of Anions on the Extraction of Lanthanides (III) by N,N'-Dimethyl-N,N'-Diphenyl-3-Oxapentanediamide // Solvent Extraction and Ion Exchange, 26: 77 – 99 c., 2008.

Super acids and acids

Super acids	H_0
$HClO_4$	-13
FSO_3H	-15,1
CF_3SO_3H	-14,1
$HSO_3F\text{-}SbF_5$	-23
HF_{abs}	-15
$HF\text{-}SbF_5$	-28

Power of acid can be described as equilibrium constant of reaction of dissociation of acid in aqueous media, named also acidity constant *Ka*

Hammet acidity function Hammet is a parameter acidity which estimated as ability of acid protonated of arbitrary basic and practically same as acidity function. For sulfuric acid acidity parameter is H_0 = -12.2. Values H_0 for classical super acids are presented in Table above.

Acids	pK_a
$HClO_4$	-10
HBr	-9
HCl	-7
HNO_3	-1.4

Power of acids, which we used in our experiemnts for sorbtion of elements at Sr-resin (100-150 μm, «Triskem International»)

$$HPF_6 > HClO_4 > HBr > HCl > HNO_3$$

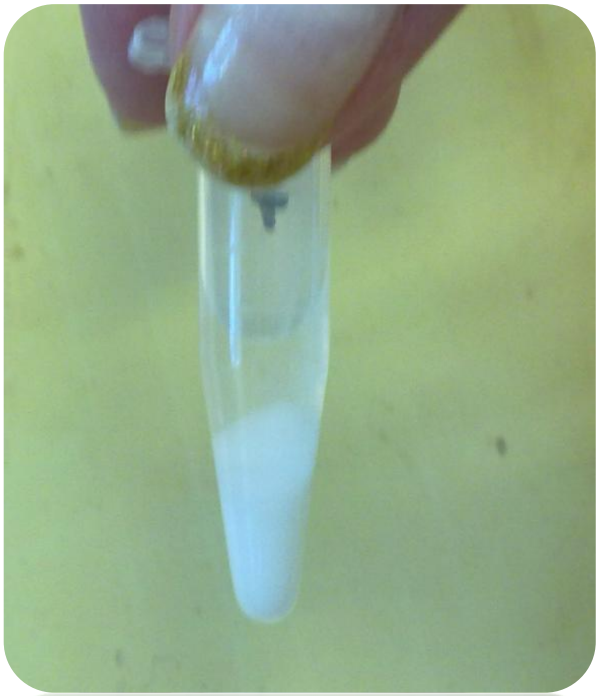
γ – lines for definition of radionuclides

Radionuclide	E, кeV	yield, %
^{82}Sr	776,5	13,4
^{131}Ba	496,3	47,1
^{133}Ba	356	62,3
^{223}Ra	270,3	23,5

Radionuclide	E, кeV	Yiled, %
^{139}Ce	165,8	79,9
^{143}Pm	742	38,3
^{169}Yb	307,7	11,1
^{173}Lu	272	13
^{225}Ac	440,4	27,5
^{88}Y	1836	99,4

- **Radionuclides were produced by high energy proton bombardment of tantalum and thorium targets**
- **No carrier-added radionuclides were applied**
- **Activity of each radionuclide was approx. 10 kBq in each sample**

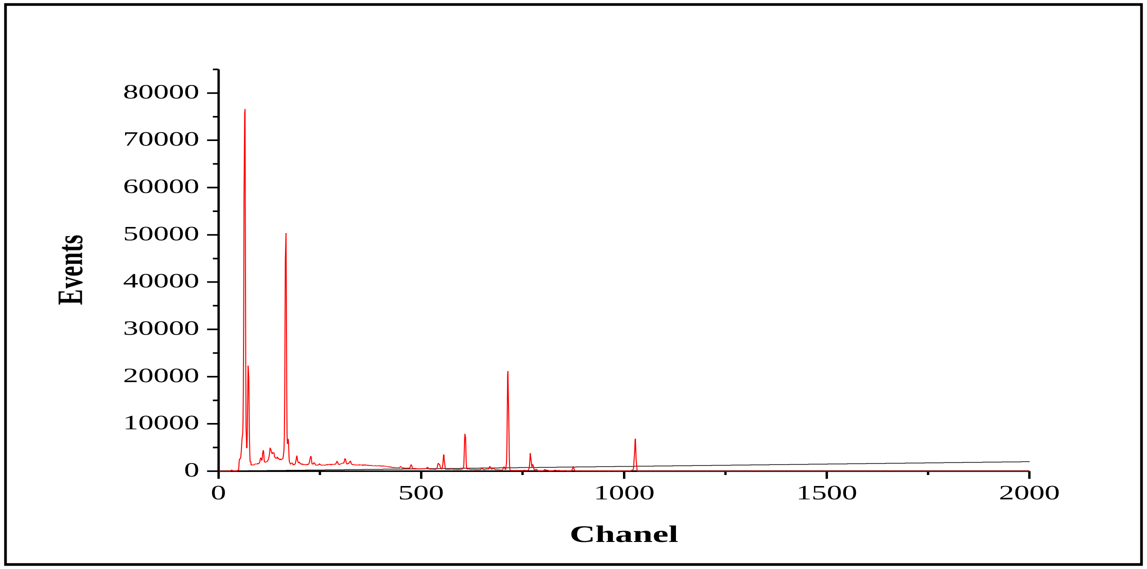
Sample proceeding



50 mg Sr-resin and 1 mL of solution

900 µL of picked solution

Example of obtained spectra



Radionuclide	Energy Kev	Yield, %
^{82}Sr	776,5	13,4
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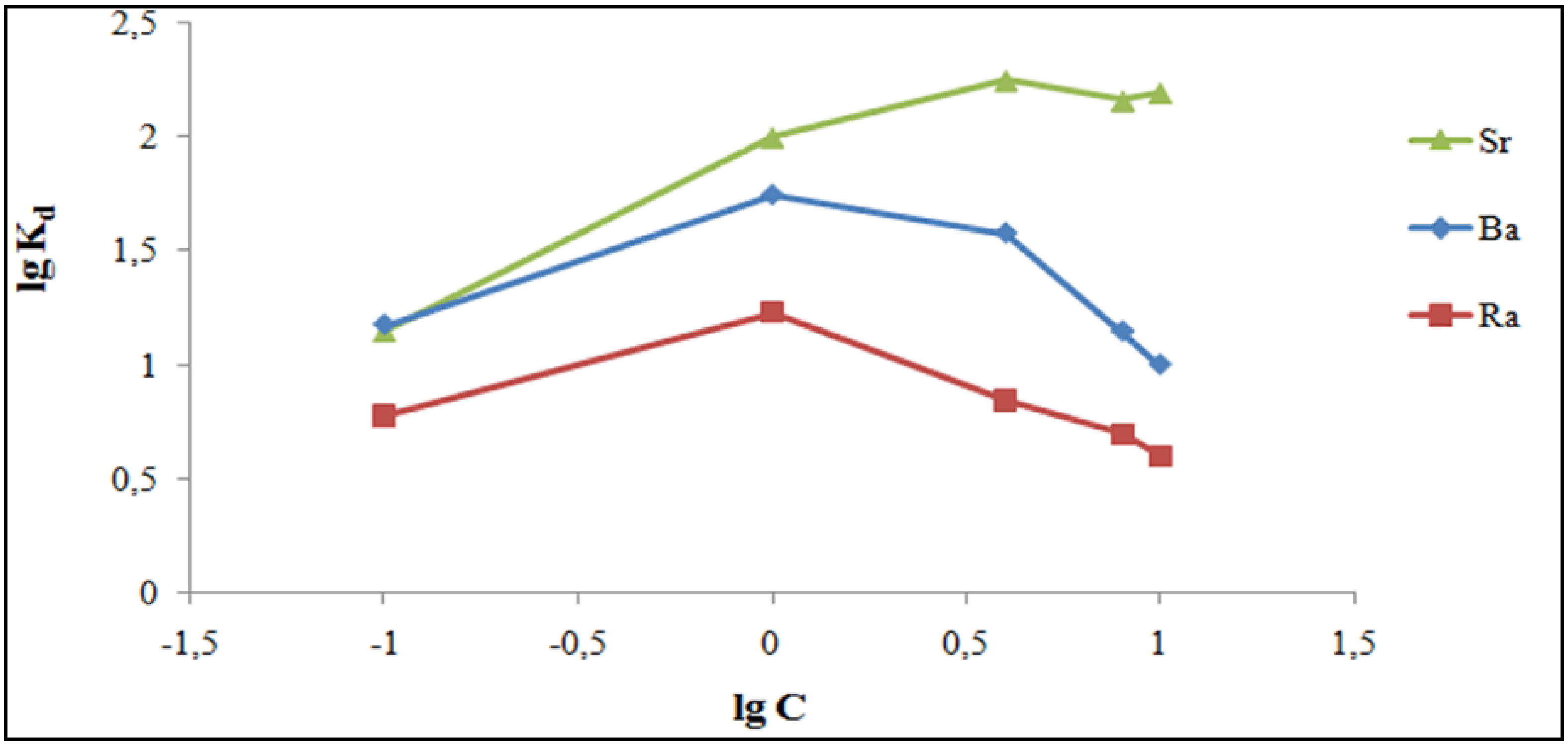
Equaition for calculation of distribution coefficients:

$$K_d = \frac{C_p(phase1)}{C_p(\mathrm{phase}2)} = \frac{A_{1g}(resin)}{A_{1mL}(solution)} = \frac{A_{50mg}(resin)}{A_{50\mu L}(solution)}$$

Where Cp(phase 1) u Cp (phase 2) – equilibrium concentrations of elements in resin and solution, $A_{50мg}$(resin) – activity (Bq) in 50 mg of resin, $A_{50\mu L}$(solution) – activity (Bq) in 50 μL of solution.

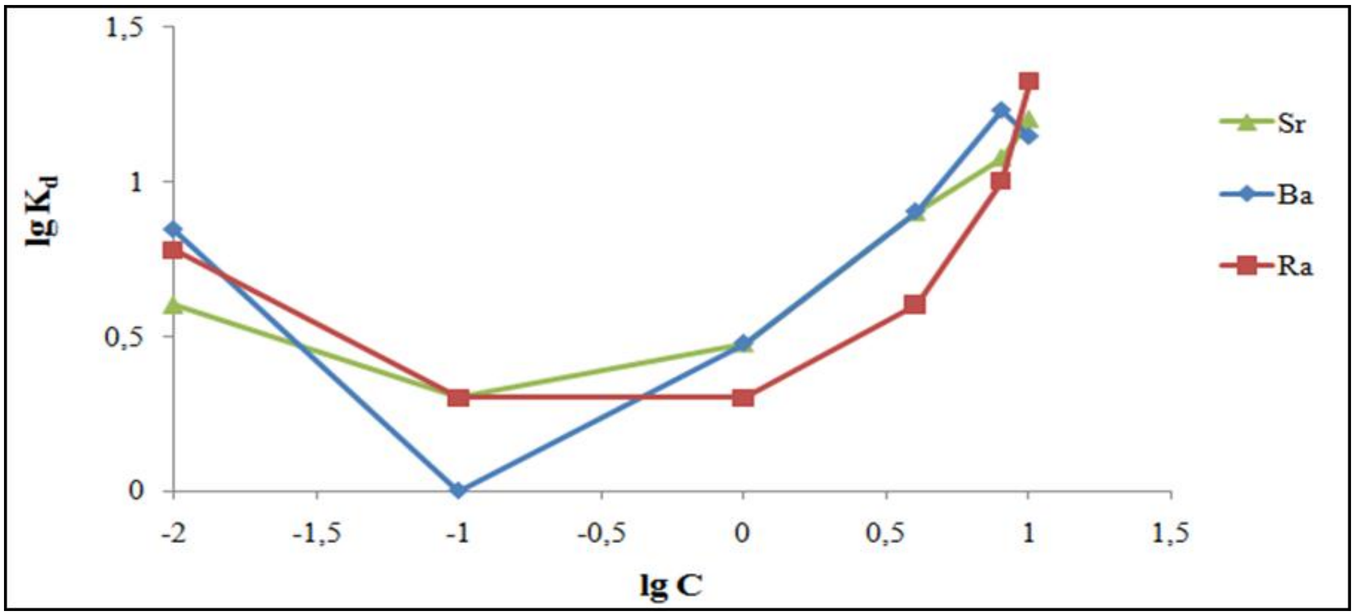
$[HNO_3]$, M	K_d		
	Sr	Ba	Ra
0,1	14	15	6
1	100	56	17
4	178	38	7
8	145	14	5
10	157	10	4

Dependence of distributions coefficients for alkaline earth elements from acid concentration in system Sr-resin- HNO_3



[HCl], M	K_d		
	Sr	Ba	Ra
0,01	4	7	6
0,1	2	1	2
1	3	3	2
4	8	8	4
8	12	17	10
10	16	14	21

Dependence of distributions coefficients for alkaline earth elements from acid concentration in system Sr-resin- HCl

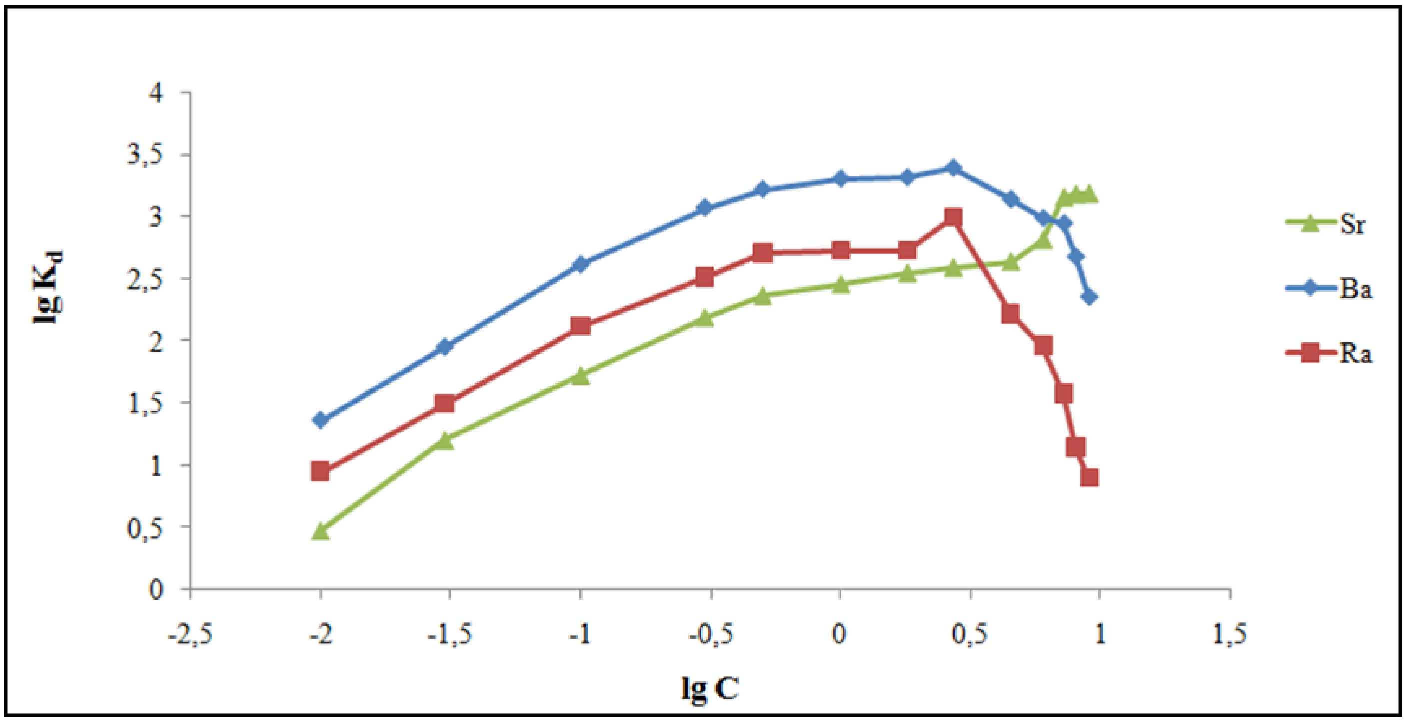


Dependence of distributions coefficients for alkaline earth elements from acid concentration in system Sr-resin- HBr

[HBr], M	K_d		
	Sr	**Ba**	**Ra**
0,01	3,8	4,3	2,5
0,03	1	4	3
0,1	1	3	4
0,3	4	5,5	5,5
0,5	6,9	7,6	7,7
1	5	12	6
1,4	5	7	5
2	5	13	5
3,5	6	12	9
5,6	11	15	9
7	9	15	10

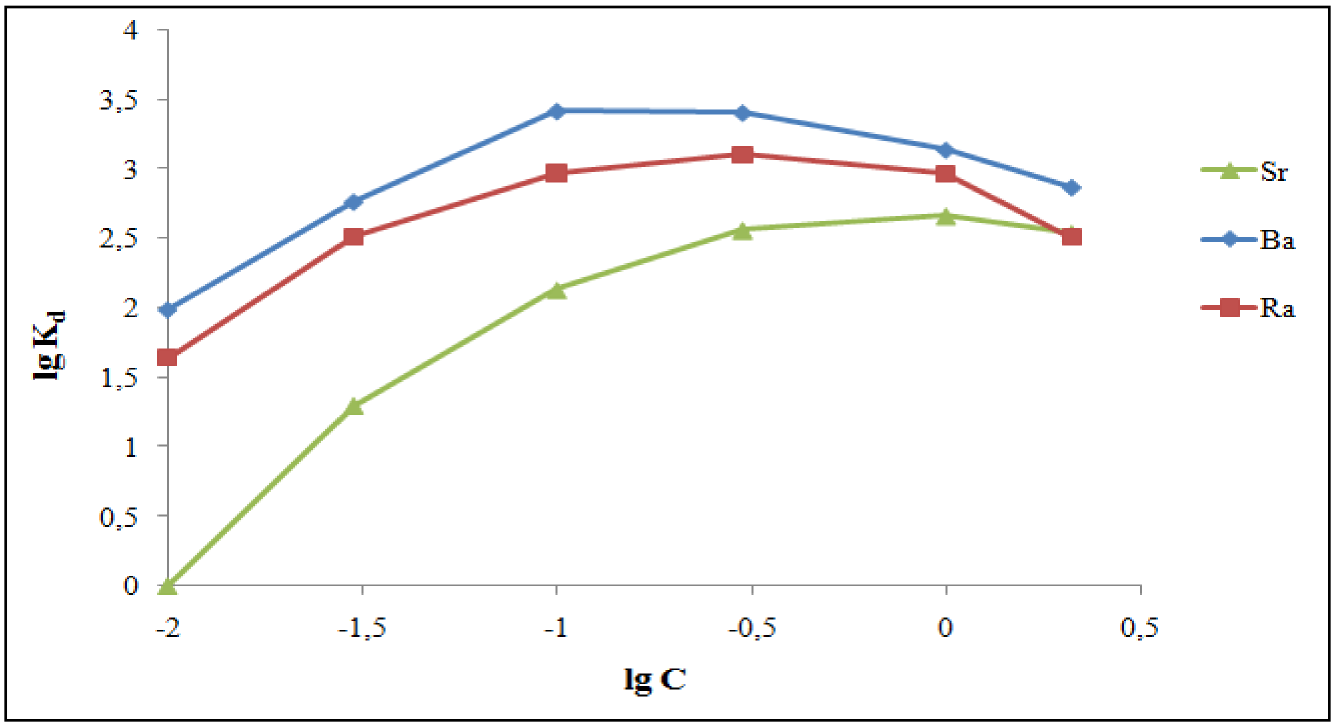
[$HClO_4$], M	K_d		
	Sr	Ba	Ra
0,01	3	23	9
0,03	16	89	31
0,1	53	409	133
0,3	156	1171	327
0,5	234	1644	512
1	289	2000	540
1,8	356	2048	541
2,7	393	2444	991
4,5	438	1364	165
6	656	963	92
7,2	1444	875	38
8	1525	473	14
9	1545	225	8

Dependence of distributions coefficients for alkaline earth elements from acid concentration in system Sr-resin- $HClO_4$

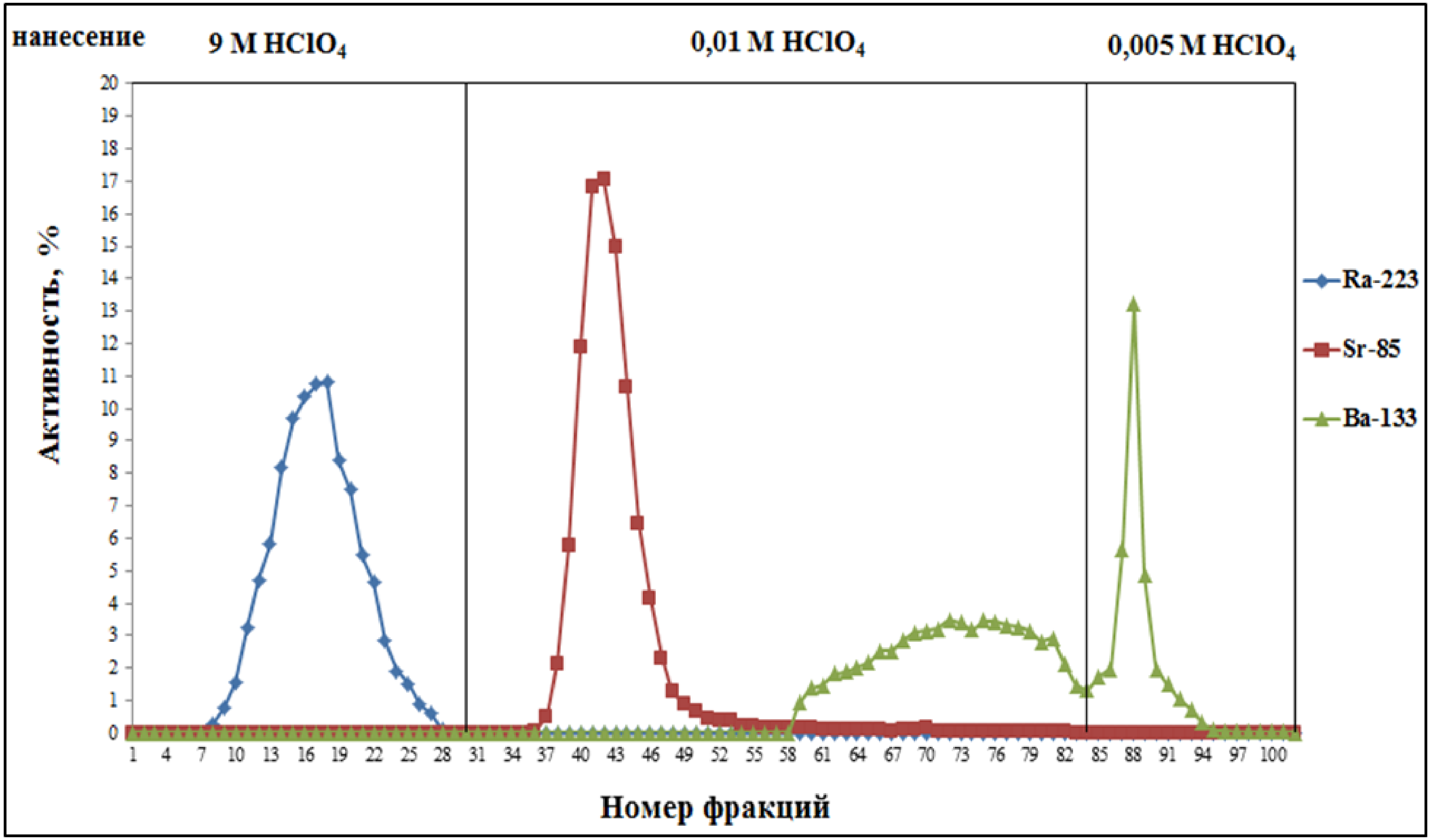


Dependence of distributions coefficients for alkaline earth elements from acid concentration in system Sr-resin- HPF_6

$[HPF_6]$, M	K_d		
	Sr	Ba	Ra
0,01	20	97	44
0,03	136	582	330
0,1	367	2629	945
0,3	466	2560	1283
1	349	1380	941
2	335	741	326
7	26	5	4

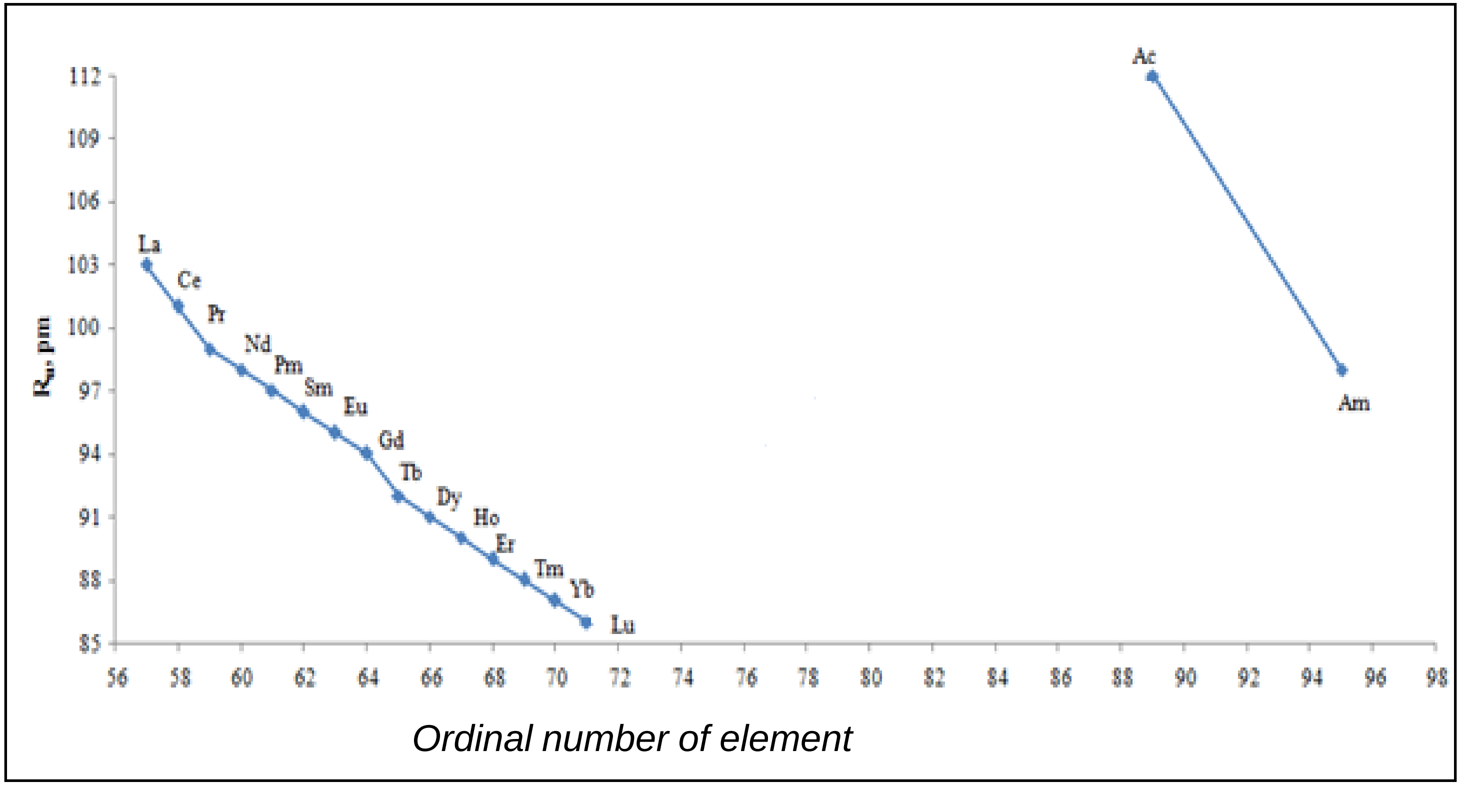


Experimental data on chromatographical separation of radionuclides ^{223}Ra, ^{85}Sr and ^{133}Ba on Sr-resin column (2 mL, 100-150 μm, «Triskem International»)



Fraction volume – 0.5 mL

Correlation between ionic radius and ordinal number of lanthanidies, americium and actinium with coordination number 6



Dependence of distributions coefficients for rare earth elements from acid concentration in system Sr-resin- HNO_3, HCl and HBr

	K_d					
[HNO_3], M	**Ac**	**Ce**	**Pm**	**Y**	**Yb**	**Lu**
0,02	7	3	1	1,03	3	2,64
0,03	4	1,78	1,71	<1	<1	2
0,1	14	13	12	10	11,9	11
0,2	3	<1	2	<1	<1	1
1	4	2	<1	3	2	<1
4	5	0,6	1,4	1,9	0,5	1,4
6	1,78	1,2	1,4	<1	2	3
8	1	<1	1	1	3	<1
10	<1	<1	<1	<1	<1	<1

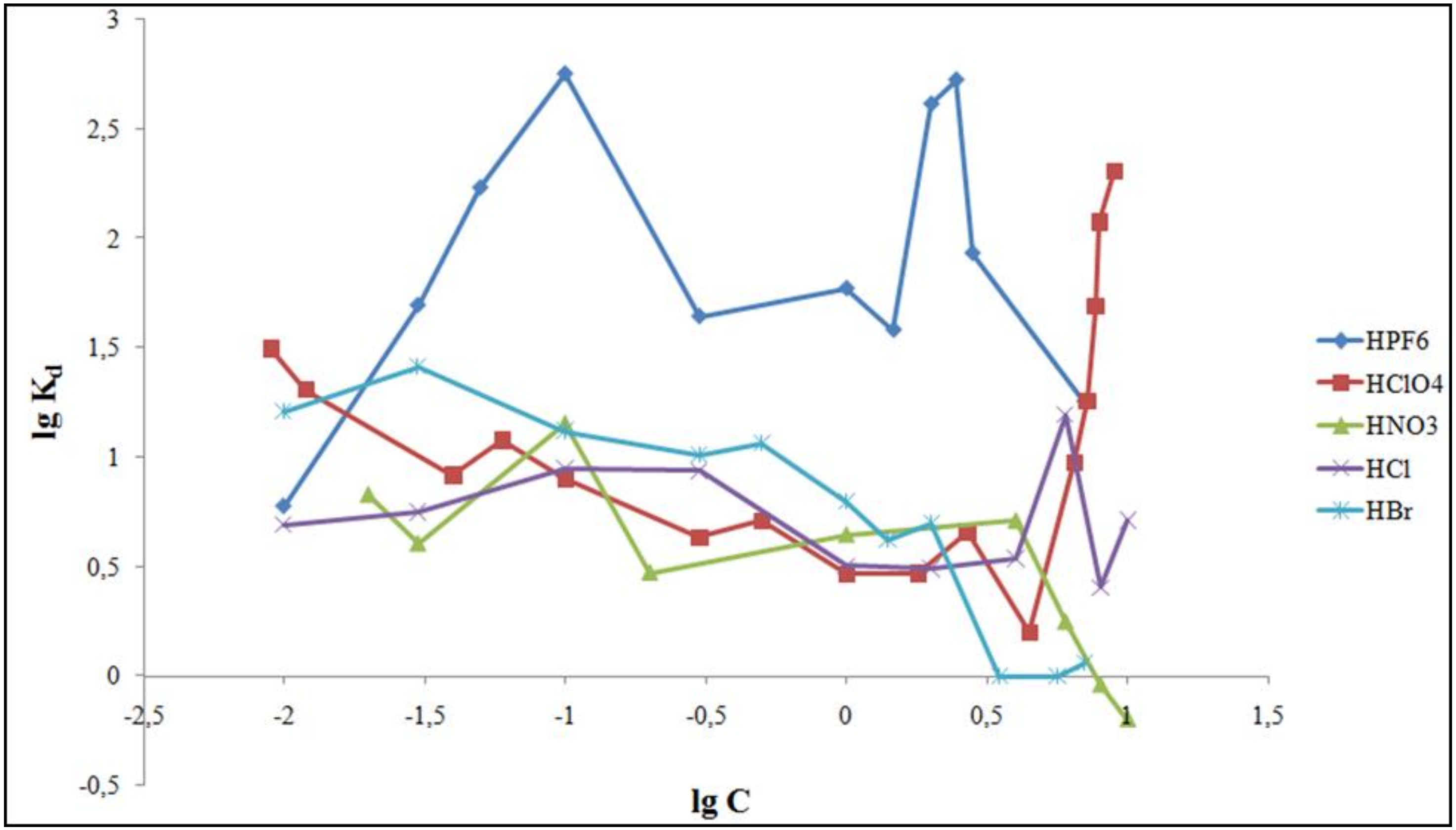
	K_d					
[HCl], M	**Ac**	**Ce**	**Pm**	**Y**	**Yb**	**Lu**
0,01	5	1,7	2	3	2,3	1
0,03	6	2,4	1,2	1,3	1	2
0,1	9	2	3	5	4	6
0,3	9	7,5	6	5	6,5	7,8
1	3	2	1	<1	<1	1,6
2	3	4	<1	<1	2,3	2,2
4	3	4	2,8	4,2	6	<1
6	16	11	10	11,2	14	5
8	3	1	1,6	2	4	<1
10	5	1,7	1,6	<1	<1	<1

	K_d					
[HBr], M	**Ac**	**Ce**	**Pm**	**Y**	**Yb**	**Lu**
0,01	16	11	6,13	10	7	6,3
0,03	26	8	15	8,76	9,23	8,91
0,1	13	2,04	1,28	4,69	2,24	2,25
0,3	10,25	2,18	3,76	3,74	3,04	3,48
0,5	11,6	7,14	7,4	5,7	4,64	5,12
1	6,28	2,03	3,74	2,09	2,26	1,41
1,4	4,18	<1	<1	2,3	1,63	1,88
2	4,98	<1	<1	<1	<1	1,38
3,5	<1	1,81	1,47	2,8	2,39	3,58
5,6	<1	<1	2,64	4,72	3,14	2,8
7	1,15	<1	2,71	1,63	4,53	3,91

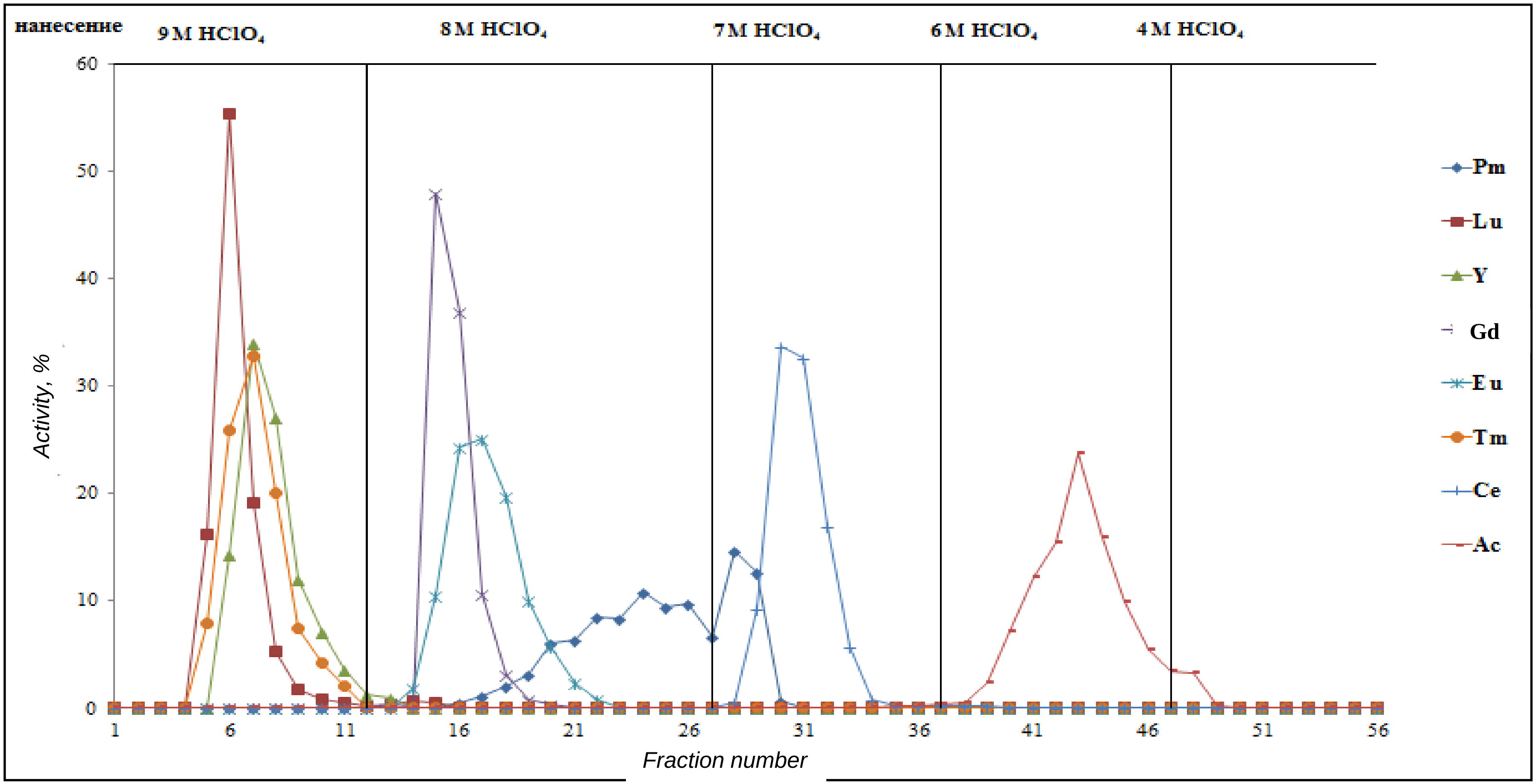
Dependence of distributions coefficients for rare earth elements from acid concentration in system Sr-resin- $HClO_4$

	K_d					
$[HClO_4]$, M	**Ac**	**Ce**	**Pm**	**Y**	**Yb**	**Lu**
0,009	31	15	18,71	19	16,1	18,23
0,012	20	9,63	7,2	8	6,4	9,89
0,04	8,25	3,62	2,07	2,36	3,69	2,48
0,06	12	8	7,27	7,12	7,03	7,46
0,1	8	4,6	5,26	4,41	4,92	3,19
0,3	4,29	3,4	2,48	<1	1,28	<1
0,5	5,11	3,18	2,39	6,74	3,22	3,75
1	2,92	<1	1,4	1,76	<1	<1
1,8	2,94	<1	<1	<1	<1	2,18
2,7	4,56	2,84	<1	<1	<1	<1
4,5	1,58	<1	<1	<1	1,57	<1
6,5	9	3,63	1,65	3	2	4,4
7,2	18	2,32	3,15	<1	<1	<1
7,7	48	5,6	2	1,2	<1	<1
8	118	19	5,74	2	<1	5,58
9	200	94	31	2,5	<1	1,02

Dependence logK_d of actinium from logC of acids concentrations in systems with Sr-resin



Chromatographical separation of radiolanthanaides and actinium on Sr-resin column(2 mL, 100-150 μm, «Triskem International»)



Fraction volume – 0.5 mL

Conclusions

- **Behavior of Y, Sr, Ra, Ba, Ac и radiolanthanides was studied on Sr-resin (100-150 µm, «Triskem International») in nitric acid (HNO_3), hydrochloric acid (HCl), perchloric acid ($HClO_4$), hydrobromic acid (HBr) and also hexafluorophosphoric acid (HPF_6) solutions.**

- **Detected strong sorption of Sr, Ra, Ba on Sr-resin in perchloric and hexafluorophosphoric acids. Distribution coefficients for Sr, Ra and Ba in hexafluorophosphoric 10 times higher then for nitric acid, while Ba has strongest sorption.**

- **Results showed that for nitric and hydrobromic acid with Sr-resin in wide concentration spectra Kd values of Ac and lanthanides are low (less then 10).**

Conclusions

- **High sorption of Ac and lanthanides on Sr-resin in perchloric and hexafluorophosphoric acid media**

- **Based of Kd values separation strategy was developed for separation Sr, Ra and Ba between each other and also from Ac in system Sr-resin-$HClO_4$**

- **Strong adsorbtion of AEE, REE and Ac on Sr-resin in perchloric and hexafluorophosphoric acid media can be explained by formation of noncontact (separated) ionic pairs in organic media. Therefore metals complexes with crown ethers in organic solvents are solvated (contacted) with molecules of organic solvents. Ion exchange mechanism of extraction**