TrisKem International

Characterization of new calixarene containing resins for the separation of Cs and Rb

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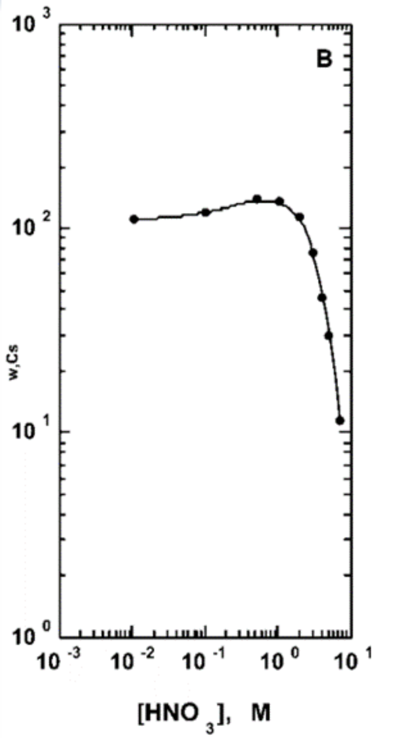
TRISKEM
Expertise in Separation Chemistry

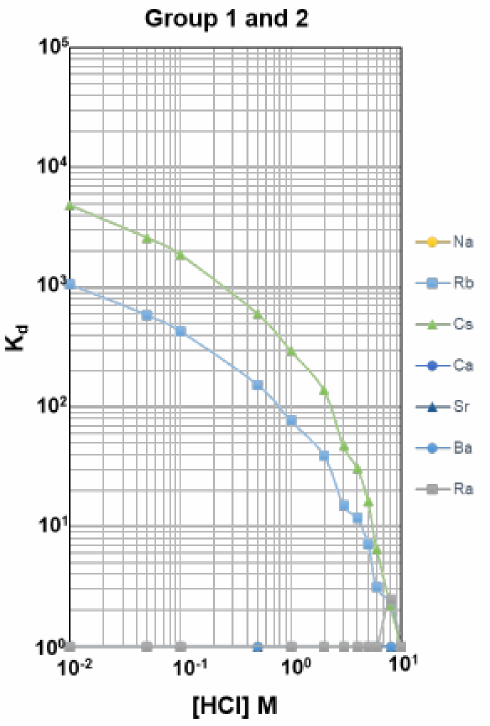
Review of literature

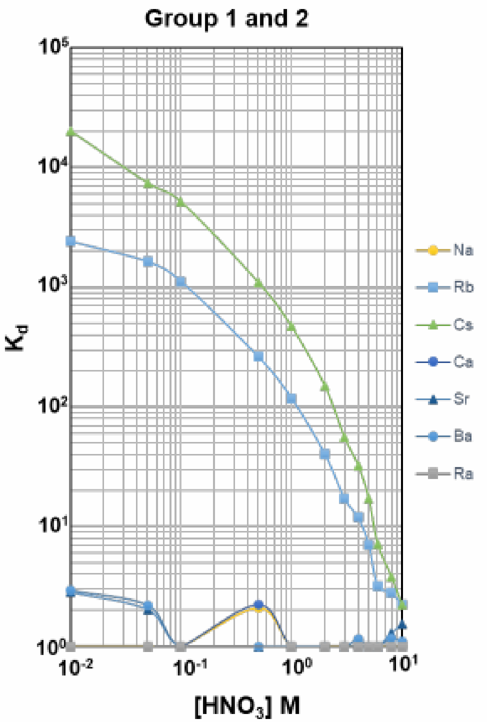


Cs sorption on 0.05 M BC6I
in 1,2-DCE
supported on Amberchrom
CG-71 m
[Dietz, 2006].

TK300 resin

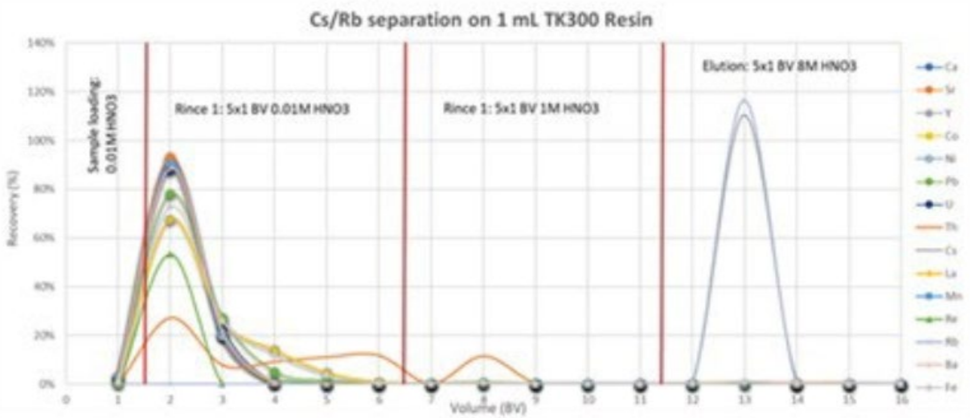
- Calixarene based
- High selectivity for Cs and Rb over other elements at low to medium acid
- Interference by K^+
- Limited capacity
- Work on additional resins





All data provided by B. Russel et al. (NPL)

- Cs and Rb loaded from 0.01 – 1M HNO_3
- Rinse with 1M HNO_3 to remove impurities
- Elution at high HNO_3
- Cs/Rb separation possible if needed
- Preferably use for low K samples (e.g. decommissioning samples)



Our goals

To develop new resins based on different calixarenes and diluents for:

► separation of Cs and Rb from weak acid solutions with possibility of elution with strong acid,

► separation of Cs and Rb from strong acid solutions with possibility of elution with water or weak acid.

It is necessary to perform follow experiments to achieve these goals:

► to prepare prototypes based on the different calixarenes

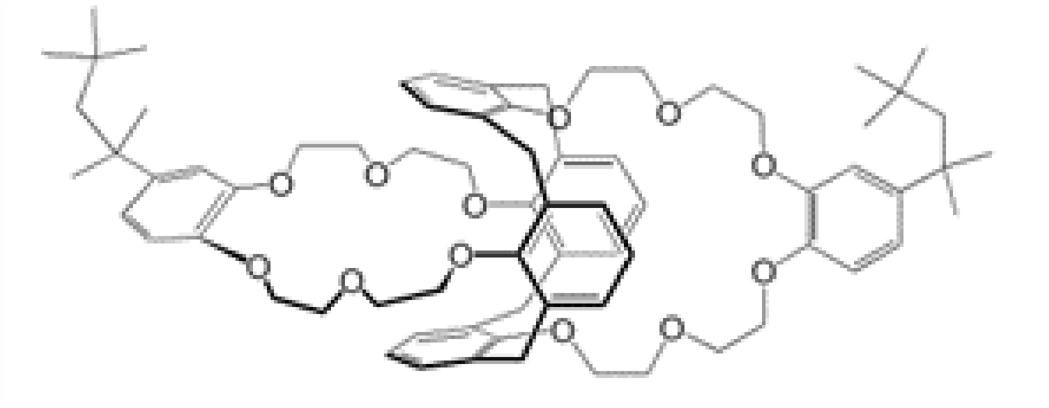
► to study dependence of D_w of different element on prototypes in HNO_3 and HCl

► to study influence of interferenting ions (like potassium) on Cs separation

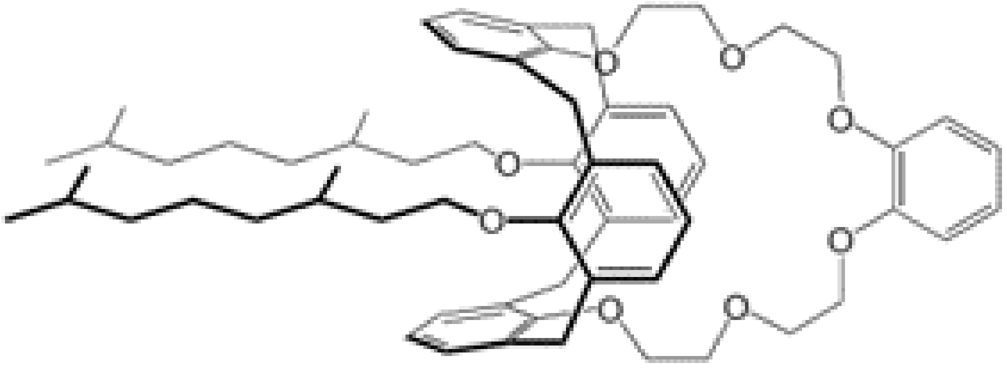
► to determine breakthrough and full capacities of prototypes

► to perform elution tests for Rb and Cs separation

Materials



Calix[4]arene-bis(tert-octylbenzocrown-6, $C_{72}H_{92}O_{12}$ (BOBCalix)



1,3-alt-25,27-Bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6, $C_{62}H_{82}O_{8}$ (MAXCalix)

Calix[4]arene-bis[4-(2-ethylhexyl)benzo-crown-6], $C_{72}H_{92}O_{12}$ (BEBHCalix)

Composition of prototypes

Table 1. Compositions of the sorbents.

Prototype	CA	Capacity
PR1	MAX	High (>14 mg Cs/g)
PR2	BEBH	High
PR3	BOB	Low (<3 mg Cs/g)
PR4	BOB	Low
PR5	MAX	Low
PR6	BEBH	Low
PR7*	MAX	High
PR8*	BEBH	Low
PR9*	MAX	High
PR10*	BEBH	High
PR11*	BEBH	High
PR13	BEBH	High

* – prototypes based on IL.

D_W of Cs, Rb and Tl in HNO_3

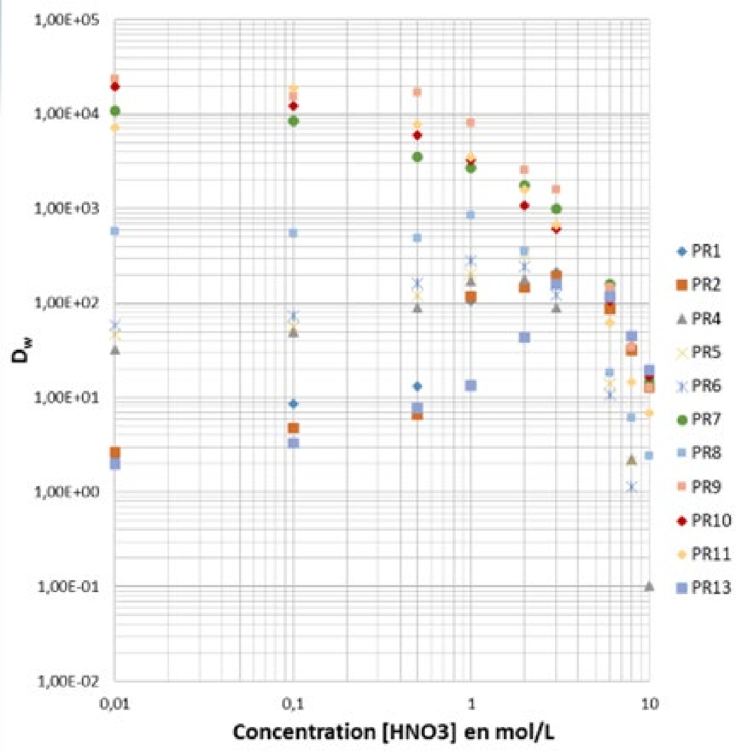


Fig. 1: Acid dependency of Dw for Cs ion on PR1-13 in HNO_3

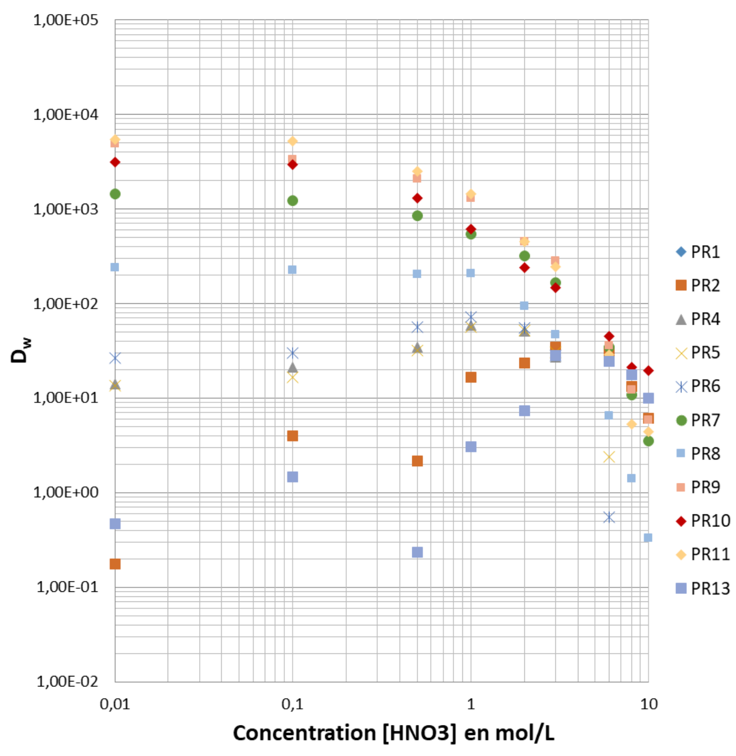


Fig. 2: Acid dependency of Dw for Rb ion on PR 1-13 in HNO_3

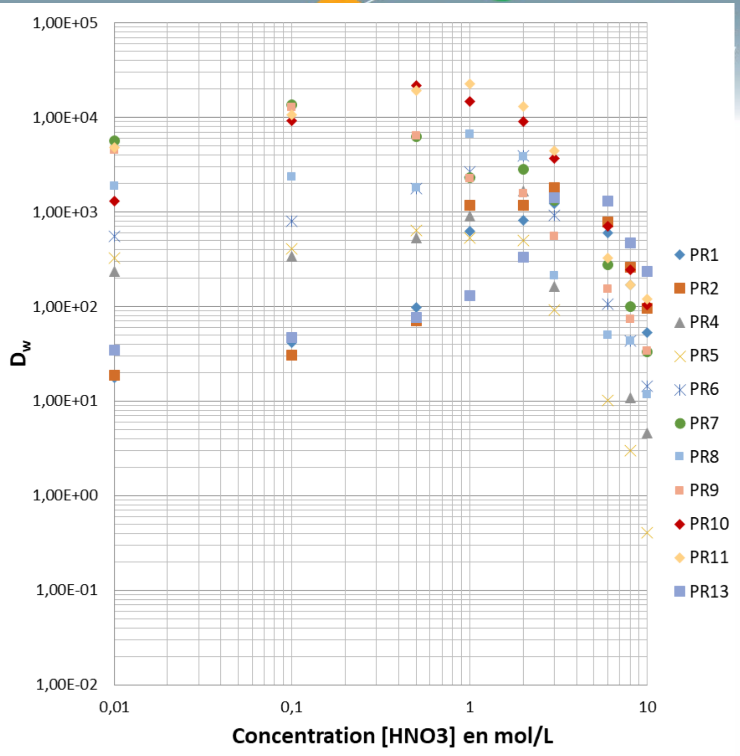


Fig. 3: Acid dependency of Dw for Tl ion on PR1-13 in HNO_3

- Most of element are not sorbed in HNO_3
- Maximum of D_w Cs, Rb in 2-3 M HNO_3 for PR1-6
- Decrease of D_w Cs, Rb for IL PR7,9-11
- Cs > Rb
- PR7,9-11 > PR1-6,8,13

D_W of elements in HCl

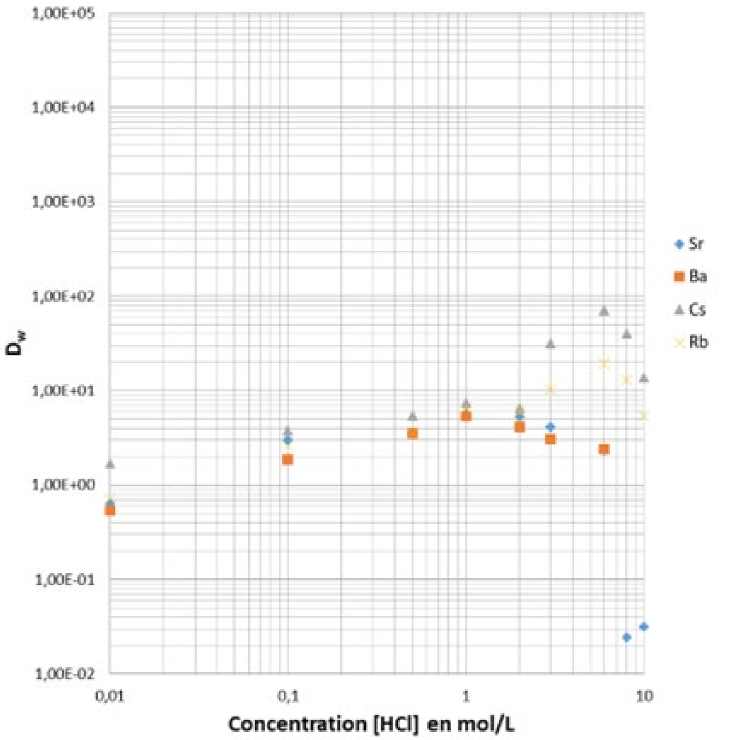


Fig. 4: Acid dependency Dw for various ions on PR1 in HCl

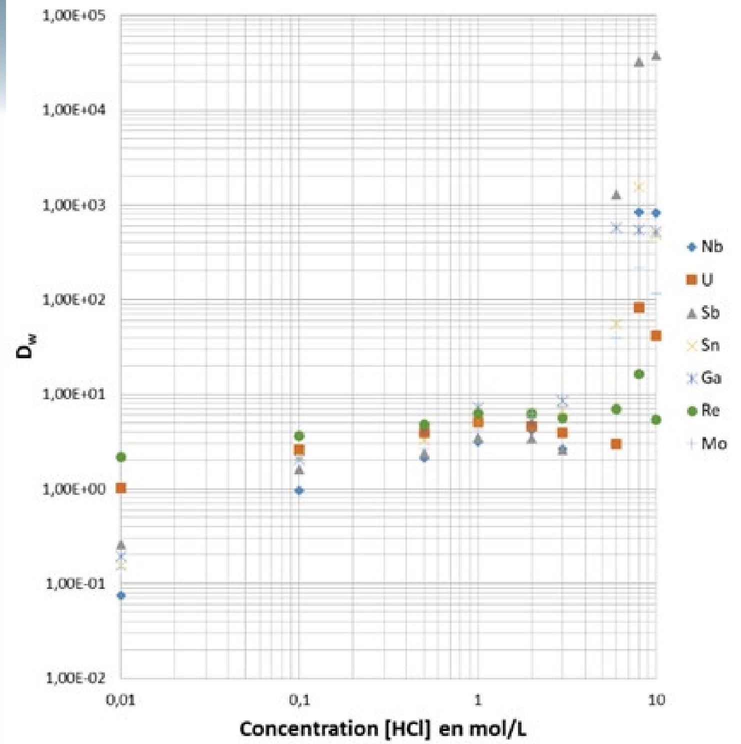


Fig. 5: Acid dependency Dw for various ions on PR1 in HCl

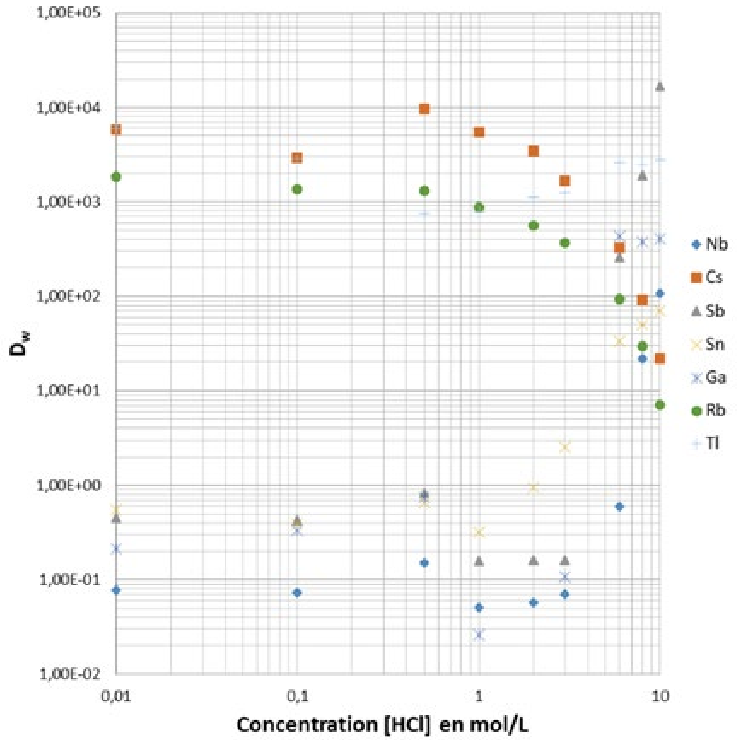


Fig. 6: Acid dependency Dw for various ions on PR7 in HCl

► PR1 weakly sorb Cs from HCl and only at high concentration
► Dependences of Cs and Rb D_w on IL PR7 in HCl are like HNO_3
► Elements which form chloride complexes sorb at high concentration of HCl

KNO_3 dependency of Dw for Cs ion

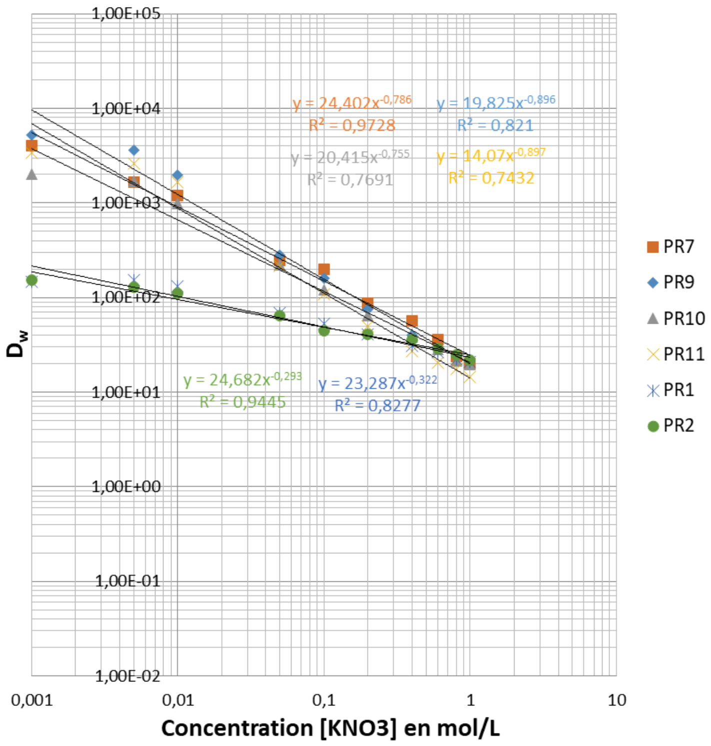


Fig. 7: KNO_3 dependency of Dw for Cs ion on high-capacity PR 1,2,7-11 in 1 M HNO_3

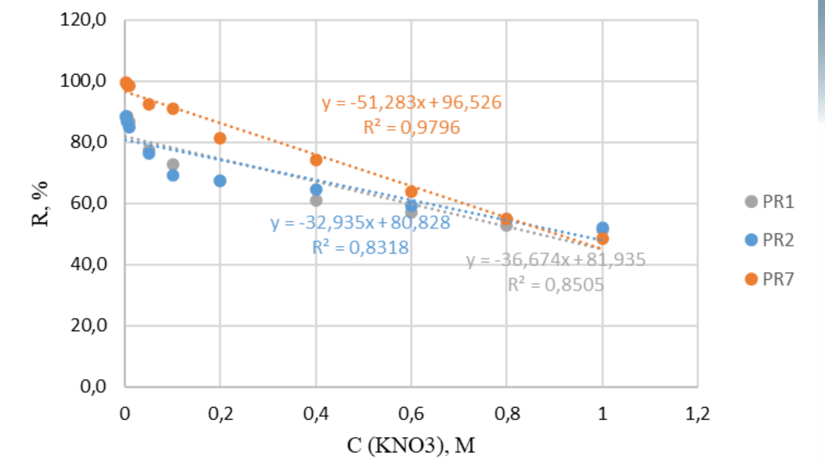


Fig. 8: KNO_3 dependency of efficiency of sorption on high-capacity PR 1,2,7 in 1 M HNO_3

►Efficiency of sorption decreases by 50% in 1 M KNO_3

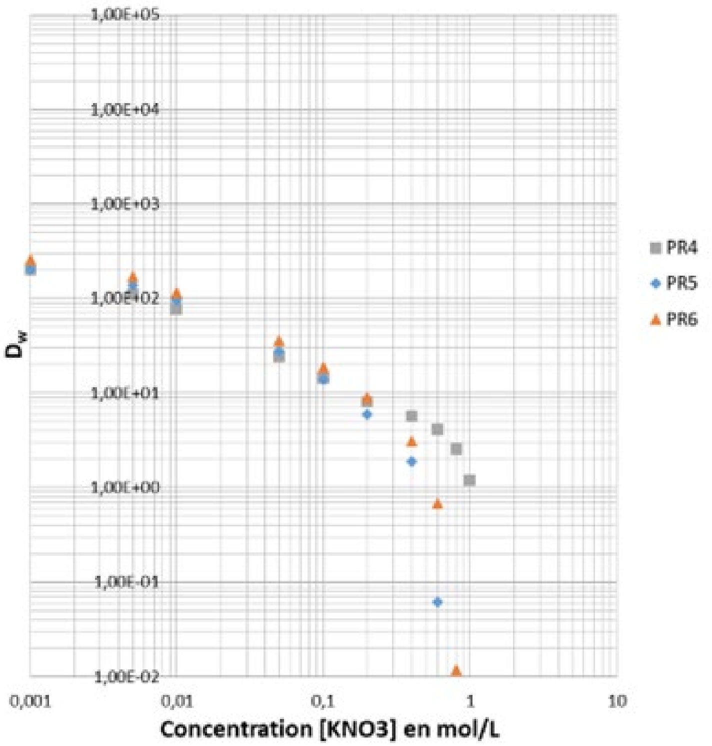


Fig. 9: KNO_3 dependency of efficiency of sorption on low-capacity PR 4-6 in 1 M HNO_3

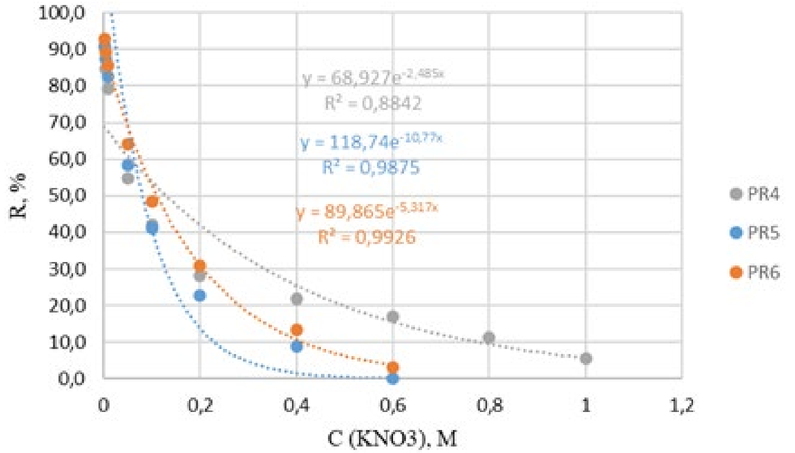


Fig. 10: KNO_3 dependency of efficiency of sorption on low-capacity PR 4-6 in 1 M HNO_3 in the presence of KNO_3

► There are no sorption in 1 M KNO_3

Capacity of prototypes (column experiment)

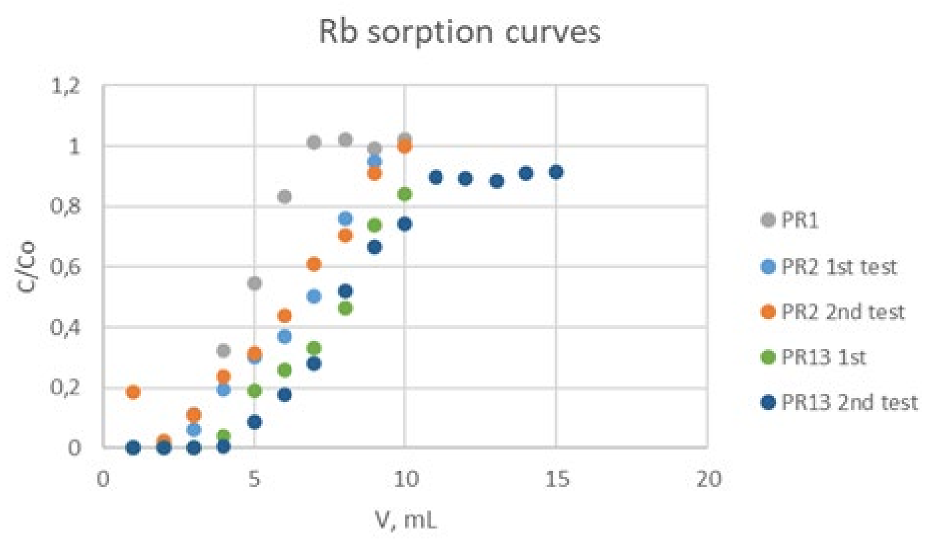


Fig. 11: Sorption curves of Rb on high-capacity prototypes in 3 M HNO_3. Initial concentration of Rb is 2,5 mg/mL.

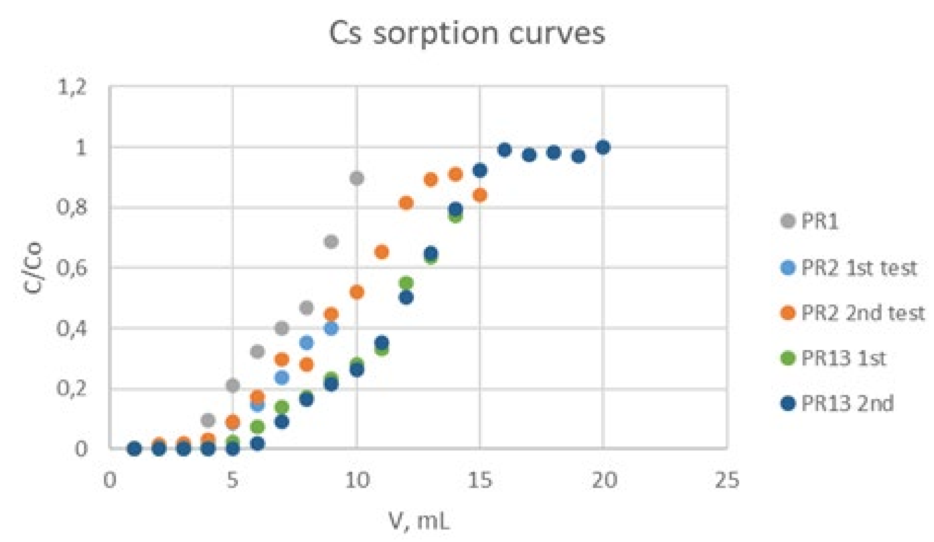


Fig. 12: Sorption curves of Cs on high-capacity prototypes in 3 M HNO_3. Initial concentration of Cs is 2,5 mg/mL.

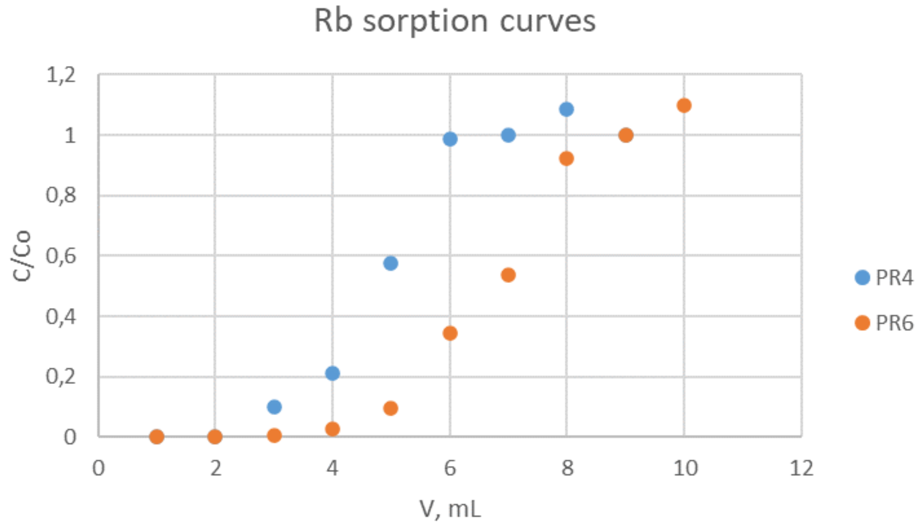


Fig. 13: Sorption curves of Rb on low-capacity prototypes in 3 M HNO_3. Initial concentration of Rb is 0,25 mg/mL.

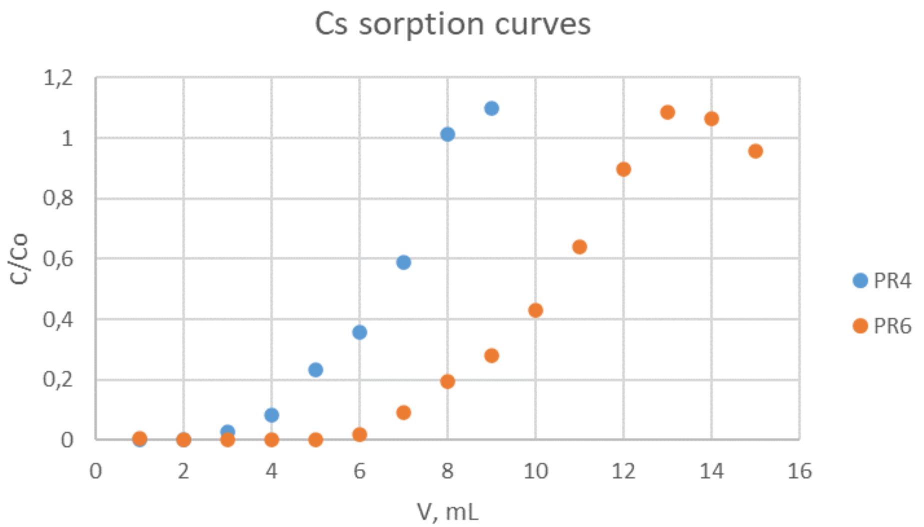


Fig. 14: Sorption curves of Cs on low-capacity prototypes in 3 M HNO_3. Initial concentration of Cs is 0,25 mg/mL.

Capacity of IL prototypes (column experiment)

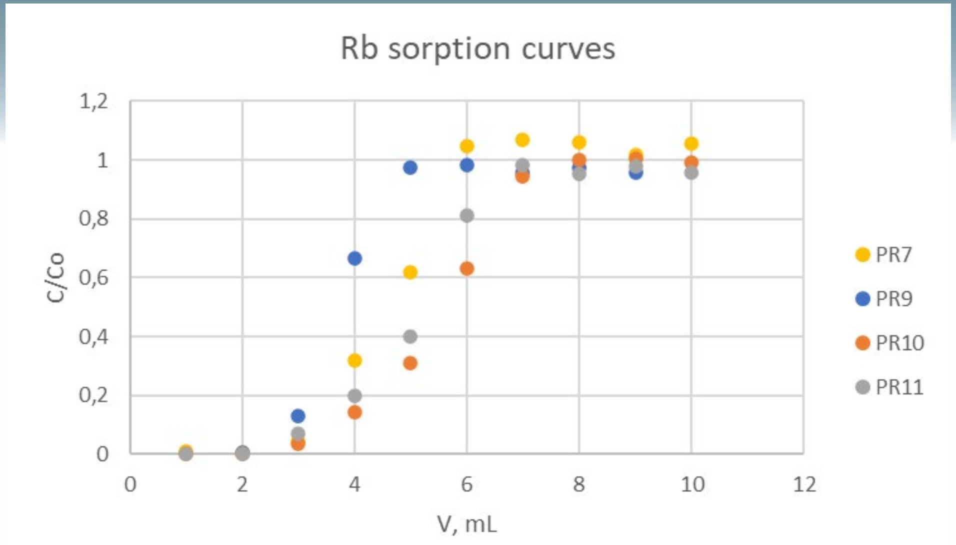


Fig. 15: Sorption curves of Rb on high-capacity prototypes in 1 M HNO_3. Initial concentration of Rb is 2,5 mg/mL.

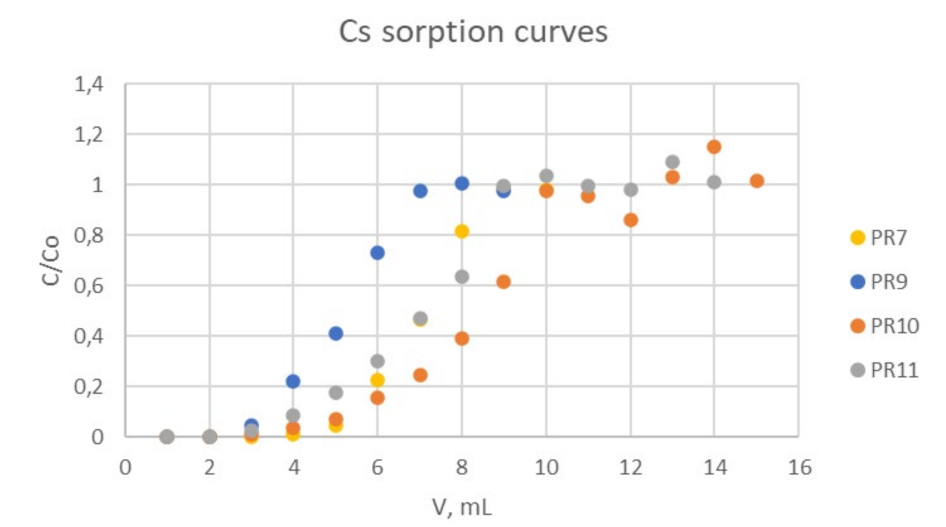
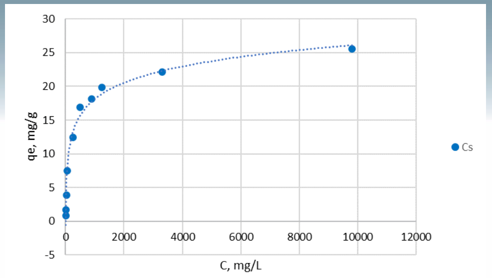


Fig. 16: Sorption curves of Cs on high-capacity prototypes in 1 M HNO_3. Initial concentration of Cs is 2,5 mg/mL.

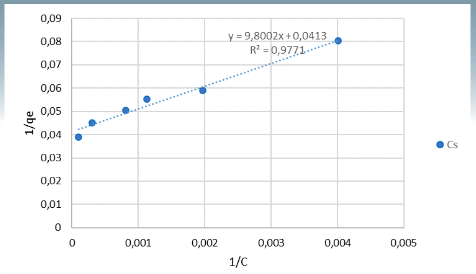
Table 2. Capacities of all prototypes

PR	Ion	DEC, $mg \cdot g^{-1}$	FDEC, $mg \cdot g^{-1}$	g_{theor}, $mg \cdot g^{-1}$	C (CA), mol/L	Elution
3 M HNO_3						
PR1	Rb	6,0	12,6	13,1	0,5	112,0 (H_2O)
PR2	Rb	5,8	**17,6**	12,2	0,5	106,9 (H_2O)
PR4	Rb	0,63	1,29	1,82	0,1	69,2 (0,01 M HNO_3)
PR6	Rb	1,3	1,9	1,8	0,1	73,4 (0,01 M HNO_3)
PR13	Rb	14,1	**26,9**	17,3	1,0	62,7 (H_2O)
1 M HNO_3						
PR7	Rb	8,9	12,0	12,5	0,5	96,0 (10 M HNO_3)
PR9	Rb	6,5	**10,4**	8,1	0,3	104,0 (10 M HNO_3)
PR10	Rb	10,3	**17,3**	11,7	0,5	96,5 (10 M HNO_3)
PR11	Rb	6,9	**15,8**	7,8	0,3	94,1 (10 M HNO_3)
3 M HNO_3						
PR1	Cs	9,3	21,5	20,4	0,5	106,3 (H_2O)
PR2	Cs	13,2	**30,3**	19,0	0,5	87,2 (H_2O)
PR4	Cs	0,86	1,66	2,84	0,1	87,5 (0,01 M HNO_3)
PR6	Cs	1,9	3,1	2,8	0,1	68,2 (0,01 M HNO_3)
PR13	Cs	19,0	**35,1**	26,9	1,0	92,7 (H_2O)
1 M HNO_3						
PR7	Cs	12,2	19,6	19,5	0,5	106,9 (10 M HNO_3)
PR9	Cs	9,3	**14,4**	12,6	0,3	91,7 (10 M HNO_3)
PR10	Cs	13,3	**25,2**	18,2	0,5	97,4 (10 M HNO_3)
PR11	Cs	10,0	**21,2**	12,1	0,3	97,4 (10 M HNO_3)

Capacity of PR2 (static experiment)



a



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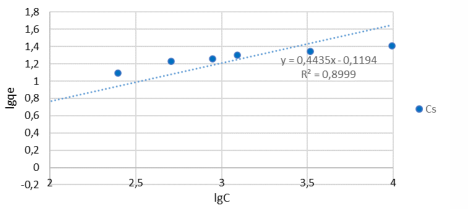
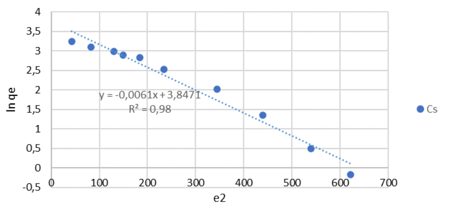


c



d

Fig. 17. Cs sorption isotherms with PR2: qe – C plot (a), linearized in coordinates1/qe – 1 / C plot (b), lgqe – lgC (c), lnqe – e2 (d).

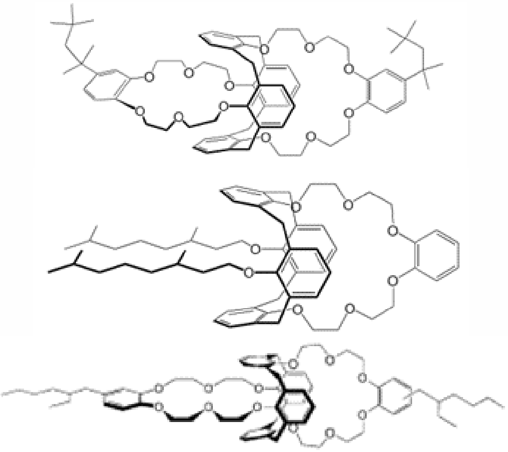
Table 3. Capacity data of PR2.

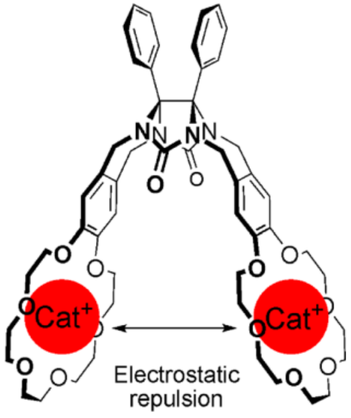
Element	Capacity in column experiment, mg/g	DEC, mg/g	TDEC, mg/g	Langmuir maximum capacity, mg/g	Maximum theoretical capacity, mg/g
Rb	16.2*	6.3	18.6		12.2
Cs	26.8*	13.2	30.3	24.2	19.0

* – sorption from 20 mL of 2,5 mg/mL Rb (Cs) solution, Rb and Cs quantitatively desorbed by 10 mL of water.

Table 4. – Parameters of the sorption isotherms of Cs on PR2

Resin	Langmuir isotherm			Freundlich isotherm			Dubinin-Radushkevich isotherm			
	g_m, mg/g	K_L, L·mg^{-1}	r^2	K_F, mg·g^{-1}	n	r^2	g_m, mg g^{-1}	β, mol^2 kJ^{-2}	E, kJ mol^{-1}	r^2
	Cs									
PR2	24.2	0.0042	0.98	0.76	2.25	0.9	46.9	0.0061	9.1	0.98

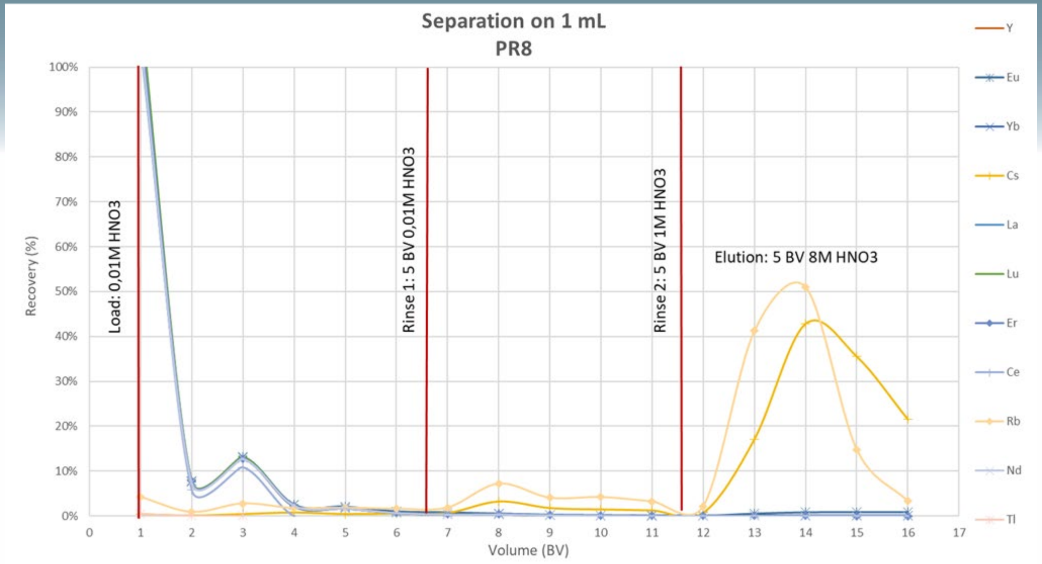




c

- ► For the most of prototypes full Cs and Rb capacities are near theoretical.
- ► For PR2 full Cs and Rb capacities are higher than theoretical according of three experiments and may be related with complex formation of 1 molecule of CA with 2 ions of Cs, because of the second crown-ether ring.
- ► Excess of theoretical capacity for PR9 may be related with participation of IL in the sorption of Cs and Rb, because of high content of IL, for PR11 both CA and IL.

Elution tests with low- (PR8) and high-capacity (PR7) IL prototypes



g. 18: Separation of Rb and Cs on PR8 from weak acid (0,01 M HNO_3) solution

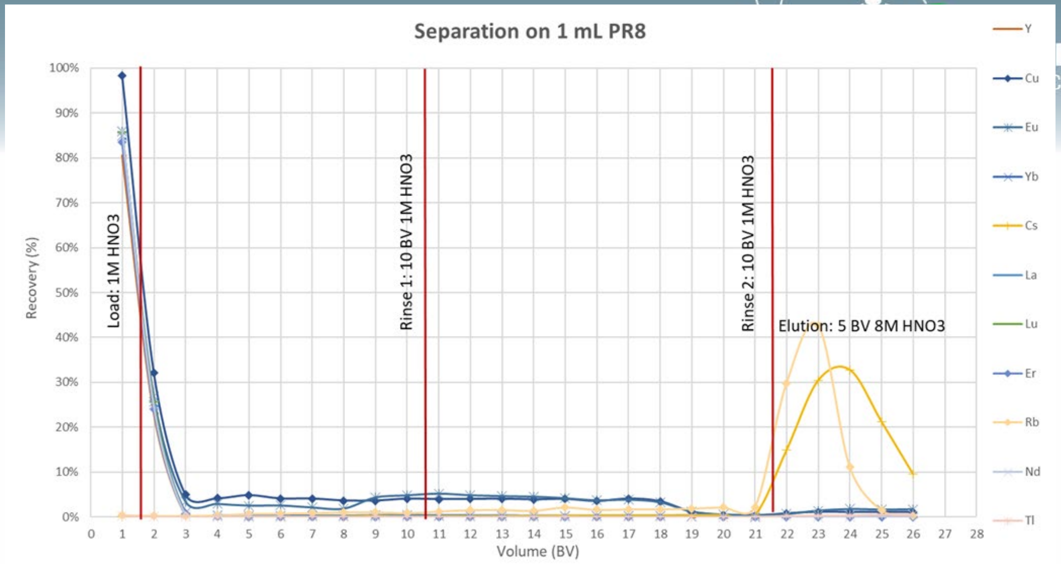
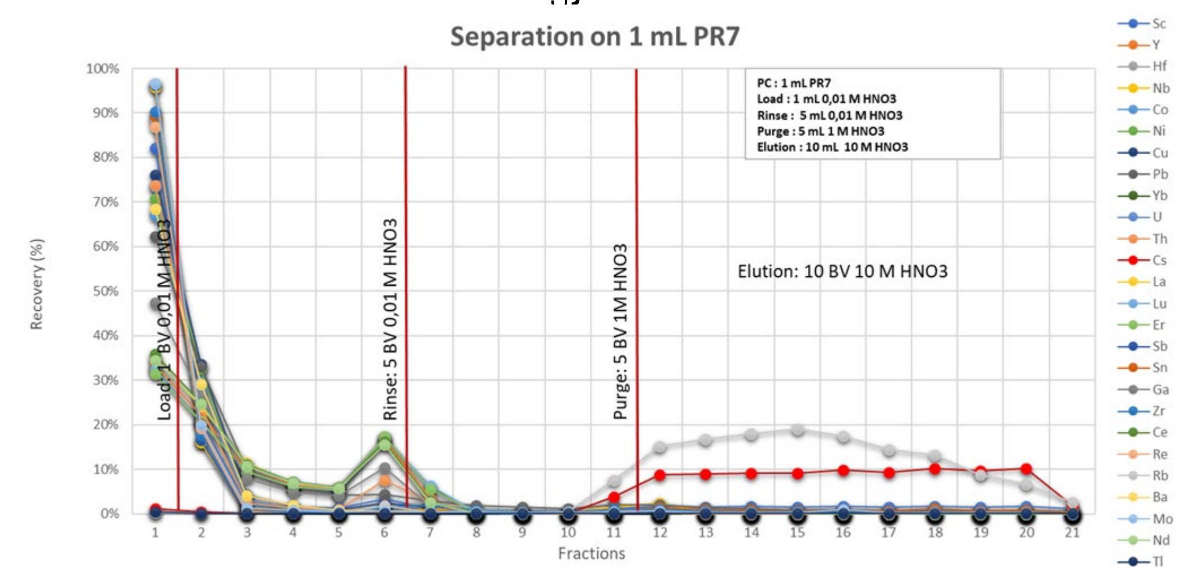


Fig 19: Separation of Rb and Cs on PR8 from 1 M HNO_3 solution



ig. 20: Separation of Rb and Cs on PR7 from weak acid (0,01 M HNO_3) solution

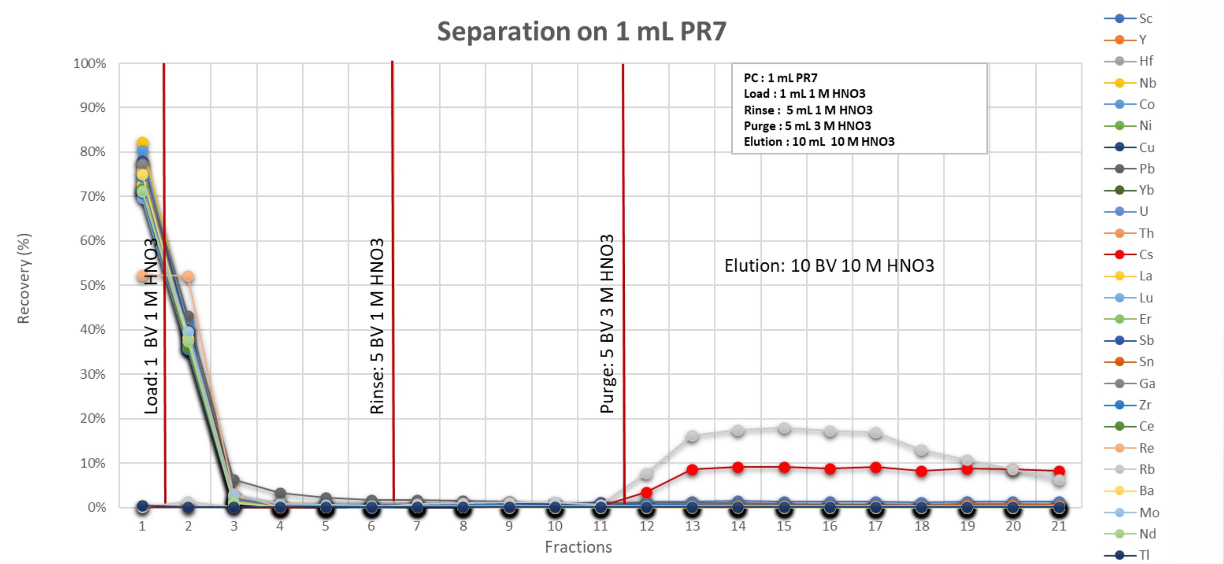


Fig. 21: Separation of Rb and Cs on PR7 from 1 M HNO_3 solution

Elution tests with high-capacity prototype (PR2)

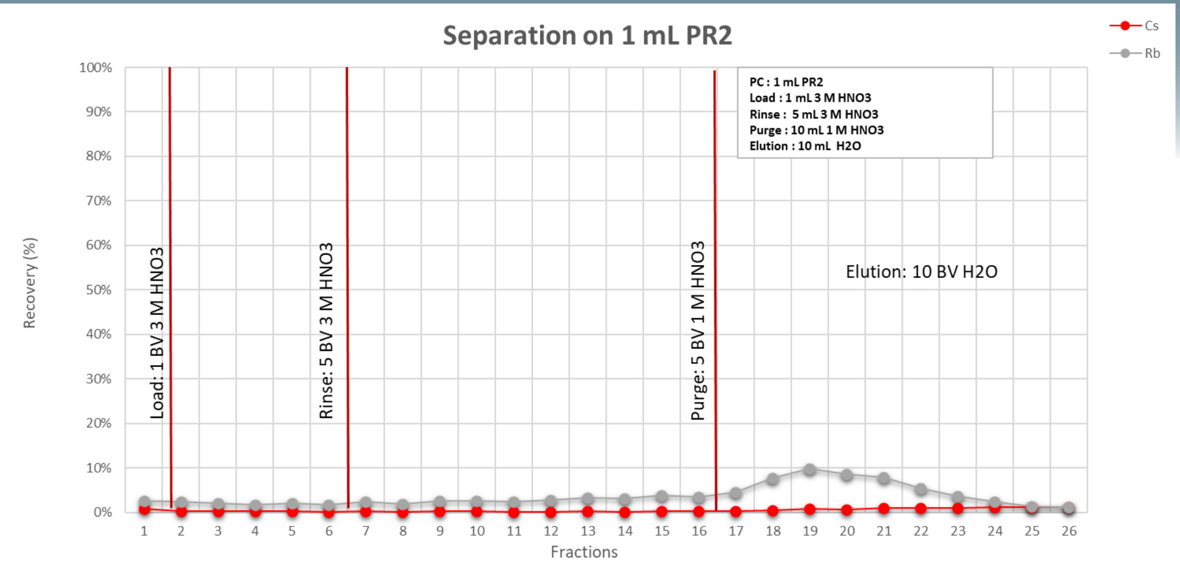


Fig. 22: Separation of 1 µg Rb and Cs on PR2 from 3 M HNO_3 solution

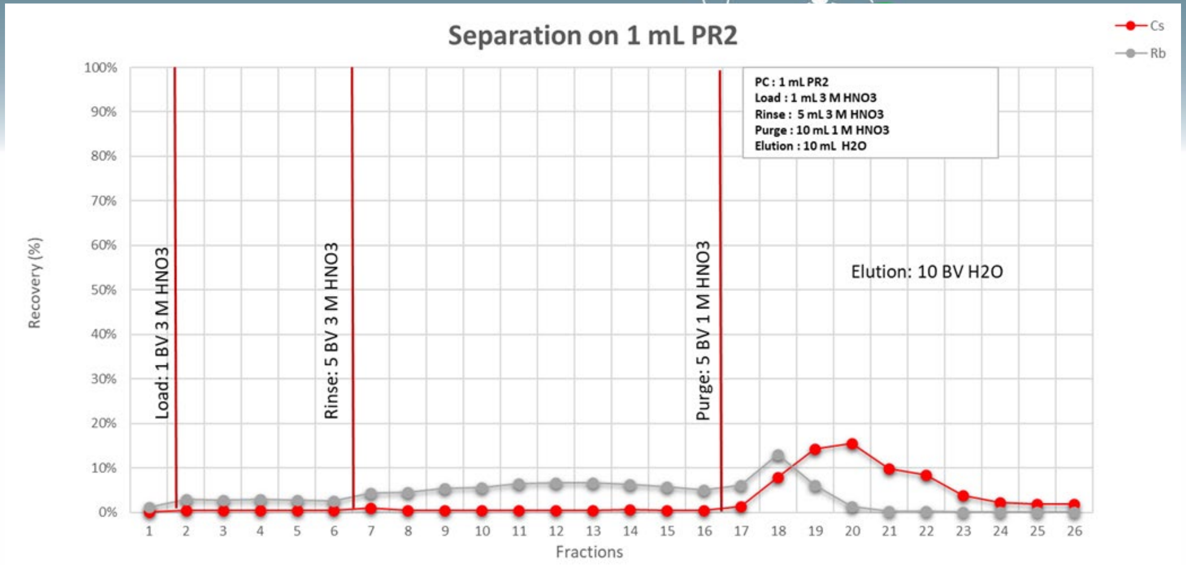


Fig. 23: Separation of 100 µg Rb and Cs on PR2 from 3 M HNO_3 solution

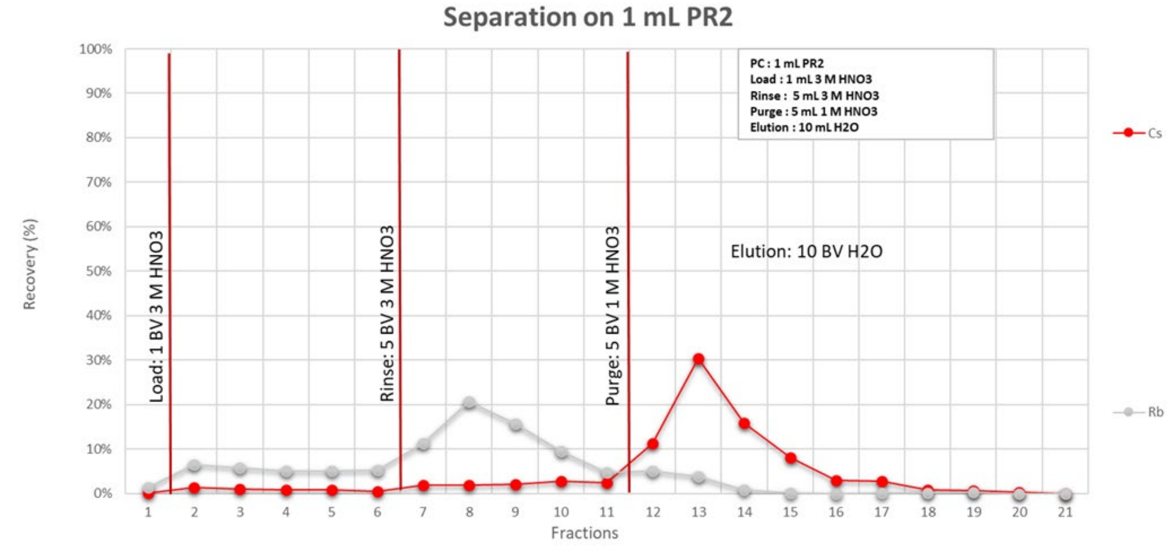


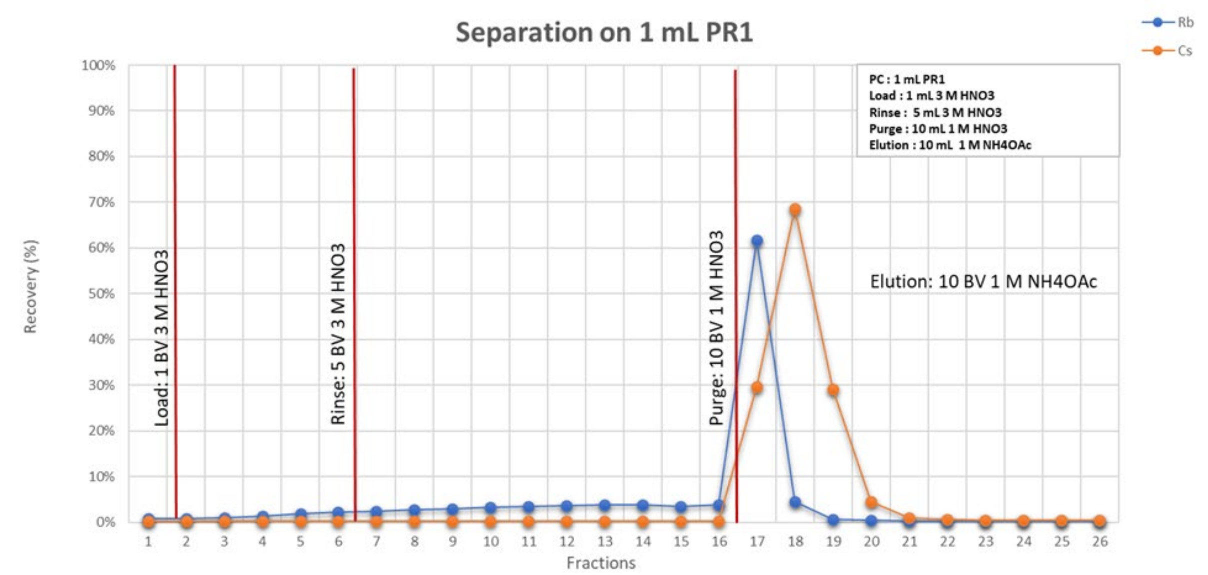
Fig. 24: Separation of 1000 µg Rb and Cs on PR2 from 3 M HNO_3 solution

► There is no elution of µg amounts of Rb and Cs from the PR1, PR2 and PR4 with water or weak acid. This contradicts the capacity and Dw ME experimental data.

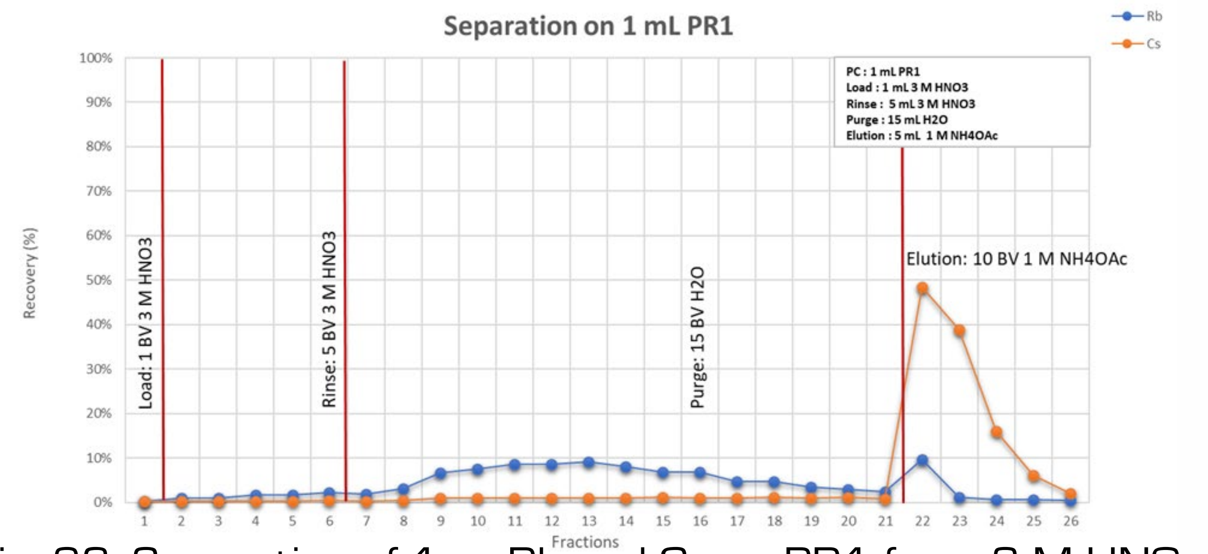
► Most likely ppb concentrations of Rb and Cs on PR1,2, 4-6 cannot be eluted with water or 0,01 M HNO_3.

► It is possible to separate "high" amounts (100 µg, 1000 µg) of Rb and Cs with PR1 and PR2. Elution of Rb is possible with 1 M HNO3, elution of Cs is possible with H2O (with "tail" of Rb in Cs fraction).

Elution tests with high-capacity prototype PR1



ig. 25: Separation of 1 µg Rb and Cs on PR1 from 3 M HNO_3 solution



ig. 26: Separation of 1 µg Rb and Cs on PR1 from 3 M HNO_3 solution

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Determination of low-level ^{135}Cs and $^{135}Cs/^{137}Cs$ atomic ratios in large volume of seawater by chemical separation coupled with triple-quadrupole inductively coupled plasma mass spectrometry measurement for its oceanographic applications

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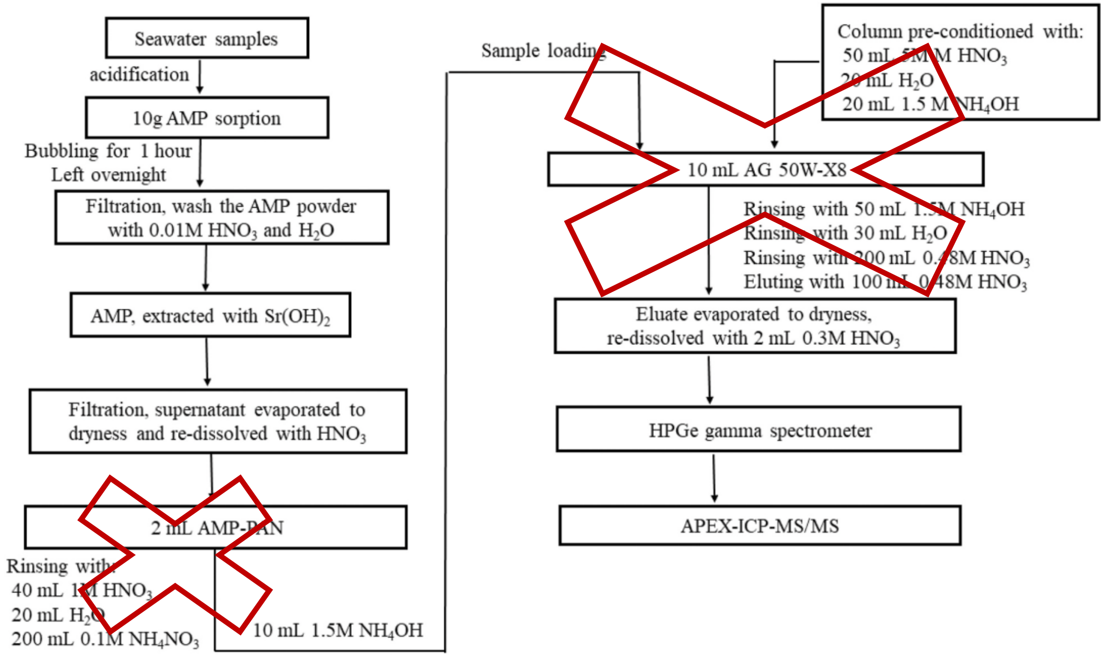


Fig. 3. Chemical procedure for separation of cesium form large volume seawater sample

Direct sorption of Rb and Cs from seawater with 2 mL cartridges IL prototypes

Flow rate is 1 BV/min

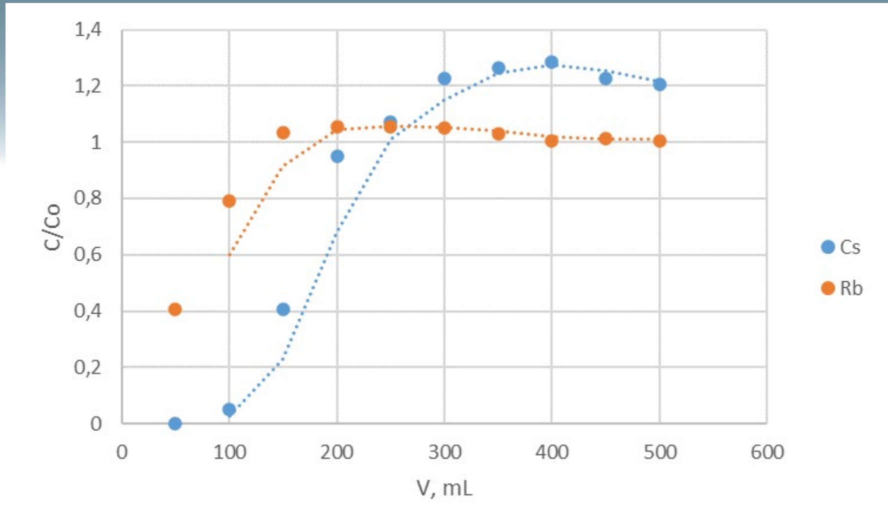


Fig. 27. Sorption curves of Cs and Rb on PR7 from seawater (pH 2).

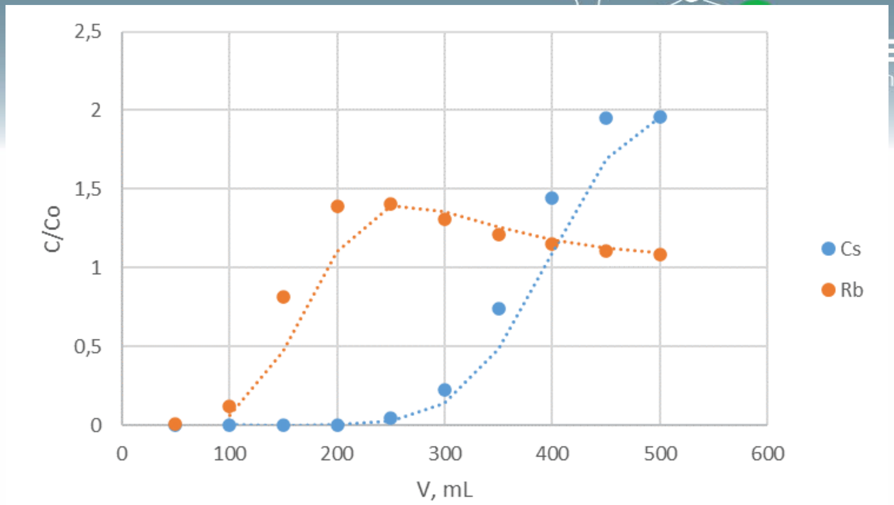


Fig. 28. Sorption curves of Cs and Rb on PR9 from seawater (pH 2).

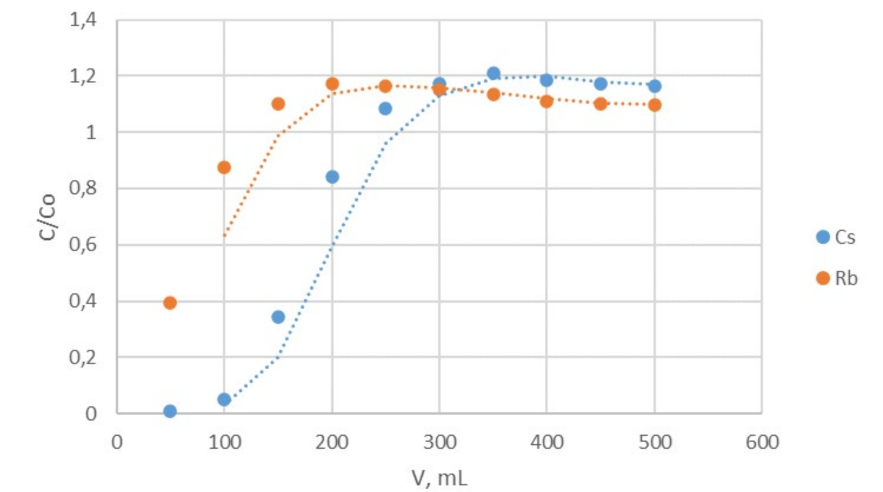


Fig. 29. Sorption curves of Cs and Rb on PR7 from seawater (pH 7,9).

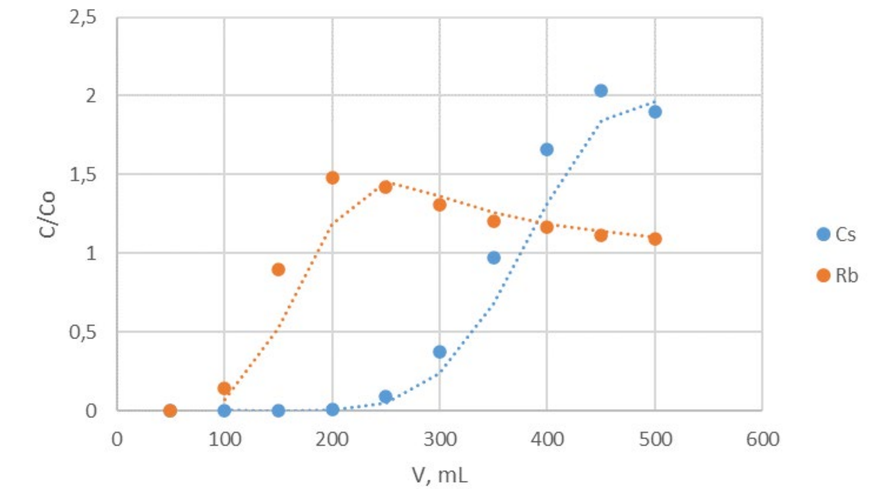


Fig. 30. Sorption curves of Cs and Rb on PR9 from seawater (pH 7,9).

Direct sorption of Rb and Cs from seawater with 2 mL cartridges IL prototypes

Flow rate is 1 BV/min

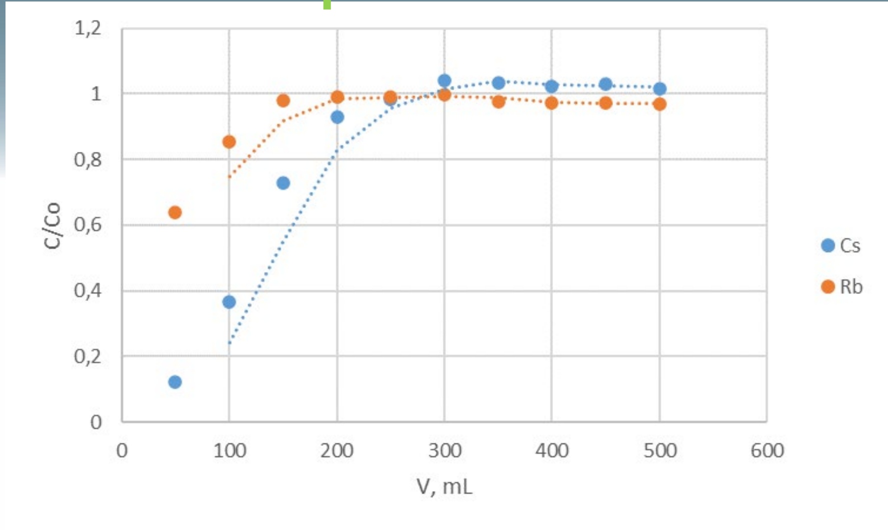


Fig. 31. Sorption curves of Cs and Rb on PR10 from seawater (pH 2).

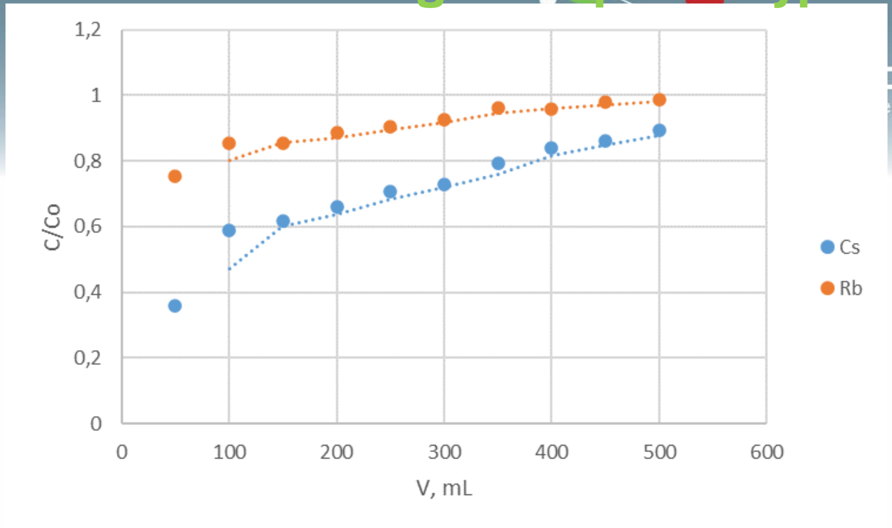


Fig. 32. Sorption curves of Cs and Rb on PR11 from seawater (pH 2).

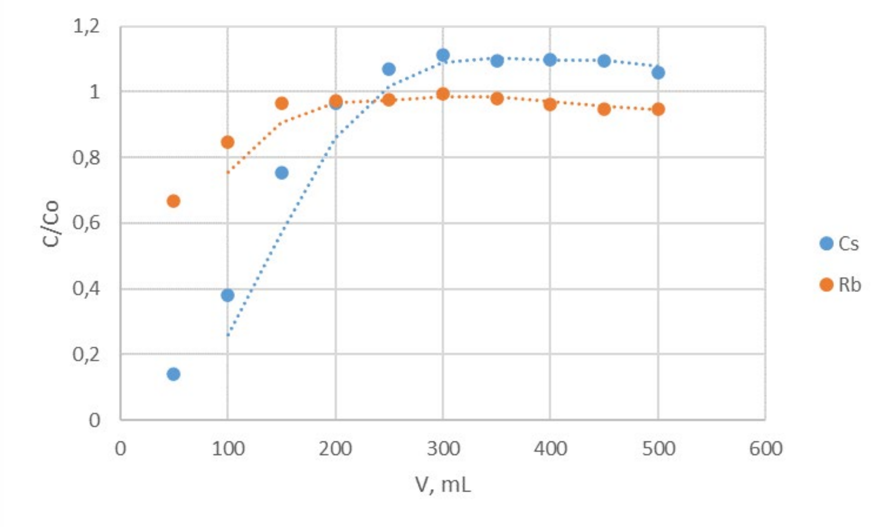


Fig. 33. Sorption curves of Cs and Rb on PR10 from seawater (pH 7,9).

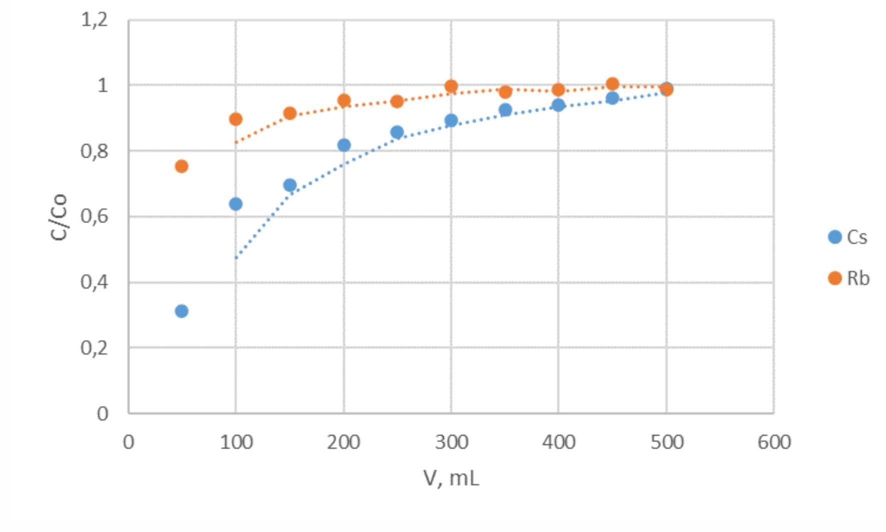


Fig. 34. Sorption curves of Cs and Rb on PR11 from seawater (pH 7,9).

Conclusions

► Calixarene based prototypes show high selectivity for Rb and Cs in wide range of HNO_3 concentrations.

► For the most of prototypes full capacities are close to theoretical, but for PR9 and BEBH PR2, 10,11 they are higher.

► Four calixarene and ionic liquids based prototypes with high-capacity (PR 7, 9-11) were developed for separation of Rb and Cs from HNO_3 solutions in wide range of concentration (0,01 – 1 M). It is possible to eluted Rb and Cs with 10 M HNO_3.

► Ionic liquids prototype PR9 can be used for direct separation of Rb and Cs from seawater.

► Two prototypes with high-capacity (PR 1,2) were developed for separation of Rb and Cs from 3 M HNO_3. But elution of Rb and Cs with water are strongly dependent on initial concentration of metals. It is no possible to elute them with water after sorption from 1 µg/L solutions.

► Efficiencies of sorption for Cs on PR 1, 2, 7, 9-11 are near 50% even in 1 M KNO_3.

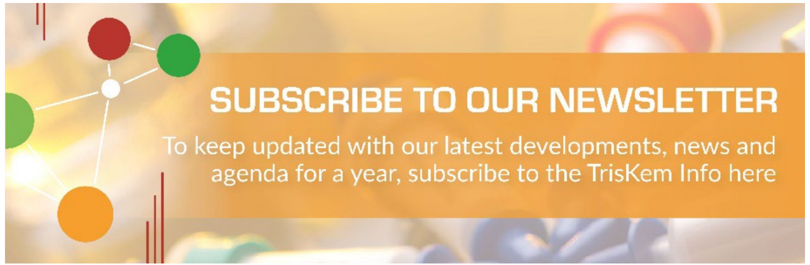
These prototypes can be used for:

► concentrating and separating of Cs and Rb isotopes from low (PR 7, 10) and elevated (PR 1, 2, 13) HNO_3 solutions for analysis of the environmental and decommissioning samples with ICP-MS and γ-spectroscopy.

► direct sorption of Cs and Rb isotopes from seawater samples for analysis with ICP-MS (PR 9).

► direct sorption of Cs and Rb isotopes from 3 M HNO_3 solutions of spent nuclear fuel processing (PR 1, 2, 13).

Thank you for your attention!



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