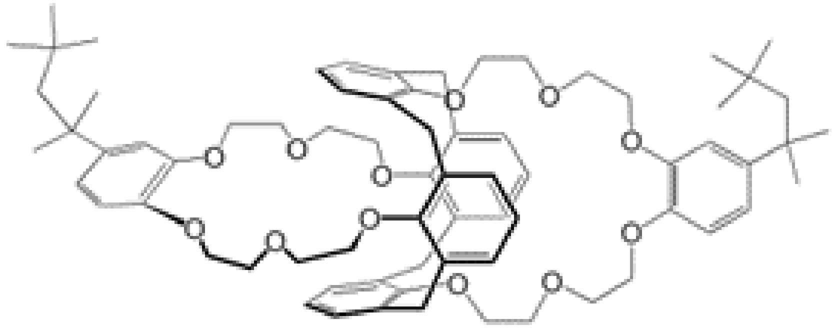
Calixarene based Cs resins

Illarion Dovhyi

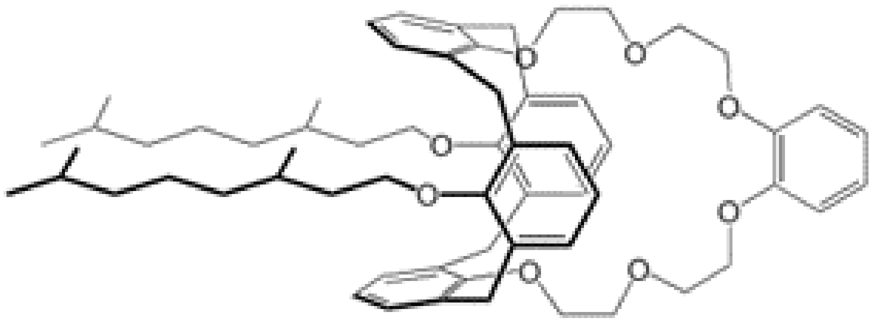
Raddec-Triskem International Technical Workshop, 18th April 2024

TRISKEM
Expertise in Separation Chemistry

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)

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 elevated acid solutions with possibility of elution with water or weak acid.

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

► to prepare prototypes based on the different calixarenes

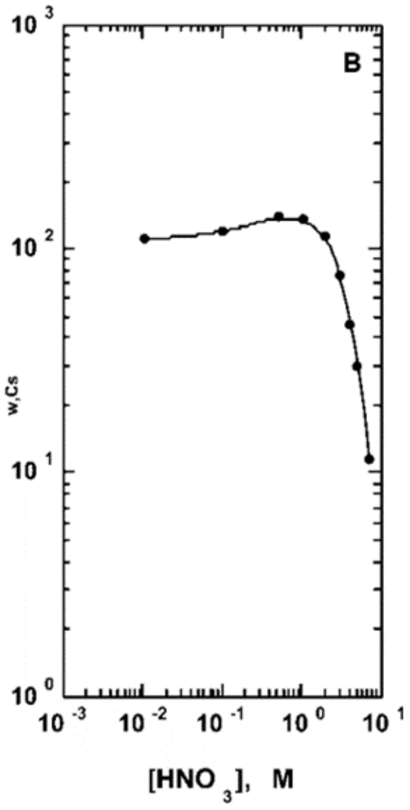
► to study dependence of D_w of different element on prototypes in HNO_3 and HCl

► 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

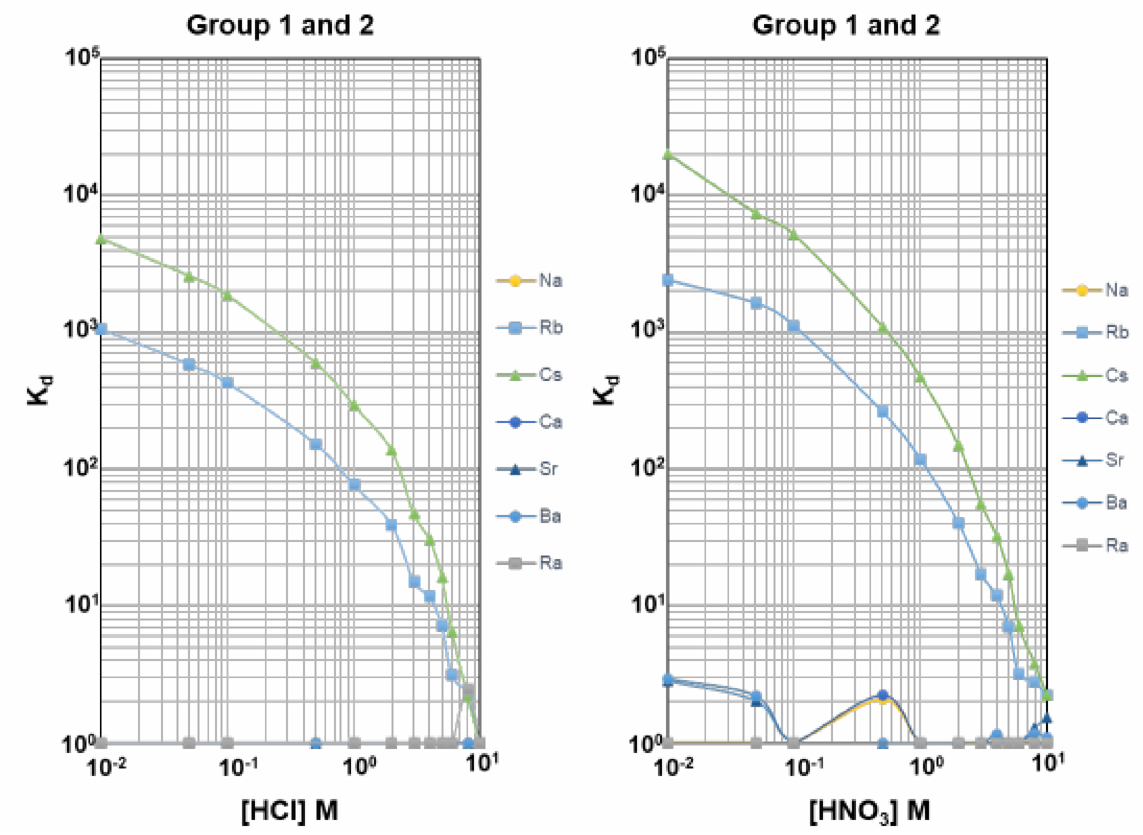
LITERATURE REVIEW



Cs sorption on 0.05 M BC6B in 1,2-DCE supported on Amberchrom CG-71 m [Dietz, 2006].

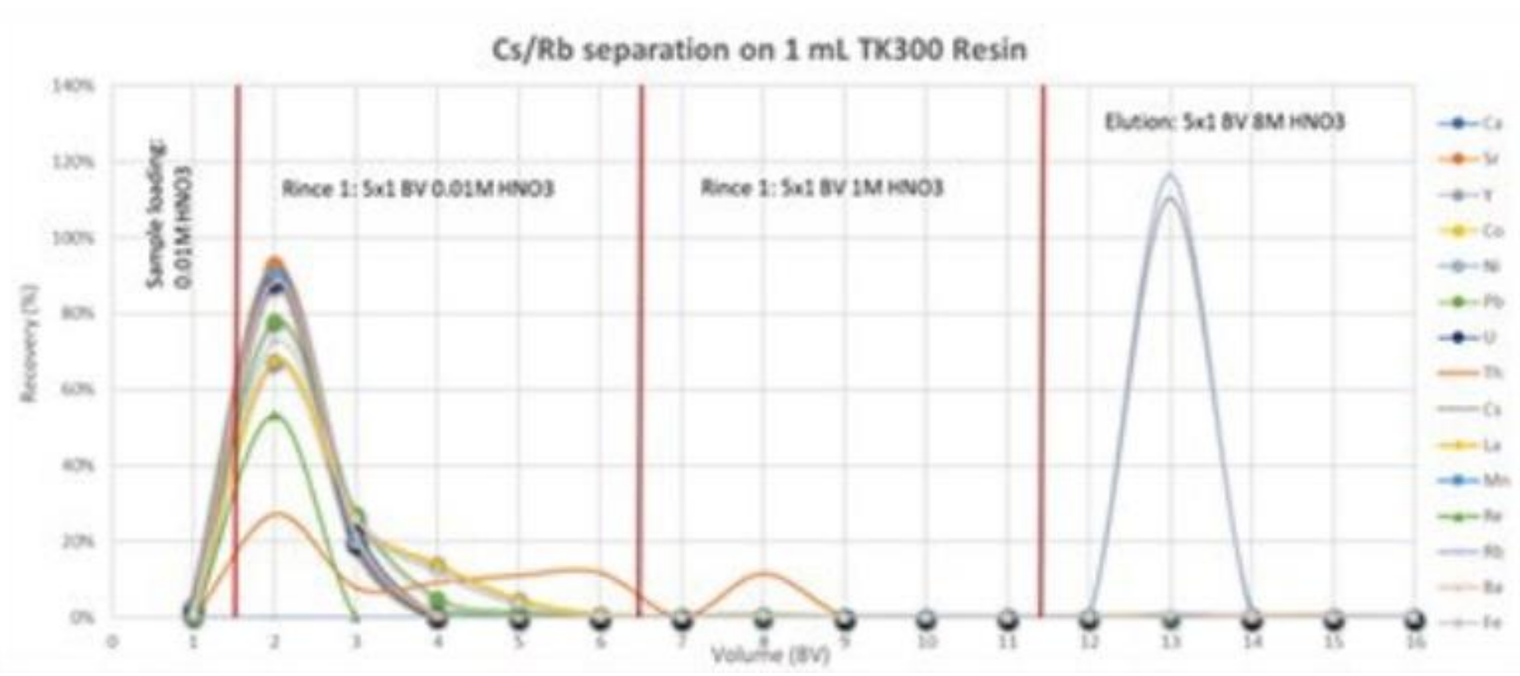
TK300 resin

- 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)

LITERATURE REVIEW



- 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)

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

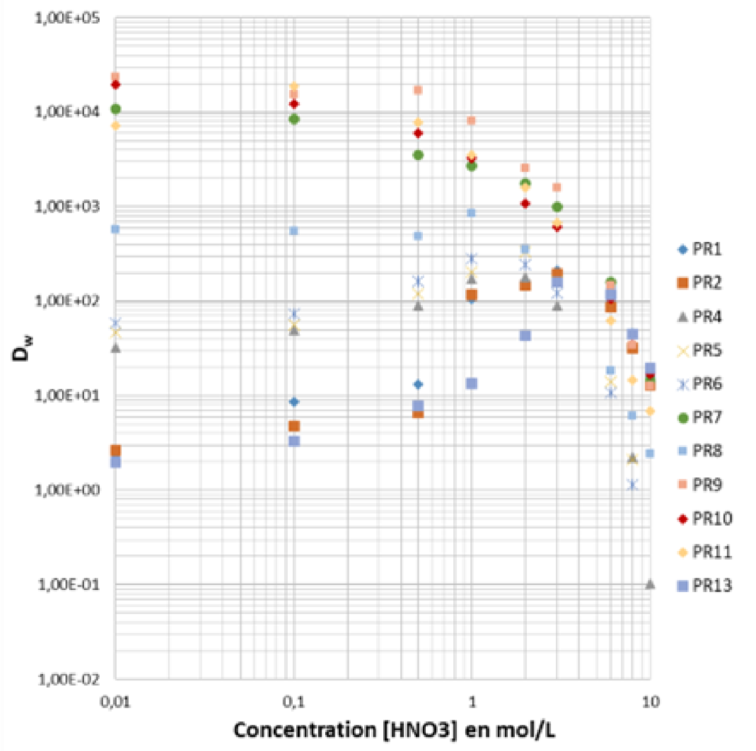


Fig. 1: Acid dependency of Dw for Cs^+ on PR1-13 in HNO_3

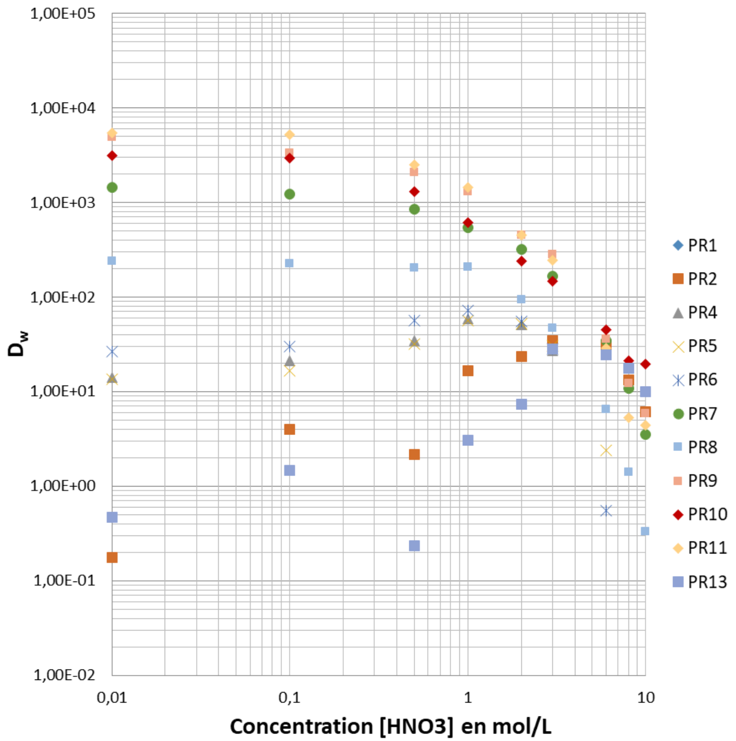


Fig. 2: Acid dependency of Dw for Rb^+ on PR 1-13 in HNO_3

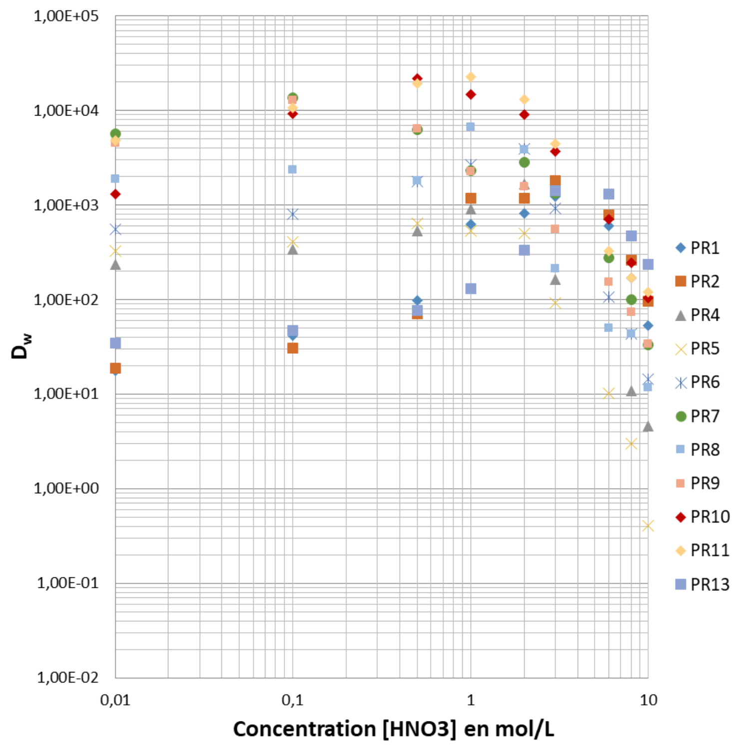


Fig. 3: Acid dependency of Dw for Tl^+ on PR1-13 in HNO_3

Most of element were not sorbed in HNO_3
Dw Cs > Dw Rb
PR7,9-11 > PR1-6,8,13

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

D_W of elements in HCl

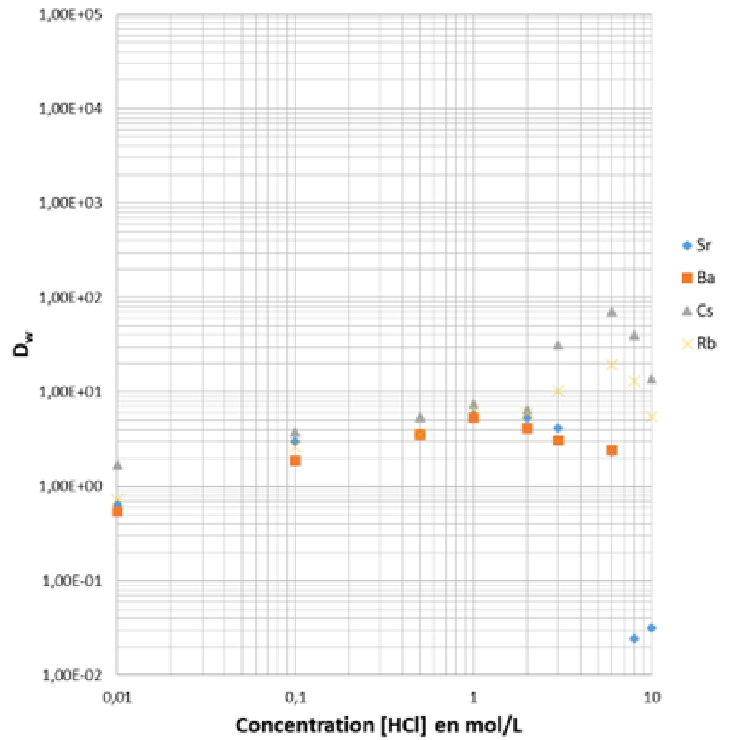


Fig. 4: Acid dependency Dw for various ions on PR1 in HCl

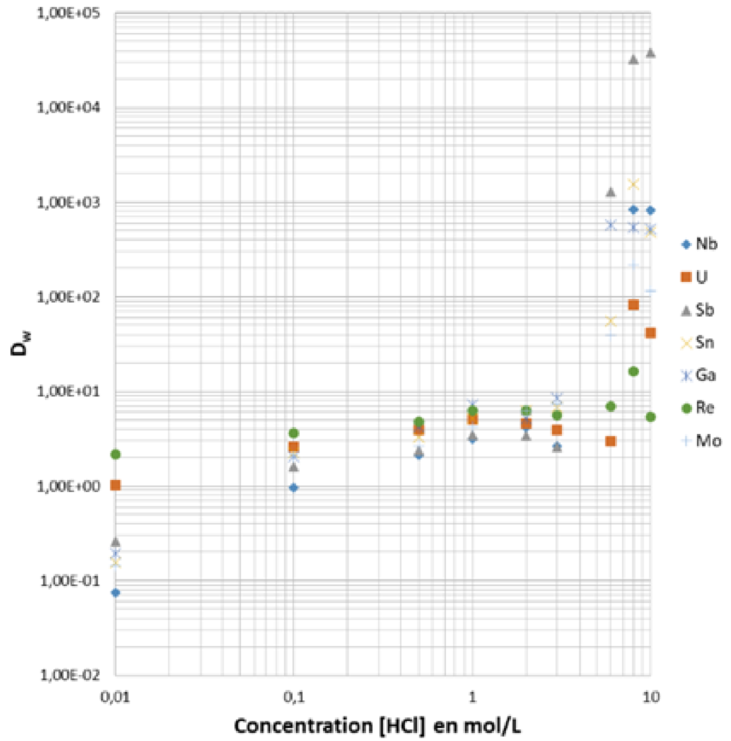


Fig. 5: Acid dependency Dw for various ions on PR1 in HCl

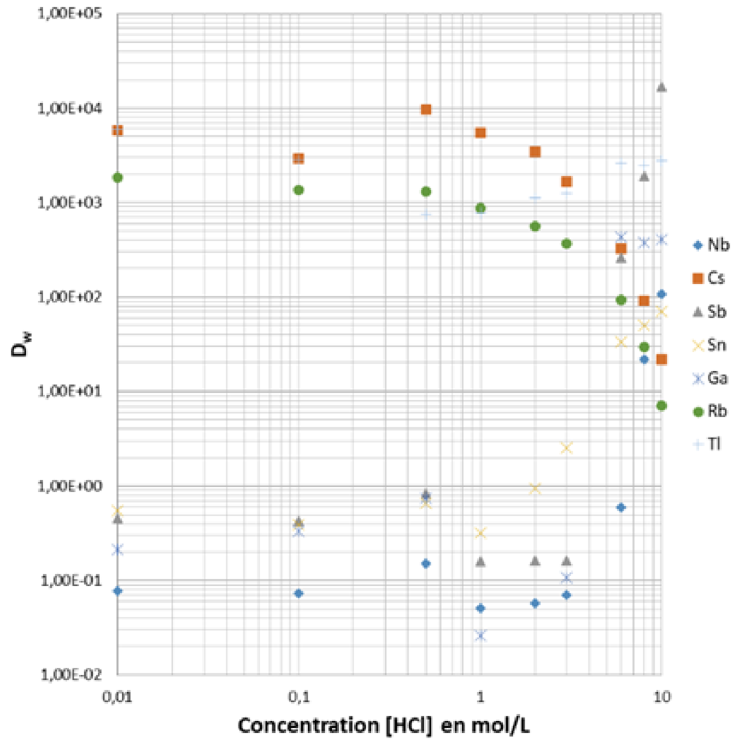


Fig. 6: Acid dependency Dw for various ions on PR7 in HCl

- 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

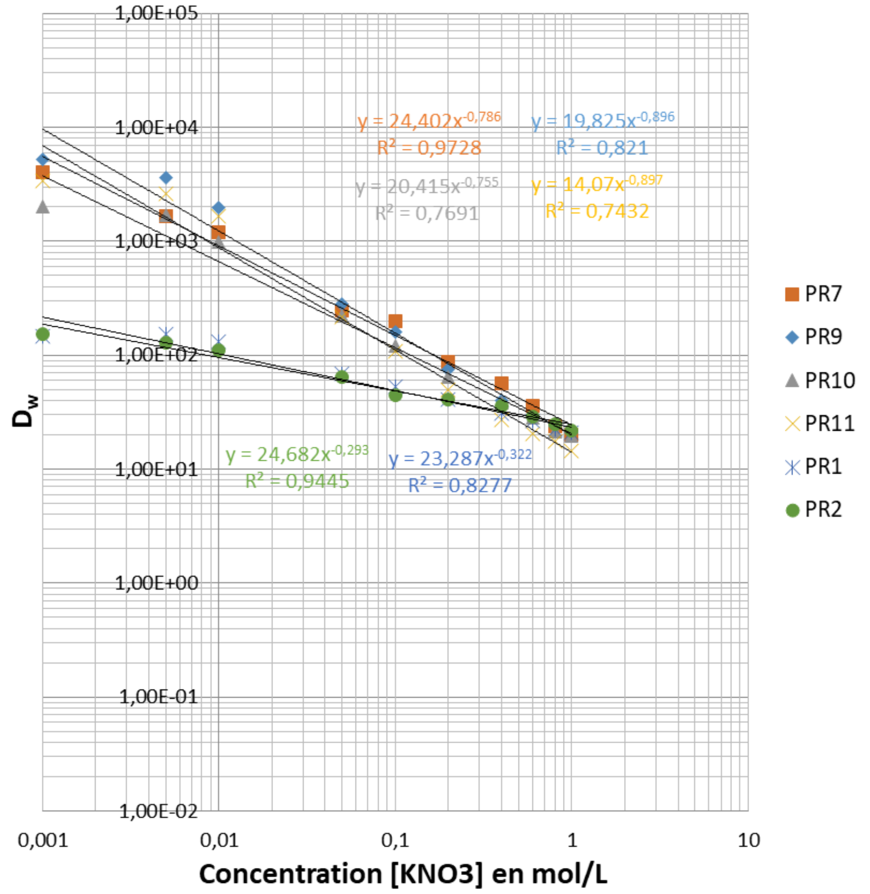


Fig. 7: KNO_3 dependency of Dw for Cs ion on high-capacity PR 1,2,7-11 in 1 M HNO_3

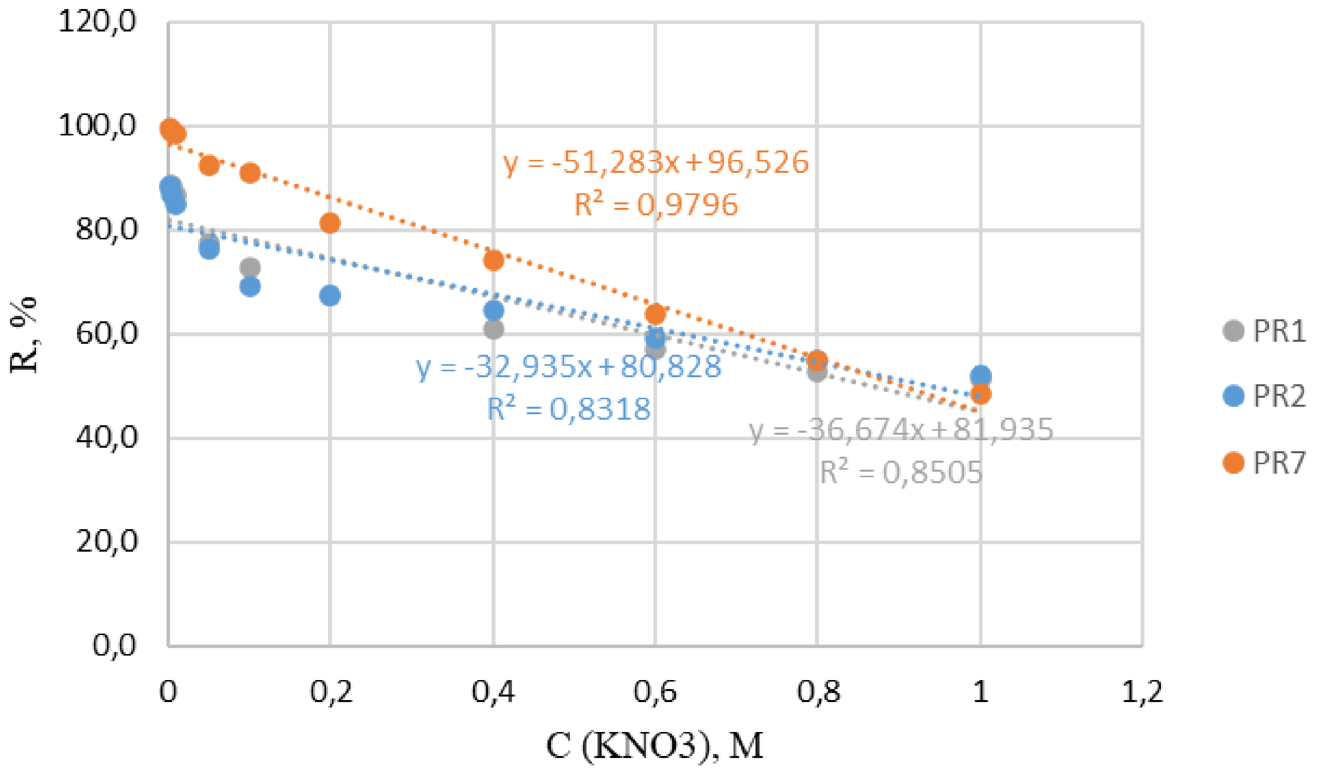


Fig. 8: KNO_3 dependency of efficiency of sorption on high-capacity PR 1,2,7 in 1 M HNO_3

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

KNO_3 dependency of Dw for Cs ion

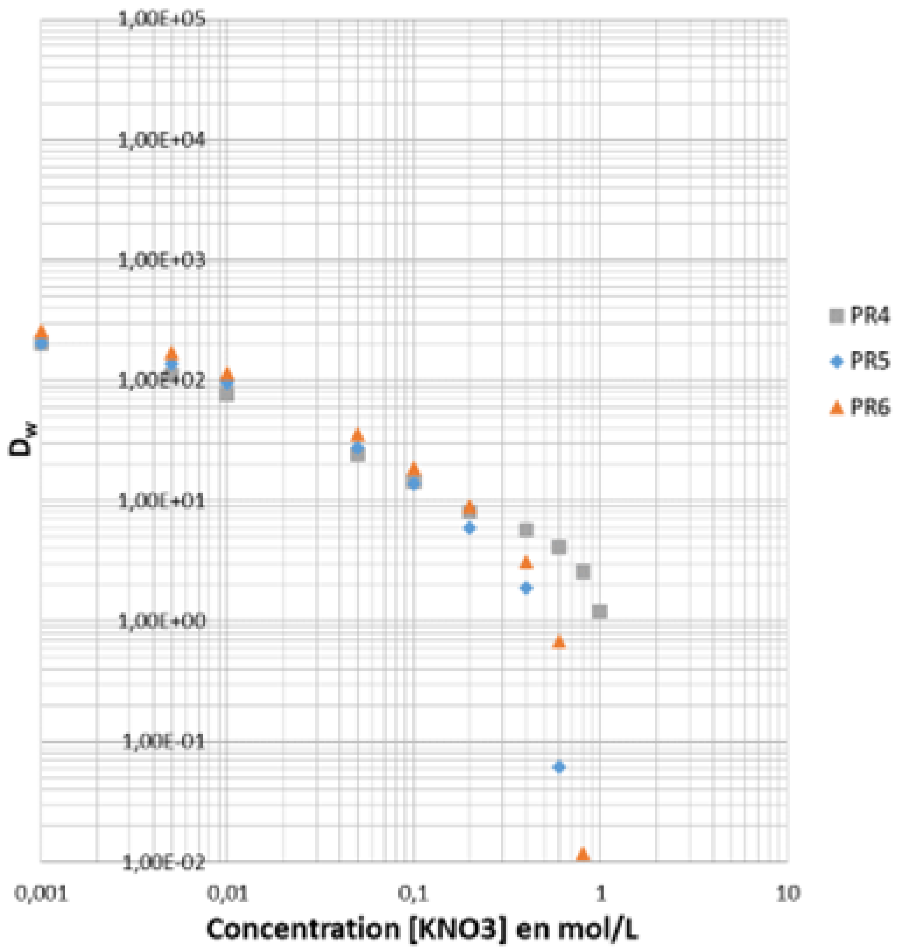


Fig. 9: KNO_3 dependency of efficiency of sorption on low-capacity PR 4-6 in 1 M HNO_3

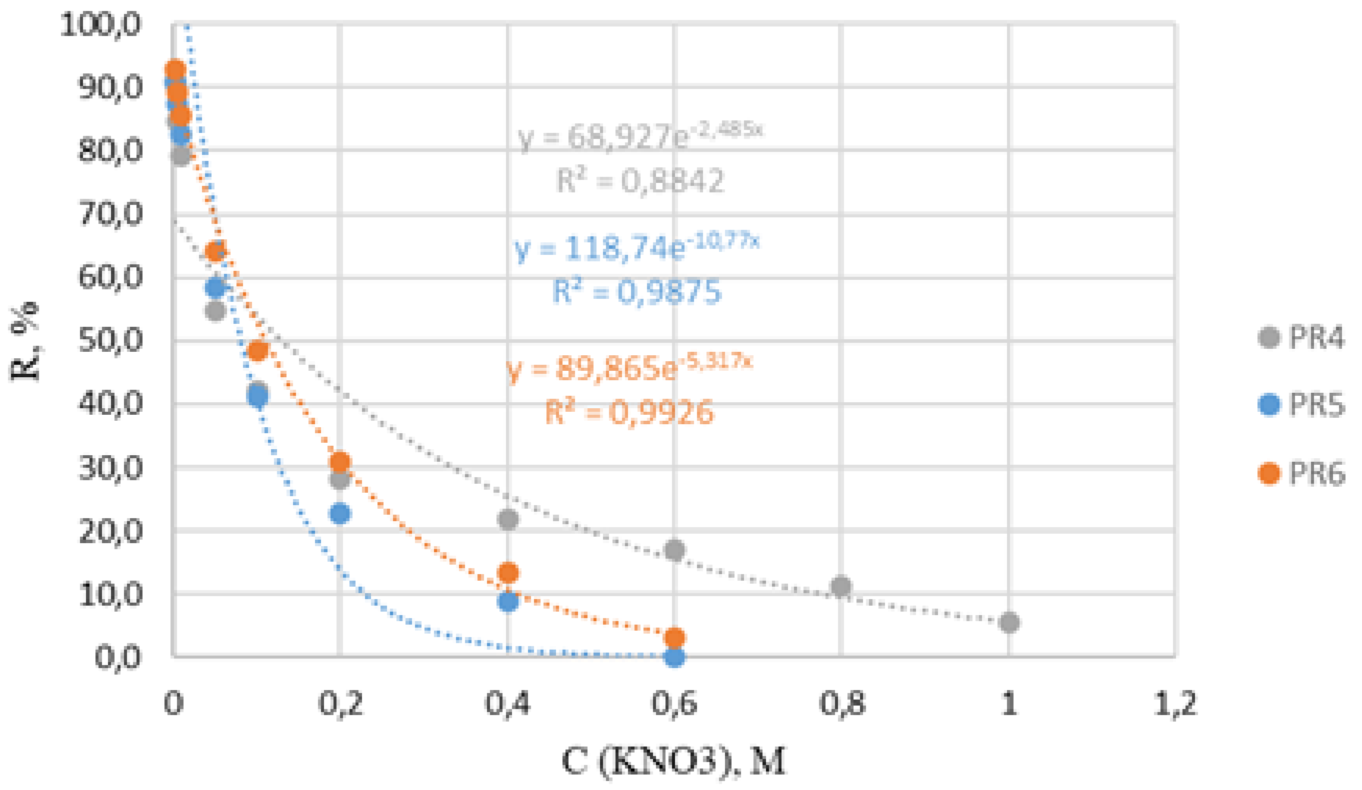


Fig. 10: KNO_3 dependency of efficiency of sorption on low-capacity PR 4-6 in 1 M HNO_3 in the presence of KNO_3

► There are no sorption in 1 M KNO_3

Capacity of prototypes (column experiment)

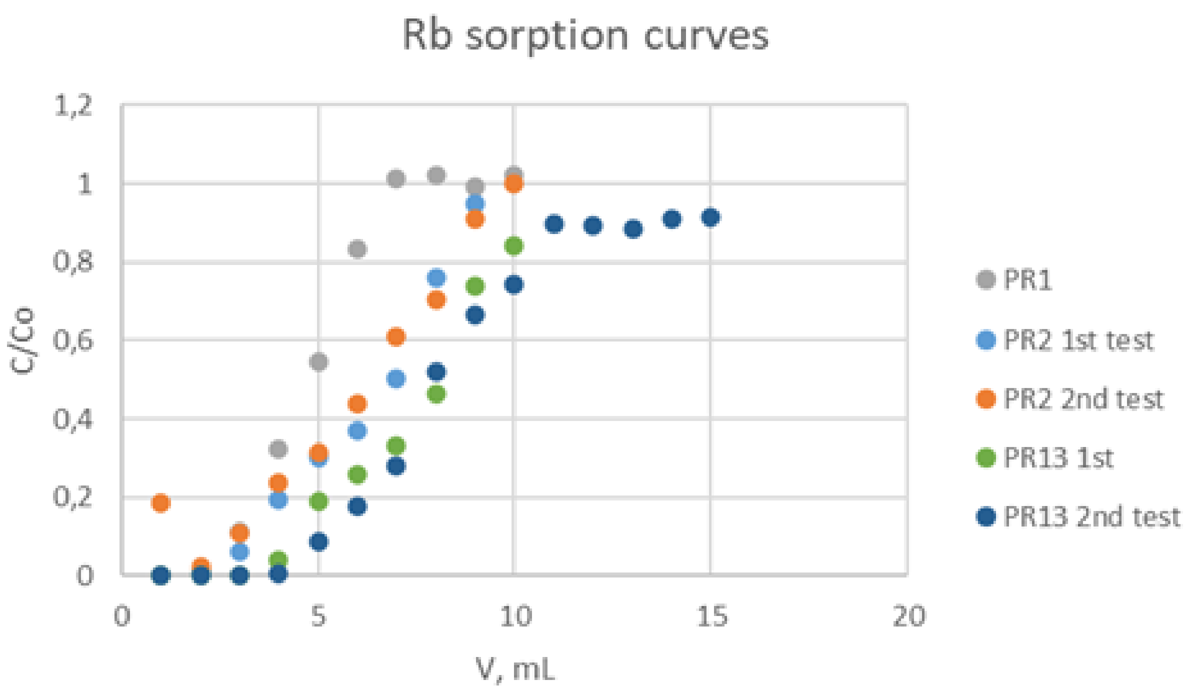


Fig. 11: Sorption curves of Rb on high-capacity prototypes in 3 M HNO_3. Initial concentration of Rb is 2,5 mg/mL.

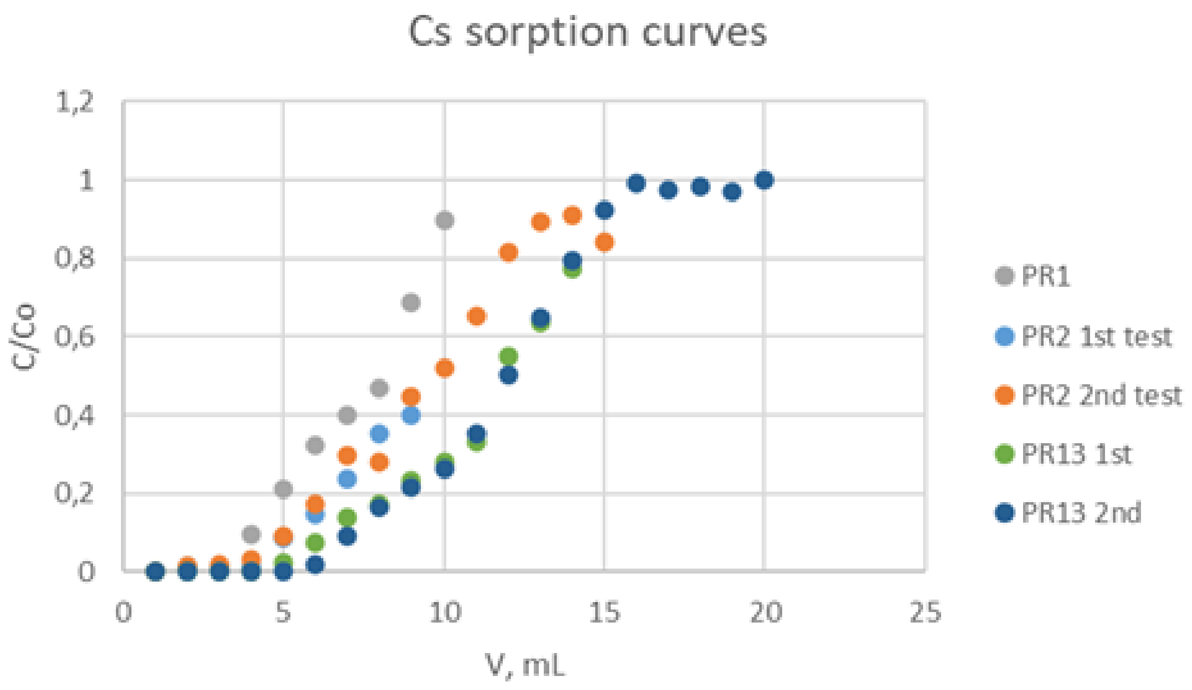


Fig. 12: Sorption curves of Cs on high-capacity prototypes in 3 M HNO_3. Initial concentration of Cs is 2,5 mg/mL.

Capacity of prototypes (column experiment)

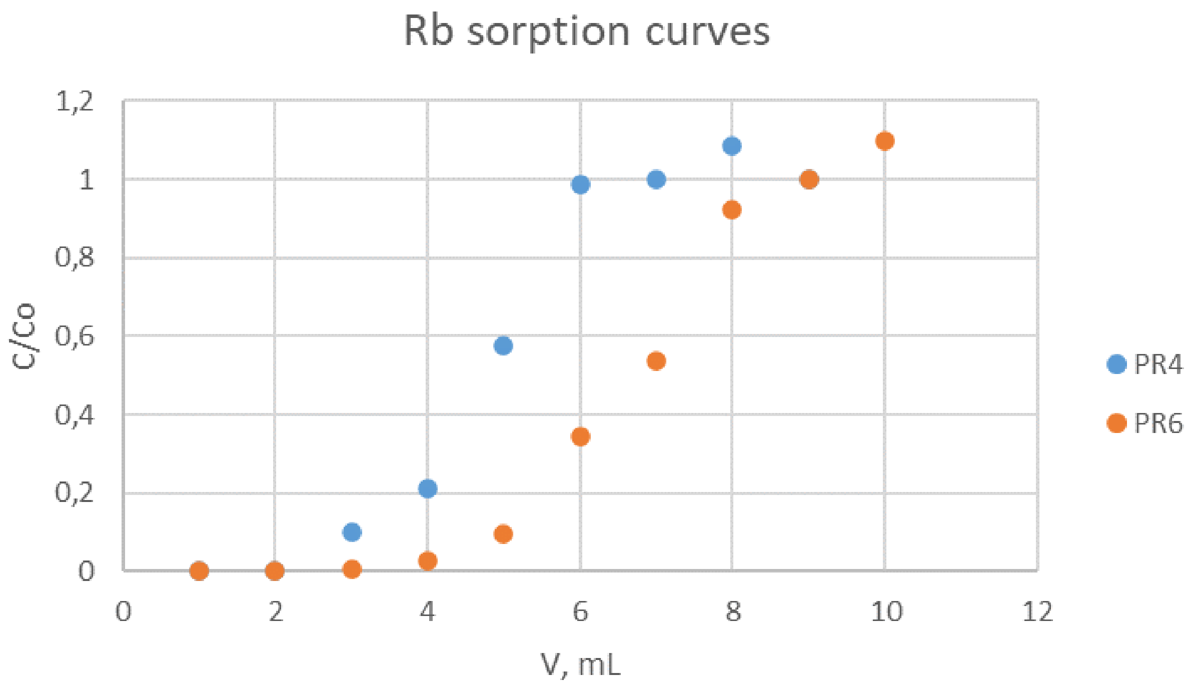


Fig. 13: Sorption curves of Rb on low-capacity prototypes in 3 M HNO_3. Initial concentration of Rb is 0,25 mg/mL.

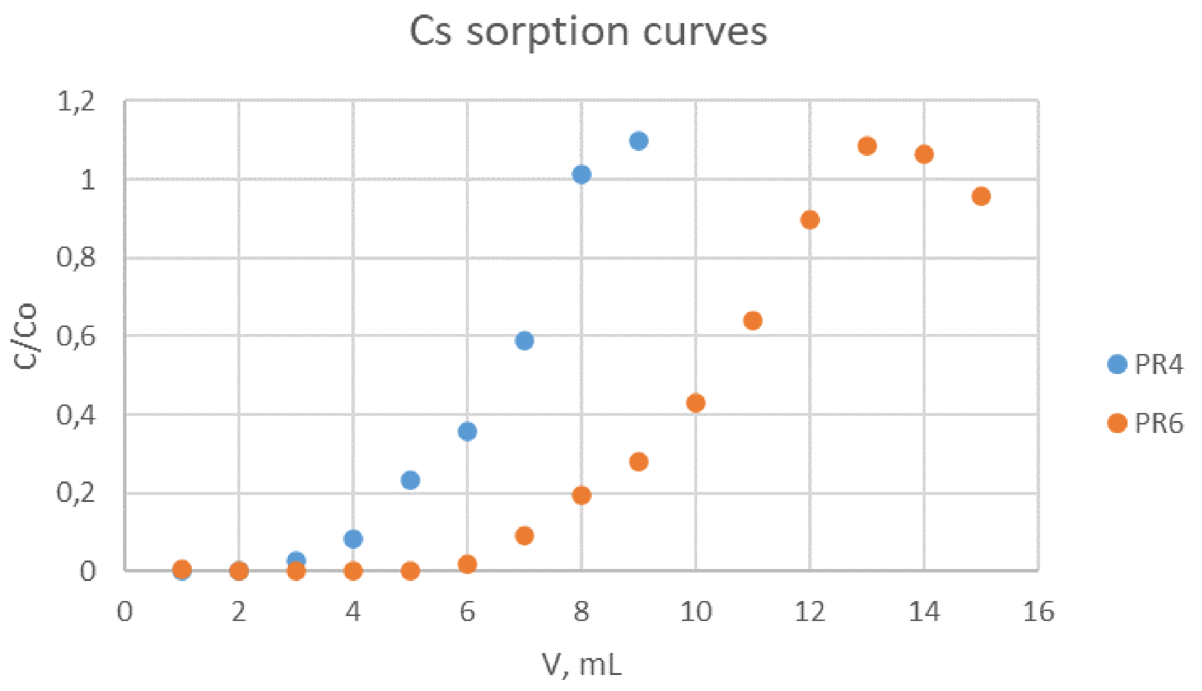


Fig. 14: Sorption curves of Cs on low-capacity prototypes in 3 M HNO_3. Initial concentration of Cs is 0,25 mg/mL.

Capacity of IL prototypes (column experiment)

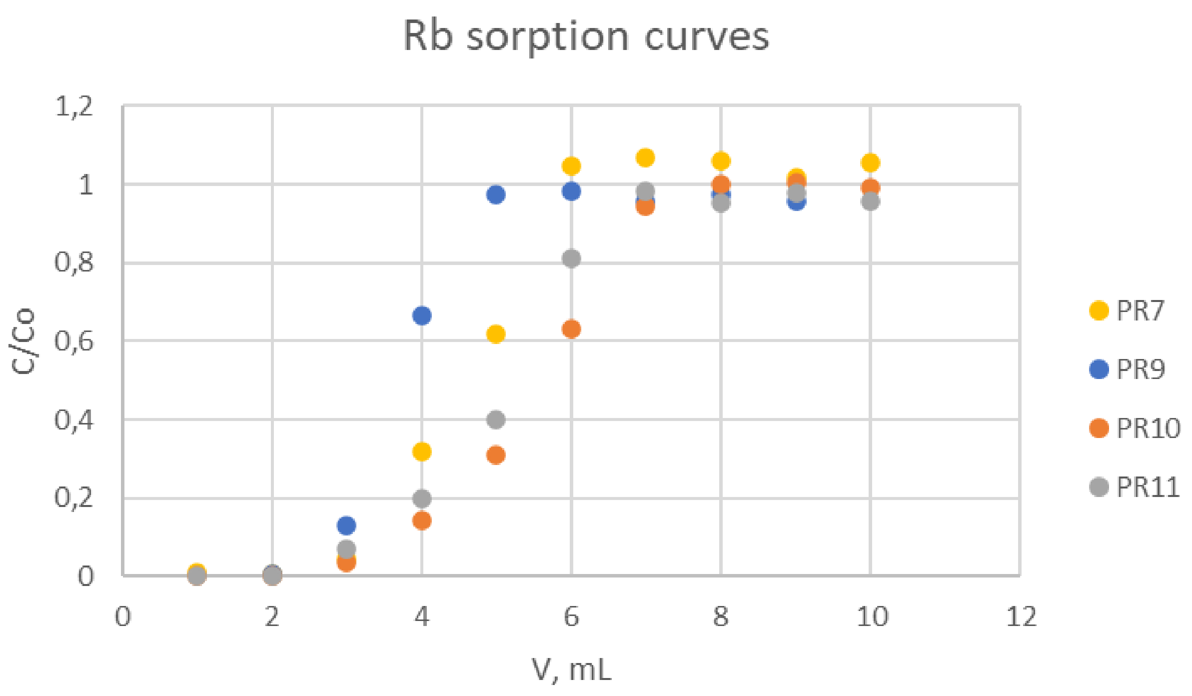


Fig. 15: Sorption curves of Rb on high-capacity prototypes in 1 M HNO_3.
Initial concentration of Rb is 2,5 mg/mL.

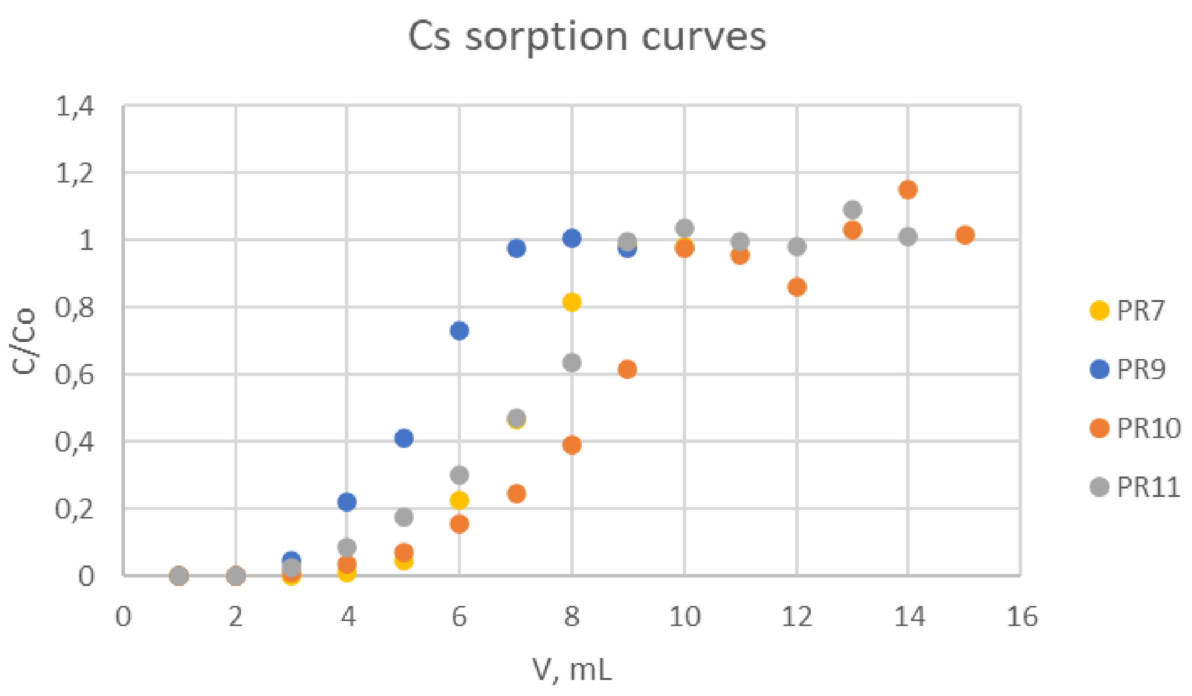


Fig. 16: Sorption curves of Cs on high-capacity prototypes in 1 M HNO_3.
Initial concentration of Cs is 2,5 mg/mL.

Capacity of IL prototypes (column experiment)

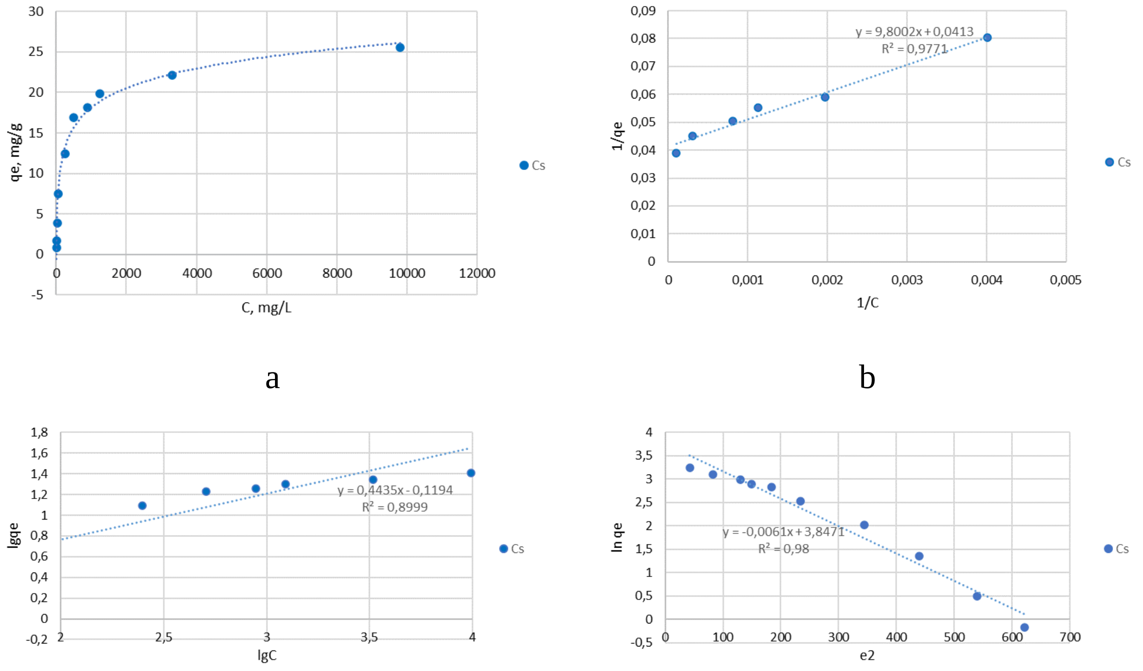
Table 2. Capacities of prototypes

PR	Ion	DEC, mg · g^{-1}	FDEC, mg · g^{-1}	g_{theor}, mg · 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)

Table 2. Capacities of prototypes

PR	Ion	DEC, mg · g^{-1}	FDEC, mg · g^{-1}	g_{theor}, mg · g^{-1}	C (CA), mol/L	Elution
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)



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.

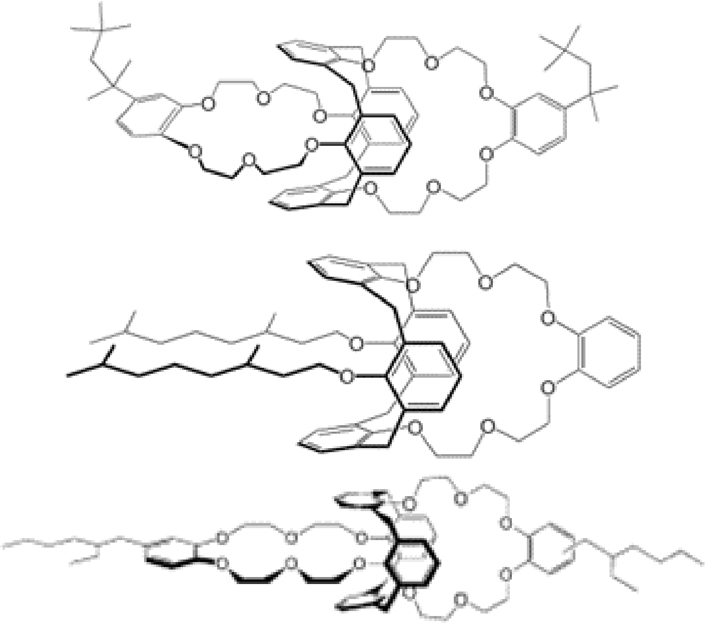
Capacity of PR2 (static experiment)

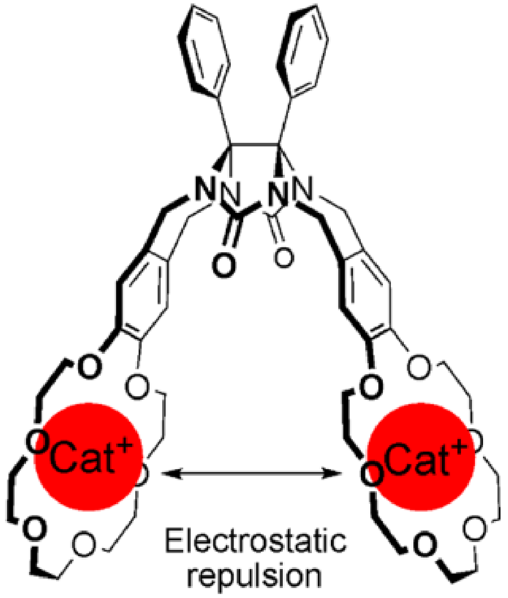
Table 4. – Parameters of the sorption isotherms of Cs on PR2

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

► For the most of prototypes full Cs and Rb capacities are close to 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.





C

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

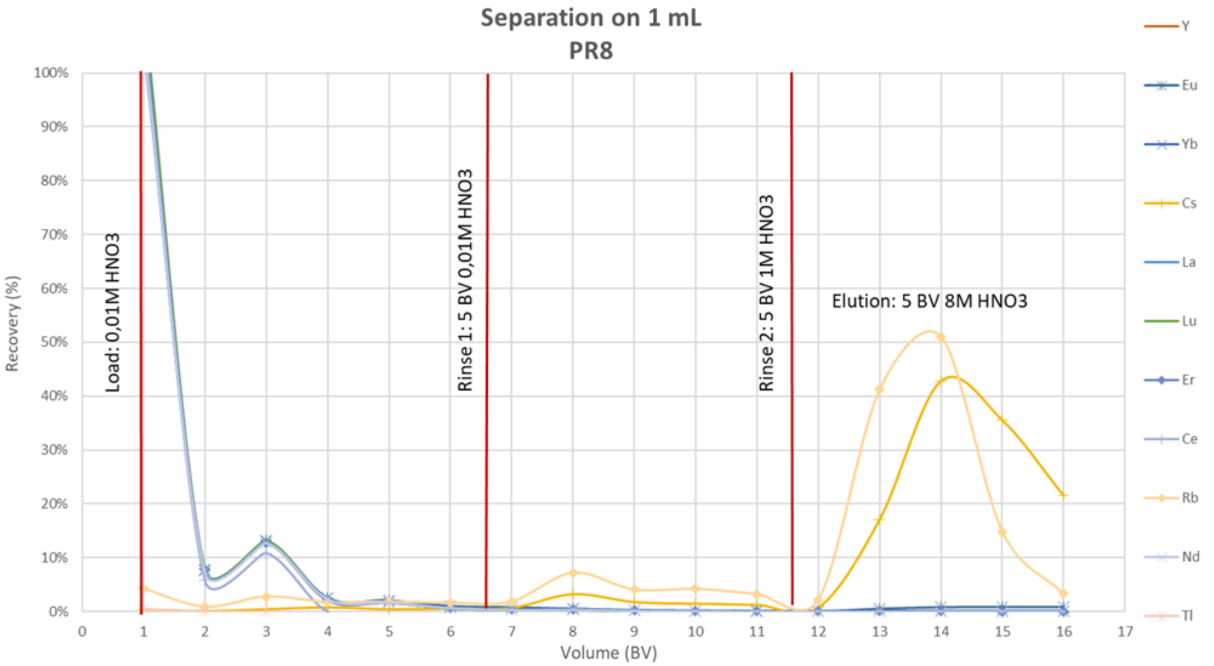


Fig. 18: Separation of Rb and Cs on PR8 (loading in 0,01 M HNO_3)

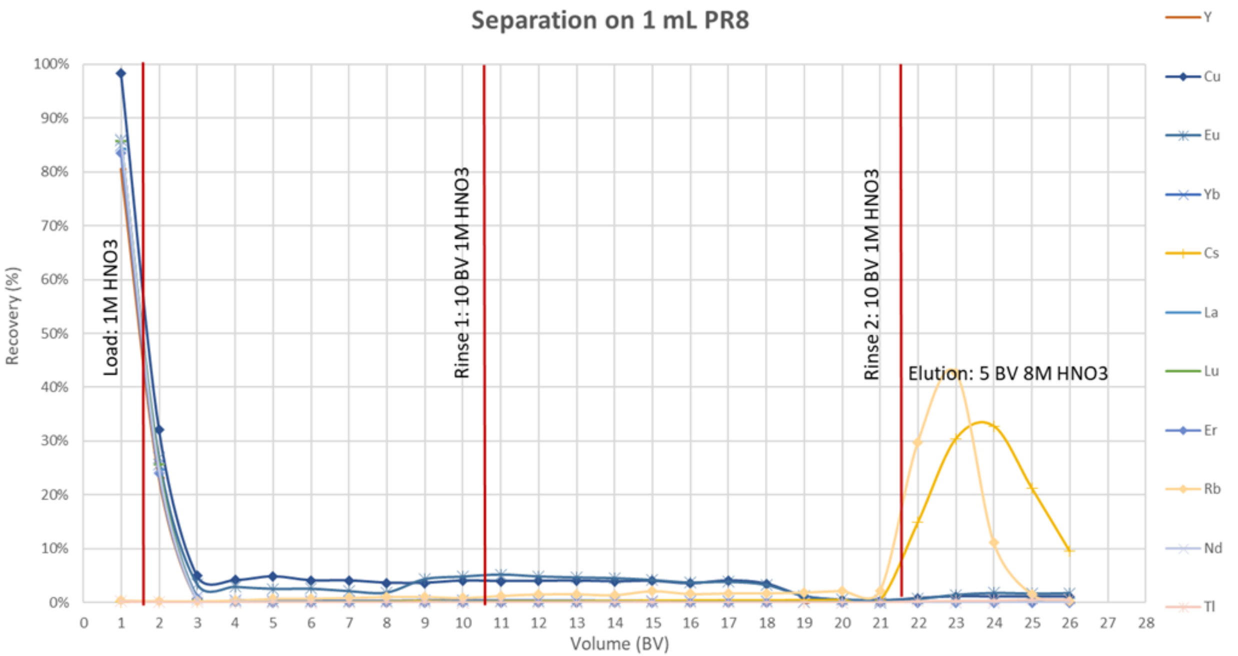


Fig 19: Separation of Rb and Cs on PR8 (loading in 1 M HNO_3 solution)

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

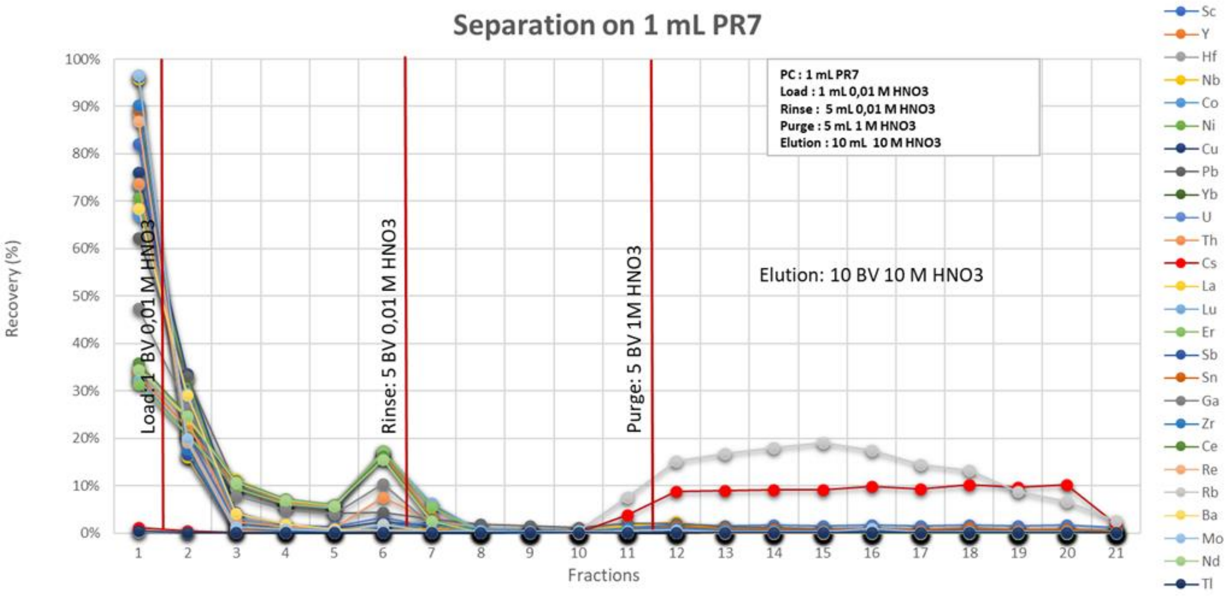


Fig. 20: Separation of Rb and Cs on PR7 (loading in 0,01 M HNO_3)

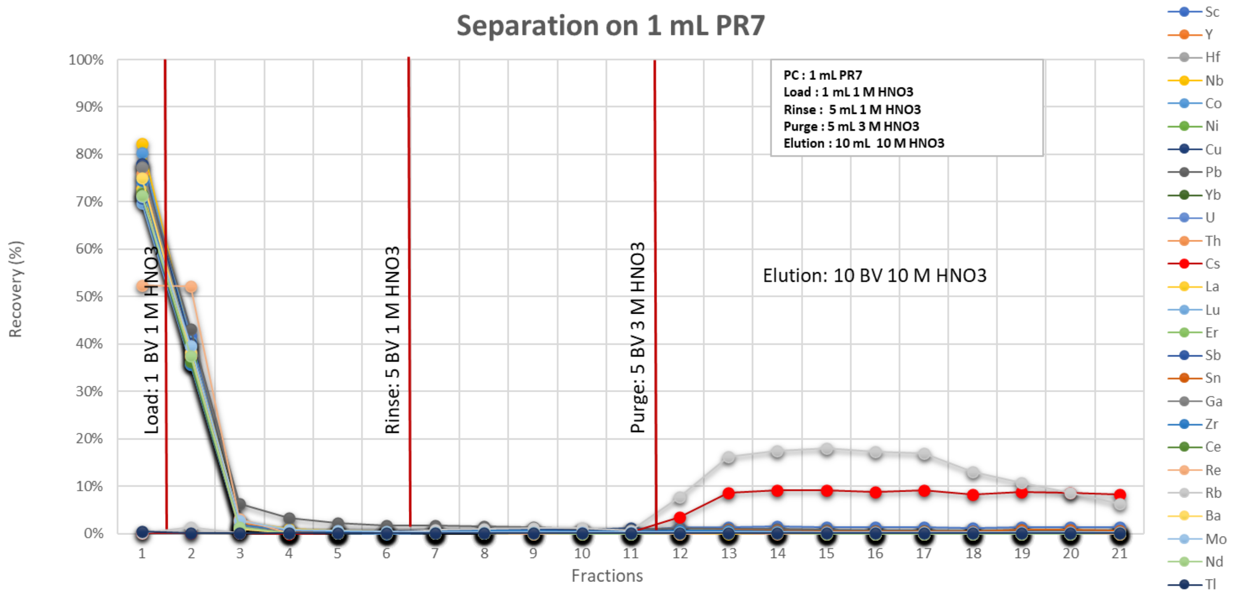


Fig. 21: Separation of Rb and Cs on PR7 (loading in 1 M HNO_3 solution)

Elution tests with high-capacity prototype (PR2)

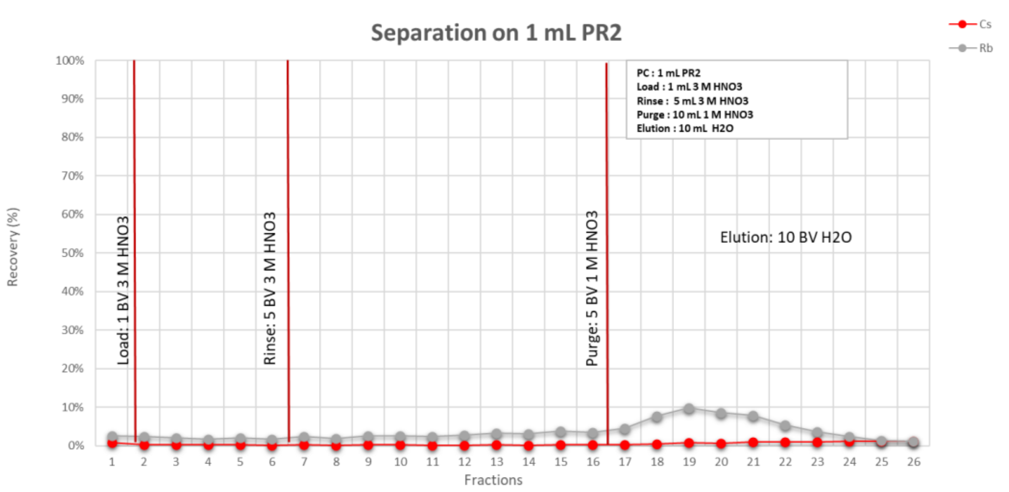


Fig. 22: Separation of **1 µg** Rb and Cs on PR2

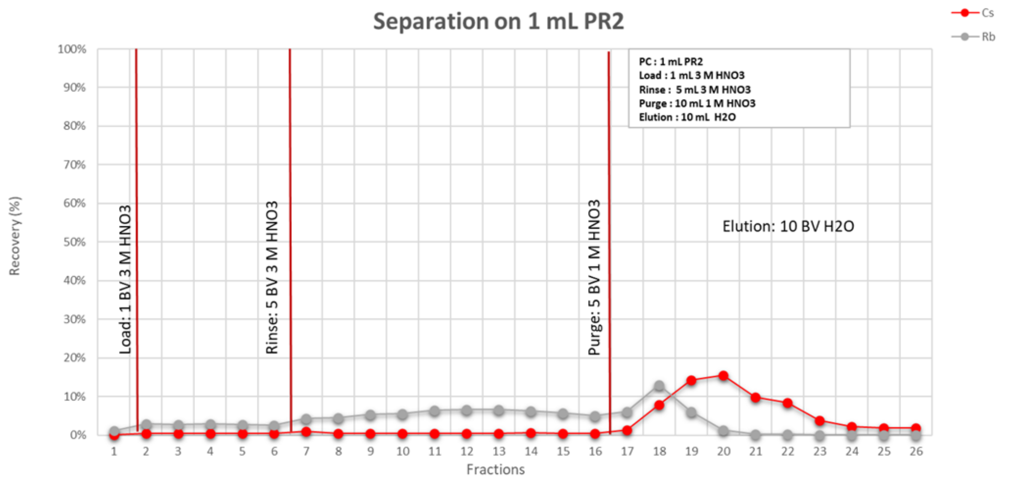


Fig. 23: Separation of **100 µg** Rb and Cs on PR2

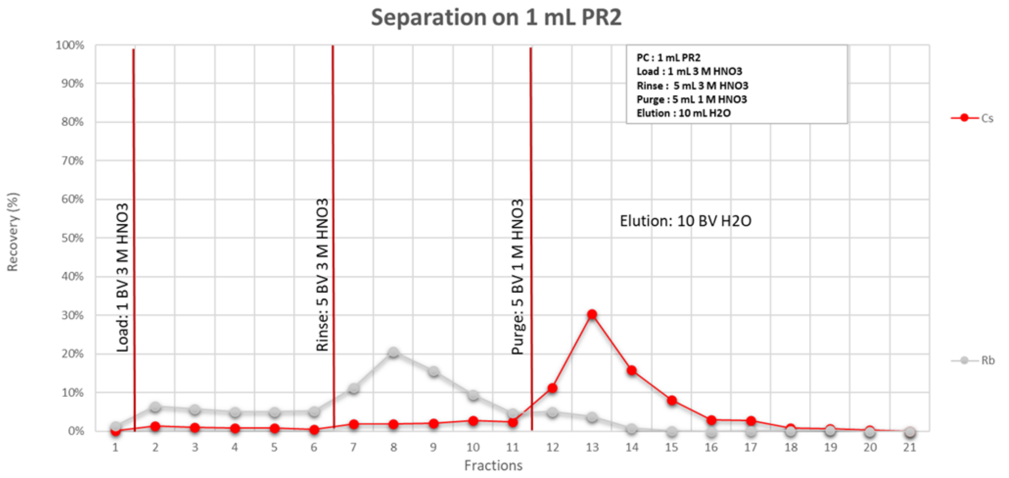


Fig. 24: Separation of **1000 µg** Rb and Cs on PR2

► 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.

► ppb concentrations of 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

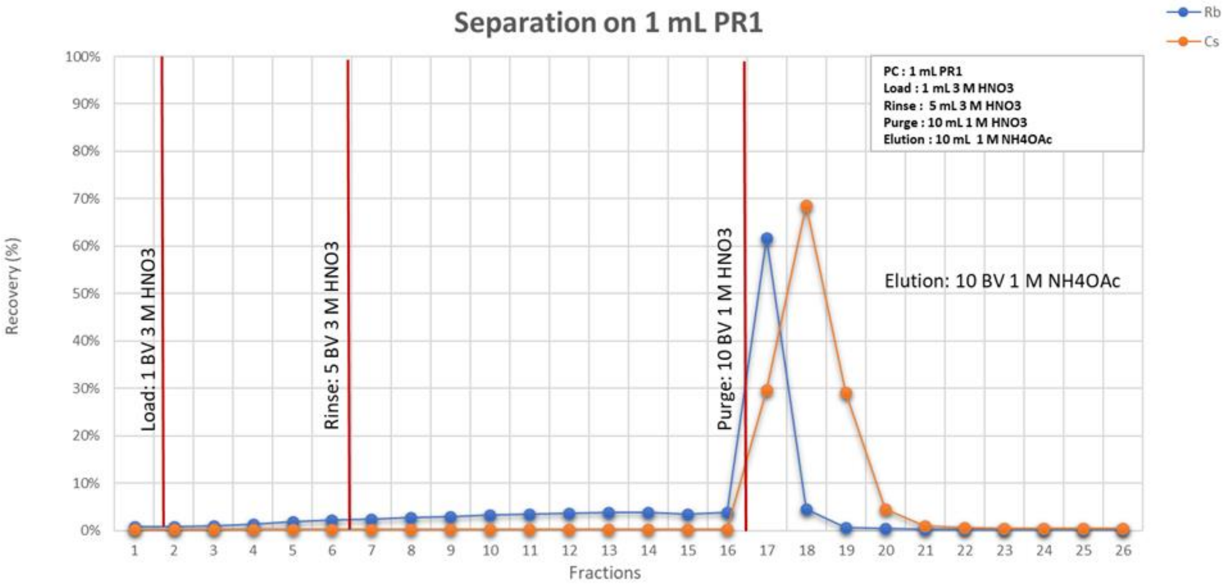


Fig. 25: Separation of 1 µg Rb and Cs on PR1

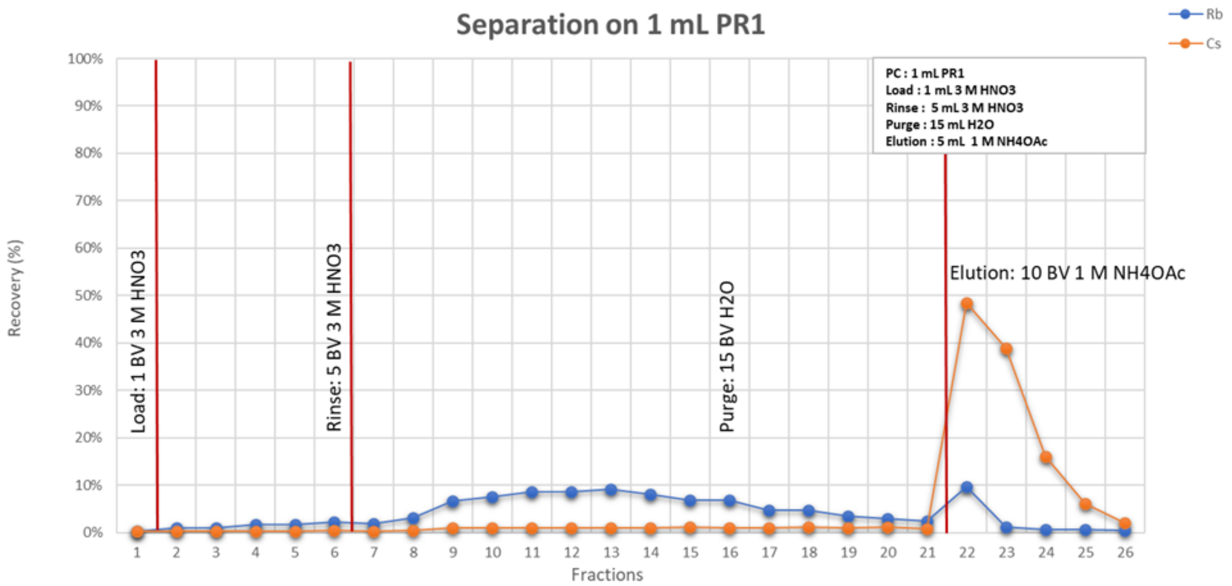


Fig. 26: Separation of 1 µg Rb and Cs on PR1

Elution tests with high-capacity prototype PR1

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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

Liuchao Zhu, Xiaolin Hou [*], Jixin Qiao

Technical University of Denmark, Department of Environmental Engineering, Risø Campus, Roskilde, DK-4000, Denmark

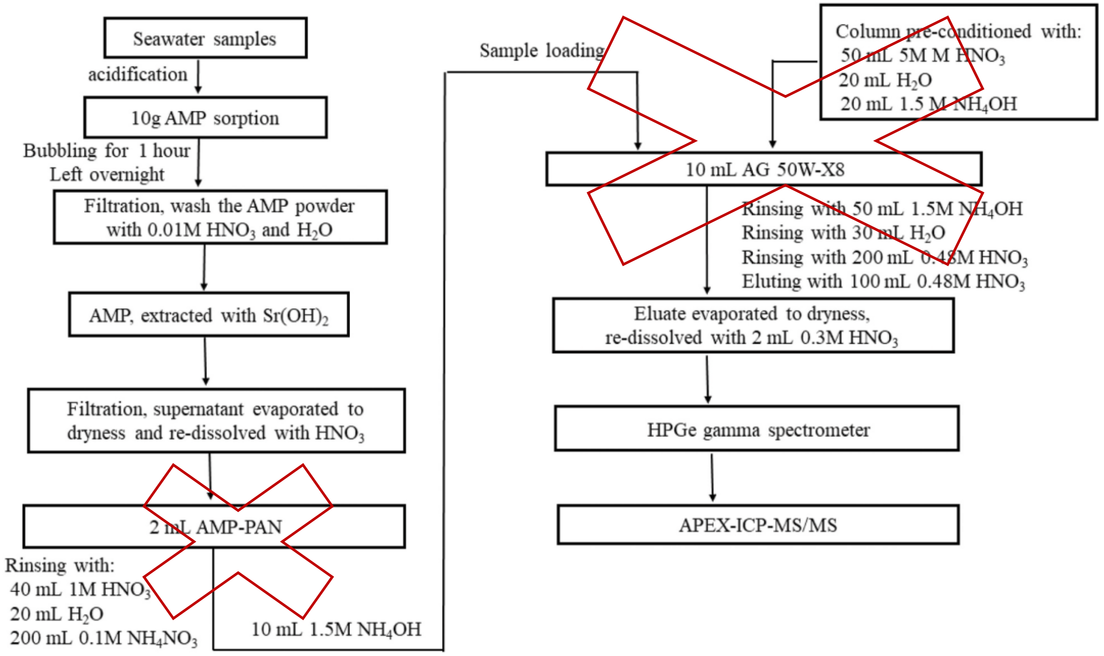


Fig. 3. Chemical procedure for separation of cesium form large volume seawater sample.

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

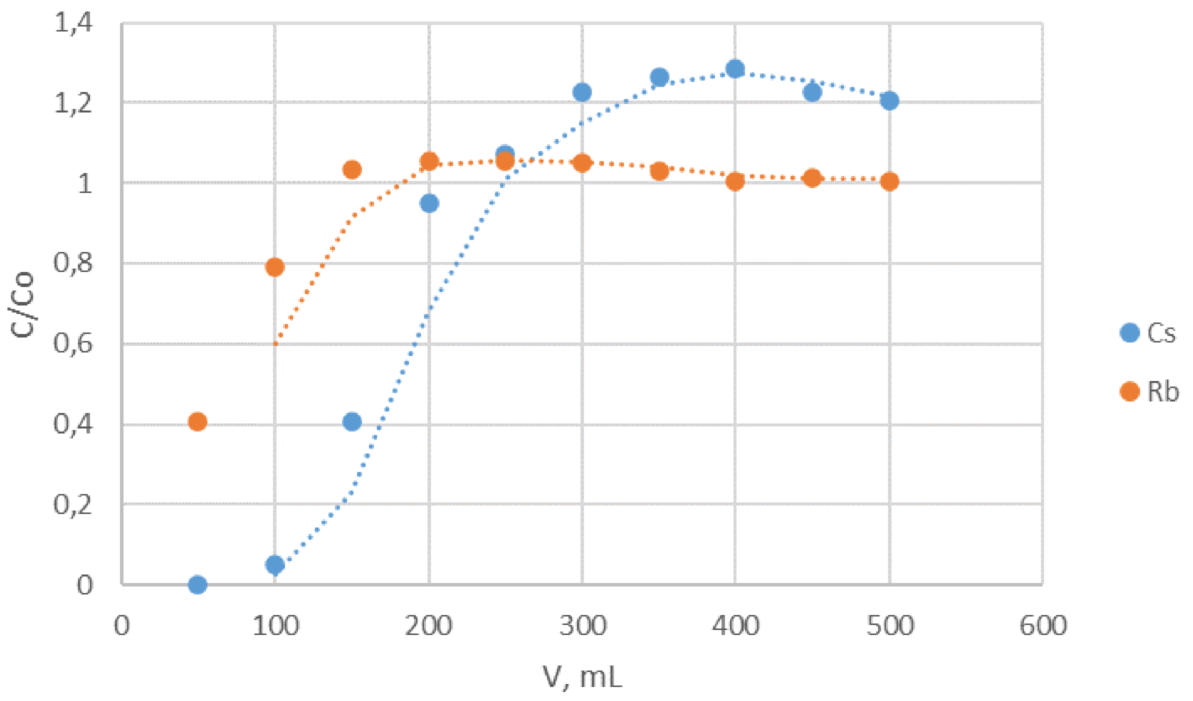


Fig. 27. Sorption curves of Cs and Rb on PR7 from seawater (pH 2).

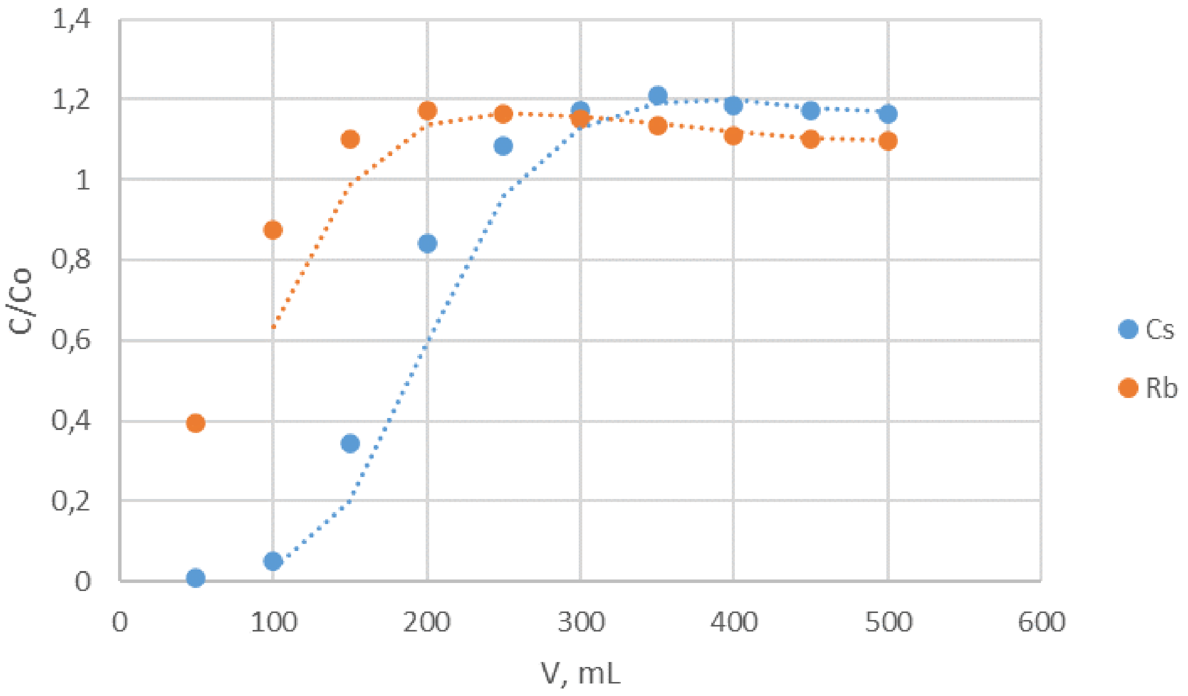


Fig. 28. Sorption curves of Cs and Rb on PR7 from seawater (pH 7,9).

Flow rate is 1 BV/min

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

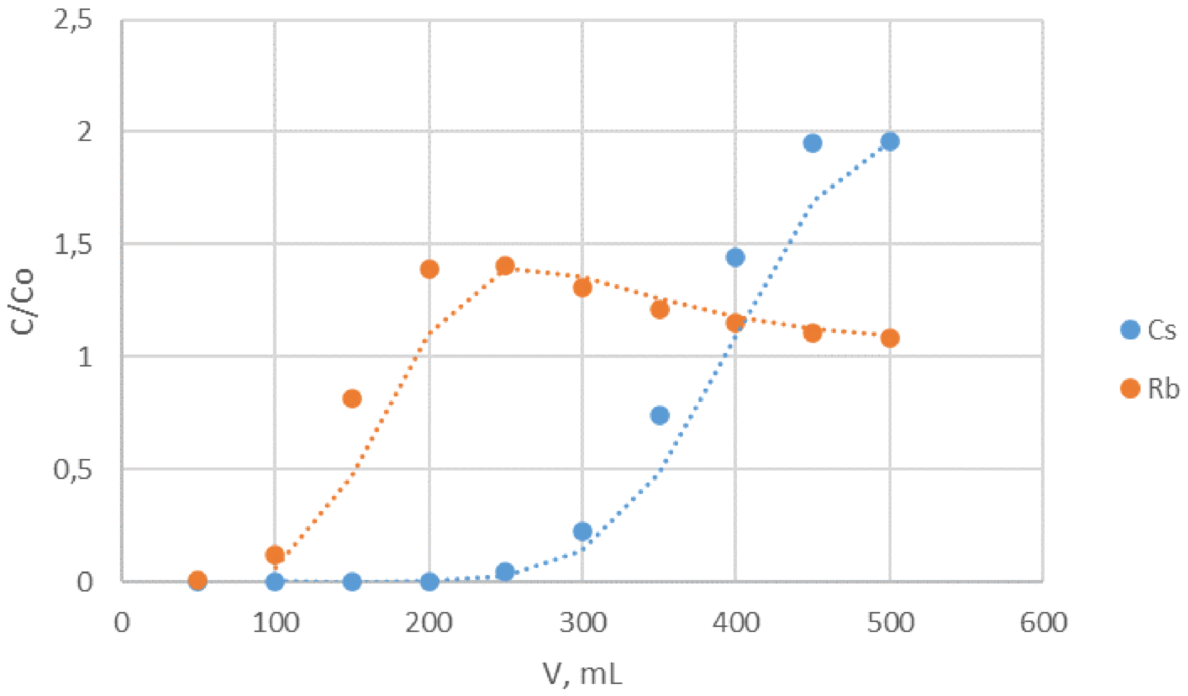


Fig. 29. Sorption curves of Cs and Rb on PR9 from seawater (pH 2).

Flow rate is 1 BV/min

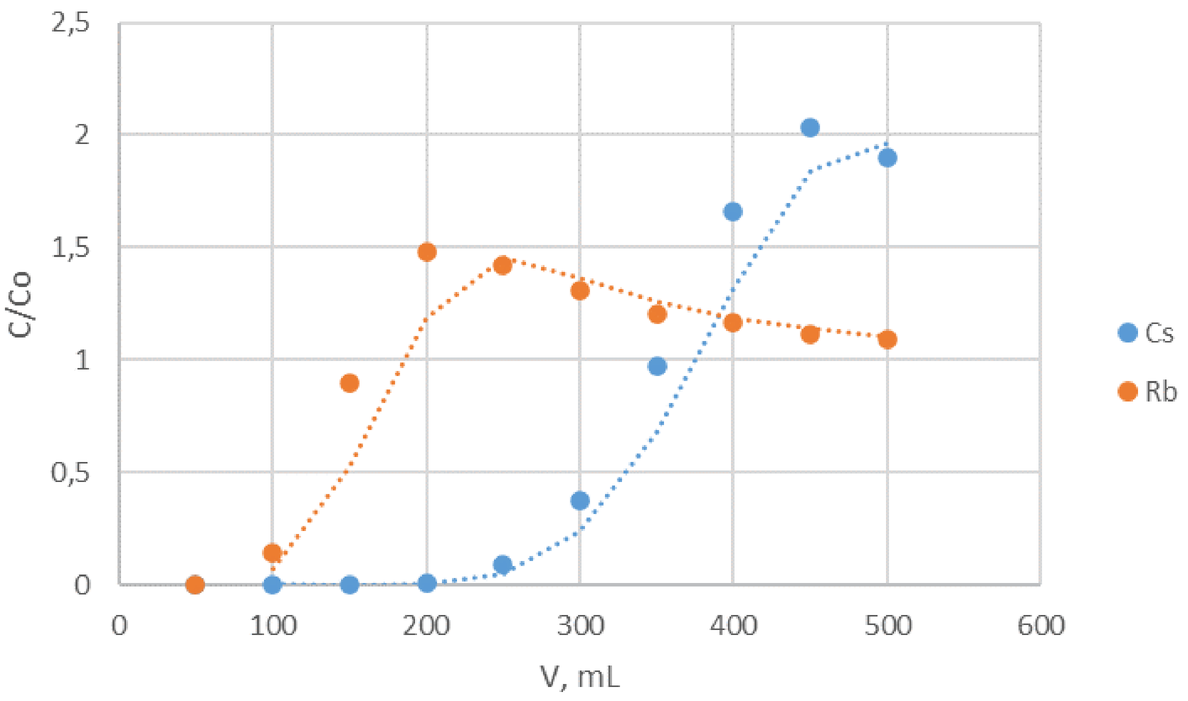


Fig. 30. Sorption curves of Cs and Rb on PR9 from seawater (pH 7,9).

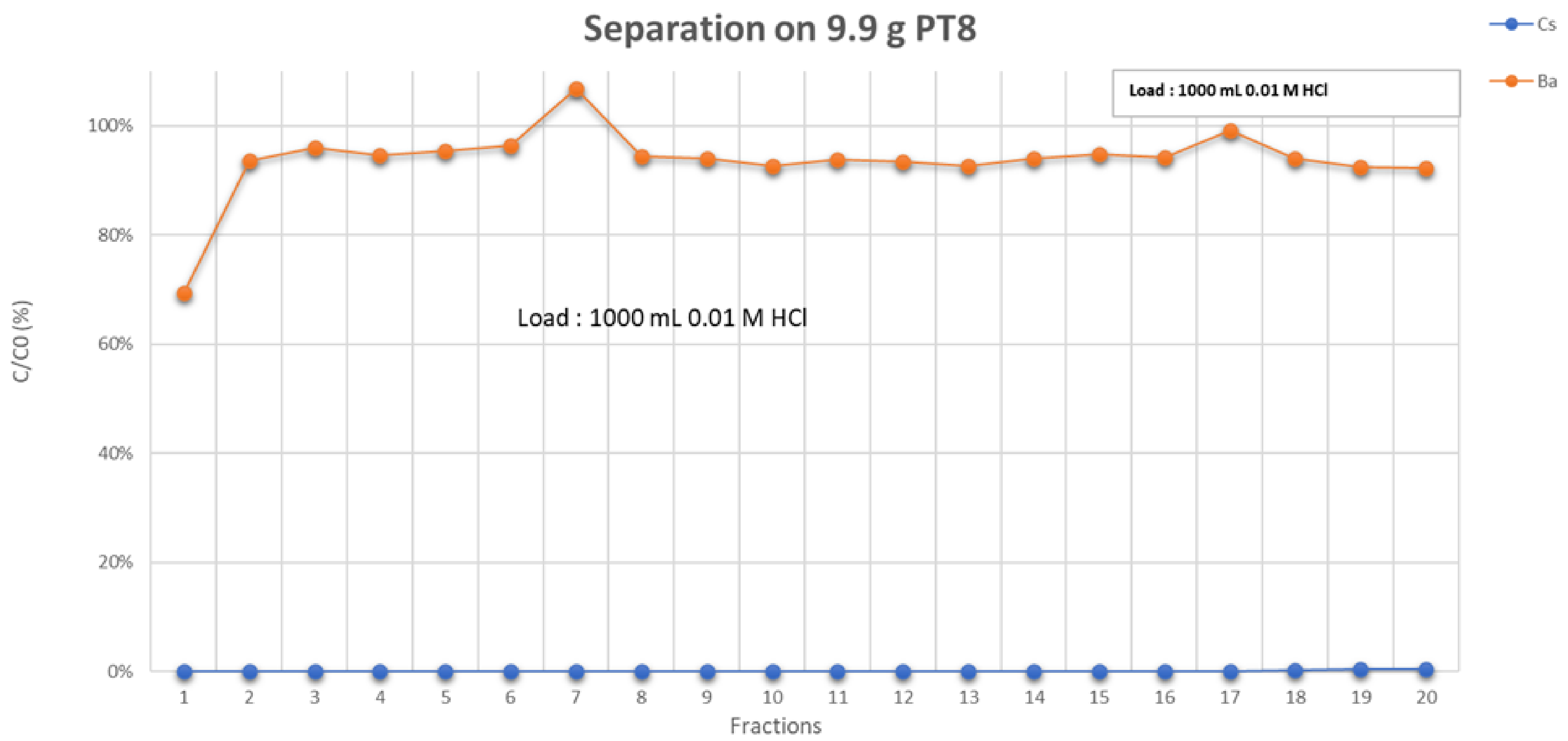
More than 100 BV for Cs breakthrough on the most effective PT9

The PT10 and PT11 are less effective

No difference between seawater with (pH 2) and without (pH 7,9) acidification

Nature of maximum in the beginning retention of Cs and after substitution of Cs with Na, K etc

Cs capture on PT8



– 1 mg of Cs and Ba were load with 1 L of 0.01 M HCl on 20 mL cartridges of PT8 (9.9 g);

– 50 mL of 0.01 M HCl were used for precondition of resin

– 50 mL of 0.01 M HCl were used for rinsing of resin

– 2*50 mL of 0.5 M $(NH_4)_2CO_3$ were used for elution of Cs

– fractions were diluted 10 times

– flow rate is 10 mL/min.

With loading of 1 mg of Cs:

- there is no breakthrough of Cs.

- elution of Cs is full.

CONCLUSIONS

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

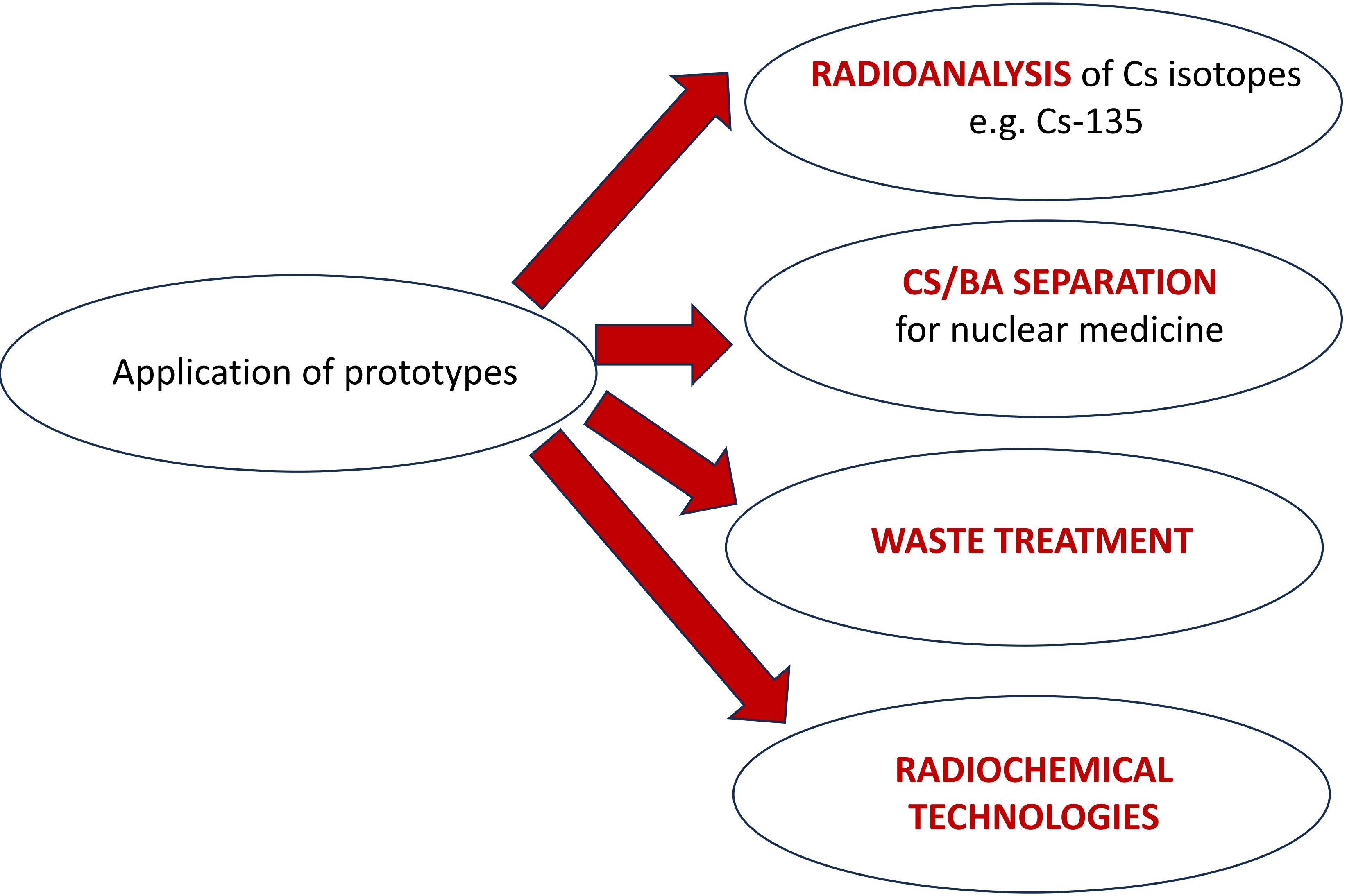
► The breakthrough capacities up to 19 mg/g resin were achieved. For the most of prototypes full capacities are close to theoretical, but for PR9 and BEBH-based PR2, 10,11 they are higher.

► Four ionic liquids-based prototypes with high (PR 7, 9) and low capacity (10-11) 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.

► Three high-capacity prototypes (PR 1, 2, 13) were developed for separation of Rb and Cs from 3 M HNO_3. But elution of 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.

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

POSSIBLE APPLICATION



► separation of Cs and Rb isotopes from low (PR 7,9- 11) and elevated (PR 1, 2, 13) HNO_3 solutions for analysis of the environmental and decommissioning samples

► Cs-131 production (low-capacity PT8)

► direct separation of Cs isotopes from seawater-based waste (high-capacity PR 9).

► direct separation of Cs 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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