PRODUCT SHEET

TK100 / TK101 Resins

Main Applications

- Direct separation of Sr from water samples (TK100)

- Direct separation of Pb from water samples (TK101)

Packing

Order N°.	Form	Particle size
TK100-B25-A, TK100-B50-A, TK100-B-100-A, TK100-200-A	25g, 50g, 100g and 200g bottles TK100 resin	100-150 µm
TK100-C20-A, TK100-C50-A	20 and 50 2 mL TK100 resin columns	100-150 µm
TK101-B25-A, TK101-B50-A, TK101-B-100-A, TK101-B200-A	25g, 50g, 100g and 200g bottles TK101 resin	100-150 µm
TK101-C20-A, TK101-C50-A	20 and 50 2 mL TK101 resin columns	100-150 µm

Physical and chemical properties

Capacity : 8 mg Sr/g TK100 Resin

Conditions of utilization

Recommended T of utilization : 20-25°C

Flow rate: A grade: 0.6 – 5 mL/min, utilization with vacuum or with pressure possible

Storage: Dry and dark, T<30°C

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TK100 / 101 RESINS

Crown-ether based extraction chromatographic resins such as the SR and PB Resins are frequently used for the separation and determination of Sr-90 and Pb-210 in aqueous samples via liquid scintillation (LSC) or gas proportional counting (GPC).

These resins only show significant Sr and Pb retention at moderate to high acid concentrations; thus not allowing for direct loading of the analytes from filtered raw or acidified water samples. This makes the additional use of pre-concentration steps such as ion exchange or co-precipitation necessary.

In order to simplify the Sr-90 and Pb-210 separation, two new extraction chromatographic resins with an extended uptake pH range were developed, allowing for direct loading of water samples (pH 2 - 8) and the subsequent purification of the analytes on the same column.

Further TK100 and TK101 allow for Ra separation, including from Ba.

TK100 Resin

The TK100 Resin consists of a crown-ether with high selectivity for Sr and Pb and HDEHP a liquid cation exchanger (see fig. 1).

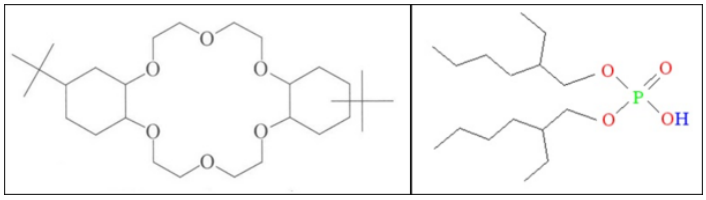

Figure 1: Extractant system TK100: Di-t-butyl dicyclohexyl-18-crown-6 and Di(2-ethyl-hexyl) phosphoric acid (HDEHP)(1)

Jake Surman from Lancaster University characterized the TK100 Resin[1,2] which results are summarized in graphs 2 – 8.

The uptake kinetics of the resin (fig. 2) are comparable to the kinetics of other extraction chromatographic resins[3].

Surman et al. further characterized the resin with respect to D_W values of Sr at different pH values ≥ pH 2 (fig. 3), as well as at HNO_3 and HCl concentrations higher than 0.01M (fig. 4). Further D_W values of various other elements were determined at pH 7 (fig. 7).

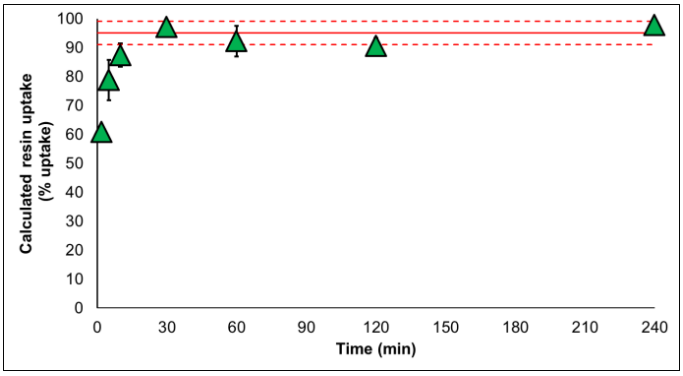

Figure 2: Sr uptake kinetics TK100 Resin[1]

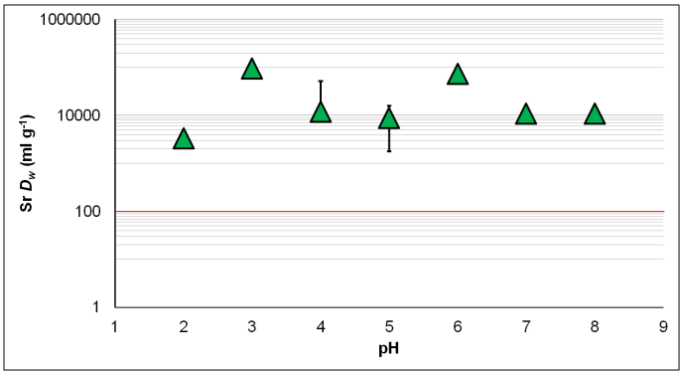

Figure 3: D_W values Sr on TK100 Resin, varying pH values[1]

The TK100 Resin shows high D_W values for Sr in a pH range between 2 and 8.

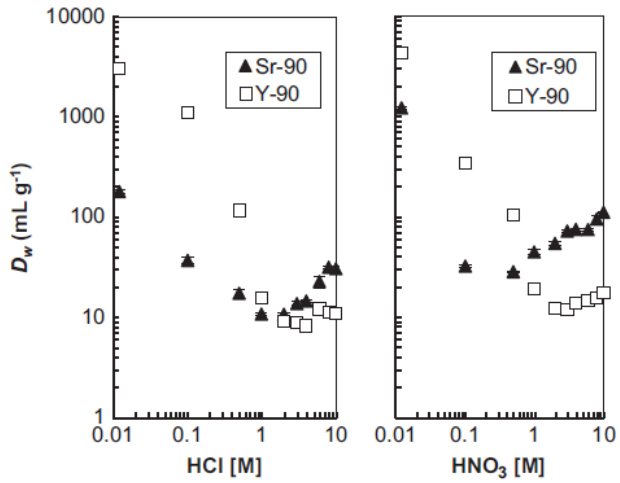

Figure 4: D_W values Sr and Y on TK100 Resin, varying HNO_3 and HCl concentrations[2]

As also shown in figure 4, the Sr uptake at pH 2 is high, especially in HNO_3. It is thus advisable to use nitric acid for the conservation of the water samples

in case they cannot be treated directly. Between acid concentrations of 0.01M and ~1M, Y shows higher retention than Sr.

Both Sr and Y, show a steep decline of their D_W values in this pH range, typical for a cation exchange mechanism, a behaviour that can be attributed to the HDEHP. For higher acid concentrations Y shows, in HCl as well as in HNO_3, a plateau at approx. D_W ~10.

Sr shows a slight increase of its D_W values in HCl up to a D_W of about 30 or 40, insufficient for use in Sr separation. In HNO_3 on the other hand an increase up to a D_W value of about 100 at 8 – 10M HNO_3 can be observed. The TK100 Resin is thus behaving very similar to the SR Resin under these conditions.

As Sr elution with water or dilute nitric acid is not possible, a number of other eluting agents were tested accordingly (fig. 5), 2M HCl, 3M HCl and 0.1M EDTA were found to be most suitable of all tested[1].

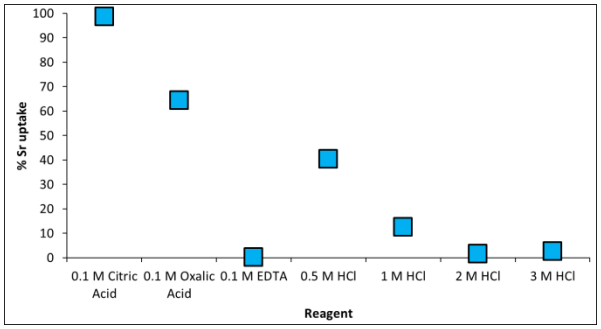

Figure 5: Sr uptake in potential eluting agents[1]

Sr / Y separation is possible using the resin, as was shown by Surman and co-authors (fig. 6), also showing that 2M HCl is indeed a suitable elution solution for Sr.

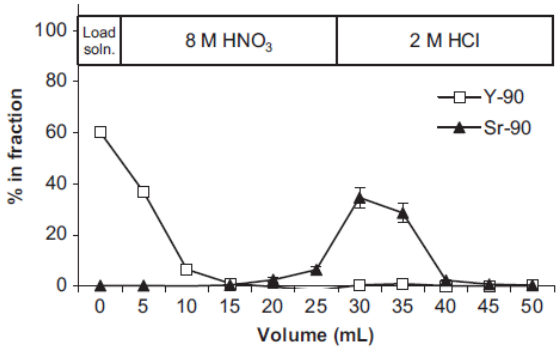

Figure 6: Sr / Y separation on TK100 Resin[2]

As expected, a number of other elements show an affinity to the TK100 resin at pH 7, making separation chemistry necessary in order to obtain a clean Sr fraction (fig. 7).

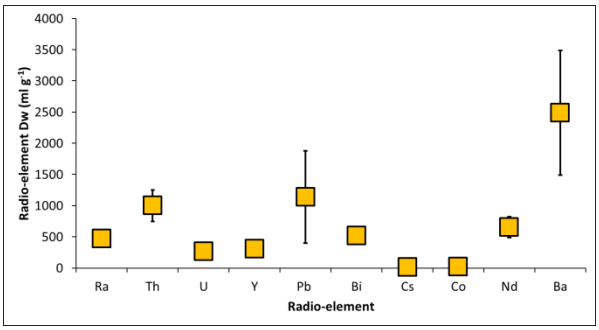

Figure 7: D_W values of selected elements on TK100 Resin[1]

As the resin is not only showing selectivity for Sr, the influence of several typical matrix elements on its uptake onto the TK100 resin at pH 7 was tested. Results are summarized in figures 8 to 10.

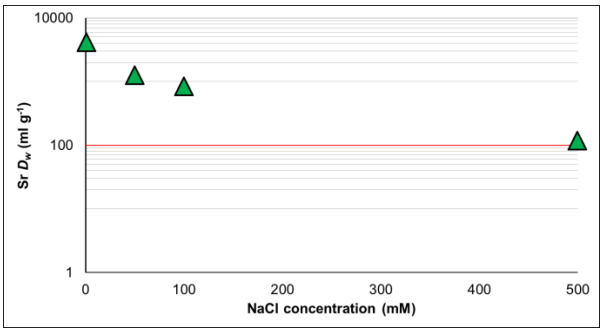

Figure 8: Sr D_W on TK100 Resin as function of NaCl concentration[1]

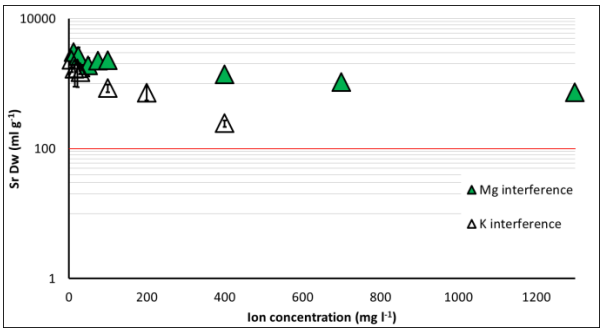

Figure 9: Sr D_W on TK100 Resin as function of K and Mg concentration[1]

Even though high salt contents indeed interfere with Sr uptake, even at NaCl concentrations of 500 mM, K concentrations of 400 mg/L, Mg concentrations of 1300 mg/L and Ca concentrations of 500 mg/L the D_W values for Sr remain greater than 100.

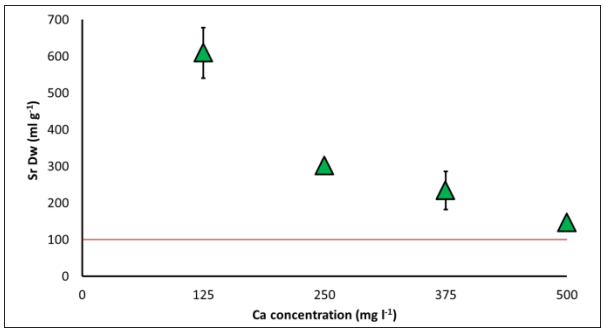

Figure 10: Sr Dw on TK100 Resin as function of Ca concentration[1]

Even if the limiting concentrations will be lower for combinations of the interferences, the resin seems well suited for surface and especially drinking waters.

It could further be shown that the resin allows for the separation of Sr from a number of elements such as Ca, K, Mg, Ba, Co, Am, Cs and Pb, as indicated in the elution studies summarized in figures 11 and 12. It should be noted that Pb is not eluting under the chosen conditions.

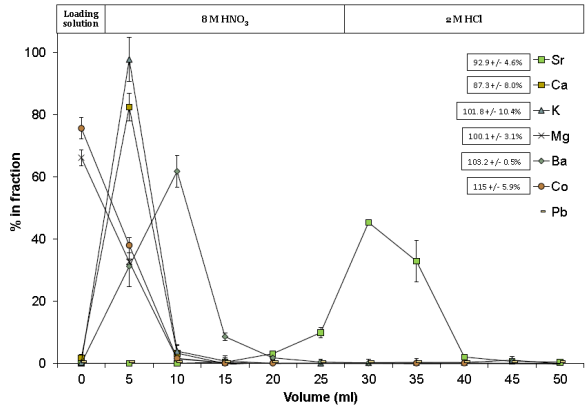

Figure 11 : Elution study, various elements, TK100 Resin[1]

Additional studies performed by Dirks et al. with 1L samples at pH 7 loaded onto a 2 mL TK100 column by aliquots of 100 mL at a flow rate of 5 mL/min (fig. 13) showed that K and Ca directly breakthrough during load without being retained.

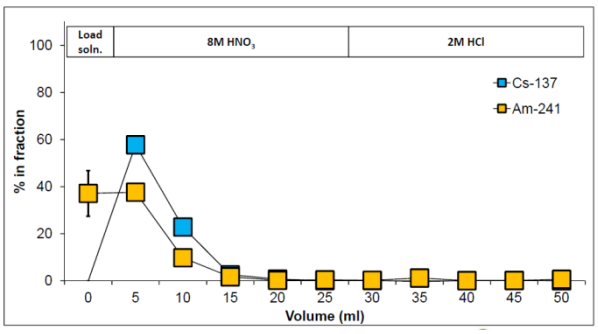

Figure 12: Elution study, Am and Cs, TK100 Resin[1]

Unfortunately a Sr breakthrough starts occurring after a loading volume of approx. 600 mL indicating that the maximum sample volume to be loaded onto the 2 mL column for Sr analysis is 500 mL. Y, Pb and U on the other hand are very well retained, even when a sample of 1L is loaded.

Y can be quantitatively removed using 8M HNO_3. Pb and U remain retained even after the Sr elution step and can be eluted using 6M HCl e.g. for Pb-210 determination via α/β discrimination LSC.

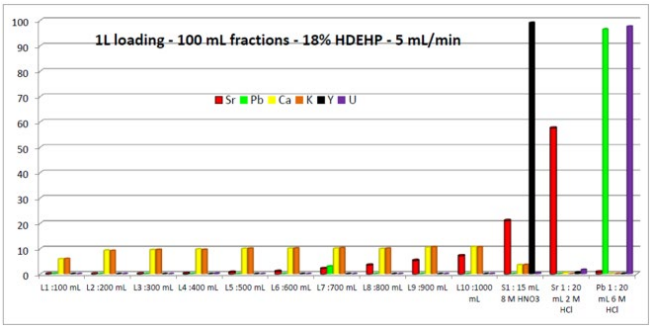

Figure 13: Elution study, various elements, 1L sample, 100 mL aliquots, TK100 Resin

Work for the separation of Pb and U on TK100 are ongoing, however, another resin called TK101 allows for facile separation of Pb from other elements.

Dirks et al. could show that Sr can be separated from 250 mL (95.2% +/- 2.5%, N=3) – 500 mL (88.2 +/- 4.3, N=3) water samples with high yields even at sample loading flow rates of 5 – 10 mL/min.

Van Es et al. could further show that the TK100 resin can be used to concentrate and separate Ra from water samples[4].

TK101 Resin

Dietz et al.[6] showed that the mechanism of Sr extraction by crown-ethers in ionic liquids strongly depends on the chain-length of the ionic liquid. Long chained ionic-liquids favor liquid-liquid extraction mechanism with high Sr uptake at high nitric acid concentrations. Whereas short chained ionic liquids introduce an additional cation exchange mechanism, leading to a very high Sr retention at low pH values. Sr retention then decreases with increasing acid concentrations to a minimum at about 1M HNO_3. At higher HNO_3 concentrations the D values increase as expected for a liquid-liquid extraction mechanism (fig.14).

This behavior corresponds very well to the behavior of the crown-ether / HDEHP system. However, as very little additional selectivity is introduced by the ionic liquid, compared with TK100 resin, it is much easier to obtain a clean Pb fraction. Unfortunately the Sr retention turned out to be significantly weaker than for the TK100 Resin, limiting the application of this system to the separation of Pb. The crown-ether / ionic liquid based extraction chromatographic resin is further referred to as TK101 Resin.

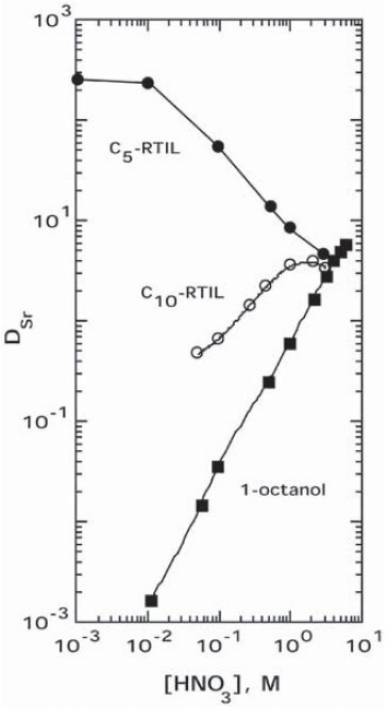

Figure 14: D_{Sr} values for various crown-ether based extraction systems in nitric acid[3].

An elution study (fig. 15) performed by Dirks et al.[5] showed that indeed a clean Pb fraction can be obtained applying the same separation scheme employed for the TK100 Resin. High Pb yields are obtained even when loading 1L samples or more at flow rates of 5 – 10 mL/min using the TK101 Resin.

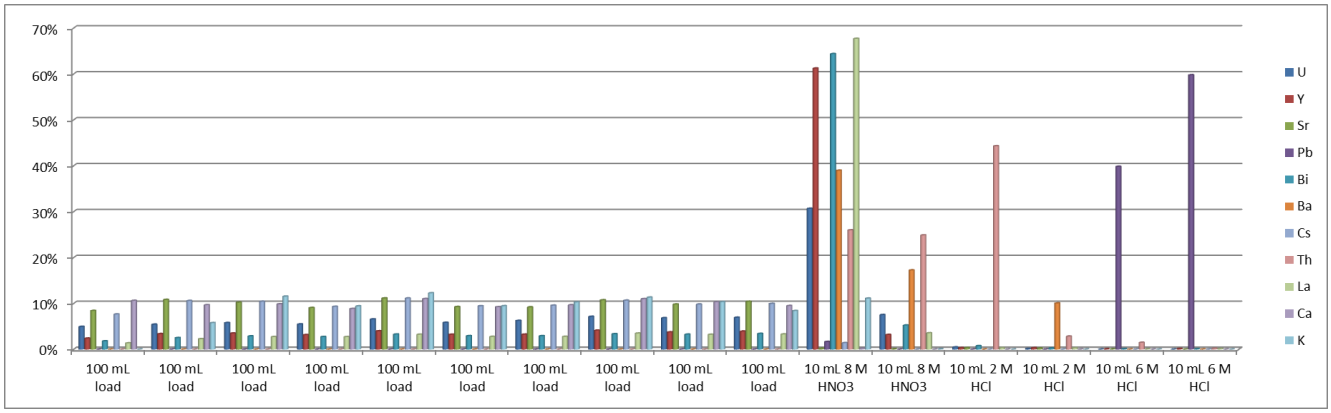

Figure 15: Elution study, 1L sample, 100 mL aliquots, TK101 Resin .

As indicated before, the TK101 Resin is based on the same crown-ether that is also used in the SR, PB and TK102 Resin. The hact that an ionic liquid is employed, this leads to a quite significant change in its selectivity at low acid concentrations, as can be seen in the following graphs.

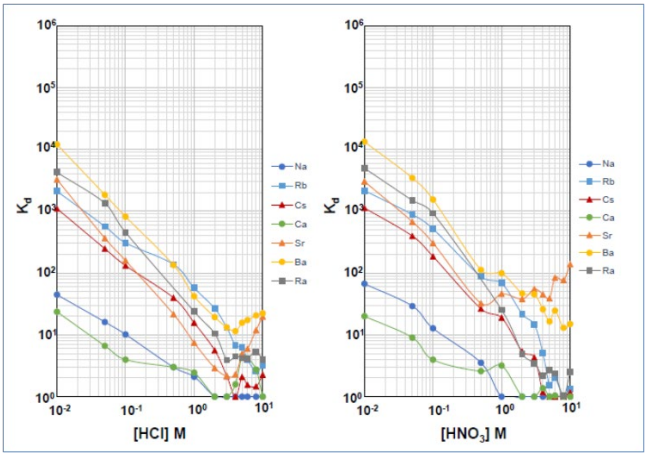

Figure 16 : Dw values of selected elements on TK101 in HNO_3. Data courtesy of Ben Russel (NPL)

While SR, PB and TK102 Resins show no selectivity for Sr, Ba, Ra at low acid concentrations TK101 does.

In dilute HNO_3 as well as in HCl Ba, Ra and Sr are very well retained from ≤0.01M to approx. 0.05M. Their retention decreases significantly as the acid concentration increases though. Sr retention in HNO_3 is an exception as it shows increasing retention at HNO_3 concentrations >3M. It should be noted that, while Ra and Ba behave similar at lower acid concentrations, they do show differences at higher acid concentrations, notably at 3M HNO_3, where the K_d Ba is higher than K_d Ra, thus allowing for a Ra/Ba separation.

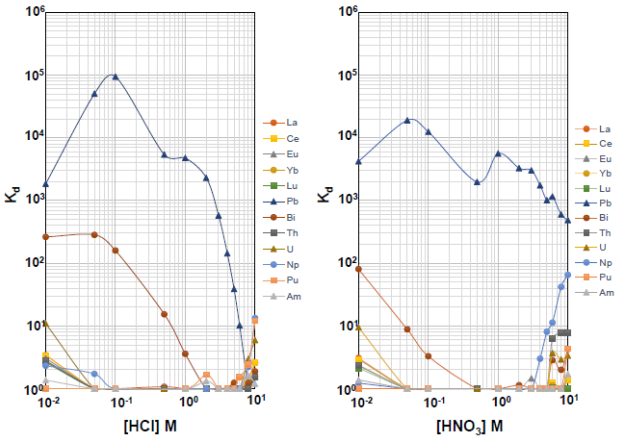

Figure 17 : Dw values of selected elements on TK101 in HNO_3. Data courtesy of Ben Russel (NPL)

Pb is very well retained over the whole HNO_3 concentration range. It is also very well retained from HCl up until approx. 3M HCl. It's retention then decreases very sharply as the HCl increases, making HCl of high concentration suitable for Pb elution.

Out of the elements shown in the graph above only Bi is also retained, particularly from dilute HCl at elevated acid concentrations. It can be very easily removed though, especially using HNO_3. Lanthanides and actinides are not retained on TK101 not in HCl neither in HNO_3.

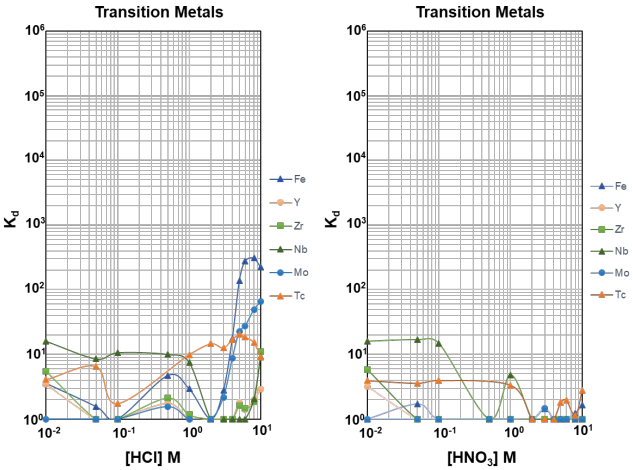

Figure 18 : Dw values of selected elements on TK101 in HNO_3. Data courtesy of Ben Russel (NPL)

Out of the tested transition metals only Nb shows some retention at high HCl, all other elements tested show very low K_d values.

The graph below shows the result of an elution study performed with amongst others Th, Ce, Pt, Ir, Ba, Ra and Pb.

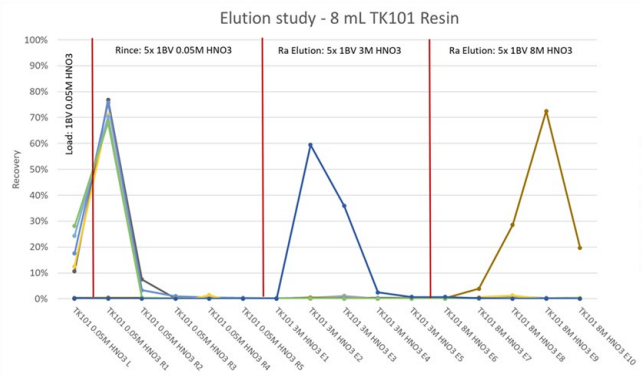

Figure 19 : Elution study of selected elements on TK101. Ra data courtesy of Nora Vajda (RadAnal)

Other elements tested than Ba, Ra and Pb are removed during load and rinse with dilute acid (here 0.05M HNO_3). Ra is then eluted with 3M HNO_3, while Ba and Pb remain retained. Ba is eluted with 8M HNO_3. Pb is still retained under these conditions and may then be eluted with 6 – 8M HCl or citrate/citric acid.

Bibliography

(1) Jake Surman, Jackie Pates, Hao Zhang and Steffen Happel: "Development of a new resin for the rapid determination of strontium-90 in environmental waters", oral presentation at the INTERNATIONAL SYMPOSIUM ON ENVIRONMENTAL RADIOACTIVITY, PLYMOUTH (UK), 4-5 September, 2012

(2) J.J.Surman, J.M.Pates, H.Zhang, S.Happel: "Development and characterisation of a new Sr selective resin for the rapid determination of ^{90}Sr in environmental water samples", Talanta, 129 (2014) 623–628

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(4) Carina Dirks, Jake Surman, Jackie Pates, Steffen Happel: Rapid determination of Pb-210 and Sr-90 in water samples using new crown-ether based extraction chromatographic resins", oral presentation, TrisKem International UGM, 6.10.14, Moscow (RU), http://www.triskem-international.com/ru/iso_album/8_rapid_determination_of_pb-210_and_sr-90_in_water_samples_using_new_crown-ether_based_extraction_chromatographic_resins.pdf

(5) van Es, E.M., Russell, B.C., Ivanov, P. et al. The behaviour of 226Ra in high-volume environmental water samples on TK100 resin. J Radioanal Nucl Chem 312, 105–110 (2017). https://doi.org/10.1007/s10967-017-5203-4

(6) Mark L. Dietz, Julie A. Dzielawa, Ivan Laszak, Blake A. Young and Mark P. Jensen: „Influence of solvent structural variations on the mechanism of facilitated ion transfer into room-temperature ionic liquids", Green Chemistry, 2003, 5, 682–685