TRISKEM
Expertise in Separation Chemistry

EXTRACTION CHROMATOGRAPHY

Technical Documentation - Radiopharmacy

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TRISKEM INTERNATIONAL

TrisKem International develops, manufactures and commercializes highly selective resins for the separation of a large variety of elements in numerous domains.

Triskem Resins are used for:

- the recuperation of high value elements (production of radio metals for medical use and recuperation of their respective target materials and recovery of critical metals)
- quality control of final and intermediary products in numerous industries including radiopharmacy
- the removal of particular elements before effluent release
- the analysis of precious samples (environmental monitoring, radiation protection, bioassay)
- the high precision determination of isotope ratios (dating/geochronology)

TrisKem International products have now become the standard technology in the field of radiochemistry, geochemistry and radiopharmacy with methods used by accredited laboratories (Orano, BNFL, CEA, NNL,...) and regulatory organizations (IRSN, IAEA, BRGM,...) and many other customers working on radionuclide and element separation and purification.

We also commercializing a complementary range of accessories such as vacuum box systems and products used for sample preparation like LSC cocktails, filters and discs for alpha spectrometry, and Pyrolyser systems for the determination of H-3, C-14, Cl-36, I-129,... in a variety of matrices including decommissioning samples.

Our technical support is carried out by a worldwide recognized scientific team consisting of radiochemistry PhDs who are amongst others members of the French nuclear equipment standardization agency (BNEN), ISO workgroups, and external IAEA experts and lecturers.

APPLICATIONS

Radiopharmacy

TrisKem manufactures selective resins for Lanthanides (e.g. Lu-177, Tb-161,...), Cu, Zr, Ga, Ac, Ge, Ti, Sc, Tc and many other radionuclides for medical purposes. We develop rapid, highly specific separation techniques for:
- Separation of radionuclides from irradiated targets
- Quality control of radionuclides for medical use
- Post-generator purification
- Radioprotection and Radioanalysis

Environmental monitoring and Bioassay

TrisKem's extraction chromatographic resins allow the separation and determination of radionuclides (e.g. actinides and fission products) from bioassay samples and environmental matrices e.g. soil, sediment, vegetation and seawater samples. Their use allows a rapid and precise determination of radionuclides in emergency and routine situations, as well as, combined with suitable sample preparation methods, to obtain very low detection limits through analysis of large volume samples.

Decommissioning

The high selectivity of our resins not only allows the analysis of standard alpha and beta emitters (actinides, Sr-89/90, Ni-63, Tc-99,...) from high matrix samples including concrete, spent resin, but also the determination of so called difficult-to-measure (DTM) radionuclides such as Sn-121m/Sn-126, Zr-93,...
We are constantly working on developing new methods according to your needs. Methods for the following radionuclides are currently under development: Se-79, Sb-125, Cs-135, Nb-93m/Nb-94, Ag-108m, Pd-107, ...

Geochemistry and Metals Separation

TrisKem's expertise in separations and it's variety of different resins with varying selectivities provides a number of opportunities to solve analytical problems through sample preparation. With our broad offer of products and long experience, TrisKem can help you meet lower detection limits with less uncertainty. The problems encountered are frequently centered on removing matrix that interferes with the instrumental measurement. ICP-MS is an example. Isobaric interferences often have to be removed in order to allow accurate determination of your analytes. Selectivity for the analyte of interest is important in these cases. Extraction chromatography is already widely used in various applications including geochronology, isotope ratio determination and provenancing.

A number of ready-to-use methods are available through our new website: www.triskem.com

CL Resin

The CL Resin is based on an extraction system that is selective for soft cations such as palladium, gold and silver and it is mainly used for the separation of chloride and iodide, especially in the context of Cl-36 and I-129 analysis, the separation of iodine isotopes and the removal of radioiodine from effluents.

The selectivity for halides is introduced by loading the resin with Ag^+ allowing good selectivity for anions, especially halides, forming sparsely soluble or insoluble Ag complexes. Since the resin retains Ag^+ over a wide range of pH values it also allows loading chloride and iodide from various conditions, from slightly (chloride) to highly alkaline (iodide) to strongly acidic (both), ideally under reducing conditions to ensure their presence as halides.

Radioiodine is considered to be one of the most dangerous radioelements in terms of radiological effects in case of accidental release. Accordingly efforts are made to capture iodine from liquid effluents already during the production process before waste storage, to avoid a possible gas release from stored liquid waste at a later date.

Caroline Decamp of the Intitute of Radioelements (IRE) has developed a method for the removal of radioiodine from acidic (1M HNO_3) radioactive process waste solutions. The IRE combined the CL Resin with XAD-4 resin and packed this mix (4g XAD-4 and 3g CL Resin) into columns. These mixed bed columns were then introduced into their process setup in order to remove radioiodine from their multi-curies production process solutions.

One prerequisite of the removal step was that it should not slow down the process; the radioiodine removal was thus tested at the same flowrates applied during the process. Flow rates up to > 180 mL/min and effluent volumes between 12L and 17L were tested, and it was found that under these conditions between 85 and more than 95% (overall mean retention yield for all solution volumes is 88% ± 5% (N = 14, k = 1)) of the radioiodine present were retained on the column, thus lowering the I-131 activity of the effluents by a factor of 10 from 100 GBq/L to about 10 GBq/L. 2000 GBq of I-131 could be removed per decontamination cycle and stored as solid waste.

Mastren et al. used the CL Resins for the separation of Ag-111 from a proton irradiated thorium target. In a second paper they have further shown that the CL Resin may be used to separate Pa from a bulk thorium matrix.

Besides the removal of radioiodine from effluents the CL Resin is also used for analytical purposes. It allows for the preconcentration of I isotopes e.g. from waste water upfront to gamma spectrometry and, more importantly, for the determination of I-129 and Cl-36, both long-lived, volatile radionuclides, in environmental and decommissioning samples.

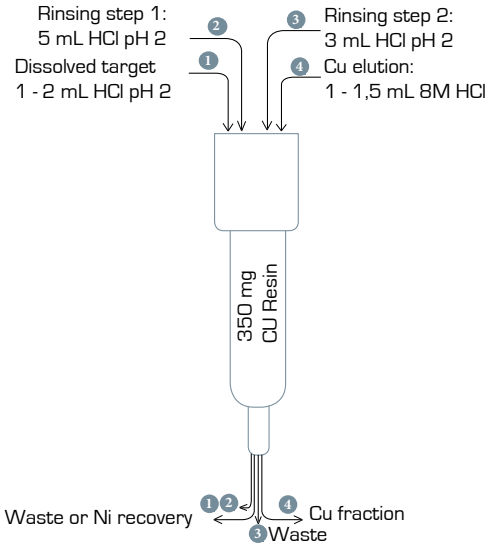
In case of analytical applications, after loading and rinsing of the resin (removal of matrix elements and interferents), chloride can be easily eluted from the resin using dilute SCN^- solutions whereas iodide remains fixed. Iodide can then be eluted from the resin using a moderately concentrated S^{2-} solution.

Main Applications

- Separation and removal of radioiodine
- Ag separation
- Pa separation
- Cl-36 and I-129 separation

CU Resin

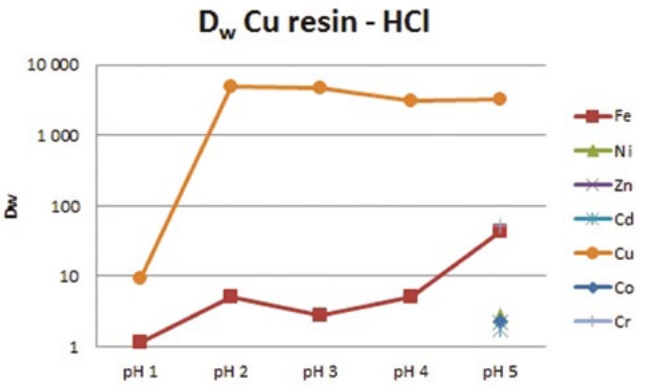
The CU Resin is used for the separation of Cu and is based on a Cu selective extraction system.
The extraction behaviour of the CU Resin towards a number of elements in three different acids at varying acid concentrations is presented here.
Overall the resin shows high selectivity for Cu over all tested cations including Ni and Zn. Cu uptake is generally high at pH values greater than 2 while it can be easily eluted with mineral acids of elevated concentrations. Accordingly it is well suited for liquid target work. For Cu separation from solid Ni targets on the other hand the TK201 resin is more suitable.
Further the resin shows high robustness against interference of elevated amounts of Zn and Ni, even at 1 g of Zn or Ni per g of CU Resin employed the D_W(Cu) remains greater than 1000.
A simple and fast method for the separation of Cu from irradiated targets was developed by Dirks. et al. allowing to obtain highly pure Cu in a very small volume in less then 10 min.
DeGraffenreid et al. could show that the Cu Resin allows separating Cu from very large Zn targets in high yields and purity. It may be combined with the TK201 Resin to convert the obtained Cu fraction from high acid concentration to dilute acid.



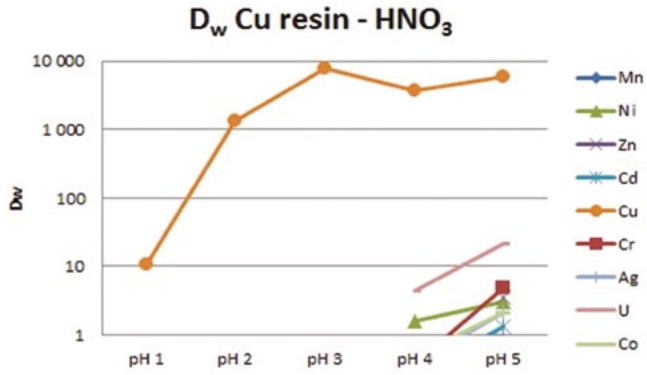
Optimized Cu separation method

Main Applications

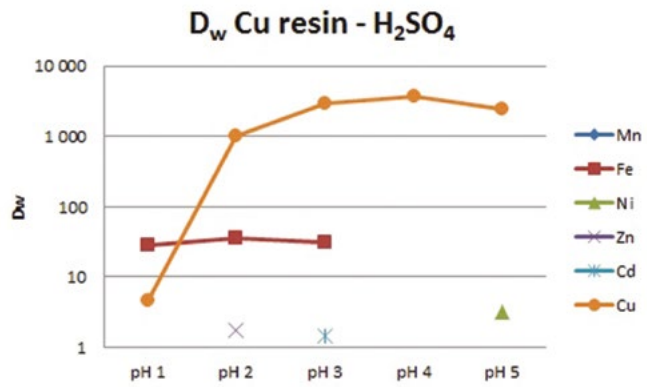
- Separation of Cu-64/67 from irradiated targets
- Concentration and separation of Cu from environmental matrices
- Purification of target materials



D_W of Cu and selected elements on Cu Resin in HCl in varying pH values.



D_W of Cu and selected elements on Cu Resin in HNO_3 in varying pH values.

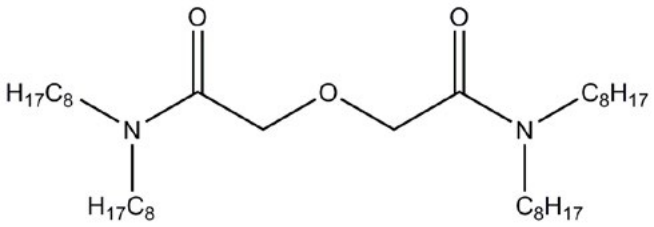


D_W of Cu and selected elements on Cu Resin in H_2SO_4 in varying pH values.

Thieme et al. showed that removing traces of stable Cu from Ni targets will result in a higher specific activity of Cu isotopes produced from such targets.

It could further be shown that Cu can be concentrated, and separated, from other high-matrix samples such as sea water, biological and mining samples with high yield and purity.

DGA Sheets



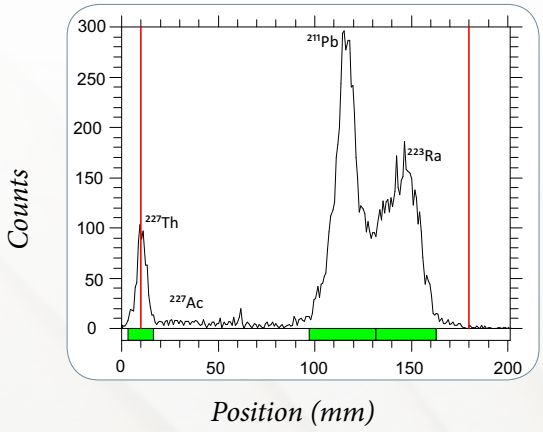
Radionuclide separation and radionuclidic purity determination was never easier. Separation of generator isotopes and radionuclide mixtures on DGA impregnated chromatographic paper, which has been developed at the CVUT, including mixtures like Ac-227/Th-227/Ra-223, Sr-90/Y-90, Ge-68/Ga-68, Mo-99/Tc-99m, Pb-212 and Ac-225/Bi-223 is now...

and Ac-225, Bi-213 is now possible using one separation material, just by changing the composition of the mobile phase (diluted mineral acids like 1M HNO_3 or HCl). The chromatographic paper is impregnated with DGA with variable active compound loading (0.1-10%).

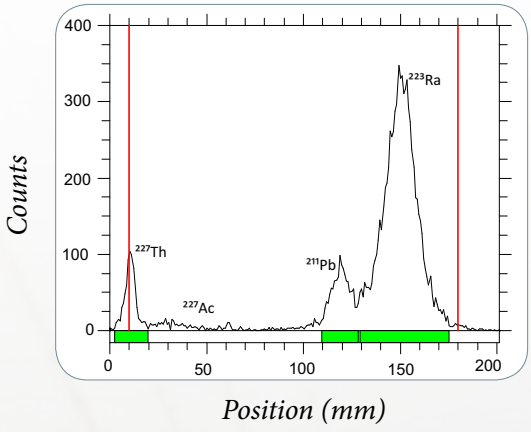
The method is easy to validate and TLC scanners or alternatively, after cutting the paper, common radiometers may be used to determine radionuclidic purity of a generator eluate or a purified radionuclide product.

Proposed standard sheet dimensions are 5 x 20 cm, 10 x 10 cm or 20 x 20 cm. Other formats and custom dimensions are however also available upon request.

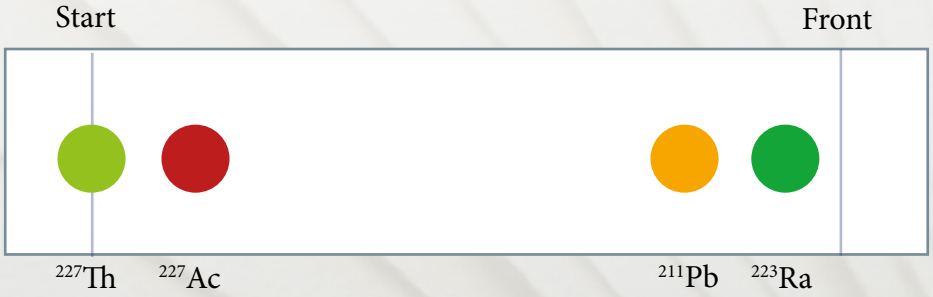
You'll find two application notes on our website.



Radiochromatogram measured immediately after separation



Radiochromatogram measured one hour after separation



Scheme of a chromatographic separation of a mixture of Ac- 227 and its descendents. Th-227 remains on start, Ac-227 has a retention factor R_f of ca. 0.2, Pb-212 of ca. 0.7 and Ra-223 of ca. 0.9.

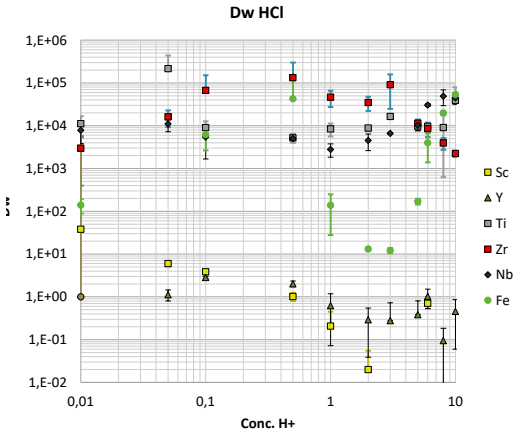
All data provided by J. Kozempel and M. Vlk, CVUT

Application notes available on our website: www.triskem.com /tki-methods.php

ZR Resin

The ZR Resin is based on the hydroxamate functionality frequently used for the separation of Zr-89 from Y targets for use in radiopharmaceutical applications.
Dirks et al. have characterized the resin with respect to its selectivity for selected elements in HNO_3, HCl and oxalic acid.

The ZR Resin shows i.a. high selectivity for Zr, Ti and Nb over a wide range of HCl concentrations (0.01M – 10M), Fe(III) is strongly retained at low and elevated HCl concentrations, retention is weaker from 1 – 6M HCl. As expected the resin shows very little selectivity for Sc and Y, a separation of e.g. Zr from Y and Ti from Sc is thus possible.

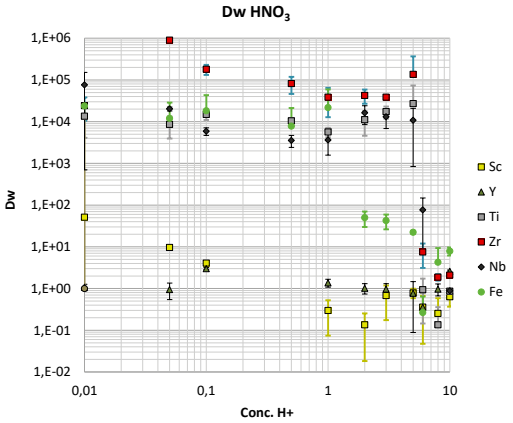


The resin shows rather similar selectivity in HNO_3, Zr, Ti and Nb are well retained up to 5M HNO_3, Fe(III) is well retained up to 1M HNO_3. At higher HNO_3 concentrations the nitric acid starts attacking the extractant, indicated by a colour change of the resin from white to brown; accordingly the resin shows no significant selectivity towards the tested cations under these conditions. As in HCl, Y and Sc show no significant retention on the ZR Resin in HNO_3.

Oxalates are very strong complexing agents for Zr, accordingly they are very frequently used for the elution of Zr.

It could be shown that oxalic acid concentrations above 0.05M lower the D_W value of Zr on the ZR Resin strongly; they are thus suitable eluting agents for Zr. It was further observed that Nb shows high D_W values even at 0.05M oxalic acid, Zr and Nb may thus be separated by adjusting the oxalic acid concentration accordingly.

Zr can be recovered near quantitatively in 1.5 mL dilute oxalic acid even in presence of up to 300 mg stable Y (using a 100 mg ZR Resin column).



D_W values, ZR Resin, HNO_3,various elements

As discussed before the ZR Resin also shows very interesting selectivity for Ti, especially with respect to Sc, which makes it interesting p.ex. for Ti-44 and Ti-45 production. While Sc is not retained e.g. from 10M HCl Ti is very well fixed. 0.1M citric acid, 0.2M oxalic acid or dilute H_2O_2 may then be used to elute Ti from the resin.

As Ti is retained over a very wide range of HCl concentrations, including dilute HCl, accordingly its potential use as support for a Ti-44/Sc-44 generator is currently being evaluated.

Besides for the separation of Zr the ZR Resin is also very often used for the separation of Ga-68 from liquid or solid Zn targets, generally in combination with the TK200 Resin. The ZR Resins' selectivity allows for its use as well in dilute HNO_3 (liquid targets) as in HCl of elevated concentration (>5.5M HCl) making it a versatile tool for Ga production on a cyclotron. The TK200 Resin is used in both cases to allow recovering Ga in dilute HCl.

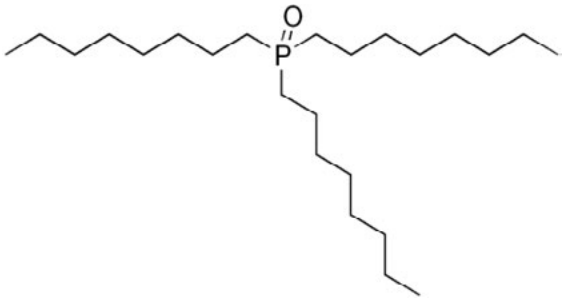
Further to the before mentioned elements the ZR resin also shows, under suitable conditions, very interesting selectivity for Ge over Ga in HCl, HNO_3 and H_2SO_4 allowing for its separation from macro quantities of Ga.
A method for the separation of Ge-68 from large quantities of GaNi or GaCo is currently being developed. This method also involves the use of the Guard Resin.

Main applications:

- Separation of zirconium
- Separation of gallium
- Separation of germanium
- Separation of titanium

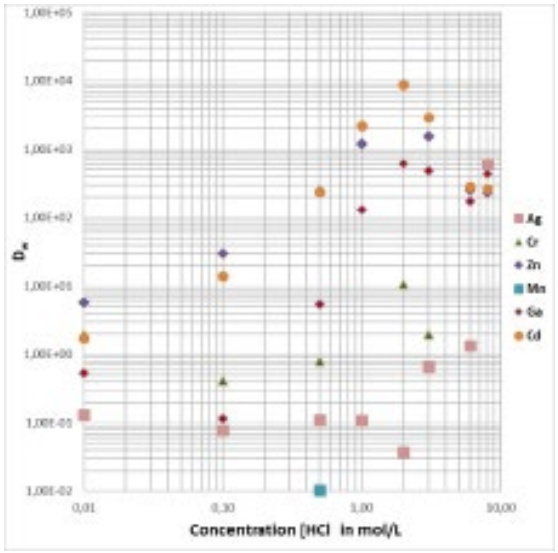
TK200 Resin

The TK200 Resin is based on TriOctylPhosphine Oxide (TOPO) an extractant widely used in the extraction of metal ions.



Trioctylphosphine oxide (TOPO)

Some examples of D_w values determined in HNO_3 and HCl using ICP-MS are shown below.



D_w values of selected elements on TK200 Resin in HCl

Cd, Zn and Ga are very well retained at HCl concentrations >1M. This is especially interesting with respect to Ga separation chemistry as Ga is not retained at 1 – 2M HCl on most resins.

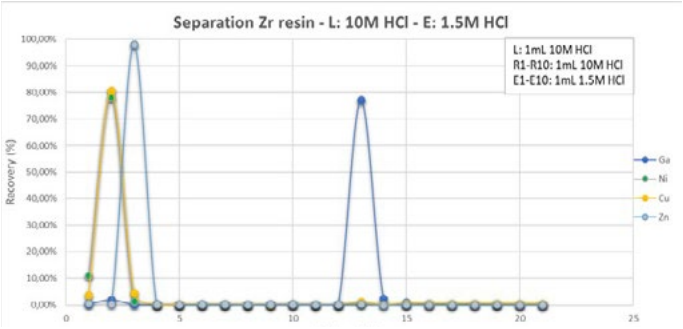
In HNO_3 none of these elements are retained incl. e.g. Ga and Zn.

D_w values for a wide range of additional elements may be found in the corresponding product sheet.

A typical example of the use of the TK200 Resin is the separation of Gallium isotopes (especially Ga-68) from irradiated Zn targets for medical use in combination e.g. with the ZR Resin.

ZR Resin is very well suited for the separation of Ga from Zn matrices, under low acid conditions (e.g. 0.1M HNO_3 often employed for liquid targets) as well as at high acid concentrations (e.g. >5.5M HCl conditions often used for the dissolution of solid Zn targets).

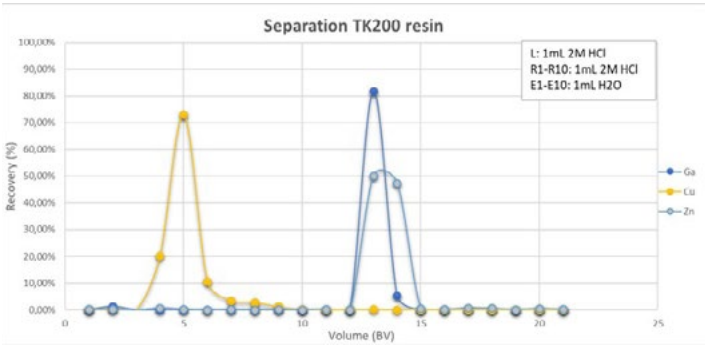
The following elution study shows the separation of Ga from Zn and potential impurities on ZR Resin:



Ga/Zn separation on ZR Resin - load from 10M HCl

Ga is eluted from the ZR Resin in a small volume (1 – 2 column volumes) of 1.5M HCl, conditions too acidic for direct use in labelling reactions.

The TK200 Resin on the other hand allows for Ga extraction at 1.5M HCl, followed by Ga elution using aqueous solutions.

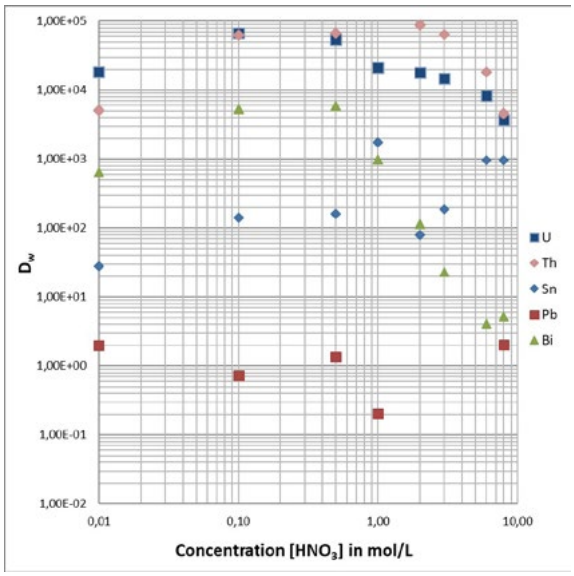


Ga elution from TK200 resin with water following load from 1.5M HCl

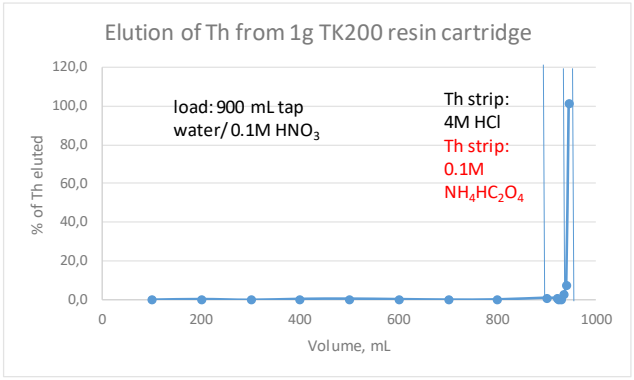
It should be noted though that only very little additional Ga/Zn separation is taking place on the TK200 Resin.

Another typical application of the TK200 Resin is the determination of actinides such as U, Th and Pu in water samples

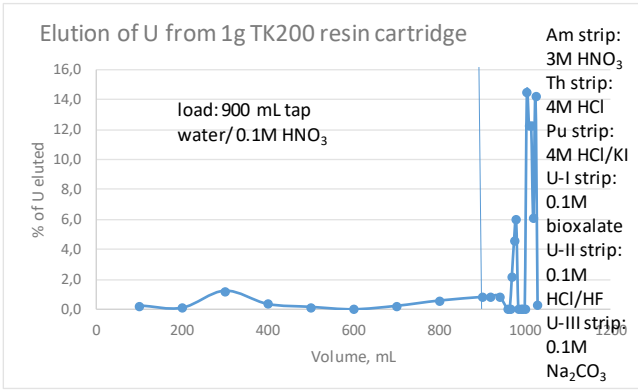
As shown in the following figure, U and Th are very well retained over the whole HNO_3 concentration range, including 0.01M.



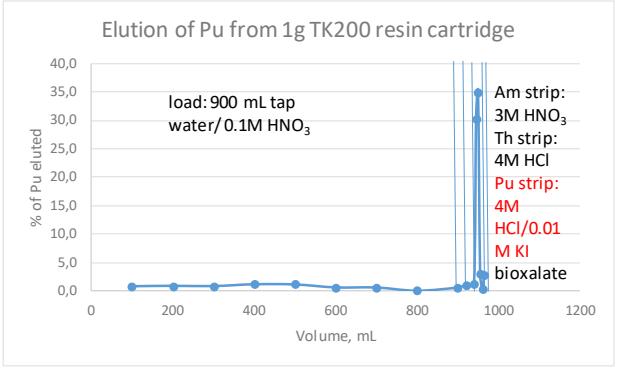
D_w values of selected elements on TK200 Resin in HNO_3



Elution study Th retention and elution on TK200 Resin (data courtesy of Nora Vajda)



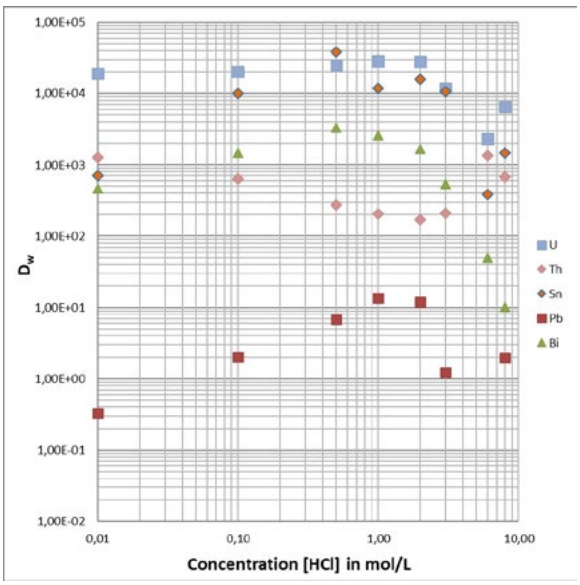
Elution study U retention and elution on TK200 Resin (data courtesy of Nora Vajda)



Elution study Pu retention and elution on TK200 Resin (data courtesy of Nora Vajda)

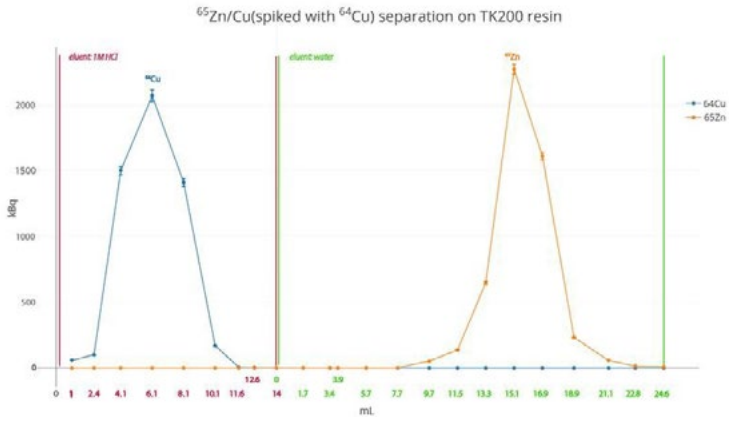
This allows for using the TK200 resin for the preconcentration of actinides from acidified water samples, and their subsequent separation on the same column.

U and Th are also very well retained from HCl.



D_w values of selected elements on TK200 Resin in HCl

A number of other methods are currently being tested, including the separation of Sc from Ca targets, the separation of Pt from Ir targets and Zn from Cu targets.



Zn-65 separation. Data provided by Fedor Zhuravlev, DTU

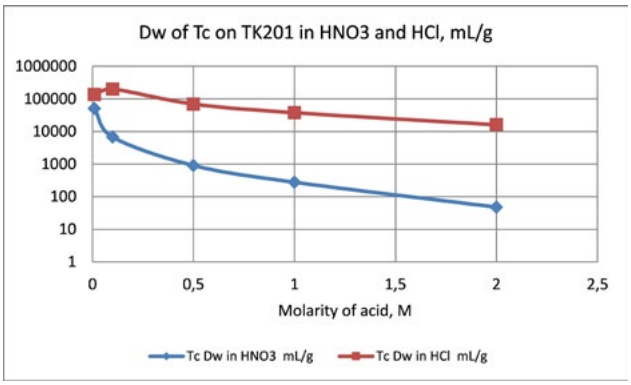
Main applications:

- Ga-68 separation from Zn targets
- Zn separation from Cu targets
- U, Pu, Th concentration and separation

TK201 Resin

The TK201 Resin is based on a tertiary amine, it further contains a small amount of a long-chained alcohol (radical scavenger) to increase its radiolysis stability. The TK201 Resin acts as a weaker ion pair binding agent compared to the TEVA Resin, accordingly it is generally possible to elute it under softer conditions.
Its main applications are the separation of anionic species such as Tc(VII) or Re(VII) and the separation of Cu isotopes from solid Ni targets.

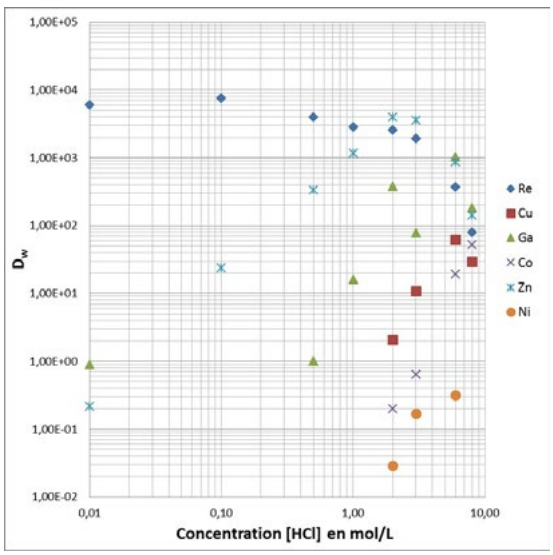
The following graph shows the D_w values for Tc in HNO_3 and HCl.



D_w values of Tc on TK201 Resin in HCl and HNO_3, obtained by LSC, data provided by N. Vajda (RadAnal)

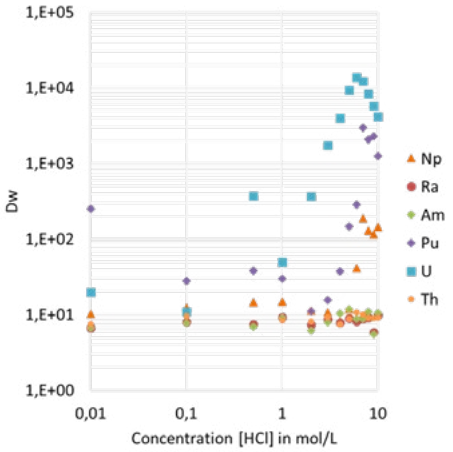
Tc(VII) is very well retained at low acid concentrations. Its retention is generally significantly higher in HCl than in HNO_3, even at elevated HCl concentration such 2M it remains very strongly retained. In HNO_3 on the other hand its retention is rather low at concentrations above 2M.

The following graphs show the selectivity of the TK201 Resin for a wide range of elements in HCl and HNO_3. All D_w shown in these graphs were obtained through ICP-MS measurements.



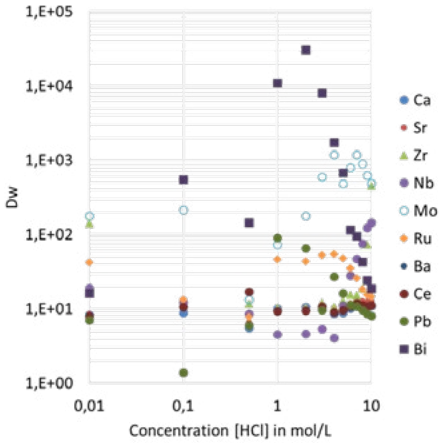
D_w values of selected elements on TK201 Resin in HCl

As expected, the TK201 Resin shows strong Re(VII) retention in HCl even at high concentrations.
Further Zn, Ga and Cu are retained, especially the latter allows for its use in radiopharmaceutical applications.



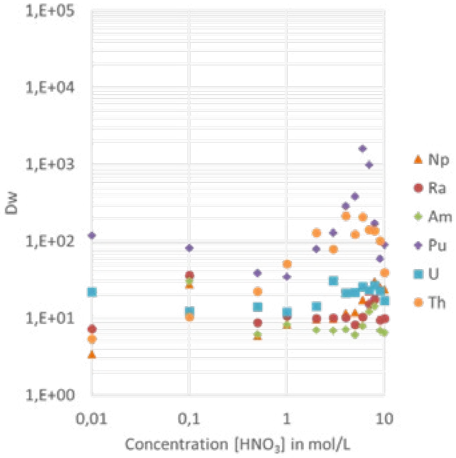
Dw values of selected elements on TK201 Resin in HCl, data provided by Russel et al. (NPL)

The TK201 Resin also shows strong retention of U and Pu at elevated HCl concentrations, both might subsequently be eluted in dilute acid.



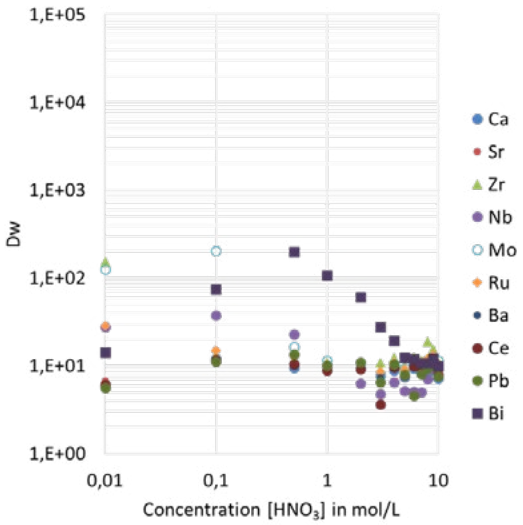
D_w values of selected elements on TK201 Resin in HCl, data provided by Russel et al. (NPL)

The TK201 Resin further strongly retains Bi and Mo at elevated HCl concentrations, while other elements tested show no or only very low retention (Ru, Nb).



D_w values of selected elements on TK201 Resin in HNO_3, data provided by Russel et al. (NPL)

The TK201 Resin generally shows rather limited selectivity in HNO_3, besides for Re and Tc at low acid concentration. At elevated HNO_3 concentrations Pu is well retained and Th fairly well, other actinides are not retained under these conditions.

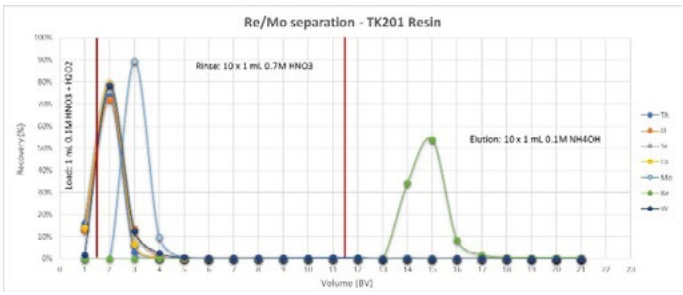


D_w values of selected elements on TK201 Resin in HNO_3, data provided by Russel et al. (NPL)

Out of the other elements tested only Bi (at about 0.5M HNO_3) and Mo (at low HNO_3 concentrations) are retained significantly. It is important to note that Mo is not retained at HNO_3 concentrations above 0.5M while Tc and Re are well retained (shown on the 1st figure), allowing for their clean separation.

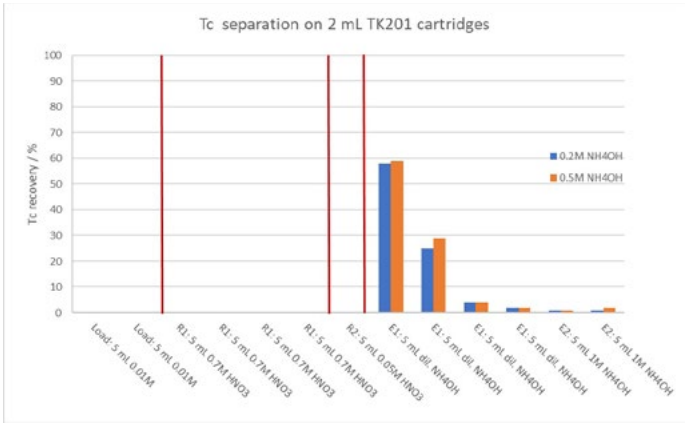
It could further be shown by Vajda et al. that D_w values for Tc(VII) are very low in dilute NH_4OH: in 0.1M NH_4OH Tc(VII) shows a D_w of only ~2, accordingly it is easily eluted by ≥ 0.1M NH_4OH.

Additional elution studies indicated that an efficient Mo separation from Re is possible using 0.7M HNO_3 for Mo removal and dilute NH_4OH for Re elution.



Elution study, Re separation from various elements (incl. Mo and W).

Vajda et al. could confirm that Tc is, like Re, not eluted in 0.7M HNO_3, validating that Re is a good surrogate for Tc and thus also allowing an efficient Mo/Tc separation. Most suitable conditions for Tc elution were found to be NH_4OH greater or equal to 0.2M.

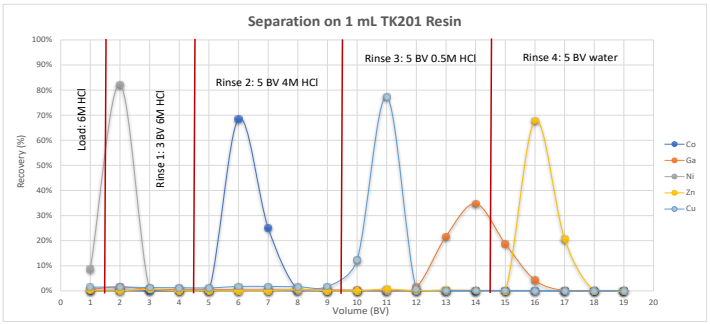


Elution study, Tc separation on 2 mL TK201 cartridges, data provided by N. Vajda (RadAnal)

The other main application of the TK201 Resin is the separation of Cu isotopes (e.g. Cu-64) from solid Ni targets. Other than the CU Resin the TK201 Resin allows for Cu retention from high HCl (e.g. 6M), while letting Ni pass for subsequent recycling. Other potential impurities (e.g. Co) may be removed through rinses with 4 – 5M HCl. Cu may then be eluted in dilute HCl leaving Zn on the column.

A typical separation is shown in the graph below. In order to remove Fe and Ga impurities potentially present the dissolved Ni target (6M HCl) may first be loaded through a small TBP (or TK400) cartridge which will retain both elements while letting Ni, Cu and Zn pass onto TK201 for further purification. Cu may then be eluted from TK201 e.g. in 0.05M HCl.

TK201 may also be used to convert the Cu fraction eluted from the CU Resin (e.g. for the separation of Cu isotopes from Zn targets) from a highly acidic solution (e.g. 6 - 8M HCl) to conditions more suitable for labeling (e.g. dilute HCl) as indicated in the following figure. TK201 will retain Cu e.g. from 6M HCl and can then be eluted with dilute HCl. This will also ensure further Zn removal.



Elution study, Cu separation and conversion on TK201 Resin

Main applications:

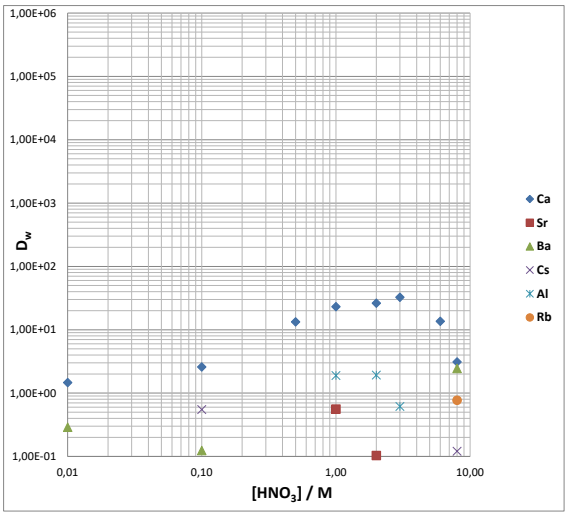
- Separation of Cu isotopes from solid Ni targets
- Separation of technetium
- Separation of rhenium

TK221 Resin

The TK221 Resin is based on a mixture of a diglocylamide and a phosphine oxide. It further contains a small amount of a long-chained alcohol and the organic phase is impregnated onto an inert support containing aromatic groups for increased stability against radiolysis.

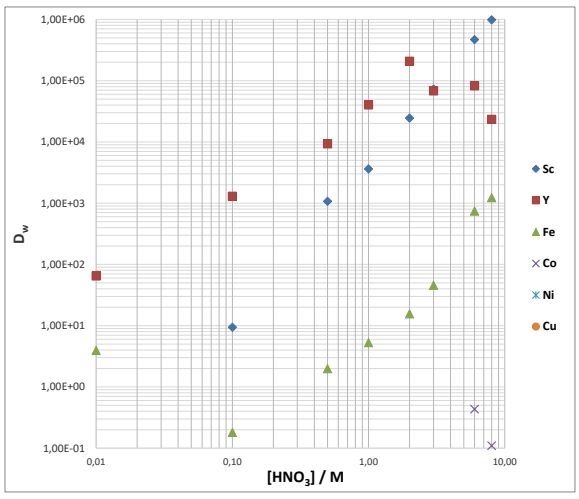
The following graphs show the selectivity of the TK221 Resin for a wide range of elements in HNO_3 and HCl.

Out of the tested elements only Ca is weakly retained on the TK221 Resin in HNO_3. Other alkaline, earth-alkaline elements and Al are not retained.



D_w values of selected elements on TK221 in HNO_3

Y and Sc are very strongly retained from HNO_3 of elevated concentration. Fe(III) is also well retained at HNO_3 concentration ≥ 3M HNO_3.

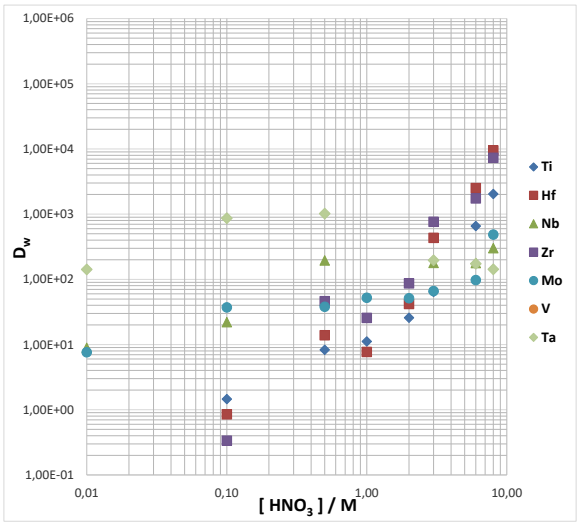


D_w values of selected elements on TK221 in HNO_3

A wide range of transition metals such as Zn, Ga, Co, Ni and Cu are not retained from nitric acid.

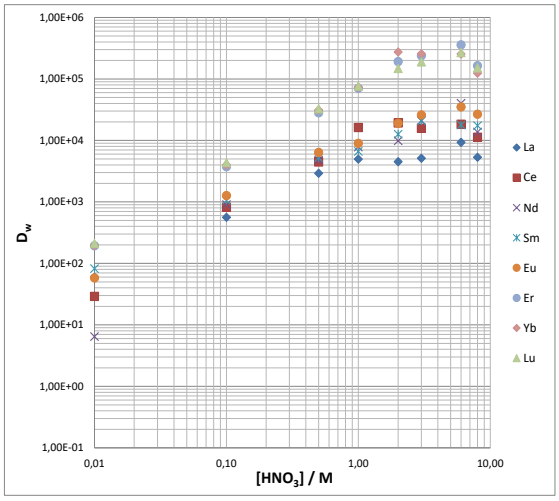
The TK221 Resin generally retains tetravalent elements such as Zr and Hf at elevated HNO_3 concentrations.

The TK221 Resin shows very high retention of lanthanides at HNO_3 concentrations ≥ 0.1M HNO_3, heavy lanthanides are even well retained in more dilute HNO_3 (≥ 0.01M). The retention of the lanthanides is significantly stronger than on TRU Resin.



D_w values of selected elements on TK221 in HCl

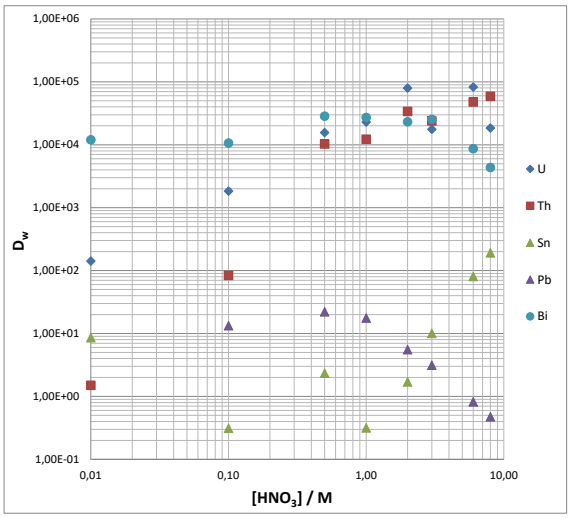
U and especially Bi are well retained over the whole HNO_3 concentration range, while Th is well retained at HNO_3 > 0.1M. U retention is significantly higher than on other diglycolamide based resins such as DGA Resin. Pb and Sn are only weakly retained.



D_w values of selected elements on TK221 in HCl

In HCl medium, none of the tested alkaline and earth-alkaline elements were retained on the TK221 Resin the same is true for Al.

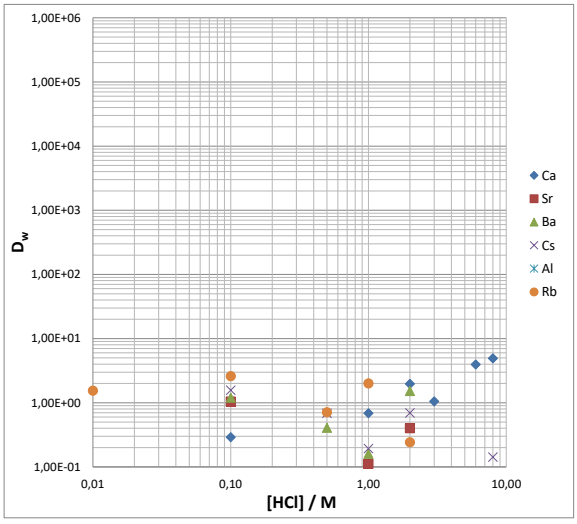
Y and Sc are very strongly retained from HCl at elevated concentration (≥ 2M HCl). Fe(III) is also well retained at HCl concentration ≥ 3M.



D_w values of selected elements on TK221 in HCl

Elements with a valency of +IV and higher such as Nb, Zr, Hf and Mo are very well retained at elevated HCl concentrations.

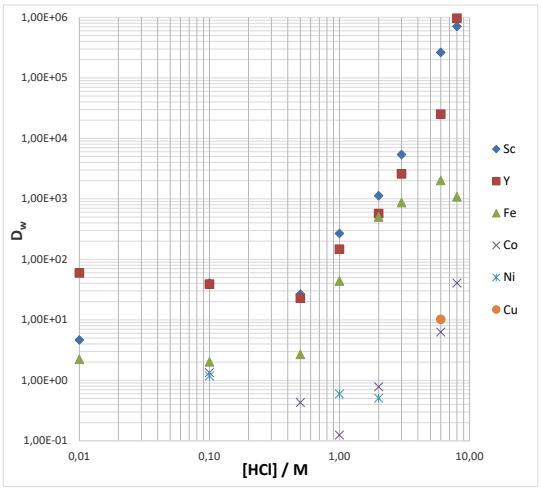
Other than many other transition metals, Zn and Ga are very well retained from ≥ 2M HCl. Both may be easily eluted in dilute HCl.



D_w values of selected elements on TK221 Resin in HCl

U, Sn and Bi are well retained over the whole HCl concentration range, while Th is only well retained at ≥ 3M HCl. Pb is generally only very weakly retained.

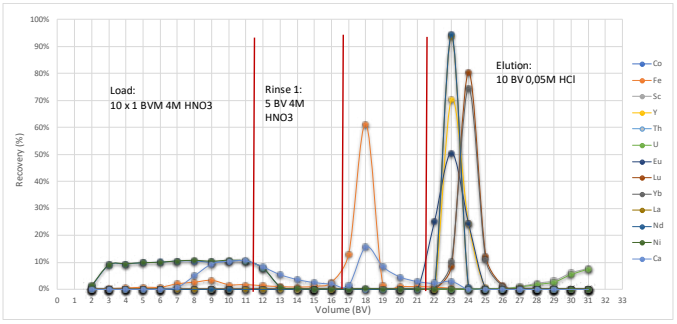
Lanthanides are generally very well retained at HCl concentrations ≥ 3M HCl, heavy lanthanides even at ≥ 1M, and they may be eluted in dilute HCl.



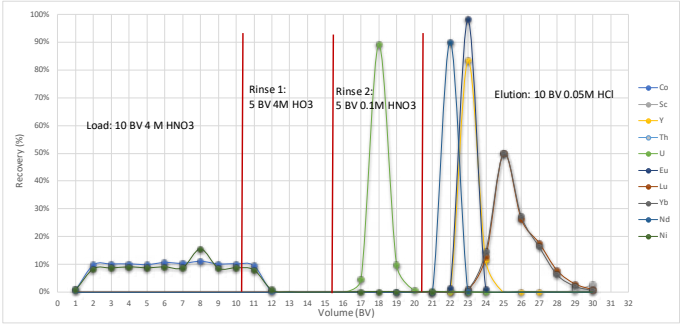
Elution study, various elements on TK221

One of the main applications of TK221 Resin is the concentration, purification and conversion of heavy lanthanides such as Lu from highly acidic solutions into dilute HCl (typically ≤0.05M HCl) conditions.

It allows e.g. to elute Lu in a smaller volume than DGA,N Resin. Accordingly, it may e.g. find use in the production of Lu-177.



Elution study, various elements on DGA, normal Resin



Elution study, various elements on TK221

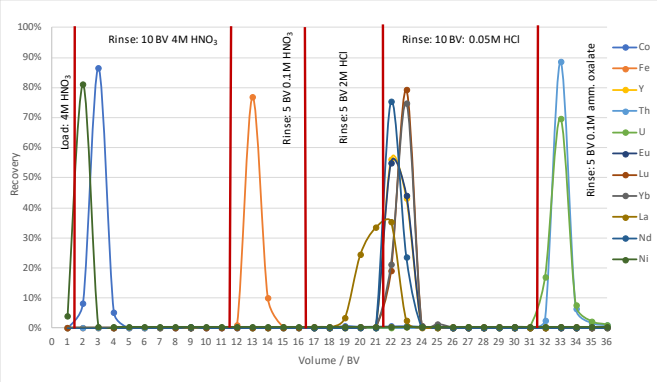
A number of separation methods based on the TK221 Resin are currently being developed particularly for ca and nca Lu-177 purification, as well as the use of TK221 as part of the separation of nca Lu-177 from up to 500 mg Yb-176.

The final product obtained using the TK221 Resin in the latter separation is typically additionally passed through a 1 mL A8 cartridge for trace nitrate removal.

Such a separation should also be applicable to the purification of Ac-225.

The fact that the TK221 Resin is showing higher U retention compared to e.g. DGA,N Resin might further allow for its use in a two column separation method for sequential actinides separation.

The following figure shows an elution study of several elements including U on TK221.



Elution study, various elements on TK221

U is very well retained under all employed HNO_3 and HCl concentrations and may finally be eluted in 0.1M oxalate. Am is expected to be eluted before U in dilute HCl.

With respect to the TK221 selectivity a stacked TEVA/TK221 method for the separation of U, Th, Pu, Am/Cm and Np seems very well possible.

In such a case Np(IV), Pu(IV) and Th(IV) would be retained, and separated, on TEVA while U and Am would pass through TEVA onto TK221 where both would be retained. It should then be possible to first elute Am with dilute HCl and finally U with dilute oxalic acid.

The development such a method is currently on-going.

Main applications:

- Separation and concentration of lanthanides (e.g. ca and nca Lu-177)
- Separation of actinides
- Separation of actinium

TK211/2/3 Resins

The TK211, TK212 and TK213 Resins are based on different mixtures of organophosphoric, organophosphonic and organophosphinic acids. It could be shown that under certain conditions and for certain lanthanide pairs, such mixtures can show increased selectivity compared to the respective pure compounds.

The organic phase further contains a small amount of a long-chained alcohol that will act as radical scavenger to increase the radiolysis stability of the resin.
The inert support onto which the organic phase is impregnated contains aromatic groups which will also contribute to the increase of the radiolysis stability of the resins.

The inert support further shows an elevated capacity for the extractants. Accordingly, this allows the TK211/2/3 Resins to have a higher extractant load compared to e.g. the LN Resin series.

The TK211/2/3 Resins show, like the LN Resins differences in their respective acidities. TK211 is the most acidic resin, accordingly it will extract lanthanides, and other elements, at higher acid concentrations than e.g. TK212 and TK213. TK212 on the other hand is more acidic than TK213 (order of acidity: TK211 > TK212 > TK213).

The selectivity and retention of the lanthanides is generally very similar in HNO_3 and HCl on all three resins, accordingly both acids may be employed for the separation of lanthanides.

This difference in the relative acidity of the resins can be exploited to facilitate otherwise more complex lanthanide separations.
This will particularly be the case for the separation of very small amounts of one lanthanide from a large excess of its neighbouring lanthanide.

Typical examples are the production of nca Lu-177 (separation from irradiated Yb-176 targets) and nca Tb-161 (separation from irradiated Gd-160 targets).

By performing a first separation on a 'less acidic resin' such as TK212 followed by direct elution of the lanthanide fraction to be further purified onto a more acidic resin such as TK211 for further purification ("sequential separation") it is possible to eliminate intermediary steps such as the use of TK221 (or DGA) Resin to convert the lanthanide fraction from higher acid concentration to low acid concentration.

In an ideal case even a fully sequential three column separation might be possible (TK213 => TK212 => TK211).

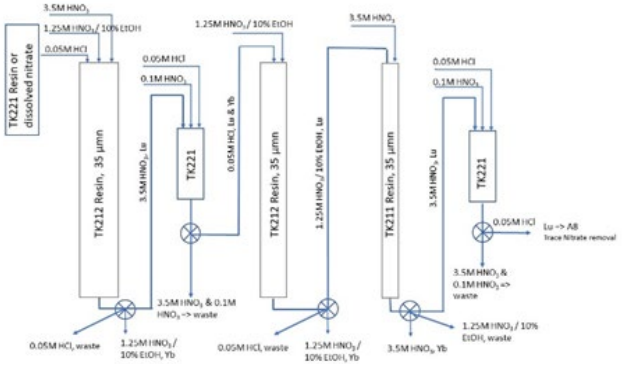
Two examples of the use of such sequential separation steps will be shown in the following.

The production of nca Lu-177 is rapidly gaining importance due to its increased use in nuclear medicine. Reliable, preferably easy to automize methods that allow for its separation from irradiated Yb-176 targets of elevated size (≥500 mg) are thus of increasing importance.

Horwitz et al. describe a method based on three LN2/ DGA cycles for the separation of nca Lu-177 from 300 mg Yb-176 targets. While this method gives good yields (~73%) in a short separation time (~4h) the fact that an elevated number of columns are required complicates its automatization. Further it has only been tested for up to 300 mg of target material.

By introducing a sequential separation step this method can be partially simplified.

It could be shown that the method described in the following figure allows for separating Lu from up to 500 mg of Yb with elevated Lu recovery (~85%) and a very low amount of residual Yb in the final Lu fraction.

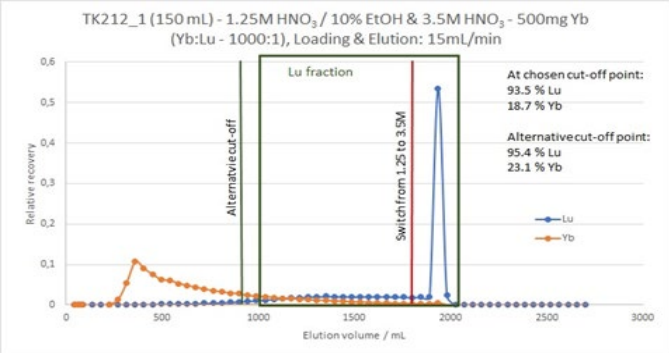


Scheme of a method for the separation of Lu from 500 mg Yb using TK212, TK221 and TK211

The increased Lu recovery is, other than the use of TK212 instead of LN2, also due to the adjustment of the eluting agent used for the chromatographic separation of Lu and Yb on the first TK212 column from 1.3M HNO_3, as suggested by Horwitz et al., to 1.25M HNO_3 / 10% EtOH.

It should be noted that adding EtOH only showed an improvement for the 1.25M HNO_3 but not for the 3.5M HNO_3. Further, mixing 3.5M HNO_3 with EtOH should be strictly avoided for safety purposes.

The following figures show typical chromatograms obtained during the separation of Lu from 500 mg of Yb (initial Lu:Yb ratio: 1:1000). All experiments were performed using stable elements, fractions of defined sizes were collected, diluted, and analysed off-line by ICP-MS. Relative recoveries were calculated for Lu and Yb and plotted against the elution volume.



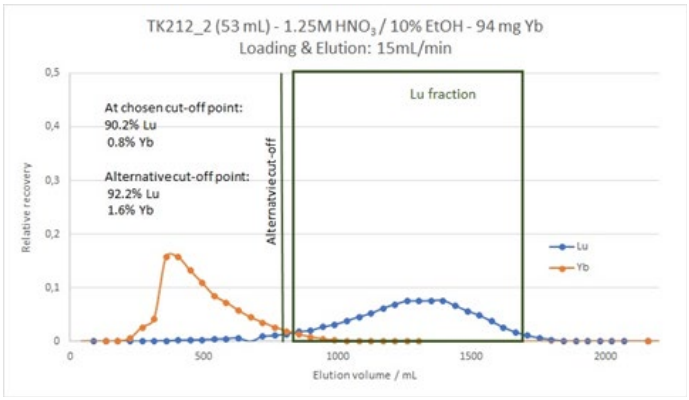
Example of a Lu separation from 500 mg Yb on a TK212 column (2.5 x 30 cm, 150 mL) using 1.25M HNO_3 / 10% EtOH and 3.5M HNO_3 e of a method for the separation of Lu from 500 mg Yb using TK212, TK221 and TK211

It should be noted that the switch to 3.5M HNO_3 in the given example was made at a rather late stage of the separation. In the final version of the process it should take place earlier, ideally triggered via radiation detection, close to the chosen cut-off point (left end of the green frame).

Indeed, the moment of the switch will have, especially on the first column, a considerable influence on the Lu recovery and Yb carry-over. This is mainly due to the significant tailing introduced by the macro-amount of Yb.

The fractions comprised in the green frame ("Lu fractions") were combined and passed through a 5g TK221 cartridge for conversion to ≤0.05M HCl. The Lu fraction thus obtained in dilute HCl was then loaded onto the next TK212 column (1.5 x 30cm, 53 mL).
Due to the lower of amount of Yb present on the column the tailing of the Yb and Lu elution is less pronounced than on the first TK212 column.

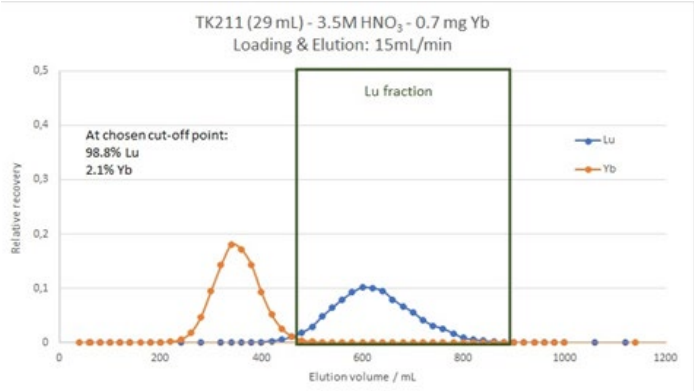
Although this would be possible, in this example the Lu containing fractions (green frame) are not eluted



Example of a Lu separation fraction, obtained from a first TK212 separation from 94 mg Yb, on a second TK212 column (1.5 x 30 cm, 53 mL) using 1.25M HNO_3 / 10% EtOH

in HNO_3 of elevated concentration (as described in the Horwitz method), passed through a TK221 (or DGA) cartridge and eluted in dilute HCl for another load onto TK212.

Instead the combined fractions are directly loaded onto a TK211 column (1.1 x 30 cm, 29 mL) for the final purification of the Lu.



Example of a Lu separation fraction, obtained from the second TK212 separation from <1 mg Yb, on a second TK212 column (1.1 x 30 cm, 29 mL) using 3.5M HNO_3

Lu is finally obtained following separation/elution e.g. with 3.5M HNO_3.

As final step the obtained Lu fractions (as indicated in the green frame) were combined and loaded onto a 2 mL TK221 cartridge, any last potentially present impurities are removed through consecutive rinsed with 3.5M HNO_3 and 0.1M HNO_3. Lu is then finally eluted using ≤0.05MHCl.

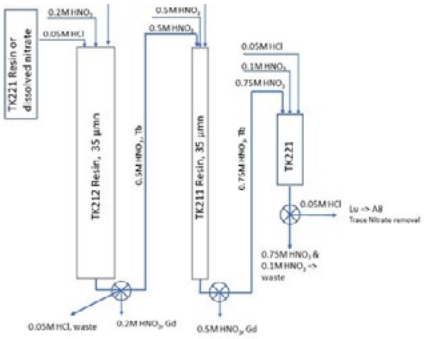
Last traces of nitrates that might still be present will be removed via a 1 mL anion exchange cartridge (A8 Resin).

A further upscale of this separation process is currently being finalized.

Another radiolanthanide increasingly finding use is Terbium. As Tb isotopes may be used for PET imaging (Tb-152), SPECT imaging (Tb-155), alpha therapy (Tb-149) and beta therapy (Tb-161) it is also referred to as the 'swiss army knife' of nuclear medicine.
Particularly the interest in Tb-161 is currently increasing significantly, accordingly methods for the separation of Tb from irradiated Gd targets of elevated size are needed.

The development, and later upscale, of methods for the separation of Tb from 500mg Gd is currently on-going. The next figure shows a scheme of a suggested separation process.

As may be seen the separation is more straightforward compared to the separation of Lu from Yb targets.

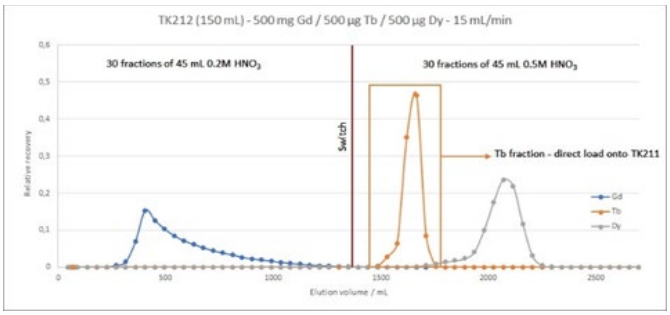


Scheme of a method currently under development for the separation of Tb from 500 mg Gd using TK212 and TK211

The following two figures show typically obtained chromatograms (stable Gd, Tb and Dy, with an original ratio of 1000:1:1).

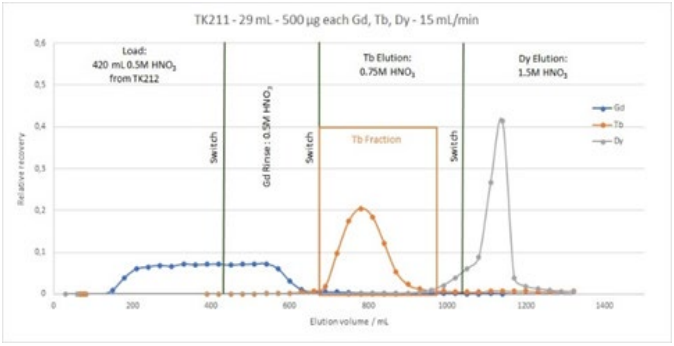
Like for the Lu separation the separations were performed using stable elements, fractions of defined volumes were taken and analysed by ICP-MS.

A first separation is performed on a TK212 column. This step allows for an initial separation of Tb from Gd and Dy.
The obtained Tb fractions (indicated by the orange frame) were then combined and directly loaded onto a TK211 column for final purification of the Tb.
As may be seen in the next figure under the chosen conditions most of the Gd is breaking through during the load, any Gd remaining on the columns is rinsed of with 0.5M HNO_3.
It could be shown for the Lu separation process that the addition of small amounts of EtOH (10% v/v) improves the separation, this is currently also being tested for the Tb separation.



Example of a Tb separation from 500 mg Gd on a TK212 column (2.5 x 30 cm, 150 mL) using 0.2M HNO_3 and 0.5M HNO_3

Increasing the concentration of the mineral acid (in this example to 0.75M HNO_3) will lead to the elution of Tb, leaving potentially remaining traces of Dy on the columns. In case the presence of Dy can be ruled out this elution can be performed at higher acid concentrations, thus lowering the elution volume.



Example of a Tb separation from 500 µg Gd on a TK211 column (1.1 x 30 cm, 150 mL) using 0.5M HNO_3 and 0.75M HNO_3

As a final step the Tb will be concentrated on a 2 mL TK221 cartridge, any last potentially present impurities are removed through consecutive rinsed with 0.75M HNO_3 and 0.1M HNO_3. Tb is the finally eluted using ≤0.05M HCl.

Last traces of nitrates that might still be present will be removed via a 1 mL anion exchange cartridge (A8 Resin).

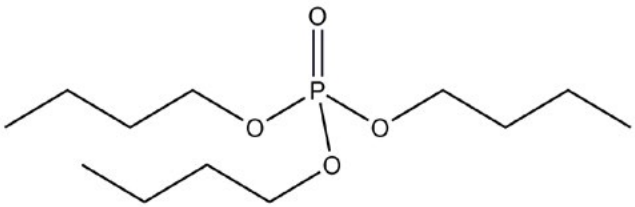
The indicated method is currently undergoing further optimisation and upscale.

Prepacked TK211/212/213 columns of various sizes (e.g. 150 mL, 53 mL and 29 mL) are currently being developed.

Main Applications :

- Lanthanide separation e.g. nca Lu-177 and nca Tb-161

TBP Resin



TriButylPhosphate (TBP)

The TBP Resin is comprised of an inert support impregnated with Tributylphosphate (TBP). TBP is a widely used extractant, it finds e.g. application in the Purex process, the reprocessing of U and Pu from spent fuel. Other applications include, amongst others, the separation of yttrium for analytical purpose.

The TBP Resin has been characterized with respect to the uptake of various elements in HNO_3 and HCl.

Beside Pu(IV) and Np(IV) several other elements such as Au, Hf, Fe, Sn and Ga also show high affinity for the TBP Resin in HCl.

While Au remains retained under all tested conditions, making its elution rather difficult in HCl, the other elements only show high D_W values at elevated acid concentrations, and low D_W values at lower concentrations.

In 1M HCl for example only Sn shows elevated D_W values whereas Fe, Ga, Sb... show very little affinity to the resin, allowing for its separation from these elements. Sn can then be eluted e.g. with 0.1M HCl.

The TBP resin generally shows very good selectivity for Sn over Te (Te-126 is an isobaric interference for the mass spectrometric determination of a long-lived beta emitter Sn-126, frequently determined in decommissioning and radioactive waste samples) and Cd which is frequently used as target material for the production of Sn-117m, a conversion electron emitter used in nuclear medicine. The resin also shows interesting selectivity for Sb, however its oxidation state needs to be carefully controlled.

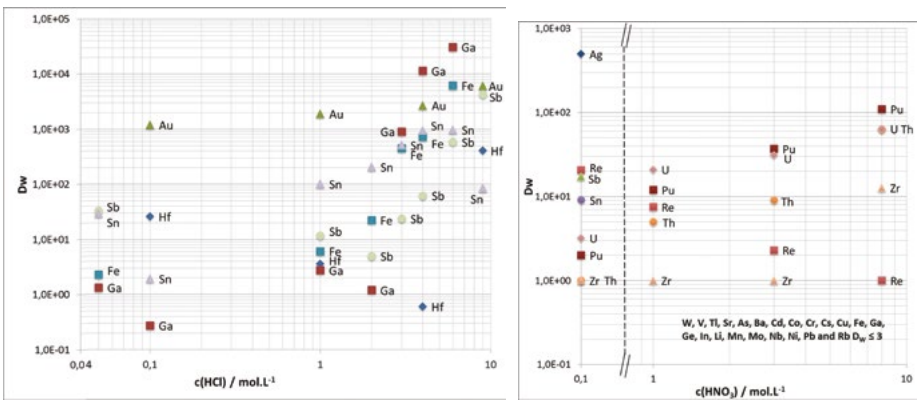
It has further been employed for the separation of Zr-89 from Y targets and for the separation of Sc from Ca targets. In both cases the products were retained from high HCl and eluted in dilute HCl.

In HNO_3 of all tested elements only the actinides (at elevated HNO_3 concentrations), and Ag (at low HNO_3 concentrations), are retained on the resin. Based on the obtained data, Dirks et al. have developed a procedure for the separation of Sn from various elements.

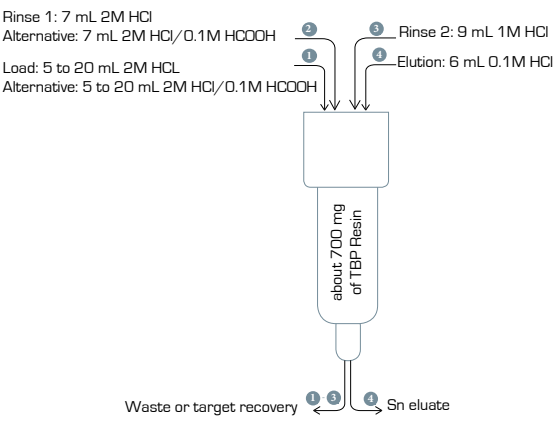
Most of the tested elements are not retained during load and first rinse. Sn and part of the Ga and Fe are retained. The latter two are first removed with 1M HCl, Sn is then quantitatively eluted with 6 mL 0.1M HCl in high purity. For samples containing elevated amounts of Fe it will be necessary to either remove Fe before loading (e.g. by anion exchange) or to assure complete reduction of Fe to Fe(II).

Main Applications :

- Separation of tin
- Separation of zirconium
- Separation of scandium
- Separation of actinides



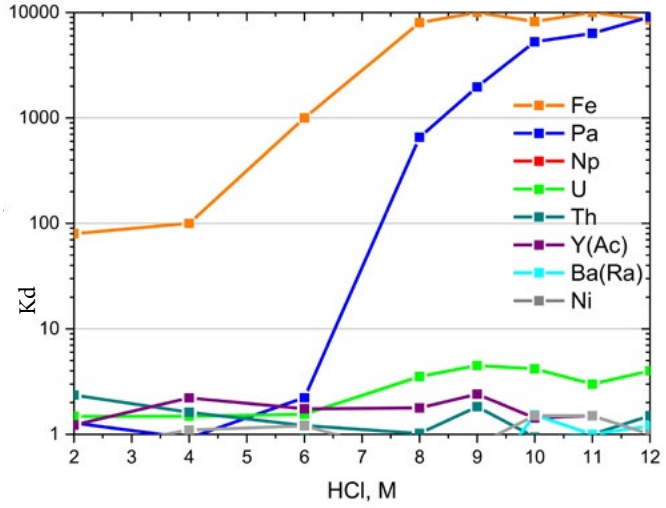
D_W values of selected elements on TBP Resin in HCl and HNO_3 .



Separation scheme Sn separation on TBP Resin.

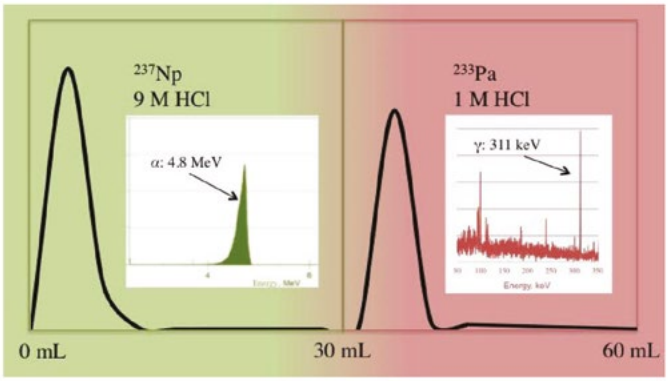
TK400 Resin

The TK400 Resin is an extraction chromatographic resin that is comprised of a long-chained alcohol impregnated onto an inert support. Knight et al. showed that long-chained alcohols, especially octanol, show very interesting selectivity towards Pa at high HCl concentrations, allowing for facile Pa/Np separation using column chromatography. Jerome and al. characterized the TK400 Resin with respect to its selectivity for



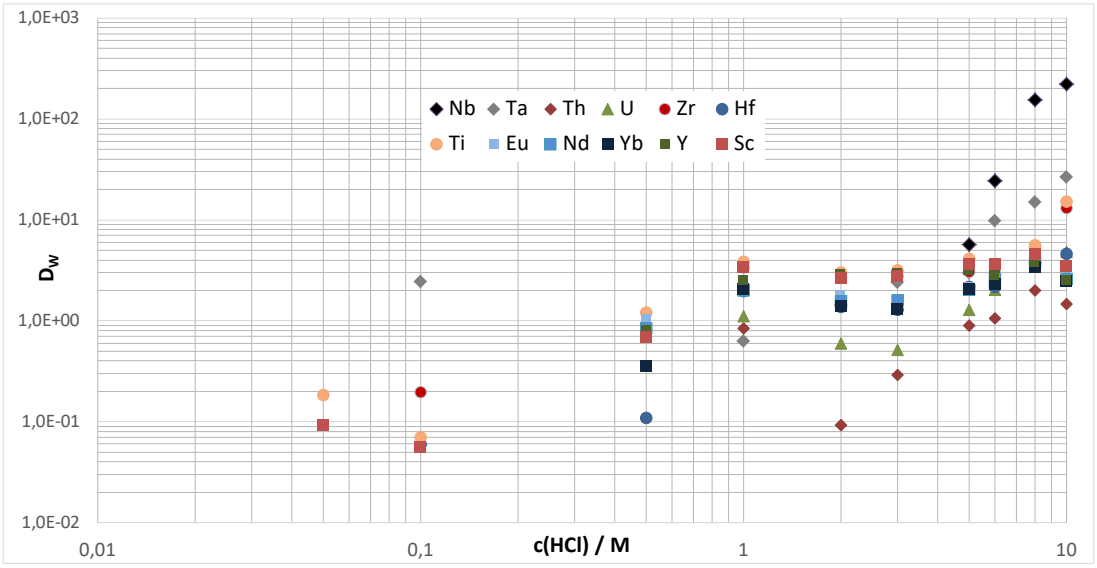
D_W values of selected elements on TK400 Resin in HCl at varying concentration [Data provided by Ivanov et al]

They found that Pa retention sharply increases at high (≥ 9M) HCl concentrations whereas other elements tested are not retained. At HCl concentrations < 8M HCl on the other hand D_W values of Pa were found to be low allowing for its elution in a small volume. Ostapenko et al. found a similar trend for Pa retention with k' values being high for Pa at high HCl concentrations (9M). These results correspond overall well to the selectivity observed by Knight et al. when performing Np/Pa

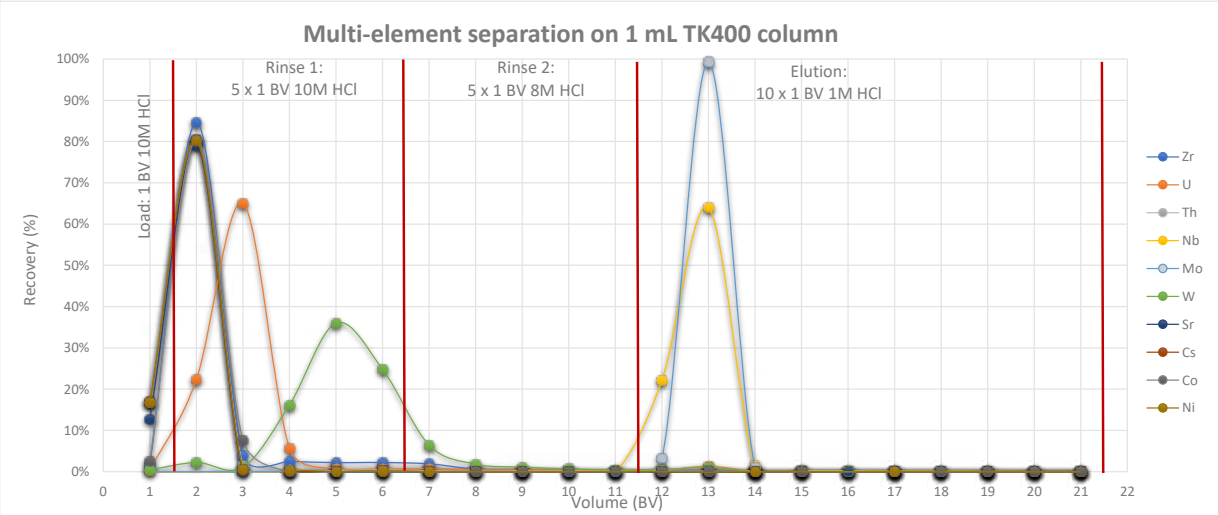


Elution study, Np/Pa separation on long-chained alcohol resin [Taken from Knight et al.]

The resin shows high selectivity for Nb at high HCl concentrations over other elements tested such as Ta, Zr, Hf and lanthanides which are not, or only very poorly as in the case of Ta, retained by the resin.



D_W values of selected elements on TK400 Resin in HCl at varying concentration

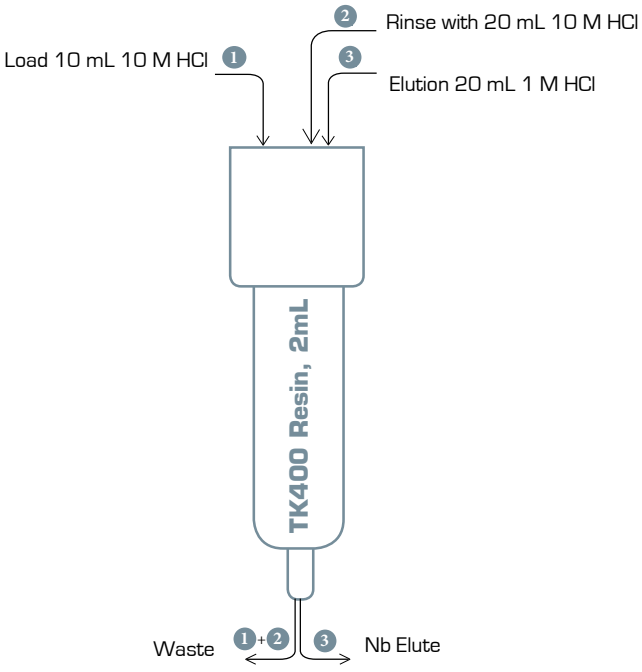


Elution study, Nb separation from selected cations, 2 mL TK400 column

With respect to its selectivity the TK400 Resin shows the potential for allowing a number of interesting separations such as Nb/Zr, Mo, Po and Pa/U/Th. The results of an elution study on the separation of Nb from a number of elements, including Zr, and the separation method used to obtain these results are shown in following figures. Jerome et al. employed the TK400 Resin for the separation of Pa from its descendants following the procedure shown here. They found that U, Th, Ac, Ra and Pb were removed from the resin during load and rinse, allowing for obtaining a clean Pa fraction with high chemical yield (~83%).

The TK400 Resin further shows a very high Fe(III) retention (and capacity) in HCl of elevated concentration which might make the TK400 suitable for Fe separation or removal (e.g. when used in combination with the TBP Resin for Zr-89 separation).

Tieu et al showed that the TK400 Resin may be used in a single column separation of Ga-68 from Zn targets, allowing to directly recover the Ga in dilute HCl. The Purity of the Ga-68 obtained was lower than that of a Ga-68 obtained using the ZR Resin/TK200 combination though.



Nb separation on TK400 Resin

Main Applications :

- Separation of protactinium
- Separation of gallium
- Separation of niobium
- Separation of iron

Guard Resin

The Guard Resin is a hydrophobic, highly crosslinked, porous polydivinylbenzene based adsorbent. Due to its high hydrophobicity it will remove certain organic impurities, notably organic impurities that are hydrophobic, more efficiently than e.g. the Prefilter Resin. The Guard Resin is generally used in reversed phase chromatography and solid phase extraction, and for the adsorption of biomolecules of up to 14 kDa. It has a surface area of > 600 m^2/g and a typical porosity in the order of 300 – 500 Å. The resin shows high mechanical and chemical stability, and it may be used over the whole pH range.

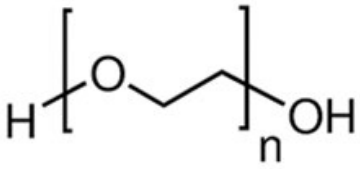
The Guard Resin is TSE/BSE/GMO free.

Another application of the Guard Resin is the separation, in combination with the ZR Resin, of Ge-68 from GaNi or GaCo targets. The actual separation of Ge from the target material is performed on two consecutive ZR Resin cartridges. The Guard Resin may then be used in the final step of the purification, namely the conversion of final product Ge-68 from dilute citric acid to dilute hydrochloric acid.

Main Applications :

- Removal of organic impurities
- Ge-68 (in combination with ZR Resin)

Upcoming: TK202 Resin

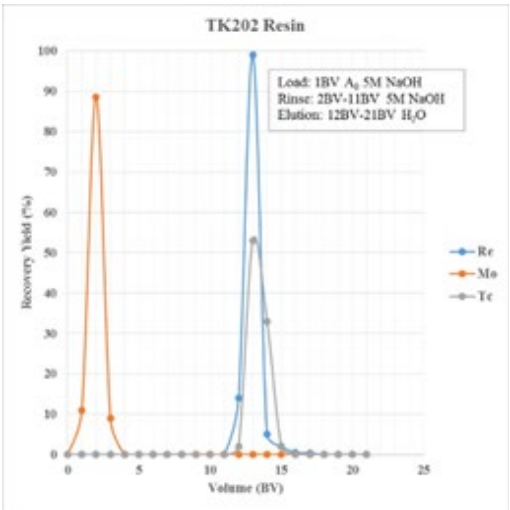


PEG functionality

The new, upcoming TK202 Resin is based on PolyEthylene Glycol (PEG) functional groups that are covalently bound to the surface of an inert support.
Its main application is the separation of Tc from Mo under highly alkaline conditions (preferably 5M NaOH) e.g. for the direct Tc-99m production from irradiated Mo targets. It may further be used for the separation and determination of Tc-99 in decommissioning samples e.g. following alkaline fusion.
In both cases, after retention and purification of the Tc it is eluted with water. In case of the radiopharmaceutical application it is preferable to pass the Tc fraction through an additional aluminium oxide column to remove last traces of Mo.

Cieszykowska et al. could show that the Tc retention increases in presence of higher amounts of Mo. They could show that for simulated Mo targets a Tc recovery > 90% for 6 – 8g Mo per g of TK202 could be achieved, and > 80% for 12g Mo per g of TK202

Additionally it could be shown that Tc and Re behave very similarly on the TK202 Resin, making the TK202 resin also suitable for Re separation.



Elution study Tc/Re separation from Mo

Main applications:

- Tc-99m separation from Mo targets
- Determination of Tc-99 in decommissioning samples

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Products	Applications *
CL Resin	I removal from effluents, Ag, Pa, Cl-36/I-129
CU Resin	Cu from liquid targets and solid Zn targets
DGA Sheets	Quality control of Ra-223, Pb-212, Ac-225/Bi-213, Ge-68/Ga-68
ZR Resin	Zr, Ga, Ge, Ti
TK200 Resin	Ga-67/8, Zn, Actinides
TK201 Resin	Cu from solid Ni targets, Tc,
TK221 Resin	Actinides, Lanthanide separation and purification (e.g. Lu-177), Ac-225 purification
TK211/2/3 Resins	Lanthanide separation (e.g. nca Lu-177, nca Tb-161)
TBP Resin	Sn, Zr, Sc, Ga, Actinides
TK400 Resin	Pa, Ga, Fe, Nb, Mo, Po
Guard Resin	Removal of orgnic impurities, Ge-68
TK202Resin	Tc separation from Mo under alcaline conditions

*the main applications are shown in orange

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