LN / LN2 / LN3 resins

Main Applications

- Separation of Lanthanides
- Separation of Actinium

Packing

Order N°.	Form	Particle size
LN-B25-A, LN-B50-A, LN-B100-A, LN-B200-A	25g, 50g, 100g and 200g bottles LN resin	100-150 µm
LN-C20-A, LN-C50-A	20, 50 and 200 2 mL LN resin columns	100-150 µm
LN5-C20-A, LN8-C20-A, LN10-C20-A	20 5mL, 8mL, 10mL LN resin columns	100-150 µm
LN-B10-S, LN-B25-S, LN-B50-S, LN-B100-S, LN-B100-S	10g, 25g, 50g, 100g, 200g bottles LN resin	50-100 µm
LN-R50-S, LN-R200-S	50 and 200 2ml cartridges LN resin	50-100 µm
L2-R10-S	10 2ml cartridges LN2 resin	50-100 µm
L3-R10-S	10 2ml cartridges LN3 resin	50-100 µm
LN-B10-F	10g bottle LN resin	20-50 µm
L2-B25-F, L2-B50-F, L2-B100-F, L2-B200-F	25g, 50g, 100g, 200g bottles LN2 resin	20-50 µm
L3-B25-F, L3-B50-F, L3-B100-F, L3-B200-F	25g, 50g, 100g, 200g bottles LN3 resin	20-50 µm

Physical and chemical properties

Density: LN resin: 0.38g/ml; LN2 resin: 0.37g/ml; LN3 resin: 0.39g/ml

Capacity: LN and LN2 Resin: 0.16 mmol/ml resin (trivalent actinides and lanthanides)
LN3 Resin: 0.18 mmol/ml resin (trivalent actinides and lanthanides)

Conversion factor D_W/k' :   LN resin: 1.75; LN2 resin: 1.82; LN3 resin: 1.67

Conditions of utilization

Recommended T of utilization :   /

Flow rate: A grade: 0.6 – 0.8 mL/min, utilization with vacuum or with pressure for s grade resin
Storage: Dry and dark, T<30°C

For additional information see enclosed literature study

Methods*

Reference	Description	Matrix	Analytes	Support
RAW01	Ra-228 in water	water	Ra-228	columns
RAW03	Radium in water	water	Ra-226, Ra-228	columns

*developped by Eichrom Technologies Inc.

LN Resin

The LN resin (LaNthanides) is composed of di(2-ethylhexyl)orthophosphoric acid (HDEHP) (fig. 1) impregnated onto an inert support.
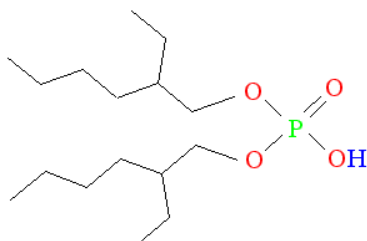
Figure 1 : Di(2-ethylhexyl)orthophosphoric acid

The following exchange equilibrium is assumed :

$$M^{3+} + 3\overline{(HY)_2} \leftrightarrow \overline{M(HY_2)_3} + 3H^+$$

Phil Horwitz studied the retention of different elements on this resin, figure 2 summarizes the results he obtained [1].

Ln resin is mainly used for two types of applications: radium separation and determination, and the separation of lanthanides for a wide range of applications.
The determination of Ra isotopes in water samples is of high importance due to their radiotoxicity and their tendency to accumulate in bones, this is especially the case for Radium-226 which is a long lived (1600 years) alpha emitter.

Table 1 : Information about radium isotopes (http://nucleardata.nuclear.lu.se/database/masses/).

Radio-nuclide	Half-life	Principle emission	Daughter nuclide
Ra-226	1600 ± 7 a	100% α	Rn-222
Ra-224	3,66 ± 0,04 d	100% α	Rn-220
Ra-228	5,75 ± 0,03 a	100% β	Ac-228
Ac-228	6,15 ± 0,02 h	100% β	Th-228

B. Burnett et al.[2] proposed a method allowing the determination of the activity of the different Ra isotopes (226, 223/224, and 228 by measurement of Ac-228) in water samples:

1/ 0,5 to 2 L of the water sample are acidified, and a small amount of stable Barium as well as Ba-133, as internal standard for Radium, are added.
2/ Barium is precipitated as sulfate and then converted into the carbonate form.

3/ The precipitate is dissolved in 0,095M HNO3 and allowed to stand for at least 30 hours for Ac-228 ingrowth. In case a yield determination via Ce is performed a known amount of Ce is added at this point.

4/ The sample is loaded onto LN resin and the resin is rinsed with 0,095M HNO3. The sample load solution and the rinsing solution contain Ra-226, Ra223/4, Ra-228 and Ba-133. Ra-226 and Ra-223/4 can be determined from this solution by different methods (e.g. alpha spectrometry or emanation methods).

5/ Ac-228 is eluted using 0,35M HNO$_3$ for measurement, after CeF$_3$ co-precipitation, by gas proportional counting. The chemical yield of the Ac separation can be determined e.g. gravimetrically via the internal standard Ce.

The preconcentration step via Barium sulfate/carbonate can be replaced either by a cation exchange resin or by using MnO$_2$ resin.

Recently Benkhedda et al.suggested a method for the automized separation and measurement of Ra-226 from water samples consisting of a preconcentration by flow injection and a on-line measurement by ICP-MS [3].
Each water sample is adjusted to a pH of 10.6, followed by the addition of EDTA. Ca and Mg form stable complexes with EDTA under these conditions, which are not retained on the LN resin. The earth alkalines retained on the LN resin (Sr, Ba and Ra) are eluted with 5M HNO$_3$. Ba and Sr are finally separated from Ra by passing the solution through SR resin. Ba and Sr are retained while Ra passes, allowing an interference free determination of Ra-226 in the sample load solution.
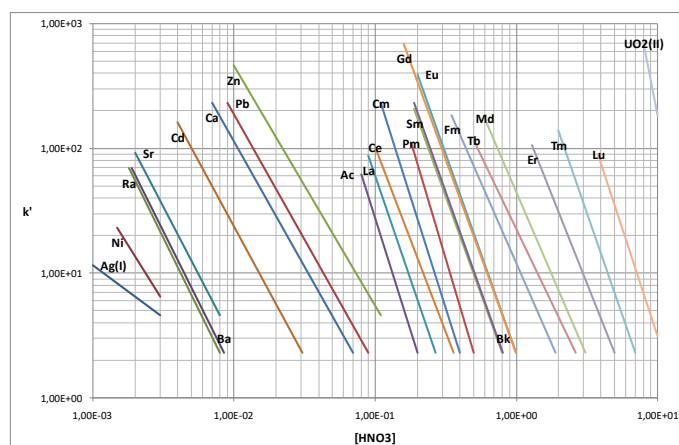

Figure 2: Retention of different elements on LN resin as a function of the HNO3 concentration (Horwitz 1975)[1]

Ln resin is also used for the determination of light rare earth elements. C. Pin et al. showed the possibility to sequentially separate La, Ce, Pr, Nd, Sm and Eu[4].

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For matrices with very high iron content an iron/rare earth separation is performed upfront using a 50WX4 type cation exchange resin. The obtained sample is then redissolved, after further treatment, in HNO_3.

In a first separation step the sample is passed through TRU resin in order to eliminate unwanted matrix elements and to remove remaining traces of iron, while the REEs stay retained. To further purify the REEs the TRU resin is rinsed with 1M HNO_3.

The light rare earth elements are then eluted with 0.05M HNO_3 and directly passed onto LN resin, which was previously conditioned with 0.05M HNO_3. At this acid concentration the REEs are retained on the LN resin. La, Ce Pr et Nd are eluted using 0.25M HCl in the cited order; Sm and Eu are then eluted using 0,75M HCl. The described separation was performed using 0.3 g of LN resin with a particle size of 50-100µm.

Ln resin can also be used in more specific applications: Hidaka et al. use LN resin for the determination of Sm/Gd ratios in moon rock samples[5].

Beside the normal LN resin two more resins exist: LN2 and LN3 (fig. 3a et 3b)[6].

HEH[EHP] (LN2)

H[TMPeP] (LN3)
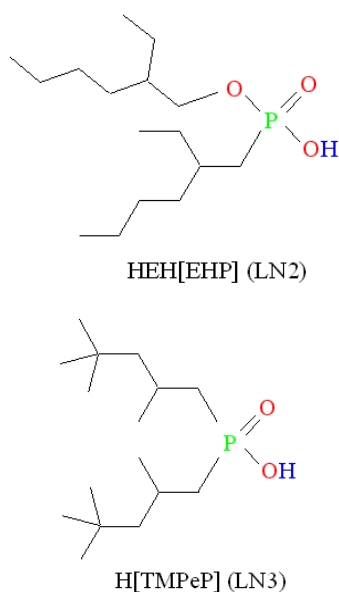
Figure 3: Extractants used for the LN2 and LN3 resins

The acidity of the impregnated extractants is diminishing in the order LN>LN2>LN3. This difference in acidity is having an impact on the retention behavior of the resins as figures 4 and 5 show.
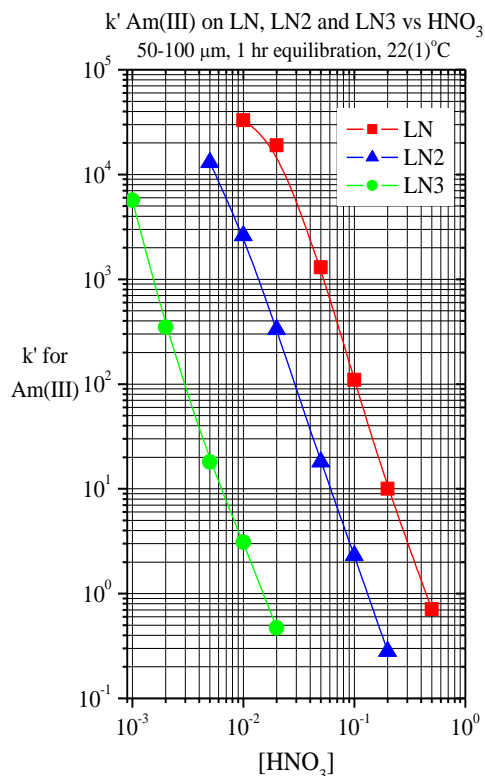
Figure 4: Capacity factors k' of Americium on the different LN resins (experiments performed at 22+/-1°C, particle size 50-100µm)[6].
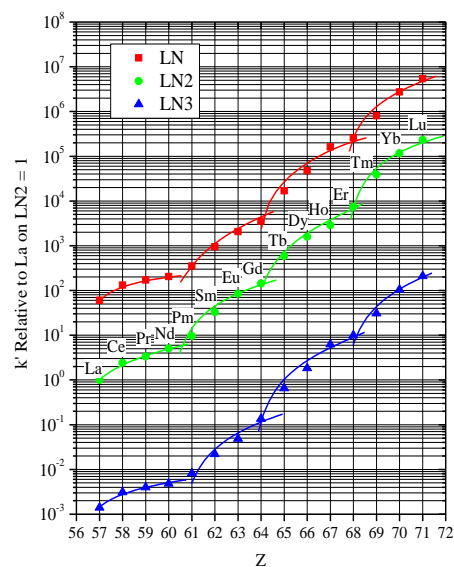
Figure 5: Relative capacity factors k' of rare earth elements normalized to La retention on LN2 resin (k'La/LN2=1)[6]

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k' vs. [HNO₃] LN, LN2 or LN3 Resin

50-100 µm, 1 h contact time, 25(2) °C

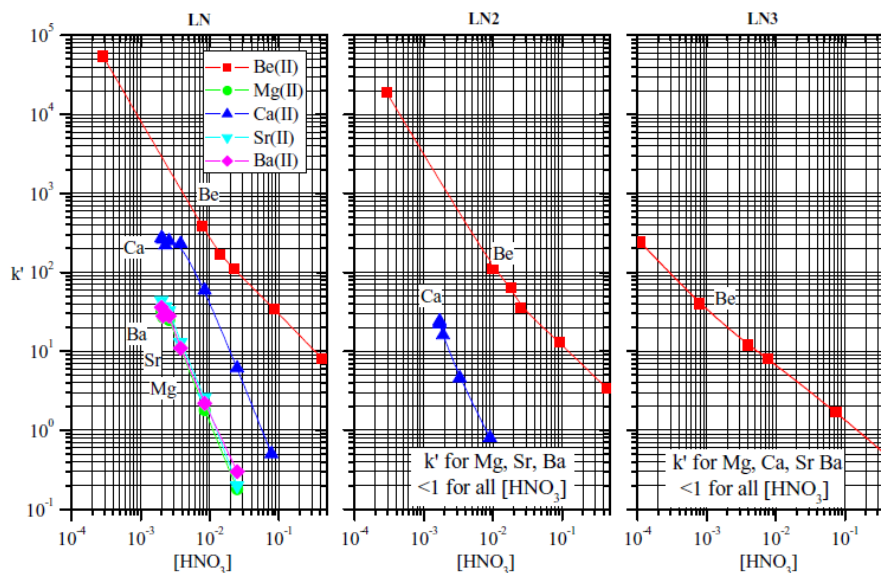**Figure 6: Capacity factor k' of earth alkalines in HNO₃ on LN / LN2 / LN3 resin.**

k' vs. [HCl] LN, LN2 or LN3 Resin

50-100 µm, 1 h contact time, 25(2) °C
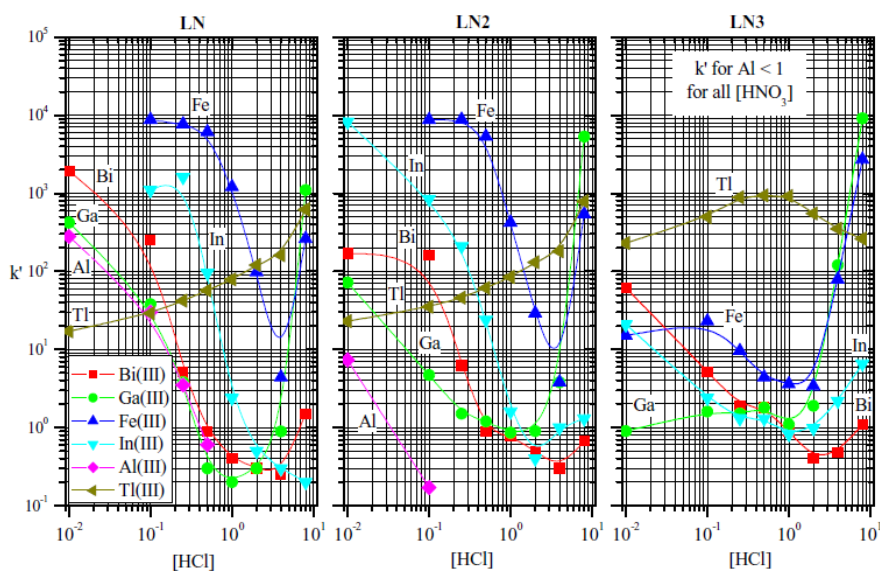
Figure 7: Capacity factor k' of various cations in HCl on LN / LN2 / LN3 resin
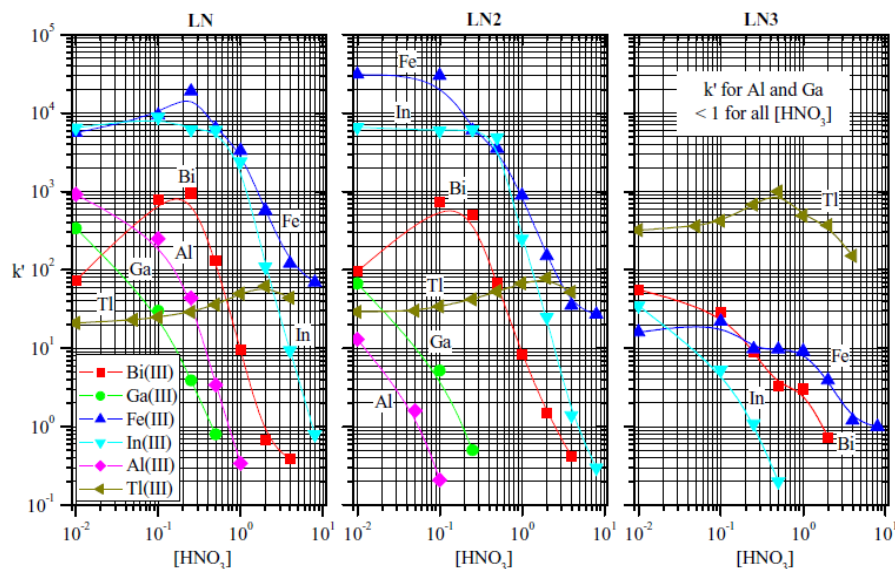
Figure 8: Capacity factor k' of various cations in HNO₃ on LN / LN2 / LN3 resin.
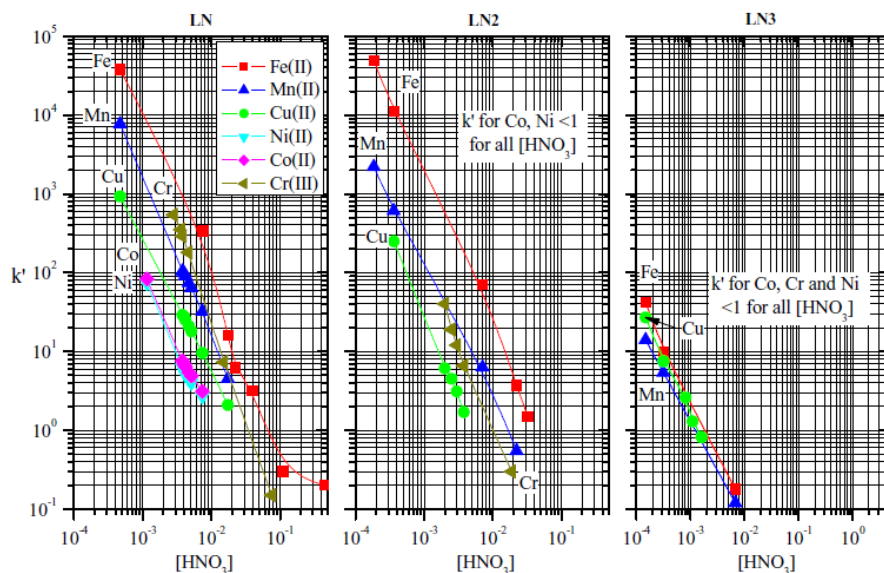
Figure 9: Capacity factor k' of various cations in HNO₃ on LN / LN2 / LN3 resin.

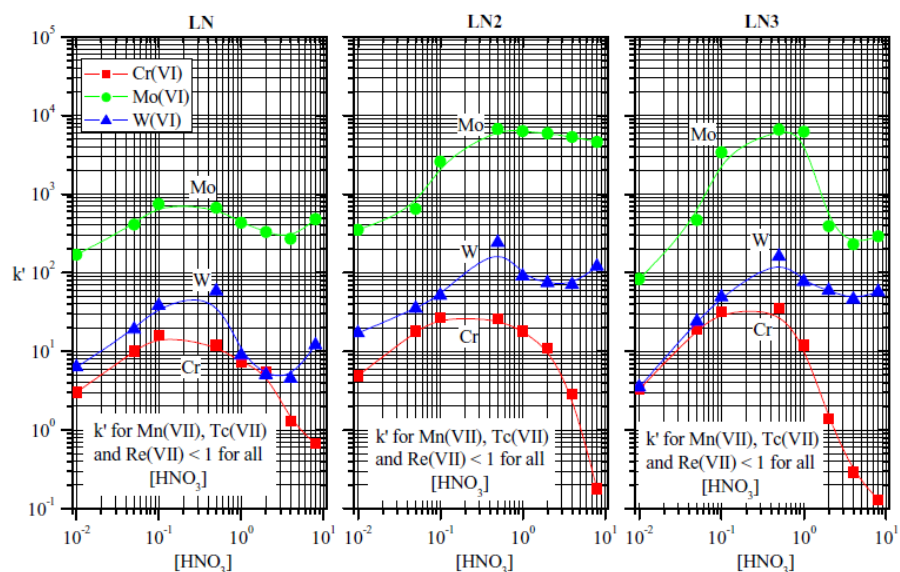## k' vs. [HNO₃] LN, LN2 or LN3 Resin

50-100 µm, 1 h contact time, 25(2) °C

Figure 10: Capacity factor k' of various cations in HNO₃ on LN / LN2 / LN3 resin.

k' vs. [HNO₃] LN, LN2 or LN3 Resin

50-100 µm, 1 h contact time, 25(2) °C
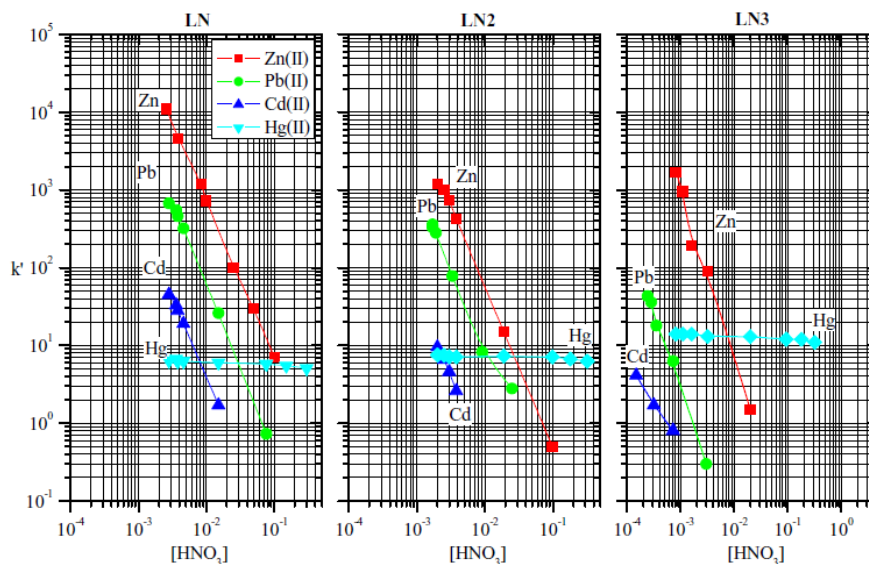
Figure 11: Capacity factor k' of various cations in HNO₃ on LN / LN2 / LN3 resin.

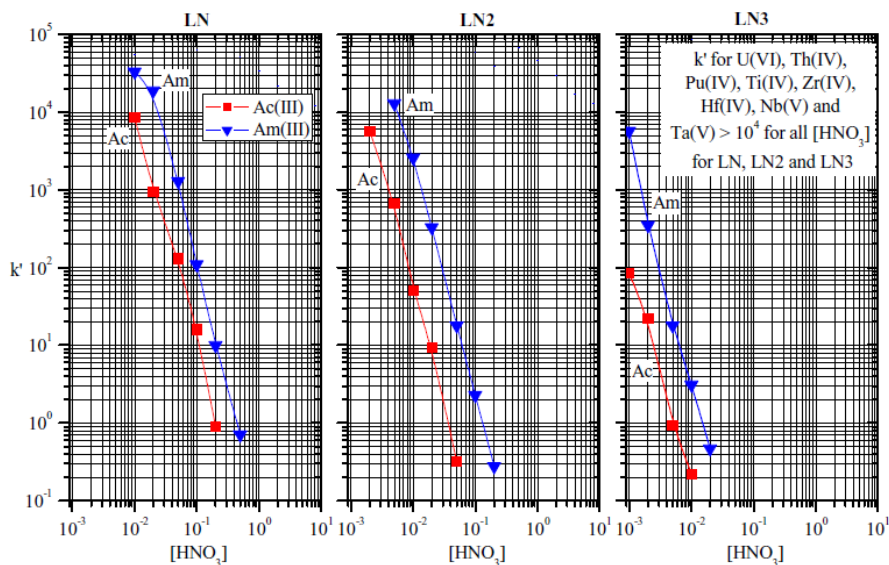## k' vs. [HNO₃] LN, LN2 or LN3 Resin

50-100 μm, 1 h contact time, 25(2) °C

Figure 12: Capacity factor k' of Ac and Am in HNO₃ on LN / LN2 / LN3 resin.

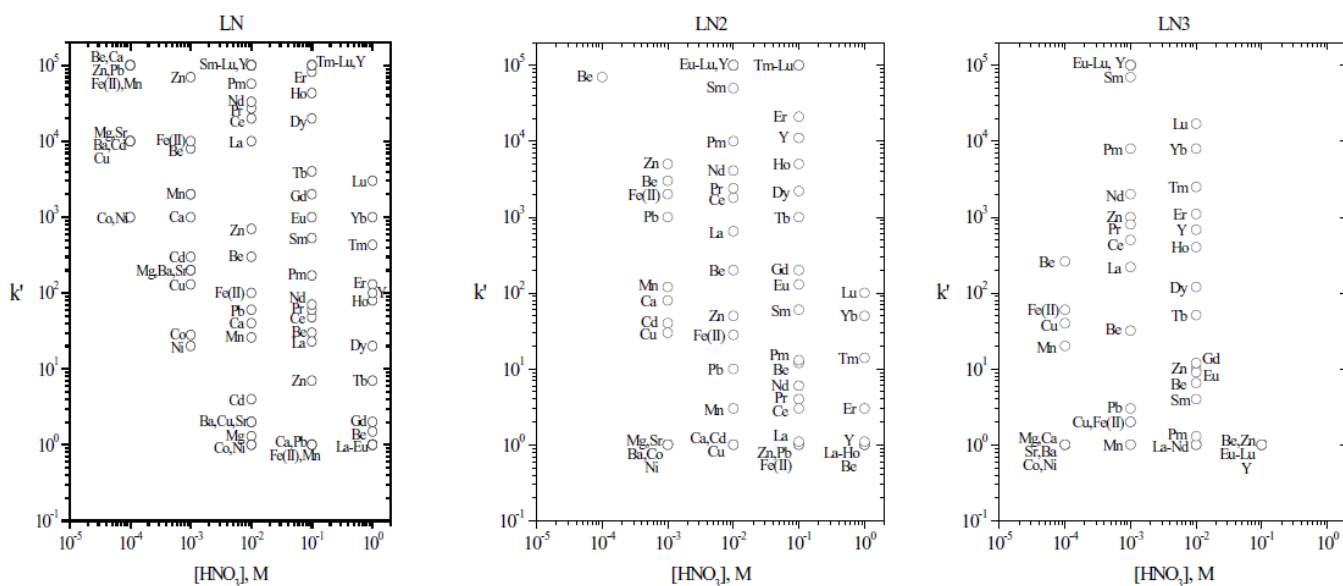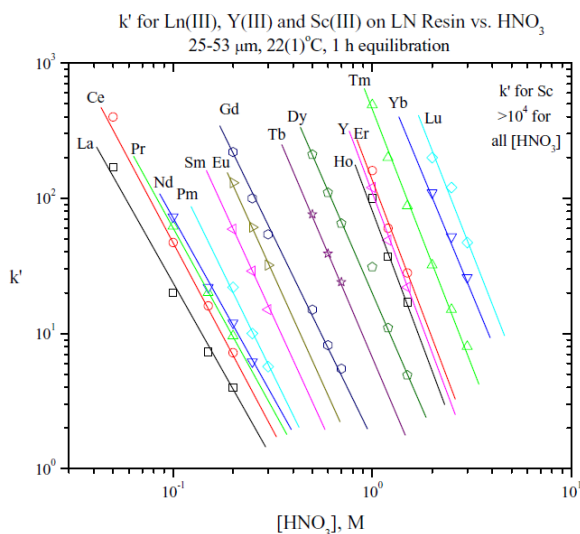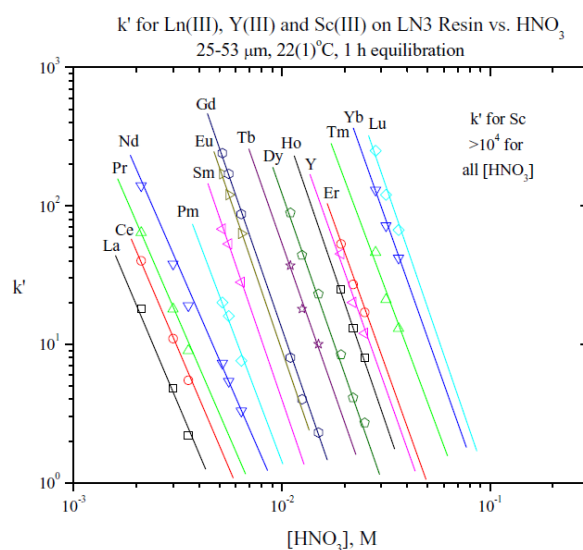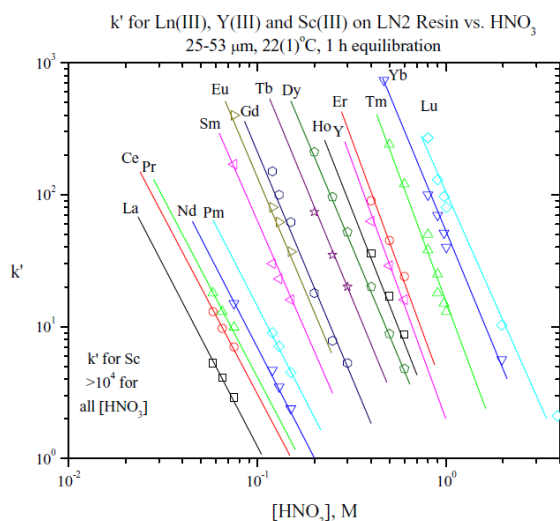**Figure 13: Capacity factor k' of various cations in HNO₃ on LN / LN2 / LN3 resin.**

Figure 14: Capacity factor k' of various lanthanides in HNO₃ on LN resin.

Figure 16: Capacity factor k' of various lanthanides in HNO₃ on LN3 resin.


Figure 15: Capacity factor k' of various lanthanides in HNO₃ on LN2 resin.

Different applications/separations have been presented during the Users' Group Meeting in Madrid (May 2008) and can be consulted on our website www.triskem-international.com.

One application increasingly finding interest is the use of the LN Resin series for the separation and purification of radio-lanthanides for their application in nuclear medicine, typical examples are i.a. Tb isotopes such as Tb-161 and especially nca Lu-177.

Horwitz et al. [7] showed that by using LN2 Resin, in combination with i.a. DGA Resin nca Lu-177 could successfully be separated from 300 mg Yb-176 targets. They reported a chemical yield for Lu-177 in the order of 73%, a decontamination factor for Yb in the order on 10^6 and a separation time of approx. 4h. Fig. 17 shows an overview of the developed process.
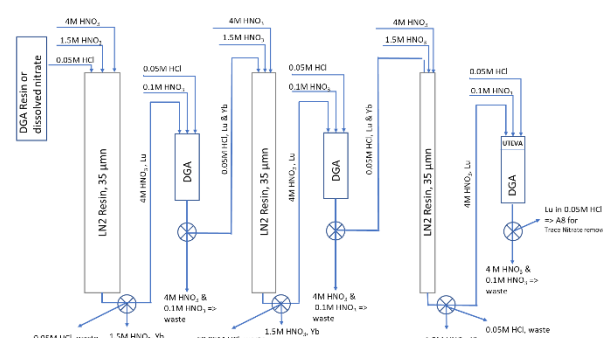
Figure 17: nca Lu-177 separation scheme according to Horwitz et al. [7]

A potential drawback of this process is the large number of different columns, making the automatization of the process challenging.

Further only up to 300 mg of Yb were tested, typically larger targets (~500mg) need to be treated. Work on the upscale of this method to 500 mg is currently being finalized.

Using the different acidities of the respective LN Resins (LN, LN2 and LN3) may allow the simplification of this process by eluting from a column filled with a resin working at lower acid concentration directly onto a column containing a resin retaining the lanthanides at higher acid concentrations (e.g. from LN2 onto LN Resin). This corresponds to a direct sequential separation.

Two methods taking advantage of this principle for the separation of nca Lu from up to 500 mg Yb targets are currently being developed, both are shown in Fig. 18 and 22. To be noted, the method shown in Fig. 18 is using TK221 Resin instead of DGA Resin as it allows for nca Lu-177 elution in a smaller volume.

The acid concentrations given in the graphs are indications only and are currently object of further optimization. HNO_3 and HCl may be employed with HNO_3 being the preferred option.

Both methods may be run, similar to the Horwitz paper, at 25 mL/min, however it could be shown that slower flow rates may result in improved separation.

Fig. 18 shows a LN2/TK221/LN2/LN based method, including one sequential separation step (LN2 => LN). The development of this method for 500 mg Yb targets is currently being finalized.
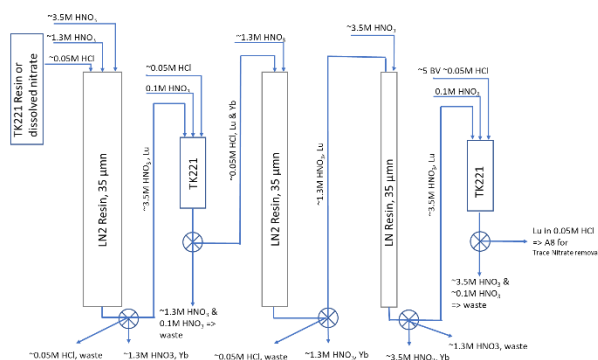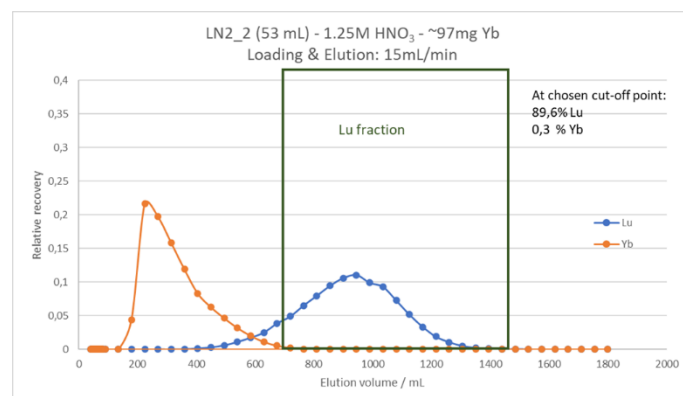

Figure 18: LN2/TK221/LN2/LN based method for the separation of Lu from up to 500 mg Yb
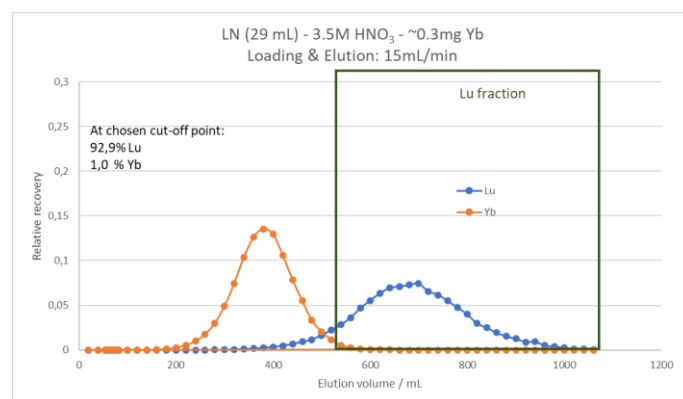
Figures 19 – 21 show some typical chromatograms obtained during the method development.
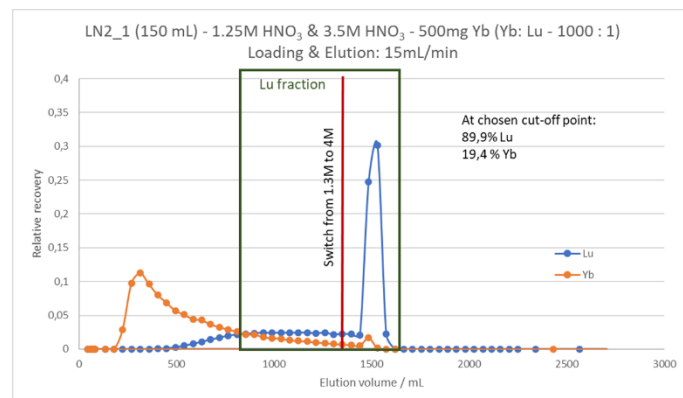
Figure 19: Elution study, stable Lu and Yb, first LN2 column.

**Figure 20: Elution study, stable Lu and Yb, second LN2 column.**

Figure 21: Elution study, stable Lu and Yb, LN column.

As can be seen, the presence of larger amounts of Yb will lead to an earlier start of the elution of Yb and Lu, and a stronger peak tailing.

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Fig. 22 shows a fully sequential LN3/LN2/LN method thus avoiding the use of intermittent TK221 (or DGA) columns. This method will require greater care with respect to the acid concentration, especially on the LN3 column. It could be shown that this method generally allows separating Lu from Yb, further method development and upscale is on-going.
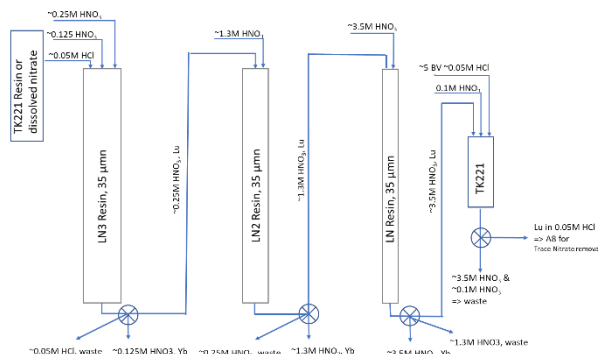
Figure 22 : LN3/LN2/LN based method for the separation of Lu from up to 500 mg Yb

The feasibility of the sequential separation approach has also been demonstrated for Tb separation e.g. from Gd targets, the upscale of a corresponding method is also currently on-going.

Ready to use prepacked 150 mL, 53 mL and 29 mL columns are currently under development.

Bibliography

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4   Pin C., Analytica Chimica Acta, Vol. 399, 79-89 (1996)
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7   E.P. Horwitz et al.: A Process for the Separation of Lu-177 from Neutron Irradiated Yb-176 Targets, Applied Radiation and Isotopes, Vol 63, pp 23-36, (2005)