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## Dear customers,

We are proud to announce that Triskem participates in the Consortium for Alpha Radiotherapy Applications (CARAT). The project will be financed under the French future investment program managed by the Commissariat Général à l'Investissement (CGI) and operated by Bpifrance.

Classified as a decisive R&D project for competitiveness (PSPC), CARAT aims to develop the production of lead-212 for treatments of cancers that currently have limited therapeutic options.

Coordinated by AREVA Med, CARAT unites, beside TrisKem, the company EVEON, the Limoges university hospital, the CRIBL laboratory at Limoges university and Subatech.

The participation in this project allows us to enhance our R&D and to integrate new experts in our team, which corresponds to Triskem business development strategy.

> Michaela Langer TRISKEM CEO

# TK100 and TK101 Resins

In order to simplify the Sr-90 and Pb-210 separation, TrisKem has developed TK100 and TK101 extraction chromatographic resins. They can be used over a pH range from pH 2 to 8, allowing for direct loading from water samples and subsequent purification of the analytes on the same column.

The **TK100 Resin** consists of a crown-ether with high selectivity for Sr and Pb and HDEHP a liquid cation exchanger (see fig. 1). Jake Surman from Lancaster University characterized the TK100  $\text{Resin}^{(1,2)}$  whose 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<sup>(3)</sup>.



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

Surman et al. further characterized the resin with respect to  $D_w$  values of Sr at different pH values  $\ge$  pH 2 (fig. 3), as well as at HNO<sub>3</sub> and HCl concentrations higher than 0.01M (fig. 4).

The TK100 Resin shows high  $D_w$  values for Sr in a pH range between 2 and 8. As also shown in figure 4, the Sr uptake at pH 2 is high, especially in HNO<sub>3</sub>. 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.





*Figure 2:* Sr uptake kinetics TK100 Resin<sup>(1)</sup>

Figure 3:  $D_w$  values Sr on TK100 Resin, varying pH values<sup>(1)</sup>

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<sub>3</sub>, a plateau at approx.  $D_w \sim 10$ .





#### News

**New resin:** ZR Resin under characterization for the separation of Zr.

**New accessories:** Empty PEEK columns are available upon request.



For further information please contact contact@triskem.fr

Literature:

You'll find hereafter some publications released recently that might be of interest for you on the determination of 226Ra in water samples and the use of alkaline fusion for the determination of U/Th in soil samples:

• Lorenzo Copia et al., Journal of Analytical Science and Technology, 2015, 6:22 - DOI: 10.1186/s40543-015-0062-5 (http://www.jast-journal.com/ content/6/1/22)

• Silvia Dulanská et al., Journal of Radioanalytical and Nuclear Chemistry, 2015, Vol. 303 (1), pp 47-51 – DOI: 10.1007/s10967-014-3454-x (http://link. springer.com/article/10.1007/s10967-014-3454-x)

• Sherrod L. Maxwell et al., Journal of Radioanalytical and Nuclear Chemistry, 2015, Vol. 305 (2), pp 631-641 – DOI: 10.1007/s10967-01 (http://citations. springer.com/item?doi=10.1007/s10967-015-3972-1)

• Sherrod L. Maxwell et al., Journal of Radioanalytical and Nuclear Chemistry, 2015, Vol. 305 (2), pp 599-608 – DOI: 10.1007/s10967-015-3992-x (http://link. springer.com/article/10.1007/s10967-015-3992-x)

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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<sub>3</sub> on the other hand an increase up to a  $D_w$  value of about 100 at 8 – 10M HNO<sub>3</sub> can be observed. The TK100 Resin is thus behaving very similar to the SR Resin under these conditions.



*Figure 4:* D<sub>W</sub> values Sr and Y on TK100 Resin, varying HNO, and HCl concentrations<sup>(2)</sup>

*Figure 5:* Sr / Y separation on TK100 *Resin*<sup>(2)</sup>

As Sr elution with water or dilute nitric acid is not possible, a number of other eluting agents were tested such as 0.1M citric acid, 0.1M oxalic acid,0.5M HCl, 2M HCl, 3M HCl and 0.1M EDTA. Amongst these tested solutions 2M HCl, 3M HCl and 0.1M EDTA were found to be most suitable <sup>(1)</sup>.

Sr / Y separation is possible using the resin, as was shown by Surman and co-authors (fig. 5), also showing that 2M HCl is indeed a suitable elution solution for Sr.

As expected, a number of other elements show an affinity to the TK100 resin at pH 7 such as Ra, Th, Bi, Nd and Ba, making separation chemistry necessary in order to obtain a clean Sr fraction.

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 6 to 8.



Figure 6: Sr  $D_w$  on TK100 Resin as function of NaCl concentration at  $pH7^{(1)}$ 

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 9 and 10. It should be noted that Pb is not eluting under the chosen conditions.

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Additional studies performed by Dirks et al.<sup>(4)</sup> 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. 11) showed that K and Ca directly breakthrough during load without being retained.

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<sub>3</sub>. 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  $\alpha/\beta$  discrimination LSC.

In order to improve the separation of Pb from U and the matrix it was tried to replace HDEHP, which introduces the additional selectivity for U, by ionic liquids.



Figure 11: Elution study, various elements, 1L sample, 100 mL aliquots, TK100 Resin<sup>(4)</sup>



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Dietz et al.<sup>(5)</sup> showed through the example of Sr that the mechanism of 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<sub>3</sub>. At higher HNO<sub>3</sub> concentrations the D values increase as expected for a liquid-liquid extraction mechanism.

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**.

An elution study (fig. 12) performed by Dirks et al.<sup>(4)</sup> 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 12: Elution study, 1L sample, 100 mL aliquots, TK101 Resin<sup>(4)</sup>

## Bibliography

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(5) 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

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