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### ● Edito :

Dear Users,

We hope that you and all that are close to you are in good health. Travel constraints and virtual conference have unfortunately restricted the direct contact with you, but we are always very pleased to answer any of your questions via phone, e-mail, or video call.

We would like to use this newsletter to present two new resins.

The TK202 Resin, which is based on an aqueous biphasic system, mainly finds application in the separation of Tc from alkaline samples such as dissolved Mo targets or digested decommissioning samples.

The TK-TcScint Resin is the first of a series of new resins which are based on the impregnation of selective extractants on plastic scintillating microspheres (developed with the University of Barcelona). This new resin allows the direct measurement of the Tc-99 retained on the cartridge without elution or addition of a scintillator cocktail which increases safety while reducing hands-on and turn-around time as well as costs.

Please get in touch with our technical support team for more information on both products. Last year we invited you to a virtual Users' Group Meeting during the virtual CARM conference organized by the NPL. Due to the success of this meeting, we have decided to renew this experience, again as part of NPLs CARM. We would be very glad if you would participate, and contribute, to this meeting!

Michaela Langer, president

### ● TK-TcScint Resin

The TK-TcScint Resin is the first of a range of resins based on "Impregnated Plastic Scintillation microspheres" developed by García, Tarancón and Bagán at the University of Barcelona<sup>[1-5]</sup>.

This range of new products will be comprised of plastic scintillation microsphere (PSm), supplied by the group at the University of Barcelona, that are impregnated with selective extractants.

The TK-TcScint Resin is, as the name indicates, mainly dedicated to the quantification of Tc-99. The extractant used in its fabrication is Aliquat336, it further contains small amounts of a long-chained alcohol. Accordingly, its selectivity will generally be very similar to the TEVA Resin.

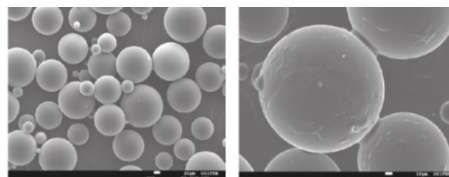


Figure 1 (a and b): left - non-impregnated plastic scintillation microspheres (PSm), right - impregnated PSm (TK-TcScint). Taken from [4]

Figure 1 (a and b) show SEM pictures of the non-impregnated PSm, and the impregnated microspheres (TK-TcScint), respectively.

The TK-TcScint is generally employed as pre-packed 2 mL cartridges for use with vacuum box systems, or

automized separation equipments based on pump systems<sup>[1, 5]</sup>.

The PSm support employed in the TK-TcScint Resin is itself acting as scintillating medium, this allows for a direct measurement of the Tc-99 retained on the cartridge, no elution and mixing of the eluate with a liquid scintillation cocktail is necessary.

This has a number of advantages:

- Gain of time which is particularly interesting in emergency situations
- No mixed liquid radioactive waste
- No Tc elution with HNO<sub>3</sub> of elevated concentration and no evaporation / aliquoting of the eluate
- No cutting of columns or cartridges to push the resin into LSC vials

Especially the latter two points are interesting in terms of radiation protection when samples of elevated activity are being analyzed.

Ideally the chemical yield is determined via ICP-MS or ICP-OES using Re as internal standard.

Fig. 2 compares this new approach based on impregnated PSm Resins such as the TK-TcScint with classical methods. In order to easily handle and avoid contaminating the LSC counter the cartridges should be placed in a standard 20 mL LSC vial for its measurement.

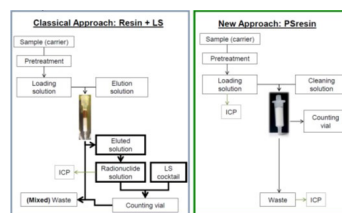


Figure 2: Overview classical radioanalytical method and PS Resin approach. Taken from [5]

Typical samples analysed include urine and various types of water sample. In case of surface water samples generally a breakthrough volume of > 200 mL can be achieved using 2 mL cartridges,

making this technique not only interesting in emergency situations or as screening tool in decommissioning, but also for use in routine biomedical or environmental monitoring. For water samples the chemical yield is generally >98.8%.

The detection efficiency for Tc-99 obtained with the TK-TcScint is very high, in the order of 89.5(0.6)%, while the background of the standard 2 mL cartridges is low with ~1.09

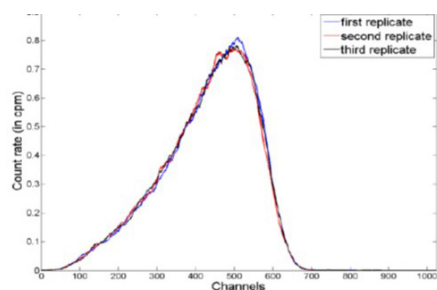


Figure 3: Liquid Scintillation Spectrum of Tc-99 on TK-TcScint. Taken from [5]

Figure 3 shows typically obtained Tc-99 spectra, as can be seen spectra obtained for three replicates match very well.

The analysis of water samples such as e.g. river and sea water (typically 50 mL) using TK-TcScint cartridges is rather straightforward [1, 5].

After filtration, if necessary, samples are heated to 90°C for 60 min after addition of a few mL of 30% H<sub>2</sub>O<sub>2</sub> to assure that Tc is present as pertechnetate. The solutions are then adjusted to 0.1M HCl using conc. HCl. Once the samples reach room temperature, they are ready for separation.

After loading of the sample the cartridge is typically rinsed successively with 0.1M HCl, 0.1M HNO<sub>3</sub>/0.1M HF (only necessary in case Th is expected to be present) and finally water. These rinses allow eliminating possible interferences while Tc (and the internal standard Re) remain on the cartridge. Load and rinse fractions are combined and analysed for Re content to allow calculating the chemical yield of the separation. The TK-TcScint cartridge can then be directly counted on an LSC counter.

The authors found very good match between expected and measured activities, for the spiked water samples as well as for two spiked MAPEP samples<sup>[1]</sup>.

Using 50 mL samples and 180 min counting time allowed the authors obtaining a limit of detection of 0.15 Bq.L<sup>-1</sup>.

As could further be shown by the authors, this method can easily be automatized. In their case they developed their own separation unit called OPENVIEW-AMSS, a modular, vacuum box based equipment. They could show that both, manual and automatized separations allow for obtaining high chemical yields and detection efficiencies, no significant differences were observed when analysing samples in parallel. However, with respect to hands-on time and radiation protection automatization provides significant advantages.

Further to the unit developed by the authors the TK-TcScint cartridges are also compatible with commercially available equipment such as the Hidex Q-Are 100<sup>[4]</sup>.

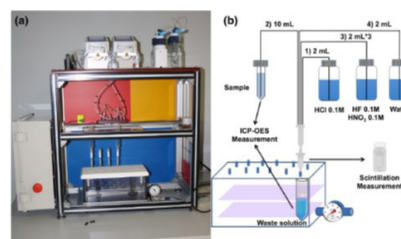


Figure 4: OPENVIEW-AMSS system and scheme of a typical separation of water samples. Taken from [1].

Besides water samples urine samples were also analysed using TK-TcScint cartridges<sup>[5]</sup>.

With respect to their higher matrix load this kind of samples requires a thorough sample pre-treatment. The described method is based on 100 mL urine samples that are first wet-ashed using conc. HNO<sub>3</sub>, followed by an additional ashing step in a muffle furnace at 550°C.

The obtained ash is then dissolved in 3 mL of conc. HNO<sub>3</sub> and diluted to 100mL using deionized water. To assure Tc is present as pertechnetate the solutions are heated, after addition of a few mL hydrogen peroxide, to 90°C for 60min. As described before, Re was used as internal standard.

By analysing spiked urine samples the authors could show that accurate results can be obtained using the impregnated PSm approach. A minimum detectable activity (MDA) of 0.036 Bq.L<sup>-1</sup> for 100mL samples and 24h counting was reported.

Further to the analysis of Tc-99, PSm Bagán et al.<sup>[6]</sup> showed that Aliquat 336 impregnated resins may also be used for the analysis of [<sup>14</sup>C]SCN<sup>-</sup> used as radiotracer for study of oil reservoir dynamics.

With respect to the selectivity of the Aliquat extractant, the compound giving TEVA Resin<sup>[7]</sup> its selectivity, a use of the TK-TcScint cartridges for the screening of other radioelements such as e.g. Pu isotopes or Po-210 seems well possible.

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## ● News :

Following the very positive feedback on last years virtual Users Group Meeting, kindly arranged by NPL, we have decided to again organise a virtual Users Group Meeting this year (24/11/2021), once more in cooperation with the NPL as part of their CARM conference (22/11 – 26/11/2021).

You are cordially invited to participate in this meeting (the participation will be free of charge). We would be even more glad if you would kindly agree to present your work. Please don't hesitate to contact [shappel@triskem.fr](mailto:shappel@triskem.fr) in this case! We will get back to you with more details about the meeting very soon. You will also find updates about the vUGM here: <https://www.triskem-international.com/users-group-meetings.php>

## ● TK202 Resin

The TK202 Resin is based on Polyethyleneglycol (PEG, fig. 1) groups, with high molecular weight, that are covalently bound onto a polymer support.

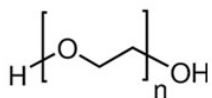


Figure 1: PolyEthyleneGlycol (PEG).

The TK202 Resin is based on an aqueous biphasic system (ABS) extraction mechanism with the covalently bound PEG acting as solid separation support. In presence of aqueous solutions with high ionic strength and high content of water-structuring (kosmotropic) anions like  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , as well as  $\text{MoO}_4^{2-}$  or  $\text{WO}_4^{2-}$  (1), it will extract chaotropic ions notably  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$ , while other non-chaotropic elements will not be retained, molybdenum being an important example.

Accordingly, Tc (and Re) retention will improve with increasing concentration of these anions.

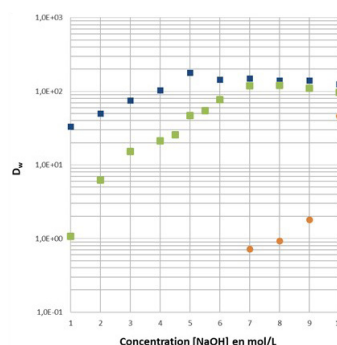


Figure 2: Dw values for Tc, Re and Mo on TK202 Resin, at varying NaOH concentrations. Tc data taken from Cieszykowska et al.<sup>(2)</sup>.

Fig. 2 shows Dw values for Tc, Re and Mo on TK202 Resin at increasing OH concentrations.

Ideally the NaOH concentration should be between 5 and 7M NaOH during load and rinse, as Tc (and Re) retention is highest while Mo retention is very low.

As mentioned before,  $\text{MoO}_4^{2-}$  itself is a kosmotropic anion. Accordingly, increasing its concentration will lead to higher Tc (and Re) retention in ABS systems like the TK202 Resin, as shown in Fig. 3. A distinct increase of the Tc retention with increasing amounts of Mo is observed.

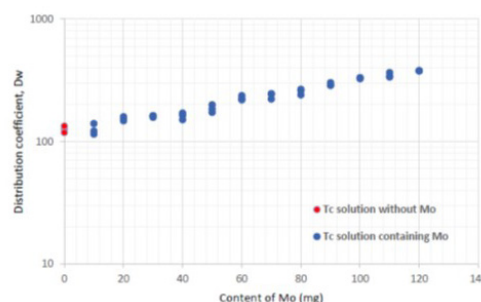


Figure 3: Dw values for Tc in 5M NaOH using 40 mg TK202 Resin, increasing amounts of Mo. Data taken from Cieszykowska et al.<sup>(2)</sup>.

This is particularly relevant in case of the separation of Tc from elevated amounts of Mo (e.g. irradiated Mo targets).

Cieszykowska et al.<sup>(2)</sup> estimated from column studies that 6 to 8g of Mo per g of TK202 Resin allow obtaining high Tc recovery (> 90%). Further increasing the amount to 12g Mo/g of resin lead to a decrease of the Tc recovery to ~82% in their experiments.

The retained Tc and Re can then be eluted with water as the ABS systems breaks down, due to the low concentration of kosmotropic anions, under these conditions.

As mentioned, one potential application of the TK202 Resin is the separation of Tc-99m from irradiated Mo targets. Accordingly, its high selectivity for Tc over Mo, and the fact that the presence of elevated amounts of Mo in solution increases the Tc retention, makes the TK202 Resin particularly suitable for this type of applications.

Indeed, besides the production of Mo-99 for the fabrication of Mo-99/Tc-99m generators via U-235 fission there are several other ways to produce Mo-99<sup>(3)</sup>, and thus Tc-99m. Three of these methods are based on the irradiation of Mo targets :

- Neutron activation of Mo-98 via (n,  $\gamma$ ) reactions (Mo-98 (n,  $\gamma$ ) Mo-99), preferably performed in a reactor with high neutron flux.
- Photon-induced ( $\gamma$ , n) reaction of Mo-100 (Mo-100 ( $\gamma$ , n) Mo-99) using photons ( $\gamma$ ) obtained through irradiation of heavy targets (converter) e.g. with electron beams.
- Direct Tc-99m production on a cyclotron using Mo-98 targets (Mo-98 (p, 2n) Tc-99m)<sup>(4)</sup>. This latter method represents, with respect to the short half-life of Tc-99m, certain logistical challenges and will generally rather allow for supplying users close to the production facility. This method requires a clean, and very rapid, separation of the produced Tc-99m from the target material.

The first two described methods tend to result in Mo-99 of limited specific activity, especially compared to Mo-99 obtained from U fission. Accordingly using them e.g. in alumina column based generator systems will, due to the generally limited Mo capacity of these columns, result in rather lower activity Mo-99/Tc-99m generators.

In such cases employing a resin, such as the TK202 Resin, to extract the Tc-99m originating from Mo-99 decay while letting Mo pass through (“inverted generator”) is often a preferred option.

It should be noted that in all three cases the recovery and recycling of the enriched Mo is of very high importance due to the pricing and limited availability of the target material.

The production methods described above all require the use of a resin with high selectivity for Tc over large amounts of Mo. Ideally, as the Mo targets are very frequently dissolved in NaOH solutions of elevated concentration, the resin should show this selectivity under these conditions.

This is the case for the TK202 Resin. As indicated before, Tc may then be recovered using water, although further separation steps will be necessary to adjust pH and Na<sup>+</sup> concentration of the final product.

Initial elution studies using Re instead of Tc confirmed the high selectivity for Re (and, as could be confirmed in separate tests, also Tc) over Mo.

Fig. 4 shows an elution study performed with trace amounts of Mo and Re. As it can be seen, a clean separation of both elements is obtained. Mo is removed during load and following rinses (both may be performed with 5 – 7M NaOH), while Re elutes in a small water volume.

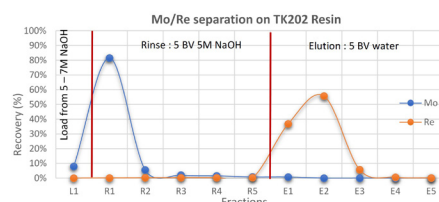


Figure 4: Elution study, trace amounts of Mo and Re on a 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

As the general selectivity could be confirmed further tests were performed using larger amounts of Mo.

Fig. 5 shows the separation of traces of Re from 2g of Mo, as e.g. typically required in case of Tc-99m production from Mo-98 irradiation in a cyclotron<sup>(4)</sup>.

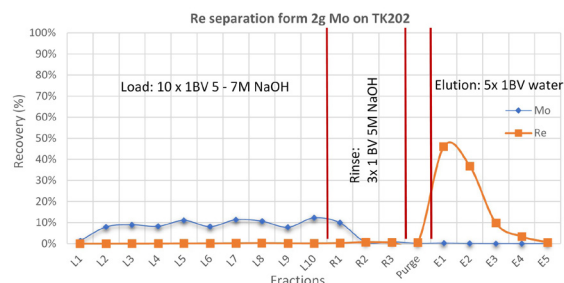


Figure 5: Elution study, separation of trace Re and 2g Mo on a 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

It should be noted that purging the resin, e.g. with air, after the rinse and before its elution with water, to remove NaOH from the cartridge/column, is of high importance to reduce the Na<sup>+</sup> and OH<sup>-</sup> load of the final Tc/Re fractions. It could further be shown that lower flow rates during elution of the TK202 Resin will result in narrower elution peaks, and thus lower elution volumes.

As discussed previously, the TK202 Resin may also be used to extract Tc-99m from Mo-99 decay present in an alkaline solution. In such cases much larger Mo targets are generally irradiated.

With respect to this, the separation of trace of Re from

100g Mo was tested. As Fig. 6 shows a clean separation of Mo and Re could be obtained here, too. Nevertheless, with respect to the very large amount of Mo present, an additional purification of the obtained Tc will be required. Methods for the separation of Tc from larger Mo amounts (e.g.  $\geq 200\text{g}$ ) are currently being tested.

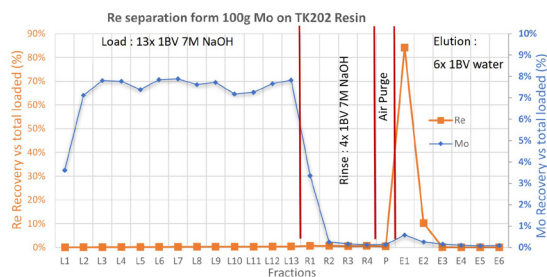


Figure 6: Elution study, separation of trace amounts of Re and 100g Mo on a 75 mL TK202 Resin cartridge, load at 0.5 BV/min, rinse at 1 BV/min, elution at 0.2 BV/min.

As shown e.g. by Bénard et al.<sup>(4)</sup>, one convenient option for this additional Tc purification is the use of a cation exchange resin (for  $\text{Na}^+$  removal and pH adjustment to below pH 7), followed by an alumina cartridge (for Re/Tc concentration and further Mo removal).

Especially for the cation exchange cartridge it is important to adjust the size of the cartridge to the amount of Mo previously present in the sample/and so to the size of the TK202 Resin cartridge employed.

For the size of the alumina cartridge the amount of residual Mo is a decisive parameter.

Fig. 7 shows the continuation of the 2g Mo separation test shown in Fig. 5.

The obtained Re fractions (E1 – E4) were combined and loaded through a C8 cation exchange resin cartridge which was then rinsed with water. The load fractions and the first rinse were collected, analyzed, and then combined for the final step of the separation, as they contain all the Re (or Tc).

As stated before, at this stage the Re fraction should be below pH 7 (typically 3 – 5) and largely free of  $\text{Na}^+$  cations.

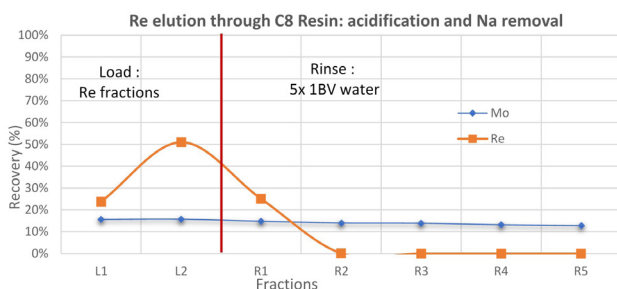


Figure 7: Continuation of the separation of Re from 2g Mo (see Fig. 5).  $\text{Na}^+$  removal and pH adjustment of Re fractions on 2 mL C8 Resin cartridge, load and rinse at 2 BV/min.

It could be shown that under these conditions, acidic alumina will retain Re/Tc (and Mo). A 0.9% NaCl solution then allows eluting Re/Tc in a small volume (2 – 3 BV) while Mo remains very strongly retained, thus further improving the purity of the recovered Re/Tc. The indicated air purge is not necessary in case of the AlOxAl Resin (acidic alumina).

This further has the advantage of allowing to obtain the Tc in the same matrix (0.9% NaCl) as delivered by a Mo-99/Tc-99m generator.

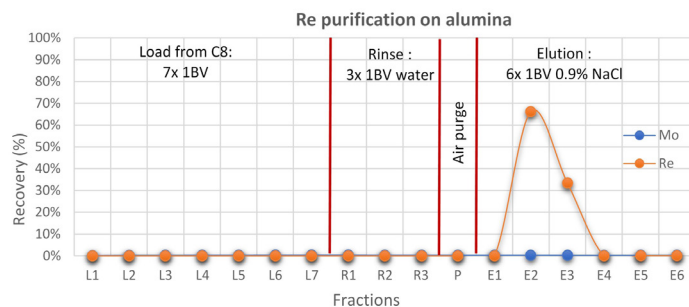


Figure 8: Re concentration, purification and conversion to 0.9% NaCl solution on 1 mL AlOxAl Resin at 2 BV/min.

Overall, in the cold tests Re recoveries in the order of  $>90\%$  could be obtained.

A schematic overview of the suggested separation method is given in Fig. 9. The method may be applied for the separation of Tc from Mo targets of various sizes, cartridge/column volumes will need to be adjusted accordingly.

Further to the TK202 Resin TrisKem also supplies C8 Resin, AlOxAl Resin.

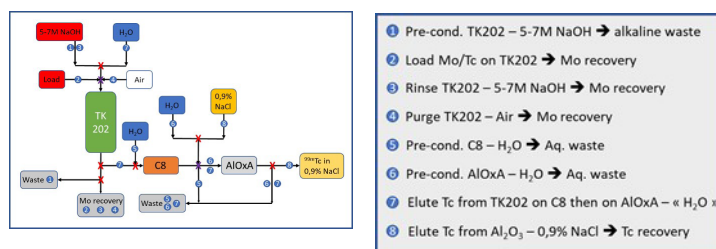


Figure 9: Schematic overview, Tc separation from Mo.

All resins are available in various columns and/or cartridges of different sizes (depending on the size of the Mo target).

Please contact us for further information.

Besides the described radiopharmaceutical use the TK202 Resin may also be employed in radioanalytical applications, notably in the analysis of Tc-99 in samples that were solubilized via alkaline fusion.



In such cases the solubilized samples (e.g. concrete samples resulting from decommissioning work) may, after removal of insoluble material, be adjusted to 5 – 7M NaOH and then passed through TK202 Resin to separate Tc.

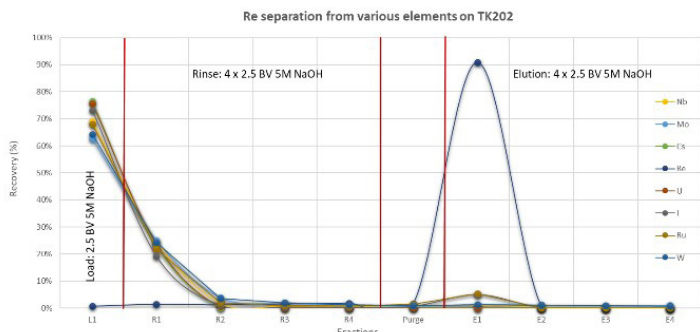


Figure 10: Re separation from selected elements on 2 mL TK202 Resin cartridge, load and rinse at 1 BV/min, elution at 0.25 BV/min.

In order to further increase the purity of the obtained Tc fraction it might be passed, as described above, through a C8 Resin, and potentially even AlOx Resin.

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## Agenda :

Please find here below a listing of the conferences at which we'll participate this year.

The majority of the conference we had planned to attend have been postponed for security reasons. We understand and support these measures.

You'll find an updated list with the new conference dates (if known) on our web site under: <https://www.triskem-international.com/ma/events>.

- EANM 2022 virtual congress, 20 – 23/10/2021, <https://eanm21.eanm.org/>

Please don't hesitate to contact Dr. Steffen HAPPEL to organize a video conference or chat during this event via e-mail [shappel@triskem.fr](mailto:shappel@triskem.fr) or Calendly [https://calendly.com/shappel\\_tki/eanm](https://calendly.com/shappel_tki/eanm).

- World Nuclear Exhibition (WNE), Pavillon France, 30/11 – 02/12/2021, Paris-Nord Villepinte, <https://www.world-nuclear-exhibition.com/en-gb.html>
- TrisKem vUGM, 24/11/2021, as part of the NPL organized CARM conference, 22/11 – 26/11/2021, <https://www.triskem-international.com/users-group-meetings.php>



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