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**MULTIPLE ION EXCHANGE COLUMN TESTS FOR TECHNETIUM  
REMOVAL FROM HANFORD TANK WASTE SUPERNATE (U)**

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**ABSTRACT**

Five cycles of loading, elution, and regeneration were performed to remove technetium from a Hanford waste sample retrieved from Tank 241-AW-101 using SuperLig<sup>®</sup> 639 resin. The waste sample was diluted to 4.95 M Na<sup>+</sup> and then was processed to remove <sup>137</sup>Cs through dual ion exchange columns each containing 15 mL of SuperLig<sup>®</sup> 644. To remove <sup>99</sup>Tc, the cesium decontaminated solution was processed downwards through two ion exchange columns, each containing 12 mL of SuperLig<sup>®</sup> 639 resin. The columns, designated as lead and lag, each had an inside diameter of 1.45 cm and a height of 30 cm. The columns were loaded in series, but were eluted and then regenerated separately. The average technetium loading for the cycles was 250 BV at 10% breakthrough. There was no significant difference in the loading performances among the five cycles. The percent removal of <sup>99</sup>Tc was > 99.94% and the average decontamination factor (DF) was ~ 1.7 x 10<sup>3</sup>. Approximately 99% of the <sup>99</sup>Tc loaded on the resin was eluted with < 15 BV of de-ionized water at 65 °C.

## INTRODUCTION

The River Protection Project -Waste Treatment Plant (RPP-WTP) is contracted by the United States Department of Energy (DOE) to develop, build, and operate a high level nuclear waste treatment facility at the Hanford Site in Richland, Washington. At this site, millions of gallons of high-level and low-level radioactive waste are stored in underground storage tanks. A large portion of the waste exists as liquid solution (supernatant) and it contains soluble radionuclides, such as  $^{137}\text{Cs}$  ( $t_{1/2} = 30$  y),  $^{99}\text{Tc}$  ( $t_{1/2} = 2.13 \times 10^5$  y), and  $^{90}\text{Sr}$  ( $t_{1/2} = 30$  y). Technetium, as  $\text{TcO}_4^-$ , is highly soluble in water and readily mobile in the environment (1, 2). This mobility, along with its long half-life makes technetium primarily a long-term hazard. Removal of  $^{99}\text{Tc}$  from the bulk waste is required to produce a low activity waste (LAW) that can be vitrified into low-level waste glass. The separated  $^{99}\text{Tc}$  is concentrated into a relatively small volume and incorporated into high-level waste sludge. This sludge is vitrified into high-level waste (HLW) glass logs suitable for permanent disposal in a federal repository.

The RPP-WTP project identified ion exchange as the optimal treatment method for removal of  $^{99}\text{Tc}$  from the Hanford waste solutions. Anion exchange using SuperLig<sup>®</sup> 639 resin from IBC Advanced Technologies, American Fork, Utah, was selected to remove  $^{99}\text{Tc}$  from the waste solutions. The resin, which is supported on polystyrene beads and covalently bonded crown ether ligands remove technetium as a ligand- $\text{NaTcO}_4$  complex (3). Extensive experimental investigations conducted at Savannah River Technology Center (SRTC) and at Battelle, Pacific Northwest National Laboratory (PNNL) with actual waste samples from Tanks 241-AW-101, 241-AN-103, 241-AN-102,

241-AZ-102, 241-AN-107, and 241-AP-101 showed that SuperLig<sup>®</sup> 639 resin was effective to remove technetium, as  $\text{TcO}_4^-$  from highly alkaline Hanford waste solutions (4-9). The chemical and radiation stability of resin was found to be excellent (10, 11). The objective of the present study was to demonstrate the SuperLig<sup>®</sup> 639 ion exchange resin performance and process steps to treat radioactive waste solution in multiple cycles. The study was also aimed at producing cesium and technetium decontaminated solution for use in LAW glass vitrification experiments.

## **EXPERIMENTAL**

### **Hanford Tank Waste Sample**

A total of thirty 500-mL glass jars of waste samples from Tank 241-AW-101 was received from the Hanford site in January and March 2001. The 500-mL grab samples were obtained from riser 22 of the 241-AW-101 waste tank in July, 2000. The as-received 241-AW-101 samples were homogenized, and then diluted with de-ionized water to provide a 4.95 M  $\text{Na}^+$  concentration in the supernatant. After dilution, the bulk solution was filtered through 0.1-micron sintered metal Mott filter to remove entrained solids. A total of 15 L of the AW-101 filtrate at 4.95 M  $\text{Na}^+$  was available for multiple ion exchange column testing. Duplicate aliquots of the bulk solution were analyzed by gamma energy counting to determine the concentration of  $^{137}\text{Cs}$ , and inductively coupled plasma – atomic emission spectroscopy (ICP-AES) to determine  $^{99}\text{Tc}$  (total) and metal ions. The  $^{99}\text{Tc}$  (pertechnetate) was determined by chemical separation/beta counting method. The nitrate and free hydroxide concentrations in the diluted bulk waste samples were 1.56 and 1.81 M, respectively. The  $^{99}\text{Tc}$  concentration in the solution was 0.066

$\mu\text{Ci/mL}$ . The diluted feed sample contained 0.46 M  $\text{K}^+$ , which is high compared to majority of the Hanford site tank waste solutions. Table 1 shows the chemical composition of the AW-101 waste sample.

### **Ion Exchange Material**

The RPP-WTP considers SuperLig<sup>®</sup> 639 resin as the baseline ion exchange resin for  $^{99}\text{Tc}$  removal from Hanford tank waste solutions. The resin was supplied by IBC Advanced Technologies, American Fork, Utah. The SuperLig<sup>®</sup> 639 resin (batch # I-R2-03-27-02-20-45) was received wet in de-ionized water. A small mass of the resin was dried under nitrogen at room temperature for use in batch and column testing. The physical properties measured for the resin were bulk density, particle (skeletal) density, F-factor, and particle size distribution. The bulk density was determined by weighing a small mass of nitrogen-dried resin into a graduated cylinder filled with de-ionized water and measuring the resin volume after tapping the cylinder walls to obtain uniform packing. The skeletal density was determined through the use of pycnometer. The F-Factor (ratio of oven-dried mass to nitrogen-dried mass of the resin) was determined by weighing approximately (1.0 g) of resin and drying in a vacuum oven at  $45 \pm 5$  °C until a constant mass was obtained. The metals content ( $\text{Na}^+$  and  $\text{K}^+$ ) of the resin was determined by digesting a sample of “as-received” resin and analyzing the solution by ICP-AES method. The particle size was determined by dry sieve analysis on nitrogen-dried resin. The wet particle size distribution of the resin was determined using Lazentec instrument. The physical properties of the SuperLig<sup>®</sup> 639 resin are shown in Table 2.

## Apparatus

The experimental apparatus for the ion exchange column tests were dual glass columns, FMI pumps, auto-sampling units, and a constant temperature water-bath circulator. The apparatus was placed in a radiochemical hood in SRTC. The columns were made of borosilicate glass tubing with adjustable plungers on the top. The inside diameter of the columns was 0.57-inch (1.45-cm) and the total length was 6 inches (15 cm). When connected in series, the primary column was referred to as the “lead” while the secondary column was referred to as the “lag”. The outside of the column walls was coated with a layer of clear polyvinyl chloride to reduce hazards associated with potentially pressurizing the columns. A ruler affixed to the column walls allowed visual observation of the resin bed height and liquid level changes during column runs. The adjustable plungers at the top of the columns were used to eliminate freeboard (headspace) liquid and to minimize the volumes of secondary waste generated. The columns were equipped with SRTC patented 200-mesh screens to hold the resin in place. The column temperature was adjusted to 25 °C with a circulating water bath hooked to the jackets around the columns. All tubing connections were made of polypropylene lines, which had Teflon<sup>®</sup> quick-connect fittings attached to each end. Solutions were passed downward through the columns.

Liquid delivery into the columns was accomplished using FMI metering pumps (model RP-1, Fluid Metering, Inc. Oyster Bay, NY). The pump heads had shaft sizes of 1/18", 1/4", and 3/8" to produce a wide range of flow rates. The pumps were run at the desired flow rates by specifying the rotational speed of the motor (RPM), which was

driven by direct current (D.C). The pump controllers readout were located outside the hood. Volumetric flow rates were determined from the mass of lag column effluent composite fractions, the density, and the time to collect the effluent composite fractions.

### **Sampling and Analysis**

The sampling of the ion exchange columns was accomplished using custom-designed auto-sampling apparatus. The apparatus consisted of assembled pieces that can be easily installed in the hood. The main piece was an electrically actuated six-position rotary valve with 1/16" flangeless tubing. The valve was mounted on an aluminum plate, 3" tall x 3" wide. At the bottom of the valve, six holes were drilled on the back of a second support plate (6" tall x 6" wide) and six stainless steel tubes (1/16" ID) were connected through ball head fittings. Polypropylene tubing (1/16" ID) was used to connect the rotary valve to the stainless steel tubing, which directed samples into sample vials. The carousel slipped into a section-groove (5/8" deep x 3" long) in the middle of a solid polyethylene block (4 1/2" long x 3" wide x 2 1/2" high) for support. The carousel and the solid block were then raised by a small jiffy-jack to align the vials with the stainless steel tubings, which delivered the sample into the sample vials in a way that minimized evaporation during sampling. Instructions were provided to allow the rotary valve to be programmed for unattended.

The basic sampling mechanism was to divert small aliquots (~ 6 mL) of the column effluent into one of five sampling valve positions and collect in the vial. A valve opened periodically at predetermined time intervals to collect samples into an 8-mL glass vial for a predetermined time. Dilution of each sample by the residual liquid in the valve tubing during a sampling event was less than 10%.

Samples of the effluent were collected from the lead column in 10 BV increments during loading. The lag column was also sampled every 20 BV during loading. The samples were analyzed by two methods: (1) Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) and (2) chemical separation followed by beta counting. In the latter method, a 1-milliliter aliquot of the AW-101 sample was spiked with  $^{99m}\text{Tc}$  tracer and diluted with nitric acid to adjust the concentration to 0.2 M  $\text{HNO}_3$ . The 0.2 M  $\text{HNO}_3$  solutions were added to pre-conditioned Eichrom TEVA columns. The columns were rinsed successively with dilute nitric and 1 M NaOH. The  $^{99}\text{Tc}$  in the sample was eluted from the columns using 2 successive additions (5 mL) of 9 N  $\text{HNO}_3$ . The eluate was neutralized with NaOH and poured through Eichrom TEVA Discs, which were pre-conditioned with 0.1 N nitric, prior to assay. The Eichrom TEVA Discs were added to a liquid scintillation cocktail, analyzed by gamma spectrometry (to quantify Tc- $^{99m}$  recoveries); and then after a suitable decay period, liquid scintillation (LS) spectrometry was applied to quantify the  $^{99}\text{Tc}$  (pure beta emitter) in the sample. The gamma measurements were conducted using a NaI well counter in conjunction with a Canberra Industries Genie2K gamma spectroscopy platform. Liquid scintillation analyses

were conducted using a Packard Industries 2750AB Liquid Scintillation Analyzer. The details of this separation and beta counting method were reported by Sigg (12).

### **Procedure**

The experiments for  $^{99}\text{Tc}$  ( $\text{TcO}_4^-$  form) loading, elution, and regeneration were carried out in a radiochemical hood and the experimental conditions are shown in Table 3. The lead and lag columns were preconditioned separately using 12 BV of 0.25 M NaOH at 3 BV/h. After preconditioning, the columns were connected in series and the feed solution was pumped down flow at 3 BV/h. The column loading was considered to start when the feed contacted the liquid on top of the resin bed in the lead column. The initial 3 BVs of the effluent from the lag column, which contained 0.25 M NaOH solution, were discarded into a waste bottle. The loading of the columns was continued until approximately 250 BVs of the feed solution were processed.

After loading, the residual feed in the columns was displaced with 0.1 M NaOH. The feed displacement was performed at a flow rate of 3 BV/h. Samples of the effluent feed displacement solution were collected at 0.5 BV increments from the bottom of the lead column. After the feed displacement, the lead and lag columns were disconnected and eluted separately with de-ionized water. Elution was carried out as downward flow at  $\sim 1$  BV/h and at  $65^\circ\text{C}$ . Samples of the eluate were collected via the auto-samplers every 1 BV for the first 5 BVs and every 2 BVs until a total of 15 BVs was processed. When elution was complete, each resin bed was rinsed with 4 BVs of de-ionized water at a flow rate of 1 BV/h. The concentrations of  $^{99}\text{Tc}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  in the feed displacement and eluate samples were determined by ICP-AES, the concentration of  $\text{NO}_3^-$  was determined ion chromatograph (IC). The concentration of  $^{99}\text{Tc}$  in selected samples was also

determined by chemical separation, followed by beta counting. The  $\text{NO}_3^-$  concentration in selected samples was determined by ion chromatography (IC). The columns were then regenerated with 12 BV of 0.25 M NaOH to prepare for the next cycle.

## RESULTS AND DISCUSSION

Batch contact tests with actual sample from a Hanford site tank 241-AW-101 were conducted prior to the small-scale multiple ion exchange column tests to verify the SuperLig<sup>®</sup> 639 resin had the necessary exchange capacity to provide a minimum performance requirement. The batch tests were performed in duplicate at liquid to solid ratio of 100 and 10 mL/g, at contact times of 48 h. The equilibrium distribution coefficients ( $K_d$ ) were calculated according to the following equation:

$$K_d = \left[ \left( \frac{C_o}{C_e} \right) - 1 \right] \left[ \frac{V}{M * F} \right]$$

Where

$C_o$  and  $C_e$  = the  $^{99}\text{Tc}$  concentration in the feed sample before and after contacting with resin

$V$  = the volume of solution used

$M$  = the mass nitrogen-dried resin

$F$  = the F-factor defined as the ratio of the as-received resin mass to that of the oven-dried mass.

The distribution coefficients ( $K_d$ s) for  $^{99}\text{Tc}$  are presented in Table 4. The  $K_d$  values of 802 and 238 mg/L were the average of duplicate measurements for  $^{99}\text{Tc}$  (pertechnetate) at phase ratios of 100 and 10 mL/g, respectively. The reason for the decline of the  $K_d$  obtained at the phase ratio of 10 mL/g is not known. However, we suspect that the floating of the resin during the batch contact testing could have resulted in relatively poor contact of the resin and solution. The floating was caused by nearly identical resin and feed solution densities. The  $K_d$  of 802 mL/g obtained in this study was 47% less than the  $K_d$  value previously reported for the Hanford waste sample from tank 241-AW-101 by Kurath et. al. (13).

Figure 1 shows the  $^{99}\text{Tc}$  breakthrough curves for SuperLig<sup>®</sup> 639 lead column using a Hanford site sample from tank 241-AN-103. The  $C/C_0$  ( $^{99}\text{Tc}$  concentration in the effluent/concentration in the feed sample) for all cycles was plotted in the same graph as a function of the cumulative number of bed volumes (BV's) of feed passed through the lead column. The concentration of  $^{99}\text{Tc}$  in the feed sample was  $6.62 \times 10^{-2}$   $\mu\text{Ci/mL}$ . Since  $^{99}\text{Tc}$  is adsorbed only as  $\text{TcO}_4^-$  on the SuperLig<sup>®</sup> 639 resin, the  $^{99}\text{Tc}$  measured and plotted represent the pertechnetate fraction only. The shape of the curves was generally sigmoid. The onset of the breakthrough was observed between 80 and 100 BV. The mean BV values processed for each of the five cycles are shown in Table 3. These values were interpolated for  $C/C_0$  of 0.1 with 95% confidence interval. It should be noted that the average loading at the 10% breakthrough for all cycles was generally better than 250 BV. Although cycles #1 and #3 appear to outperform the remaining cycles (#2, #4 and #5),

the statistical difference in the loading performance of the resin is not significant. In other words, the resin performance was nearly the same for all the cycles.

Figures 2-6 show the  $^{99}\text{Tc}$  elution curves for the five cycles. In these figures, a  $C/\text{Co}$  target of 0.01 (i.e. 1% feed concentration) was selected to indicate a complete elution of the column. The open circles show the  $^{99}\text{Tc}$  (pertechnetate) as determined by chemical separation/beta counting; the open triangles represent the  $^{99}\text{Tc}$  (total) measured by inductively coupled plasma – atomic emission spectroscopy (ICP-AES). The ICP-AES and the chemical separation/beta counting methods provide near identical results. Since the SuperLig<sup>®</sup> 639 adsorbs only  $^{99}\text{Tc}$  in  $\text{TcO}_4^-$  form, the results by the two methods should nearly be the same. The elution of the SuperLig<sup>®</sup> 639 resin showed the same pattern for all cycles; the  $^{99}\text{Tc}$  elution produced a sharp peak using a small volume of eluent (3 to 4 BV). The  $C/\text{Co}$  value at the peak was 94, 92, 91, 77, and 128 for cycles #1, #2, #3, #4, and #5, respectively. This value depends primarily on the degree of column loading and the efficiency of elution. As shown in Figures 2-6, a target  $C/\text{Co}$  of 0.01 (i.e. 99% recovery of  $^{99}\text{Tc}$  from the column) was reached using  $< 16$  BV of eluent.

Figures 7-11 show the molar concentrations of  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{NO}_3^-$  in the feed displacement and eluate samples for the five cycle tests. As expected, the  $\text{K}^+$  and  $\text{Na}^+$  concentration decreased sharply during the feed displacement step. The  $\text{Na}^+$  curve decreased to 0.1 M indicating a complete feed displacement from the column. It then continues to decline sharply due to further dilution by the de-ionized water front until the  $^{99}\text{Tc}$  elution peak emerged. The  $\text{K}^+$  curves exhibited a broad elution peak after processing

3 to 4 BV of eluate. It is quite possible that this peak is associated with the  $^{99}\text{Tc}$  peak described earlier since  $\text{K}^+$  salts are adsorbed as  $\text{KTcO}_4$  during the column loading. It has long been assumed that the SuperLig<sup>®</sup> 639 resin adsorbs nitrate ion as the primary competitor with technetium. The  $\text{Na}^+$  curves exhibited no distinct peaks although small humps were occasionally observed at the end tail of the curve. In fact, it would be very difficult to observe the  $\text{Na}^+$  elution peak due to the high background from the 0.1 M NaOH feed displacement solution. Although the  $\text{K}^+$  and  $\text{Na}^+$  peaks are not sufficiently resolved, it is apparent that  $^{99}\text{Tc}$  was present on the resin as a mixture of  $\text{NaTcO}_4$  and  $\text{KTcO}_4$  salts. This suggests that the resin is more effective for pertechnetate removal in the presence of excess  $\text{K}^+$  in the waste solution.

The results of the resin performance are shown in Table 6. This table shows the volume of effluent product collected, the concentration of  $^{99}\text{Tc}$  in the effluent composite product, the percent removal of  $^{99}\text{Tc}$ , and the decontamination factors achieved in each of the five cycles. The average  $^{99}\text{Tc}$  removed from the feed sample was more than 99.9%. The decontamination factors achieved for  $^{99}\text{Tc}$  in cycles 1, 2, 3, 4, and 5 were 1810, 1100, 1570, 1770, and 2250 respectively. The RPP-WTP requires a DF of 30 for the Hanford tank waste solution from tank 241-AW-101.

## CONCLUSION

Five cycles of loading, elution, and regeneration were performed to demonstrate the removal of technetium from Hanford tank waste using SuperLig<sup>®</sup> 639 resin in a small dual ion exchange column system. The resin showed good loading and elution performances for all five cycles. The percent removal of <sup>99</sup>Tc was > 99.9%, and the average decontamination factor (DF) achieved for five cycles was ~1700. This DF was 30 times higher than those previously observed for older batches of SuperLig<sup>®</sup> 639 tested Hanford waste samples AW-101. The feed displacement and elution data suggested that the resin retained pertechnetate in the form of sodium and potassium salts. The elution of the <sup>99</sup>Tc with de-ionized water at 65 °C was effective; Less than 1% of the <sup>99</sup>Tc remained on SuperLig<sup>®</sup> 639 resin after 16 BV.

## **ACKNOWLEDGMENTS**

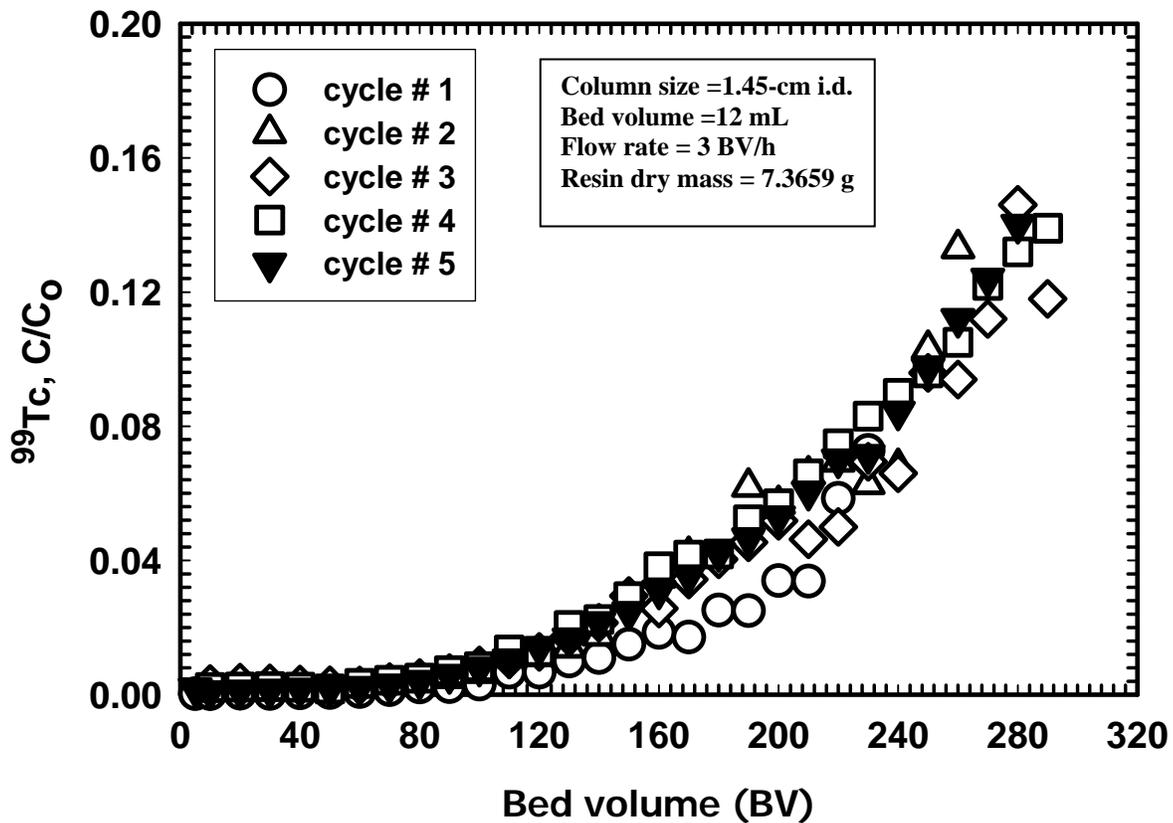
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# FIGURES



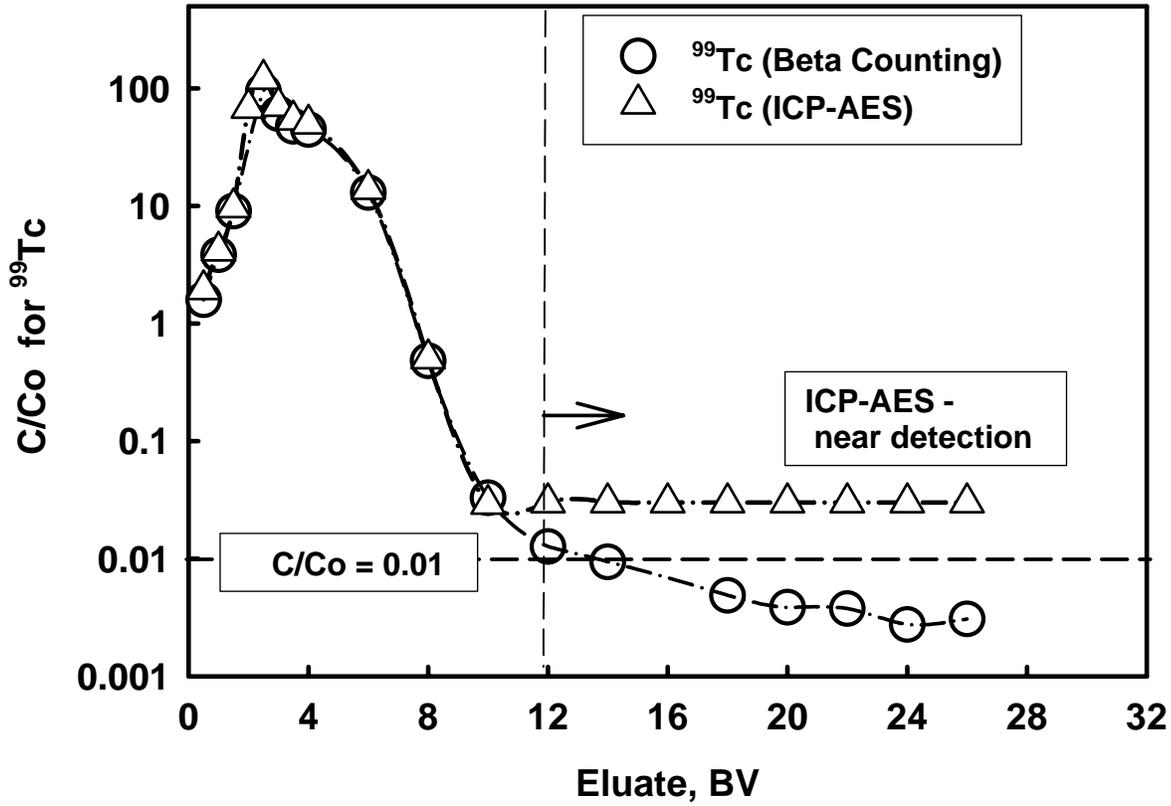


Fig. 2.  $^{99}\text{Tc}$  Elution Curves - Cycle #1

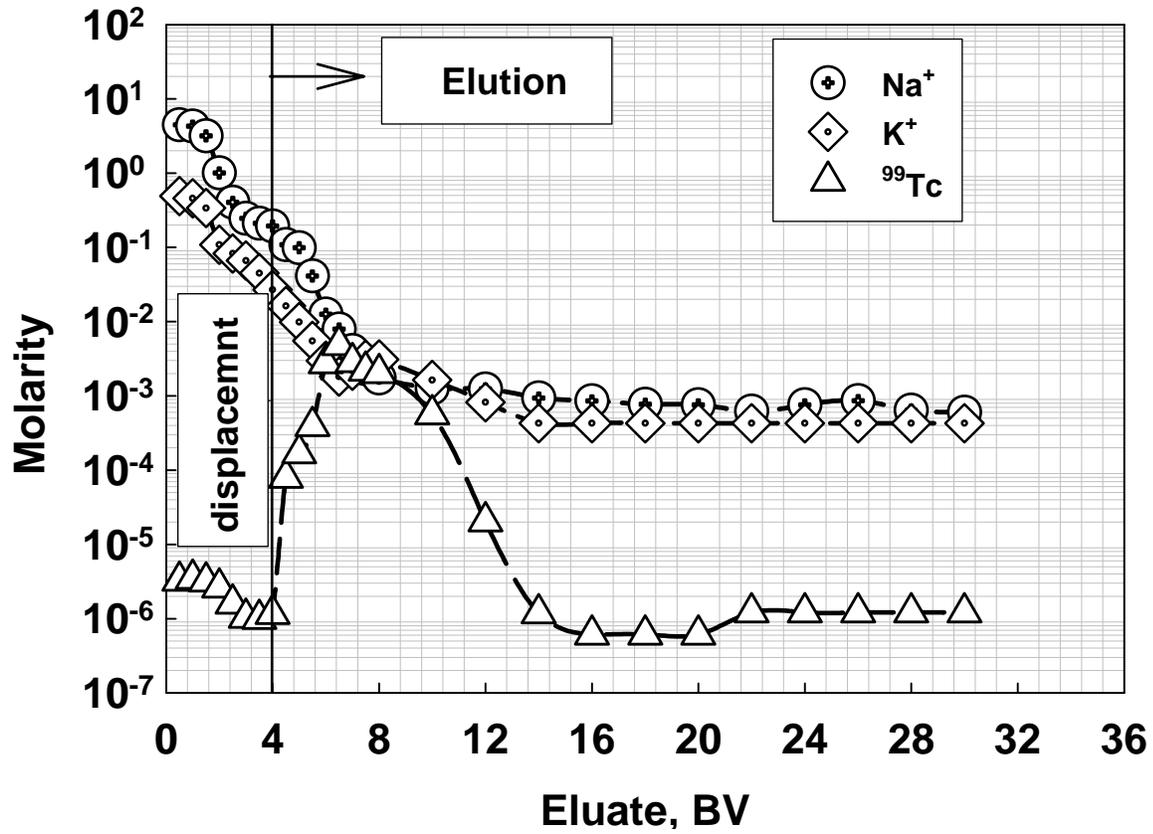


Fig. 3. Feed Displacement and Elution - Cycle #1

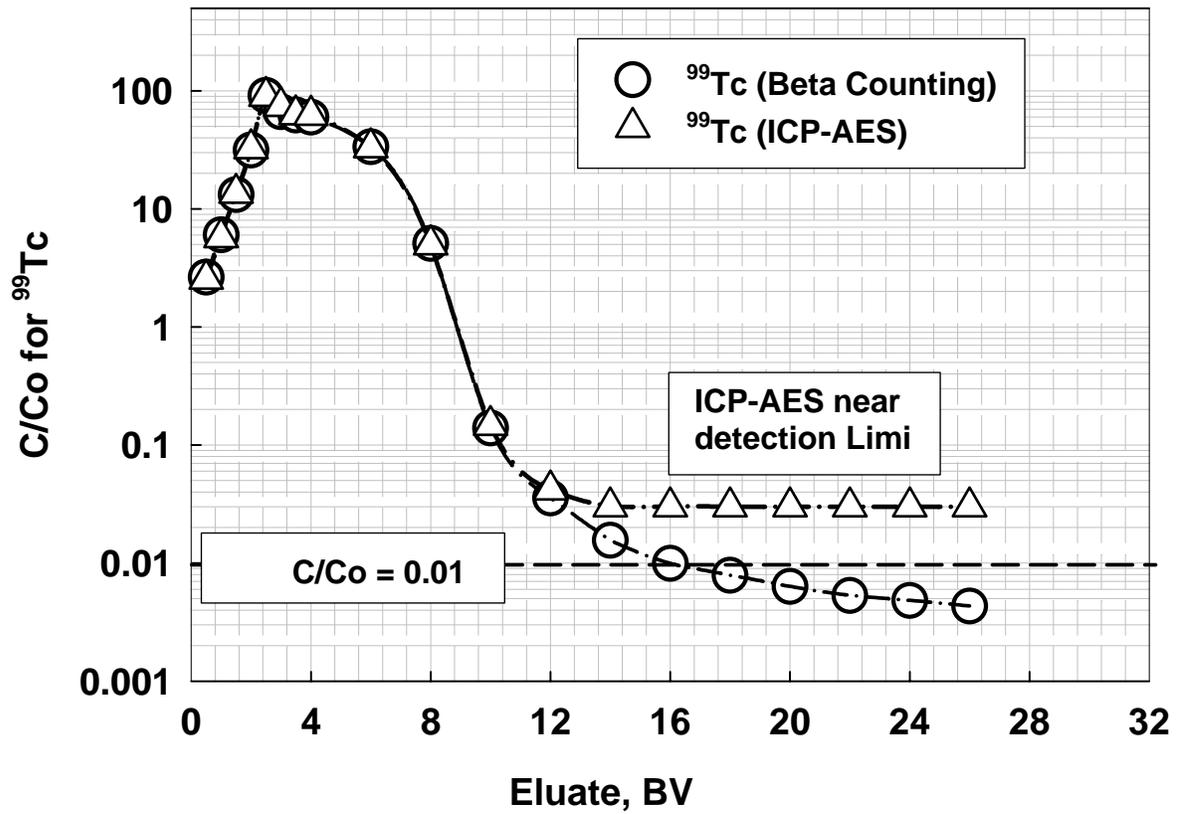


Fig. 4.  $^{99}\text{Tc}$  Elution Curve – Cycle # 2

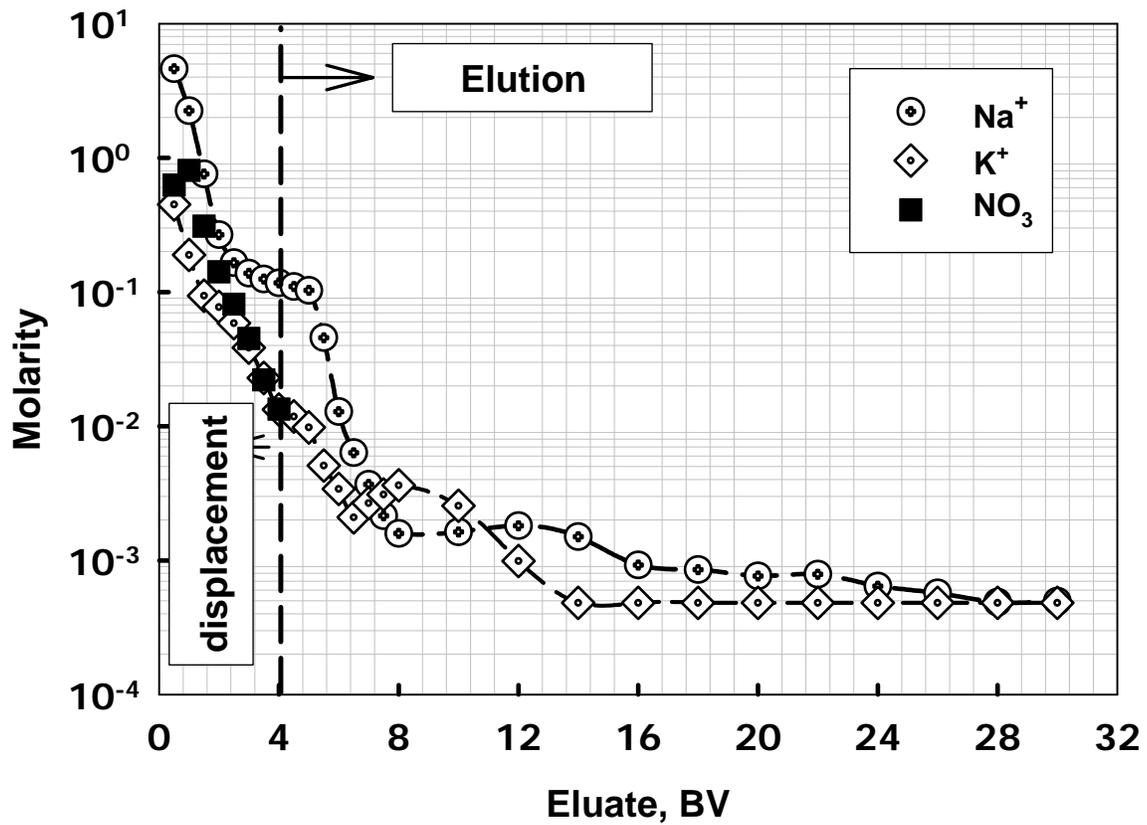


Fig. 5. Feed Displacement and Elution - Cycle # 2

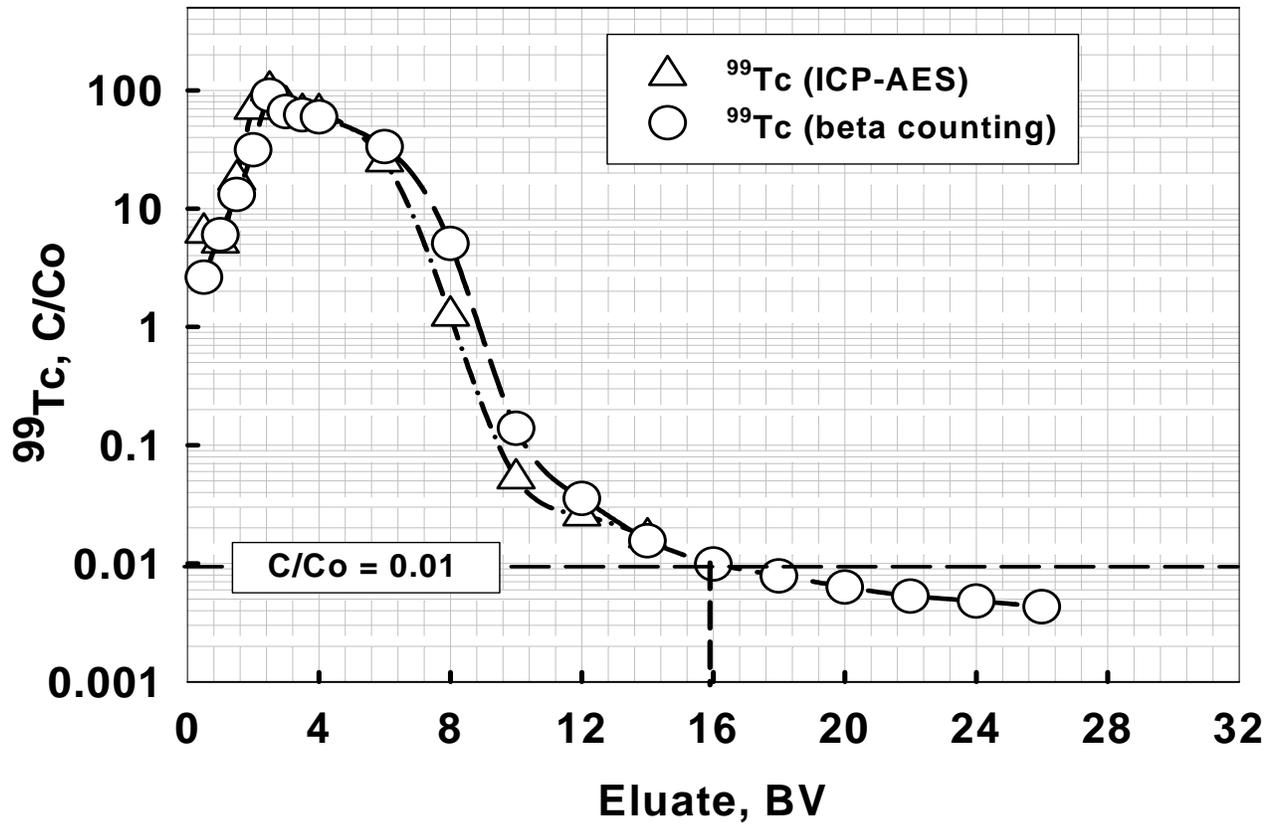


Fig. 6.  $^{99}\text{Tc}$  Elution Curve - Cycle # 3

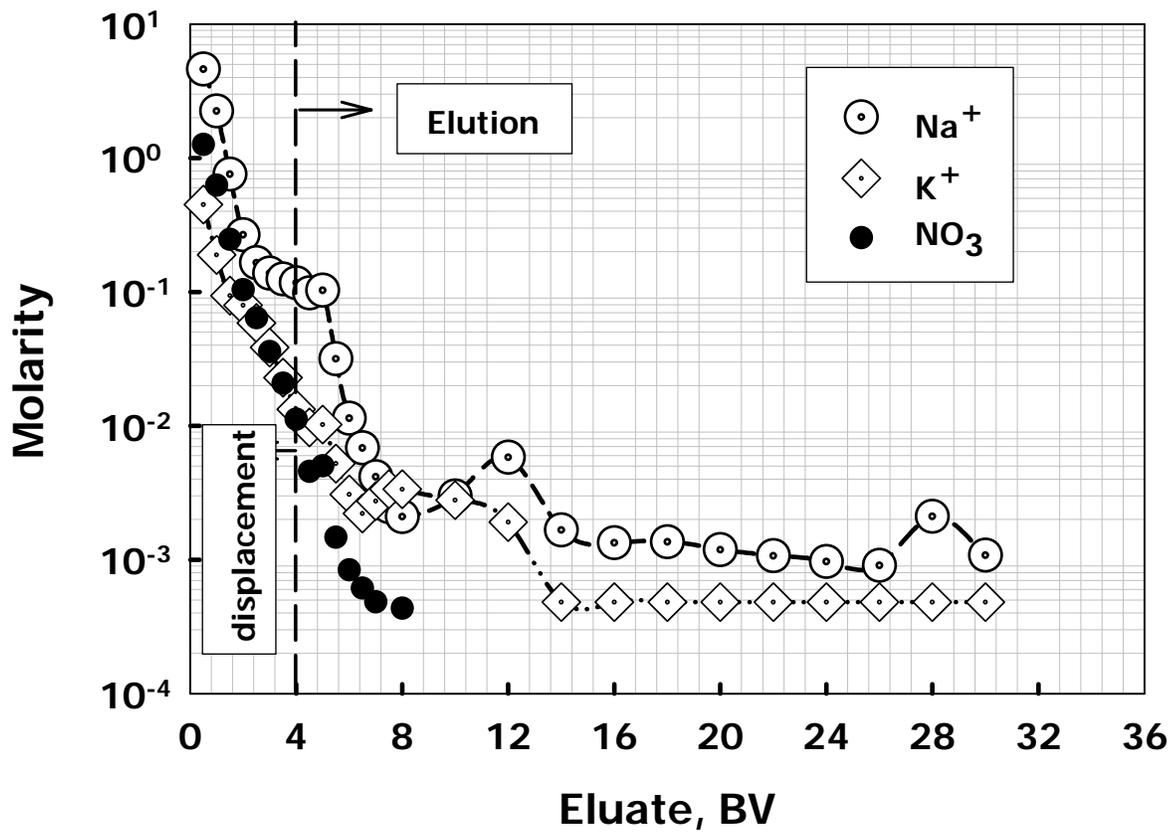


Fig. 7. Feed Displacement and Elution - Cycle # 3

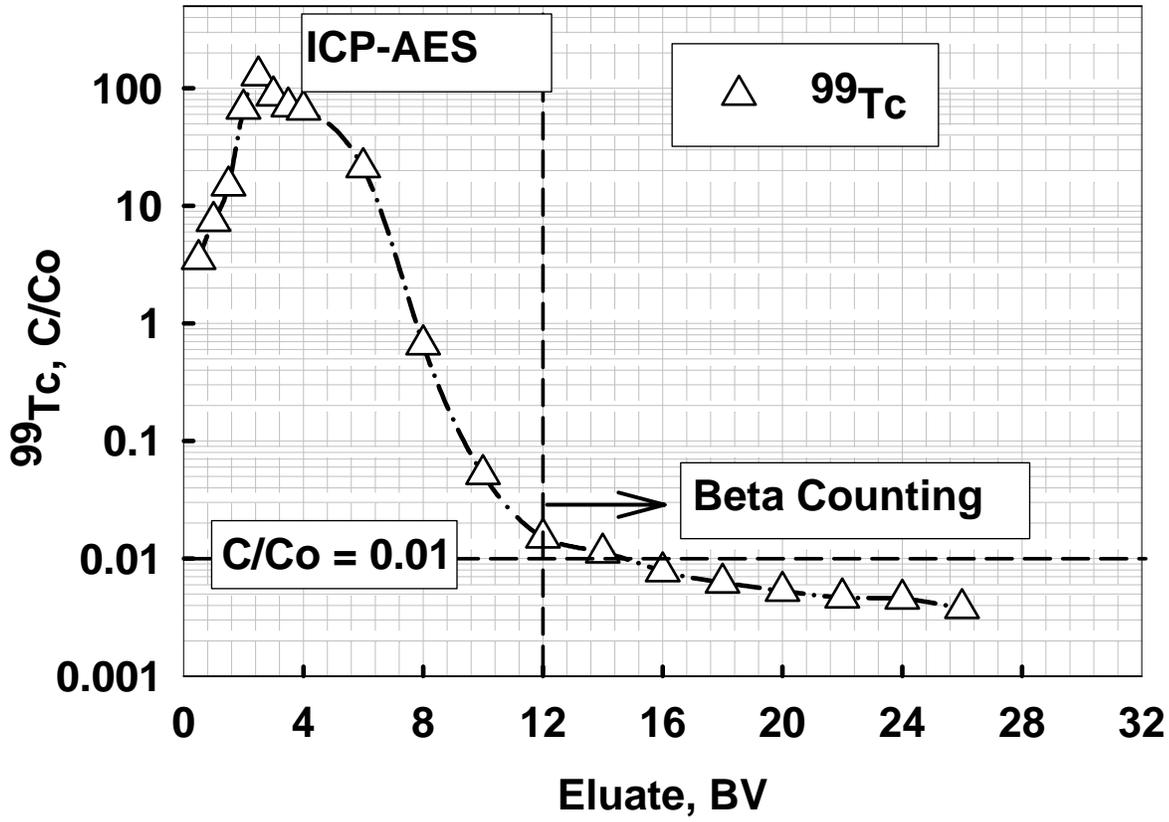


Fig. 8.  $^{99}\text{Tc}$  Elution Curve - Cycle # 4

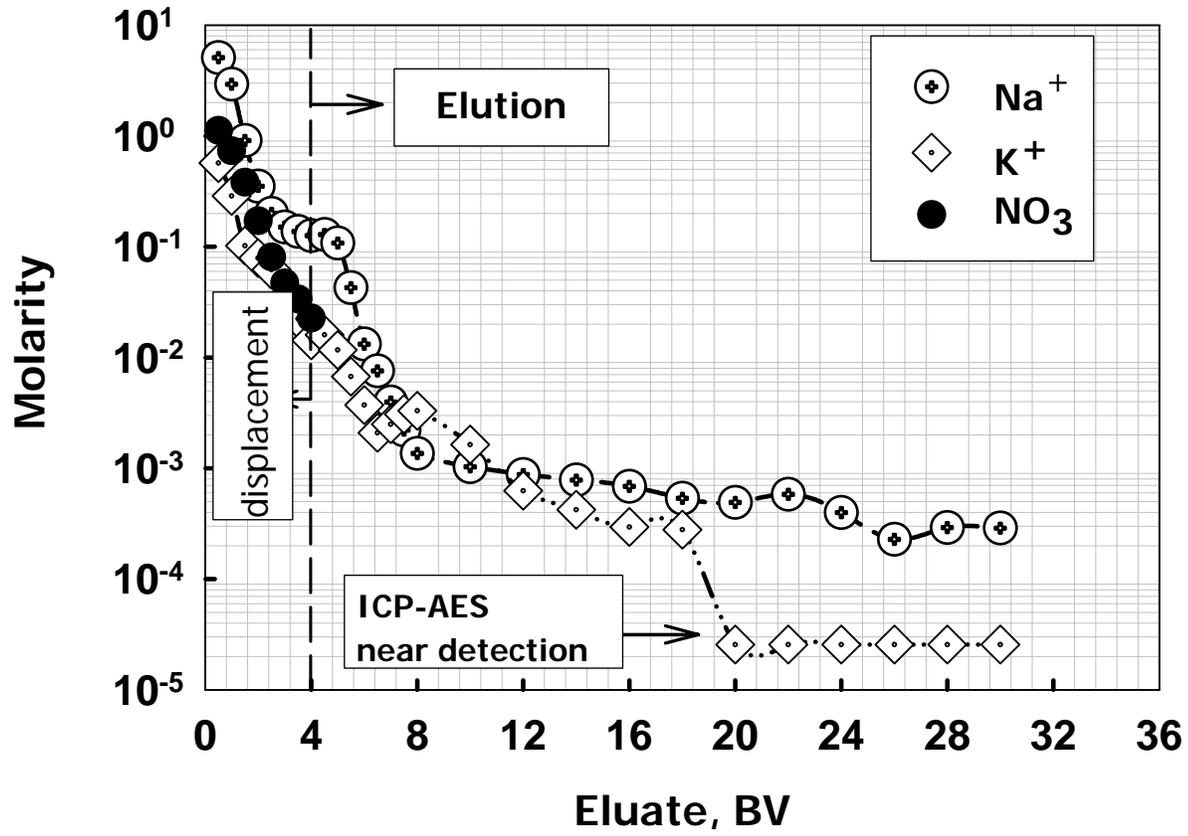


Fig. 9. Feed Displacement and Elution - Cycle # 4

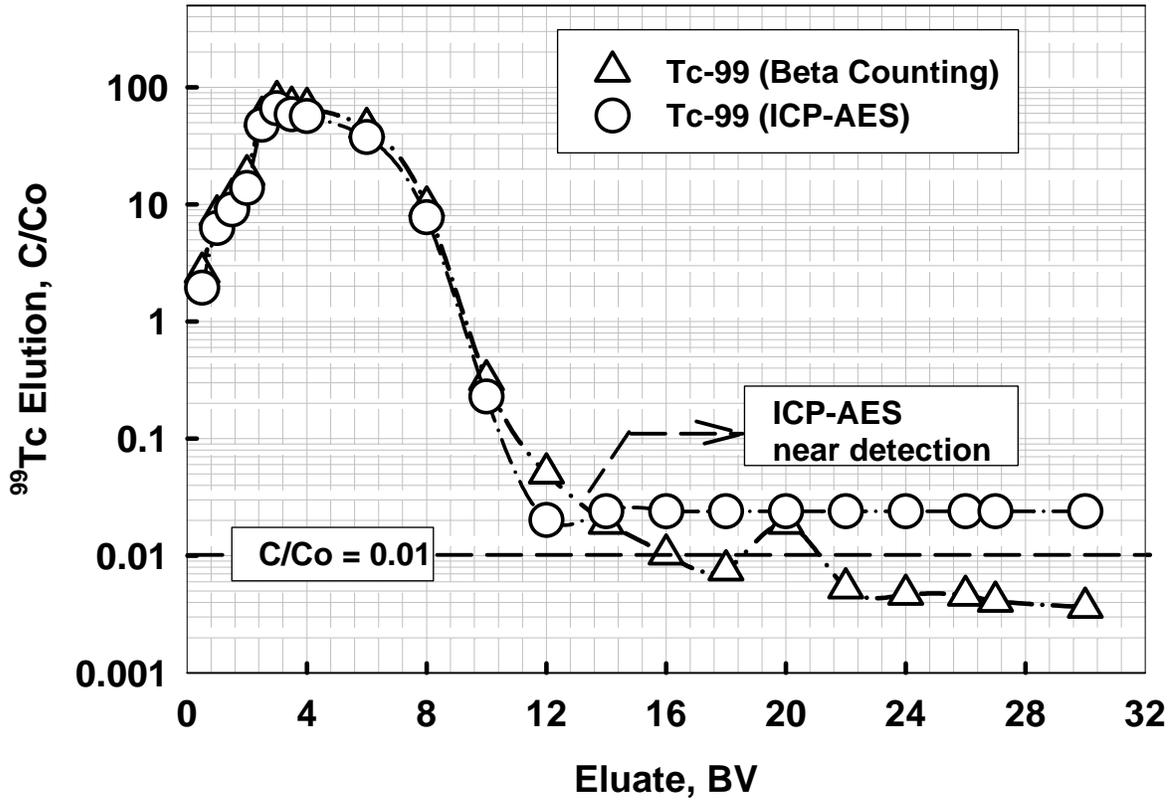


Fig. 10. <sup>99</sup>Tc Elution Curves - Cycle # 5

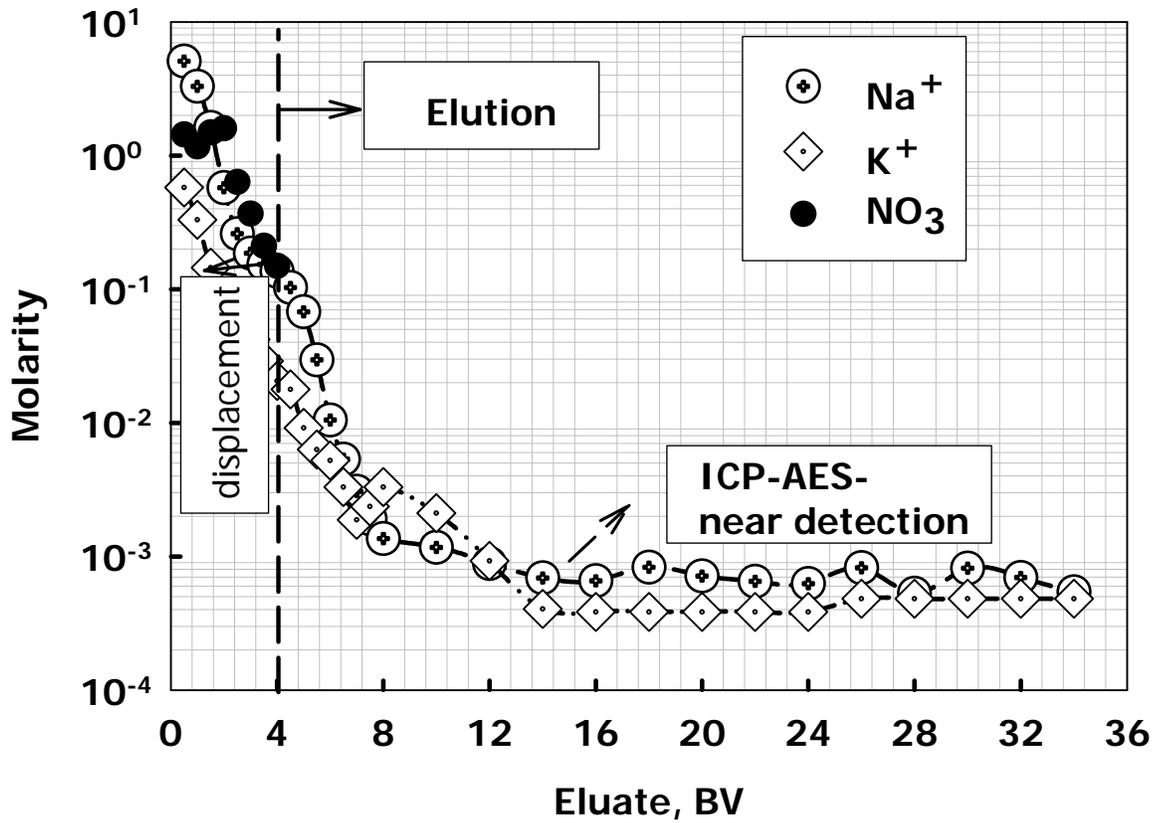


Fig. 11. Feed Displacement and Elution - Cycle # 5

# TABLES

**Table 1. Composition of Hanford waste sample (Tank 241-AW-101)**

| Analyte                              | Concentration | Analyte  | Concentration |
|--------------------------------------|---------------|--|---------------|
| <sup>99</sup> Tc, $\mu\text{Ci/mL}$  | 6.62E-04      | Total carbon, $\mu\text{g/L}$                              | 2.21E+03      |
| <sup>137</sup> Cs, $\mu\text{Ci/mL}$ | 1.75E+02      | TIC, $\text{mg/L}$   | 8.52E+02      |
| <sup>133</sup> Cs, $\mu\text{g/L}$   | 4.16E+03      | TOC, $\text{mg/L}$   | 1.36E+03      |
| <sup>135</sup> Cs, $\mu\text{g/L}$   | 1.46E+03      | Free OH-, M  | 1.81E+00      |
| <sup>136</sup> Cs, $\mu\text{g/L}$   | 9.22E+01      | <sup>238</sup> U/Pu, $\mu\text{g/L}$                       | 1.56E+03      |
| <sup>137</sup> Cs, $\mu\text{g/L}$   | 2.05E+03      | Specific gravity   | 1.22E+00      |
| Total Cs, $\mu\text{g/L}$            | 7.76E+03      |  |               |
| Total Cs, M                          | 5.84E-05      |  |               |
|                                      |               |  |               |
| IC (anions), M                       |               |  |               |
| Cl <sup>-</sup>                      | 6.94E-02      | NO <sub>2</sub> <sup>-</sup>                               | 9.97E-01      |
| F <sup>-</sup>                       | 9.48E-02      | (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> <sup>-</sup> | 2.58E-03      |
| HCOO <sup>-</sup>                    | 2.43E-02      | PO <sub>4</sub> <sup>-</sup>                               | 4.70E-03      |
| NO <sub>3</sub> <sup>-</sup>         | 1.56E+00      | SO <sub>4</sub> <sup>-</sup>                               | 1.77E-03      |
|                                      |               |  |               |
| Metals (ICP-AES), M                  |               |  |               |
| Al                                   | 4.74E-01      | Fe   | 5.64E-06      |
| B                                    | 1.68E-04      | K  | 4.68E-01      |
| Ba                                   | 2.58E-06      | Na   | 5.09E+00      |
| Ca                                   | 1.97E-05      | Na/K   | 1.09E+01      |
| Cd                                   | 3.07E-07      | Na/Al  | 1.08E+01      |
| Cr                                   | 9.17E-05      | Na/Cs  | 8.81E+04      |
| Cu                                   | 9.08E-06      | K/Cs   | 8.11E+03      |

**Table 2. Properties of SuperLig<sup>®</sup> 639 Resin**

|                               |             |
|-------------------------------|-------------|
| F-Factor                      | 0.98        |
| Bulk density (nitrogen-dried) | 0.41 g/mL   |
| Skeletal density              | 1.21, g/mL  |
| Particle size range           | 20-45 mesh  |
| Mean particle size            | 475 microns |

**Table 3. Operating Conditions**

|                              |                           |
|------------------------------|---------------------------|
| AW-101 Column Tests          | SuperLig <sup>®</sup> 639 |
| Column size, cm              | 1.45                      |
| Dual column set-up           | Lead & lag                |
| Bed volume, mL               | 12                        |
| Mass of resin/column, g      | 7.3659                    |
| Preconditioning solution     | 0.25 M NaOH               |
| Displacement solution        | 0.1 M NaOH                |
| Flow rate, BV/h              |                           |
| Loading                      | 3.0                       |
| Displacement                 | 3.0                       |
| Elution                      | 1.0                       |
| Column temperatures          |                           |
| Loading                      | 25 °C                     |
| Elution                      | 65 °C                     |
| Eluent                       | De-ionized water          |
| [ <sup>99</sup> Tc]o, μCi/mL | 0.0662                    |

**Table 4. Technetium Distribution Coefficients ( $K_d$ s) for AW-101 Waste and SuperLig<sup>®</sup> 639 Resin**

| AW-101 actual waste | phase       | $[^{99}\text{Tc}]_0$ | $[^{99}\text{Tc}]_e$ | $K_d$  | avg. $K_d$ |       |
|---------------------|-------------|----------------------|----------------------|--------|------------|-------|
| Sample ID           | Ratio, mL/g | ( $\mu\text{g/L}$ )  | ( $\mu\text{g/L}$ )  | (mL/g) | (mL/g)     | % RSD |
| Kd-1                | 96          | 4725                 | 492                  | 839    |            |       |
| Kd-1D               | 90          | 4725                 | 508                  | 766    | 802        | 6.4   |
| Kd-2                | 9.5         | 4725                 | 190                  | 231    |            |       |
| Kd-2D               | 9.5         | 4725                 | 181                  | 245    | 238        | 4.1   |

**Table 5. Average BV Processed at C/Co = 0.1**

| Cycle # | Mean value (BV) | Lower Limit (BV) | Upper Limit (BV) |
|---------|-----------------|------------------|------------------|
| 1       | 262             | 251              | 282              |
| 2       | 250             | 240              | 267              |
| 3       | 258             | 252              | 265              |
| 4       | 251             | 249              | 252              |
| 5       | 251             | 248              | 253              |

**Table 6. SuperLig<sup>®</sup> 639 Resin Performance**

| Cycle # | Effluent composite <sup>a</sup> collected (mL) | <sup>99</sup> Tc in the effluent composite (μCi/mL) | <sup>99</sup> Tc percent removal (%) | Decontamination Factor <sup>b</sup> |
|---------|--|---|--------------------------------------|-------------------------------------|
| 1       | 2,964  | $3.66 \times 10^{-5}$                               | 99.94                                | 1,810                               |
| 2       | 3,570  | $5.95 \times 10^{-5}$                               | 99.91                                | 1,100                               |
| 3       | 3,600  | $4.20 \times 10^{-5}$                               | 99.94                                | 1,570                               |
| 4       | 3,650  | $3.70 \times 10^{-5}$                               | 99.94                                | 1,770                               |
| 5       | 3,630  | $2.94 \times 10^{-5}$                               | 99.90                                | 2,250                               |

<sup>a</sup> Effluent product is defined as the treated effluent solution collected from the lag column

<sup>b</sup> The DF is defined as the concentration of <sup>99</sup>Tc in the feed solution before treatment divided by the concentration in the effluent composite solution after treatment.

**Table 7. Composition of Effluent Solutions**

| Radionuclides                              | cycle #1 | cycle #2 | cycle #3 | cycle #4 | cycle #5  |
|--|----------|----------|----------|----------|-----------|
| <sup>137</sup> C, $\mu\text{Ci/mL}$        | 3.48E-04 | 3.72E-03 | 2.87E-03 | 4.50E-03 | 4.01E-03* |
| <sup>99</sup> Tc, $\mu\text{Ci/mL}$        | 3.66E-05 | 5.95E-05 | 4.20E-05 | 3.73E-05 | 2.94E-05  |
| <sup>99</sup> Tc, $\mu\text{g/L}$ (ICP-MS) | 1.73E+02 | 1.73E+02 | 1.99E+02 | 1.34E+02 | 1.25E+02  |
| Total carbon, mg/L                         | 2.30E+03 | 2.26E+03 | 2.34E+03 | 1.62E+04 | 1.52E+04  |
| TIC  | 1.01E+03 | 9.18E+02 | 1.08E+03 | 1.51E+04 | 1.41E+04  |
| TOC  | 1.29E+03 | 1.34E+03 | 1.26E+03 | 1.11E+03 | 1.05E+03  |
| Total base, M                              | 2.79E+00 | 2.83E+00 | 2.79E+00 | 2.88E+00 | 2.83E+00  |
| Free OH, M                                 | 2.05E+00 | 2.01E+00 | 1.84E+00 | 2.10E+00 | 2.09E+00  |
| wt. % dissolved solids                     | 3.15E+01 | 3.22E+01 | 3.24E+01 | nm**     | nm**      |
| specific gravity                           | 1.23E+00 | 1.23E+00 | 1.23E+00 | 1.23E+00 | 1.23E+00  |
| IC (anions), M                             |          |          |          |          |           |
| Cl-  | 6.22E-02 | 6.35E-02 | 6.18E-02 | 6.60E-02 | 6.46E-02  |
| F-   | 9.64E-03 | 6.92E-03 | 6.87E-03 | nm**     | 4.90E-03  |
| HCOO-                                      | 1.31E-02 | 6.74E-03 | 7.09E-03 | 1.15E-02 | 1.15E-02  |
| NO3-                                       | 1.35E+00 | 1.28E+00 | 1.22E+00 | 1.32E+00 | 1.25E+00  |
| NO2-                                       | 8.97E-01 | 9.12E-01 | 8.95E-01 | 9.27E-01 | 9.25E-01  |
| (C2O4)2-                                   | 2.11E-03 | 1.93E-03 | 1.84E-03 | 1.92E-03 | 2.14E-03  |
| PO4-                                       | 2.42E-03 | 1.96E-03 | 2.04E-03 | 2.38E-03 | 2.73E-03  |
| SO4-                                       | 1.65E-03 | 1.39E-03 | 1.30E-03 | 1.17E-03 | 1.43E-03  |
| by ICP-AES, $\mu\text{g/mL}$               |          |          |          |          |           |
| Ag   | 3.57E-01 | 3.79E-01 | 4.12E-01 | 2.98E-01 | 3.33E-01  |
| Al   | 1.37E+04 | 1.40E+04 | 1.40E+04 | 1.15E+04 | 1.17E+04  |
| B  | 1.85E+01 | 1.91E+01 | 1.89E+01 | 1.68E+01 | 1.72E+01  |
| Ba   | 5.38E-01 | 5.82E-01 | 5.80E-01 | nm**     | nm**      |
| Ca   | 5.95E+00 | 6.22E+00 | 6.23E+00 | 5.00E+00 | 5.30E+00  |
| Cd   | 9.82E-01 | 1.07E+00 | 1.03E+00 | 7.84E-01 | 8.20E-01  |
| Ce   | 4.17E+00 | 4.42E+00 | 4.76E+00 | 3.88E+00 | 4.21E+00  |
| Cr   | 3.73E+01 | 4.32E+01 | 4.16E+01 | 3.54E+01 | 3.68E+01  |
| Cu   | 3.78E+00 | 2.50E+00 | 2.65E+00 | 1.59E+00 | 1.20E+00  |
| Fe   | 1.45E+00 | 1.77E+00 | 1.80E+00 | 1.58E+00 | 1.86E+00  |
| K  | 2.13E+04 | 2.19E+04 | 2.18E+04 | 1.75E+04 | 1.77E+04  |
| La   | 7.75E-01 | 7.92E-01 | 8.54E-01 | 5.84E-01 | 6.10E-01  |
| Mo   | 4.27E+01 | 4.36E+01 | 4.39E+01 | 3.47E+01 | 3.54E+01  |
| Na   | 1.16E+05 | 1.21E+05 | 1.20E+05 | 1.01E+05 | 1.04E+05  |
| Ni   | 2.46E+00 | 2.53E+00 | 2.35E+00 | 2.19E+00 | 2.16E+00  |
| P  | 1.46E+02 | 1.49E+02 | 1.49E+02 | 1.30E+02 | 1.36E+02  |
| Pb   | 1.50E+01 | 1.62E+01 | 1.56E+01 | 1.30E+01 | 1.38E+01  |

|    |          |          |          |          |          |
|----|----------|----------|----------|----------|----------|
| Sb | 3.94E+01 | 4.07E+01 | 4.09E+01 | 3.09E+01 | 3.22E+01 |
| Si | 9.15E+01 | 8.96E+01 | 8.99E+01 | 6.73E+01 | 6.86E+01 |
| Sn | 7.70E+01 | 7.91E+01 | 7.89E+01 | 6.02E+01 | 6.16E+01 |
| Sr | 2.00E+00 | 2.07E+00 | 2.08E+00 | 1.59E+00 | 1.81E+00 |
| Zn | 4.58E+00 | 4.69E+00 | 4.85E+00 | 3.98E+00 | 4.08E+00 |
| Zr | 4.44E+00 | 6.06E+00 | 5.44E+00 | 4.95E+00 | 5.24E+00 |