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Recent Developments in the Analysis of Techetium-99

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Analysis of ^{99}Tc using an extraction chromatographic resin to isolate technetium from other elements, followed by liquid scintillation counting has become common worldwide. The method is robust and has been applied to a wide variety of matrix types. Recently, high biases have been reported when samples with high levels of naturally occurring uranium were analyzed. The problem was traced to incomplete decontamination of the technetium fraction from ^{234}Th (daughter of ^{238}U) present in the samples. A variety of protocol modifications to the load and rinse solutions were attempted in order to improve the decontamination of the technetium fraction. It was determined that complexing agents were required to remove thorium from the column. Oxalate solutions provided better decontamination than nitric acid and hydrochloric acid solutions alone for samples with low levels of natural uranium. However, fluoride was found to be necessary to ensure adequate decontamination from samples containing up to 44 Bq of natural uranium.

1. Introduction

In recent years the use of extraction chromatography has grown significantly in methodologies for technetium-99 measurement. An aliphatic quaternary amine, impregnated on a polymeric support, trade named TEVA® Resin[1] has become a standard in separating and pre-concentrating pertechnetate prior to technetium-99 measurement by liquid scintillation or ICP-MS.

TEVA Resin has a very high affinity for pertechnetate anion from low acid and even basic solutions. Figure 1 shows the uptake of TcO_4^- as a function of nitric acid and HCl concentration. It can be seen that the TcO_4^- uptake increases with decreasing acid concentration, while all the actinide elements show declining retention. This behavior indicates that the TEVA Resin can be used to separate pertechnetate anion from a wide variety of potentially interfering radionuclides. The k' values in the range of 10^4–10^5 show that the resin can be used to pre-concentrate pertechnetate from very large volume samples (e.g. up to 4 liters of water.)

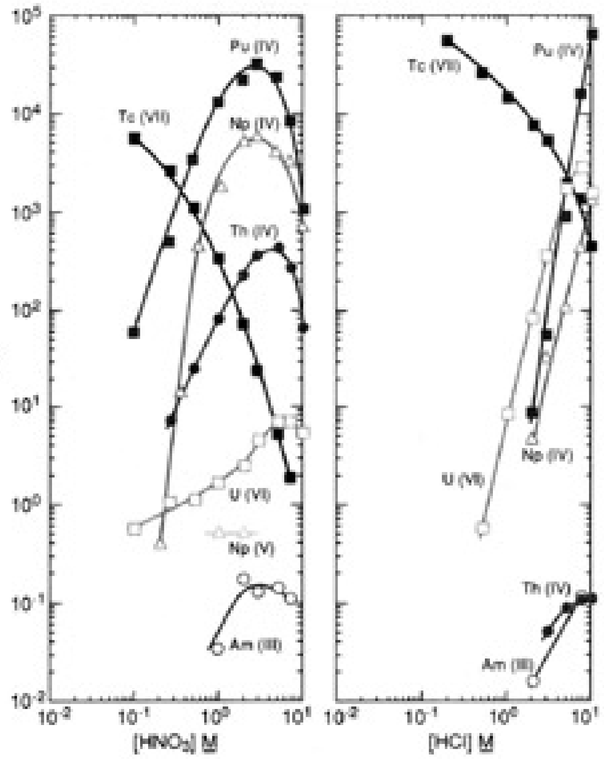

Figure 1. The acid dependency of k' for various ions at 23 °C, TEVA Resin (published by Horwitz, et al.[1])

The technique has been applied to a variety of matrices including water, soil, urine and waste samples. It has also been applied to process control samples in nuclear fuel reprocessing and waste treatment applications.[1–5] TEVA Resin has been used in several formats: slurry-packed columns for gravity flow use, dry packed cartridges for us in vacuum manifold systems, and glass fiber filter discs to process very large liquid samples with fast flow rate (~100 mL/min.)

As this methodology has been applied to broader and broader sample types, several challenging matrix interferences have been encountered that have made accurate measurements difficult. One example of a matrix challenge is the effect of high levels of Th-234 present in natural uranium samples on the quantitation of Tc-99 in the sample. In this case, the beta emissions from the interfering isotope are measured in the Tc-99 window of the LSC. This can lead to a bias in the measurement of Tc-99.

2. Experimental

All experiments were conducted using reagent grade materials. TEVA Resin packaged in columns is commercially available from Eichrom Technologies (Darien, IL, USA.) UltimaGold® LLT liquid scintillation counting cocktail was obtained from PerkinElmer Life Sciences (Boston, MA, formerly Packard Instrument Company.)

Technetium-99 was loaded onto a 2 mL pre-packed column of TEVA Resin from 0.01 M HNO_3. The column was then rinsed with 0.01 M HNO_3 (typically 20–25 mL.) The resin was then removed from the plastic column and transferred to a plastic 20 mL scintillation vial. UltimaGold LLT cocktail was added. Samples vials were placed in a Packard 2750 Liquid Scintillation Counter and allowed to equilibrate to the dark. Count time was 30 minutes. Typical counting uncertainly was

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5–10%. Reagent blanks were determined by rinsing a TEVA Resin column with 0.01 M HNO_3, removing the resin and transferring to a scintillation vial. UltimaGold LLT was added and the vial counted for 30 minutes. Since blank levels were very consistent between experiments and lots of resin, blanks were not run with all experiments.

3. Results and Discussion

A number of customer comments about high spikes recoveries in samples from nuclear facilities lead to an internal investigation at Eichrom. A hypothesis emerged that thorium-234 present in natural uranium samples was causing a high bias in the counts observed in the technetium-99 window of the LSC spectrum. Initially, this seemed improbable since the retention of both uranium and thorium is quite low on the TEVA Resin under the load and rinse conditions of the method. Extrapolation of the Th uptake curve in the nitric acid graph in Figure 1, indicates that thorium should have a k' of less than10^{-1}. (The dimensionless value, "k'", represents the retention of an element on a chromatographic column as a multiple of free column volumes to peak maximum.) It would be expected that at this uptake level, there should be no thorium present on the column if loaded and rinsed with sufficient 0.01 M HNO_3 (40–50 mL.) However, the problem was replicated in our internal technical support laboratory and confirmed to be reproducible on multiple replicates of several different lots of TEVA Resin. Table 1 shows results of natural uranium spiked(3.6 Bq) into 0.01 M HNO_3, loaded onto TEVA Resin columns, rinsed and counted as indicated above. No technetium-99 was spiked into these samples. Net counts in the technetium-99 region were in the range of 0.2 to 0.4 cps. Counting efficiency was not measured for this experiment, but typically is in the range of 90%.

TABLE 1: Effect of Natural Uranium Spikes on Counts in the Tc-99 Window in LSC

TEVA Resin Lot #	Natural uranium spike/Bq	Blank counts/cps	Mean counts Tc-99 region/cps	σ/cps. n = 3
10170	3.6	0.23	0.62	0.10
11270	3.6	0.23	0.53	0.06
08280	3.6	0.26	0.47	0.05

To resolve this problem various options were considered. The uptake of thorium is lower from HCl than from nitric acid and use of HCl in load or rinse solution would be expected to elute the thorium more completely from the column. Additionally, various complexants including oxalate and fluoride should keep the thorium in a complexed state and prevent loading on the resin. Various concentrations and volumes of these solutions were tried and the results are shown in Tables 2–4.

TABLE 2: The Effect of Various Load/Rinse Combinations Containing Hydrochloric Acid on Counts in the Tc-99 Region Due to Natural Uranium Spike

Natural uranium spike/Bq	Load (20 mL)	Rinse (25 mL)	Blank counts/cps	Mean counts Tc-99 region/cps	σ/cps
3.6	0.01 M HCl	0.01 M HCl	0.24	1.18	0.08 (n = 9)
3.6	0.5 M HNO_3	0.05 M HCl	ND	0.92	0.21 (n = 5)
8.9	0.5 M HNO_3	0.05 M HCl	ND	0.93	0.13 (n = 5)
3.6	0.01 M HNO_3	0.1 M HCl	ND	1.13	0.05 (n = 4)

Attempts to reduce the thorium-234 bias in the technetium-99 fraction using HCl were not successful. Despite the indication that Th would be less strongly retained from HCl, the bias in the technetium-99 window actually increased. Results were reproducible between various numbers of replicates.

The use of oxalate as a complexant actually helped to reduce the problem but did not eliminate it completely. The data for this experiment are shown in Table 3. Higher spikes of natural uranium ($^{234}U/^{238}U$) were added, in this case 37.4 Bq. Various concentrations and volumes of oxalic acid in the rinse solution were evaluated. With no oxalate and 25 mL of rinse, the same conditions as the initial experiments which replicated the problem, 5.4 cps were observed in the technetium-99 window. Addition of oxalate in the range of 0.05 M to 0.5 M with rinse volumes of 25 and 50 mL reduced the counts in the Tc-99 window to 1.1 cps or less. However, in the best case, 50 mL of 0.5 M oxalic acid, there were still approximately 0.3 net cps. This is a marked improvement and may be acceptable as a solution in cases were the amount of interfering thorium-234 is low. However, a universal solution that can address even very high levels of thorium-234 is desirable.

TABLE 3: The Effect of Increasing Concentration and Volume of Oxalic Acid Rinses on the Counts in the Technetium-99 Window

Natural uranium spike/Bq	Oxalic acid conc.	Rinse volume	Blank counts/cps	Mean counts Tc-99 region/cps	σ/cps n = 2
37.4	None	25 mL	0.27	5.4	1.1
37.4	0.05 M	25 mL	0.25	1.1	0.01
37.4	0.1 M	25 mL	0.25	0.78	0.2
37.4	0.1 M	50 mL	0.25	0.64	0.11
37.4	0.5 M	25 mL	0.25	0.80	0.13
37.4	0.5 M	50 mL	0.24	0.53	0.09

Fluoride added as HF was evaluated next. The results of this experiment are shown in Table 4. In this case, the load solution was 0.01 M HNO_3 and the rinse was 25 mL of 0.5 M HF/0.02 M HNO_3. Varying spike levels of natural uranium were added. At all of these levels the net counts in the technetium-99 region were effectively zero. Subsequent evaluations of actual samples and technetium-99 spikes indicated that the HF in the rinse solution did not adversely affect technetium-99 recoveries.

TABLE 4: Counts in the Technetium-99 Region for Various Spikes of Natural Uranium where the Load Solution was 0.01 M HNO_3 and the Rinse Solution was 25 mL 0.5 M HF/0.02 M HNO_3

Natural uranium spike/Bq	Blank counts/cps	Mean counts Tc-99 region/cps	σ/cps
3.6	0.26	0.25	0.004 n = 3
22	0.27	0.26	0.003 n = 2
44	0.26	0.22	0.005 n = 4

4. Conclusion

The use of complexants is necessary to eliminate the thorium interference caused by samples containing natural uranium. Oxalic acid may be sufficient to solve the problem for cases where the amount of thorium-234 is not large relative to the technetium-99 content. Further experimentation would be required to determine the limits of thorium-234 concentration for which this solution would be acceptable. Addition of fluoride as hydrofluoric acid to complex the thorium seems to solve this problem even at concentrations of natural uranium as high as 44 Bq. Though not shown here, use of sodium fluoride was also found acceptable and may be suitable in cases where the hazards of HF are to be avoided.

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