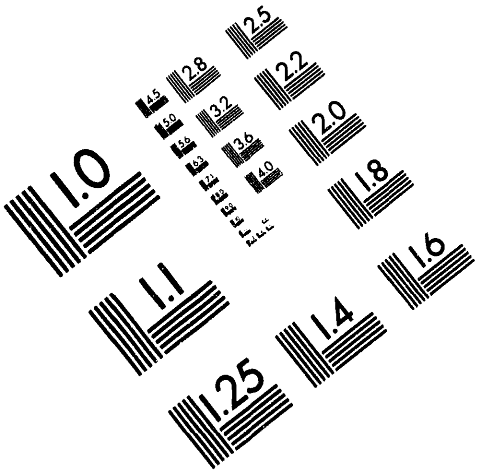

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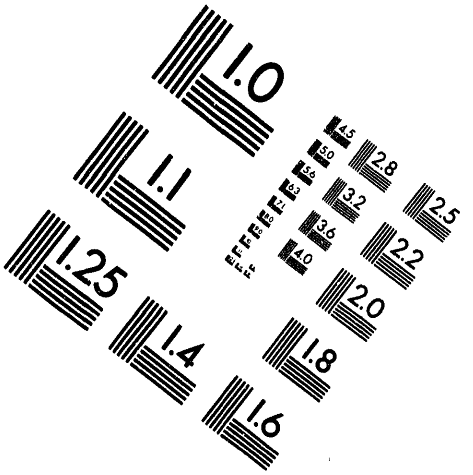

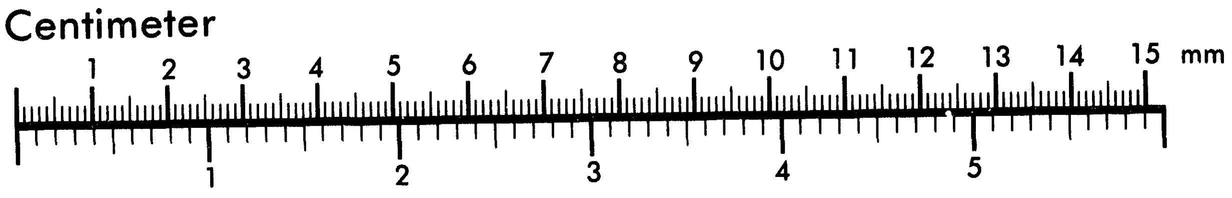

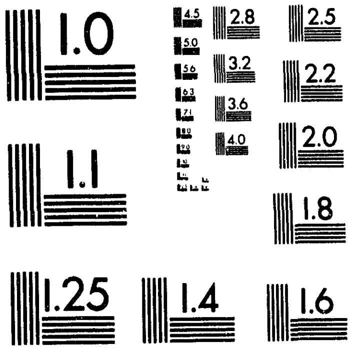

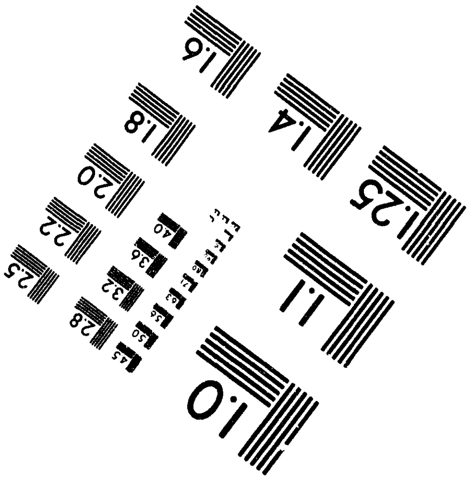

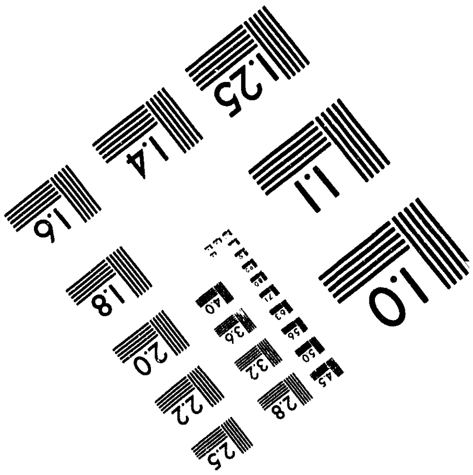

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MEASUREMENT OF ACTINIDES AND STRONTIUM-90 IN HIGH ACTIVITY WASTE (U)

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Measurement of Actinides and Strontium-90 in High Activity Waste

by

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The reliable measurement of trace radionuclides in high activity waste is important to support waste processing activities at SRS (F and H Area Waste Tanks, Extended Sludge Processing (ESP) and In-Tank precipitation (ITP) processing). Separation techniques are needed to remove high levels of gamma activity and alpha/beta interferences prior to analytical measurement. Using new extraction chromatographic resins from EiChrom Industries, Inc., the SRS Central Laboratory has developed new high speed separation methods that enable measurement of neptunium, thorium, uranium, plutonium, americium and strontium-90 in high activity waste solutions. Small particle size resin and applied vacuum are used to reduce analysis times and enhance column performance. Extraction chromatographic resins are easy to use and eliminate the generation of contaminated liquid organic waste.

Introduction

The Savannah River Site stores approximately 35 million gallons of high level liquid waste as sludge, saltcake, or salt solution. The waste will eventually be converted to a glass form in the Defense Waste Processing Facility (DWPF) and the decontaminated liquid converted to concrete at the Saltstone Facility. Because of difficult sample matrices and time consuming separation methods required, the analysis of high activity waste for trace actinides can place challenging demands on laboratory resources. Separation techniques that enable the rapid, cost effective measurement of trace actinides and other radionuclides are needed to meet customer needs in a timely manner.

In the SRS Central Laboratory, rapid separation methods are required to enable timely analytical support for F and H Area Waste Tanks, Extended Sludge Processing (ESP) and In-Tank precipitation (ITP) processing. In response to this need, R.N. Mahannah and S.L. Maxwell developed methods for rapid measurement of trace fissile material (uranium-235 and plutonium -239) in high activity liquid waste at the Savannah River Site using high speed TEHP (tri(2-ethylhexyl) phosphate columns and anion exchange resin [1].

To provide a wider range of rapid separation methods for high activity waste, new high speed separation methods using resins from EiChrom Industries have been developed. The overall separation schemes are also applicable to environmental samples and bioassay samples after appropriate sample pretreatment.

Separation Methods Developed

The SRS Central Laboratory has developed separation methods that enable the measurement of neptunium, strontium, thorium, uranium, plutonium and americium in high activity liquid waste solutions. To reduce analysis cycle times and enhance column separation performance, small particle size resin (20 to 50 micron and 50 to 100 micron) and applied vacuum were used. Column flow rates are typically 2 to 4 mL/minute, much faster than gravity flow rates of approximately 0.5 mL/minute. Extraction chromatographic resins are more efficient than classical solvent extraction, easy to use and eliminate the generation of contaminated liquid organic waste.

Neptunium-237

A new method to measure neptunium-237 and thorium isotopes in high activity waste using TEVA•Spec® resin was developed. After sample cleanup, neptunium-237 is measured by alpha spectrometry. Figures 1 illustrates the neptunium -237 separation scheme. Thorium is eluted using 6M hydrochloric acid prior to stripping the neptunium from the resin.The method is rapid, provides high recovery of neptunium and effective removal of other actinides and matrix components. The separation can be performed using 2 to 3 molar (M) nitric acid instead of the 8M nitric acid concentration typically used in traditional anion resin methods. This allows separation of plutonium from neptunium in a nitric acid matrix by reducing plutonium to the Pu(III) valence state. This method has been found to be more rapid and convenient that the traditional TIOA (tri-iso octyl amine) solvent extraction method previously used in the Central Laboratory. This separation scheme has also been applied to the measurement of trace neptunium-237 and thorium in a high level americium/ curium solution in a SRS F-Canyon tank.

Strontium-90

A new high speed strontium-90 method was also developed. Strontium-90 is separated from alpha/beta/gamma interferences in waste using Sr•Spec® resin and measured by liquid scintillation counting. Figure 2 illustrates the strontium-90 separation scheme. Barium isotopes, which are very difficult to separate from strontium using traditional precipitation methods, are separated easily using Sr•Spec® resin in a 8M nitric acid matrix. It was found that plutonium (IV), cerium (IV) and neptunium (IV), which would otherwise be retained by the Sr•Spec® resin, are removed easily by adding a 3M nitric acid-0.05M oxalic acid rinse.

Three Column Method for Actinides

In addition to using EiChrom resins for single column actinide separations, the SRS Central Laboratory has used these columns in series to achieve maximum separation power and optimum chemical recovery. By using three separate columns, collecting the rinse from the first column and loading it to the next column in the series, actinides can be rapidly separated from the same sample solution with excellent removal of interferences and chemical recovery.

The use of TEVA•Spec® resin and U-TEVA• Spec® resin in series has been demonstrated at SRS to effectively separate neptunium, thorium and uranium from other actinides and matrix components[2]. Neptunium and thorium are retained and separated using TEVA•Spec® resin, while uranium is rinsed through the TEVA• Spec® resin column and collected quantitatively on U-TEVA• Spec® resin. If TRU•Spec® resin is added to this series, americium and plutonium can also be recovered from the sample[3]. Plutonium is rinsed through the TEVA•Spec® and U-TEVA• Spec® columns as Pu (III), using ferrous sulfamate as a reductant. Figure 3 illustrates this three column scheme.

Sequential actinide separations have been performed by some DOE and commercial laboratories using only one resin, TRU•Spec ®; however, high resolution separations are more difficult with TRU•Spec ® alone, particularly when one or more actinides is present in large quantity[4]. In addition, since actinides are retained on three separate columns rather than one, this scheme provides additional column capacity.

One key advantage of using TEVA•Spec® resin over traditional anion resin schemes is that plutonium and neptunium can be separated easily from each other in a dilute nitric acid matrix. In the 8M nitric acid anion exchange method traditionally used, plutonium and neptunium separation is difficult. With TEVA•Spec®, however, the plutonium valence can be easily maintained as Pu (III) in 2 to 3 molar nitric acid to enable plutonium-neptunium separation. Thorium elution is also relatively easy with 6M hydrochloric, without the residual "tailing" that sometimes occurs in conventional anion resin methods. Uranium is rinsed through TEVA•Spec® with less nitric acid rinse volume than is used in typical anion resin methods and is collected on U-TEVA•Spec ®. Plutonium (III) and americium are rinsed through the U-TEVA•Spec ® column. Ascorbic acid is added to the rinse solution to reduce ferric ions to ferrous ions. This solution is loaded onto the TRU•Spec ® column to recover americium and plutonium, which are eluted separately using 4M hydrochloric acid and 0.1 M ammonium bioxalate respectively.

The separation scheme is flexible. If neptunium is not likely to be present (or if Pu and

Np are desired together), plutonium can be retained on the TEVA•Spec® cartridge by adjusting the plutonium valence to Pu (IV) in the initial sample solution with ferrous ammonium sulfate followed by sodium nitrite. Figure 4 illustrates this alternative scheme.

New Approach

The three column method is an extremely effective way to recover five actinides from one sample solution. However, to reduce analysis time even further, the SRS Central Laboratory has shown that the three column method can be combined into a single multistage column. In addition, Sr•Spec® resin can be added to the series to also recover strontium-89/90 from the sample solution. One sample solution can be loaded to the multistage column to recover thorium, neptunium, uranium, plutonium, americium and strontium are separated with high recovery and efficient removal of interferences. The multistage column is split apart at the luer connections to allow separate stripping of the respective radionuclides.

The sample solution is, in effect, added to four columns at once, instead of passing the solution through one column at time. This technique also significantly reduces the volume of load plus rinse solution that is added to the later columns in the series. The Sr•Spec® option, for example, could not be added to the original three column method without evaporating the large rinse volume collected from the final TRU•Spec® column. Minimizing the volume of total load and rinse solution loaded to these columns ensures good chemical recoveries of actinides.

This technique can be applied to high activity waste samples, trace environmental samples and bioassay samples after appropriate sample pretreatment. For example, actinides can be precipitated from large water or urine samples using calcium phosphate precipitation while actinides can be analyzed in soil and fecal samples after cleanup with Diphonix™ resin and dissolution of the resin using hydrogen peroxide with an iron or vanadium catalyst[5].

Single Multistage Column

The multistage column consists of a TEVA•Spec® cartridge, U-TEVA•Spec® cartridge, TRU•Spec® cartridge, and, optionally, a Sr•Spec® cartridge in series. Figures 5 and 6 show the multistage column method.

Thorium and neptunium are removed by the TEVA•Spec® cartridge, uranium by the U-TEVA•Spec® cartridge, plutonium and americium are removed by the TRU•Spec® cartridge and, if desired, strontium can be isolated using a Sr•Spec® cartridge.

In this multistage column procedure, the load solution is adjusted to matrix conditions compatible with all four cartridges. The caustic high activity waste sample is acidified to 1.5 to 3 molar nitric acid and the total nitrate concentration adjusted to 3 to 5 molar nitrate. Ferrous sulfamate and ascorbic acid are used to control the valence states of plutonium and neptunium.

The sample solution is loaded to the multistage column, rinsed with a 2.5 molar nitric acid- 0.1 molar ferrous sulfamate-0.1M ascorbic acid mixture, and then split apart into separate cartridges for stripping of the respective analytes. Fission products and matrix components are rinsed through multistage column by the initial load and rinse solution. After the gamma level in the waste sample is reduced significantly, the column can then be removed from the shielded cells and the analytes stripped in a hood or radiobench. This method minimizes radiation exposure to technicians by effectively removing gamma isotopes from the sample inside the shielded cells.

In the load and rinse solutions, the ferrous sulfamate adjusts the plutonium valence to Pu (III) and the neptunium valence to Np (IV). The sulfamate scavenges any nitrite present in the sample or the nitric acid matrix that will oxidize Pu (III) to Pu (IV). The ascorbic acid reduces any ferric ion present back to ferrous ion to prevent ferric iron retention and interference on the TRU•Spec® cartridge. The additional nitrate is added as aluminum nitrate to enhance actinide retention, particularly thorium, on TEVA•Spec®. In addition, the aluminum added complexes any fluorides, phosphates, oxalates or sulfates present in the sample matrix to facilitate the actinide extractions. The nitric acid concentration is kept low enough to allow the ferrous ions to maintain the plutonium as Pu (III), so that the plutonium will pass through the TEVA•Spec® and U-TEVA•Spec® columns and be retained by the TRU•Spec® cartridge.

The separation scheme is flexible. If neptunium is not likely to be present (or if Pu and Np are desired together), plutonium can be retained on the TEVA•Spec® cartridge by adjusting the plutonium valence to Pu (IV) in the initial sample solution with ferrous ammonium sulfate followed by sodium nitrite. Figure 6 illustrates this approach.

After the initial loading and rinsing steps, the single multistage column is removed from the shielded cells and the cartridges are separated at their luer connections and handled individually. New reservoirs are added to each cartridge and after small volume rinses specific for each cartridge are completed, the actinides and strontium are stripped from the respective cartridges and measured.

Thorium/Neptunium

For a 2 mL volume of resin, one free column volume (FCV) is 1.35 mL. Rinse volumes are given as approximate free column volumes so that rinse volumes for any size resin column can be calculated. After the TEVA•Spec® cartridge is removed from the multistage column, the TEVA•Spec® cartridge is rinsed with 5 FCV's of 3M nitric acid. To elute the thorium, 11 to 15 FCV's of 6M hydrochloric acid are added to the

TEVA•Spec® cartridge. Neptunium (or plutonium, if adjusted to Pu (IV) in the load solution) is then stripped with 7 to 10 FCV's of 0.02M nitric-0.02M hydrofluoric acid. For development testing, neptunium was counted in solid state silicon surface alpha counters after mounting on a planchet and thorium was measured by direct current emission spectrometry.

Uranium

The U-TEVA•Spec® cartridge is rinsed with 4 FCV's of 3M nitric acid-0.05 M oxalic acid to remove any residual neptunium that may have passed through the TEVA•Spec® cartridge, followed by approximately 6 FCV's of 3M nitric acid to complete the rinse. Uranium is then eluted with 7 or more FCV's of 0.01 M nitric acid. Total uranium was measured by a Chemchek laser kinetic phosphescence analyzer; however, uranium concentration and isotopics in liquid waste may be determined by adding a U-233 spike and measuring the spiked sample using thermal ionization mass spectrometry[6]. For laser phosphorescence measurements, the ferrous ion must be rinsed well from the U-TEVA•Spec® resin prior to stripping of the uranium to prevent quenching of the uranium phosphorescence.

Americium and Europium

Europium was added as an chemical analog for americium to provide an additional verification of americium recovery using this column scheme. The TRU•Spec® cartridge is rinsed with 4 FCV's of 3M nitric acid-0.1M sodium nitrite to ensure formation of Pu (IV) after loading the plutonium as Pu (III). After the cartridge is rinsed with 4 FCV's of 3M nitric acid, americium or europium is stripped with 1.5 FCV's of 9M hydrochloric acid and 9 FCV's of 4M hydrochloric acid. Plutonium is eluted from the resin with 10 to 15 FCV's of 0.1M ammonium bioxalate. Americium was counted by alpha spectrometry after mounting on a planchet and europium was measured by direct current emission spectrometry. Plutonium, after acidification of the bioxalate solution with 8M nitric acid, was measured by mounting on a planchet and counting by alpha spectrometry.

Strontium-90

The Sr•Spec® cartridge is rinsed with 2 FCV's of 3M nitric acid-0.05 M oxalic acid to remove any residual Pu (IV), Np (IV), Ce (IV), Ru (IV) that may have passed through the other cartridges. 4 FCV's of 8M nitric acid are added to rinse the cartridge. If additional barium removal is required, the volume of 8M nitric acid rinse can be increased slightly. The strontium is eluted with approximately 6 FCV's of 0.05 M nitric acid. 0.05 M nitric acid is used instead of water to ensure radioactive lead remains on Sr•Spec® resin during strontium elution[7]. Although a cesium-137 removal factor of 10,000 to 100,000 is often observed with only one Sr•Spec®column separation, additional cesium-137 removal is usually required because cesium-137 levels are typically many orders of magnitude greater than strontium-90 in the liquid sampled above the waste tank sludge. The eluant solution containing strontium-90 is acidified to 4 to 8M nitric acid and loaded to the same well-rinsed Sr•Spec® cartridge again to remove additional cesium-137. The strontium -90 is stripped from the column as before and one milliliter of solution is added to the vial containing scintillation cocktail.

The strontium is counted using the liquid scintillation counter within two hours of elution to minimize yttrium-90 ingrowth. Because of its relatively short half-life, Sr-89 is not typically present in high activity liquid waste at SRS. If Sr-89 measurement is required, however, Sr-89 and Sr-90 may be measured by Cerenkov counting or by separation of the Y-90 using after at least one week ingrowth using the same Sr•Spec® cartridge. The Sr-90 can be determined from the Y-90 and the Sr-89 calculated by subtracting the Sr-90 from the total Sr counted prior to Y-90 ingrowth [8].

Verification Testing and Results

Neptunium Separation on TEVA•Spec®

Figure 7 shows results obtained using TEVA•Spec® for Np-237 measurement in liquid waste. A 2 mL volume of 50 to 100 µm resin was used with a flow rate of 2 to 4 mL/minute. 1 x 10 ^{5} dpm neptunium-237, 5 x 10 ^{7} dpm plutonium added and 5 ug thorium was added to test the column cleanup capability. A Tank 38 caustic waste sample with a caustic level of 6 M NaOH was spiked with neptunium-237 to test spike recovery.

Strontium-90 Separation on Sr•Spec®

Figure 8 shows recovery data obtained using Sr•Spec® for Sr measurement in liquid waste as well as results from removal tests. A 1.5 mL column of 20-50 µm Sr•Spec® was used with a 5 mL/min. flow rate. Sodium levels were tested as high as 1.6 M in the load solution. 5 mg of Sr and 500 mg barium were added to tests strontium recovery and barium removal. Plutonium (5 x 10 ^{6} dpm) and neptunium (2 x 10 ^{5} dpm) were added to test removal of these removal of these actinides from Sr•Spec®.

Multistage Column Scheme for Actinides and Strontium-90

Figure 9 shows the standard recovery obtained using the multistage column scheme for actinide and Sr-90 separation when standards were added to a simulated waste solution (4.5 M NaOH).

Figure 10 shows the spike recovery obtained using the multistage column scheme for actinide and Sr-90 separation when actinide and Sr-90 spikes are added to Tank 26 or Tank 46 high activity liquid waste sample solutions. The cesium-137 levels for these solutions were approximately 3 X10^8 dpm/mL and the caustic level was approximately 1M NaOH.

The standard and spike recoveries demonstrate the method provides good chemical recovery of the actinides and strontium-90 from simulated waste solution and actual high activity waste tank samples.

Time Savings

The rapid extraction methods for actinide separations typically used in the SRS Central Laboratory are usually performed at least five times faster than gravity flow column methods. For multiple actinide separations, it is estimated the cartridge technique reduces the analytical time by an additional factor of three.

Summary

The SRS Central Laboratory has developed new high speed extraction chromatographic methods that enable rapid separation of actinides and strontium-90 in high activity liquid waste. Neptunium-237 and thorium are separated from the waste matrix using TEVA•Spec® resin while strontium -90 is separated using Sr•Spec® resin. A three column scheme using TEVA•Spec®, U-TEVA•Spec® and TRU•Spec® columns has been shown to separate neptunium, thorium, uranium, plutonium and americium effectively and rapidly from one sample solution. In this technique the rinse solution from the first column is passed through the next column in the series to recover individual actinides. A recent innovation using a single multistage column consisting of TEVA•Spec®, U-TEVA•Spec®, TRU•Spec® and Sr•Spec®cartridges in series was shown to give excellent recoveries for actinides and strontium -90. A single sample solution plus initial rinse solution is loaded to the multistage column to reduce analysis time significantly.

Acknowledgements

The authors wish to recognize the contribution of Roger Mahannah for his valuable feedback regarding these column separation schemes and Matt Hammett for his help performing the column separations. They also wish to acknowledge Mary Benton, Phil Baker, Martha Settles and Pat Woods for their help in coordinating analyses by DCAP spectrometry.

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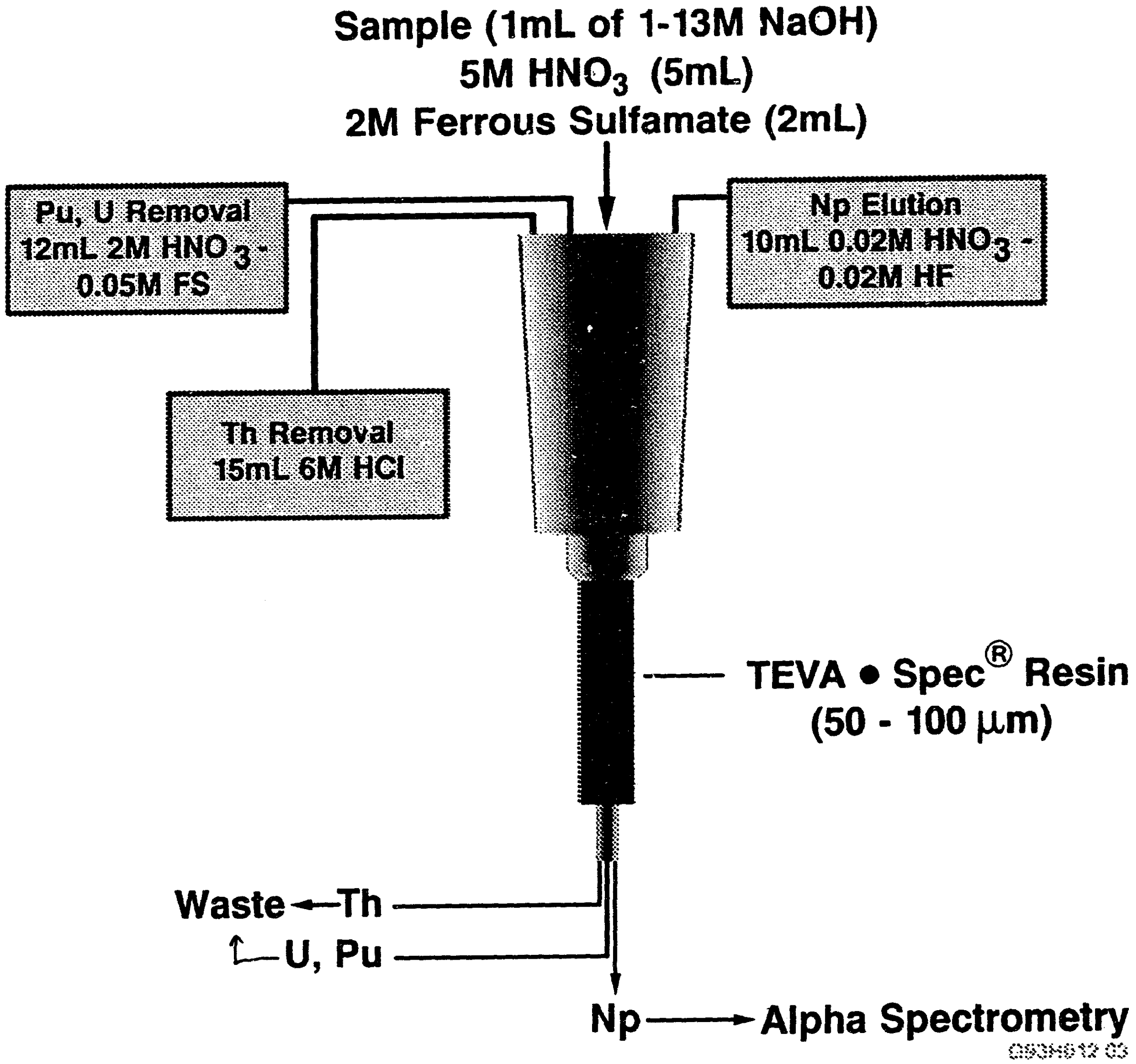
6) R.N. Mahannah and S.L. Maxwell, III, "Measurement of Trace Uranium-235 and Plutonium-239, 240 in Waste Tank Material at Savannah River Site", Proceedings of the 33rd Annual INMM Meeting, 1992, pg. 83, Orlando, FL.

7) Personal communication, Don Nelson, Argonne National Laboratory, Argonne, IL

8) EiChrom Industries, Inc. Analytical procedures

Figure 1 Np-237 Separation Scheme

~~Np-237 Separation~~



Sample (1mL of 1-13M NaOH)
5M HNO_3 (5mL)
2M Ferrous Sulfamate (2mL)

Pu, U Removal
12mL 2M HNO_3 - 0.05M FS

Th Removal
15mL 6M HCl

Np Elution
10mL 0.02M HNO_3 - 0.02M HF

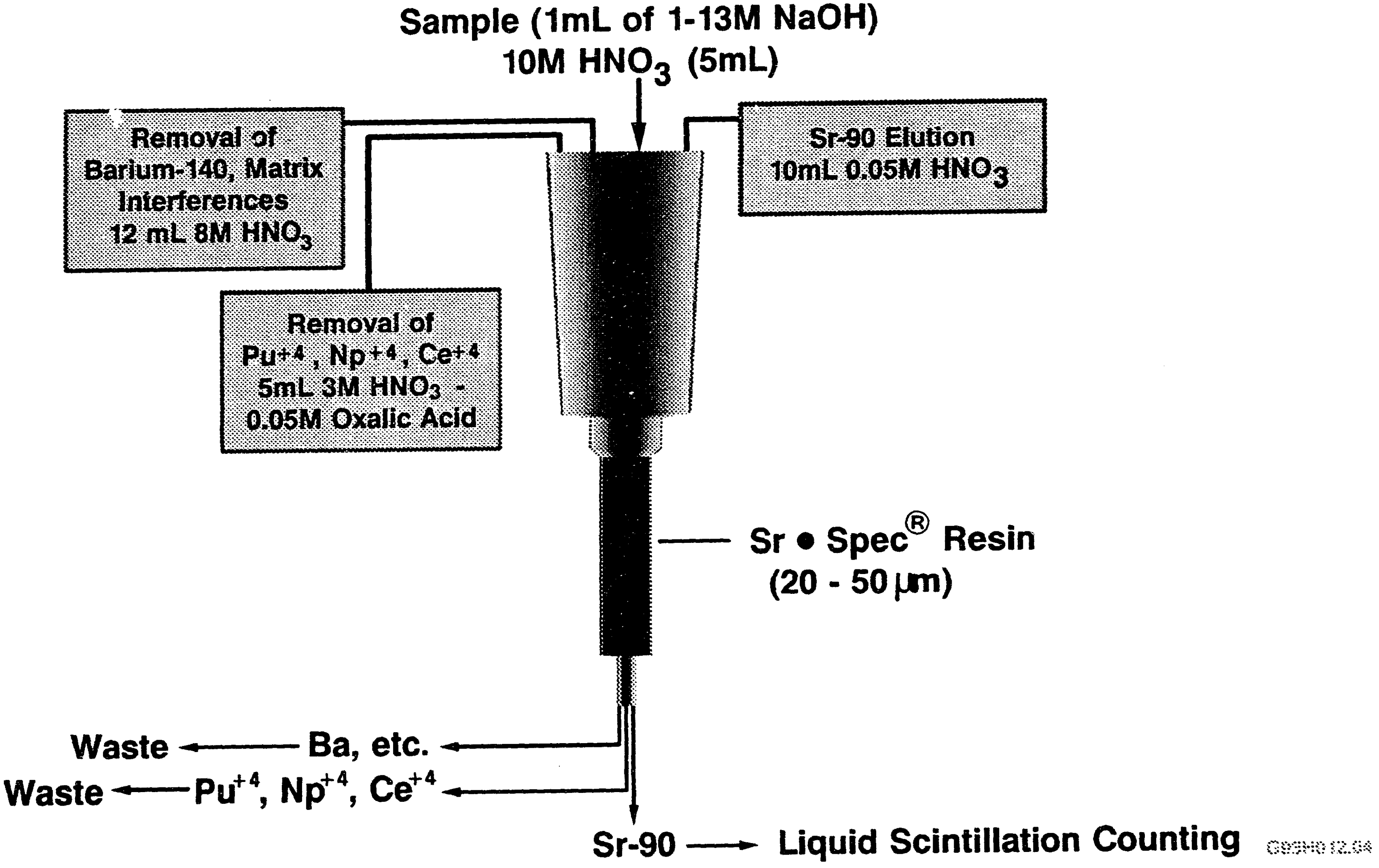
TEVA • Spec® Resin
(50 - 100 µm)

Waste ← Th
↑— U, Pu

Np → Alpha Spectrometry

C93H012.03

Figure 2 Sr-90 Separation Scheme



Sample (1mL of 1-13M NaOH)
10M HNO_3 (5mL)

Removal of
Barium-140, Matrix
Interferences
12 mL 8M HNO_3

Removal of
Pu^{+4}, Np^{+4}, Ce^{+4}
5mL 3M HNO_3 -
0.05M Oxalic Acid

Sr-90 Elution
10mL 0.05M HNO_3

Sr • Spec® Resin
(20 - 50 µm)

Waste ← Ba, etc.

Waste ← Pu^{+4}, Np^{+4}, Ce^{+4}

Sr-90 → Liquid Scintillation Counting

G93H0 12.94

Figure 3 Three Colum Actinide Method

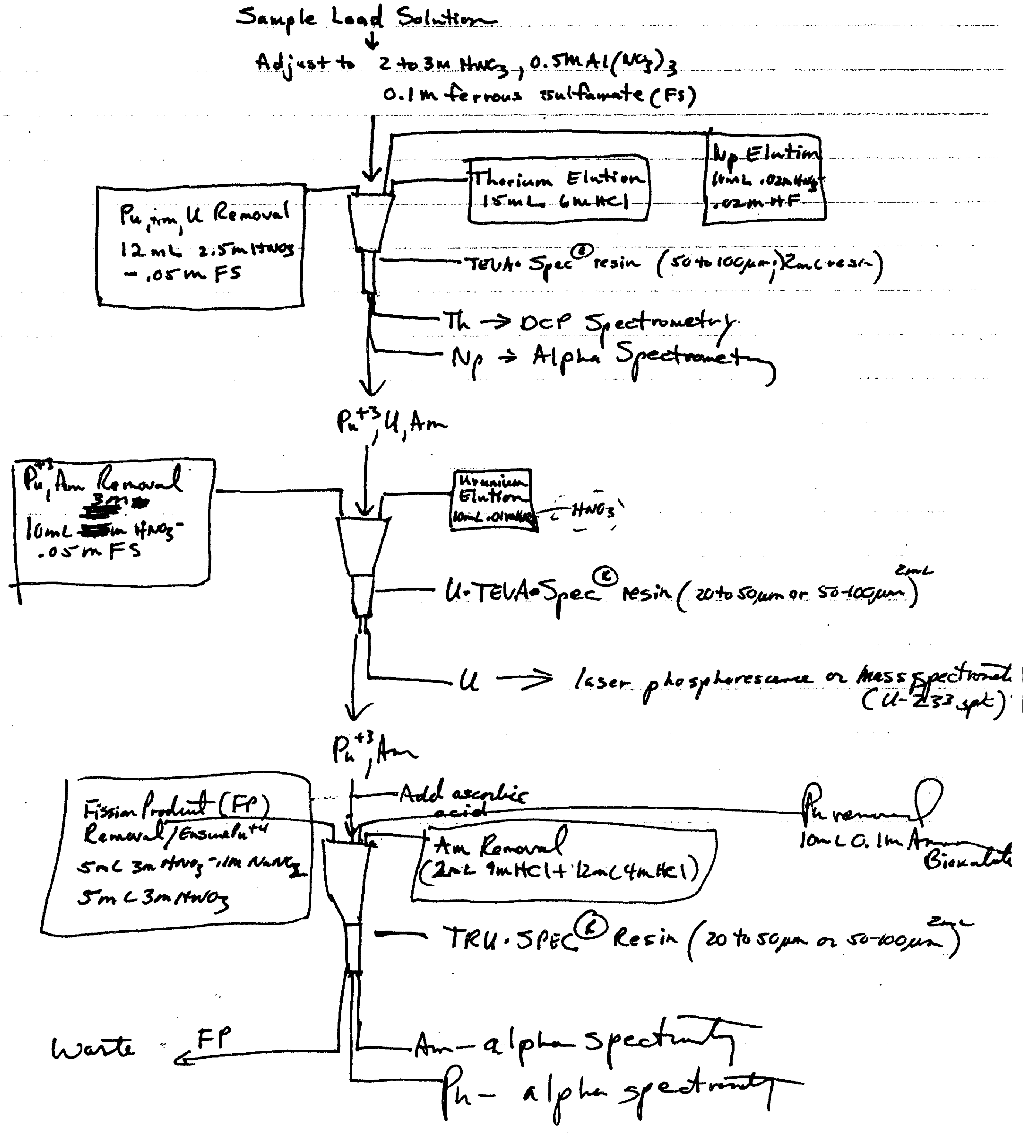


Figure 4
Alternative Three Column Scheme

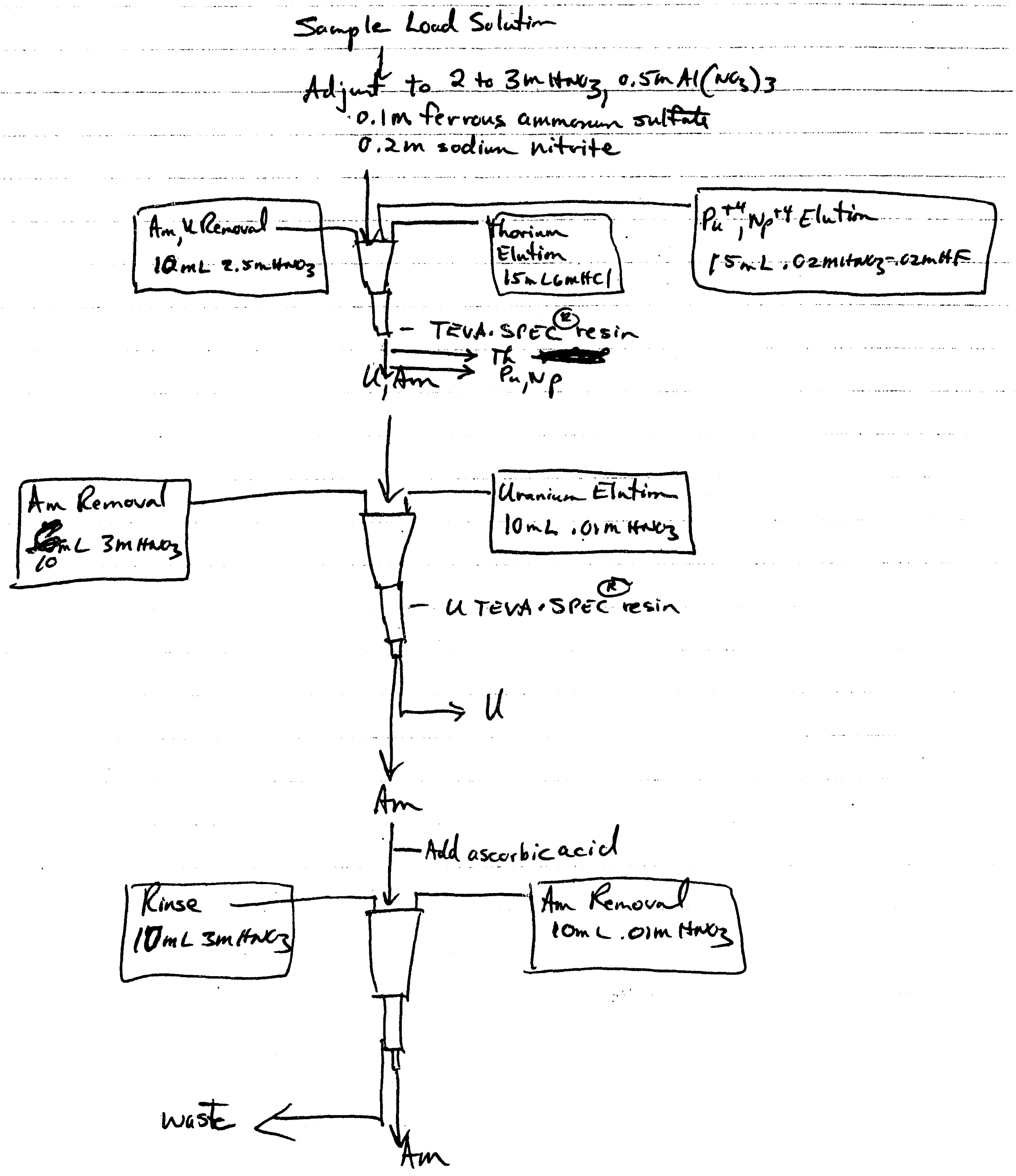
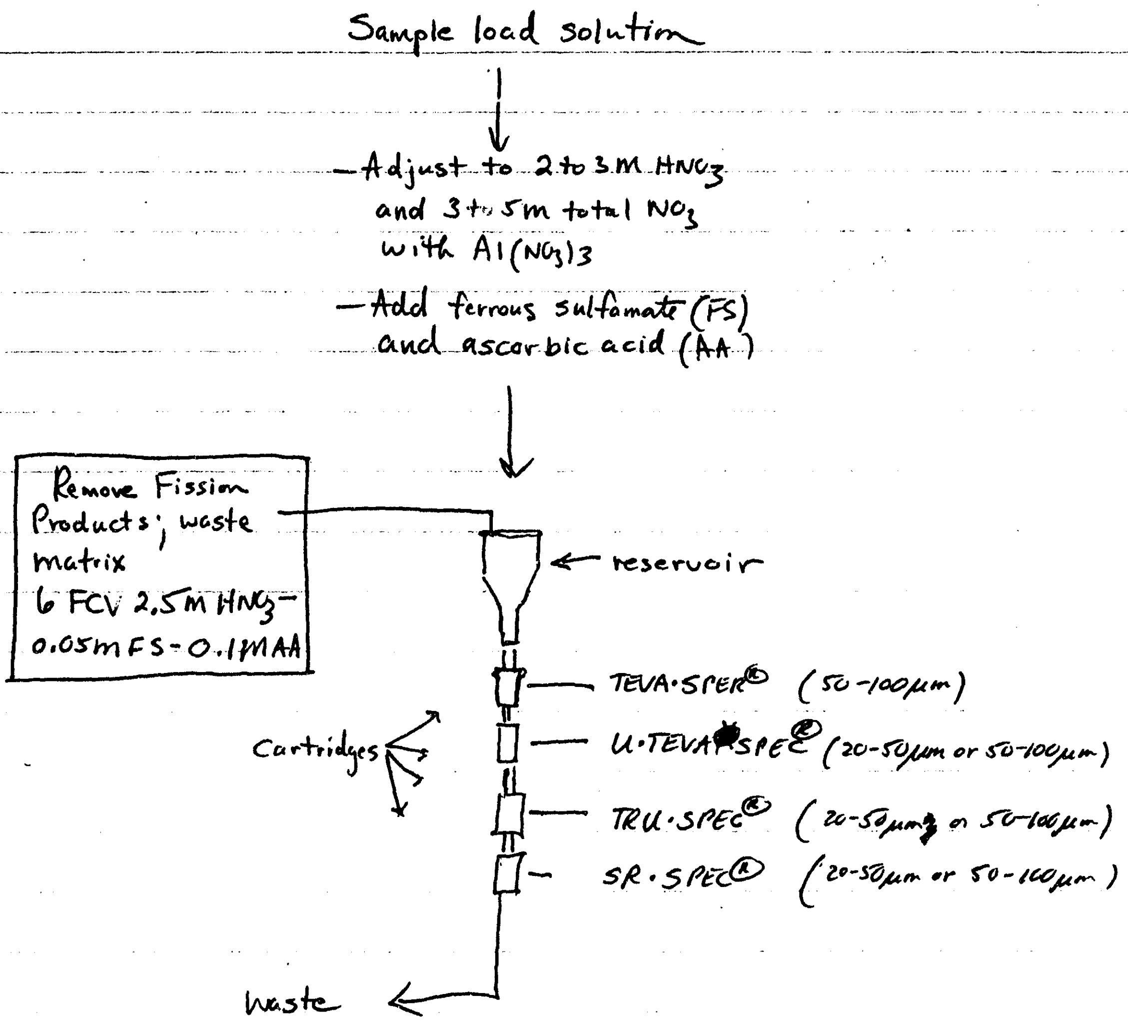


Figure 5 Multistage Column Method - Load and Initial Rinse



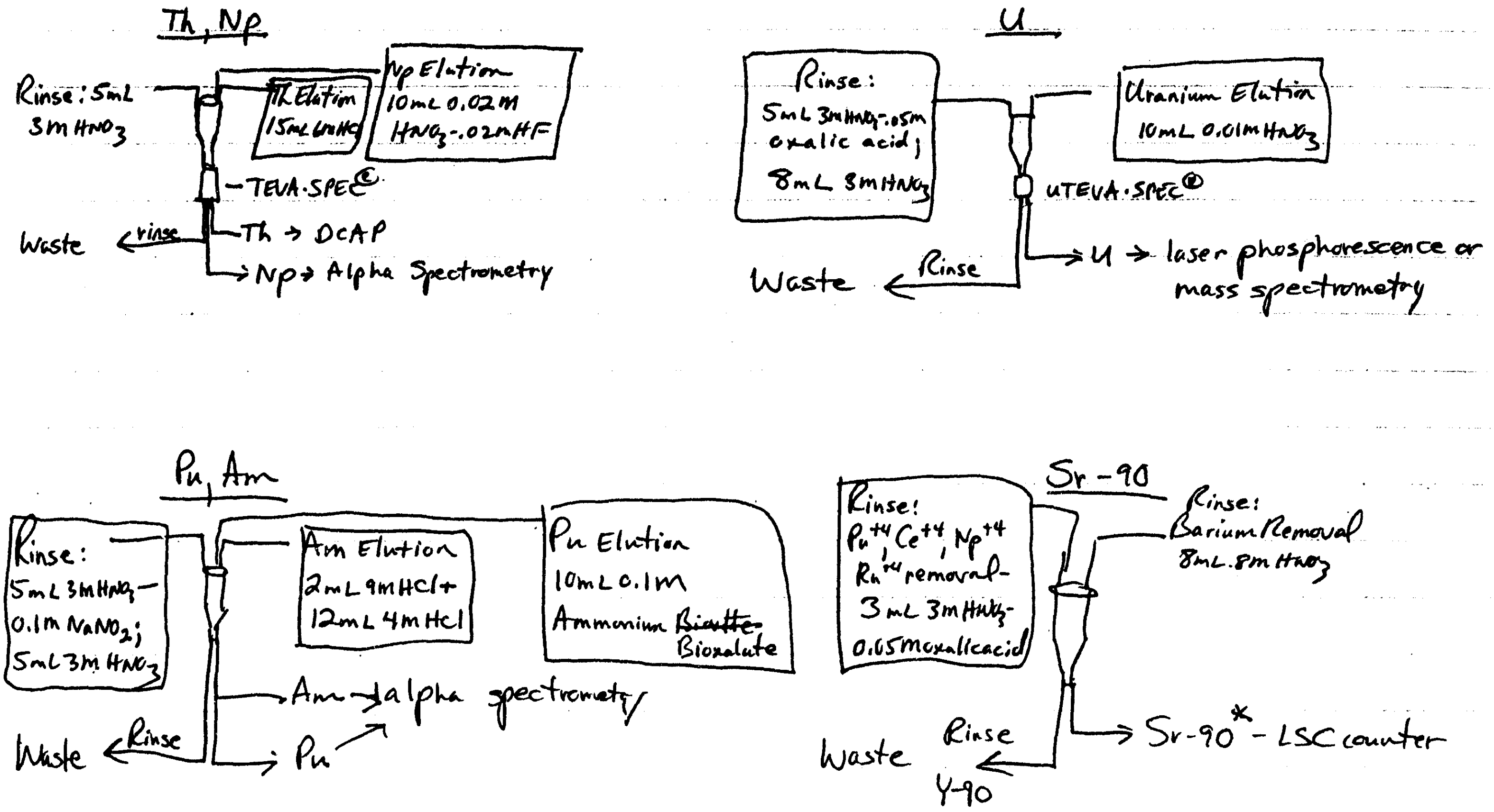


Figure 6 Multistage Column Rinses and Elutions

* may require additional Cs-137 removal

Figure 7 Neptunium Recovery Using TEVA•Spec® Method

% Np Recovery- Standards	% Np Spike Recovery -Waste Tank 38
95%	93%
92%	96%
94%	--
101%	--
Avg.= 96% ± 5% RSD	Avg.= 94% ± 2% RSD

Thorium removal= >99.9%
Plutonium removal = 99.9%
Thorium recovery in 6M HCL elution = 95%

Figure 8 Strontium Recovery Using Sr•Spec® Method

%Sr Recovery- Standards	% Sr Spike Recovery - Waste Tank 26
96%	106 %
99%	104%
94%	Avg.= 105% ± 1 % RSD
95%	
99%	
98%	
Avg.= 98% ± 2.5% RSD	

Barium removal= 99.9%
*Plutonium removal = >99.9%
*Neptunium removal = >99.9%
*Cerium removal = >99.9%

* If additional 5 mL rinse of 3M nitric acid-0.05M oxalic acid used

Figure 9 Standard Recoviers - Simulated Waste

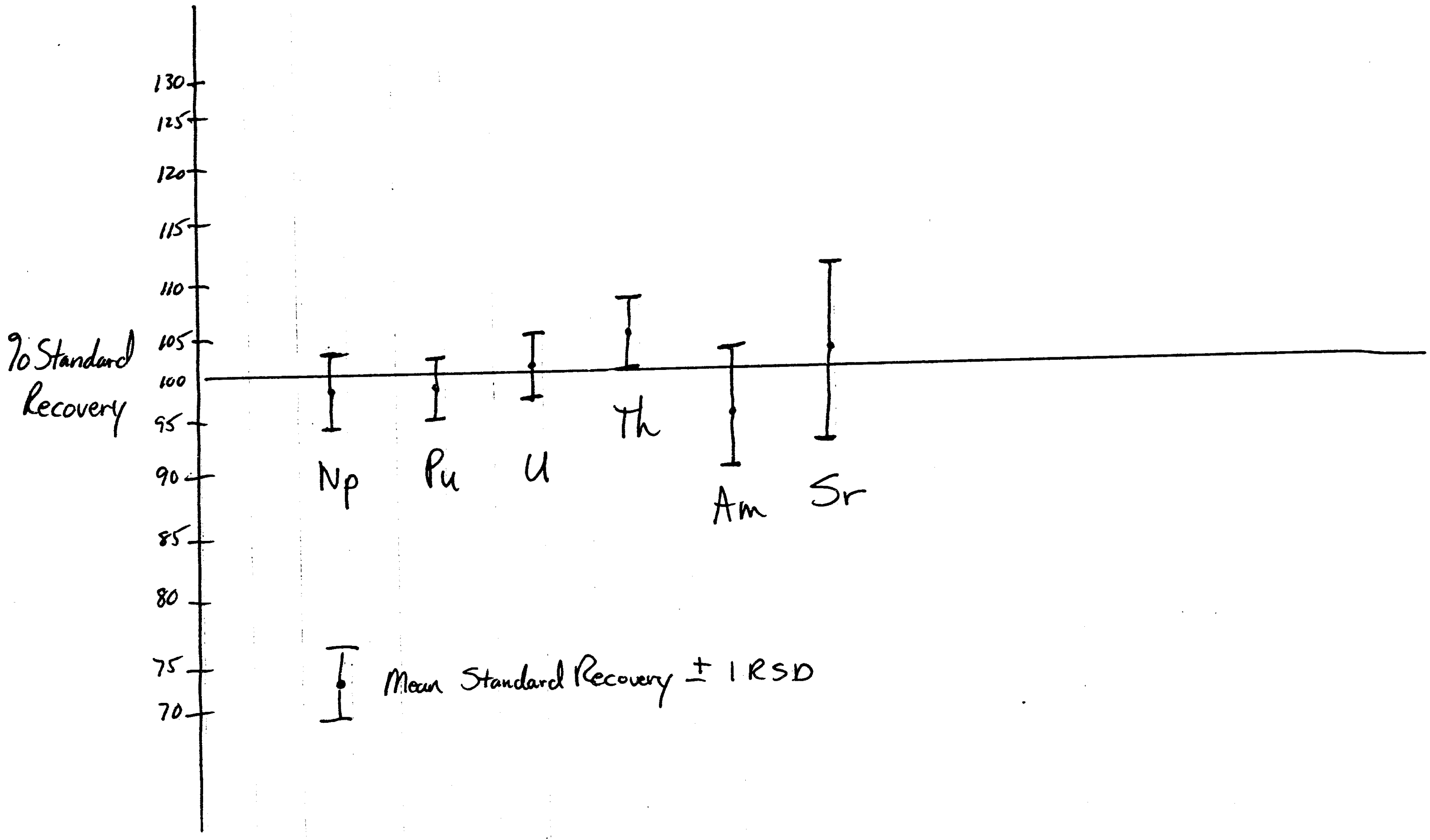


Figure 9

Actual Numbers

Np	97 ± 5%
Pu	97 ± 4%
U	101 ± 3%
Th	106 ± 6%
Am	96 ± 8%
Sr	103 ± 10%

Figure 10 Spike Recoveries - ~~Multistage Column~~ High Activity Waste

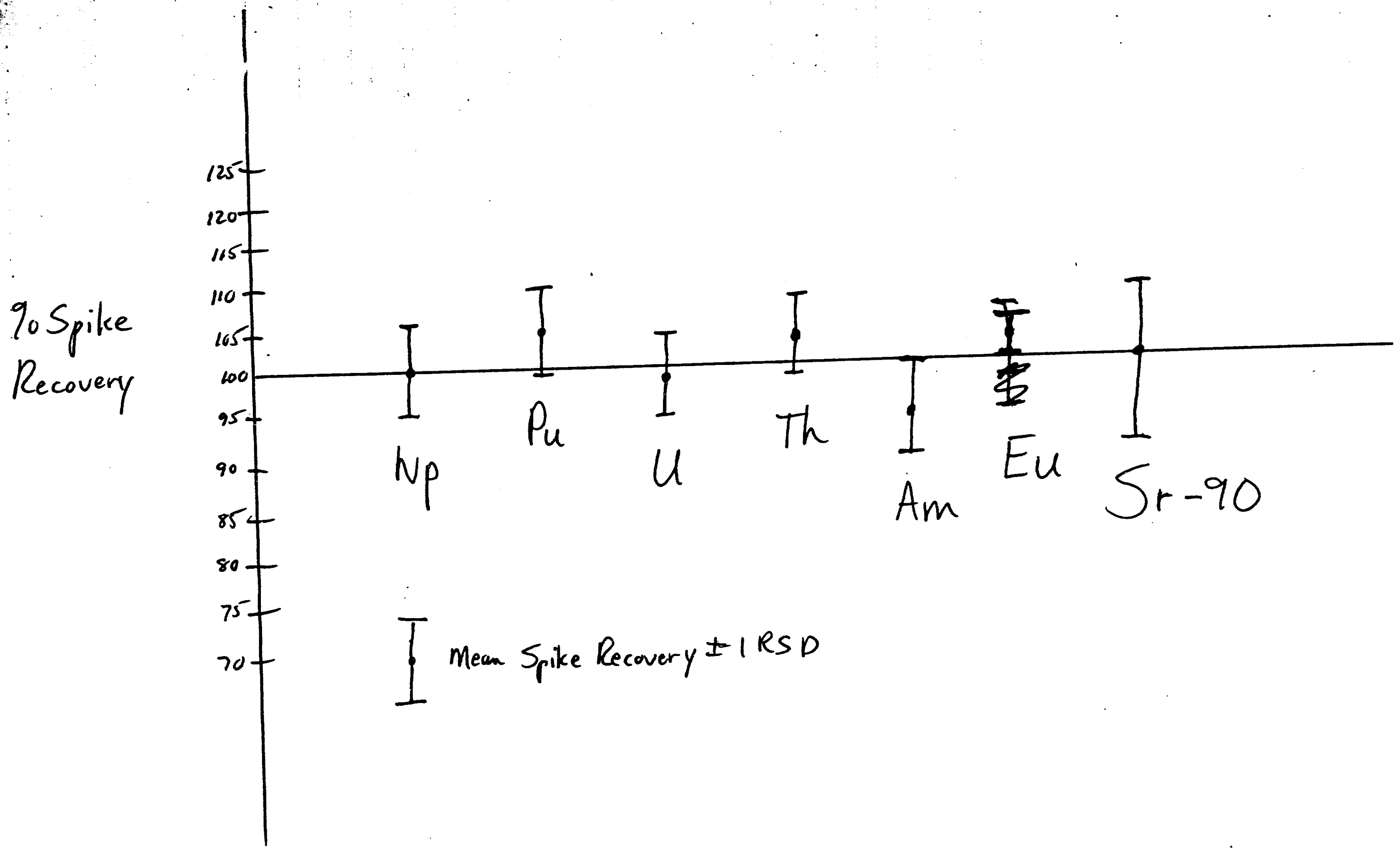


Figure 10

Actual #'s to help draw graph

Np	100 ± 6%
Pu	105 ± 6%
U	98 ± 4%
Th	104 ± 5%
Am	94 ± 6%
Eu	104 ± 2%
Sr-90	~~100~~ 97 ± ~~10~~ 12%

DATE
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8/25/94

END