Identification of Non-Pertechnetate Species
In
Hanford Tank Waste,
Their Synthesis, Characterization,
And
Fundamental Chemistry

DE-FG07-01ER63281

Final Report
September 15, 2001 through September 14, 2004

Kenneth R. Ashely;
903-886-5381; Ken_Ashley@TAMU-Commece.edu

And

Norman Schroeder, Principal Investigator
505-667-0967;Nschroeder@lanl.gov

Jose A. Olivares
5056655190; Olivares@lanl.gov

Brian Scott
5056670065; bscott@lanl.gov

December 10, 2004

Dept. of Chemistry
Texas A&M University-Commerce
Commerce, Texas 75429-3011

FINAL REPORT
Identification of Non-Pertechnetate Species in Hanford Tank Waste, Their Synthesis,
Characterization, and Fundamental Chemistry

Executive Summary

This proposal had three major goals: (1) develop capillary electrophoresis mass spectrometry as a characterization technique, (2) separate a non-pertechnetate fraction from a waste sample and identify the non-pertechnetate species in it by CEMS, and (3) synthesize and characterize bulk quantities of the identified non-pertechnetate species and study their ligand substitution and redox chemistry.

The development of capillary electrophoresis mass spectrometry as a characterization technique for these technetium species was unsuccessful. We were unable to gain access to the necessary instrumental to pursue this aspect of the research. We were able to separate a non-pertechnetate fraction from a waste sample and remove much (>99 %) of the radioactivity. But, we were unable to identify the species(s). We did not have access to the necessary instrumentation. Since we were unable to identify the technetium specie(s), we were unable to synthesize and characterize bulk quantities of the non-pertechnetate species and study their ligand substitution and redox chemistry. The majority of the effort was devoted to devising a separation scheme for the nor-pertechnetate species. We were able to devise a scheme.

This report is comprised of three sections. The first is the "Re-Examination of a Procedure for the Analyses of ^{99}Tc in Hanford Waste Tank Samples." This work was performed to ensure that the analytical procedure that we use for technetium determinations was accurate. The second section reports on the work of the undergraduate students and was performed at TAMU-Commerce. It is a detailed investigation of the separation method employed in the section. It is entitled "The Separation of Werner Type Complexes Using Gel Permeation Chromatography." The third part of the report is "Separation of Non-Pertechnetate Species from Hanford AN-107 Tank Waste."

The analytical procedure for the analyses of total ^{99}Tc in an AN-107 Hanford Waste Tank sample has been verified to be accurate and reliable. The general approach of the method was to: (1) add a known amount ^{95m}Tc yield tracer to a sample, (2) oxidize exhaustively the sample with Ce(IV) in HNO$_3$, (3) remove the ^{90}Sr and ^{137}Cs using a Dowex 50W cation exchange column, (4) adsorb the TcO$_4^-$ onto a Reillex-HPQ anion exchange column, (5) remove the TcO$_4^-$ by reductively elution with a solution of 1 M (NaOH/H$_2$NC$_2$H$_4$NH$_2$)/5 mM SnCl$_2$, (6) add the eluent to Ultima Gold (UG) liquid scintillation (LS) cocktail, (7) acquire the ^{95m}Tc counts/min (cpm) using a NaI gcounter, (8) acquire the ^{95m}Tc and ^{99}Tc cpm using a LS counter, (9) subtract the ^{95m}Tc LS cpm from the total LS cpm to give the number of LS cpm for ^{99}Tc. An untreated ^{95m}Tc standard is used to determine the (LS cpm/g cpm ratio for ^{95m}Tc and the chemical yield.

The additively of the LS spectra of ^{99}TcO$_4^-$ and ^{95m}TcO$_4^-$ has been established. There are no serious quenching problems in the determination of the LS cpm in (9 mL water/11 mL UG) to (1 mL water/19 mL UG) and and with various amounts of Sn^{2+}/NaOH/en in the solutions. The complete analyses, including the oxidation procedure, for ^{99}Tc was performed with five known samples varying from 195,000 to 20,000 cpm ^{99}Tc. The error between the experimentally determined cpm of ^{99}Tc and that taken was (+3.9 ± 3.9)%

We have established that a Sephadex G-10 (a size exclusion chromatographic material) column can separate various inorganic ions based on some interaction other than size. The maximum

elution volume should have been 32.2 mL for a particular column. However, the elution volume varied from 36.8 mL for $Cr(C_2O_4)_3^{3-}$ to 41 mL for $Co(NH_3)_6^{+3}$ to 91.4 mL for $Co(NH_3)_3(NO_2)_3$ These data imply that more than size is effecting a separation. Also, it appears that charge on the complex is not the deciding factor.

The significance of these results are quite profound in the field of aqueous ion chemistry. This chromatographic technique gives a method to separate large amounts of various ions without the addition of extraneous ions , such as necessary in ion exchange chromatography.

A sample AN–107 was treated with of Zn^{2+} to remove the complexing reagent from strontium and other metal ions and then passed through a cation column. The effluent was chromatographed on a BioGel P-2 column. The column was eluted with water followed by 1.00 M $NaNO_3$. The fractions were added to Ultama Gold and LS counted. There are three peaks for the water elution. These are at elution volumes of 14, 22, 25 mL with estimated K values are 0.79, 1.24, and 1.41, respectively. There were two peaks eluted with the $NaNO_3$. An examination of the LS spectra revealed that the first peak contained nickel. The second, third, and fourth peak contained strontium and yttrium. The fifth peak contained technetium. This procedure removed more than 99 % of the radioactivity. However the identity of the technetium species was not established,

FINAL REPORT
Identification of Non-Pertechnetate Species in Hanford Tank Waste, Their Synthesis,
Characterization, and Fundamental Chemistry

Project Objective
This proposal has three major goals: (1) develop capillary electrophoresis mass spectrometry as a characterization technique, (2) separate a non-pertechnetate fraction from a waste sample and identify the non-pertechnetate species in it by CEMS, and (3) synthesize and characterize bulk quantities of the identified non-pertechnetate species and study their ligand substitution and redox chemistry.

Background
Technetium, as pertechnetate (TcO_4^-), is a mobile species in the environment. This characteristic, along with its long half-life, (^{99}Tc, $t_{1/2}$ = 213,000 a) makes technetium a major contributor to the long-term hazard associated with low level waste (LLW) disposal. Thus, technetium partitioning from nuclear waste tanks at DOE sites (Hanford, etc.) may be required so that the LLW forms meet DOE performance assessment criteria. Technetium separations assume that technetium exists as TcO_4^- in the tank waste. However, work with actual Hanford waste indicates that much of the technetium exists in a form other than TcO_4^- and that these unidentified technetium species are not readily converted to pertechnetate by oxidation.

Technetium was introduced into the tanks as the pertechnetate anion. However, years of thermal, chemical, and radiolytic digestion in the presence of organic material, including complexants such as EDTA, NTA, citrate, and oxalate, has transformed much of the TcO_4^- into stable, reduced, technetium complexes. To successfully partition technetium from tank wastes, it will be necessary to either remove these non-pertechnetate species with a new process, or re-oxidize them to TcO_4^- so that conventional pertechnetate separation scheme will be successful. The success of the Department of Energy's (DOE's) technetium management strategy lies in knowing what these non-pertechnetate species are and understanding their chemistry.

This research will use the technetium complexes prepared under our original EMSP proposal to develop a capillary electrophoresis mass spectrometry (CEMS) technique that will be used to identify non-pertechnetate species in actual waste samples. The model technetium complexes will be used as standards to establish the operational parameters for CEMS for the types of technetium compounds we speculate are in the waste. Development of this technique is even more critical to resolving the non-pertechnetate problem since many of the technetium complexes synthesized in our original proposal are too easily oxidized or show less stability in caustic media compared to the actual non-pertechnetate species in the waste.

Status
The development of capillary electrophoresis mass spectrometry as a characterization technique for these technetium species was unsuccessful. We were unable to gain access to the necessary instrumental to pursue this aspect of the research.

We were able to separate a non-pertechnetate fraction from a waste sample and remove much (>99 %) of the radioactivity. But, we were unable to identify the species(s). We did not have access to the necessary instrumentation.

Since we were unable to identify the technetium specie(s), we were unable to synthesize and characterize bulk quantities of the non-pertechnetate species and study their ligand substitution and redox chemistry.

The majority of the effort was devoted to devising a separation scheme for the non-pertechnetate species. We were able to devise a scheme.

Overview of Report
The work reported in this final report was the results of a collaboration among Dr. Kenneth Ashley (TAMU-Commerce), Dr. Norman Schroeder (Los Alamos National Laboratory), and undergraduate students Mathew McKinney (TAMU-Commerce) and Tamara Mitrofanenko (TAMU-Commerce). This report is comprised of three sections. The first is the "Re-Examination of a Procedure for the Analyses of ^{99}Tc in Hanford Waste Tank Samples." This work was performed to ensure that the analytical procedure that we use for technetium determinations was accurate. The second section reports on the work of the undergraduate students and was performed at TAMU-Commerce. It is a detailed investigation of the separation method employed in the section. It is entitled "The Separation of Werner Type Complexes Using Gel Permeation Chromatography." The third part of the report is "Separation of Non-Pertechnetate Species from Hanford AN-107 Tank Waste." It is abstracted from a paper that has been submitted for publication. The work for the first two sections was performed at Los Alamos National Laboratory.

Re-Examination of a Procedure for the Analyses of ^{99}Tc in Hanford Waste Tank Samples

Introduction
The radioanalytical procedure for determining ^{99}Tc in fission waste was developed and tested on the Melton Valley and 101-AW Hanford tank waste simulant. It has been used to analyze the 101-SY and 103-SY samples received from Pacific Northwest National Laboratory (PNNL). The method insures that the measurement of ^{99}Tc is quantitative. The principal features of the procedure are to trace the sample with [95m]Tc, to insure isotopic exchange between the ^{99}Tc and the [95m]Tc, and to produce a radiochemically clean sample for counting. The samples are wet ashed with a solution of concentrated nitric acid and Ce(IV) to ensure complete oxidation of the technetium to pertechnetate (TcO_4^-). The sample is counted for gamma activity (from the [95m]Tc) using a high efficiency NaI crystal and/or Ge detector and beta activity using liquid scintillation. Corrections for the conversion electrons from the [95m]Tc are made in the liquid scintillation counting (LSC).

This method has been used for some time and all internal checks such as inductively coupled plasma-mass spectrometer y and ^{99}Tc nuclear magnetic resonance methods indicate that the method is accurate. However, we have never performed a detailed verification of the method. Since we are constantly using this method to study samples of Hanford Tank Waste, we determined that the method warranted a more detailed study. This reports is the results of that study

Experimental
The same stock solution of [95m]TcO_4^- and of [99]TcO_4^- were used throughout this study to ensure internal consistency. The desired dilutions were made. Aliquots of these solutions the added to the LS vials containing the chosen amount of Ultima Gold™ liquid scintillation cocktail and water to give a total volume of 20.0 mL.

The net cpm of [99]Tc ($^0A_{99}$ in the sample was converted to ng ^{99}Tc by the relationship: {(cpm [99]Tc + 98)/37.2 = ng [99]Tc} This equation was derived from a calibration curve established previously with an Amersham ^{99}Tc standard (Amersham Corporation, Arlington Heights, IL).

The technetium analyses were performed in the following manner. Into a 250 mL beaker was placed a 0.100 to 0.200 mL weighted sample of the material to be analyzed. To this, was added an accurately measured amount of the [95m]TcO_4^- tracer to give about 400-800 cpm in the NaI counter (165-245 keV window). Then 3 mL of conc. nitric acid and 5 m of water were added to the beaker and it was set on a hot plate. A small surface thermometer was used to ensure that at no time the surface temperature exceed 200°C. After the solution begin to fume, 0.10 M ceric ammonium nitrate in 0.10 M nitric acid was added dropwise until the yellow color of the ceric ion persisted. The sample was hearted to evaporate it. The yellow color of the ceric ion was maintained with the dropwise addition of the ceric solution throughout all of the evaporation process. The sample was evaporated to incipient dryness. The sample was removed from the hot plate just as the last drop of liquid was evaporating. Two mL of conc. nitric acid was added to the sample and it was again taken to dryness as above. The process was repeated twice more for a total of four times.

Finally, 5 mL of conc. nitric was added and the solution was evaporated to dryness as above. Then, 5 mL of water was added and the solution was evaporated to incipient dryness. The sample was taken up with 5 x 1 mL of water and passed through a 0.7 x 4 cm bed of AG 50W-x 8, 100-200 mesh cation exchange resin. Each mL was added to the column and allowed to run

into the top of the resin bed before the addition of the next mL. Each 1 mL aliquot was added to the beaker in an attempt to wash out all of the technetium. The column removes the bulk of the cations, ^{137}Cs in particularly in the Hanford Waste samples. The eluent and washings were collected and neutralized with base (1 M NaOH); this was checked with pH strips.

The solution was contacted for one to two hours with 0.5 g of Reillex-HPQ resin in a 25 mL LSC vial. The resin was poured into an Econocolumn and eluted with 5 x 1 mL aliquots of water. The resin was eluted with 3 x 5 mL aliquots of 1 M nitric acid and then with 5 x 1 mL aliquots water. The eluents and washings were collected in a LSC vial. The resin was counted on the NaI counter to insure that all ^{137}Cs was removed (^{137}Cs has a peak at 667 keV). Other foreign activity was also checked for in the NaI spectrum.

The technetium was eluted into a LSC vial, containing 2 mL of water and 16 mL of Ultima Gold, with 10 x 0.100 mL of Sn/en/OH$^-$ solution. The 0.005 M Sn (II)/1 M ethylenediamine (en)/1 M NaOH solution (Sn/en/OH$^-$ solution) was prepared each day by adding 19 mg SnCl$_2$ to 20 mL of a 1 M ethylenediamine (en)/1 M NaOH solution. The solution needs to be made fresh to ensure that the tin is as Sn^{2+} is still reduced. The column was eluted with 10 x 0.100 mL of water into the LSC vial. The NaI spectrum was check for any foreign activity.

The solution was counted on the NaI and liquid scintillation counters. The LSC used channels 6-660 (0.11-172.1 keV), which encompassed >99.9% of the activity in the ^{99}Tc spectrum. The numbers of counts per minute for each sample and for several blanks (background, bkg) were recorded.

The treatment of data for radiochemical determination of ^{99}Tc was as follows. The contribution of ^{95m}Tc to the LSC of the sample was determined by preparing the same size aliquot of ^{95m}Tc as used in the samples and LS counting it in the same geometry as an actual sample. This included the ^{95m}Tc spike, water to give the same volume as a sample, and the Ultima Gold cocktail. The sample was counted, and background subtracted, on the liquid scintillation counter ($^{LS}A_{95m}$) and sodium iodide counter ($^{g}A_{95m}$).

For the actual sample, the activity, with the background subtracted, in the sodium iodide counter ($^{g}B_{95m}$) was made. The chemical yield (CY) as determined by ^{95m}Tc was given as CY = ($^{g}B_{95m}/^{g}A_{95m}$). These yields were always >50% and usually about 70%. The activity of ^{99}Tc ($^{o}A_{99}$) in the sample was determined with the following equation where A_{99} was the net LSC cpm of the sample:

$$^{o}A_{99} = \{A_{99} - (^{LC}B_{95m} * CY)\} / CY \qquad (1)$$

Results and Discussion

The analyses of ^{99}Tc in samples ranging from the Hanford Waste Tanks to effluents from column separations results in various volumes of differing solutions being added to the Ultima Gold™ liquid scintillation cocktail. We normally used 16.0 mL of Ultima Gold™ (UG) and 4.0 mL water/solution to give a total of 20.0 mL for the cocktail. Hence, we examined the effect of UG, water, and solutions on the LS cpm and the LS spectra as a function of various volumes of these reagents.

Fig. 1 shows the additively of the LS spectra of ^{99}TcO$_4^-$ and ^{95m}TcO$_4^-$. The calculated spectrum is identical to the measured one. Next were measured the LS spectra of solutions of variable volumes of water (V_W) and of Ultima Gold™ (V_{UG}) with a constant amount of ^{99}TcO$_4^-$ or ^{95m}TcO$_4^-$

such that the volumes summed to 20.0 mL These spectra are illustrated in Figs. 2 and 3. As V_W increases and V_{UG} decreases the LS spectral peaks move to a lower energy. With the exception of the 0.10 mL of water spectrum for $^{99}TcO_4^-$ all of the spectra are contained in the 6- 660 (0.11-172.1 keV) channel window. Fig. 4 gives the cpm as a function of volumes from Figs. 2 and 3. Notice that other then the lowest cpms at lower V_W, a condition that is never experimentally encountered, the cpm is essentially constant. The other important observation is the constant $\{^{95m}Tc_{LSC}/^{95m}Tc_g\}$ cpm ratio. This is very important because this ratio is used to determine the ^{95m}Tc LS cpm from the ^{95m}Tc g cpm in the solution containing both ^{99}Tc and ^{95m}Tc.

In the actual determination of total technetium, the counting solution contains water and the Sn/en/OH⁻ solution, the eluent from the Reillex-HPQ columns. The effect of the variable Sn^{2+} and NaOH/en concentrations upon the LS spectra is important to know. Hence, the LS spectra of constant amount of $^{99}TcO_4^-$ or $^{95m}TcO_4^-$ were measured in varying volumes of Sn^{2+} (V_S) and NaOH/en (V_{NE}), and V_W such that the volumes summed to 4.0 mL and 16 mL of Ultima Gold. In Figs. 5 and 6 are the LS spectra for $^{99}TcO_4^-$. In Figs. 7 and 8 are the results for the $^{95m}TcO_4^-$ for the same type of experiment.

In Figs. 5 and 7, the NaOH/en was 50 mM and the $[Sn^{2+}]$ was varied from 4.7 to 0.13 mM. In Figs. 6 and 8, the [NaOH/en] was varied from, 25 to 195 mM and the $[Sn^{2+}]$ was varied from 0.15 to1.15 mM. For both $^{99}TcO_4^-$ and $^{95m}TcO_4^-$, the spectra are variable but are all within the 6- 660 (0.11-172.1 keV) channel range. The average total cpm for the 10 samples of $^{99}TcO_4^-$ is (20,363 ± 551) cpm and for the $^{95m}TcO_4^-$ is (3,873 ± 81) CPM. The uncertainties are one standard deviation of the sample set.

While the shapes of the LS spectra change as a function of the variable Sn^{2+} and NaOH/en concentrations, the spectra all stay in the 6-660 channel range (0.11-172.1 keV). The fact that the cpm for all of the solutions are the essentially the same while the shapes of the LS spectra change is a consequence of the fact that the cpms are measured in a range that contains all of the counts. That is, as the LS spectra change they are still within the counting range. The cpm is the same only the energy distribution pf the photons counted changes.

Solutions containing different amounts of $^{99}TcO_4^-$, $^{95m}TcO_4^-$, and water were prepared to a total volume of 4.00 mL in LS vials. To these vials were added 16 mL of Ultima Gold™ and then they were NaI and LS counted. The amount of $^{99}TcO_4^-$ in each solution was determined using Eq. 1 with CY =1.00. The results are shown in Table 1. The average difference (error) is (–4.81 ± 2.35)%. There seem to be no correlation between the ratio of $\{^{99}TcO_4^-/^{95m}TcO_4^-\}$ and the error. However there is a 5% negative bias that we can not explain at this time.

Solutions of known amounts of $^{99}TcO_4^-$ were $^{95m}TcO_4^-$, were taken through the oxidation procedure as described in the Experimental Section. The results are reported in Table II. The per cent difference is (+3.88 ± 3.90)% While this error is similar to the untreated samples it is a positive bias.

The final set of experiments that were performed was one in which known amounts of $^{99}TcO_4^-$ were added to an Hanford Tank Waste AN-107 sample and then taken through the oxidation procedure and analyzed. Table III contains the results of these analyses. The analyses of four samples of AN-107 gave a result of (3.48 ± 0.09) x 10^{-9} mole ^{99}Tc/0.100 mL. Samples of AN-107 were analyzed with added ^{99}Tc. With 8.51 x 10^{-9} mole added ^{99}Tc, the ^{99}Tc in the waste was determined as 3.51 x 10^{-9} mole^{99}Tc/0.100 mL. With 16.3 x 10^{-9} mole added ^{99}Tc, the ^{99}Tc in the waste was determined to be 3.67 x 10^{-9} mole ^{99}Tc/0.100 mL. With 25.1 x 10^{-9} mole added ^{99}Tc,

the ^{99}Tc in the waste was determined to be 3.75 x 10^{-9} mole ^{99}Tc/0.100 m. Again we see a positive bias in the results that increases as the amount of added ^{99}TcO$_4^-$ increases.

Summary

The analytical procedure for the analyses of total ^{99}Tc in an AN-107 Hanford Waste Tank sample has been verified to be accurate and reliable. The general approach of the method was to: (1) add a known amount ^{95m}Tc yield tracer to a sample, (2) oxidize exhaustively the sample with Ce(IV) in HNO$_3$, (3) remove the ^{90}Sr and ^{137}Cs using a Dowex 50W cation exchange column, (4) adsorb the TcO$_4^-$ onto a Reillex-HPQ anion exchange column, (5) remove the TcO$_4^-$ by reductively elution with a solution of 1 M (NaOH/H$_2$NC$_2$H$_4$NH$_2$)/5 mM SnCl$_2$, (6) add the eluent to Ultima Gold (UG) liquid scintillation (LS) cocktail, (7) acquire the ^{95m}Tc counts/min (cpm) using a NaI gcounter, (8) acquire the ^{95m}Tc and ^{99}Tc cpm using a LS counter, (9)subtract the ^{95m}Tc LS cpm from the total LS cpm to give the number of LS cpm for ^{99}Tc. An untreated ^{95m}Tc standard is used to determine the (LS cpm/g cpm ratio for ^{95m}Tc and the chemical yield.

The additively of the LS spectra of ^{99}TcO$_4^-$ and ^{95m}TcO$_4^-$ has been established. The spectrum calculated from the mathematical addition of the ^{99}TcO$_4^-$ and ^{95m}TcO$_4^-$ spectra is identical to the experimental determined one.

An examination of the ^{99}Tc and ^{95m}Tc LS energy spectra revealed that the position of the peak(s) vary as a function of water and UG present in LS cocktail. The shapes are almost constant. However, the total LS cpm is constant between (9 mL water/11 mL UG) and (1mL water/19 mL UG).

The LC spectra of both ^{99}Tc and ^{95m}Tc are dependent upon the amount of Sn^{2+}/NaOH/en in the solutions. However, the total LS counts in the measurement window is almost constant. That is, there are no serious quenching problems in the determination of the LS cpm.

The analyses, no oxidation procedure, for ^{99}Tc was performed with 12 known samples varying from 1,995 to 199,500 cpm of taken ^{99}Tc and 318 to 39,200 cpm of added ^{95m}Tc. The difference between taken and found ^{99}Tc was (-4.81 ± 2.35)% with no observable trend.

The complete analyses, including the oxidation procedure, for ^{99}Tc was performed with five known samples varying from 195,000 to 20,000 cpm ^{99}Tc. The error between the experimentally determined cpm of ^{99}Tc and that taken was (+3.9 ± 3.9)%

The analyses of four AN-107 samples that were subjected to the oxidation procedure gave a result of (3.48 ± 0.09) x 10^{-9} mole ^{99}Tc/0.100 mL AN-107. Three AN-107 samples with standard additions of 8.51, 16.3, and 25.1 nanomoles of ^{99}TcO$_4^-$ were found to contain 3.53, 3.67, and 3.75 nanomoles ^{99}Tc/0.100 mL AN-107, respectively.

Table I. The results of ^{99}Tc analyses of prepared ^{99}Tc and ^{95m}Tc solutions are reported.

		LS Counts		
Total	^{95m}Tc Added	Found ^{99}Tc	Taken ^{99}Tc	% Diff.
5,903	4,088	1,815	1,995	-9.01
11,622	1,915	9,707	9,974	-2.67
28,358	19,167	9,191	9,974	-7.85
19,796	318	19,478	19,947	-2.35
23,189	3,997	19,192	19,947	-3.78
23,176	3,899	19,277	19,947	-3.36
23,407	4,027	19,380	19,947	-2.84
23,461	4,073	19,399	19,947	-2.80
57,522	39,213	18,309	19,947	-8.21
96,202	1,976	94,226	99,735	-5.52
114,549	19,712	94,837	99,735	-4.91
194,529	3,883	190,645	199,470	-4.42
			Ave.	**-4.81**
			Std. Div.	**2.35**

Table II. The results of ^{99}Tc analyses in standard solutions are tabulated.

^{99}Tc, cpm		
Found	Taken	% Difference
192,846	195,350	-2.31
157,269	156,280	+0.63
71,531	78,140	-8.46
36,155	39,070	-7.46
19,178	19,535	-1.83
	Ave.	**-3.88**
	Std. Dev.	**3.90**

Table III. The results of ^{99}Tc analyses of AN-107 with added known amounts of ^{99}Tc Added. The amount of Found ^{99}Tc reported has the added amount of ^{99}Tc subtracted.

Added ^{99}Tc, 10^{-9}, mol	Found ^{99}Tc, 10^{-9}, mol/0.100 mL
None	3.48 ± 0.09
8.51	3.51
16.3	3.65
25.1	3.73
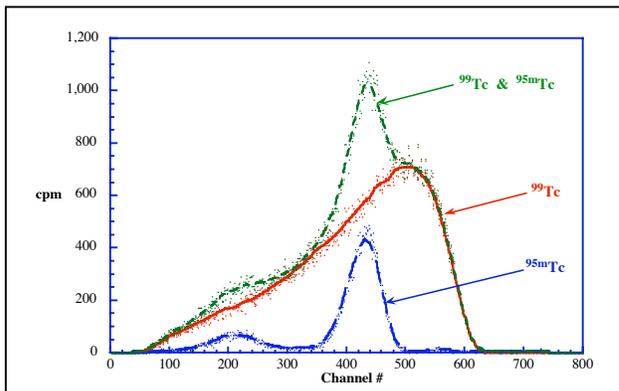
Figure 1. The LS spectra of ^{99}Tc and ^{95m}Tc show the additively. The bottom spectra is that of ^{95m}Tc, the middle one is that of ^{99}Tc, and the top spectra is that ^{99}Tc and ^{95m}Tc of combined.
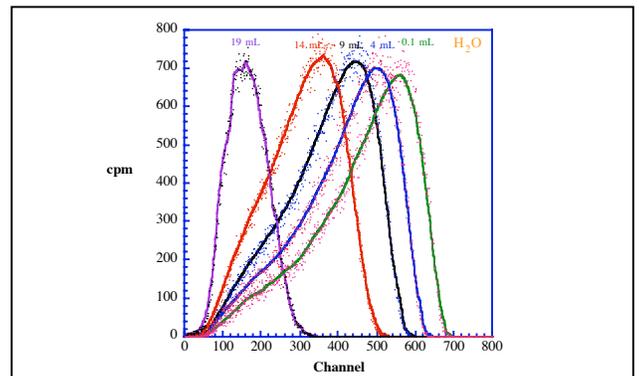

Figure 2. The LS spectra of ^{99}TcO$_4^-$ with various amounts of water and Ultima Gold are displayed. The volume is constant at 20 mL. The volume of water, from left to right is 19, 14, 9, 4, and 0.1 mL. The volume of Ultima Gold is 20–(water volume).
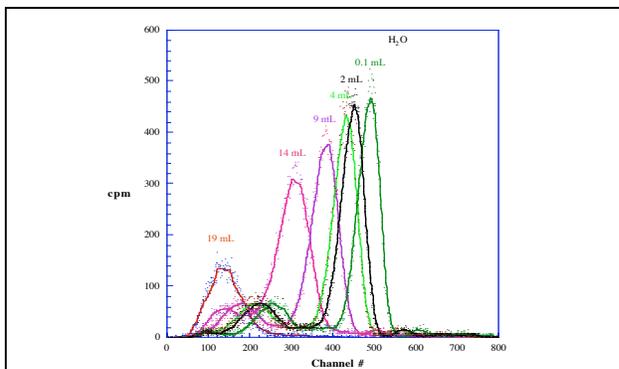
Figure 3. The LS spectra of ^{95m}TcO$_4^-$ with various amounts of water and Ultima Gold are displayed. The volume is constant at 20 mL. he volume is constant at 20 mL. The volume of water, from left to right is 19, 14, 9, 4, and 0.1 mL. The volume of Ultima Gold is 20–(water volume).
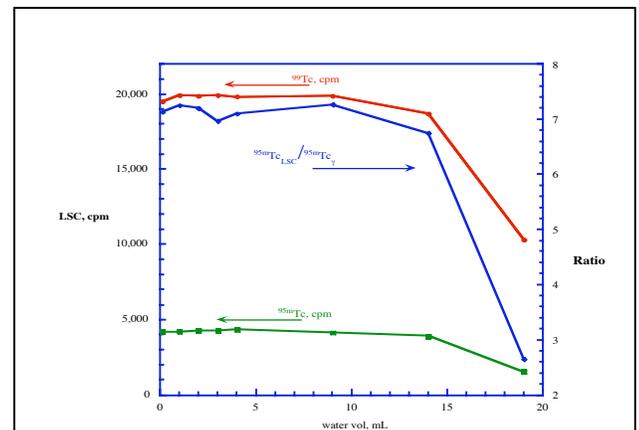


Figure 4. The graph showing the LSC cpm for ^{99m}TcO$_4^-$ (top) and ^{99}Tc O$_4^-$ (bottom) and the {^{95m}Tc$_{LSC}$/^{95m}Tc$_g$} cpm ratio (middle) as a function of various volumes of H$_2$O and Ultima Gold in a 20 mL total volume.
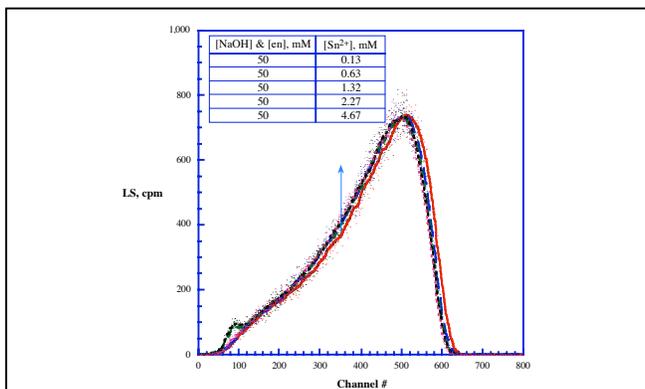
Figure 5. The dependence of the ^{99}Tc O$_4^-$ LSC spectrum on [Sn^{2+}] at a constant NaOH/en concentration of 50 mM. The [Sn^{2+}] concentration varies from 0.13, 0.63, 1.32, 2.37, and 4.67 mM bottom to top on the left side.
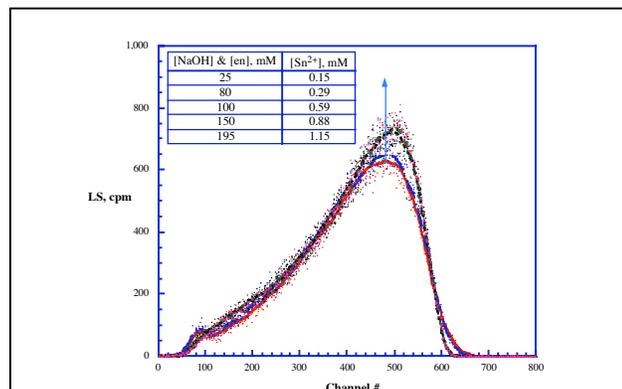
Figure 6. The dependence of the ^{99}Tc O$_4^-$ LSC spectrum on variable [Sn^{2+}] and [NaOH/en] concentrations. The [NaOH/en] : [Sn^{2+}] concentrations varies from 25 : 0.15, 80 : 0.29, 100 : 0.59, 150 :0.88 and 195 : 1.15 mM top to bottom at the center.
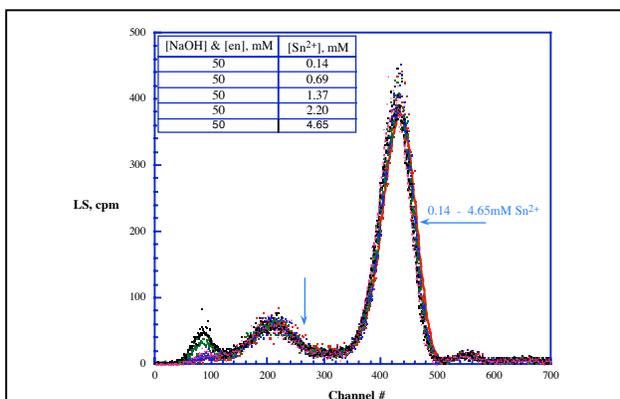
Figure 7. The dependence of the ^{95m}Tc O$_4^-$ LSC spectrum on [Sn^{2+}] at a constant NaOH/en concentration of 50 mM. The [Sn^{2+}] concentration varies from 0.14, 0.69, 1.37, 2.20, and 4.65 mM bottom to top on the left side.
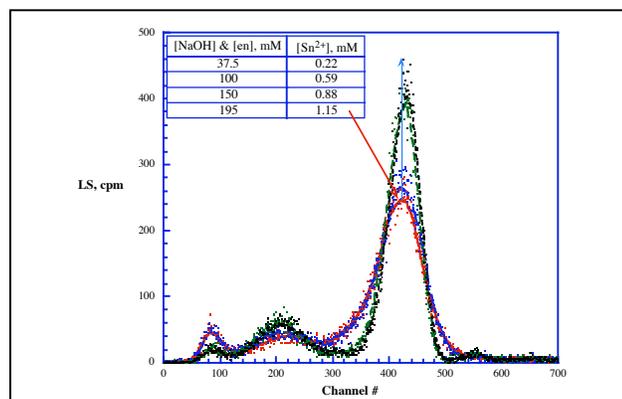
Figure 8. The dependence of the ^{95m}Tc O$_4^-$ LSC spectrum on variable [Sn^{2+}] and [NaOH/en] concentrations. The [NaOH/en] : [Sn^{2+}] concentrations varies from 37.5 : 0.22, 100 : 0.59, 150 : 0.88, and 195 : 1.15 mM top to bottom at the center.

The Separation of Werner Type Complexes Using Gel Permeation Chromatography

Introduction
The technique of gel permeation chromatograph depends on the separation of molecules by their size. The solid phase has pores of varying sizes in it. Small molecules diffuse into the pore and take longer, greater elution volume, to move down the column. Large molecules are excluded from the pores and come through the column the quickest. The basic chromatographic equation is Eq. 2. V_e is the elution volume. This is the volume that is passed through the column

$$V_e = V_o + KV_i \qquad\qquad (2)$$

at the point of the concentration maxima of the solute being eluted. V_o is the void volume. This is the volume between the gel particles. V_i is the interstitial volume. This is the volume in the pores of the gel. K is the distribution coefficient and for no gel-solute interaction has a value of from 0 to 1.00. For a large molecule that is excluded form the solid phase, K = 0.00 and V_e = V_o. For a small molecule that enters into all of the pore volume, K = 1.00 and V_e = V_o + V_i. The width of the elution peak is estimated and is called width at half height maximum,$W_{1/2}$.

Sephadex G–10 is a dextran cross–linked with glycerin made by Pharmacia Fine Chemicals. Inc. The G–10 has a fractionation range to 700 g/mol. Small ions do not vary much in size. Hence, the V_e for most ions should be vary similar. This is especially true of first row transition metal coordination complexes, Werner type compounds.

In the separation of the Hanford Tank Waste using Sephadex G–10, it was discovered that separation based only on size could not explain the separations. It appeared as if there were some specific interactions between the ions and the solid phase. This third section of the results gives preliminary data for the separation of some Werner complexes using Sephadex G–10.

Experimental
The chromatography equipment consisted of a pump that allowed control of the rate of flow of the eluent. The outlet from the pump was attached through a 1.0 mL injection loop and then through a flow adaptor to a 1.00 x 50 cm column. The effluent stopcock was attached to a drop-counter on a fraction collector. The fraction collector could be set to collect the desired number of counts and then change the collection tuber.

The chromatography column was filled with a slurry of Sephadex G-10 in water. The Sephadex G-10 powder and water was prepared and allowed to stand for 24 hours in order to hydrate the gel. The slurry was then poured into the column and allowed to settle while excess water drained out through the open bottom stopcock. This was repeated until the gel was at a height of 45 cm. This gave a bed volume of 35.3 cm^3.

For a particular chromatographic separation, the flow rate was first adjusted. This was done by collecting a fraction of water in a particular time (usually 1.3-2.0 minutes/fraction) and determining the mass of the fraction. For the purposes of these experiments, it was assumed that 1.000 mL water/1.000 g water. The flow rate then was the ml/fraction divide by the minutes/fraction that was set in the fraction counter. The fraction collection was repeated until a constant desired flow rate was attained.

A solution of the selected compound was injected into the 1.0 ml loop and then the values turned to introduce the loop into the flow of eluent that was being pumped through the column. Once the solution has been separated on the column (the Werner complexes are colored and

can be seen) then an analysis was done of the fractions containing colored solutions. Each of the fractions in turn was transferred into a curette and the absorbance in measured at the desired wavelength using a Shimadzu uv/visible Spectrophotometer.

The flow rate was again measured during the elution by obtaining the mass of 10 fractions of water before the band appears at the bottom of the column and 10 fractions afterwards. These masses are averaged and converted to the flow rate.

The void volume (V_o) was determined by adding a solution of Dextrin Blue and determining the elution volume (V_e). Since for blue dextrin K = 0.00, the value of V_e is the same as V_o.

Results

The results obtained are summarized in Table I. The V_e are almost independent of flow rate.

Table I. Data for the separation of Werner complexes using Sephadex G-10 with water as the eluent.

Compound	MW, g/mol	Flow rate, mL/min	V_e
Blue Dextrin	2×10^6	0.686	32.2
$Co(NH_3)_6^{3+}$	161	1.01	40.5
$Cr(C_2O_4)(H_2O)_4^+$	204	0.80	47.3
$Co(NH_3)_3(NO_2)_3$	248	1.06	91.4
cis-$Cr(C_2O_4)_2(H_2O)_2^-$	264	1.32	42.8
$Cr(C_2O_4)_3^{3-}$	316	1.32	36.8

The V_o is 32.2 mL, the V_e for Blue Dextran. If the Sephadex G-10 column were separating based on size as does for gel permeation chromatography, then there should be very little difference in the V_e for the various compounds. Clearly a V_e of 91 mL for $Co(NH_3)_3(NO_2)_3$ versus 41 mL for $Co(NH_3)_6^{+3}$ and 37 mL for $Cr(C_2O_4)_3^{3-}$ implies that more than size is effecting a separation. Also, it appears that charge on the complex is not the deciding factor.

In an attempt to systematically vary the complexes, the series $Co(NH_3)_{6-n}(NO_2)_n^{+(3-n)}$ is being synthesized. The values of V_e will be determined. Additionally, other cobalt complexes with various size chelating ligand will be synthesized and the values of V_e will be determined. Additional separation data will give insight into the molecular/ion parameters that determine individual ion V_e.

The significance of these results are quite profound in the field of aqueous ion chemistry. This chromatographic technique gives a method to separate large amounts of various ions without the addition of extraneous ions , such as necessary in ion exchange chromatography.

Separation of Non-Pertechnetate Species from Hanford AN-107 Tank Waste

A significant amount of the technetium in the Hanford tank waste exists as unidentified, stable, reduced, technetium complexes. Our project seeks to identify these species using capillary electrophoresis mass spectrometry (CEMS). In order to do this we must first separate the non-pertechnetate fractions from a waste sample. Separation of these fractions involves two major steps: 1) cation exchange to remove the gross activity, and 2) size exclusion chromatography to remove residual activity and to separate the various non-pertechnetate fractions from each other. Our first series of experiments with AN-107 tank waste studied the effect of pH on the cation separation. Although successful at low pH, this approach runs the risk of altering the non-pertechnetate species that exist in the caustic tank waste. We have developed a new procedure using Zn^{2+} that allows us to do the cation separations without acidifying the sample. Although technetium recovery was ~50% through the two step process, we obtained a technetium fraction essentially free of residual gross activity that should allow doing a CEMS analysis on the fraction. Observation of a consistent loss of technetium to the cation column suggests that some technetium is cationic.

Introduction

Technetium, as pertechnetate (TcO_4^-), is a mobile species in the environment.[1] This characteristic, along with its long half-life, (^{99}Tc, $t_{1/2}$ = 213,000 a) makes technetium a major contributor to the long-term hazard associated with low level waste (LLW) disposal.[2] Technetium partitioning from the nuclear waste at DOE sites will be required so that the LLW forms meet DOE performance assessment criteria. Current technetium separations assume that technetium exists as TcO_4^- in the waste. However, years of thermal, chemical, and radiolytic digestion in the presence of organic material, has transformed much of the TcO_4^- into unidentified, stable, reduced, technetium complexes. Some tanks that have a high organic content have >50% of their technetium in this form.[3, 4] To successfully partition technetium from tank wastes, it will be necessary to either remove these technetium species with a new process, or reoxidize them to TcO_4^- so that conventional pertechnetate separation schemes can be used.

Our research seeks to identify these unknown non-pertechnetate species (TcN) using capillary electrophoresis mass spectrometry (CEMS). However, for operation and safety reasons, we must first separate the TcN fractions from the actual waste, which is a caustic, high salt ($\mu \approx 5$ M), matrix. This paper reports on the progress we have made on this separation.

Experimental

A 250 mL sample of diluted, cesium free, Hanford waste from tank AN-107 was sent to us in 1998 by Pacific Northwest National Laboratory. The general experimental procedures, the procedures for $^{95m}TcO_4^-$ solution preparation, technetium counting methods, the methods for determining the free OH^-, NO_2^-, and NO_3^- concentrations, the methods used for measuring the apparent technetium ($^{app}K_d$) and true pertechnetate ($^{true}K_d$) distribution coefficients, the equation that relates the normalized $^{app}K_d$ and $^{true}K_d$ to the percent non-pertechnetate in a sample, and the radiochemical method for determining the total ^{99}Tc c in waste samples, have been described previously.[3-6] In the development of this paper we have noticed that the radiochemical method for total ^{99}Tc, which uses a ^{95m}Tc chemical yield tracer, has a negative bias. The measured ^{99}Tc cpm values are low by 3-9% and the bias is greater for samples that have a

^{95m}Tc/^{99}Tc activity ratio > 2, a situation that was common to this paper. An Orion semi-micro pH electrode and an EA 940 meter were used to measure pH values.

A Packard A5530 NaI γ-counter was used to measure the ^{95m}Tc (204 keV γ-ray) content of analytical samples and to monitor the gross activity of waste samples as they were processed. The gross activity, which is mostly beta activity and has no discernable spectral structure, was measured from 15–2000 keV. In contrast to ^{95m}Tc measurements, the gross activity readings were highly dependent on the sample volume from 0.1 to 20 mL; the beta activity was attenuated logarithmically with increasing volume. Any quantitative relationship within an experiment and between experiments must be made at the same volume. A Wallac Guardian 1414 Liquid Scintillation Counter (LSC) was used to measure ^{99}Tc and ^{95m}Tc in analytical samples. Packard Ultima Gold^{TM} A/B (UG) cocktail was used to prepare LSC samples.

Dowex$^®$ AG50Wx8, H$^+$ form, 100-200 mesh, cation exchange resin was obtained from Bio–Rad. Cation resin beds of the desired length and volume were prepared in Bio-Rad Poly–Prep columns by washing them with 20 bed volumes (BV) of water. If a Na$^+$ form bed was needed it was prepared by washing the H$^+$ form with ten sequential bed volumes of 1.00 M NaOH. In some of the experiments, the 1.00 M NaOH solution was left in the column and in other experiments the column was washed with water to remove the NaOH.

Cation exchange was used to separate TcN fractions from the gross activity in AN-107. The general procedure was to take a 0.1-1.0 mL aliquot of AN–107 (12645-126447 cpm total ^{99}Tc), adjust it to a desired pH (12.5, 10.0, 7.00, 3.02, or 1.00) with 1.0 M HNO$_3$, and pass it through a 5-10 mL Dowex H$^+$ or Na$^+$ form resin column. The column was washed with water until the combined effluent volume was 20 mL. The effluent was γ-counted and then either analyzed for total technetium or diluted to 25.00 mL. In the latter case two 2-mL aliquots were analyzed for total technetium, the remaining 21.00 mL were added to a Sephadex G-10 column (see below). In some cases the water elution was followed with 1 and 8 M HNO$_3$ elutions.

Some pH 3.01 adjusted 1.00 mL aliquot samples, after passing through a 5 mL H$^+$ form resin column, had a pH of 1.10. These were readjusted to pH 3.65 and run through a second 5 mL H$^+$ form column. This effluent, which had a pH of about 1.4, was evaporated to 0.5 mL at ambient temperature (four days). The color of the solution was light yellow and the estimated acidity was 2.5 M. This was then added to a 1 x 40 cm Sephadex G-10 column (see below).

Some experiments were performed in which 0.100 or 0.200 mL of AN-107 were diluted to 1.00 or 2.00 mL and brought to 0.17 M in Zn^{2+}. The zinc concentration was based on the TOC level in the sample (20.7 g/L). Assuming the TOC represents chelating ligands and that there are 2 carbons/chelator then there were 0.0864 mmole of chelators in the 0.100 mL sample. This would require an equivalent amount of Zn^{2+} to be added to the sample in order to form a 1:1 Zn^2+/chelator complex; for insurance we added twice that amount. Fortuitously, this yielded a solution close to the original sample pH, ~12. A precipitate of Zn(OH)$_2$ was observed. After setting for two hours the solution and white precipitate, Zn(OH)$_2$, were added to a Na$^+$ form cation column and eluted with the desired amount of water and nitric acid solutions.

Sephadex G-10 for gel filtration chromatography of molecules <700 MW was obtained from Aldrich Chemical Company. The effluents from the cation columns were added to G-10 columns to separate the technetium fractions from each other and from the residual gross activity. The G-10 was slurred and equilibrated with water for at least 24 hours before use. Beds were prepared in 1 cm diameter columns of variable length. All elutions were with water. Large scale separations on 1 x 40 cm beds had a calculated total volume of 31.4 mL. The free volume of the

bed, V_o, was found to be 13.0 mL using the blue dextran (MW = 2 x 10^6) method.[7] Likewise the sum of V_o and V_i (the pore volume) was found to be 18.0 mL using a $CoCl_2$ (MW = 129.8) solution. This latter measurement assumes that there is no interaction between the Co^{2+} and the Sephadex G-10. The elution volume, V_e, is given by the Eq. 1. For this particular

$$V_e = V_o + KV_i \qquad\qquad (1)$$

G-10 column Eq. 2 can be written with K depending on the degree of entry into the pores of the

$$V_e = V_o + KV_i = 13.0 \text{ mL} + K (5.0 \text{ mL}) \qquad\qquad (2)$$

gel and ranging between 0 (no entry) and 1 (total entry). In many of these separations the V_e exceeds 18 mL. This implies a specific interaction of the species and the G-10 gel.

Some experiments dissected the G–10 column to examine it for residual activity. Sections of the column consisting of the G-10 and the resident water were added to 1.0 mL of water and 14 mL of UG. The sections were counted by both methods.

Our use of the BioGel P-2 as a chromatographic material is very similar to the use of Sephedex G-10. In our continuing efforts to separate the various technetium containing species in the Hanford AN-107 Waste Tank Sample, we chose to examine BioGel P-2, a polyacrrylamide gel copolymer of acrylamide and N, N'-methylene-bis-acrylamide with a fractionation range 100 to 1,800 Dalton. For the 1.90 mL BioGel columns that we used, Eq. 2 is applicable. That is, the maximum V_e should be when K = 1.0 or 1.68 mL and the minimum

$$V_e = V_o + KV_i = 0.471 \text{ mL} + K(1.21 \text{ mL}) \qquad\qquad (3)$$

elution volume should be 0.47 mL when K = 0.0. For a 2.0 mL column, the numbers are 1.27 mL for V_i, 0.496 mL for V_o, and 1.77 mL for V_e. Any elution volume greater than 1.68 (1.77 mL) mL implies that there are specific interactions and the BioGel is not behaving in a strict size exclusion mode. For a 20 mL BioGel, the value for V_i is 12.7 mL for V_o is 4.96 mL. Hence, the values for V_e should range from 4.96 to 17.7 mL. If values of V_e are larger then 17.7 mL, K>1.00 and this implies a specific interaction of the solute with the BioGel P-2.

Exploratory experiments were performed to elucidate the interaction of technetium compounds with the BioGel P, a polyacrylamide gel.

Results and Discussion

The sample of AN-107 waste that was received in 1998 is a reddish brown solution that has some solid material in it. Table 1 shows some of the content of the sample. Comparing our measured density, pH, nitrate and ^{99}Tc analysis to other dilutions of AN-107 indicates that the sample is a 1:2 dilution of the original waste.[3] The TOC content shows that AN-107 waste is classified as "a high organic tank" containing numerous compounds such as EDTA, oxalate, acetate, glycolate and gluconate.

In July 1999 the waste sample was analyzed for total technetium. Five aliquots taken from a well stirred bottle of AN-107 that contained both solution and solid gave 122,045 ± 2,795 cpm ^{99}Tc/mL; the uncertainty is the standard deviation of the sample set. A sample of this stirred mixture was centrifuged for 2.0 hours. Five aliquots of the supernatant analyzed for total

technetium gave 125,995 ± 2,885 cpm/mL. There is no significant difference in these two averages at the 95% confidence level. The combined result is 124,020 ± 2,840 cpm/mL. These results imply that all of the technetium species in the waste, pertechnetate and non-pertechnetate, are soluble. In July 2002, the analysis of centrifuged AN-107 was repeated and gave 129,480 ± 8,030 cpm/mL. There is no significant difference between the averages of the 1999 and 2002 results. Thus over three years all the technetium is remaining in solution. The composite average and uncertainty is 126,447 ± 4,655 cpm/mL The technetium concentration is $(3.39 ± 0.13) \times 10^{-5}$ M.

In June 1998, the apparent distribution coefficient ($^{app}K_d$) between Reillex^{TM}-HPQ and the as received waste was 4.42 ± 0.70 mL/g. The $^{app}K_d$ is a gross measure of how technetium distributes between the phases when a solution contains both TcO_4^- and TcN. The $^{true}K_d$ for pertechnetate in this sample, obtained by adding $^{95m}TcO_4^-$ to the sample, was found to be 315 ± 41 mL/g. Thus the percent TcN in this waste is estimated to be 66 ± 9%, which is consistent with our other samples of AN-107.[3] In July 2002, the $^{app}K_d$ value was found to be 5.82 ± 0.30 mL/g; the TcN had decreased to 60 ± 8%. Thus within experimental error the sample is stable. We have seen previously that the percent TcN in Hanford waste samples can be maintained if they are not heated and/or their exposure to air is limited.[4]

In order to identify the TcN species by CE/MS we first need to obtain a TcN fraction from AN-107. From an operational and safety perspective we are required to remove the gross activity from the AN-107 sample. Since the major activity in the waste is ^{90}Sr, 56.8 mCi/L, it was reasonable to use cation exchange to remove this activity.

The effectiveness of this was tested by adjusting aliquots of AN-107 to desired pH values with HNO_3, adding them to H^+ or Na^+ form cation columns, and eluting with water. The eluents were counted and/or analyzed for technetium. Figure 1 shows that the gross activity in the effluent drops dramatically as the sample pH is reduced. For example, below pH 1 more than 90% of the activity remains on the column. When the H^+ form of the resin is used in combination with a sample adjusted to pH 3, the effluent activity has only ~1% of the initial activity. The greater decontamination observed in the latter case is the result of the lower pH that the H^+ form of the cation resin ultimately gives to the sample. These observations are consistent with ^{90}Sr being released from its ligands (i.e. EDTA) at low pH and then sorbed on the cation resin.

We have observed a serious problem with the pH adjustment procedure in that technetium is being lost to the cation resin. For example, with the Na^+ form of the resin, losses have ranged from 8% to 20% at pH 7.00 to 2.95, respectively. When the H^+ form was used, 24% losses have been seen at pH 3.01. Since the H^+ form adds to the ultimate acidity of the sample it might be expected that higher acid is causing some unknown technetium species to become cationic and sorb onto the resin. As we have mentioned in the experimental section these losses may be exaggerated by 3-9% because of the bias in the ^{99}Tc analytical procedure. However, the general nature of the loss across a pH range suggests that there may be a cationic technetium species that is a component of the waste.

Once the sample is free of most of its gross activity it needs to cleaned up from the residual activity salts and be separated from pertechnetate and into TcN fractions. Sephadex G–10 gel is a dextran, a partially hydrolyzed starch, which is cross-linked with epichlorohydrin and is useful for size separations for molecules less than 700 MW. Preliminary experiments determined that pertechnetate, whether dissolved in water or in a solution of 1.50 M $NaNO_3$/1.00 M NaOH, is not retained by 2 ml G-10 columns. In a similar experiment, a 0.100 mL AN-107 sample loses 25%

of its technetium to the column. If AN-107 is ≈ 60/40 TcN/TcO$_4^-$ and if it is assumed that the pertechnetate elutes, it appears that approximately half of the TcN is sticking to the column. Thus G-10 has some interaction with the TcN species and offers the possibility of separating these species from themselves and from pertechnetate.

Preceding the G-10 column with a Dowex, Na$^+$ form, cation column gave similar results. For example, an AN–107 sample adjusted to pH 10.00, 7.00 or 3.02 and passed through a cation column and then a G-10 column had 33.1, 31.3, and 33.3% of the technetium removed. The slightly higher technetium removal probably is due to the combined losses from the cation and G-10 columns.

A large-scale separation of the technetium species from 1 mL of AN-107 (126,447 cpm total ^{99}Tc, ~43000 cpm TcO$_4^-$ and 83500 cpm TcN) was tried using a sequential cation/G-10 procedure. After passing the pH 3.00 adjusted sample through two cation columns only 3% of the gross activity remained. The concentrated cation effluent, which had a light yellow color and an acidity of 2.4 M, was passed down a G-10 column and eluted with water. Figure 2 shows the elution patterns for the residual gross activity and the technetium activity coming off this column. There are two major technetium peaks, the first elutes with the residual gross activity (fractions 6-15, 9075 cpm ^{99}Tc) and is probably pertechnetate, while the second peak (fractions 16-28, 22508 cpm ^{99}Tc) elutes essentially free of other activity. Unfortunately only 32,311 cpm of ^{99}Tc, or 26% of the added technetium, were found in these fractions, far lower than expected. Figure 3 shows the activity present in nine sections of the dissected G-10 column. The residual gross activity maximizes at the top of the column and steadily declines down the column. In contrast, the LSC data shows a definite peak from 14 to 30 cm, and these spectra suggest that they could be due to ^{99}Tc. If free of other activity, these spectra may contain 31,889 cpm of ^{99}Tc. This total may be low by 15% due to quenching on the ^{99}Tc signal by G-10; thus 29% of the total technetium may still be on the G-10 column. Unfortunately, even with a quench correction, only 68,983 cpm, or 55%, of the total ^{99}Tc can be accounted for. A possible explanation is that a significant amount of technetium was lost to the cation columns. Since we have observed that 20-24% of the technetium can be lost to a single cation column at pHs below 3.00 it is not unreasonable to expect higher losses for two columns; a 40-48% loss complements the percent recovery. In addition, the H$^+$ form columns produced effluents with pH values of 1.10 and 1.37; the acid generated in the sample could be facilitating the production of a cationic technetium species.

The above experiments demonstrate that the gross activity can be removed from the sample. It is suspected that protonating the chelating ligands (polyaminocarboxylates, i.e. EDTA) that bind cations such as ^{90}Sr^{2+} causes the ligand to release the cationic aqua species that can be sorbed by the resin. However, lowering the pH may also be altering the unknown technetium species and allowing them to sorb on the resin. It is suspected that the reduced non-pertechnetate species could also be complexed by polyaminocarboxylates or alkoxide ligands. Protonation of these ligands at low pH values would be possible and would result in a species change from the initial basic solutions. Hence, an alternate approach to the conversion of the complexed metal ions into cations is needed.

Zn^{2+} has a larger stability constant with EDTA than Sr^{2+}; log K= 16.5 vs. log K = 8.74.[8] If Zn^{2+} were added to the waste solution, it is possible that the Zn^{2+} could displace EDTA type ligands chelating Sr^{2+} and allow the cation to be sorbed by the Na$^+$ form of the cation resin. Little or no pH change would be expected from the metathesis reaction.

In the experiment using 0.100 mL of AN-107, the cation column was eluted with 10 BV of water, then 4 BV of 1.0 M HNO_3, and finally 8 BV of 8.0 M HNO_3. The results depicted in Figure 4 show that ~2% of the gross activity came off the column with water, ~1% with 1.0 M HNO_3, and ~97% with the 8.0 M HNO_3 elution. Although, the 1.0 M HNO_3 dissolved the white $Zn(OH)_2$ precipitate, very little activity was removed by this eluent; this suggests that the $Zn(OH)_2$ precipitate is not sorbing the gross activity. When compared to the data in Figure 1, it is clear that Zn^{2+} is effecting a decontamination from the gross activity in the waste that is equivalent to adjusting the pH to ~1. Thus we get the equivalent decontamination with a much lower probability of altering the TcN species identity.

But where is the technetium? The experiment was repeated and the fractions were collected and analyzed for gross activity and total technetium. Table 2 shows that 29 mL of water eluted 73% of the technetium and left behind 88% of the gross activity. It is interesting that 9.4% of the technetium comes off with acid and half of this with 8.0 M HNO_3. Only 82% of the technetium that was in the initial sample was recovered. Although this loss may be exaggerated by 3-9% the data from this experiment, especially the fact that 8 M HNO_3 removes ^{99}Tc activity from the column, suggests that there is a cationic technetium species in the waste.

A larger test (0.20 mL of AN-107) of the Zn^{2+} decontamination procedure coupled to the G-10 separation was tried to determine how well the method could decontaminate and isolate the various TcN fractions. The cation column effluent was added to a 1 x 40 cm G-10 column and eluted with water. Figure 5 shows a plot of the residual gross activity as a function of elution volume; most of this elutes as large band centered at 17.0 mL. Figure 5 also shows how the technetium eluted from this column. A major band centered at 19.5 mL contains 27% of the technetium added to the experiment while another major band at 21.5 mL contains 14%. This latter band is essentially separated from the residual gross activity and is an improvement in the separation relative to Figure 2. Integration of the technetium fraction accounts for 53% of the added technetium. The missing technetium is on the cation column (10-20%) and on the G-10 column (30%). Technetium elution from the G-10 column might be improved by using an eluent such as ethylene glycol that could compete with the dextran alcohol functionalities.

Behavior of Technetium Compounds with BioGel P-2

When $^{95m}TcO_4^-$ in water was added to the top of the 1.90 mL column, it was not eluted with water within 18 mL (K = 14.5). The same behavior with K>14.5.was observed when a $^{99}Tc(gluconate)_x^{-n}$ complex in water was added to the top of the column. A solution of $^{95m}TcO_4^-$ in 2.0 M $NaNO_3$ was added to the top of the column. It was eluted with 2.0 M $NaNO_3$ in ≈ 4.0 mL (K ≈ 2.9). A solution of $^{95m}TcO_4^-$ in 2.0 M $NaNO_3$ was added to the top of the column. It was not eluted with water within ≈ 8.0 mL (K ≈ 6.2). It was eluted within 1.9 mL (K ≈ 1.2) when 0.50 m$NaNO_3$ was added.

It is clear that the interaction of TcO_4^- with the BioGel P-2 is altered in the presence of $NaNO_3$. Two possibilities are that (1) the $NaNO_3$ interacts with the TcO_4^- or that (2) the $NaNO_3$ interacts with the BioGel P-2 and results in a different behavior for the TcO_4^-. This phenomenon is of interest in itself but has not been pursued at this point.

We were able to separate a solution of $^{95m}TcO_4^-$ and $^{99}Tc(gluconate)_x^{-n}$ complex into two clearly resolved bands (Figure 7.). A 0.20 mL solution containing ≈ 1.5 x 10^{-5} M $^{95m}TcO_4^-$ and $^{99}Tc(gluconate)_x^{-n}$ complex each was added to a 2.0 mL BioGel P-2 column. A 2.0 mL fraction of water was added as eluent then a solution of 0.100 M $NaNO_3$ was added with 1.0 mL fractions collected. The activity of the fractions was measured using the Liquid Scintillation counter. As seen in Figure 7, there were maximum amounts of activity at elution volumes of 4 mL (K = 2.75)

and 6 mL (K = 4.32). The summation of the cpm in each band indicated that the $^{95m}TcO_4^-$ eluted first followed by the $^{99}Tc(gluconate)_x^{-n}$.

A 0.50 mL sample of AN-107 that had been contacted with CH_3CN was added to the top of 2.0 mL of BioGel P-2 column. The sample was eluted with water, 0.50 mL fractions collected, and the fractions were counted in the 165-255 keV range on the NaI counter. Fraction #3 contained 14 %, fraction #4 contained 80 %, and fraction #5 contained 3 % of the total activity. The high salt contact and the relatively high loading volume did not allow for retention of the activity. However, the fate of the $^{99}TcO_4^-$ on the column is unknown.

Release and Removal of Activity from AN-107

The AN-107 contains a variety of metal ions, many of them radioactive. However, these ions cannot be removed by simple cation exchange procedures from the AN-107 sample. This is a combination of the high salt concentration ($NaNO_3$) and the fact that they are not simple aqua ions; they are complexed to a variety of ligands. Hence, the chelating ligands must be removed from the ions before the ions can be removed by ion exchange. This task must be performed without changing the pH or solution conditions. The technetium species present must not be altered.

The general approach is to add Zn^{2+}, in the form of $ZnSO_4$, which will complex the chelating reagents and release the Sr^{2+} and other cations. The sulfate anion might also precipitate some of the metal cations. Then the cations can be removed on a cation resin column, Dowex 50Wx8. The anionic technetium compounds will come through the column and be separated from the activity.

First, the amount of Zn^{2+} to add to the solution of AN-107 must be decided. Assuming 39 g/L of carbon, in 0.1 mL of the AN-107 there are (39g/1000 mL) x (0.10 mL) x (1 mole/12 g carbon) = 0.325 mmoles carbon. Assuming 2 moles of carbon/chelate results in 0.1625 mmoles of chelator. Assume 1 chelator/zinc ion. Then want 0.1625 mmoles of $ZnSO_4.7H_2O$. At 287.5 g/mol, this is 0.0467 g/0.100 mL AN-107.

In order to examine the behavior of the AN-107 with this treatment, the following experiment was performed. A solution containing 0.100 mL of $^{95m}TcO_4^-$ was placed in a LS vial and counted on the NaI counter. For this $^{95m}TcO_4^-$ solution, there was 4,255 cpm in the 165-255 keV range and 124,223 cpm in the 5-2000 keV range. A total of 0.100 mL of AN-107 was added to the LS vial and the combined solution counted. There were 163,450 cpm in the 165-255 keV range and 1,628,338 cpm in the 5-2000 keV range. A 0.800 mL solution containing 0.0468 g of $ZnSO_4.7H_2O$ was added to the AN-107/$^{95m}TcO_4^-$ solution and the combined solution set for 2 hours. A precipitate developed. The solution was added to the top of a 2.0 mL Dowex 50WX8 Na^+ form column and eluted by the addition of 1 mL of water at a time. The eluents were collect in LS vials and count on the NaI counter. In the first 3.0 mL of elution volume, there were 4,371 cpm in the 165-255 keV range. This is all of the $^{95m}TcO_4^-$ solution, as would be expected for an anion. With the addition of 10 mL of water total, no additional activity is eluted. Then 8.0 M HNO_3 was used as the eluent for 5.0 mL and 16 M HNO_3 for 4.0 mL. A total of 68% of the activity in the 5-2000 keV range was recovered. This implied that 32% of this activity went with the Zn^{2+} precipitate. The conclusion is that the $ZnSO_4$ precipitation and Dowex 50W chromatography removes most of the unwanted activity.

The water elutions from above were combined and air evaporated. The residue was taken up in 10 x 0.100 mL of water. Each 0.100 mL was added to the top of a 2.0 mL BioGel P-2 column. The column was eluted with 1.0 mL fractions of water and the fraction LS counted. The activity

begins to be eluted with the second mL of water and peaked at 5 mL of water (fraction 5). This gives a value for K of 3.53. An examination of the LS spectra reveals that there are several different radioactive species in the effluent solutions. However, the important point is that most of the activity has been removed from the solution. The question that is unanswered is "Did any of the technetium species also get removed?"

A small sample of a solution of AN-107 that had been treated with Zn^{2+} (equivalent to 0.002 mL of the original sample) was brought to dryness twice on a 180 °C hotplate. The LS spectrum was compared to an equivalent unheated sample. There was no difference in the spectra. The conclusion is that there is no volatile species present.

A series of experiments were performed using the AN-107 to determine the amount of activity and technetium removed by various treatments. In these experiments, a 2.00 mL sample of AN-107 was treated with $ZnSO_4$ and added to a Dowex cation column. The water eluents was combined, reduced in volume, and diluted to 25.00 mL. All of the numbers given will be normalized to this dilution. The original AN-107 sample has 749,580/mL in the 15-2000 keV range and (9,558 ± 268) cpm/mL of ^{99}Tc. Upon treatment with $ZnSO_4$/Dowex cation column, the sample contained 16,760 cpm/mL in the 15-2000 keV range and (8,258 ± 246) cpm/mL of ^{99}Tc. This is a 97.8 % removal of the 15-2000 keV range activity and (13.7 ± 0.7) % of the technetium. Upon a second pass through the Dowex column, he sample contained 3,039 cpm/mL in the 15-2000 keV range and 7,879 cpm/mL of ^{99}Tc. This is an 81.9 % removal of the 15-2000 keV range activity and 4.59 % removal of technetium. A total removal of 99.6 % of the 15-2000 keV range activity and 17.6 % of the technetium was effected.

A sample was also treated a second time with $ZnSO_4$ and then passed through a second Dowex cation column. The 16,760 cpm/mL in the 15-2000 keV range was reduced to 927 cpm/mL, an additional 94.1 % removal. The 8,258 cpm/mL of the technetium was reduced to 7,196 cpm/mL, an additional 12.9 % removal. The overall removal of the activity in the 15-2000 keV range was 99.9 % and 24.7 % of the technetium.

Technetium removal
In a second sample, 14.7 % of the technetium was removed by the Zn^{2+}/two cation column treatment. Of the remaining 85.3 % technetium, (82.6 ± 3.9) % of it was removed by passing it into a Reillex-HPQ anion resin column. This leaves 17.4 % of the remaining technetium not sorbed by the cation or anion column. On a total technetium basis, 14.7 % was removed by the initial treatment, 70.4 % of the technetium has been removed after the Reillex-HPQ NO_3^- form column and 14.9 % of the technetium remains. The remaining technetium species are neutral or if they are charged species they are not sorbed because of the high salt concentration.

Isotope Dilution
One of the high activity isotopes in the AN-107 is ^{90}Sr. An attempt to dilute the sample with natural Sr was made by adjusting the $Sr(NO_3)_2$ concentration to 1.0 M in a sample of AN-107 that had been treated by Zn^{2+}/Dowex column method. The sample was then passed through a Dowex 50Wx8 K^+ form cation resin column. When compared to a sample with no added $Sr(NO_3)_2$ but also passed through a cation column, there was no additional removal of activity. The conclusion is that after the Zn^{2+}/Dowex column there is little $^{90}Sr^{2+}$ left in the solution.

Anion Exchange Column Separation
A Zn^{2+}/Dowex column treated sample of AN-107 was passed through a Dowex 50Wx8 Na^+ form cation exchange column. The activity of all of the fractions was measure using the LS counter. The initial sample activity of 52,390 cpm/mL (15-2000 keV range) was reduced by 65 percent to

18,252 cpm/mL after passing through the cation column with water elution. This effluent was added to a Dowex 1x8 anion NO_3^- form exchange column. The column was successively eluted with water, 0.10 M $NaNO_3$, 1.0 M $NaNO_3$, 1.0 M HNO_3, water, and finally an Sn^{2+}/NaOH/en solution. Figure 7 is plot of the results. There is no definite conclusion other then there appears to be at least five different species that are eluted. No identification could be made.

BioGel P-2 Column Separations
A 1.00 mL sample of Zn^{2+}/Dowex column treated AN-107 was added to the top of a 20 mL (0.7 x 52 cm) column of BioGel P-2. The column was eluted with water at a flow rate of 0.43 mL/min and 1.0 mL fractions were collected. The fractions were added to Ultama Gold and LS counted. The cpm/mL are for the entire 15-2000 keV range. Figure 8 contains the elution results. There are three peaks for the water elution. These are at elution volumes of 14, 22, 25 mL. The estimated K values are 0.79, 1.24, and 1.41. After 1.00 M $NaNO_3$ was begun as the eluent, a peak emerged at 18 mL (78 mL total elution volume) and at 28 mL (88 mL total elution volume). Figure 9 shows the cpm versus channel numbers for the peaks.

References

1. N. C. Schroeder, D. Morgan, D. J. Rokop, and J. Fabryka-Martin, *Radiochimca Acta*, 60 (1993) 203.
2. S. A. Barker, C. K. Thornhill, and L. K. Holton, Pretreatment technology plan, Westinghouse Hanford Company Report WHC-EP-0629, 1993.
3. N. C. Schroeder, S. D. Radzinski, K. R. Ashley, A. P. Truong, and P. A. Szczepaniak, in *Science and Technology for Disposal of Radioactivity Tank Waste*, Edited by W. W. Schulz and N. J. Lombardo, Plenum Press, New York, 1998.
4. K. R. Ashley, A. P. Truong, G. D. Whitener, N. C. Schroeder, and S. D. Radzinski, *J. Radioanalytical Nuc. Chem. Articles, 250* (2001) 271.
N. C. Schroeder, S. D. Radzinski, J. R. Ball, K. R. Ashley, S. L. Cobb, B. Cuttrell, J M. Adams, C. Johnson, G. D. Whitener, Technetium partitioning for the Hanford tank waste remediation system: anion exchange studies for partitioning technetium from synthetic DSSF and DSS simulants and actual wastes (101-SY and 103-SY) using Reillex™-HPQ resin, Los Alamos National Laboratory Report LA-UR-95-4440, Los Alamos, NM, 1995.
6. N. C. Schroeder, S. D. Radzinski, J R. Ball, K. R. Ashley and G. D. Whitener, *Progress in Metal Ion Separation and Preconcentration: Progress and Opportunities*, Edited by A. H. Bond, M. L. Dietz, and R. D. Rogers, ACS Symp. Ser. 716, Washington, D. C., 1999.
7. D. A. Skoog, F. J. Holler, and T. A. Nieman, *Principles of Instrumental Analysis*, 5th Ed. Philadelphia: Harcourt Brace College Publishers, 1998.
8. R. M. Smith and A. E. Martell, *Critical Stability Constants*, Vol. 6, Plenum Press, New York, NY, p. 96 (1989).

Table 1. AN-107 waste composition, concentrations, and activities

Species	M	Species	M	Species	mCi/L
Na	4.96	K	0.0266	^{241}Am	0.40[a]
Ca	0.010	PO_4^{3-}	0.0076	^{137}Cs	0.034[a]
Fe	0.0094	Al	0.0245	^{239}Pu	0.07[a]
CO_3^{2-}	0.25	free OH^-	0.087[a]	^{90}Sr	56.8[a]
NO_2^-	0.756 ± 0.088[a]	pH	12.4[a]	^{60}Co	0.12[a]
NO_3^-	3.09 ± 0.51[a]	TOC (g/L)	20.74	^{99}Tc	0.0569[a]
^{99}Tc	(3.39 ± 0.13) x 10^{-5} M			^{99}Tc (cpm/mL)	126447 ± 4655[a]
		density (g/mL)	1.253 ±0.003[a]		

[a]determined at LANL

Table 2. Technetium accountability in the Zn^{2+} metathesis decontamination procedure

Fraction #	Eluent	Fraction Vol., mL	^{99}Tc cpm	% Recovered ^{99}Tc	NaI, cpm
1	H_2O	5	8,326	66	22,565
2	H_2O	8	586	4.6	20,314
3	H_2O	8	240	1.9	13,599
4	H_2O	8	38	0.3	7,142
5	1.0 M HNO_3	12	611	4.8	21,056
6	8.0 M HNO_3	16	573	4.5	441,854
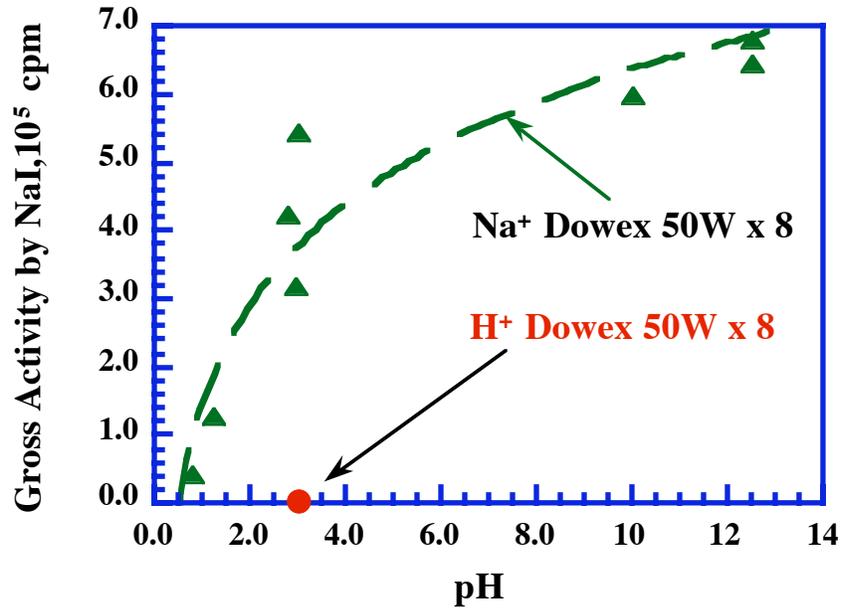
Figure 1. Gross activity in the cation exchange columns eluents as a function of sample pH.
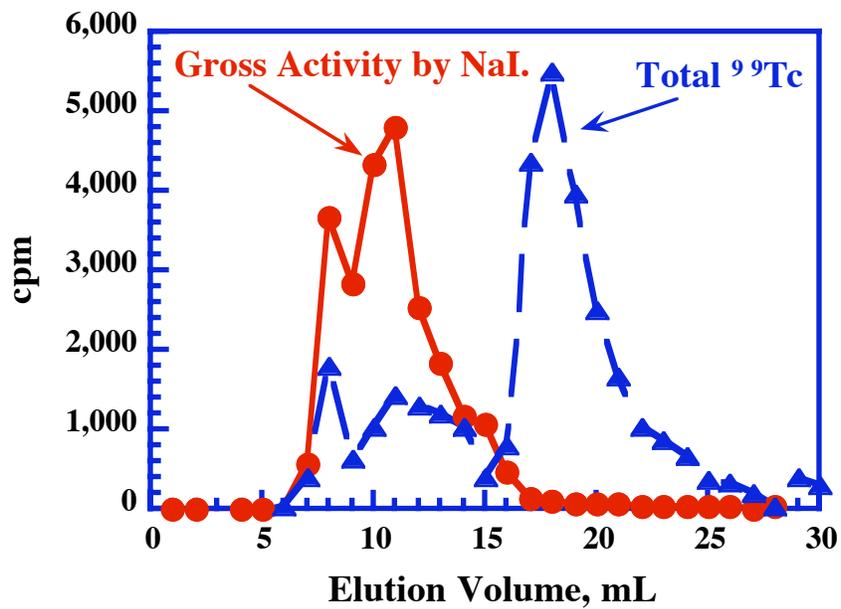
Figure 2. The residual gross activity and the technetium activity eluting off a G-10 column after prior acidification and cation exchange column separation.
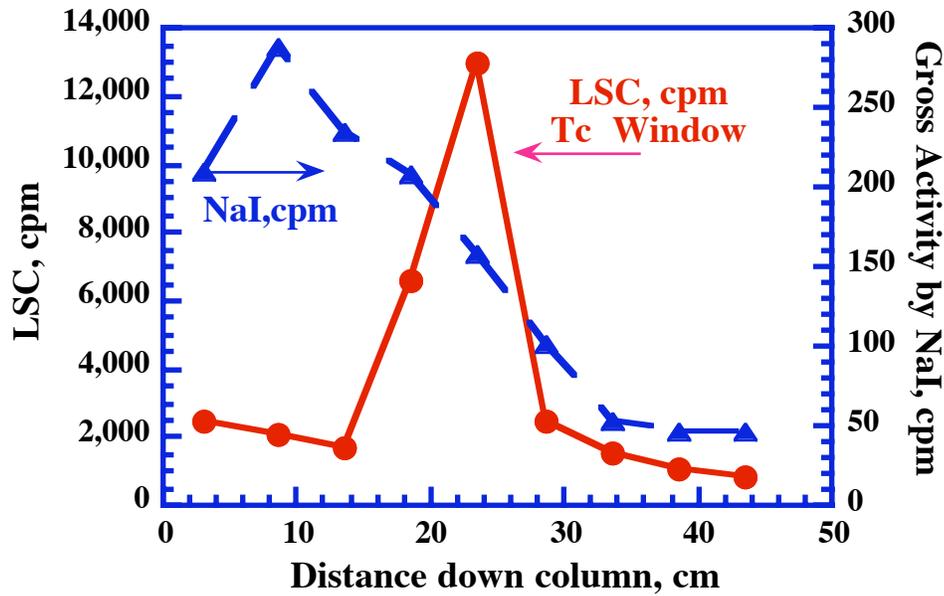
Figure 3. Activities as a function of distance down a G-10 column after elution of the technetium.
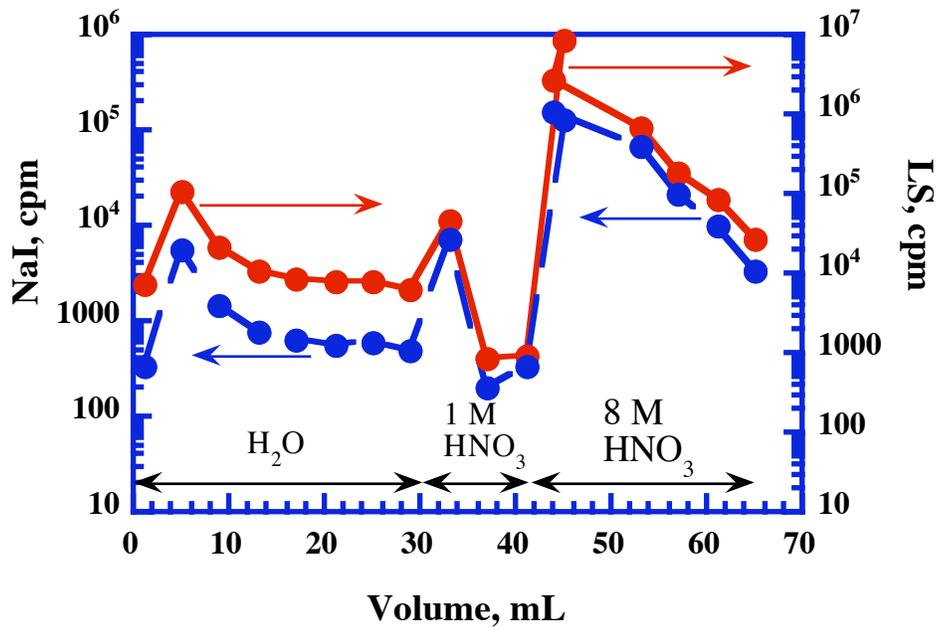
*Figure 4.* Elution of the cation column after sample treatment with Zn^{2+} ion.
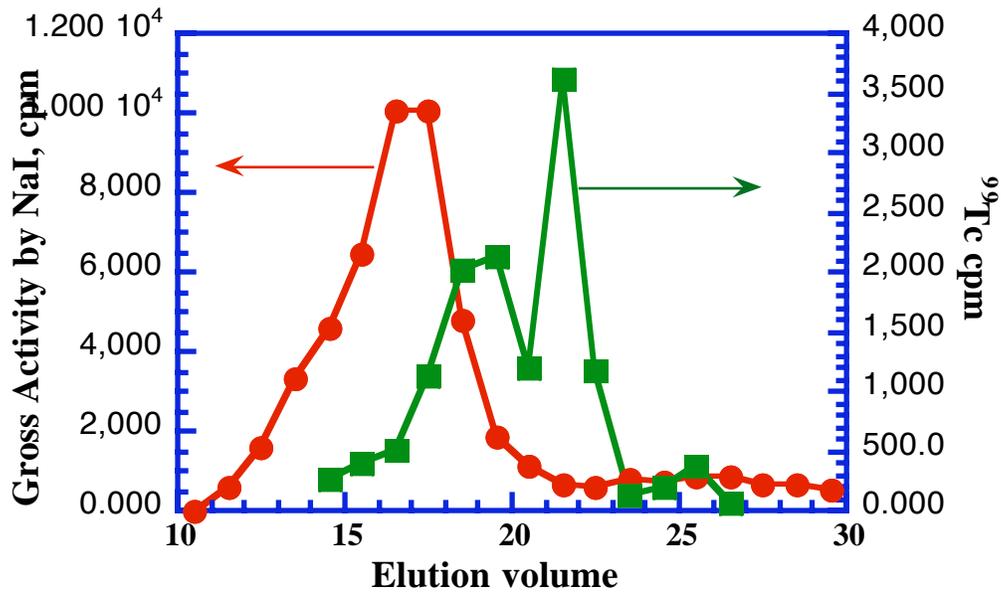
Figure 5. Elution of the G-10 column after prior sample treatment with Zn^{2+} ion and cation exchange column separation.
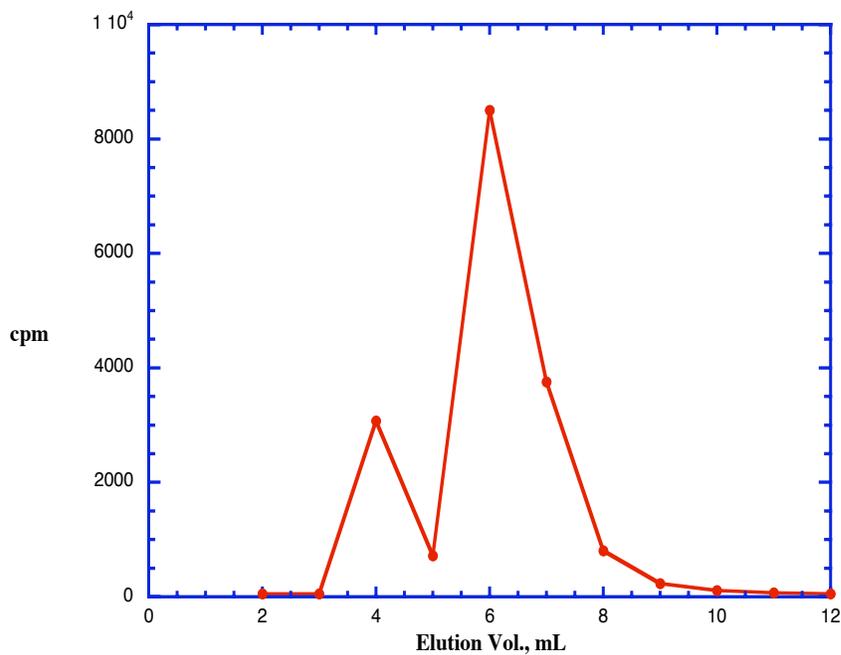
Figure 6. The elution with water of $^{95m}TcO_4^-$ (first peak) and then the $^{99}Tc(gluconate)_x^{-n}$ complex from a 2.0 mL BioGel P-2 column is depicted. The cpm is the activity as measured on the LS counter.
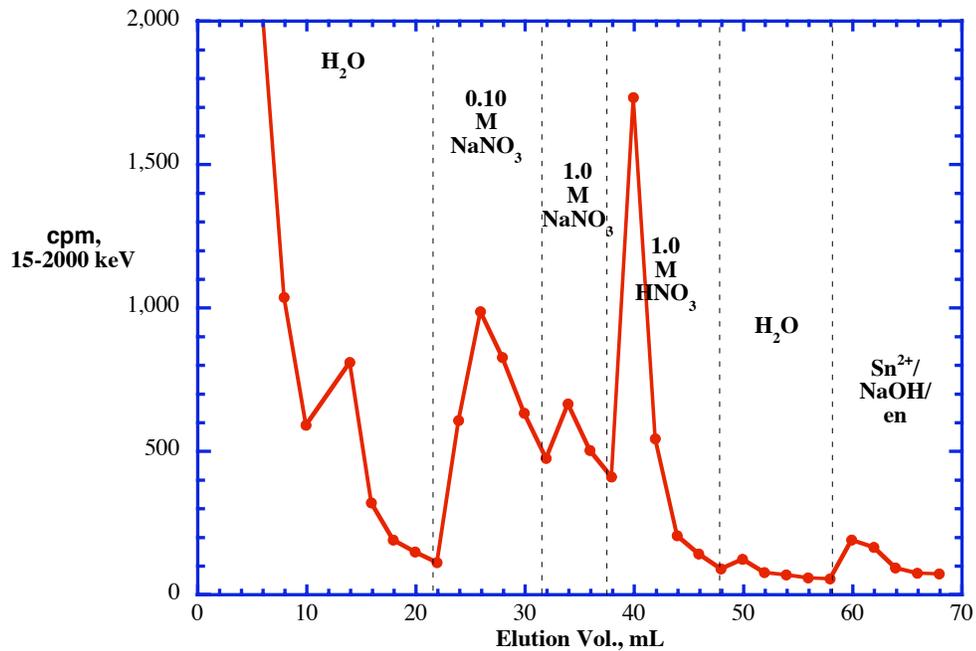
Figure 7. A Zn^{2+}/Dowex column treated sample of AN-107 passed through a second cation column and the effluent added to a Dowex 1x8 anion NO_3^- form exchange column. The eluents are indicated in the Figure.
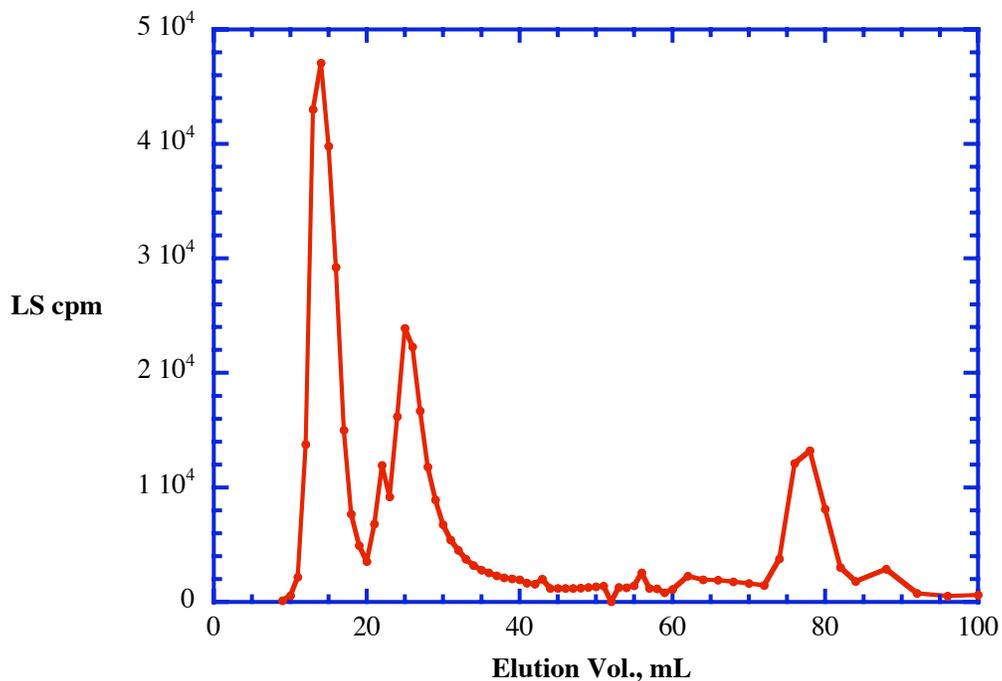

Figure 8. The LS cpm as a function of the elution volume from a 20 mL BioGel P-2 column is graphed. The LS spectra of each peak are in Figure 4.
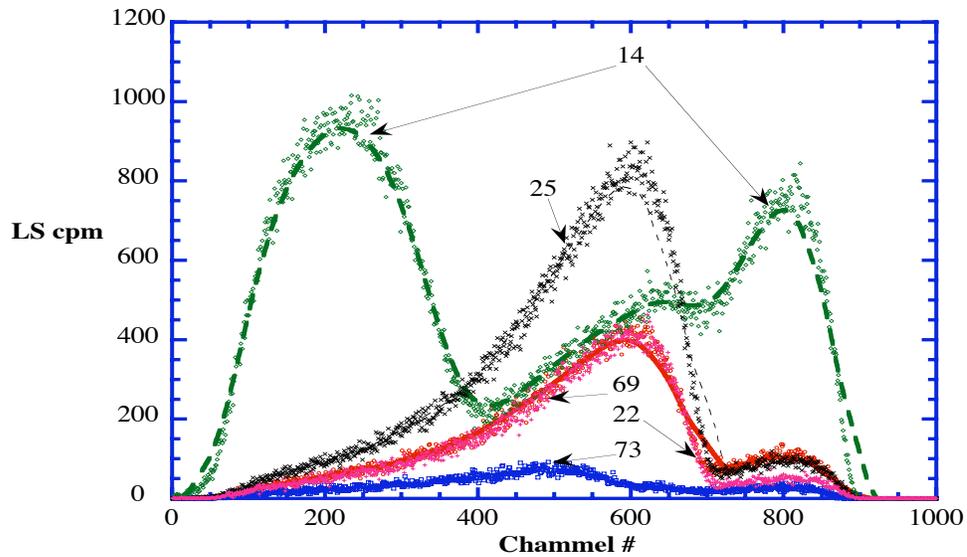
Figure 9. The LS spectra of the peak fractions (numbers in the Figure).The peak at channel # 200 indicates nickle, at channel # 600 indicates strontium, at channel # 850 indicates yttrium, and at channel # 500 indicates technetium.