2

Conf-9209120--1

WSRC-MS--92-141

DE92 040832

Determination of Technetium-99 in Aqueous Samples by Isotope Dilution Inductively Coupled Plasma-Mass Spectrometry (U)

D.M. Beals

A paper proposed for Presentation/Publication
at the 3rd International Conference on
Nuclear and Radiochemistry
Vienna, Austria
7 - 11 September 1992

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U. S. Department of Energy under contract No. DE-AC09-89SR18035

DISCLAIMER

DETERMINATION OF TECHNETIUM-99 IN AQUEOUS SAMPLES BY ISOTOPE DILUTION INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Abstract

An isotope dilution/inductively coupled plasma mass spectrometric method (ID/ICP-MS) for measuring the concentration of technetium-99 in aqueous samples was developed at the Savannah River Technology Center (SRTC). The procedure is faster than radiometric techniques, is also less subject to interferences, and has equal or better detection limits. It is currently being used to measure the concentration of ^{99}Tc in samples of Savannah River water collected in the vicinity of the Savannah River Site.

In this method, one liter samples of water are spiked with ^{97}Tc. After equilibration, the technetium is extracted from the sample with a chromatographic resin. Interfering elements, molybdenum and ruthenium, are either not retained by the resin or are washed off with dilute nitric acid. The technetium is then eluted with more concentrated nitric acid, and the $^{99}Tc/^{97}Tc$ ratio in the eluant is measured with an ICP-MS. The ^{99}Tc concentration in the original sample is calculated from the $^{99}Tc/^{97}Tc$ ratio. The chemical recovery of the extraction procedure is greater than 90%. The detection limit of the instrument, taken as three times the background counts at m/z = 99, is 0.6 part per trillion (ppt). The detection limit of the procedure, taken as three times the standard deviation of several reagent blank analyses, is 0.33 pCi/L.

Introduction

Technetium-99 is produced by the fission of ^{235}U and ^{239}Pu. It is primarily released to the environment through nuclear fuel processing and nuclear weapons testing. Technetium-99 has a half life of 2.12×10^5 years. It is a beta emitter with an E_{max} of 0.292 MeV. In an oxidizing environment technetium exists as the pertechnetate ion, TcO_4^- (Turcotte, 1982). This ion is very mobile in groundwater and surface water. Technetium behaves as a nutrient analog and may be concentrated by plants (Matsuoka, et al., 1990) either through their roots or by absorbing technetium which had been deposited on their outer membranes. In humans and animals the pertechnetate ion localizes in the gastrointestinal tract and thyroid gland (Till, et al., 1979). Analyses of environmental samples are therefore routinely performed near nuclear facilities to monitor the concentration of ^{99}Tc in the environment.

Several methods have been used to analyze for ^{99}Tc in the environment. These methods include concentration of the technetium by anion exchange (Riley and Siddiqui, 1982; Chen, et al., 1990), organic extraction (Golchert and Sedlet, 1969; Chiu, et al., 1992) and/or selective precipitation (Matsuoka, et al., 1990). Technetium-99 activities are often determined with a liquid scintillation spectrometer or gas-flow beta proportional detector. Chemically, technetium is similar to rhenium, another group VIIB element, thus they are difficult to separate from each other. Ruthenium is also difficult to separate from technetium. Ruthenium-106, also a beta emitter, may be released with technetium during nuclear fuel processing. Any radioactive rhenium or ruthenium not separated from technetium may bias results if samples are counted by liquid scintillation or beta proportional detection.

The technetium separation and concentration techniques mentioned above are not quantitative. Chemical recovery of technetium is difficult to determine because technetium has no stable isotope with which to perform gravimetric yield determinations. Technetium-99m (half life of six hours) has been used as a yield tracer (Chen, et al., 1990). The ^{99m}Tc recovery is measured by gamma spectrometry followed by beta counting of the ^{99}Tc one week later. Other procedures call for the analysis of duplicate samples, one spiked with ^{99}Tc. The chemical yield is assumed to be the same for the spiked and the unspiked sample.

Anderson and Walker (1980) developed a procedure to measure ^{99}Tc by thermal-ionization mass spectrometry. Technetium-97 could then be used as a yield tracer and concentration determination by isotope dilution. Recently, Morita, et al, (1991) measured ^{99}Tc by inductively coupled plasma mass spectrometry (ICP-MS). They performed a chemical separation of the technetium to remove the isobaric interference of ^{99}Ru Chemical yield was determined by gamma spectrometry using ^{95m}Tc as a yield monitor. Crain and Gallimore (1992) measured ^{99}Tc by ICP-MS in unconcentrated samples, with a reported detection limit of 6 ppt (part per trillion). However they were measuring the technetium in spiked solutions free of ruthenium.

At the Savannah River Technology Center (SRTC), part of the Savannah River Site (SRS) in Aiken South Carolina, USA, operated by the Westinghouse Savannah River Company for the U.S. Department of Energy, we have developed a procedure to measure ^{99}Tc by ICP-MS, employing a ^{97}Tc tracer for determination of concentration by isotope dilution. A chemical separation technique has been developed which concentrates technetium from one liter water samples. The developed technique also offers decontamination of technetium from ruthenium and molybdenum, which have isobaric interferences at mass 99 and 97, respectively. Using this new

technique we have analyzed river water samples from near the SRS, as well as reagent blank and spike samples.

The detection limit of the developed procedure is less than 0.5 pCi/L. This is similar to procedures which use liquid scintillation or beta proportional counting to measure the ^{99}Tc concentration. However, with the mass spectrometric technique, isotope dilution can be used to correct for chemical recovery through the separation procedure. Also, any ruthenium not separated from the technetium may be identified using mass spectrometry so as not to bias the ^{99}Tc calculated result, rhenium will not interfere with the mass spectrometric measurement of ^{99}Tc. The chemical separation procedure takes approximately one day. Using the autosampler on the ICP-MS, up to four samples per hour can be analyzed which is much faster than counting techniques.

PROCEDURE DEVELOPMENT

Reagents Used

The ^{97}Tc tracer used for sample analyses was prepared at the SRS by neutron activation of calutron enriched ^{96}Ru obtained from Oak Ridge National Laboratory. Approximately 400 ng of ^{97}Tc were produced from the ruthenium. After a cool down period the ^{97}Tc was separated from the ruthenium. The ^{97}Tc concentration of the final solution was calibrated by thermal ionization mass spectrometry and ICP-MS against a dilution of a National Institute of Standards and Technology (NIST) ^{99}Tc standard reference material. All reagents used in the ^{97}Tc separation were ACS reagent grade. Deionized water, when used in this paper, was purified through a Millipore RO unit, providing ASTM type I water. The ^{99}Tc from NIST was diluted to a working concentration with 0.15M NH_4OH, reagent grade NH_4OH in deionized water.

The TEVA-Spec chromatographic resin is commercially supplied by EIChroM Industries, Inc., Darien, IL, with a particle size of 80-160 microns. Columns used to hold the chromatographic resin were Bio-Rad Poly-Prep Chromatography Columns, Richmond, CA. The nitric acid used in the technetium separation procedure was purchased from Seastar Chemicals (Seattle, WA). The Seastar acid was found to have the lowest molybdenum concentration of the commercial acid suppliers.

Equipment Used

ICP-MS measurements were made with a Turner Scientific TS Sola (Manchester England), equipped with both a Faraday detector and an electron multiplier. Due to the unique design features of this instrument detection limits for many elements are in the low to sub ppt range. A Meinhard Type C nebulizer (Precision Glassblowing, Englewood, CO) is used for sample introduction into a Scotts water-cooled spray chamber.

The ICP-MS is housed in a facility operating under class 1000 specifications. A class 100 work area is available for preparing standard dilutions. Argon gas, which has less than 0.001% oxidizable impurities, is supplied to the ICP-MS for use as the plasma gas.

Technetium-99 was used as a spike during procedure development. Mass scans were performed using the electron multiplier detector with a 32 msec dwell time, 16 channels per amu and 16 passes per scan. The instrument sensitivities for technetium, ruthenium and molybdenum were calculated daily. The "direct concentration match" option of the TS Sola software was used to calculate the test samples' concentrations. Test results were averaged over four successive scans. For sample analyses a 16 msec dwell time is used, 16 channels per amu, and 10 passes per scan. The isotope ratio of $^{99}Tc/^{97}Tc$ is determined in 10 successive scans. The TS Sola software allows the use of custom elemental equations. A ^{97}Mo correction is made on the ^{97}Tc based on the ^{95}Mo peak. A correction for ^{99}Ru is made on the ^{99}Tc peak based on the ^{102}Ru peak.

Separation Procedure

A chromatographic extraction resin is used to separate technetium from ruthenium and molybdenum. As seen in Figure 1 TEVA-Spec chromatographic extraction resin (EIChrom Industries, Inc.) has a very high distribution coefficient for retention of technetium at low acid concentrations. Sullivan, et al. (1991) used this property to concentrate technetium from borehole waters. In our initial tests deionized water was spiked with 25 pCi of ^{99}Tc. The laboratory in which this work was performed is not permitted to use higher level radioactive spikes. Following Sullivan, et al. (1991), hydrogen peroxide was added to the sample to ensure the technetium existed as the pertechnetate ion. The samples were then boiled for one hour to decompose the hydrogen peroxide. Samples of up to several hundred milliliters were passed through a column containing two milliliters of the TEVA-Spec resin. The flow rate through the column is extremely slow, thus for 1L or greater samples a batch extraction technique is used. A two milliliter equivalent amount of TEVA-Spec resin is added to the sample and the solution is stirred overnight.

More than 95% of the technetium was absorbed onto the resin as confirmed by analyzing the waste solution on the ICP-MS for remaining ^{99}Tc.

Sullivan, et al. (1991) rinsed the TEVA-Spec with 1M HNO_3 prior to counting the resin by liquid scintillation for ^{99}Tc. The EIChroM Industries product literature states that molybdenum will be eluted off the resin with 2M HNO_3. After the sample had passed through the resin, the column was washed with 50 mL of 1M HNO_3. If the sample was batch extracted with the resin, the resin was allowed to settle and the supernate decanted. The remaining solution and resin were then transferred to a column for the 1M HNO_3 rinse and elution. Less than 5% of the technetium was eluted with 50 mL of 1M HNO_3.

To elute the technetium from the resin various concentrations of nitric acid were tested. More than 70% of the technetium was eluted using 20 mL of 4M HNO_3, more than 90% of the technetium was eluted using either 20 mL of 6 or 8M HNO_3. By increasing the 4M HNO_3 volume to 30 mL more than 90% of the technetium was eluted from the resin (Table 1).

Decontamination Studies

Due to the isobaric interferences of ^{97}Mo with the ^{97}Tc tracer and ^{99}Ru with the ^{99}Tc to be measured the decontamination factors for these elements for the previously described procedure were determined. Molybdenum and ruthenium were added to deionized water to make the final concentration 10 ppb of each element. The initial solution contained 1.4 ppt of ^{99}Tc (24 pCi/L). The instrument is sensitive enough to measure ^{99}Tc at 1.4 ppt, but the signal would be masked by the ^{99}Ru peak. The samples were then passed through the TEVA-Spec column, washed with 50 mL of 1M HNO_3, and finally eluted with 30 mL of 4M HNO_3. All fractions were analyzed by ICP-MS.

An ICP-MS mass spectrum from each fraction is shown in Figures 2-4. As seen in Figure 2 ruthenium was not retained by the TEVA-Spec resin. The major peaks of ruthenium are present in the correct ratios in the column waste solution (the 18.7% peak at mass 104 was not measured). Upon washing the column molybdenum was eluted from the resin but not technetium as shown in Figure 3. The ^{92}Mo and ^{94}Mo peaks were not measured but all other molybdenum peaks are present in the correct ratios in the 1M HNO_3 wash solution. A small amount of ruthenium was also present in the wash solution. Figure 4 shows the recovered ^{99}Tc spike peak in the final 4M HNO_3 elution solution. More than 99% of the starting molybdenum was separated from the final technetium elution, more than 99.6% of the initial ruthenium was separated.

In an attempt to improve the decontamination factors for ruthenium and molybdenum from technetium some variations on the above separation scheme were performed. 1M HCl was substituted for the 1M HNO_3 column wash. The ruthenium decontamination was unchanged however only 10% of the molybdenum was washed from the column with the dilute HCl. The remaining molybdenum eluted off the column with the technetium in the 4M HNO_3 solution. The chemical recovery of the technetium was decreased by increasing the 1M HNO_3 to 100 mL or using 50 mL of 2M HNO_3 as a wash solution. The decrease in yield was not offset by a significant increase in molybdenum decontamination.

The procedure was chosen that resulted in high chemical recoveries of technetium and acceptable decontamination from ruthenium and molybdenum, as described below. The sample is passed through a column containing two milliliters of TEVA-Spec resin, washed with 50 mL of 1M HNO_3, eluted with 30 mL of 4M HNO_3. Depending on the starting solution a small amount of ruthenium and molybdenum may remain in the final solution to be analyzed by ICP-MS, as seen in Figure 4. The molybdenum and ruthenium concentration, as well as isotopic ratios, of a sample can be determined prior to sample analysis. Then the appropriate amount of ^{97}Tc tracer to be added to the sample can be calculated such that the final molybdenum contribution at m/z = 97 can be kept to less than 10% of the ^{97}Tc contribution. If a large amount of ruthenium is present in the starting solution an additional ruthenium decontamination by organic extraction is needed to achieve the desired detection limit. In stream samples collected near the SRS the initial ruthenium and molybdenum concentrations are less than 1 ppb and so additional ruthenium decontamination was not required.

SAMPLE ANALYSES

The instrument response factor (RF) for technetium was determined by measuring the counts per second at m/z = 99 of a solution of known ^{99}Tc concentration.

$$RF = (\text{counts/second})\ (\text{mass})/(\text{concentration in ppm})$$

Under our operating conditions of the TS Sola the response factor for ^{99}Tc on the electron multiplier detector averages 1.2×10^9. The instrument detection limit, defined as three times the background counts/sec at m/z = 99, was calculated to be 0.6 ppt. A typical scan of deionized water in the technetium mass region is shown in Figure 5. The peak at mass m/z = 96 is most likely Ar_2O^+. The peak at m/z = 104 is suspected to be SrO^+.

Figure 6 shows a spectra of a reagent blank prepared by the procedure discussed above. The ^{97}Tc tracer peak is more than ten times greater than the ^{97}Mo at m/z = 97 based on the ^{95}Mo peak. The source of the molybdenum contamination in this blank is not clear. After correcting the peak at m/z = 99 for ruthenium, based on the ^{102}Ru peak, and correcting the m/z = 97 peak for molybdenum, the $^{99}Tc/^{97}Tc$ is 0.0025. The calculated ^{99}Tc concentration for this blank is 3 pg per sample, or 0.05 per Ci/L.

When analyzing several samples consecutively it was noted the background at m/z = 99 rose steadily. Between sample analyses 10% HNO_3 and deionized water washes were each passed through the tubing of the autosampler to the nebulizer and the spray chamber for three minutes. Crain and Gallimore (1992) noted a memory effect when analyzing higher levels of ^{99}Tc but believed it to be a chemical effect as changing from 10% HNO_3 to 2% HNO_3 lowered the m/z = 99 background. Decreasing the nitric acid concentration did not reduce the apparent background, however we found that rinsing the sample intake tubing, nebulizer and spray chamber with 10% NH_4OH decreased the m/z = 99 background to baseline values.

The sample analysis procedure at the SRTC consists of purging the autosampler tubing, nebulizer and spray chamber with 10% HNO_3, deionized water, 10% NH_4OH, and then again deionized water (three minutes each) prior to introducing the sample to the plasma for the $^{99}Tc/^{97}Tc$ measurement. The actual sample analysis, including sample introduction, takes approximately three minutes resulting in four samples analyzed per hour. As the ICP-MS is easily programmed for automatic analysis this is an acceptable sample throughput.

River samples to be analyzed for ^{99}Tc by the SRTC are collected in precleaned plastic bottles by hand dipping the mouth of the bottle below the water surface. Upon returning to the lab the sample volume is measured, typically 1 L of sample is used for analysis, and the sample transferred to a glass beaker and a known quantity of ^{97}Tc (1.2 ng for 1 L stream samples) is added to the sample. Hydrogen peroxide is added to the sample in amount equal to 1% by volume. The sample beaker is covered with a watch glass and brought to a boil for one hour. After cooling, the technetium is adsorbed onto the TEVA-Spec resin. The resin is washed with 50 mL of 1M HNO_3 and the technetium is eluted with 30 mL of 4M HNO_3. The diluted nitric acid is made with the Seastar acid. The eluant is collected in precleaned plastic bottles and transferred to the ICP-MS lab to be analyzed as described above.

Samples collected from the Savannah River, which flows along the border of the SRS, were analyzed by the above procedure. Technetium-99 concentrations varied from 0.31 to 0.72 pCi/L as shown in Table 2. The mean and standard deviation (1 sigma) of several blank samples are 0.22 ± 0.11 pCi/L. Some samples of deionized water were spiked with known amounts of ^{99}Tc and then analyzed by the developed procedure. The calculated and the expected results are shown in Table 3.

A procedure is also being developed to analyze acid digested samples for ^{99}Tc. Air filters, that had been digested in strong acids, were spiked with ^{97}Tc , neutralized with NH_4OH and analyzed by the above procedure. The chemical recovery of the technetium appears to be similar to that of the water samples. There is also an interest in analyzing the leachate from vegetation and soil samples for ^{99}Tc. It appears that after leaching, the acid may be neutralized with NH_4OH and then analyzed as a water sample.

Conclusions

A procedure was developed at the SRTC to determine the ^{99}Tc concentration in aqueous samples. We are currently measuring the ^{99}Tc concentration in streams in the vicinity of the SRS in South Carolina, USA, using ID/ICP-MS. We plan to extend the technique to measure ^{99}Tc concentrations in air filters, stack monitors, vegetation and soil. The procedure detection limit, while sensitive enough for environmental monitoring purposes, may be made more sensitive by increasing the sample size or using an ultrasonic nebulizer for sample introduction into the ICP-MS. ID/ICP-MS can be used to map the global distribution of ^{99}Tc. It can be used to measure fallout from nuclear weapons testing and to monitor the release of ^{99}Tc to the environment from nuclear facilities.

Acknowledgements

The author would like to extend her thanks to Sara Green and Sharon Redd, Senior Laboratory Technicians, who performed many of the chemical separations for these analyses. Turner Spectrometry offered many helpful suggestions on setting up the ICP-MS protocol.

The information contained in this manuscript was developed during the course of work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

References

Anderson, T. J. and R. L. Walker, 1980, "Determination of Picogram Amounts of Technetium-99 by Resin Bead Mass Spectrometric Isotope Dilution", *Analytical Chemistry, Vol. 52, No. 4, pp. 709-713.*

Chen, Qingjiang, H. Dahlgaard, H. J. M. Hansen and A. Aarkrog, 1990, "Determination of ^{99}Tc in Environmental Samples by Anion Exchange and Liquid-Liquid Extraction at Controlled Valency", *Analytica Chimica Acta, Vol. 228, pp. 163-167.*

Chiu, Jih-Hung, Tieh-Chi Chu and Pao-Shan Weng, 1992, "Extraction of Technetium-99 by Complexation with Ammonium Tetramethylenedithiocarbamate into Chloroform and its Application to the Determination of Technetium-99 in Low-Level Radioactive Wastes", *Analytica Chimica Acta, Vol. 256, pp. 293-299.*

Crain, J. S. and D. L. Gallimore, 1992, "Inductively Coupled Plasma-Mass Spectrometry of Synthetic Elements: ^{99}Tc, *Applied Spectroscopy, Vol. 46, No. 3, pp 547-549.*

Golchert, N. W. and Jacob Sedlet, 1969, "Radiochemical Determination of Technetium-99 in Environmental Water Samples", *Analytical Chemistry, Vol. 41, No. 4, pp 669-671.*

Matsuoka, N., T. Umata, M. Olamura, N. Shiraishi, N. Momoshima and Y. Takashima, 1990, "Determination of Technetium-99 from the Aspect of Environmental Radioactivity", *Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 140, No. 1, pp. 57-73.*

Morita, S., C. K. Kim, Y. Takaku, R. Seki and N. Ikeda, 1991, "Determination of Technetium-99 in Environmental Samples by Inductively Coupled Plasma Mass Spectrometry", *Appl. Radiat. Isot., Vol. 42, No. 6, pp. 531-534.*

Riley, J. P. and S. A. Siddiqui, 1982, "The Determination of Technetium-99 in Seawater and Marine Algae", *Analytica Chimica Acta, Vol. 139, pp. 167-176.*

Sullivan, T., D. Nelson and E. Thompson, 1991, "Determination of Technetium-99 in Borehole Waters Using an Extraction Chromatographic Resin", *From the Workshop on Extraction Chromatography presented at the 37th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, Ottawa, Canada.*

Till, J. E., F. O. Hoffman and D. E. Dunning, Jr., 1979, "A New Look at ^{99}Tc Releases to the Atmosphere", *Health Physics, Vol. 36 (January), pp. 21-30.*

Turcotte, M.S., 1982, "Environmental Behavior of Technetium-99", DP-1644, *E.I. du Pont de Nemours & Co., Savannah River Laboratory, DOE Contract # DE-AC09-76SR00001.*

Table 1

Elution of Tc from TEVA-Spec resin

Acid Concentration	Volume (mL)	% Tc removed (average)
4M HNO_3	20	74
6M HNO_3	20	91
8M HNO_3	20	93
4M HNO_3	30	91

Table 2

^{99}Tc Results from the Savannah River

location	concentration (at 95% CL)
Shell Bluff	0.31 ± 0.21 pCi/L
Above Vogtle	0.65 ± 0.13 pCi/L
Below Vogtle	0.53 ± 0.27 pCi/L
Hwy 301	0.72 ± 0.46 pCi/L

Table 2

^{99}Tc Spike Results

expected	calculated (at 95% CL)
0.48 pCi/L	0.57 ± 0.20 pCi/L
2.39 pCi/L	2.12 ± 0.50 pCi/L
9.58 pCi/L	6.74 ± 1.57 pCi/L

Figure Captions

Figure 1. Acid Dependency of TC Retention TEVA-Spec

Figure 2. Column Waste

Figure 3. 1M HNO_3 Wash

Figure 4. 4 M HNO_3 Elution

Figure 5. Deionized Water Blank

Figure 6. Process Regeant Blank

Figure 7. Typical Sample Spectra

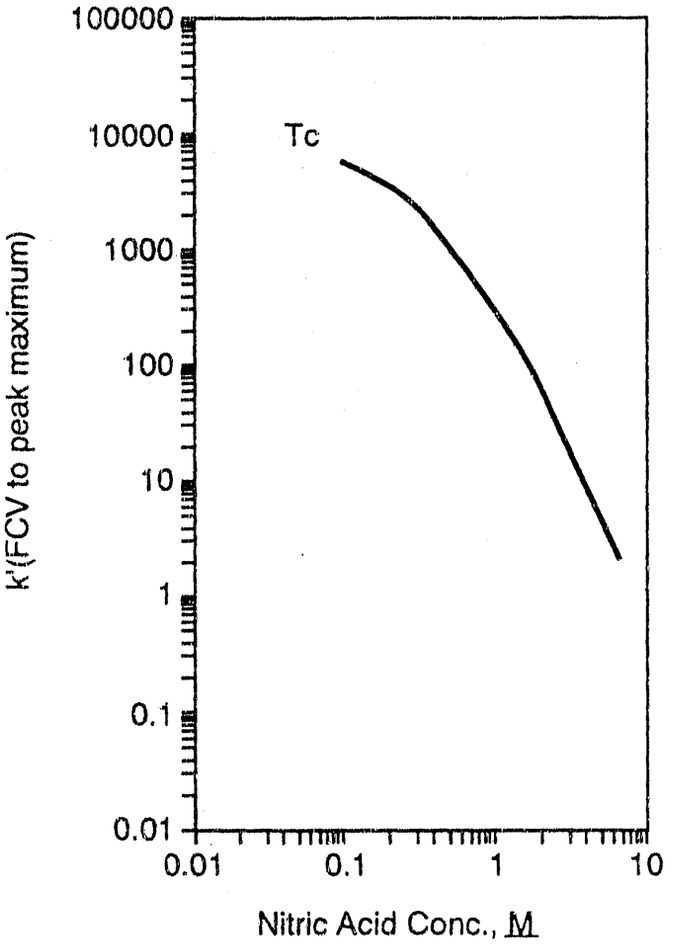

FIGURE 1. Acid Dependency of TC Retention TEVA•Spec

M92G035.01

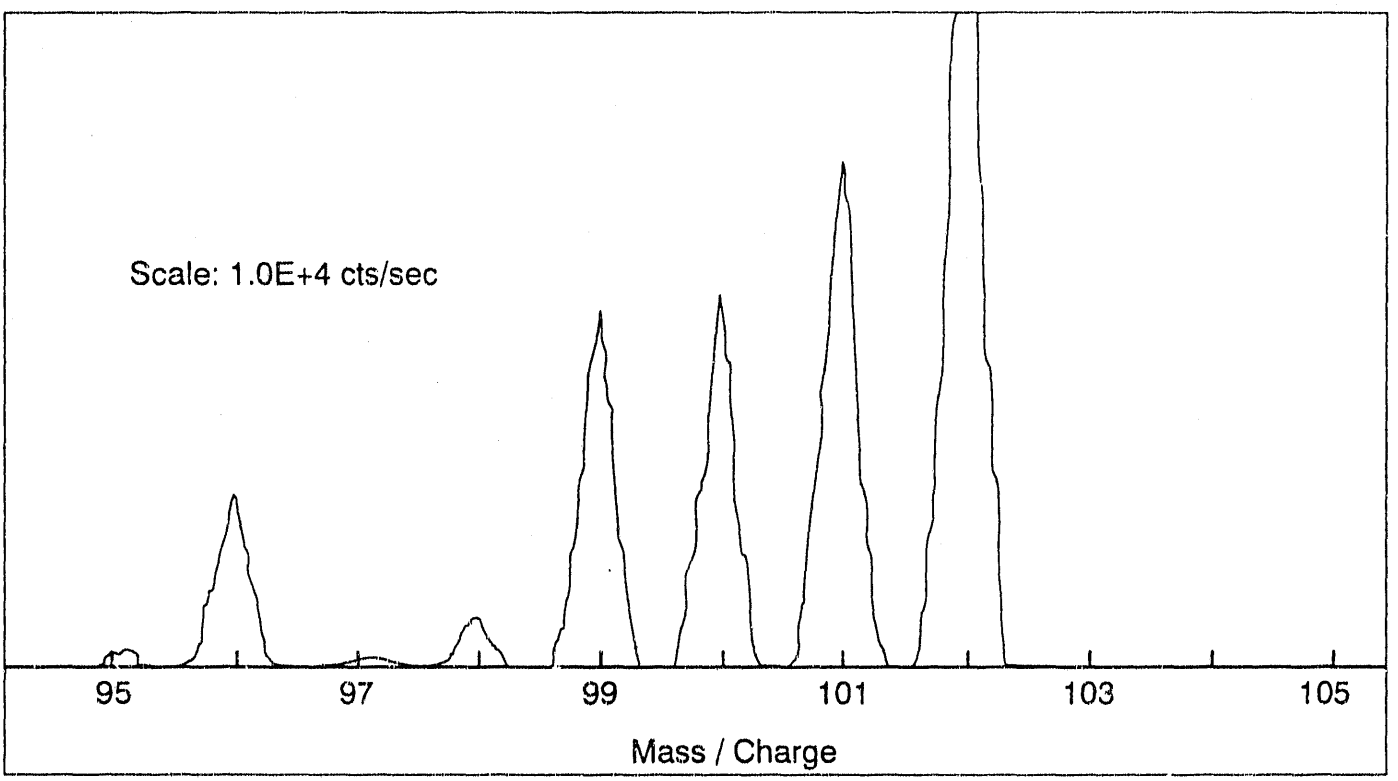

Figure 2. Column Waste

M92G035.02

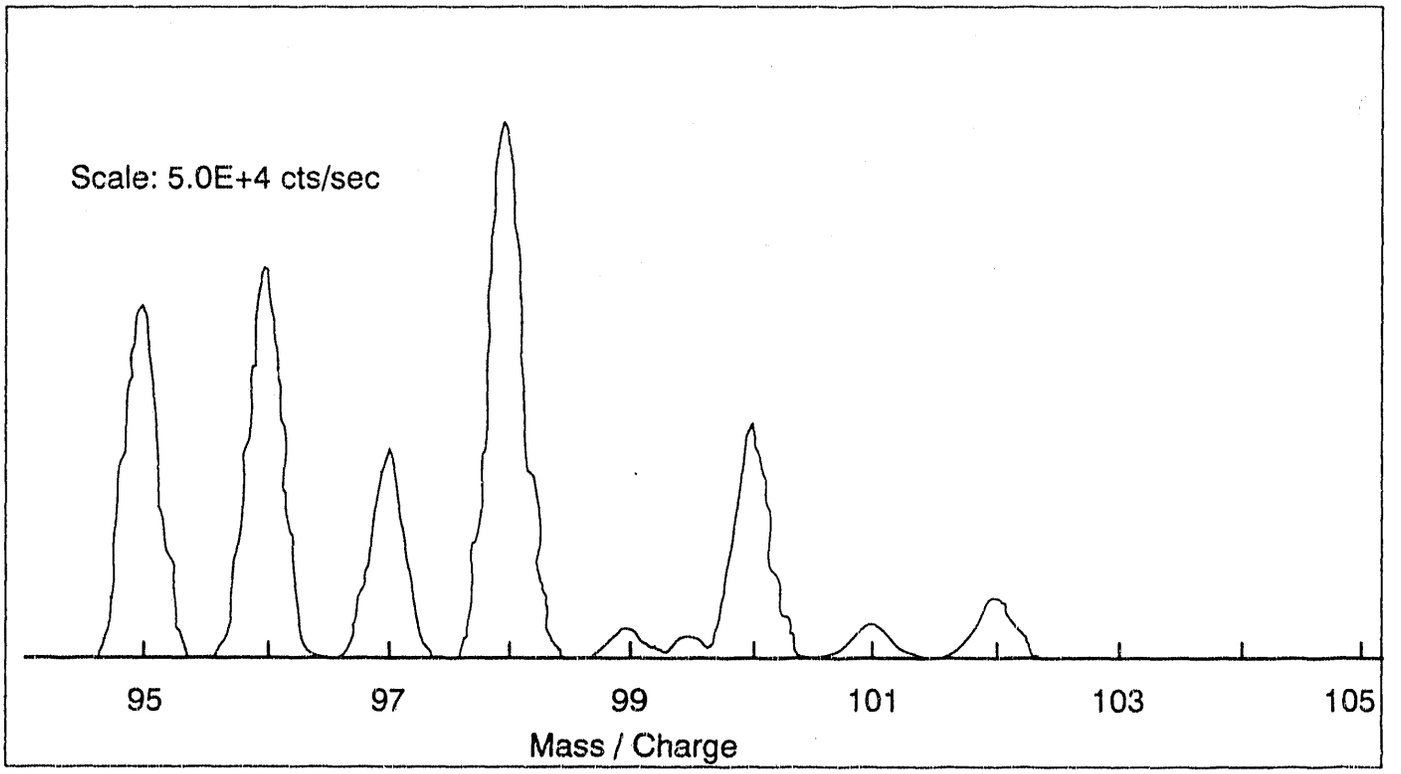

Figure 3. 1M NNO_3 Wash

M92G035.03

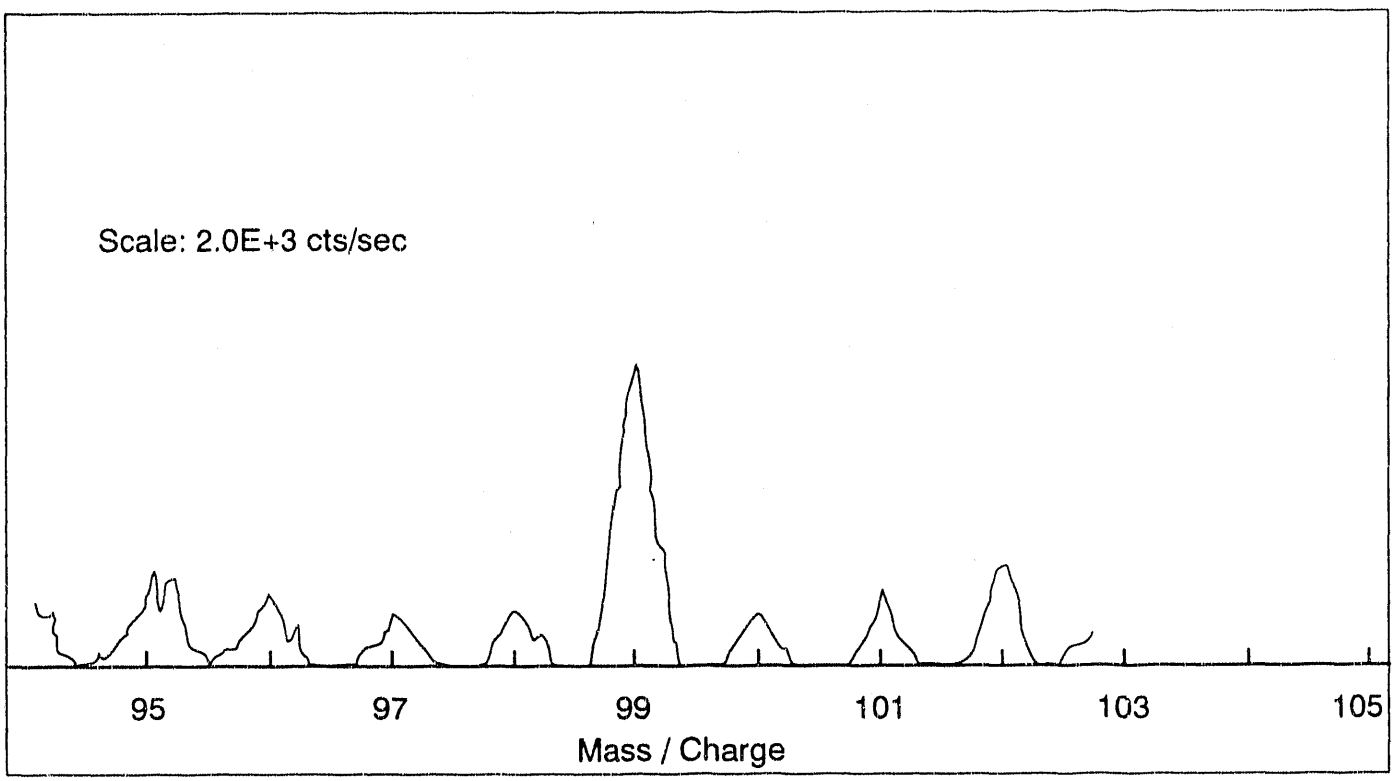

Figure 4. 4M HNO_3 Elution

M92G035.04

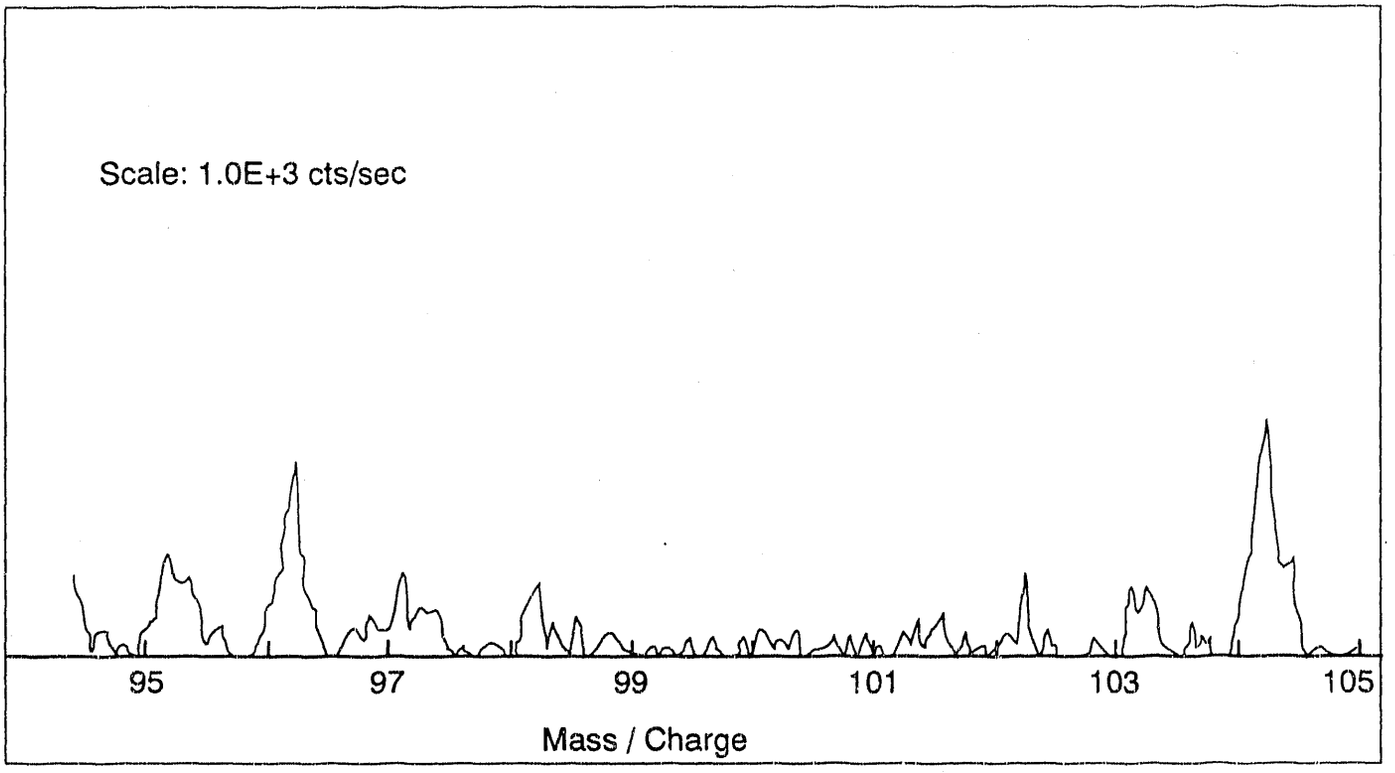

Figure 5. Deionized Water Blank

M92G035.05

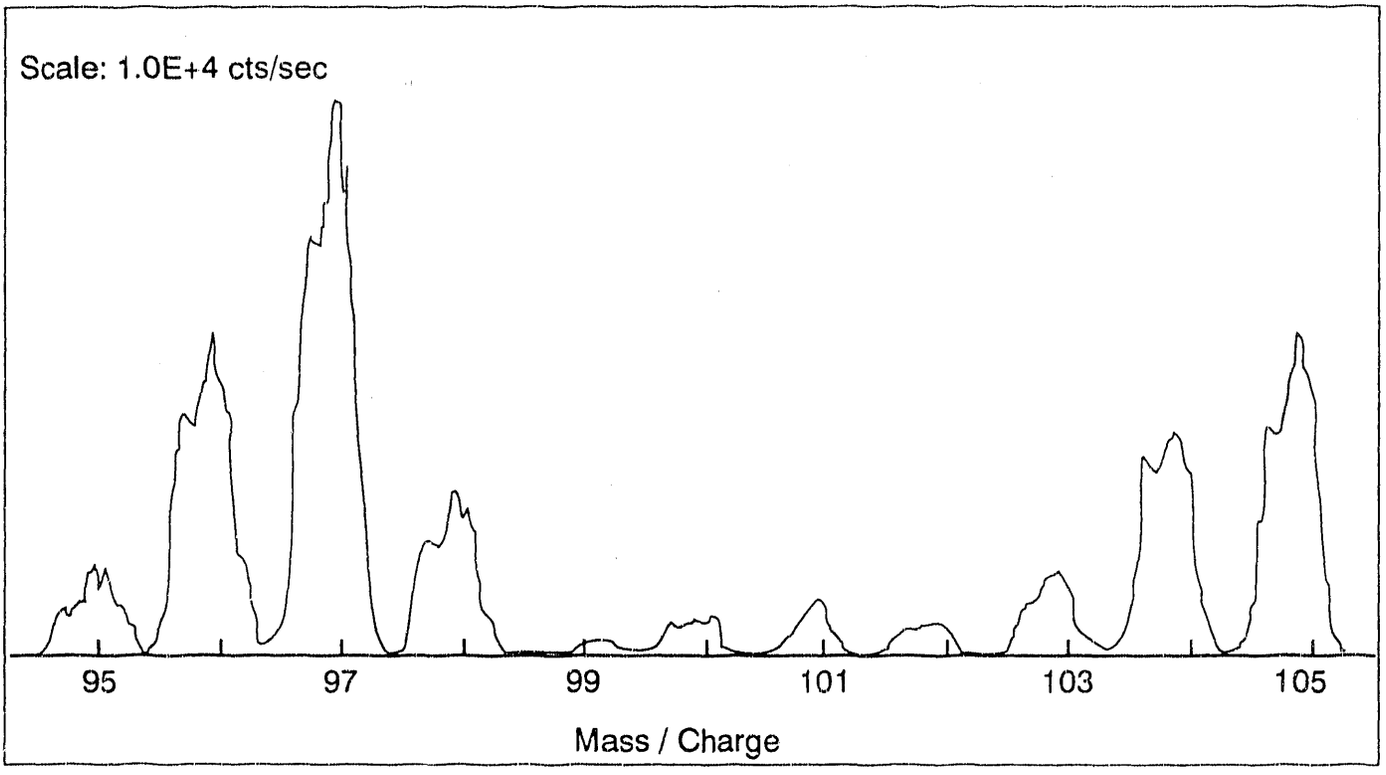

Figure 6. Process Regeant Blank

M92G035.06

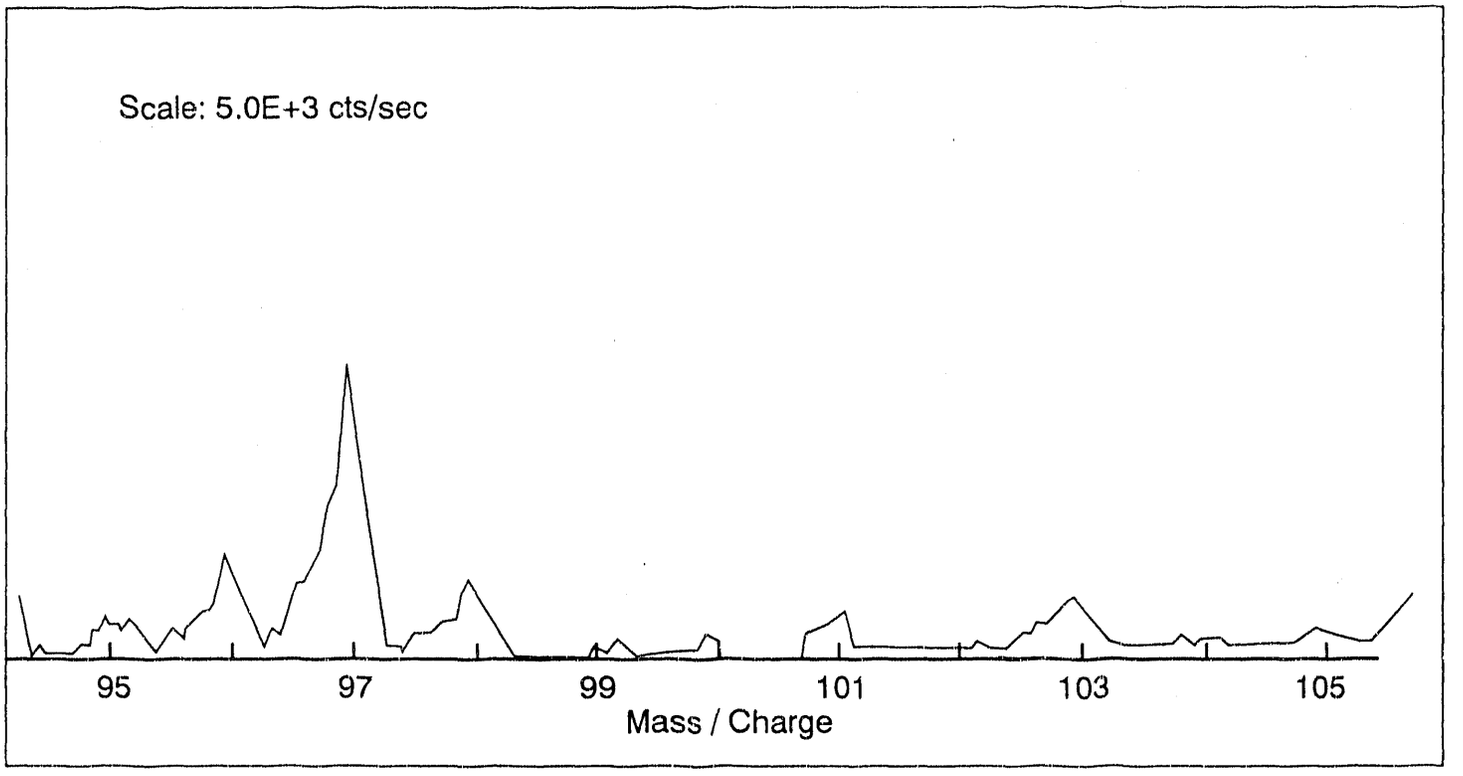

Figure 7. Typical Sample Spectra

M92G035.07

END

DATE FILMED

11/17/92