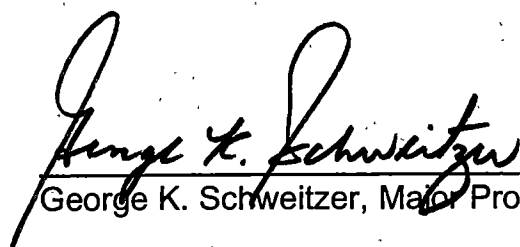
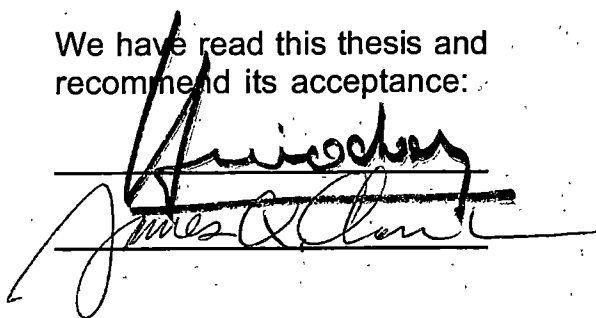


To the Graduate Council:

I am submitting herewith a thesis written by Juli L. Miranda entitled "Determination of ^{99}Tc in Urine by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID/ICP-MS)." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.


George K. Schweitzer, Major Professor

We have read this thesis and
recommend its acceptance:


James A. Clark

Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

**DETERMINATION OF ^{99}Tc IN URINE BY ISOTOPE DILUTION
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ID/ICP-MS)**

**A Thesis
Presented for the
Master of Science Degree**

The University of Tennessee, Knoxville

**Juli L. Miranda
December 1999**

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ABSTRACT

A method for the determination of ^{99}Tc in urine employing isotope dilution inductively coupled plasma mass spectrometry (ID/ICP-MS) was developed. In this procedure, the urine sample was spiked with a known amount of ^{97}Tc and digested using peroxide and nitric acid. Isobaric interferents, ^{97}Mo and ^{99}Ru , were removed using extraction chromatography. Mass to charge ratios of 95, 97, 99 and 102 were monitored for quantitating the concentration of ^{99}Tc in the samples. Measurements made at the 10^{-9} M level for ^{99}Tc had with an average relative error of 4% for a known concentration, an average relative standard deviation of 3% for twelve runs, and a detection limit of 1.1×10^{-11} M for 3 s.

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CHAPTER I

INTRODUCTION

Technetium, element 43, was first synthesized and isolated in 1937 by Perrier and Segrè.¹ There are no stable isotopes of technetium in nature. Of the known 21 radioisotopes of technetium, all but three have half-lives ($t_{1/2}$) less than 60 days.² ^{97}Tc , ^{98}Tc and ^{99}Tc have half-lives of 2.6×10^6 y, 4.2×10^6 y and 2.1×10^5 y, respectively. ^{99}Tc is the decay product of ^{99}Mo which is formed by the activation of stable molybdenum³ or by the fission of ^{235}U and ^{239}Pu . The nuclear fission of ^{235}U and ^{239}Pu produces high yields (6.3% and 6.1%, respectively)⁴ of ^{99}Tc . ^{99}Tc eventually decays to ^{99}Ru . The decay scheme for ^{99}Tc is seen in Figure 1. Due to its long half-life and large fission production yield, ^{99}Tc is one of the most important nuclides to be monitored in environmental samples.

^{99}Tc is released into the environment mainly due to nuclear fuel reprocessing, nuclear power production, nuclear weapons testings, and to a lesser extent by disposal of $^{99\text{m}}\text{Tc}$ from medical diagnostic procedures. The gamma decay of $^{99\text{m}}\text{Tc}$, $t_{1/2} = 6.0$ h, leads to the formation of ^{99}Tc . In the environment, technetium is found as the volatile heptaoxide, Tc_2O_7 , or as the very soluble and highly mobile pertechnetate ion, TcO_4^- . The ease of mobility results in accumulation in plants through their roots or absorption through their outer membranes.^{3, 5-7} In humans and animals, the pertechnetate ion is found to localize in the thyroid gland, gastrointestinal tract, stomach, liver and

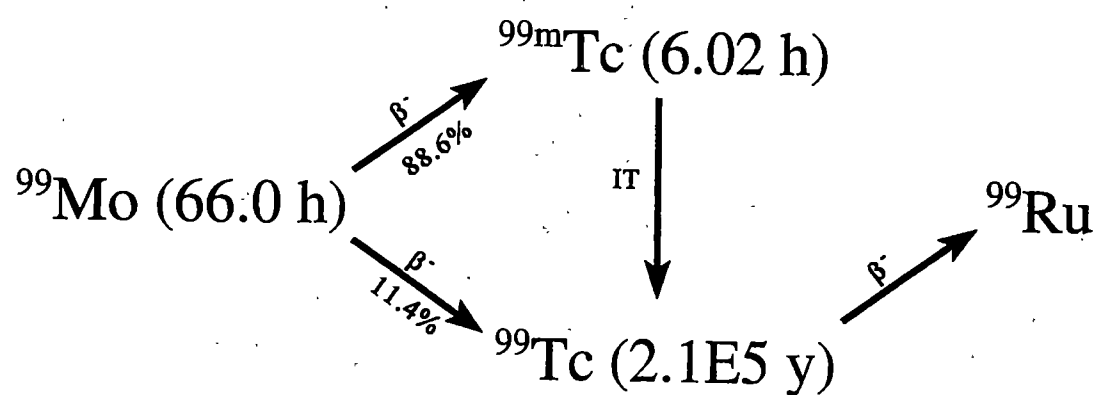


Figure 1. Decay Scheme for ^{99}Tc

Source: Kocher, D.C., Radioactive Decay Data Tables, Office of Scientific and Technical Information U.S.D.O.E., DOE/TIC-11026, (1988).

bladder.⁸⁻¹⁰ The determination of ^{99}Tc , a pure beta emitter with a maximum energy of 293.6 keV and an average energy of 84.6 keV, is conventionally performed using radiochemical analysis. An alternative method is inductively coupled plasma-mass spectrometry (ICP-MS), which is based on the mass to charge ratio (m/z) of the ions involved and can be used to determine the activity of nuclides with long half-lives.

A. RADIOMETRIC METHODS OF ^{99}Tc DETECTION

Beta decay includes the processes of positron emission (β^+), negatron emission (β^-) and/or electron capture (EC). In all beta decay, the mass number of the nucleus remains unchanged while the atomic number changes. In β^- emission, negative electrons are emitted, and the atomic number is increased by one unit, whereas the atomic number is decreased by one unit in β^+ emission.¹¹ The atomic number is also decreased by one unit in EC decay, but through the spontaneous incorporation of an atomic electron into the nucleus.

The activity of ^{99}Tc in a sample is usually determined using a liquid scintillation spectrometer¹²⁻¹³ or a low background gas-flow proportional counter.^{3, 14-24} Sample preparation for liquid scintillation counting or gas-flow detection is typically carried out in a fashion such that attenuation, self-absorption, and/or chemical or color quenching is at a minimum. Chemical separation of ^{99}Tc from interfering β -emitting radionuclides that may be present in the sample must be performed in addition to extracting the nuclide from the

sample matrix. Techniques that are used for the isolation of ^{99}Tc include ion exchange,^{7, 13 - 16, 18, 25} coprecipitation,^{3, 7, 12, 14 - 16, 18 - 22, 24 - 25} and solvent extraction.^{3,}

^{14 - 25} Any interferent not removed prior to analysis will invalidate results.

Neutron activation analysis (NAA) can also be performed for the determination of picogram amounts of ^{99}Tc using a thermal neutron flux of about $5 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.²⁶ After irradiation, ^{99}Tc is determined from the activity of ^{100}Tc , $t_{1/2} = 16 \text{ s}$, which is produced by the (n, γ) reaction. Other activation analyses based on the formation of $^{99\text{m}}\text{Tc}$ in an (n, n') reaction²⁷ and in a (γ, γ') reaction with bremsstrahlung radiation²⁸ are also used for the determination of ^{99}Tc . Although activation analysis is very sensitive, only a limited number of laboratories have the facilities to perform this type of analysis.

Chemical recovery, by means of gravimetric yield, is difficult to determine because technetium has no stable isotopes. Studies have been conducted using rhenium as an internal tracer,^{14 - 16} as well as several of the short-lived technetium isotopes, including $^{97\text{m}}\text{Tc}$ ¹⁴ and $^{99\text{m}}\text{Tc}$,^{3, 17 - 23} as internal yield monitors. Using these isotopes requires delayed analysis employing other detection methods like gamma spectroscopy and low background Geiger-Muller counting. Another method of yield determination involves adding a known activity of ^{99}Tc to one of a pair of samples and analyzing both in an identical manner.^{7, 24} In this carrier-free radiochemical method, it is assumed that the factors that influence recovery are the same in both samples.

A variety of matrices, including soil,¹⁶ water, e.g., sea,^{7, 16 - 18, 22} surface,^{3, 14, 15, 24} and waste,^{3, 13, 20} vegetation, e.g., lichens,³ seaweed,^{5, 7, 16, 18, 22} and vegetables,²³ air filters,^{3, 21} low level radioactive waste,¹⁹ and urine¹² samples have been analyzed for ⁹⁹Tc by radiometric methods.

B. MASS SPECTROMETRIC METHODS OF ⁹⁹TC DETECTION

The ICP-MS method of analysis is based on the measurement of the mass of the nuclide rather than its radioactive emission. In ICP-MS the sample in solution is nebulized and passed through a spray chamber into an argon plasma. The high temperature of the plasma, about 7000 K, causes atomization and ionization of the sample. The ions produced are introduced into a quadrupole mass spectrometer where they are separated according to their m/z .⁶

ICP-MS is usually less susceptible to spectral interferences than inductively coupled plasma-optical emission spectrometry (ICP-OES). Isobars, species having the same mass number but different atomic numbers, are the major interferences in ICP-MS, and therefore, a chemical separation is often necessary to achieve accurate results. A variety of methods can be performed to achieve the separation and include ion exchange,^{2, 4, 29 - 39} chromatographic extraction,^{40, 41} coprecipitation,^{6, 29, 33, 35} and solvent extraction.^{4, 6, 26, 29 - 33, 35, 42} The formation of doubly charged or polyatomic ions in the plasma or ion extraction

interface with the same m/z of the nuclide of interest can also cause problems in the analysis.

Determination of ^{99}Tc in a urine matrix by ICP-MS has not been reported in the literature, but other matrices such as environmental samples (water and soil) and various nuclear waste forms have been tested.^{4, 29 - 33, 37, 38, 40 - 42} As with radiochemical determination of ^{99}Tc , the ICP-MS method necessitates an internal yield monitor for quantitation of the nuclide of interest. Several researchers employ the use of $^{95\text{m}}\text{Tc}$,^{29, 31, 33, 42} while another uses $^{99\text{m}}\text{Tc}$.³² Both internal yield monitors require radiochemical determination in addition to determining ^{99}Tc by ICP-MS. The method of standard addition can be used to circumvent the need for an internal yield monitor.³⁷ Another useful technique is isotope dilution. In this method, a known concentration of a nuclide is spiked into all samples and the samples are analyzed. The ratio of the counts from both nuclides, the one of interest and the spike, is multiplied by the concentration of the known nuclide to give the concentration of the unknown nuclide. In order to perform isotope dilution, no isobaric interferences can be present in the peaks measured. This procedure is used for the determination of ^{99}Tc in a water matrix using ^{97}Tc for isotope dilution.^{40, 41}

C. PROPOSED PROBLEM

From a radiological protection perspective, all employees that perform decommissioning and decontaminating processes at nuclear sites

contaminated with the long lived ^{99}Tc isotope require monitoring for exposure. As stated previously, few articles have been published concerning ^{99}Tc in urine using conventional radioanalytical methods, and none have been published determining ^{99}Tc in urine by ID/ICP-MS. Presently, at the Oak Ridge, TN Department of Energy Y-12 Site, ^{99}Tc in urine is determined using a standard addition method by spiking one of a pair of identical urine samples with a known concentration of ^{99}Tc , analyzing both samples using ICP-MS, determining the percent recovery, and calculating the analytical result based on the recovery.

A numerical example of this method is illustrated. In the standard addition method aliquot 1 is urine while aliquot 2 is urine with a known concentration, 200 pM, of ^{99}Tc added. After preparation and analyzing both samples by ICP-MS, aliquot 1 is found to contain 50 pM ^{99}Tc and aliquot 2 is found to contain 240 pM ^{99}Tc . The difference of between the two acquired numbers, 190 pM, is the experimentally determined concentration of ^{99}Tc that was added to aliquot 2. Dividing 190 pM by the known concentration of ^{99}Tc added, 200 pM, the percent recovery, 95%, is calculated. Assuming that any factors that influence recovery are the same in both samples, the actual concentration of ^{99}Tc in aliquot 1 can be ascertained by dividing the acquired value for aliquot 1, 50 pM, by the percent recovery in decimal form, 0.95, thus yielding 53 pM.

The objective of this research is to develop a method for the determination of ^{99}Tc in a urine matrix using ^{97}Tc as a reference isotope and isotope dilution inductively coupled plasma-mass spectrometry (ID/ICP-MS) for analysis. Isotope dilution measures the change in the ratio of signal intensities for two selected isotopes of an element of interest after the addition of a known quantity of one of these isotopes.

For comparison purposes, a numerical example of the proposed method, for an ideal sample, for ^{99}Tc is depicted. A known concentration, 125 pM, of ^{97}Tc is added to an aliquot of urine suspected to contain ^{99}Tc . The sample is then prepared and analyzed at m/z 99 as well as m/z 97 in a single scan. By dividing the cps of ^{99}Tc , 400, by the counts of ^{97}Tc , 2000 cps, the $^{99}\text{Tc}/^{97}\text{Tc}$ ratio is calculated, 0.20. Because a known concentration of ^{97}Tc was added prior to analysis, this value can be multiplied by the $^{99}\text{Tc}/^{97}\text{Tc}$ ratio to give the actual concentration of ^{99}Tc in the sample. $125 \text{ pM} \times 0.20 = 25 \text{ pM}$. By incorporating a method using isotope dilution, only one sample aliquot is necessary for analysis, rather than the two required for the standard addition method and a calibration curve is not needed for quantitation.

To accomplish this goal, a variety of tasks were completed including conditioning the resin, separating isobaric interferences, quantitating the ^{97}Tc solution, determining a method for urine matrix digestion, and assessing the elution acid concentration.

CHAPTER II

BACKGROUND

A. ICP-MS ANALYSIS OF ^{99}Tc

Since the first commercial ICP-MS was introduced in 1983, the technique has gained rapid and wide acceptance in analytical laboratories for the analysis of geological, environmental, water, medical, biological, metallurgical, nuclear, and industrial samples. Over the last ten years, ICP-MS has been used to determine the concentration of long-lived radionuclides. The advantages of ICP-MS over traditional radioanalytical methods include simultaneous multi-element analysis, shorter measurement times, lack of interferences caused by ionizing emissions from other radionuclides present in the sample, lower detection limits, and higher precision and accuracy. There are also disadvantages related to ICP-MS that require careful consideration. Removal of any spectral interferences such as isobars, polyatomic ions, and doubly charged ions, in addition to, the reduction of the total dissolved solid content must be accomplished during sample preparation.

The earliest research using ICP-MS for the determination of ^{99}Tc was reported in the literature by Kim et al.³⁰ In this work, soil samples are ashed at 450°C and leached using 8 M HCl. The leachate is extracted with isopropyl ether. The aqueous layer is evaporated, redissolved in 1 M HNO_3 and extracted with 5% tri-isooctylamine (TIOA). The fraction containing the technetium is then stripped with 1 M NaOH and passed through a Dowex 1-X8, OH form anion

exchange column. The column is washed with 1 M NaOH, 1 M HCl, and 0.1 M HNO₃, and the technetium is eluted with 8 M HNO₃. The mass spectrum for the soil samples contains a peak at an m/z of 99, as well as interfering peaks at 98, 100, 101 and 102. Molybdenum has naturally occurring isotopes at masses of 98 and 100 with abundances of 24.13% and 9.63%, respectively. Ruthenium isotopes are present at masses 98, 99, 100, 101 and 102 with abundances of 1.86%, 12.7%, 12.6%, 17.1% and 31.6%, respectively.

In 1991, Morita et al.³² used ^{99m}Tc to measure the chemical recovery of ⁹⁹Tc for various solvent extraction reagents. It is found that technetium can be more effectively extracted with cyclohexanone/1 M K₂CO₃ than TIOA or tributylphosphate (TBP). By adding hydrogen peroxide prior to carrying out the cyclohexanone extraction, the hydrogen peroxide oxidizes the ruthenium into an inextractable oxidation state, and the ruthenium remains in the aqueous layer during extraction. Nearly complete removal of ¹⁰¹Ru and ¹⁰²Ru is observed and confirmed by measuring the decontamination factor for ruthenium.

Ihsanullah³⁵ assessed a variety of different separation methods to determine the degree of removal of ruthenium. The separation methods include precipitation, elution with NaOH, ion exchange, and extraction into various organic compounds, including cyclohexanone, chloroform, 5%TIOA-xylene, carbon tetrachloride, and tri-n-butylphosphate. Technetium recovery (%) and ruthenium decontamination factors (DF) are calculated for each method. The DF is calculated in the following manner:

$$DF = \frac{100\% \text{ Ru added}}{\% \text{ Ru remaining}} \quad \text{Eqn. 2.1}$$

The following data are reported for each method: precipitation, 83% recovery and a DF of 345; NaOH elution, 90.6% recovery and a DF of 160; cyclohexanone extraction, 98% recovery and a DF of 1000; chloroform extraction, 1% recovery and a DF of 1; 5% TIOA-xylene extraction, 98% recovery and a DF of 700; carbon tetrachloride extraction, 90% recovery and a DF of 700; TBP extraction, 80% recovery and a DF of 4000; and ion exchange, 90% recovery and a DF of 10. Thus, adequate decontamination of ruthenium is achieved by a single or a combination of procedures.

When incorporating anion exchange as the method for removing ruthenium, significant amounts of molybdenum is observed to elute from the Dowex 1-X8 resin. Ihsanullah³⁶ performed various experiments to establish the amount of molybdenum present in the resin, as well as removal of the molybdenum from the resin. Large amounts of ⁹⁸Mo and ¹⁰⁰Mo can interfere with the determination of low level concentrations of ⁹⁹Tc due to peak overlap. To check for the presence of molybdenum, a sample containing a known amount of ⁹⁹Tc is passed through the resin, analyzed by ICP-MS over the mass range of 91 to 104 and compared to the spectrum of the same solution that is not passed through the resin. Peaks at m/z 92, 94, 95, 96, 97, 98 and 100, indicative of molybdenum, are found to be elevated in the sample that is passed through the resin and are minimal in the blank solution not passed

through the resin. Once the presence of molybdenum is established, Ihsanullah carries out several tests including elution of molybdenum from the resin using 4, 8, 12, and 16 M HNO_3 , elution of molybdenum using 2, 4, 6, and 8 mL of resin, elution of molybdenum with 1 M HCl , and elution of molybdenum with 3 M NaOH to assess the removal of molybdenum. In general, a trend of decreasing counts (corrected with ^{103}Rh) at ^{95}Mo occurs with each 10 mL aliquot of nitric acid. Also, the ^{95}Mo counts observed in the eluent increase with increasing acid concentration. For example, the first 20 mL of 4 M HNO_3 rinse show 1449 counts whereas the first 20 mL of 16 M HNO_3 rinse generate 2916 counts. It is concluded from this work and another study performed by Ihsanullah,³⁴ that 5 mL of Dowex 1-X8 resin, an eluant of 12 M HNO_3 , and an elution flow rate of 0.2 - 0.3 mL/min yield the best molybdenum removal.

Besides isobars, the formation of polyatomic and doubly charged ions and their effect on analysis is of great importance. The tendency of these spectral interferences to occur is evaluated by Crain and Gallimore.³⁹ By analyzing a prepared 10 mg/L ^{99}Tc sample in 2% (v/v) HNO_3 and comparing the ratios of oxide, hydroxide, and doubly charged ion formation for technetium with those for lanthanum and thorium, it can be concluded that technetium did not form an oxide and doubly charged ions as easily as do the lanthanide and actinide elements. This work shows that TcO^+ is observed to form at a rate of 0.03% relative to the parent ion. This percentage is not deemed to interfere significantly with the internal standard, ^{115}In , used in the work presented here.

However, the analysis did show that technetium appears to form oxides, such as TcO_2^+ , more readily than other elements.

The determination of very low-levels of ^{99}Tc in seawater by ICP-MS was developed by Momoshima et al.³¹ Because of the low concentration, it is necessary for the ^{99}Tc in the sample to be enriched prior to precipitation, separation, and quantitation. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2\text{S}_2\text{O}_5$, a reducing agent, are added to the sample. Iron hydroxide is precipitated using NaOH and dissolved using HCl and H_2O_2 . $^{95\text{m}}\text{Tc}$ is added at this point as the tracer, and the iron hydroxide is precipitated again with NaOH and scavenged. Evaluation of the background counting rates at m/z 99 show that various extracting reagents purify ^{99}Tc , including methyl ethyl ketone (MEK), cyclohexanone, and tetraphenyl arsonium chloride (TPAC). Momoshima found MEK to be the only suitable extracting reagent for very low-level ^{99}Tc analysis by ICP-MS. After extraction in 5 M NaOH , the sample solution is passed through an anion exchange resin and washed with 30 mL of 1 M HNO_3 and 30 mL of 0.1 M HNO_3 . The technetium is eluted with 30 mL of warmed 16 M HNO_3 , passed through a cation exchange resin in 1 M HNO_3 , and analyzed by gamma spectrometry for $^{95\text{m}}\text{Tc}$ and by ICP-MS for ^{99}Tc . Actual seawater samples analyzed by this procedure have an average ^{99}Tc recovery of 49.5% with concentrations of ^{99}Tc ranging from 1.1 to 7.4 $\mu\text{Bq/L}$ ($1\text{Bq/L} = 16.2\text{ pM}$ for ^{99}Tc). These are one to two orders of magnitude lower than can be obtained from radiochemical methods.

Nicholson et al.⁶ also developed a method for the determination of low levels of ^{99}Tc in seawater, seaweed, and sediment similar to that of Momoshima et al. In addition to using TBP as an extractant, Nicholson incorporates an additional extraction step using MEK. Chemical recoveries ranging from 50 - 70% are slightly improved over Momoshima et al. The instrument detection limit, based on three standard deviations of the blank, is calculated to be 30 mBq. Discrimination ratios, the ratio of the mass of the element in solution before the chemical separation to that afterwards, for several polyatomic interferences are assessed, including $\text{ZnCl}^+ = 2000$, $\text{NiCl}^+ = >2800$, $\text{CoAr}^+ = 7 \times 10^5$ and $\text{MoH}^+ = 1600$, while the isobaric ruthenium discrimination factor is determined to be 1000.

A sequential method for the determination of ^{99}Tc and ^{237}Np in soil samples was developed by Sumiya et al.³³ in 1995. The following steps are carried out in preparing the sample for analysis of ^{99}Tc by ICP-MS and of $^{95\text{m}}\text{Tc}$ by gamma spectrometry: iron hydroxide coprecipitation, solvent extraction using TBP/xylene, anion exchange separation, and a second extraction with cyclohexanone, K_2CO_3 , and carbon tetrachloride. For this procedure a decontamination factor for ^{106}Ru is calculated to be 1.9×10^5 . The use of an ultrasonic nebulizer for sample introduction results in a detection limit for ^{99}Tc of 2.1 mBq/L.

Within the past three years, the method of ID/ICP-MS has been used for the determination of ^{99}Tc in water samples by Beals.^{40, 41} In this procedure, 1 L

samples of water are spiked with a known amount of ^{97}Tc , 1% by volume of H_2O_2 is added, brought to a boil for 1 h, cooled, passed through a column containing 2 mL of TEVA-Spec resin, washed with 50 mL of 1 M HNO_3 , eluted with 50 mL of 4 M HNO_3 , and analyzed. The ^{99}Tc concentration is calculated from the $^{99}\text{Tc}/^{97}\text{Tc}$ ratio. A decontamination study of molybdenum and ruthenium is carried out because of the isobaric interferences of ^{97}Mo with the ^{97}Tc in the standard and ^{99}Ru with ^{99}Tc in the sample. After analyzing the load, rinse, and elution fractions, it is found that the ruthenium is not retained by the resin, the molybdenum is washed off the resin with the 1 M HNO_3 rinse, and the technetium is eluted with the 4 M HNO_3 . More than 99% of the starting molybdenum and 99.6% of the starting ruthenium are separated from the final technetium elution. If large amounts of molybdenum or ruthenium are present, corrections of m/z 97 and 99 can be carried out, based on the natural abundances of ^{95}Mo and ^{102}Ru peaks, respectively.

CHAPTER III

ANALYTICAL INSTRUMENTATION

The inductively coupled plasma-mass spectrometer (ICP-MS) used for this research was a Fisons Instruments VG PlasmaQuad ICP20P equipped with a Gilson sample changer. An ICP-MS^{43, 44} is comprised of 6 main components: sample introduction system, inductively coupled plasma, ion extraction interface, ion focusing lenses, quadrupole mass spectrometer, and ion detection system. Each of these components is depicted in Figure 2 and described below. The instrumental parameters used during this research are listed in Table 1.

A. ICP-MS COMPONENTS

1. Sample Introduction System

The sample is introduced into the ICP by pneumatic nebulization. A peristaltic pump delivers the sample to the spray chamber where a high velocity stream of argon gas contacts the solution and disrupts its flow creating a spray of droplets. The sample aerosol is forced through the spray chamber, where only the smallest droplets, usually less than 8-10 μm in diameter, are supplied to the plasma. Approximately 1% of the sample solution is transported into the plasma in these small droplets. Pneumatic nebulization, although inefficient, has maintained its popularity due to convenience and stability. The larger droplets that do not reach the plasma condense against

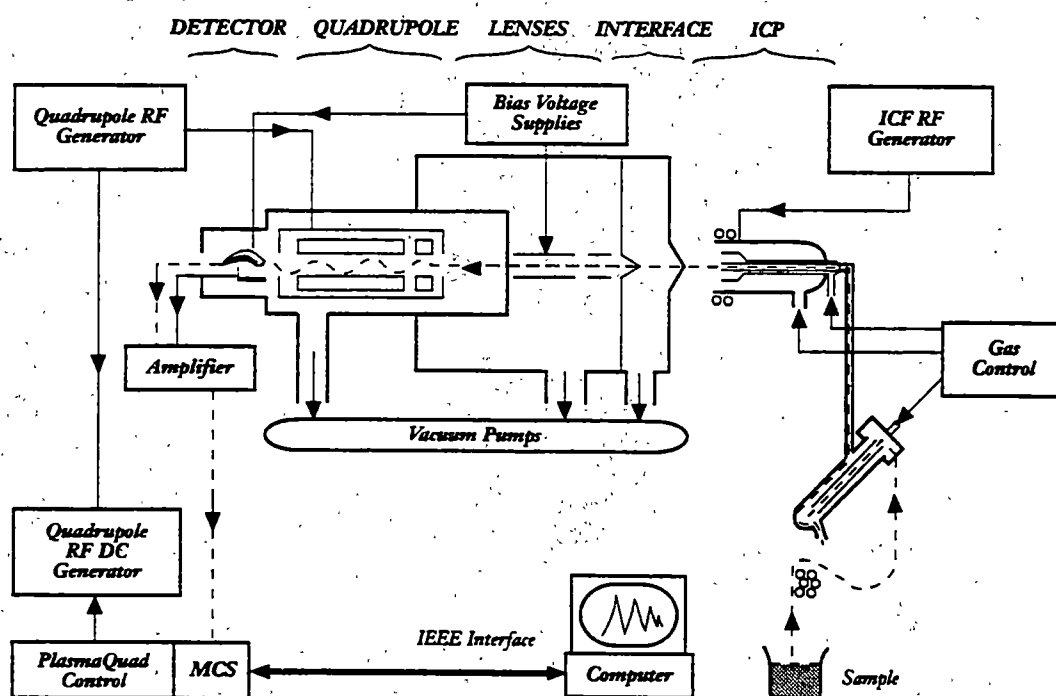


Figure 2. Diagram of ICP-MS

Source: PlasmaQuad System Manual, FI Elemental Analysis, Fisons Instrument (1992).

TABLE 1

INSTRUMENT CONFIGURATION FOR ICP-MS MEASUREMENTS

ICP-MS		
Nebulizer argon flow (L/min)		0.950
Auxiliary argon flow (L/min)		0.930
Cooling argon flow (L/min)		13.25
Power (W)		1350
Reflective power (W)		5
Sample flow (mL/min)		0.8
Interface		
Sample Cone		Nickel
Skimmer Cone		Nickel
Acquisition Parameters ^a		
Acquisition time (s)		60
Dwell time (ms)		45
Time per Sweep (s)		0.95
Scan Mode		Peak-jumping
Counting Mode		Pulse
Replicates		3
Vacuum Pressures		
Expansion (mbar)		1.9×10^0
Interface (mbar)		0.0×10^{-4}
Analyzer (mbar)		2.1×10^{-6}

^aUnless specified otherwise.

the water cooled sides of the spray chamber and are pumped out by another peristaltic pump to a waste container.

2. Inductively Coupled Plasma (ICP)

The ICP is an electrodeless discharge in argon gas at atmospheric pressure, maintained by energy coupled to it from a radio frequency generator.⁴³ The plasma is created by a spark from a Tesla coil, which provides free electrons to couple with the magnetic field. The plasma is produced at the end of and inside a quartz glass torch. The most popular torch used is a 'Scott Fassel' style which can be seen in Figure 3. A coolant gas, also argon, is pumped at a rate of 10-15 L/min into the outermost region of the torch to protect and cool the inner torch walls. An auxiliary gas flow prevents the plasma from melting the tip of the central tube and typically has a flow rate of about 1-2 L/min. A third gas flow, at 1 L/min, is the nebulizer gas which carries the aerosol from the sample introduction system into the plasma. Once in the plasma, the sample aerosol is rapidly desolvated, volatilized, dissociated, and ionized by the high temperatures.

3. Ion Extraction Interface

The ions in the plasma are sampled and transported into the ion focusing lens stack. An illustration of the ion extraction interface is shown in Figure 4. The ions in the plasma are sampled by a water cooled pure nickel

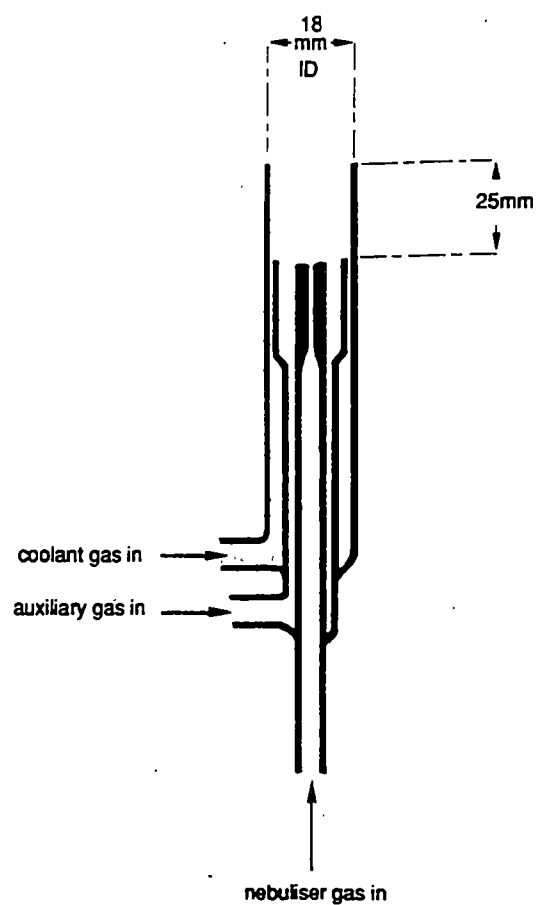
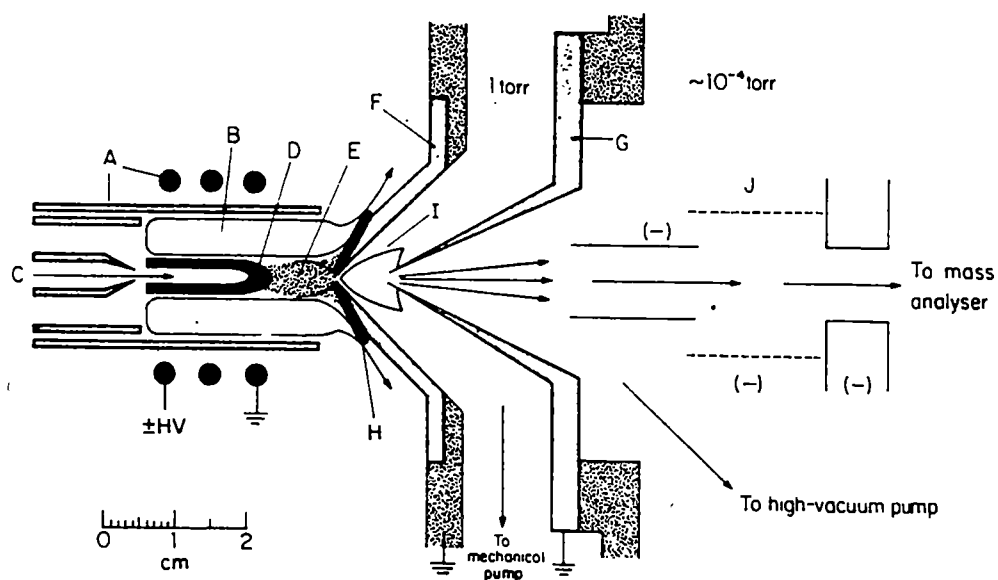


Figure 3. 'Scott Fassel' Torch Design

Source: Jarvis, K., Gray, A.L., *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, New York, NY, Chapman and Hall (1992).



A. Torch and load coil
 B. Induction region
 C. Aerosol gas flow
 D. Initial radiation zone
 E. Normal analytical zone

F. Sample cone
 G. Skimmer cone
 H. Boundary layer
 I. Supersonic jet
 J. Ion lens

Figure 4. Ion Extraction Interface

Source: Jarvis, K., Gray, A.L., *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, New York, NY, Chapman and Hall (1992).

1.0 mm aperture sample cone into a pumped vacuum system where a supersonic jet is formed due to the pressure differential across the aperture. The jet consists of a freely expanding region called the zone of silence surrounded by two shock waves called the barrel shock and Mach disc.⁴³ The central section of the zone of silence flows through a pure nickel 0.7 mm aperture skimmer cone which is seated inside the Mach disc. The region between these two cones is the expansion chamber and is maintained at a pressure of 2 mbar. As the plasma strikes the surface of the sampling cone, a boundary layer is formed. The temperature of this boundary layer is in between the temperatures of the plasma and the cone, and therefore oxide formations can result. Matrix effects occur if ions from this region are sampled. A skimmer cone with a smaller opening than the sample cone reduces these effects. The extraction process takes approximately 3 μ s under the above conditions.

4. Ion Focusing Lenses

After the ions pass through the skimmer cone, the ion optic lenses focus the charged species through a differential aperture and into the quadrupole mass filter. The ion optics system is comprised of several symmetrical electrostatic lens elements on the system axis and a lens power supply unit.⁴⁴ A negative potential applied to the extraction lens causes the ions to move at a constant velocity toward the actual lens stack. Negatively charged ions are repelled, and neutral atoms and molecules diffuse away and are pumped out

of the system by the intermediate stage pump. The intermediate chamber is evacuated to below 10^{-4} mbar. The ions are then passed through the collector electrode and around an on-axis photon-stop which prevents light and any stray neutral species from being detected by the electron multiplier. After the ions are deflected around the photon-stop, they are focused by lens elements L1 and L2 through the differential pumping aperture. Lenses L3 and L4 refocus the ions into the entrance aperture of the quadrupole mass spectrometer.

Figure 5 shows the ion lens geometry. Prior to sample analysis, the extraction lens, collector lens, and ion focusing elements L1, L2, L3, and L4 are adjusted to obtain the optimum sensitivity for different m/z ratios. Little or no m/z separation of the extracted ion beam is achieved by the ion lenses and must be performed by the quadrupole mass analyzer.

5. Quadrupole Mass Spectrometer

The quadrupole mass spectrometer is comprised of four, electrically conducting, parallel rods arranged to produce an electric field which allows stable trajectories only for ions that have a narrow range of m/z . Within the VG PlasmaQuad ICP20P, each rod is made of molybdenum and is 12 mm in diameter and 230 mm in length. As seen in Figure 6, the rods are positioned in a square array and opposite pairs are connected. DC and RF voltages of amplitude U and V , respectively, are applied to each pair. Equal and opposite

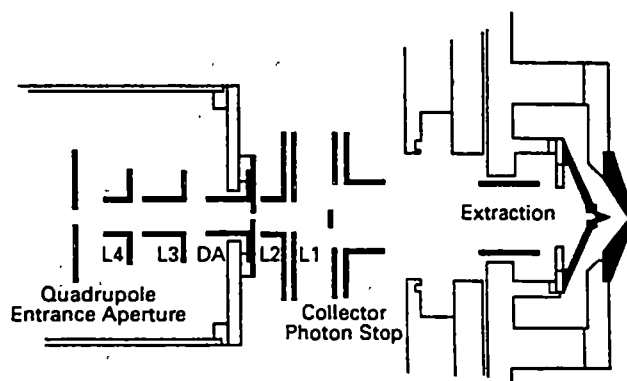


Figure 5. Geometry of Ion Lenses

Source: Jarvis, K., Gray, A.L., *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, New York, NY, Chapman and Hall (1992).

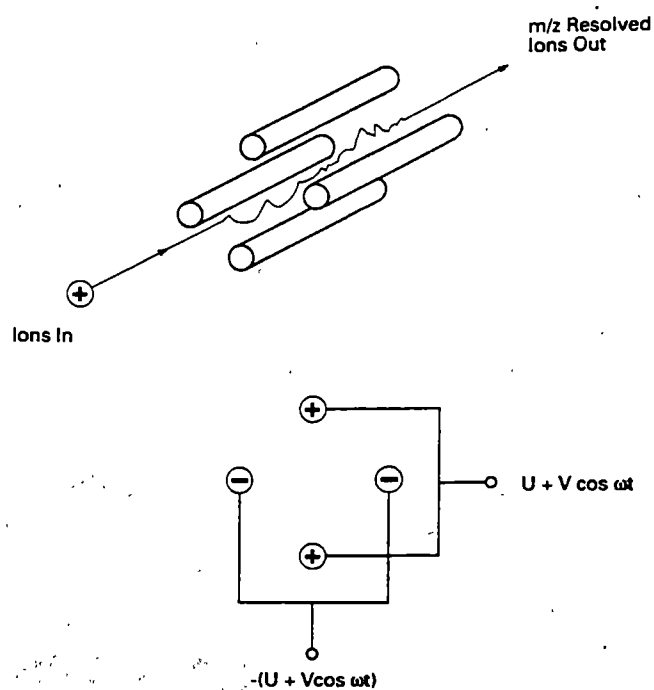


Figure 6. Quadrupole Rods and Applied Voltages

Source: Jarvis, K., Gray, A.L., *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, New York, NY, Chapman and Hall (1992).

DC voltages are applied to each pair of rods, and the RF voltages on each pair have the same amplitude but are opposite in sign.

In the positive plane, trajectories of higher mass ions are stabilized and are less able to follow the swings of the varying component, while the trajectories of lighter mass ions tend to be deflected too much and strike the rods, resulting in a high pass mass filter. In the negative plane, the trajectories of the lighter mass ions are stabilized, while the heavier mass ions tend to be lost preferentially, resulting in a low pass mass filter. The combination of both of these planes together produces a mass filter which transmits only ions at the m/z of interest. The calculation of allowed ion trajectories leads to a stability diagram, as seen in Figure 7, plotted as the variation of parameter $a \sim U/(m/z)$ with $q \sim V/(m/z)$. For values of (a,q) , outside the stable region, the DC and RF fields cause the ions to collide with the rods and are lost. For given values of U and V , a point on the scan line corresponds to one particular value of m/z .⁴³ As U and V are varied during a scan, a and q change as well, and different m/z values are selected. Therefore, the only ions that have stable paths are those that fall on the scan line and inside the sharply pointed peak of the stability diagram. Generally, as the m/z transmitted by a quadrupole is scanned, the voltages U and V are changed, but the ratio U/V is kept constant. As U and V are varied, the operating points for ions of different m/z will move into the stable region producing a mass spectrum.⁴³

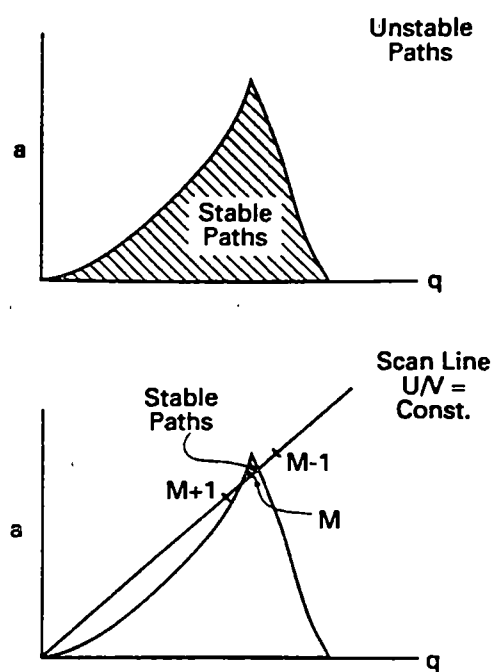


Figure 7. Stability Diagram for Ion Transmission

Source: Jarvis, K., Gray, A.L., *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, New York, NY, Chapman and Hall (1992).

The resolution of the quadrupole mass spectrometer can be expressed as $M / \Delta M$ where M is the mass and ΔM is the baseline peak width. An average resolution of 250 was calculated for the lead isotopes with M equal to 206, 207, and 208 having an average ΔM of 0.83 atomic mass units.

6. Ion Detection

The channeltron electron multiplier detects those ions that are transmitted through the quadrupole mass filter. The channeltron electron multiplier in Figure 8 is an open glass tube tapered to a cone at one end and has an interior that is coated with a lead oxide semiconducting material. The detector can be operated in pulse counting (PC) mode or analog (A) mode. The frequency of the output pulses from the multiplier corresponds to the true ion count rate emerging from the quadrupole and depends on the operating mode in use.⁴⁴ In PC mode, pulses from a comparator are selected by the multiplexer, whereas in A mode the output of the analog amplifier is converted to a pulse train by a voltage-to-frequency converter, and then these pulses are selected by the multiplexer.⁴⁴ The output from the multiplexer is sent from the head amplifier for scaling in the control unit. For detection of positive ions, a potential of ~ -3 kV is applied to the front of the multiplier which attracts ions into the cone while the back of the tube near the collector electrode is held at ground. When a positive ion strikes the cone surface, one or more secondary electrons are ejected. Because a continuous potential gradient exists within

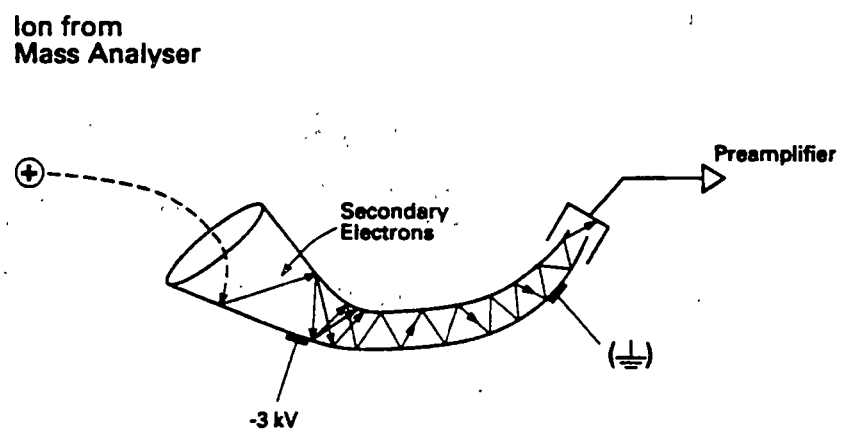


Figure 8. Channeltron Electron Multiplier

Source: Jarvis, K., Gray, A.L., *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, New York, NY, Chapman and Hall (1992).

the tube, the secondary electrons move further into the tube towards the collector electrode. As the secondary electrons collide with the walls, more secondary electrons are emitted and cascade toward the collector. This process continues until the space charge becomes large enough to inhibit further multiplication, and the result is a discrete pulse containing as many as 10^8 electrons that leave the base of the cone and are attracted to the collector electrode. This pulse is sensed and shaped by a fast pre-amplifier and in turn goes to a digital discriminator and counting circuit which counts pulses above a set threshold.

B. DATA ACQUISITION

A multichannel scaler (MCS) system includes an acquisition microprocessor, a high-speed input scaler, acquisition memory, a digital-to-analog converter (DAC), and a video display unit (VDU). This system is used to manage the pulses from the signal handling electronics. These pulses are gated into a counter for the selected dwell-time, copied into the latch, and the next dwell-period starts. As the current dwell-period accumulates pulses, the microprocessor reads the previous count from the latch and adds the contents to the appropriate location in the acquisition memory. The sequence of DAC settings and dwell-periods are sent from the computer data system to the Plasmaquad control unit via the GPIB-488 interface. Over 250 acquisition regions can be defined allowing acquisition over a range of masses or of

specific masses. Once the regions are defined, acquisition can begin. Lastly, the VDU allows instantaneous visual examination of the acquired data.

C. AUXILIARY SYSTEMS

1. Vacuum System

The ICP operates at atmospheric pressure, whereas the MS requires ions to move with minimal collisions, and therefore, the quadrupole mass filter and electron multiplier are housed within a vacuum system. Figure 9 shows the vacuum system used in the ICP-MS. In order to reach the pressure of $\sim 10^{-6}$ mbar necessary for the MS and detector to operate, the instrument is divided into three separate stages, and the pressure is gradually reduced across each stage by a technique called differential pumping. The first stage is the expansion chamber and lies between the sample and skimmer cones. 95% of the gas load entering the system is evacuated down to a pressure of 2.0 mbar in this stage using a mechanical rotary pump. Between the skimmer cone and the differential aperture, which includes ion focusing lenses L1 and L2, is the intermediate chamber. A pressure of $\sim 10^{-4}$ mbar is reached in this chamber using a turbomolecular pump. A second turbomolecular pump is used to evacuate the analyzer chamber which houses the remainder of the lens stack, the quadrupole mass analyzer and the detector to a pressure of about 2.0×10^{-6} mbar.

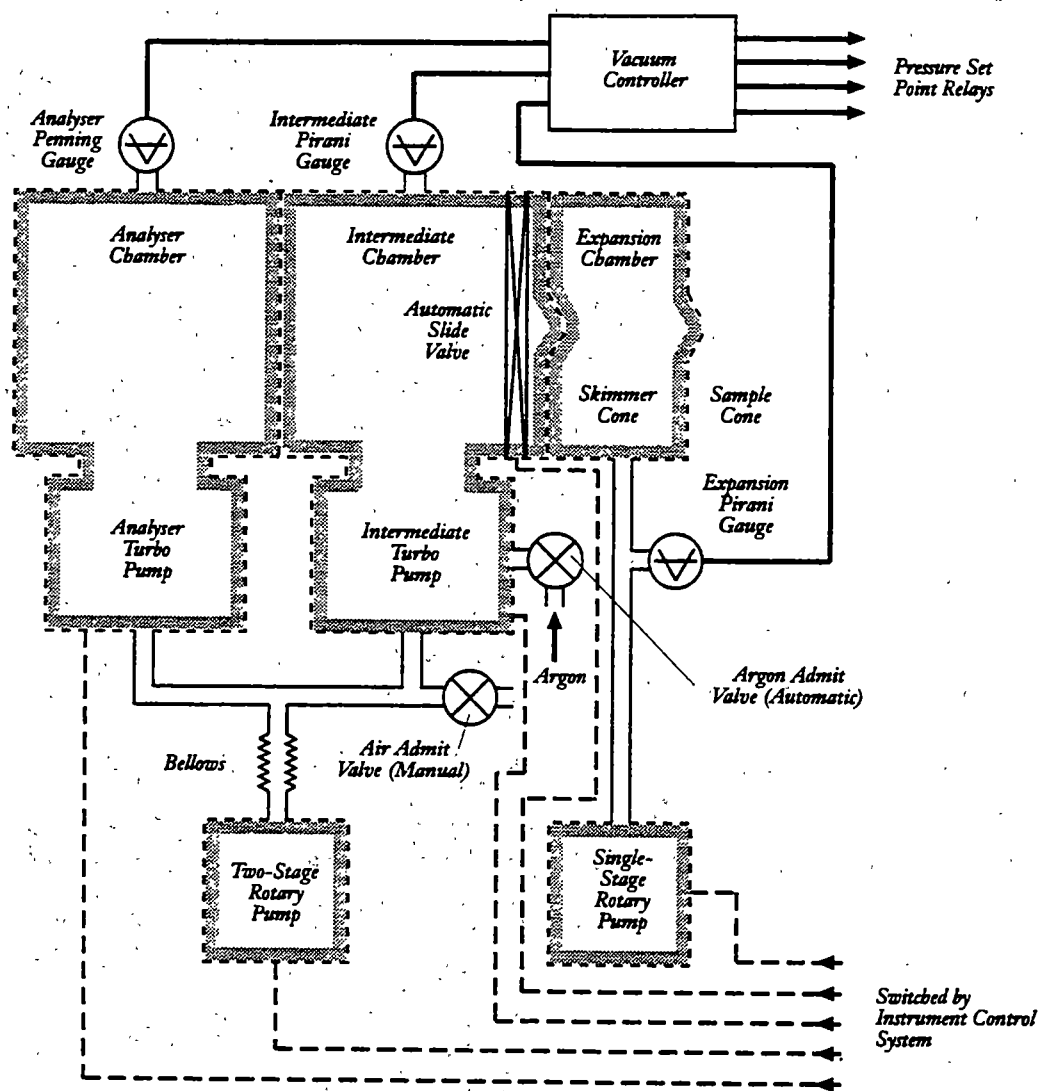


Figure 9. Vacuum System

Source: PlasmaQuad System Manual, FI Elemental Analysis, Fisons Instrument (1992).

2. Cooling System

A water cooling system ensures that instrument components which dissipate heat are maintained at their optimum operating temperature. The plasma sampling interface, ICP load coil, spray chamber, and turbomolecular pumps are all connected to the cooling system. In addition, flow switches are located in the torchbox and in water-cooled turbomolecular pump systems to shut the instrument down if insufficient cooling is detected.

D. TUNING OF INSTRUMENT

Adjustment of the torch box, gas flows, and lenses to achieve optimum signal sensitivity is performed prior to operation. The torch position relative to the sampling cone is adjusted using the lateral and vertical positioning knobs as well as the sampling depth micrometer. The voltages to each of the lenses in the lens stack, including the extraction and collector lenses, are tuned using the potentiostats for L1, L2, L3 and L4. All three gas flows also have adjustment knobs to help optimize and stabilize the signal. A short term stability test, which is comprised of 10 - 30 s acquisitions, is performed after the signal has been optimized to determine the instrument stability. A relative standard deviation of < 5% of the counts per second obtained during 10 acquisitions at selected m/z ratios is considered acceptable.

E. INSTRUMENT CALIBRATIONS

1. Mass Calibration

Prior to analyzing an unknown sample, a calibration of the mass scale is necessary to determine the digital to analog conversion setting of the quadrupole control system. Typically, a standard of six elements having a range of 9 to 238 amu is run. The instrument software matches a pre-defined mass spectrum to the output of the instrument during a mass calibration. This calibration ensures that the masses measured by the instrument for the selected standard are accurate with respect to the standard spectrum.

2. Detector Calibration

The channeltron electron multiplier detects ions in the PC and A modes, and a detector calibration correlates these modes. A detector calibration matches the analog output of the detector to the pulse counting output of the detector across the entire mass range. Detection in PC is generally limited to 6 orders of magnitude (0.01 ng/mL to 10 µg/mL), while A allows detection at two orders of magnitude above that of the PC limit. A detector calibration is necessary if sample results are obtained from both modes.

F. QUANTITATIVE ANALYSIS

1. Peak Hopping

The two main modes of data collection for ICP-MS are peak hopping and scanning. In the peak hopping mode, the peak heights are measured for specific mass positions. The position of the central point of the peak is important and is used as the starting point for the measurement of each peak. Points on both sides of the central point are taken and for each of these points, the height is measured. One advantage of the peak hopping mode is that for less abundant isotopes, the data collection times are increased to improve the counting statistics. Peak hopping has the disadvantage that no record is kept for masses not selected. Additionally, interference and matrix effects are easily missed since the whole spectrum is not available for interpretation.

2. Scanning

In the scanning mode, data are collected for all masses throughout the spectrum so that the peak shape is well defined, and the area under the curve is easily integrated. The usual mode of operation is to scan the quadrupole across the mass range and to successively build up the mass spectrum. Constant mass width and valley integration are two techniques that are used to define the peak for integration. In the constant width method, a fixed peak width is integrated regardless of the peak height, width, or resolution. This integration technique excludes the "noisier" tails on either side of the peak. In

the valley integration approach, the peak is integrated on both the high and low mass sides until a predefined single channel value is reached.⁴³ The primary advantage of the scanning mode is that information is obtained over a wide mass range and therefore permits interfering elements to be easily identified.

3. Calibration Curve

ICP-MS is a comparative method and does not give an absolute value for the concentration of the element of interest. Consequently, quantification of measured data is determined by comparing the measured counts from an unknown sample to the counts from a solution of a known concentration. In other words, a calibration curve (signal versus concentration) is established. A new calibration curve is usually generated with each set of analytical runs.

4. Internal Standards

The evaluation of one element by spiking with and monitoring another element as a reference is the basis of internal standardization. Internal standards are used to monitor and correct for fluctuations in matrix effects, instrumental drift, nebulizer and sampler orifice blockages, and aerosol transport effects. Characteristics of a suitable internal standard include being monoisotopic or having one dominant isotope, being easily ionized in the ICP without unusual chemical effects, having a similar ionization potential to the element of interest, being rarely found in real samples, and being reflective of

the mass range of interest. Examples of internal standards include ^{115}In , ^{103}Rh , ^{89}Y and ^{45}Sc .

G. ISOTOPE DILUTION

Isotope dilution measures the change in the ratio of signal intensities for two selected isotopes of an element of interest after the addition of a known quantity of one of these isotopes. Any element with at least two stable isotopes or monoisotopic elements with a suitable long-lived radioisotope can be determined using this technique. The most abundant isotope is usually used as the reference in order to obtain the best sensitivity. Also, the reference isotope is normally spiked such that the ratio is near unity to help maximize the precision by having nearly the same signal intensity as the element of interest.

The advantages of isotope dilution over other calibration methods include the compensation for any loss of the analyte due to sample preparation, the immunity to physical or chemical interferences which have the same effect on both isotopes, and inclusion of a built-in internal standard that is one of its own isotopes. As previously stated, the basic limitation with this method is that it is usually not applicable to monoisotopic elements, and enriched stable isotopes are often difficult to find and can be expensive. Additionally, the element to be determined must have at least two isotopes that are free of any isobaric interferences. With external calibration standards, a single interference-free isotope is all that is necessary.

H. INTERFERENCES

1. Spectroscopic

Interferences that affect ICP-MS are separated into two main categories: 'spectroscopic' and 'non-spectroscopic.' Spectroscopic interferences encompass isobaric overlap, polyatomic ions, including refractory oxides and doubly charged ions. As previously described, isobaric overlap occurs when two elements have stable or long-lived isotopes of the same mass number. Most elements in the periodic table have at least one, sometimes two or even three isotopes free from isobaric overlap.⁴³ The amount of overlap depends upon the sample matrix and the relative proportions of the elements involved. A correction to the mass of interest can be applied by measuring another isotope of the interfering element that is free from interferences and calculating the relative contribution to the mass of interest. Isobaric overlap also exists with ions derived from the plasma gas, Ar, and with known impurities, such as Kr and Xe, in the liquid argon supply. ^{40}Ar interferes with ^{40}K and ^{40}Ca , and Kr has an isobaric overlap with ^{84}Sr , ^{86}Sr , and three of the most abundant isotopes of Se. Xe has nine isotopes, seven of which have an isobaric overlap with Ba or Te. Polyatomic ions pose a much more serious interference problem than does isobaric overlap. Polyatomic ions result from the combination of two or more atomic species.⁴³ Argon, hydrogen, and oxygen are the dominant species in the plasma, and nitrogen, sulfur, and chlorine are the primary elements present in the acids used for sample preparation. These may

combine with each other or with elements in the sample matrix to form a polyatomic ion interferent. The amount of polyatomic ion formation depends largely upon the nature of the acid and sample matrix, and the operating parameters of the plasma and nebulizer system may also play a role.

Refractory oxides, which are also polyatomic ions, arise due to incomplete dissociation of the sample matrix or from recombination in the plasma tail. The interference can be seen at 16 (MO^+), 32 (MO_2^+) or 48 (MO_3^+) mass units above the M^+ peak. A correction for an oxide overlap is made by analyzing a solution containing only the element forming the oxide and calculating the percent contribution of the MO_x^+ ion to the analyte peak. This method of correction, however, can lead to considerable error in a result. By separating the analyte from the matrix using ion extraction chromatography, solvent extraction, or coprecipitation, the amount of interferences may be reduced or eliminated.

Like polyatomic ions, the nebulizer gas flow has a significant effect on the level of MO_x^+ ions formed. For the most part, the ICP produces singly charged ions, but multiply charged ions can also occur. Only those elements with a second ionization energy lower than the first ionization energy of argon will undergo any significant degree of dication formation. Under normal operating conditions, the formation of doubly charged ions is less than 1%, but as the nebulizer gas flow rate is varied, the amount of interfering dications also changes. The effect of doubly charged ions is a small loss of signal, and therefore, sensitivity for

the singly charged species decreases. Additionally, a number of isotopic overlaps may arise at one half of the mass of the parent ion.

2. Non-spectroscopic

High concentrations of dissolved solids is the main non-spectroscopic interference. Samples containing large amounts, $> 2000 \mu\text{g/mL}$, of either dissolved or undissolved solids lead to considerable signal drift over a short period of time and/or progressive blocking of the sampling aperture. Further dilution of the sample reduces the amount of dissolved solids and may improve the signal stability, but the sensitivity will be reduced due to the lower concentration of the isotope of interest.

CHAPTER IV

EXPERIMENTAL PROCEDURE

A. CHEMICALS

All water was obtained from a Barnstead NANOpure water purification system. J. T. Baker, Phillipsburg, NJ, Ultrex® II Ultrapure nitric acid was used to prepare all nitric acid solutions. Certified A.C.S. grade hydrogen peroxide (30%) was obtained from Fisher Scientific in Fair Lawn, NJ. The technetium extraction chromatographic resin (TEVA•Spec™) was commercially supplied by Eichrom Industries, Inc., Darien, IL, with a particle size of 100 -150 µm. Columns used to hold the chromatographic resin were purchased from Bio-Rad Poly-Prep Chromatography Columns of Richmond, CA. The columns were gravity packed with 2 mL of the resin. A simulated urine solution used in the method development was prepared according to the procedure described in Appendix I. A ^{99}Tc standard was obtained from National Institute of Standards and Technology (NIST) in Washington, DC, from which all stock and working solutions were quantitatively prepared. Spectrometric standard solutions of molybdenum and ruthenium were acquired from VHG Labs, Inc., Manchester, NH, and the internal standard, ^{115}In , was purchased from Spex CertiPrep, Metuchen, NJ, and used to normalize the raw counts. The ^{97}Tc solution was purchased from Los Alamos National Laboratory Medical Isotope Program, Los Alamos, NM. All other reagents used were of analytical grade or better.

B. ISOBARIC INTERFERENT REMOVAL

In order to accurately analyze for ^{99}Tc in urine by ID/ICP-MS using ^{97}Tc as the reference isotope, the two main isobaric interferences, ^{97}Mo and ^{99}Ru , were removed. One source of molybdenum was from the ^{97}Tc reference isotope solution itself. Natural molybdenum, which is 9.55% ^{97}Mo , was irradiated with protons and a neutron was given off to produce $^{95\text{m}}\text{Tc}$ and $^{97\text{m}}\text{Tc}$. As seen in the decay schemes for $^{95\text{m}}\text{Tc}$ and $^{97\text{m}}\text{Tc}$ in Figures 10 and 11, $^{95\text{m}}\text{Tc}$ became ^{95}Mo while the $^{97\text{m}}\text{Tc}$ decayed to ^{97}Tc . Residual molybdenum that did not react with the protons may be present in the ^{97}Tc solution. Another source of molybdenum was the chromatographic exchange resin used. There was no apparent source of ruthenium, but the removal of ruthenium from the final sample aliquot was assessed for completeness.

A water matrix was initially used to develop the method due to its ease of preparation and analysis. Once the removal of the spectroscopic interferences and elution of ^{99}Tc was established, the ^{97}Tc reference isotope was incorporated and isotope dilution analysis was performed. Artificial and real urine matrices were then carried through the method. Modifications needed for preparation and analysis were explored when necessary. For all experiments, each sample was prepared on a single resin column and analyzed by ICP-MS in triplicate.

The removal of molybdenum and ruthenium, was carried out in the following experiment. Six 10.0 mL aliquots of a solution containing 105 nM of

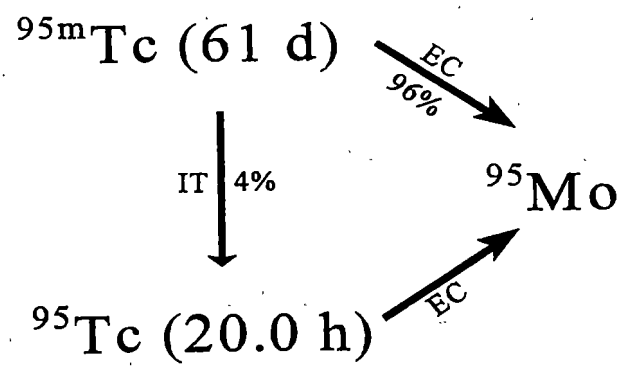


Figure 10. Decay Scheme for ^{95m}Tc

Source: Kocher, D.C., Radioactive Decay Data Tables, Office of Scientific and Technical Information U.S.D.O.E., DOE/TIC-11026, (1988).

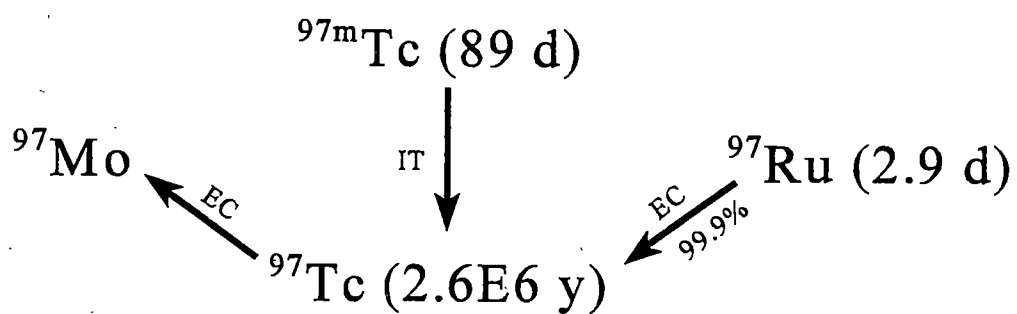


Figure 11. Decay Scheme for ^{97m}Tc

Source: Kocher, D.C., Radioactive Decay Data Tables, Office of Scientific and Technical Information U.S.D.O.E., DOE/TIC-11026, (1988).

molybdenum and 99.7 nM of ruthenium in water were oxidized with 1.0 mL of H_2O_2 , acidified with 0.10 mL of concentrated HNO_3 , and heated on a hotplate to a temperature near 95°C with a reflux condenser attached. The samples were allowed to cool to room temperature before being poured over six conditioned (10.0 mL of 0.10 M HNO_3) resin columns. Six 10.0 mL aliquots of water were digested and poured through six additional conditioned resin columns to be used as blank samples. The load fraction from each column was collected and diluted to a known volume. Each sample column and respective blank column were rinsed with 80.0 mL of one of the following nitric acid concentrations: 0.10 M, 0.50 M, 1.0 M, 2.0 M, and 3.0 M. A pair of columns were also washed with water. The rinse fraction from each column was collected and both the load and rinse fractions were analyzed for m/z 95, 97, 101, 102, and 104. Mass to charge ratios of 95 and 97 represent molybdenum isotopes, and m/z 101, 102, and 104 represent ruthenium isotopes. The concentration of molybdenum and ruthenium in each fraction and the percent removed were calculated. Because of its ability to adequately remove the molybdenum from the resin, 2.0 M HNO_3 was chosen as the rinse eluent.

Once the acid molarity of the rinse step was selected, the optimum amount of acid necessary to complete the interference removal was investigated. A 10.0 mL sample of a solution containing 105 nM of molybdenum and 99.7 nM of ruthenium in water and a blank sample of 10.0 mL of water were oxidized, acidified, digested, and poured over a pair of

conditioned columns, and the load fraction was collected. The two columns were rinsed with eight 10.0 mL aliquots of 2.0 M HNO₃ and collected. The load fraction and each 10.0 mL aliquot were analyzed for m/z 95, 97, 101, 102 and 104. Based on the cumulative percent removal of molybdenum, 40.0 mL of 2.0 M HNO₃ was selected.

C. ⁹⁹Tc ELUTION

Experiments similar to the isobaric interferent removal were performed in order to evaluate the acid molarity necessary to elute ⁹⁹Tc from the resin. Seven 10.0 mL aliquots of a 1.20 nM solution of ⁹⁹Tc in 2.0 M HNO₃ and seven 10.0 mL aliquots of water were oxidized, acidified, and digested prior to being poured over conditioned columns. All of the columns were rinsed with 40.0 mL of 2.0 M HNO₃ before eluting the technetium with one of the following nitric acid molarities: 2.0 M, 3.0 M, 4.0 M, 5.0 M, 6.0 M, 8.0 M, and 10.0 M. The load, rinse and elution fractions were collected and analyzed by ICP-MS in peak-jumping modes for m/z 99.

Optimization of the ⁹⁹Tc elution process using 3.0 M, 4.0 M, 5.0 M, 6.0 M and 8.0 M HNO₃ was carried out by oxidizing, acidifying, and digesting five 10.0 mL aliquots of a 1.20 nM ⁹⁹Tc solution and five 10.0 mL aliquots of water blanks. The solutions were poured onto 10 conditioned resin columns, rinsed with 40.0 mL of 2.0 M HNO₃, and eight 10.0 mL aliquots of each acid concentration were sequentially used to elute the technetium.

Because the selection of the optimum rinse of 40.0 mL of 2.0 M HNO_3 to remove molybdenum and ruthenium and the selection of ^{99}Tc elution conditions were determined separately, a solution containing all three elements was tested. Three 10.0 mL aliquots of a 2.0 M HNO_3 solution containing 105 nM of molybdenum, 99.6 nM of ruthenium and, 1.15 nM of ^{99}Tc were oxidized, acidified and digested. Three blank samples were also prepared using 10.0 mL of water. After cooling, the samples were poured over 6 conditioned resin columns. 40.0 mL of 2.0 M HNO_3 was used to rinse each resin, and the technetium was eluted on a pair of blank and sample columns using 40.0 mL of 4.0 M HNO_3 followed by two aliquots of 10.0 mL of 4.0 M HNO_3 . The technetium on the other two pairs of blank and sample columns were eluted with 30.0 mL of 5.0 M HNO_3 followed by two 10.0 mL aliquots of 5.0 M HNO_3 and 30.0 mL of 6.0 M HNO_3 followed by two 10.0 mL aliquots of 6.0 M HNO_3 . The load, rinse, and elution fractions were collected from each column and analyzed for ^{95}Mo , ^{97}Mo , ^{99}Tc , ^{101}Ru , ^{102}Ru and ^{104}Ru . Assessment of these results led to the selection of the elution conditions of 30.0 mL of 6.0 M HNO_3 .

D. ^{97}Tc STANDARD VALIDATION

Because of the possible presence of ^{97}Mo , ^{99}Tc , and ^{99}Ru in the ^{97}Tc standard solution, the concentrations of ^{95}Mo , ^{99}Tc and ^{102}Ru , and the $^{97}\text{Mo}/^{95}\text{Mo}$, $^{97}\text{Tc}/^{99}\text{Tc}$, and $^{99}\text{Ru}/^{102}\text{Ru}$, ratios were determined. The concentrations of ^{97}Mo ,

^{97}Tc , and ^{99}Ru were then calculated in order to properly quantitate all isotopes of interest in the ^{97}Tc standard solution.

Two replicate samples were prepared by adding 0.2012 mL of the ^{97}Tc standard solution into two aliquots of 10.0 mL of water. A 10.0 mL water blank was also prepared. The samples and blank were oxidized, acidified, and digested prior to being poured over conditioned columns. 40.0 mL of 2.0 M HNO_3 was used as the rinse solution, and 30.0 mL of 6.0 M HNO_3 was used to elute the samples. The load, rinse, and elution fractions were collected from each column and analyzed for m/z 95, 97, 99, and 102. Additionally, two other samples and a water blank were prepared in the same manner except they were not run through the resin column. (These samples will be referred to as "no column" or "NC" samples). This same experiment was repeated using three aliquots of 0.2022 mL of the ^{97}Tc standard solution, along with a blank, a no column sample, and a no column blank. The instrument acquisition and dwell times were increased from 60 s to 120 s and 45 ms to 60 ms, respectively, for experiments performed during quantitation of the ^{97}Tc standard and to assess the behavior of ^{97}Tc and ^{99}Tc in artificial and real urine matrices.

E. CONDITIONING OF RESIN FOR MOLYBDENUM REMOVAL

The presence of an excessive amount of integrated cps seen at m/z 95, assumed and later confirmed to be ^{95}Mo , during an analysis of the ^{97}Tc solution

in real urine, prompted an evaluation of the resin to determine if it was a source of molybdenum.

Three columns packed with resin were individually washed with six 10.0 mL aliquots of 0.10 M HNO₃, 2.0 M HNO₃, and 6.0 M HNO₃. Additionally, a resin column was washed sequentially with six 10.0 mL aliquots of 0.10 M HNO₃, six 10.0 mL aliquots of 2.0 M HNO₃, and six 10.0 mL aliquots of 6.0 M HNO₃. Each aliquot was analyzed for ⁹⁵Mo, ⁹⁷Mo, ¹⁰¹Ru, ¹⁰²Ru and, ¹⁰⁴Ru.

Based on the data obtained in the individual and sequential conditioning experiments, a new conditioning scheme was developed. To ensure that the new conditioning steps did not affect the molybdenum and ruthenium removal, a blank sample and two samples containing molybdenum and ruthenium were passed through columns that had been conditioned according to the new conditioning scheme. Specifically, the columns were conditioned with three 10.0 mL aliquots of 2.0 M HNO₃ to remove any molybdenum followed by four 10.0 mL aliquots of 0.10 M HNO₃ to return the resin to a low nitric acid concentration prior to loading the sample. Two 10.0 mL water samples were prepared to contain 29.2 µM of molybdenum and 31.0 µM of ruthenium. Two water blanks were also prepared. The samples and blanks were oxidized, acidified, and digested prior to one of each being poured over the conditioned columns. The other blank and sample were prepared as no column sample and blank. 40.0 mL of 2.0 M HNO₃ was used as the rinse solution, and 30.0 mL of 6.0 M HNO₃ was used to elute the sample. The load, rinse, and elution

fractions, as well as the seven 10.0 mL aliquots from the conditioning step and the two no column samples, were analyzed for ^{95}Mo , ^{97}Mo , ^{101}Ru , ^{102}Ru , and ^{104}Ru .

F. ARTIFICIAL AND REAL URINE MATRICES

The new conditioning scheme for the resin helped remove a fraction of the integrated counts per second (cps) seen at m/z 95, but additional measures were taken to further reduce the cps. In reviewing the possible options for eliminating the cps at m/z 95, the volume of the 2.0 M HNO_3 rinse was increased. While reducing the cps at m/z 95 is important, the elution of the technetium isotopes during the rinse must be minimized.

Four 10.0 mL samples in water, artificial and real urine, were spiked to contain 1.36 nM of ^{97}Tc and 1.30 nM of ^{99}Tc . Twelve matrix matched blanks were also prepared. The samples and blanks were oxidized, acidified, digested, and poured over conditioned resin columns. The spiked sample and its respective blank for the three matrices were rinsed with 40.0, 50.0, 60.0, and 70.0 mL of 2.0 M HNO_3 . All twenty-four columns were eluted with 30.0 mL of 6.0 M HNO_3 . The elution fraction of each column was analyzed for m/z 95, 97, 99, and 102.

The new resin conditioning scheme helped remove extraneous cps at m/z 95, and the new rinsing volume of 60.0 mL of 2.0 M HNO_3 further reduced the cps at m/z 95. Four samples with varying concentrations of ^{99}Tc and a

constant concentration of ^{97}Tc were prepared in water, artificial urine, and real urine. Four 10.0 mL aliquots of real urine contained ^{99}Tc concentrations of 1.63 nM, 3.23 nM, 6.34 nM, and 12.7 nM, and a constant ^{97}Tc concentration of 1.67 nM. Additionally, a reagent blank containing no technetium isotopes and a blank containing only 1.67 nM of ^{97}Tc were prepared. For the artificial urine and the water matrices, the following concentrations of ^{99}Tc were prepared in four 10.0 mL aliquots of each: 1.64 nM, 3.23 nM, 6.46 nM, and 12.9 nM, and 1.67 nM of ^{97}Tc was added to each sample. Again, a reagent blank and blank spiked with ^{97}Tc were prepared. All 18 samples were oxidized, acidified, digested, poured over the resin, rinsed with 60.0 mL of 2.0 M HNO_3 , and eluted with 30.0 mL of 6.0 M HNO_3 . Only the elution fractions were analyzed for ^{95}Mo , ^{97}Tc , ^{99}Tc , and ^{102}Ru .

CHAPTER V

RESULTS AND DISCUSSION

A. ISOBARIC INTERFERENT REMOVAL

The results of the experiments performed to measure the removal of molybdenum and ruthenium from the resin using increasing nitric acid concentrations are seen in Table 2. Contained in the table are the amounts of molybdenum and ruthenium found in the load and rinse fractions as well as the percent of molybdenum and ruthenium removed. Ruthenium was not retained on the resin because 98% of it was found in the load fraction. Molybdenum remained on the resin, but the majority of the molybdenum was rinsed off the resin with all of the acid concentrations tested. A graph in ElChroM product information, reproduced in Figure 12, indicated that technetium was eluted more effectively at higher nitric acid molarities. Therefore, a lower acid concentration for rinsing the molybdenum was preferred. 2.0 M HNO_3 was initially selected for testing the rinsing of the resin.

Table 3 displays the data obtained from determining the volume of 2.0 M HNO_3 needed to most effectively remove the molybdenum from the resin. Listed in the table are the amounts of molybdenum and ruthenium isotopes that were found in the load fraction and each of the 10.0 mL rinse aliquots. The cumulative percent of molybdenum and ruthenium that was measured in the load and each rinse fractions is also listed in the table. 40.0 mL was selected as the amount of 2.0 M HNO_3 necessary to remove a significant fraction of the

TABLE 2

MOLYBDENUM AND RUTHENIUM IN SAMPLE LOAD AND REMOVAL USING VARYING ACID RINSES

Sample ID	Blank Subtraction	⁹⁵ Mo (μg)	⁹⁷ Mo (μg)	¹⁰¹ Ru (μg)	¹⁰² Ru (μg)	¹⁰⁴ Ru (μg)	True Value Mo (μg)	True Value Ru (μg)	% Mo Removed	% Ru Removed
BLK-LOAD	-	0.0004	0.0003	0	0	0	-	-	-	-
LOAD	BLK-LOAD	0.0006	0.0006	0.0987	0.0992	0.1000	0.1008	0.1008	0	98
H ₂ O-BLK-RIN	-	0	0	0	0	0	-	-	-	-
0.1M-BLK-RIN	-	0.0012	0.0009	0	0	0	-	-	-	-
0.5M-BLK-RIN	-	0.0023	0.0022	0	0	0	-	-	-	-
1.0M-BLK-RIN	-	0.0023	0.0020	0	0	0	-	-	-	-
2.0M-BLK-RIN	-	0.0040	0.0036	0	0	0	-	-	-	-
3.0M-BLK-RIN	-	0.0026	0.0022	0	0	0	-	-	-	-
H ₂ O-RIN	H ₂ O-RIN	0	0.0019	0.0002	0.0002	0.0002	0.1008	0.1008	1	0
0.1M-RIN	0.1M-RIN	0.0925	0.0931	0.0002	0.0002	0.0002	0.1008	0.1008	92	0
0.5M-RIN	0.5M-RIN	0.0967	0.0988	0.0002	0.0002	0.0004	0.1008	0.1008	97	0
1.0M-RIN	1.0M-RIN	0.0963	0.0974	0.0004	0.0002	0.0004	0.1008	0.1008	96	0
2.0M-RIN	2.0M-RIN	0.0986	0.0984	0.0001	0.0002	0.0002	0.1008	0.1008	98	0
3.0M-RIN	3.0M-RIN	0.0993	0.1009	0.0002	0.0002	0.0002	0.1008	0.1008	99	0

% Removal for Mo was calculated based on the average of ⁹⁵Mo and ⁹⁷Mo masses.

% Removal for Ru was calculated based on the average of ¹⁰¹Ru, ¹⁰²Ru, and ¹⁰⁴Ru masses.

BLK stands for blank sample, LOAD stands for Load fraction, and RIN stands for rinse fraction.

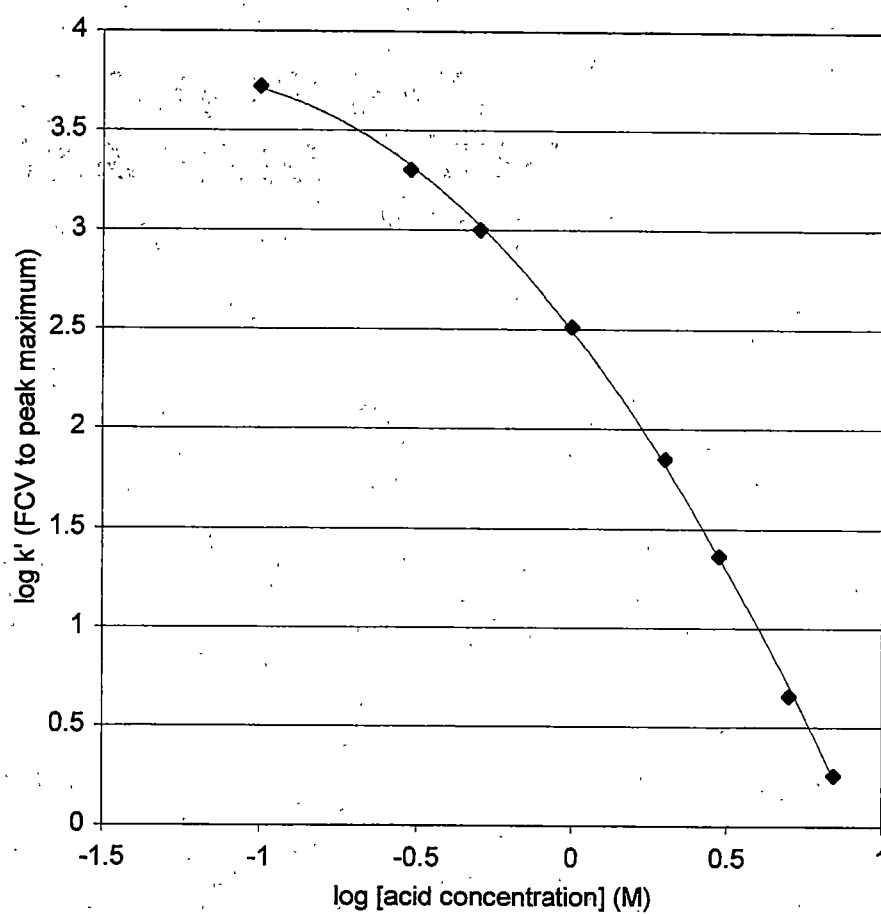


Figure 12: Nitric Acid Dependency of TEVA-Spec Resin

Source: Extraction Chromatographic Material for Rapid Separation of Tetravalent Actinides, TEVA-Spec Product Information, Eichrom Industries, Inc.

TABLE 3

OPTIMIZATION OF 2.0 M NITRIC ACID COLUMN RINSE

Sample ID	Blank Subtraction	⁹⁵ Mo (μg)	⁹⁷ Mo (μg)	¹⁰¹ Ru (μg)	¹⁰² Ru (μg)	¹⁰⁴ Ru (μg)	True Value Mo (μg)	True Value Ru (μg)	Cumulative % Mo Removed	Cumulative % Ru Removed
2M-BLK-LOAD	-	0.0009	0.0011	0	0	0.0003	-	-	-	-
2M-BLK-RIN1	-	0.0030	0.0031	0	0	0.0005	-	-	-	-
2M-BLK-RIN2	-	0.0004	0.0005	0	0	0	-	-	-	-
2M-BLK-RIN3	-	0.0002	0.0002	0	0	0	-	-	-	-
2M-BLK-RIN4	-	0.0002	0.0002	0	0	0	-	-	-	-
2M-BLK-RIN5	-	0.0002	0.0002	0	0	0	-	-	-	-
2M-BLK-RIN6	-	0.0002	0.0002	0	0	0	-	-	-	-
2M-BLK-RIN7	-	0.0002	0.0002	0	0	0	-	-	-	-
2M-BLK-RIN8	-	0.0002	0.0002	0	0	0	-	-	-	-
2M-LOAD	2M-BLK-LOAD	0.0002	0	0.0912	0.0919	0.0928	0.1008	0.1008	0	91
2M-RIN1	2M-BLK-RIN1	0.0852	0.0862	0.0002	0.0002	0.0002	0.1008	0.1008	85	91
2M-RIN2	2M-BLK-RIN2	0.0072	0.0073	0	0	0	0.1008	0.1008	92	91
2M-RIN3	2M-BLK-RIN3	0.0006	0.0006	0	0	0	0.1008	0.1008	93	91
2M-RIN4	2M-BLK-RIN4	0.0003	0.0002	0	0	0	0.1008	0.1008	93	91
2M-RIN5	2M-BLK-RIN5	0.0002	0.0002	0	0	0	0.1008	0.1008	93	91
2M-RIN6	2M-BLK-RIN6	0.0001	0.0001	0	0	0	0.1008	0.1008	93	91
2M-RIN7	2M-BLK-RIN7	0	0.0001	0	0	0	0.1008	0.1008	93	91
2M-RIN8	2M-BLK-RIN8	0	0	0	0	0	0.1008	0.1008	93	91

% Removal for Mo was calculated based on the average of ⁹⁵Mo and ⁹⁷Mo concentrations.

% Removal for Ru was calculated based on the average of ¹⁰¹Ru, ¹⁰²Ru, and ¹⁰⁴Ru concentrations.

molybdenum, with a 93% recovery. For volumes greater than 40.0 mL, no additional molybdenum was removed. The 2.0 M HNO_3 rinse at any volume did not rinse off any additional ruthenium.

B. ^{99}Tc ELUTION

The data from the tests performed to assess the elution of ^{99}Tc using a range of stronger nitric acid solutions are summarized in Table 4. Only 1% of ^{99}Tc passed through the resin during the load step and less than 1% during the rinse with 40.0 mL of 2.0 M HNO_3 . Acid concentrations of 3.0 M, 4.0 M, 5.0 M, 6.0 M, and 8.0 M HNO_3 appeared to remove the majority of the technetium, 94%, 94%, 96%, 99%, and 100%, respectively. These concentrations were investigated further.

Optimization of the selected acid concentrations can be seen in Tables 5, 6, 7, 8, and 9. The amounts of ^{99}Tc eluted with each 10.0 mL of 3.0 M, 4.0 M, 5.0 M, 6.0 M, and 8.0 M HNO_3 and the cumulative percent recovery are reported in these tables. Table 10 summarizes the amount of each acid molarity necessary to elute the majority of the technetium. In selecting the acid molarity for the elution of ^{99}Tc , the following criteria were considered: 1) minimize the final volume of the eluted technetium sample, 2) obtain the maximum percent of ^{99}Tc eluted, and 3) reduce the volume of acid needed for elution to shorten the elution time. 4.0 M, 5.0 M and 6.0 M met these criteria and were examined further.

TABLE 4
ELUTION OF ^{99}Tc
USING VARYING CONCENTRATIONS OF NITRIC ACID

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	% Recovery
BLK-LOAD	-	0.47	-	-
LOAD	BLK-LOAD	0.08	11.66	1
BLK-RIN	-	0.46	-	-
RIN	BLK-RIN	0.03	11.66	0
2.0M-BLK-ELU	-	0.89	-	-
3.0M-BLK-ELU	-	0.84	-	-
4.0M-BLK-ELU	-	0.87	-	-
5.0M-BLK-ELU	-	0.87	-	-
6.0M-BLK-ELU	-	0.86	-	-
8.0M-BLK-ELU	-	0.88	-	-
10.0M-BLK-ELU	-	0.85	-	-
2.0M-ELU	2.0M-BLK-ELU	9.04	11.66	78
3.0M-ELU	3.0M-BLK-ELU	10.94	11.66	94
4.0M-ELU	4.0M-BLK-ELU	11.02	11.66	94
5.0M-ELU	5.0M-BLK-ELU	11.23	11.66	96
6.0M-ELU	6.0M-BLK-ELU	11.54	11.66	99
8.0M-ELU	8.0M-BLK-ELU	11.72	11.66	100
10.0M-ELU	10.0M-BLK-ELU	12.06	11.66	103

ELU stands for elution fraction.

TABLE 5
OPTIMIZATION OF ^{99}Tc USING 3.0 M NITRIC ACID

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
3.0M-BLK-ELU1	-	0.05	-	-
3.0M-BLK-ELU2	-	0.04	-	-
3.0M-BLK-ELU3	-	0.05	-	-
3.0M-BLK-ELU4	-	0.04	-	-
3.0M-BLK-ELU5	-	0.05	-	-
3.0M-BLK-ELU6	-	0.05	-	-
3.0M-BLK-ELU7	-	0.05	-	-
3.0M-BLK-ELU8	-	0.04	-	-
3.0M-ELU1	3.0M-BLK-ELU1	1.11	11.66	10
3.0M-ELU2	3.0M-BLK-ELU2	4.66	11.66	49
3.0M-ELU3	3.0M-BLK-ELU3	3.62	11.66	80
3.0M-ELU4	3.0M-BLK-ELU4	1.37	11.66	92
3.0M-ELU5	3.0M-BLK-ELU5	0.33	11.66	95
3.0M-ELU6	3.0M-BLK-ELU6	0.08	11.66	96
3.0M-ELU7	3.0M-BLK-ELU7	0.02	11.66	96
3.0M-ELU8	3.0M-BLK-ELU8	0.01	11.66	96

TABLE 6
OPTIMIZATION OF ^{99}Tc USING 4.0 M NITRIC ACID

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
4.0M-BLK-ELU1	-	0.05	-	-
4.0M-BLK-ELU2	-	0.05	-	-
4.0M-BLK-ELU3	-	0.05	-	-
4.0M-BLK-ELU4	-	0.05	-	-
4.0M-BLK-ELU5	-	0.05	-	-
4.0M-BLK-ELU6	-	0.05	-	-
4.0M-BLK-ELU7	-	0.05	-	-
4.0M-BLK-ELU8	-	0.05	-	-
4.0M-ELU1	4.0M-BLK-ELU1	6.95	11.66	59
4.0M-ELU2	4.0M-BLK-ELU2	3.92	11.66	93
4.0M-ELU3	4.0M-BLK-ELU3	0.51	11.66	98
4.0M-ELU4	4.0M-BLK-ELU4	0.06	11.66	98
4.0M-ELU5	4.0M-BLK-ELU5	0.02	11.66	98
4.0M-ELU6	4.0M-BLK-ELU6	0.02	11.66	98
4.0M-ELU7	4.0M-BLK-ELU7	0	11.66	98
4.0M-ELU8	4.0M-BLK-ELU8	0	11.66	98

TABLE 7
OPTIMIZATION OF ^{99}Tc USING 5.0 M NITRIC ACID

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
5.0M-BLK-ELU1	-	0.06	-	-
5.0M-BLK-ELU2	-	0.05	-	-
5.0M-BLK-ELU3	-	0.06	-	-
5.0M-BLK-ELU4	-	0.06	-	-
5.0M-BLK-ELU5	-	0.06	-	-
5.0M-BLK-ELU6	-	0.06	-	-
5.0M-BLK-ELU7	-	0.05	-	-
5.0M-BLK-ELU8	-	0.05	-	-
5.0M-ELU1	5.0M-BLK-ELU1	8.79	11.66	75
5.0M-ELU2	5.0M-BLK-ELU2	1.93	11.66	92
5.0M-ELU3	5.0M-BLK-ELU3	0.21	11.66	94
5.0M-ELU4	5.0M-BLK-ELU4	0.02	11.66	94
5.0M-ELU5	5.0M-BLK-ELU5	0.01	11.66	94
5.0M-ELU6	5.0M-BLK-ELU6	0.01	11.66	94
5.0M-ELU7	5.0M-BLK-ELU7	0.01	11.66	94
5.0M-ELU8	5.0M-BLK-ELU8	0.01	11.66	94

TABLE 8
OPTIMIZATION OF ^{99}Tc USING 6.0 M NITRIC ACID

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
6.0M-BLK-ELU1	-	0.04	-	-
6.0M-BLK-ELU2	-	0.04	-	-
6.0M-BLK-ELU3	-	0.04	-	-
6.0M-BLK-ELU4	-	0.05	-	-
6.0M-BLK-ELU5	-	0.04	-	-
6.0M-BLK-ELU6	-	0.04	-	-
6.0M-BLK-ELU7	-	0.04	-	-
6.0M-BLK-ELU8	-	0.05	-	-
6.0M-ELU1	6.0M-BLK-ELU1	9.73	11.66	83
6.0M-ELU2	6.0M-BLK-ELU2	0.92	11.66	91
6.0M-ELU3	6.0M-BLK-ELU3	0.13	11.66	92
6.0M-ELU4	6.0M-BLK-ELU4	0	11.66	92
6.0M-ELU5	6.0M-BLK-ELU5	0.01	11.66	92
6.0M-ELU6	6.0M-BLK-ELU6	0.01	11.66	93
6.0M-ELU7	6.0M-BLK-ELU7	0	11.66	93
6.0M-ELU8	6.0M-BLK-ELU8	0	11.66	93

TABLE 9
OPTIMIZATION OF ^{99}Tc USING 8.0 M NITRIC ACID

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
8.0M-BLK-ELU1	-	0.10	-	-
8.0M-BLK-ELU2	-	0.10	-	-
8.0M-BLK-ELU3	-	0.11	-	-
8.0M-BLK-ELU4	-	0.10	-	-
8.0M-BLK-ELU5	-	0.10	-	-
8.0M-BLK-ELU6	-	0.10	-	-
8.0M-BLK-ELU7	-	0.10	-	-
8.0M-BLK-ELU8	-	0.10	-	-
8.0M-ELU1	8.0M-BLK-ELU1	10.28	11.66	88
8.0M-ELU2	8.0M-BLK-ELU2	0.59	11.66	93
8.0M-ELU3	8.0M-BLK-ELU3	0.02	11.66	93
8.0M-ELU4	8.0M-BLK-ELU4	0.01	11.66	93
8.0M-ELU5	8.0M-BLK-ELU5	0.02	11.66	94
8.0M-ELU6	8.0M-BLK-ELU6	0.05	11.66	94
8.0M-ELU7	8.0M-BLK-ELU7	0.06	11.66	94
8.0M-ELU8	8.0M-BLK-ELU8	0.06	11.66	95

TABLE 10
SUMMARY OF ACID CONCENTRATIONS AND VOLUMES
NECESSARY TO ELUTE ^{99}Tc

Nitric Acid Concentration Used	mL Necessary for Elution	% Removed
3.0 M	60	96
4.0 M	40	98
5.0 M	30	94
6.0 M	30	92
8.0 M	20	93

Three experiments using a solution containing known concentrations of molybdenum, ruthenium, and ^{99}Tc were performed using 40.0 mL of 2.0 M HNO_3 for the rinse fraction and various amounts of 4.0 M, 5.0 M, and 6.0 M for eluting the ^{99}Tc . Tables 11, 12 and 13 display the amounts of molybdenum and ruthenium found in each fraction, as well as the percent removed for both molybdenum and ruthenium for 4.0 M, 5.0 M and 6.0 M HNO_3 , respectively. The ruthenium behaved as previously seen, in that the element was not retained on the column and washed through with the load fraction. Molybdenum was partially retained with 82% being washed through the column into the load fraction, and 19% of the molybdenum was rinsed off the resin with 40.0 mL of 2.0 M HNO_3 . In Table 2, the molybdenum was found exclusively in the rinse fraction. This probably occurred because the samples in this experiment were prepared in a 2.0 M HNO_3 matrix rather than a water matrix. Tables 14, 15, and 16 display the amounts of ^{99}Tc detected in the elution fraction and the cumulative percent recovery.

After reviewing these data and assessing the three criteria, 30.0 mL of 6.0 M HNO_3 was used for the ^{99}Tc elution. A 3-fold dilution of the elution fraction was required to obtain an acid concentration of 2.0 M HNO_3 and was an acceptable sample matrix for the ICP-MS. Acid molarities higher than 2.0 M HNO_3 , are not compatible with the ICP-MS instrumentation. The final volume after dilution was 90 mL. Whereas, if 4.0 M HNO_3 was used, a final volume of

TABLE 11

SEPARATION OF MOLYBDENUM AND RUTHENIUM IN LOAD, RINSE, AND
4.0 M HNO₃ ELUTION FRACTIONS OF COMBINED STANDARD SOLUTION

Sample ID	Blank Subtraction	⁹⁵ Mo (µg)	⁹⁷ Mo (µg)	¹⁰¹ Ru (µg)	¹⁰² Ru (µg)	¹⁰⁴ Ru (µg)	True Value Mo (µg)	True Value Ru (µg)	% Mo Removed	% Ru Removed
BLK-LOAD SAM-LOAD	- BLK-LOAD	0 0.0820	0 0.0812	0 0.0958	0 0.0954	0 0.0944	- 0.1007	- 0.1007	- 81	- 94
BLK-RIN SAM-RIN	- BLK-RIN	0.0003 0.0195	0.0016 0.0189	0 0.0039	0 0.0031	0 0.0032	- 0.1007	- 0.1007	- 19	- 3
BLK-40mL-ELU SAM-40mL-ELU	- BLK-40mL-ELU	0 0	0.0008 0	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0 0	0 0	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0 0	0 0	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
Total in LOAD and RIN portions	-	0.1015	0.1001	0.0997	0.0985	0.0976	0.1007	0.1007	100	98

% Removal for Mo was calculated based on the average of ⁹⁵Mo and ⁹⁷Mo concentrations.

% Removal for Ru was calculated based on the average of ¹⁰¹Ru, ¹⁰²Ru, and ¹⁰⁴Ru concentrations.

SAM stands for sample.

TABLE 12

SEPARATION OF MOLYBDENUM AND RUTHENIUM IN LOAD, RINSE, AND
5.0 M HNO₃ ELUTION FRACTIONS OF COMBINED STANDARD SOLUTION

Sample ID	Blank Subtraction	⁹⁵ Mo (μg)	⁹⁷ Mo (μg)	¹⁰¹ Ru (μg)	¹⁰² Ru (μg)	¹⁰⁴ Ru (μg)	True Value Mo (μg)	True Value Ru (μg)	% Mo Removed	% Ru Removed
BLK-LOAD SAM-LOAD	- BLK-LOAD	0 0.0813	0 0.0808	0 0.0962	0 0.0962	0 0.0954	- 0.1007	- 0.1007	- 80	- 95
BLK-RIN SAM-RIN	- BLK-RIN	0.0002 0.0210	0.0012 0.0209	0 0.0033	0 0.0033	0 0.0032	- 0.1007	- 0.1007	- 21	- 3
BLK-30mL-ELU SAM-30mL-ELU	- BLK-30mL-ELU	0 0.0004	0 0.0005	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0 0.0001	0 0.0001	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0 0	0 0	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
Total in LOAD and RIN portions	-	0.1023	0.1017	0.0995	0.0995	0.0986	0.1007	0.1007	101	98

% Removal for Mo was calculated based on the average of ⁹⁵Mo and ⁹⁷Mo concentrations.

% Removal for Ru was calculated based on the average of ¹⁰¹Ru, ¹⁰²Ru, and ¹⁰⁴Ru concentrations.

TABLE 13

SEPARATION OF MOLYBDENUM AND RUTHENIUM IN LOAD, RINSE, AND
6.0 M HNO₃ ELUTION FRACTIONS OF COMBINED STANDARD SOLUTION

Sample ID	Blank Subtraction	⁹⁵ Mo (μg)	⁹⁷ Mo (μg)	¹⁰¹ Ru (μg)	¹⁰² Ru (μg)	¹⁰⁴ Ru (μg)	True Value Mo (μg)	True Value Ru (μg)	% Mo Removed	% Ru Removed
BLK-LOAD SAM-LOAD	- BLK-LOAD	0 0.0855	0 0.0843	0 0.0992	0 0.0988	0 0.0985	- 0.1007	- 0.1007	- 84	- 98
BLK-RIN SAM-RIN	- BLK-RIN	0.0006 0.0168	0.0016 0.0169	0 0	0 0	0 0	- 0.1007	- 0.1007	- 17	- 0
BLK-30mL-ELU SAM-30mL-ELU	- BLK-30mL-ELU	0 0.0002	0 0.0002	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0 0	0 0	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0 0	0 0	0 0	0 0	0 0	- 0.1007	- 0.1007	- 0	- 0
Total in LOAD and RIN portions	-	0.1023	0.1012	0.0992	0.0988	0.0985	0.1007	0.1007	101	98

% Removal for Mo was calculated based on the average of ⁹⁵Mo and ⁹⁷Mo concentrations.

% Removal for Ru was calculated based on the average of ¹⁰¹Ru, ¹⁰²Ru, and ¹⁰⁴Ru concentrations.

TABLE 14

SEPARATION OF ^{99}Tc IN LOAD, RINSE, AND 4.0 M HNO_3 ELUTION
FRACTIONS OF COMBINED STANDARD SOLUTION

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
BLK-LOAD SAM-LOAD	- BLK-LOAD	0.24 106.33 ^b	- 11.56	- -
BLK-RIN SAM-RIN	- BLK-RIN	0.22 3.66 ^b	- 11.56	- -
BLK-40mL-ELU SAM-40mL-ELU	- BLK-40mL-ELU	0.25 10.83	- 11.56	- 94
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0.06 0.61	- 11.56	- 99
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0.07 0.21	- 11.56	- 101

^bMeasured at m/z 99, which includes ^{99}Ru isobar.

TABLE 15

SEPARATION OF ^{99}Tc IN LOAD, RINSE, AND 5.0 M HNO_3 ELUTION
FRACTIONS OF COMBINED STANDARD SOLUTION

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
BLK-LOAD SAM-LOAD	- BLK-LOAD	0.23 107.61 ^b	- 11.56	- -
BLK-RIN SAM-RIN	- BLK-RIN	0.22 3.95 ^b	- 11.56	- -
BLK-30mL-ELU SAM-30mL-ELU	- BLK-30mL-ELU	0.18 10.90	- 11.56	- 94
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0.06 0.43	- 11.56	- 98
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0.06 0.04	- 11.56	- 98

^bMeasured at m/z 99, which includes ^{99}Ru isobar.

TABLE 16

SEPARATION OF ^{99}Tc IN LOAD, RINSE, AND 6.0 M HNO_3 ELUTION
FRACTIONS OF COMBINED STANDARD SOLUTION

Sample ID	Blank Subtraction	^{99}Tc (pmoles)	True Value ^{99}Tc (pmoles)	Cumulative % Recovery
BLK-LOAD SAM-LOAD	- BLK-LOAD	0.24 111.68 ^b	- 11.56	- -
BLK-RIN SAM-RIN	- BLK-RIN	0.22 0.10 ^b	- 11.56	- -
BLK-30mL-ELU SAM-30mL-ELU	- BLK-30mL-ELU	0.19 11.27	- 11.56	- 97
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0.07 0.37	- 11.56	- 101
BLK-10mL-ELU SAM-10mL-ELU	- BLK-10mL-ELU	0.06 0.04	- 11.56	- 101

^bMeasured at m/z 99, which includes ^{99}Ru isobar.

100 mL resulted after a 2-fold dilution of the 50.0 mL elution volume. Likewise, for 5.0 M HNO_3 , a final volume of 100 mL resulted after a 2.5-fold dilution.

C. ^{97}Tc STANDARD VALIDATION

From the product technical data sheet for the $^{95\text{m}}\text{Tc}$ solution, a significant amount of $^{97\text{m}}\text{Tc}$ was determined to be present as a radioactive impurity.

Because $^{97\text{m}}\text{Tc}$ ($t_{1/2} = 89 \text{ d}$) decays to ^{97}Tc ($t_{1/2} = 2.6 \times 10^6 \text{ y}$), this solution was used as the ^{97}Tc reference isotope source.

The $^{95\text{m}}\text{Tc}$ standard solution was produced by irradiating natural molybdenum resulting in a (p,n) process. In a (p,n) process, a proton is added, and a neutron is expelled,. Therefore, the atomic number (Z) is increased by 1 and the mass number (A) remains the same. Additionally, (2p,n), (3p,n), (4p,n), etc. reactions are also possible during irradiation. Natural molybdenum consists of the following isotopes with their abundances listed in parentheses: ^{92}Mo (14.8%), ^{94}Mo (9.3%), ^{95}Mo (15.9%), ^{96}Mo (16.7%), ^{97}Mo (9.6%), ^{98}Mo (24.1%) and ^{100}Mo (9.6%). After irradiation, the following radioactive technetium isotopes of interest, with respective half lives in parentheses, could possibly have been formed: ^{95}Tc ($t_{1/2} = 20.0 \text{ h}$), $^{95\text{m}}\text{Tc}$ ($t_{1/2} = 61 \text{ d}$), ^{97}Tc ($t_{1/2} = 2.6 \times 10^6 \text{ y}$), $^{97\text{m}}\text{Tc}$ ($t_{1/2} = 90.5 \text{ d}$), ^{98}Tc ($t_{1/2} = 4.2 \times 10^6 \text{ y}$), ^{99}Tc ($t_{1/2} = 2.11 \times 10^5 \text{ y}$), and $^{99\text{m}}\text{Tc}$ ($t_{1/2} = 6.01 \text{ h}$). In the radiochemical field, negligible activity can be assumed if the isotope has passed through ten half lives since production. For this $^{95\text{m}}\text{Tc}$ solution, over 2 y had passed since production, and only the ^{97}Tc and ^{99}Tc

isotopes should be present in the standard solution. Additionally, decay products from the six isotopes, primarily ^{95}Mo from $^{95\text{m}}\text{Tc}$ decay, and natural molybdenum that was not converted during irradiation will be present in the solution. Therefore, the possible elements at each m/z of interest in the ^{97}Tc standard solution are ^{95}Mo , ^{97}Mo , ^{97}Tc , ^{99}Tc and ^{99}Ru .

As seen in the isobaric interferent removal experiments, ruthenium was not retained on the resin and passed through with the load fraction. Molybdenum was washed off the column with the 2.0 M HNO_3 rinse, and ^{99}Tc was eluted from the resin using 6.0 M HNO_3 . The quantitation of ^{95}Mo , ^{99}Tc and, ^{102}Ru in the ^{97}Tc standard solution was determined by generating calibration curves for each of the three isotopes and analyzing each of the specific column fractions. Samples not passed through the resin (no column) were also analyzed for ^{95}Mo , ^{99}Tc and ^{102}Ru . To increase the accuracy and precision of the calculated concentrations present in the ^{97}Tc standard the cps were increased at each m/z of interest. The sample acquisition time was increased from 60 s to 120 s, and the dwell time was raised from 45 ms to 60 ms. The measured concentrations, average concentrations, standard deviations, and relative standard deviations for ^{95}Mo and ^{99}Tc are listed in Tables 17 and 18, respectively. Only background levels of cps were obtained at m/z 102 in both the no column sample and the elution fractions. Therefore, the ^{97}Tc standard solution contained no ruthenium. Consequently, the ^{99}Tc concentration can be

TABLE 17

⁹⁵MO CONCENTRATION IN ⁹⁷TC STANDARD SOLUTION

Sample ID	⁹⁵ Mo (μM)
SAM1 NC1	1.06
SAM2 NC1	1.01
SAM1 RIN1	1.10
SAM2 RIN1	1.23
SAM1 NC2	0.99
SAM2 NC2	0.96
SAM1 RIN2	1.09
SAM2 RIN2	1.18
SAM NC4	1.00
SAM1 RIN4	0.97
SAM2 RIN4	0.97
SAM3 RIN4	1.00
SAM NC5	1.03
SAM1 RIN5	0.98
SAM2 RIN5	0.98
SAM3 RIN5	0.99
SAM NC6	0.98
SAM1 RIN6	0.96
SAM2 RIN6	0.96
SAM3 RIN6	0.99
	$\bar{x} = 1.02$ $n = 20$ $s = 0.07$ RSD = 7.3%

NC stands for "no column".

TABLE 18
⁹⁹Tc CONCENTRATION IN ⁹⁷Tc STANDARD SOLUTION

Sample ID	⁹⁹ Tc (μM)
SAM1 NC2	0.24
SAM2 NC2	0.24
SAM1 ELU2	0.24
SAM2 ELU2	0.24
SAM1 NC3	0.24
SAM2 NC3	0.25
SAM1 ELU3	0.24
SAM2 ELU3	0.24
SAM NC4	0.25
SAM NC5	0.25
SAM1 ELU5	0.26
SAM2 ELU5	0.26
SAM3 ELU5	0.26
SAM NC6	0.26
SAM1 ELU6	0.34 ^c
SAM2 ELU6	0.35 ^c
SAM3 ELU6	0.35 ^c
	$\bar{x} = 0.25$ $n = 14$ $s = 0.01$ RSD = 3.6%

^c Data determined to be outliers.

quantitated without interference from ^{99}Ru in both the no column sample and elution fraction.

To quantitate the amount of ^{97}Mo and ^{97}Tc in the ^{97}Tc standard solution, the ratios of $^{97}\text{Mo}/^{95}\text{Mo}$ and $^{97}\text{Tc}/^{99}\text{Tc}$ in the ^{97}Tc standard were determined. Natural abundances of the isotopes could not be assumed due to the differing cross sections for each isotope during the irradiation process as well as the decay schemes that followed the irradiation. The $^{97}\text{Mo}/^{95}\text{Mo}$ ratio was calculated using the integrated cps in the rinse fractions of the ^{97}Tc standard validation experiment. Similarly, the $^{97}\text{Tc}/^{99}\text{Tc}$ ratio was determined from the elution fraction of the same experiments. The cps, calculated ratios, average ratios, standard deviations, and relative standard deviations are listed in Tables 19 and 20. Knowing the concentrations for ^{95}Mo and ^{99}Tc and the experimentally determined abundance ratios of $^{97}\text{Mo}/^{95}\text{Mo}$ and $^{97}\text{Tc}/^{99}\text{Tc}$, the concentrations for ^{97}Mo and ^{97}Tc were calculated using the following equations:

$$^{97}\text{Mo (moles/L)} = \left(\frac{^{97}\text{Mo (cps)}}{^{95}\text{Mo (cps)}} \right) ^{95}\text{Mo (moles/L)} \quad \text{Eqn. 5.1}$$

$$^{97}\text{Tc (moles/L)} = \left(\frac{^{97}\text{Tc (cps)}}{^{99}\text{Tc (cps)}} \right) ^{99}\text{Tc (moles/L)} \quad \text{Eqn. 5.2}$$

The determined concentrations are shown in Table 21.

In addition, from the ^{97}Tc standard validation experiment, the percent recovery of ^{95}Mo and ^{99}Tc in the rinse and elution fraction, respectively, were determined using the no column sample. Because the samples were diluted differently before being analyzed, the cps were normalized by volume, and the

TABLE 19

CPS AT M/Z 95 AND 97 AND $^{97}\text{Mo}/^{95}\text{Mo}$ RATIO

Sample ID	Blank Subtraction	Mass 95 (cps)	Mass 97 (cps)	$^{97}\text{Mo}/^{95}\text{Mo}$
BLK RIN1	-	865	514	-
SAM1 RIN1	BLK RIN1	4084	2261	0.55
SAM2 RIN1	BLK RIN1	4151	2293	0.55
BLK RIN2	-	516	326	-
SAM1 RIN2	BLK RIN2	2698	1667	0.61
SAM2 RIN2	BLK RIN2	2948	1812	0.62
BLK RIN3	-	1289	828	-
SAM1 RIN3	BLK RIN3	3814	2327	0.61
SAM2 RIN3	BLK RIN3	4079	2433	0.60
BLK RIN4	-	990	571	-
SAM1 RIN4	BLK RIN4	4297	2351	0.55
SAM2 RIN4	BLK RIN4	4213	2319	0.55
SAM3 RIN4	BLK RIN4	4170	2291	0.55
BLK RIN5	-	1162	719	-
SAM1 RIN5	BLK RIN5	4736	2820	0.60
SAM2 RIN5	BLK RIN5	4485	2696	0.60
SAM3 RIN5	BLK RIN5	4640	2808	0.60
BLK RIN6	-	897	489	-
SAM1 RIN6	BLK RIN6	3968	2086	0.53
SAM2 RIN6	BLK RIN6	3857	2030	0.53
SAM3 RIN6	BLK RIN6	3940	2065	0.52
				$\bar{x} = 0.57$ $n = 15$ $s = 0.03$ $\% \text{ RSD} = 6.2$

TABLE 20

CPS AT M/Z 97 AND 99 AND $^{97}\text{Tc}/^{99}\text{Tc}$ RATIO

Sample ID	Blank Subtraction	Mass 97 (cps)	Mass 99 (cps)	$^{97}\text{Tc}/^{99}\text{Tc}$
BLK ELU1	-	10	9	-
SAM1 ELU1	BLK ELU1	344	2670	0.13
SAM2 ELU1	BLK ELU1	344	2618	0.13
BLK ELU2	-	0	0	-
SAM1 ELU2	BLK ELU2	283	1941	0.15
SAM2 ELU2	BLK ELU2	285	1956	0.15
BLK ELU3	-	40	1	-
SAM1 ELU3	BLK ELU3	376	2946	0.13
SAM2 ELU3	BLK ELU3	396	2940	0.14
BLK ELU5	-	9	43	-
SAM1 ELU5	BLK ELU5	542	3801	0.14
SAM2 ELU5	BLK ELU5	569	3885	0.15
SAM3 ELU5	BLK ELU5	563	3932	0.14
BLK ELU6	-	9	25	-
SAM1 ELU6	BLK ELU6	395	3318	0.12
SAM2 ELU6	BLK ELU6	411	3365	0.12
SAM3 ELU6	BLK ELU6	396	3319	0.12
				$\bar{x} = 0.13$ $n = 12$ $s = 0.01$ $\% \text{ RSD} = 8.0$

TABLE 21

ACCEPTED VALUES FOR ^{97}Mo AND ^{97}Tc IN ^{97}Tc STANDARD SOLUTION

^{97}Mo (μM)	^{97}Tc (μM)
0.58 ± 0.08	0.033 ± 0.002

percent recovery was calculated. ^{95}Mo showed an average recovery of $100 \pm 9\%$, and $94 \pm 4\%$ of the ^{99}Tc was recovered.

D. CONDITIONING OF RESIN FOR MOLYBDENUM REMOVAL

Analysis of several real and artificial urine samples spiked with known concentrations of ^{97}Tc and ^{99}Tc indicated excessive cps at m/z 95. In assessing various contamination possibilities, the resin was tested as a source of ^{95}Mo . The results from the conditioning of three resins using various nitric acid concentrations are shown in Figures 13 and 14. Indicated in the first graph was that 0.10 M HNO_3 removed a portion of the ^{95}Mo , but did not completely reach a baseline level. The 2.0 M and 6.0 M HNO_3 removed between 60 and 85% more of the ^{95}Mo than 0.10 M HNO_3 with the first 10.0 mL aliquot. The 2.0 M and 6.0 M HNO_3 further reduced the cps beyond the 0.10 M HNO_3 conditioning. Both 2.0 M and 6.0 M HNO_3 removed the ^{95}Mo from the resin equally well. Because a larger volume of 0.10 M HNO_3 would be necessary to prepare the resin for sample loading after 6.0 M HNO_3 was used, 2.0 M HNO_3 was selected to condition the resin. Identical trends for the removal of ^{97}Mo are seen in Figure 14.

The results from the sequential rinsing of 0.10 M, 2.0 M and 6.0 M HNO_3 through the resin are illustrated in Figures 15 and 16. The 0.10 M HNO_3 removed a large portion of the molybdenum, and the first 10.0 mL of 2.0 M HNO_3 removed a smaller, but significant portion of the molybdenum. By the

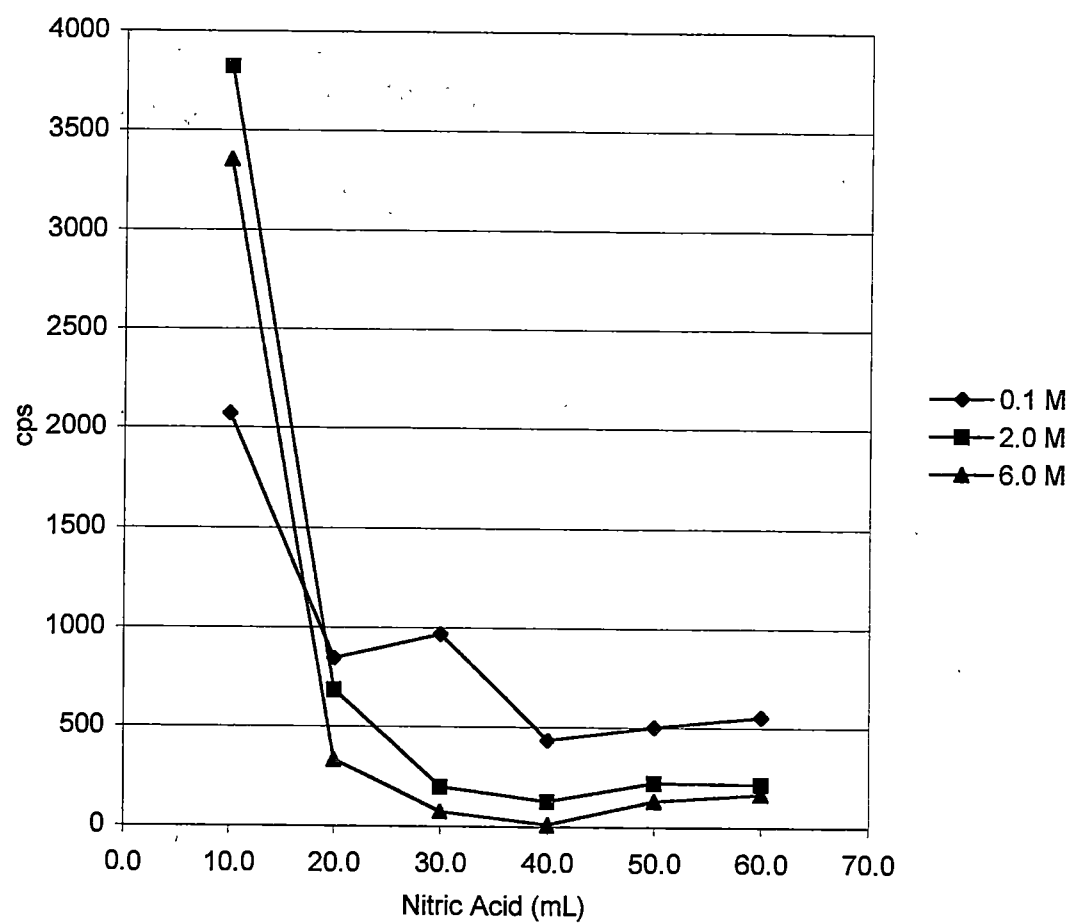


Figure 13: ^{95}Mo Removal from Individual Resin Columns using 0.10, 2.0, and 6.0 M HNO_3

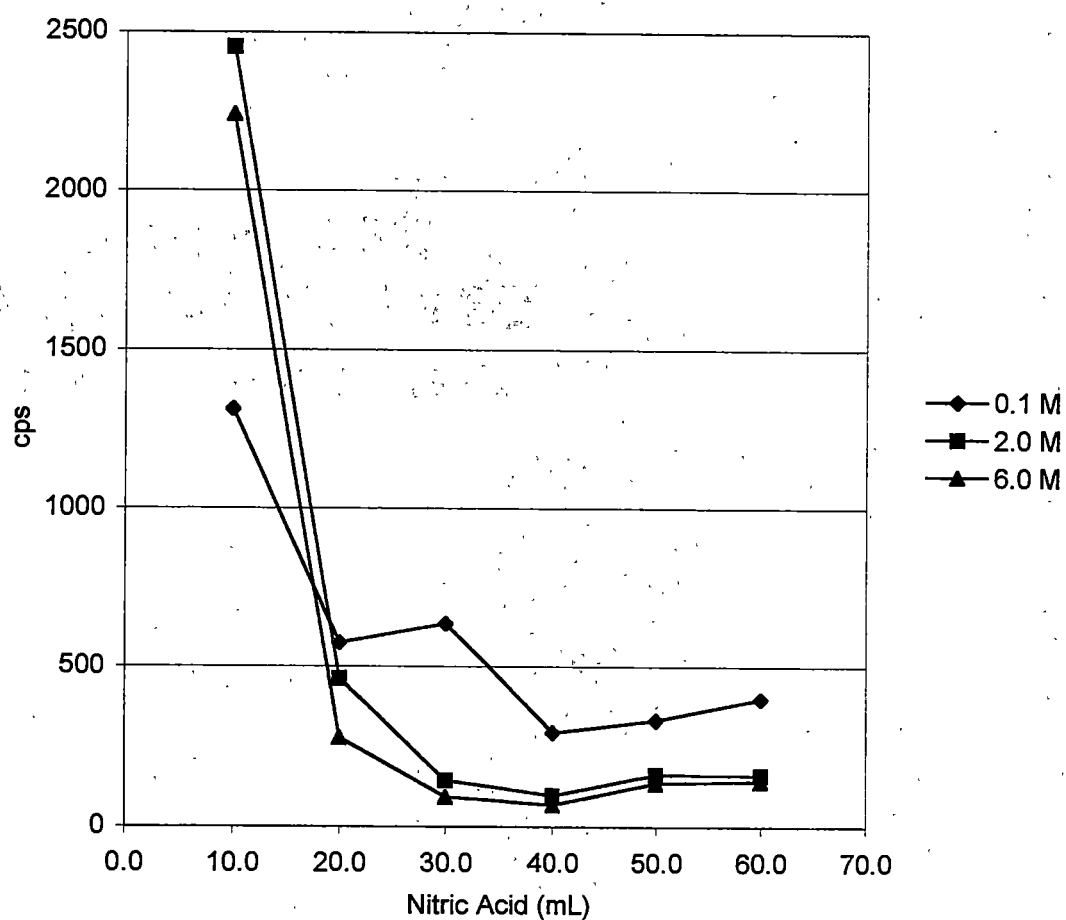


Figure 14: ^{97}Mo Removal from Individual Resin Columns using 0.10, 2.0, and 6.0 M HNO_3

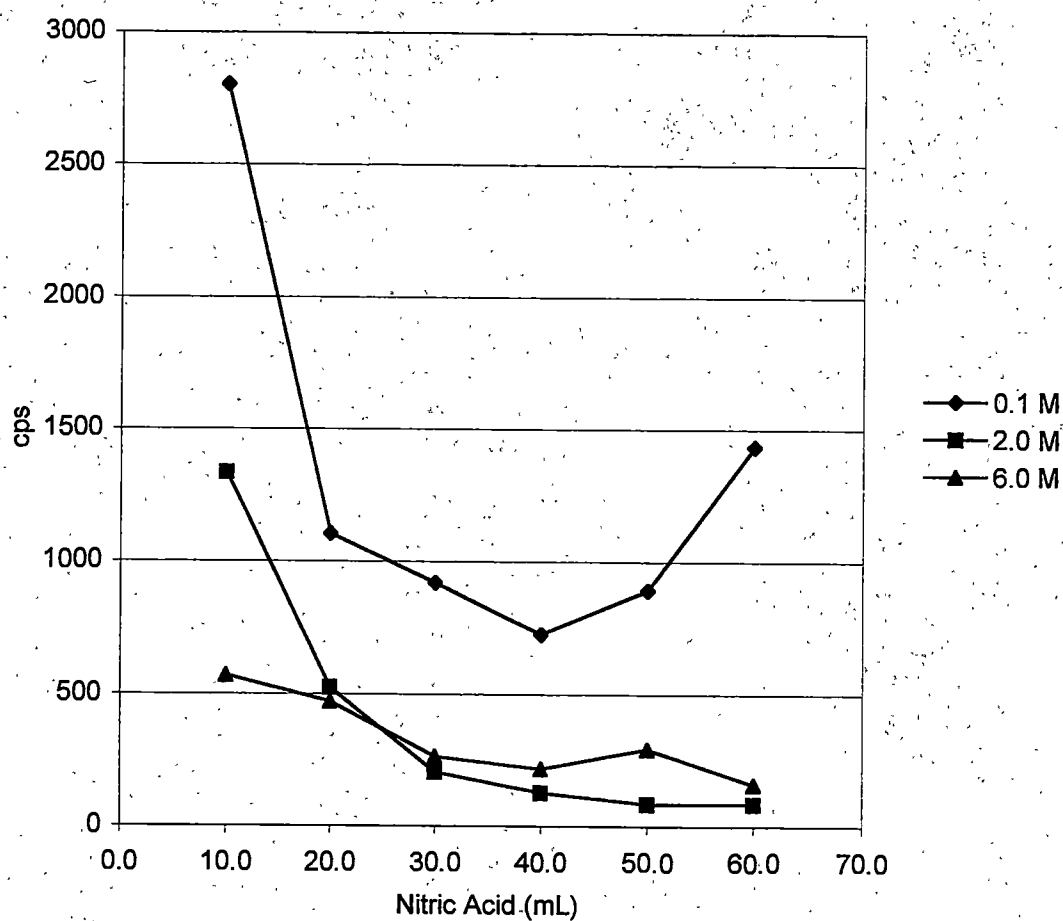


Figure 15: ^{95}Mo Sequential Removal from Resin Columns using 0.10, 2.0, and 6.0 M HNO_3

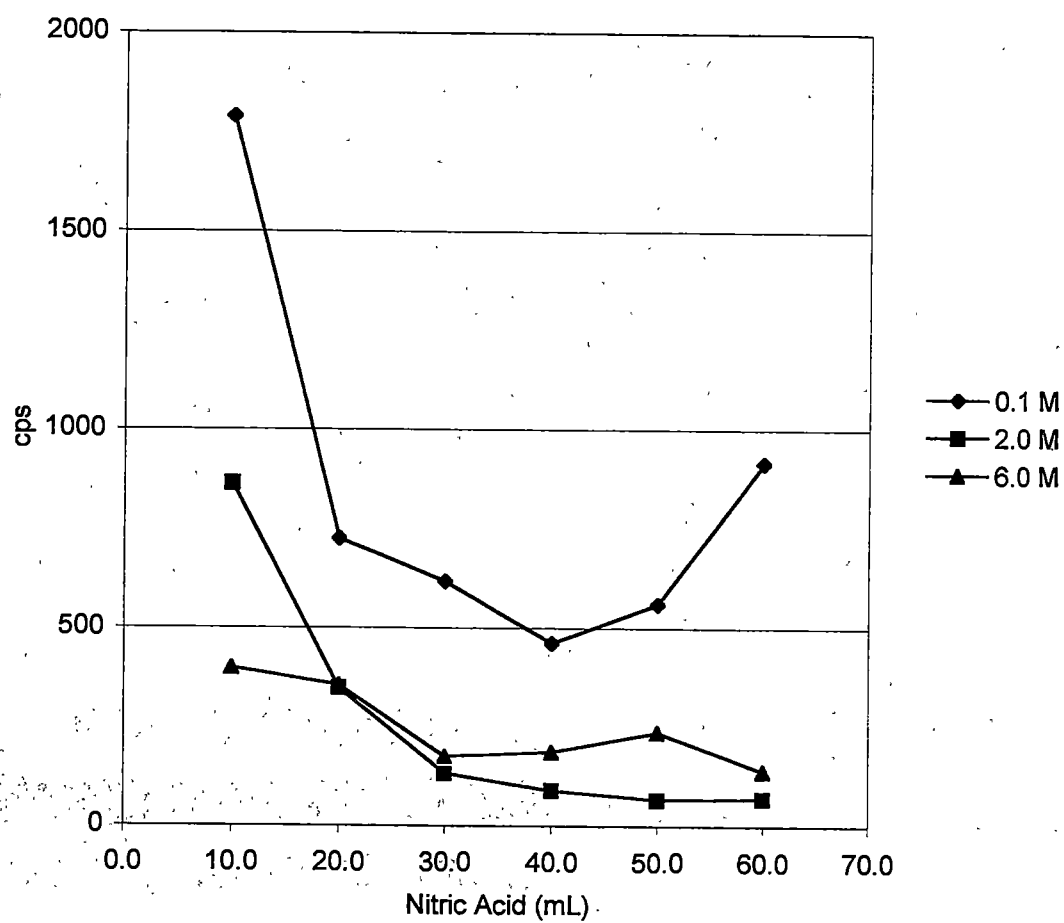


Figure 16: ^{97}Mo Sequential Removal from Resin Columns using 0.10, 2.0, and 6.0 M HNO_3

time the 60.0 mL of 6.0 M HNO_3 was passed through the column, the majority of the molybdenum had already been removed. Identical trends are seen in Figure 16 for the removal of ^{97}Mo . This study led to modification of the conditioning of the resin from the 10.0 mL of 0.10 M HNO_3 initially used. A column with resin was conditioned with three 10.0 mL aliquots of 2.0 M HNO_3 and four 10.0 mL aliquots of 0.10 M HNO_3 . These washes were analyzed for ^{95}Mo , ^{97}Tc , ^{99}Tc , and ^{102}Ru . Figures 17 and 18 show the reduction of cps at m/z 95 and 97, respectively. 30.0 mL of 2.0 M HNO_3 followed by 40.0 mL of 0.10 M HNO_3 was selected as the conditioning step of choice.

To ensure that the molybdenum and ruthenium behavior using the new conditioning scheme remained the same as previously noted, the load and rinse steps were retested, and the results can be seen in Table 22. As expected, the majority of the ruthenium was not retained on the resin, and 94% was found in the load fraction. 3% of the ruthenium and 99% of the molybdenum were observed in the 2.0 M HNO_3 rinse fraction. The elution fraction of the experiment contained only a minimal amount of the molybdenum and no ruthenium. These data compare favorably with the data listed in Table 2, where 98% of the ruthenium was passed through the column with the load fraction and 2.0 M HNO_3 rinsed out 98% of the molybdenum.

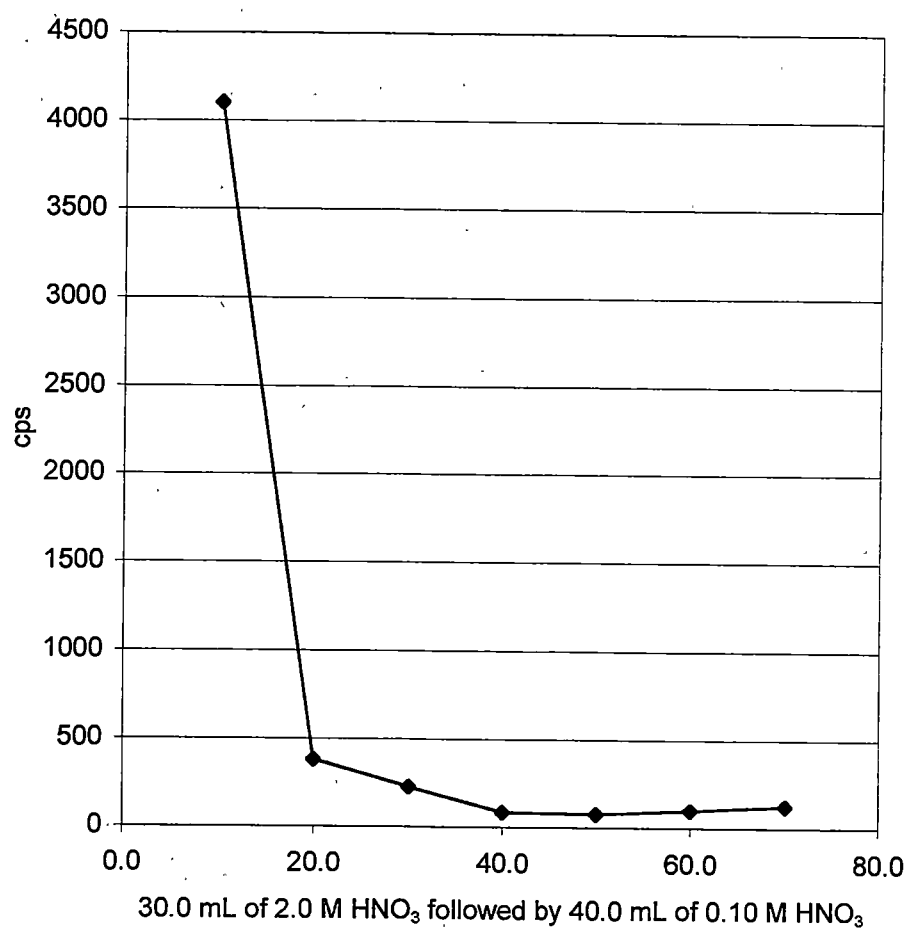


Figure 17: ^{95}Mo Removal from Resin Column using New Conditioning Scheme

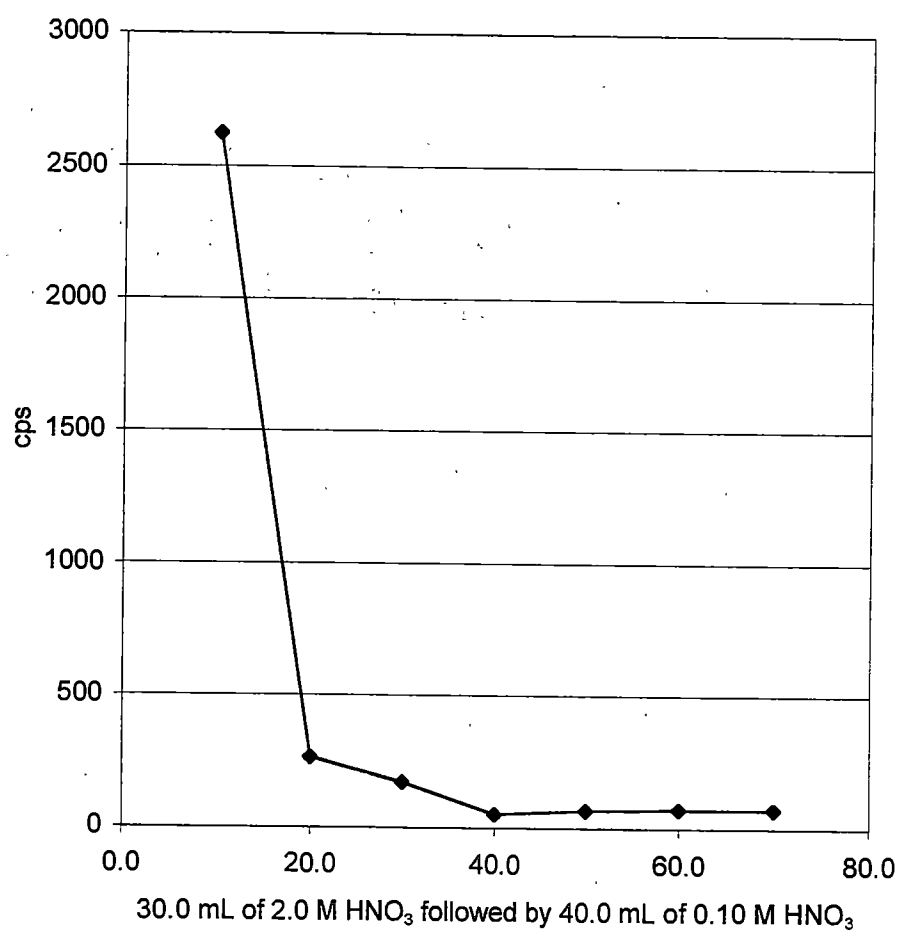


Figure 18: ⁹⁷Mo Removal from Resin Column using New Conditioning Scheme

TABLE 22

MOLYBDENUM AND RUTHENIUM REMOVAL AFTER CONDITIONING
OF RESIN WITH 2.0 M HNO₃ AND 0.1 M HNO₃ IN A WATER MATRIX

Sample ID	Blank Subtraction	⁹⁵ Mo (µg)	⁹⁷ Mo (µg)	¹⁰¹ Ru (µg)	¹⁰² Ru (µg)	¹⁰⁴ Ru (µg)	True Value Mo (µg)	True Value Ru (µg)	% Mo Removed	% Ru Removed
BLK-NC SAM-NC	- BLK-NC	0.0025 0.2944	0.0031 0.2953	0.0006 0.2947	0.0005 0.2941	0.0006 0.2970	- 0.3084	- 0.3088	- 96	- 96
BLK-LOAD SAM-LOAD	- BLK-LOAD	0.0017 0	0.0023 0.0001	0.0005 0.2891	0.0003 0.2887	0.0005 0.2891	- 0.3084	- 0.3088	- 0	- 94
BLK-RIN SAM-RIN	- BLK-RIN	0.0030 0.3051	0.0036 0.3050	0.0005 0.0089	0.0003 0.0091	0.0004 0.0093	- 0.3084	- 0.3088	- 99	- 3
BLK-ELU SAM-ELU	- BLK-30mL-E	0.0011 0.0059	0.0017 0.0055	0.0003 0.0002	0.0002 0.0002	0.0003 0.0001	- 0.3084	- 0.3088	- 2	- 0

% Removal for Mo was calculated based on the average of ⁹⁵Mo and ⁹⁷Mo concentrations.

% Removal for Ru was calculated based on the average of ¹⁰¹Ru, ¹⁰²Ru, and ¹⁰⁴Ru concentrations.

E. ARTIFICIAL AND REAL URINE MATRICES

The conditions for the load, rinse, and elution of ruthenium, molybdenum, and technetium in a water matrix were now determined. Next, artificial and real urine matrices required testing. First, the elution of ^{99}Ru was analyzed. Due to the high amount of dissolved solids in the real urine matrix and the potential clogging of the skimmer cone, only the elution fractions were analyzed. Table 23 shows that in both the artificial and real urine matrices, ruthenium was not present in the elution fraction and therefore did not interfere with the measurement of ^{99}Tc at m/z 99.

By incorporating a different resin conditioning scheme, the cps at m/z 95 were reduced, but a small amount of molybdenum still remained. Comparison of the cps at m/z 95 for water, artificial, and real urine, showed that the largest amount of molybdenum was present in the real urine matrix. To further aid in removal of molybdenum, the volume of 2.0 M HNO_3 used to rinse the resin was increased. Using a real urine matrix, the rinse volume of 2.0 M HNO_3 was increased from 40.0 mL to 50.0 mL, 60.0 mL, and 70.0 mL. The 50.0 mL 2.0 M HNO_3 rinse reduced the cps at m/z 95 by 28% over the 40.0 mL rinse, the 60.0 mL 2.0 M HNO_3 51%, and the 70.0 mL 2.0 M HNO_3 56%.

Also, during the assessment of increasing the volume of 2.0 M HNO_3 needed to reduce the cps at m/z 95, coelution of technetium with the molybdenum was monitored at m/z 99. For the water matrix, a 6% loss at m/z 99 was observed using 70.0 mL of the 2.0 M HNO_3 , 1% using 60.0 mL and 2%

TABLE 23

RUTHENIUM REMOVAL AFTER CONDITIONING OF RESIN
WITH 2.0 M HNO₃ AND 0.1 M HNO₃ IN AN ARTIFICIAL AND REAL URINE MATRIX

Sample ID	Blank Subtraction	¹⁰² Ru (μg)	True Value Ru (μg)	% Removed Ru
BLK-ARTIF-ELU	-	0.0001	-	0
SAM-ARTIF-ELU	BLK-ARTIF-ELU	0.0004	0.2058	0
BLK-REAL-ELU	-	0.0001	-	0
SAM-REAL-ELU	BLK-REAL-ELU	0.0027	0.2058	1

ARTIF stands for artificial urine matrix and REAL stands for real urine matrix.

using 50.0 mL. A similar trend was seen with the real urine matrix losing 5% with 70.0 mL, 1% with 60.0 mL, and 0% with 50.0 mL. The artificial urine matrix fluctuated with a 0.2% loss with 70.0 mL, 2% with 60.0 mL, and 0.8% with 50.0 mL. Selection of 60.0 mL of 2.0 M HNO₃ as the appropriate rinse volume removed the most ⁹⁵Mo without eluting a significant fraction of ⁹⁹Tc.

After incorporating the new conditioning scheme and increasing the rinse volume, a number of cps above the background level were still detected at m/z 95. Calculation of the ratio of m/z 97 to 95 in a real urine blank revealed that the molybdenum was present in natural abundance and was due only to the real urine matrix. Because of this, the ⁹⁷Mo/⁹⁵Mo natural abundance ratio of 0.60, was used to subtract out the molybdenum contribution to m/z 97. This natural abundance ratio was experimentally determined to be 0.60 ± 0.04 using several molybdenum calibration standards. The ratio of ⁹⁹Ru/¹⁰²Ru was also experimentally determined and found to be 0.38 ± 0.01 comparing well with the known natural abundance of 0.40. To remove the ⁹⁷Mo isobaric interferent from ⁹⁷Tc, the following calculations were applied to samples in a real urine matrix:

$$^{97}\text{Tc (cps)} = \text{total cps at m/z 97} - ^{97}\text{Mo (cps)} \quad \text{Eqn. 5.3}$$

$$^{97}\text{Mo (cps)} = \text{total cps at m/z 95} \left(\frac{^{97}\text{Mo}}{^{95}\text{Mo}} \right) \quad \text{Eqn. 5.4}$$

Because the cps at m/z 95 in the water and artificial urine matrix were from the ⁹⁷Tc standard solution and not the matrix, the ⁹⁷Mo/⁹⁵Mo ratio of 0.57 determined

from the ^{97}Tc standard solution was used rather than the natural abundance ratio.

Once the cps have been abundance corrected for molybdenum and blank subtracted for each mass, the cps due to ^{99}Tc in the ^{97}Tc standard solution must be subtracted from the total cps at m/z 99 to give the ^{99}Tc cps from the sample. The following equations were used:

$$^{99}\text{Tc (SAM cps)} = ^{99}\text{Tc (total cps)} - ^{99}\text{Tc (STD cps)} \quad \text{Eqn. 5.5}$$

$$^{99}\text{Tc (STD cps)} = ^{97}\text{Tc (STD cps)} * (7.46) \quad \text{Eqn. 5.6}$$

The constant 7.46 was the determined ratio of $^{99}\text{Tc}/^{97}\text{Tc}$ in the ^{97}Tc standard solution (See Table 21). After these corrections, the cps at m/z 97 were due to the ^{97}Tc standard solution, and the cps at m/z 99 were due to the ^{99}Tc in the sample. Their ratio was then be multiplied by the known concentration of ^{97}Tc added to the sample giving the concentration of ^{99}Tc in the sample. This is shown by,

$$^{99}\text{Tc (SAM moles/L)} = ^{97}\text{Tc (STD moles/L)} \left(\frac{^{99}\text{Tc (SAM cps)}}{^{97}\text{Tc (STD cps)}} \right) \quad \text{Eqn. 5.7}$$

The corrected cps for the ^{97}Tc , the measured cps for ^{99}Tc , the calculated cps for ^{99}Tc , the calculated concentrations for ^{99}Tc , the true value of ^{99}Tc in the sample, and the relative errors for the samples are listed in Tables 24, 25, and 26. The relative errors ranged from -29% to -16% for all three matrices.

TABLE 24
COMPARISON OF RELATIVE ERROR USING VARIOUS RINSE VOLUMES
OF 2.0 M HNO₃ IN A WATER MATRIX

Sample ID	Blank Subtraction	⁹⁷ Tc (cps)	⁹⁹ Tc (cps)	Calculated ⁹⁹ Tc (cps)	Calculated ⁹⁹ Tc (nM)	True Value ⁹⁹ Tc (nM)	Relative Error (%)
BLK-40mL SAM-40mL	- BLK-40mL	7 901	9 13693	- 6969	- 3.444	- 4.324	- -20
BLK-50mL SAM-50mL	- BLK-50mL	1 928	0 13990	- 7069	- 3.395	- 4.324	- -21
BLK-60mL SAM-60mL	- BLK-60mL	10 867	3 13565	- 7095	- 3.645	- 4.324	- -16
BLK-70mL SAM-70mL	- BLK-70mL	6 824	1 12818	- 6670	- 3.605	- 4.324	- -17

TABLE 25

COMPARISON OF RELATIVE ERROR USING VARIOUS RINSE VOLUMES
OF 2.0 M HNO_3 IN AN ARTIFICIAL URINE MATRIX

Sample ID	Blank Subtraction	^{97}Tc (cps)	^{99}Tc (cps)	Calculated ^{99}Tc (cps)	Calculated ^{99}Tc (nM)	True Value (nM)	Relative Error (%)
BLK-40mL SAM-40mL	- BLK-40mL	9 890	2 13624	- 6988	- 3.500	- 4.324	- -19
BLK-50mL SAM-50mL	- BLK-50mL	10 885	3 13522	- 6922	- 3.486	- 4.324	- -19
BLK-60mL SAM-60mL	- BLK-60mL	8 878	0 13339	- 6788	- 3.444	- 4.324	- -20
BLK-70mL SAM-70mL	- BLK-70mL	0 903	0 13650	- 6911	- 3.409	- 4.324	- -21

TABLE 26

COMPARISON OF RELATIVE ERROR USING VARIOUS RINSE VOLUMES
OF 2.0 M HNO₃ IN A REAL URINE MATRIX

Sample ID	Blank Subtraction	⁹⁷ Tc (cps)	⁹⁹ Tc (cps)	Calculated ⁹⁹ Tc (cps)	Calculated ⁹⁹ Tc (nM)	True Value (nM)	Relative Error (%)
BLK-40mL SAM-40mL	- BLK-40mL	231 978	0 14059	- 6761	- 3.079	- 4.324	- -29
BLK-50mL SAM-50mL	- BLK-50mL	194 917	2 14045	- 7207	- 3.503	- 4.324	- -19
BLK-60mL SAM-60mL	- BLK-60mL	121 912	3 13914	- 7109	- 3.472	- 4.324	- -20
BLK-70mL SAM-70mL	- BLK-70mL	125 897	2 13335	- 6644	- 3.300	- 4.324	- -24

As a final test of the developed procedure, four different concentrations of ^{99}Tc were added to four samples of each matrix along with a known constant concentration of ^{97}Tc . The samples were oxidized, acidified, digested, passed through conditioned columns, rinsed, eluted, and analyzed for ^{95}Mo , ^{97}Tc , ^{99}Tc , and ^{102}Ru . The cps obtained were abundance corrected, blank subtracted, the contribution of ^{99}Tc from the ^{97}Tc standard was removed, and the ^{99}Tc concentration due to the sample was calculated and compared to the expected ^{99}Tc concentration. A comparison of the percent relative errors for each sample can be seen in Figure 19. Although the errors were larger than expected across the different concentrations and different matrices, the water and artificial urine were similar. The figure also indicated that the real urine matrix was the poorest at all concentrations. In the calculations used to determine the ^{99}Tc result, the two main possible causes of the positive bias were: 1) the $^{99}\text{Tc}/^{97}\text{Tc}$ ratio of 7.46 used to calculate the ^{99}Tc cps due to the sample was incorrect, or 2) the method for calculating the ^{97}Tc cps due to the ^{97}Tc standard was under estimating the abundance corrections. Taking the ratio at m/z 97 to m/z 95 of a blank urine sample, a value consistent with the $^{97}\text{Mo}/^{95}\text{Mo}$ natural abundance of 0.60 was obtained. Therefore, the practice of correcting the cps using the molybdenum natural abundance value appeared to be valid. The variation in the $^{99}\text{Tc}/^{97}\text{Tc}$ ratio, however, ranged from 6.83 to 8.40 with an average of 7.46 (See Figure 20). A similar fluctuation in the $^{95}\text{Mo}/^{97}\text{Mo}$ ratio was observed (See Figure 21).

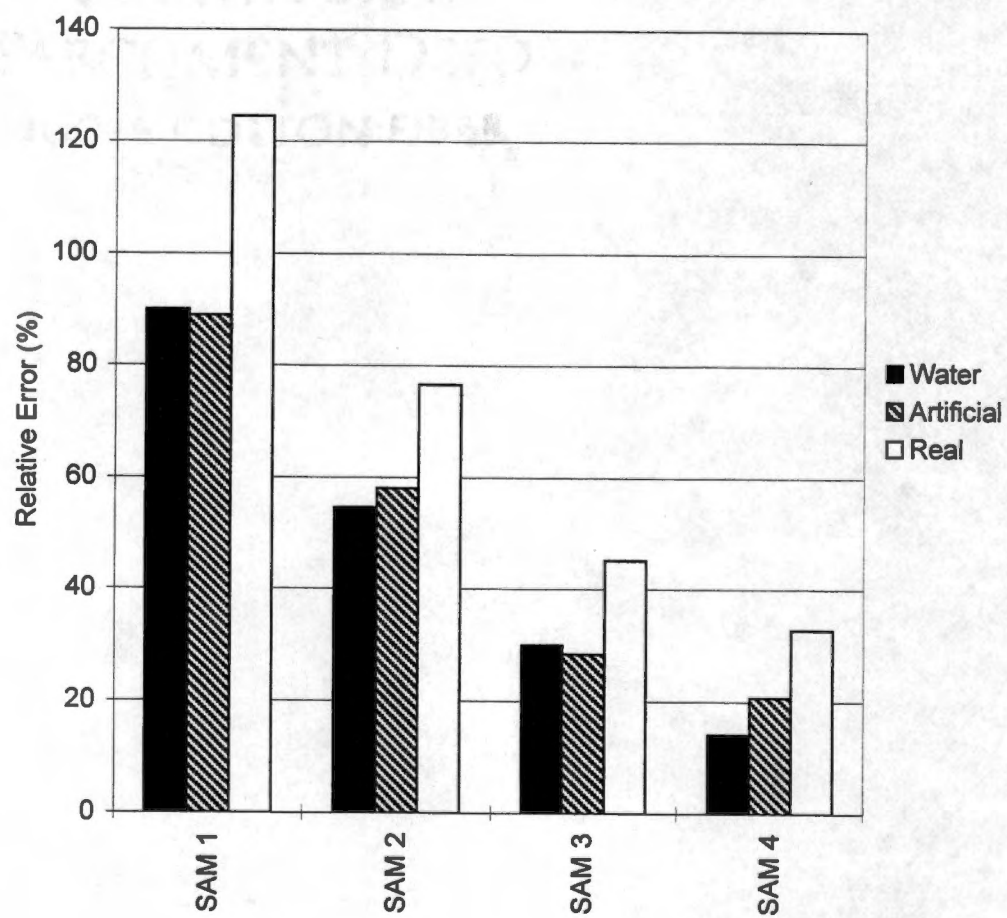


Figure 19: Comparison of Relative Errors in Various Matrices using $^{99}\text{Tc}/^{97}\text{Tc}$ Ratio

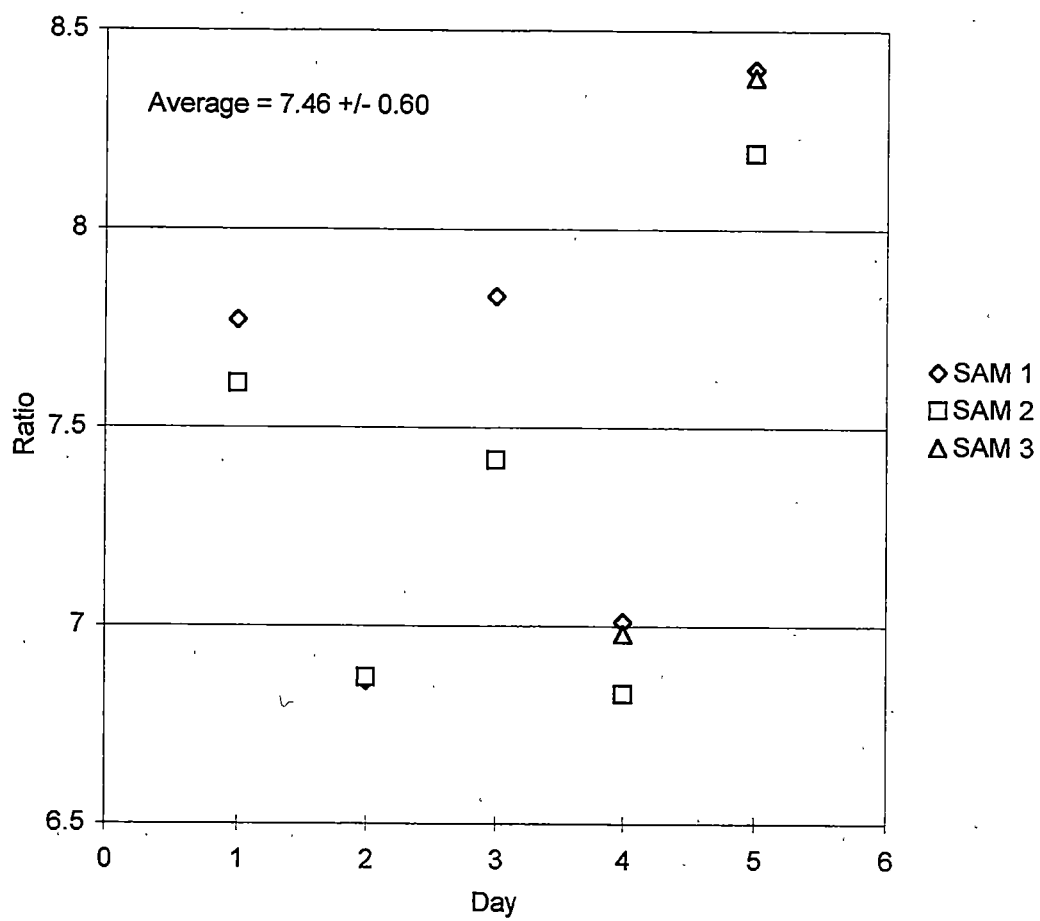


Figure 20: Variation of $^{99}\text{Tc}/^{97}\text{Tc}$ Ratio

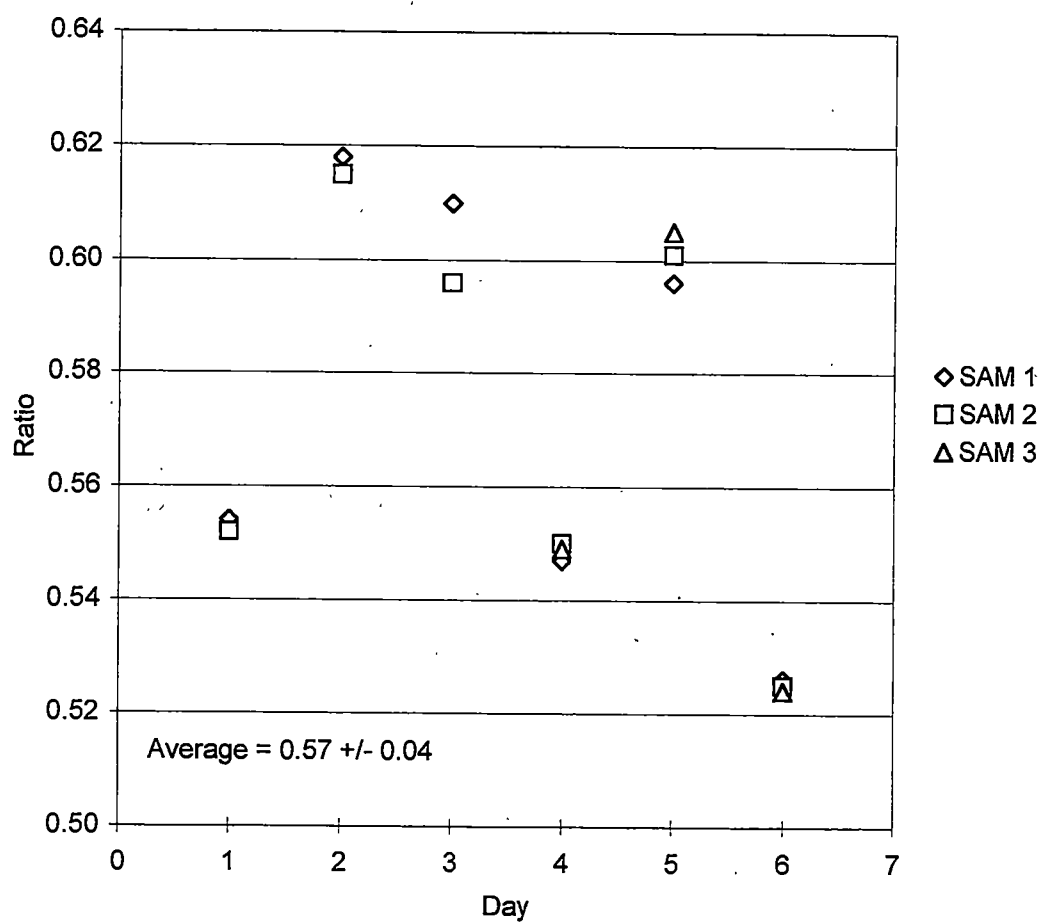


Figure 21: Variation of $^{95}\text{Mo}/^{97}\text{Mo}$ Ratio

To compensate for this $^{99}\text{Tc}/^{97}\text{Tc}$ fluctuation, a blank sample containing only the ^{97}Tc standard in each matrix was prepared and analyzed along with the spiked samples. Rather than using the ratio value of 7.46 to remove the cps at m/z 99 contributed by the ^{97}Tc standard, the cps at m/z 99 of the ^{97}Tc blank were subtracted directly from the total cps at m/z 99 of the sample. For m/z 97 the cps from the blank (reagent) were used for blank subtraction. This is as follows:

$$^{99}\text{Tc} \text{ (SAM cps)} = \text{total cps at } m/z \text{ 99} - \text{cps at } m/z \text{ 99 of } ^{97}\text{Tc} \text{ blank} \quad \text{Eqn. 5.8}$$

$$^{97}\text{Tc} \text{ (STD cps)} = \text{total cps at } m/z \text{ 97} - \text{cps at } m/z \text{ 97 of blank} \quad \text{Eqn. 5.9}$$

Once this correction was applied to the data, the determination of the ^{99}Tc concentration in the sample was calculated using Equation 5.7. Using the same raw data that produced Figure 19, but applying the direct subtraction of ^{99}Tc cps, Figure 22 results. The relative errors now ranged from -3% for SAM1 of the artificial matrix to 18% on SAM4 of the real urine matrix. SAM2 of the water matrix was excluded because of an apparent pipet error. The water matrix exhibited the least error due to minimal matrix effects, followed by the artificial urine and real urine.

The analysis order of the samples illustrated in Figures 19 and 22 were as follows: 2.0 M HNO_3 , BLK (contained only reagents), BLK97 (contained only ^{97}Tc), SAM 1, SAM 2, SAM 3, and SAM 4. To monitor instrument fluctuation during the analysis, the samples were analyzed again in the order: 2.0 M

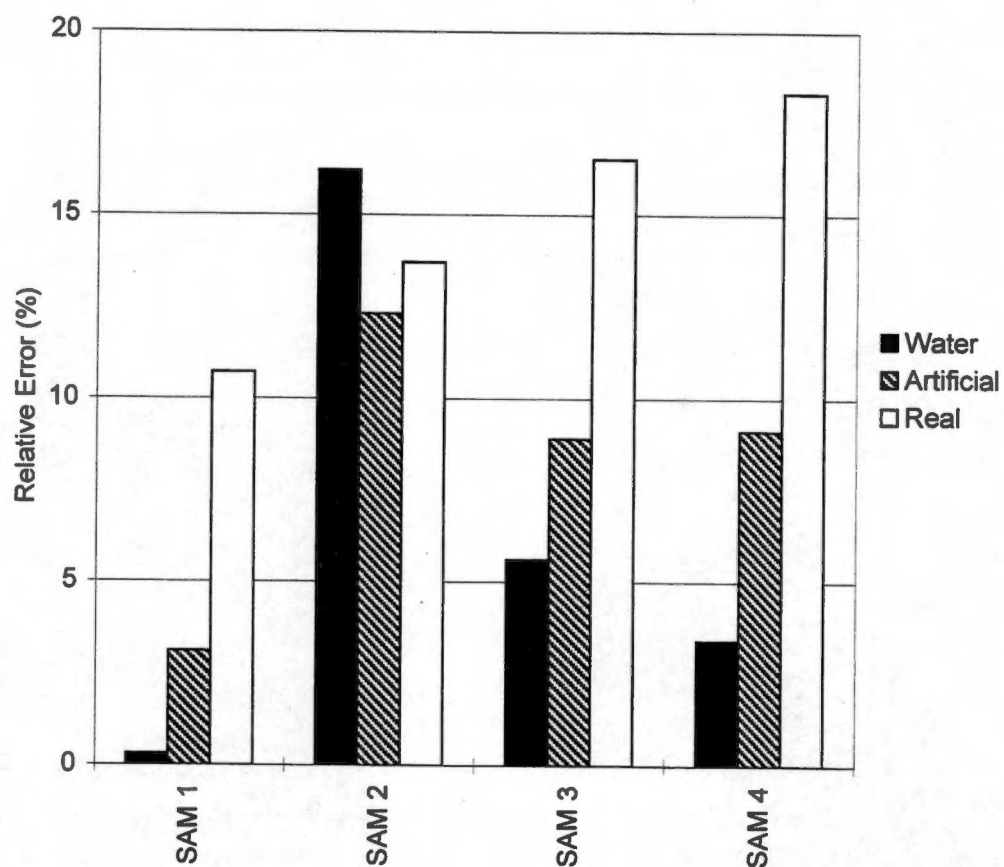


Figure 22: Comparison of the Absolute Value of Relative Errors in Various Matrices by Directly Subtracting ^{99}Tc cps due to ^{97}Tc Reference Isotope

HNO₃, BLK, BLK97, SAM 1, SAM 2, SAM 3, SAM 4, SAM 4-1, SAM 3-1, SAM 2-1, SAM 1-1, BLK97-1, and BLK-1 ("-1" indicates the second run). The average of the BLK and BLK-1 was used to blank subtract at m/z 97 and 102, and the average of BLK97 and BLK97-1 was used for subtraction at m/z 99. The average percent relative error calculated for these samples are depicted in Figure 23. Bracketing the samples with a matrix matched blank sample containing only the ⁹⁷Tc reference isotope helped to compensate for instrument fluctuations and thus reduced the relative error.

Several figures of merit were calculated for ⁹⁷Tc and ⁹⁹Tc for the different matrices and are listed in Table 27. Table 28 shows the same figures of merit for the standard addition method that is currently being used for the determination of ⁹⁹Tc in urine by inductively coupled plasma mass spectrometry. These data were obtained by averaging several months of laboratory control samples results. In comparison, the two methods performed at an approximately equal level in terms of precision, accuracy, and detection. Since only one run was necessary per sample in the isotope dilution procedure, with no calibration curve, versus two runs for each sample in the standard addition method, plus a calibration curve, the analysis time can be reduced by 37%.

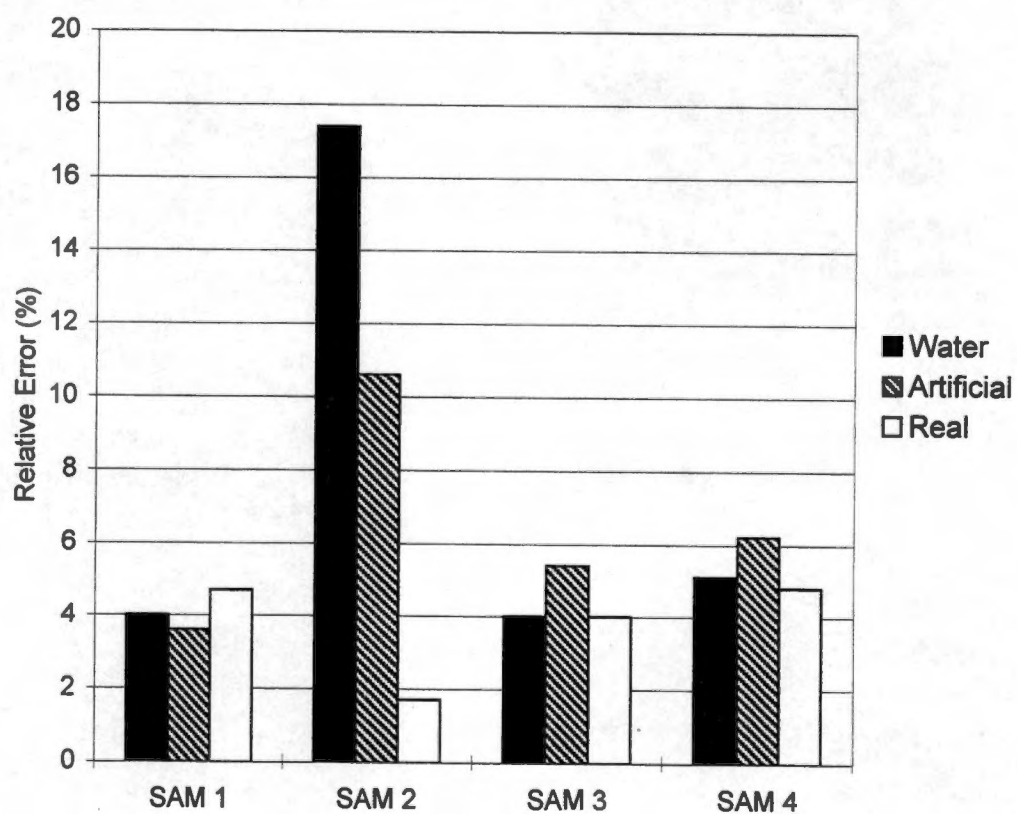


Figure 23: Comparison of Average Relative Errors in Various Matrices by Directly Subtracting Average ^{99}Tc cps due to ^{97}Tc Reference Isotope

TABLE 27

FIGURES OF MERIT FOR ^{99}Tc AND ^{99}Tc USING ISOTOPE DILUTION METHOD

Isotope	Matrix	Accuracy, Relative Error (%)	Precision, Relative Standard Deviation (%)	Detection Limit (pM)
^{99}Tc	Water	2.7	4.3	12.2
	Artificial Urine	4.7	4.1	17.1
	Real Urine	3.6	2.8	11.4
^{97}Tc	Water	-	-	22.4
	Artificial Urine	-	-	19.2
	Real Urine	-	-	47.4

TABLE 28

FIGURES OF MERIT FOR ^{99}Tc USING STANDARD ADDITION METHOD^d

Accuracy, Relative Error (%)	Precision, Relative Standard Deviation (%)	Detection Limit (pM)
1.9	6.8	9.5

^dArtificial urine matrix used for control samples.

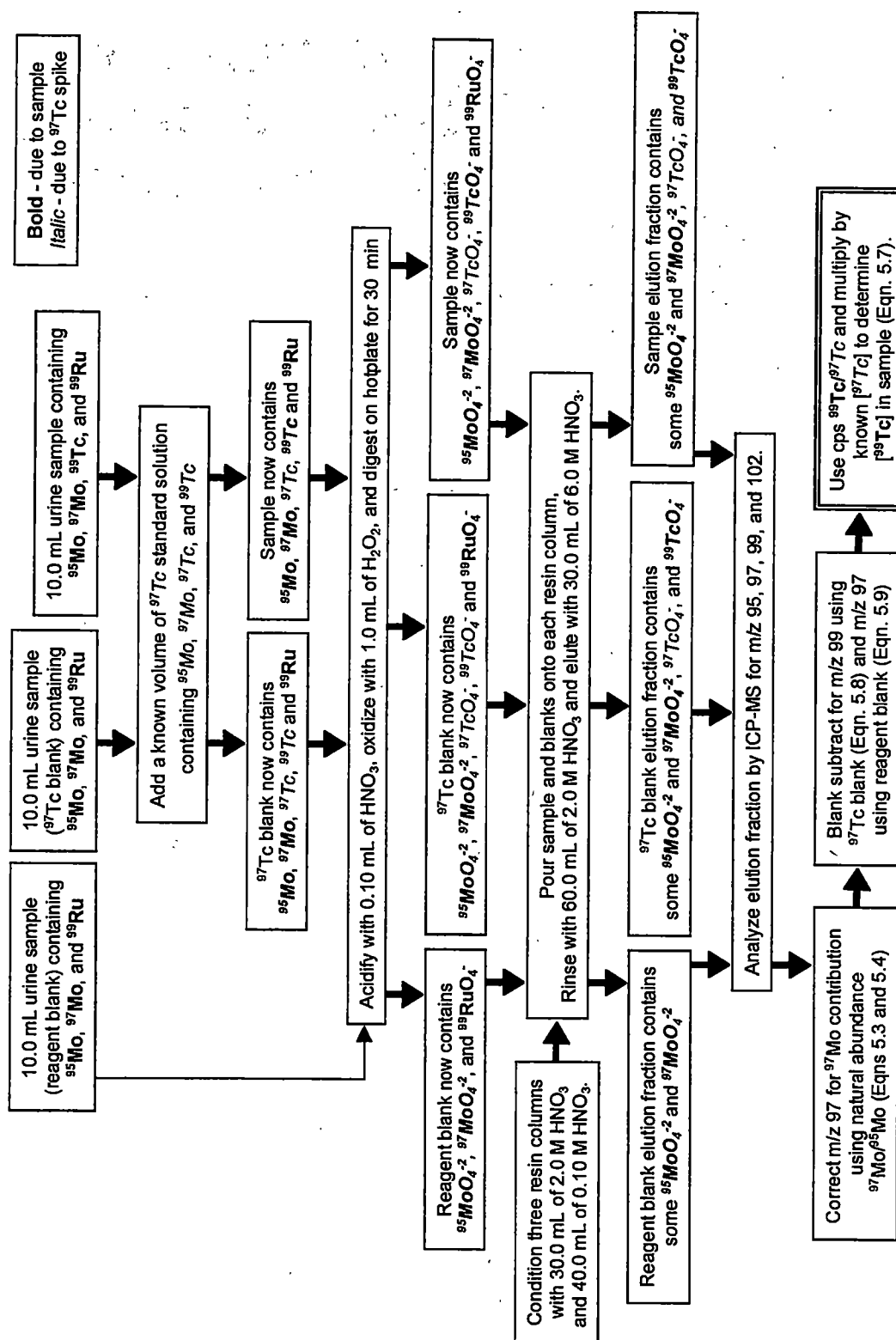
CHAPTER VI

CONCLUSION

A method for the determination of ^{99}Tc in urine by isotope dilution inductively coupled plasma mass spectrometry was developed. The research consisted of conditioning the extraction chromatographic resin to remove ^{95}Mo , quantitating the ^{97}Tc standard solution used as the reference isotope, determining the volume and acid concentration to separate the isobaric interferents, ^{97}Mo and ^{99}Ru , from the isotopes of interest, ^{97}Tc and ^{99}Tc , and optimizing the volume and acid concentration necessary to elute ^{97}Tc and ^{99}Tc . A flow diagram of this process is illustrated in Figure 24 and described below.

In summary, 10.0 mL of a urine sample containing an unknown concentration of ^{99}Tc was spiked with a known concentration of ^{97}Tc , acidified with 0.10 mL concentrated HNO_3 , oxidized with 1.0 mL of H_2O_2 , and digested on a hot plate with a surface temperature of $\sim 150^\circ\text{C}$ for 30 min. Additionally, two blank samples, one containing reagents only and one containing the ^{97}Tc reference isotope, were acidified, oxidized, and digested.

Columns containing approximately 2.0 mL of TEVA-Spec resin were conditioned with 30.0 mL of 2.0 M HNO_3 and 40.0 mL of 0.10 M HNO_3 . After conditioning, the urine samples were poured onto the resin and allowed to drain. Ruthenium, if present, not retained on the resin and was collected in the load fraction. Next, to remove the majority of the molybdenum, the resin was rinsed with 60.0 mL of 2.0 M HNO_3 . Lastly, the technetium isotopes, ^{97}Tc and

Figure 24. Flow Diagram of Determination of ^{99}Tc in Urine Using ID/ICP-MS

^{99}Tc , were eluted with 30.0 mL of 6.0 M HNO_3 . For analysis, the acid concentration was reduced from 6.0 M to 2.0 M. The blank sample containing the ^{97}Tc was analyzed before and after the actual samples. The ICP-MS instrument was set to acquire data in the peak-jumping mode at m/z 95, 97, 99 and 102 for 120 s, and the dwell time for each m/z was set to 60 ms.

The raw data were then treated in the following manner. The cps at m/z 97 were molybdenum abundance corrected using m/z 95 (^{95}Mo) using Equations 5.3 and 5.4. Blank subtraction of the samples at m/z 99 was performed using the average cps at m/z 99 of the two acquisitions of the ^{97}Tc blank (Equation 5.8). The cps at m/z 97 of the blank sample containing only reagents were then subtracted from m/z 97 of the samples (Equation 5.9). Last, the concentration of ^{99}Tc in the urine sample was calculated using Equation 5.7.

For this analysis, the real urine sample contained a large quantity of natural molybdenum, and therefore, the correction of ^{97}Mo relative to ^{95}Mo for m/z 97 was necessary to obtain accurate results. As expected, increasing the dwell times and acquisition times for all m/z decreased the relative error for each matrix. Ideally, the performance of the method would be improved if the ^{97}Tc standard solution were free of ^{97}Mo and ^{99}Tc . This would allow for improved precision in determining the contributions of the ^{97}Tc in the standard and the ^{99}Tc in the sample.

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APPENDIX

APPENDIX I

RECIPE FOR ARTIFICIAL URINE⁴⁵

Component	g/kg
Urea	16.0
NaCl	2.32
KCl	3.43
Creatinine	1.10
Na ₂ SO ₄ (anhydrous)	4.31
Hippuric Acid	0.63
NH ₄ Cl	1.06
Citric Acid	0.54
MgSO ₄ (anhydrous)	0.46
NaH ₂ PO ₄ • H ₂ O	2.73
CaCl ₂ • 2H ₂ O	0.63
Oxalic Acid	0.02
Lactic Acid	0.094
Glucose	0.48
Na ₂ SiO ₃ • 9H ₂ O	0.071
Pepsin	0.029
Concentrated (70%) HNO ₃	5.0

Note: Each kilogram of artificial urine also contains 961 g of distilled water.

VITA

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