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^{99}Tc BIOASSAY BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

A Dissertation

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DISCLAIMER

DEDICATION

The author wishes to dedicate this work to her husband, Samuel, and children, Mary Beth, Samuel, and Katherine, whose love, support, and patience made it possible to continue her education and complete this research project.

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ABSTRACT

A means of analyzing ^{99}Tc in urine by inductively coupled plasma mass spectrometry (ICP-MS) has been developed. Historically, ^{99}Tc analysis was based on the radiometric detection of the 293 keV $E_{Max.}$ beta decay product by liquid scintillation or gas flow proportional counting. In a urine matrix, the analysis of ^{99}Tc is plagued with many difficulties using conventional radiometric methods. Difficulties originate during chemical separation due to the volatile nature of Tc_2O_7 or during radiation detection due to color or chemical quenching. A separation scheme for ^{99}Tc detection by ICP-MS is given and is proven to be a sensitive and robust analytical alternative. A comparison of methods using radiometric and mass quantitation of ^{99}Tc has been conducted in water, artificial urine, and real urine matrices at activity levels between 700 and 2200 dpm/L. Liquid scintillation results based on an external standard quench correction and a quench curve correction method are compared to results obtained by ICP-MS. Each method produced accurate results, however the precision of the ICP-MS results is superior to that of liquid scintillation results. Limits of detection (LOD) for ICP-MS and liquid scintillation detection are 14.67 and 203.4 dpm/L, respectively, in a real urine matrix.

In order to determine the basis for the increased precision of the ICP-MS results, the detection sensitivity for each method is derived and measured (k vs.

λ). The detection sensitivity for the ^{99}Tc isotope by ICP-MS is 2.175×10^{-7} +/- 8.990×10^{-9} and by liquid scintillation is 7.434×10^{-14} +/- 7.461×10^{-15}. A difference by seven orders of magnitude between the two detection systems allows ICP-MS samples to be analyzed for a period of 15 s compared to 3600 s by liquid scintillation counting with a lower LOD.

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CHAPTER 1

INTRODUCTION

To date 21 isotopes of technetium with half-lives ranging from one second to several million years are known to exist. Technetium (atomic number 43) is the lightest of the artificial radioelements. The name technetium was suggested by Perrier and Segre because it was the first element to be prepared artificially.[1] ^{97}Tc ($t_{1/2}$ = 2.6E6 y), ^{98}Tc ($t_{1/2}$ = 4.2E6 y), and ^{99}Tc ($t_{1/2}$ = 2.13E5 y) are the only isotopes of technetium with half lives over 91 days.[2] Of the three longer lived isotopes, only ^{99}Tc has been obtained in weighable quantities because of the high (6.1%) fission yield.[3] ^{99}Tc is produced either directly as a fission product of ^{235}U and ^{239}Pu or indirectly as a decay product of ^{99}Mo. The release of ^{99}Tc into the environment has occurred predominately through reprocessing of nuclear fuel and testing of nuclear weapons, and to a lesser extent through use of radiopharmaceuticals and radioactive waste site contamination. Once released into the environment, it may exist as the volatile heptoxide (Tc_2O_7) or as the highly soluble and mobile pertechnetate ion (TcO_4^-). In these forms, the potential exists for technetium to be concentrated in plants and animals.[4] In humans, the pertechnetate ion localizes predominately in the thyroid gland and gastrointestinal tract.[5]

At the formerly named Oak Ridge Gaseous Diffusion Plant (ORGDP), ^{99}Tc was introduced into the gaseous diffusion cascades as a contaminant in uranium that had been reprocessed from spent nuclear fuel.[6] From a radiological protection perspective, it is imperative to control/monitor worker exposure during disassembly and decontamination processes using accurate evaluation techniques. To date few studies on ^{99}Tc bioassay have been reported. The majority of the ^{99}Tc literature reports the

evaluation of ^{99}Tc in environmental, waste, and geochemical samples using both radioanalytical and mass analysis.[7-11]

A. Radiometric Methods of ^{99}Tc Detection

Radioanalytical methods for the determination of ^{99}Tc ($\bar{B}_{Max.}$ = 293.6 keV, $\bar{B}_{Avg.}$ = 84.6 keV) are based on the detection of beta emissions using gas-flow proportional counters, surface barrier detectors, or liquid scintillation counting. Using any of the above detection methods, the removal of beta emitting interferents from the sample is essential due to the extremely low resolution of beta ray energies. The preparation of thin layer samples is necessary when detecting beta emissions using gas-flow proportional counting or surface barrier detectors to prevent attenuation, self-absorption, and back scattering effects. When detecting beta emissions by liquid scintillation counting, careful chemical preparation is necessary to prevent attenuation and self absorption through chemical or color quenching of the scintillation light.

Trace amounts of ^{99}Tc may also be detected by use of neutron activation analysis (NAA) with a thermal neutron flux of $\approx 5 \times 10^{13}$ n · cm^{-2} · s^{-1}. However, in order to employ this technique, the medium in which ^{99}Tc is irradiated must be a highly purified aqueous solution. Once irradiated, ^{99}Tc activity is determined based on the production of ^{100}Tc from the (n,γ) activation. In order to detect ^{100}Tc ($t_{1/2}$ = 15.8 s), a fast method of separation and detection of the gamma emitter is required.[11] Due to the short half-life of ^{100}Tc, other activation analyses have been proposed based on the formation of ^{99m}Tc in a (n,n′) reaction with reactor neutrons[12] and in a (γ,γ′) reaction with bremsstrahlung radiation.[13] Although these detection techniques are sensitive, activation

analysis are extremely tedious methods that are available to only a limited number of laboratories.

Because no stable isotope of technetium exists, chemical recovery by means of gravimetric yield is not possible for methods requiring chemical separation to isolate the ^{99}Tc isotope. Other isotopes of technetium have been employed (^{95m}Tc $t_{1/2}$ = 61 d and ^{99m}Tc $t_{1/2}$ = 6.02 h)[2] as internal yield monitors, but require analysis using other detection methods such as gamma spectrometry. Another method of yield determination employs the use of unspiked, spiked samples in which a known amount of ^{99}Tc is added to a duplicate sample. The difference between the spiked and unspiked values is used to determine percent recovery; however, the percent recovery is assumed to be the same in both the spiked and unspiked samples.

B. Mass Methods of ^{99}Tc Detection

To date bioassay analysis of ^{99}Tc by mass has not been reported. However, detection of ^{99}Tc in environmental, waste, and geochemical samples by mass is documented.[7-10,14,23,24] Isobaric, spectroscopic, and nonspectroscopic interferents preclude the direct analysis of ^{99}Tc, resulting in the requirement of a chemical separation procedure.

^{99}Tc isotope dilution analysis using thermal-ionization mass spectrometry (TIMS) has been reported[7] in which ^{97}Tc was used as the isotope dilution standard. The technetium was isolated chemically, and loaded onto a pair of resin beads with an approximate diameter of 0.3 mm and analyzed. The use of resonance ionization mass spectrometry (RIMS) has been utilized[14] for the ultra trace analysis of technetium in geochemical samples. A three-step, three-color, excitation and ionization scheme is

employed resulting in 1.6 fg limit of detection (LOD) for technetium. The determination of ^{99}Tc by isotope dilution inductively coupled plasma-mass spectrometry (ID/ICP-MS)[10] for aqueous samples has recently been published in which ^{97}Tc was used as the isotope dilution standard.

The chemical separation yield determination is an area of concern as well in ^{99}Tc analysis by mass. Ideally the long lived ^{97}Tc or ^{98}Tc isotopes would be used for isotope dilution analysis, however the scarcity of these isotopes precludes the extensive use of this method. Other technetium isotopes such as ^{95m}Tc have not been desirable for use in isotope dilution mass analysis because of the short half-life, high specific activity, and large quantities required for detection. A method combining the use of radioanalytical and mass detection was published.[15] ^{95m}Tc was used as an internal yield monitor and counted by gamma spectrometry, and ^{99}Tc was detected by ICP-MS.

C. Proposed Problem

As previously mentioned, safe disassembly and decontamination processes at sites contaminated with the long lived ^{99}Tc isotope require accurate personnel monitoring techniques. To date few studies on ^{99}Tc bioassay have been reported using radioanalytical methods, and no publications have been located using mass analysis. The objective of this dissertation is to evaluate the feasibility of determining ^{99}Tc in urine using inductively coupled plasma mass spectrometry (ICP-MS) and evaluate the detection sensitivity by mass compared to that by radioactive decay. In order to accomplish this objective, a chemical separation scheme must be developed to isolate the ^{99}Tc isotope from a urine matrix. In order to evaluate the detection capability of ICP-MS, the results from a ^{99}Tc mass analysis must be compared to results from a

commonly used radioanalytical method of detection, such as liquid scintillation counting. Finally, the detection sensitivities of the two methods may be compared and evaluated considering the data generated in the comparison study.

CHAPTER II

BACKGROUND

One of the major difficulties faced when working with an organic urine matrix is dealing with the high amounts of dissolved solids. Human urine when stored for only days has the potential of salting out as much as 20% by volume or higher. Because of sample inhomogeneity and potential container adsorption, many experimenters prefer to use the total sample in addition to container wall acid leaches when working with urine; however, measurements of ^{99}Tc activity per unit volume (dpm/L) require the use of exact volumes. A high dissolved solid content in the chemically separated solution has a negative effect in both radioanalytical and mass analysis. Colored urine samples also pose problems in liquid scintillation counting due to color quenching of the scintillation photon emissions. Additionally the presence of low energy beta emitting interferents, predominately ^{40}K, presents a problem in radioanalytical analysis due to the low β^- resolution and must be separated from the ^{99}Tc analyte. When determining ^{99}Tc by mass, isobaric interferents must either be removed or corrected for mathematically. Sample preparation for both radiometric and mass determinations must deal with these complex matrix issues to obtain accurate, reproducible results and maintain reasonable minimum detection concentrations (MDC).

A. Liquid Scintillation Analysis of ^{99}Tc

In 1980 Pacer[16] evaluated the ^{99}Tc counting efficiency over a 1000 fold concentration range, container adsorption tendencies, and quenching characteristics in liquid scintillation counting. At that time, he noted the lack of information available in the literature on liquid scintillation counting of ^{99}Tc, despite the major advances in counting

methodologies to cope with quenching effects and to minimize background. In this publication, ^{99}Tc as aqueous NH_4TcO_4 was analyzed by liquid scintillation over a concentration range of 10^{-4} to 10^{-7} M and found to be reproducible (relative standard deviation < 1%) with a counting efficiency greater than 94%. No adsorption of $^{99}TcO_4^-$ on glass or polypropylene containers was observed when samples ranging in concentration between 7.65×10^{-6} to 7.65×10^{-9} M were stored up to 3 months. Chemical quench was evaluated using $CHCl_3$ and was found to have only a slight effect on counting efficiency. Color quench was also evaluated using $K_2Cr_2O_7$ and found to have a pronounced effect on efficiency; however, quench corrections were successfully employed when total counts were assessed.

A method for the determination of ^{99}Tc in urine by liquid scintillation counting was published by Cattarin et al.[17] The chemical separation of ^{99}Tc was carried out using a pertechnetate coprecipitation with tetraphenylarsonium chloride ($AsPh_4Cl$) in the presence of perchlorate anion. The precipitate was dissolved in warm acetonitrile and counted by liquid scintillation. Mean separation recoveries of 98.2% for ten 1000 dpm controls and 97.4% for ten 100 dpm controls were obtained. The sample analysis was carried out using fresh, nondecomposed urine without the presence of solids or organic colloidal substances. In such samples, a peroxide digestion to oxidize organic material and acid addition to dissolve insoluble hydroxide salts before precipitation are necessary.

The analysis of ^{99}Tc in waste water from a pressurized nuclear-power reactor using liquid scintillation counting was reported by Verrezen and Hurtgen.[8] ^{99}Tc in waste water samples was adsorbed on AG 1X2 ion-exchange resin. The resin was washed

with water to remove all radioactive isotopes other than ^{99}Tc and ^{129}I. Technetium was then eluted from the column with hot (60°C) 6.0 M nitric acid. The solution was evaporated to dryness using an infrared lamp. The residue was dissolved in 1 mL of bi-distilled water, transferred into a low potassium glass vial, mixed with 19 mL of scintillation cocktail, and counted by liquid scintillation to determine the ^{99}Tc activity. Should this method be applied to urine samples, the same digestion concerns stated above would need to be addressed.

^{99}Tc analysis at the Lockheed Martian Energy Systems Center of Excellence for Bioassay was carried out using a liquid scintillation technique until the beginning of 1997. In this method developed by Khin Thein,[18] 30.0 mL of urine and 2.0 mL H_2O_2 were pipetted into 50 mL centrifuge cones and heated in an oil bath between 90 to 100 °C for one hour. The solution was cooled, acidified to 0.50 M with HNO_3, and poured over a prepared AG MP-1 anion exchange resin (NO_3^-), then washed with 0.50 M HNO_3 and 0.50 M HCl sequentially. The ^{99}Tc was eluted with 50.0 mL 4.0 M HNO_3, the volume was reduced on a hotplate without boiling to approximately 1 mL, the solution was combined with 12.0 mL scintillation cocktail, and the ^{99}Tc activity was determined by liquid scintillation counting over a region of 2.0 to 294 keV.

Thein's method proved to be accurate and reproducible; however, two areas of concern were associated with this procedure. First the vapor pressure of Tc_2O_7 is high at low temperatures (e.g., 10^{-1} mm at 100 °C),[19] so Tc(VII) is easily lost upon evaporation in acidic solutions unless a reducing agent is present or the evaporation is conducted at low temperatures. In an analytical laboratory setting with a large sample throughput and quick turnaround times, the slow solution evaporation step became

tedious and time consuming. A problem with sample loss occurred due to nonuniform heating on hotplates causing rapid evaporation and charring. Another problem area involved chemical quenching. Should small amounts of acid remain in the sample after evaporation, the solution/cocktail mixture would become extremely fluid, and quenching became so severe that quench correction techniques were not useful when counted by liquid scintillation.

B. ICP-MS Analysis of ^{99}Tc

Since the first commercial ICP-MS became available in 1983, the technique has gained wide and rapid acceptance as a simultaneous multielemental detection method for trace and ultratrace analysis. ICP-MS is increasingly being used as a tool for the measurement of long-lived radionuclides. Major advantages of ICP-MS over radioanalytical techniques include the absence of ionizing radiation interferents and rapid sample throughput. However, ICP-MS is not without faults. Interferents from isobars, polyatomic ions, and doubly-charged ions must be removed or monitored. In addition high concentration elements and large amounts of dissolved solids lead to signal suppression. A general rule in ICP-MS analysis is to maintain a total dissolved solid content of less than 0.1%.

Kim et al.[20] were one of the first groups of investigators to examine the potential for ^{99}Tc trace analysis in soil by ICP-MS. Soil samples were ashed at 450 °C, then leached with 8.0 M HCl. The leach was filtered and extracted with isopropyl ether. The aqueous layer was dried, acidified, and extracted with 5% tri-isooctylamine (TIOA)-toluene. Technetium was stripped with 1.0 M NaOH, poured over a Dowex 1-X8 column (OH-form), and washed with 1.0 M NaOH, 1.0 M HCl, and 0.10 M HNO_3. The

technetium was eluted using 8.0 M HNO_3 and analyzed by ICP-MS. Kim et al. found ^{99}Tc produced a linear calibration curve over a range of 3.2 to 42 ppt; however, molybdenum and ruthenium were present in the spectra.

In 1991 Kim et al.[21] evaluated the sequential analysis of ^{99}Tc, ^{226}Ra, ^{232}Th, ^{237}Np, ^{238}U, ^{239}Pu, and ^{240}Pu in acidic solutions using both high resolution ICP-MS (HR-ICP-MS) and ultrasonic nebulization. Kim et al. obtained ^{99}Tc LOD's of 0.23 ppt and 0.008 ppt, respectively.

The tendency of ^{99}Tc to form polyatomic and doubly-charged ions was evaluated by Crain and Gallimore[22] using 10 ppm and 100 ppb working solutions. Technetium was found not to form oxide and 2+ ions as readily as lanthanide and actinide elements, but did form higher order oxides, mimicking the behavior of W and other refractory transition elements. The following percentages of polyatomic and doubly-charged ion formation were found: TcH^+ = 0.002%, TcO^+ = 0.03%, TcO_2^+= 0.01%, TcO_2H^+= 0.002%, TcO_3^+= 0.01%, TcO_3H^+= 0.004%, and Tc^{2+} = 0.003%. Crain and Gallimore also noted a problem with memory effects using the high level technetium standards, however the memory was thought to be primarily chemical since higher-concentration acid rinse solutions raised the *m/z* background relative to a lower acid concentration rinse.

The evaluation of low-level quantities of ^{99}Tc in sea water by ICP-MS was reported by Momoshima et al.[23] ^{95m}Tc was used as an internal yield monitor and quantitated using gamma spectrometry. Technetium was concentrated from the aqueous samples by reduction to the IV state using $K_2S_2O_5$ and coprecipitation with $Fe(OH)_3$ at a pH of 9. At this point, Momoshima et al. evaluated countrates at *m/z* 99 in

blank samples prepared using methods efficient in isolating technetium, including methyl ethyl ketone (MEK), tetraphenyl arsonium chloride (TPAC), cyclohexanone, anion exchange resin, cation exchange resin, and cyclohexane. Based on background countrate data and the reported ability to remove Ru, MEK was chosen as the extraction medium. After extraction with MEK, the solution was passed over an anion exchange resin, washed with 1.0 M HNO_3, eluted with 16.0 M HNO_3, passed over a cation exchange resin, rinsed with 1.0 M HNO_3, counted by gamma spectrometry, and analyzed by ICP-MS. A 54.4% overall recovery was reported for this method and the presence of approximately 2.6 to 6.4 ppt of Ru was noted in the mass spectrum. In this study, Momoshima et al. evaluated the possible formation of a MoH^+ (*m/z* 99) polyatomic interference by spiking a HNO_3 solution with Mo and monitoring *m/z* 99. No difference in the *m/z* 99 countrate was observed between a spiked and a blank solution.

In approximately the same time period, Nicholson et al.[24] described a procedure similar to that of Momoshima et. al. for low-levels of ^{99}Tc in environmental samples in which a combination of TBP and MEK extractions were employed. Recoveries between 50 to 70%, LOD values equivalent to radioanalytical methods, and a Ru discrimination ratio ($X_{\text{Before Separation}}/X_{\text{After Separation}}$) of 4000 were obtained. In addition, discrimination ratios were determined for other possible polyatomic interferents including: $ZnCl^+$ = 2000, $NiCl^+$ >2800, $CoAr^+ = 7 \times 10^5$, and MoH^+ = 1600.

Recently the application of isotope dilution ICP-MS (ID/ICP-MS) for ^{99}Tc detection in aqueous samples was published by D. Beals.[10] In this method, a known amount of ^{97}Tc was spiked in the samples before chemical separation and the amount of ^{99}Tc was calculated from the $^{99}Tc/^{97}Tc$ ratio. To evaluate the method performance,

water samples spiked with ^{97}Tc were digested at boiling in the presence of H_2O_2 for one hour. Samples were poured over 2.0 mL equivalent amounts of TEVA-Spec resin and rinsed with 1.0 M HNO_3. Spiked ^{99}Tc samples were prepared to determine HNO_3 concentrations necessary for technetium elution. Optimum elution concentration and volumes included 20.0 mL of 8.0 M HNO_3 and 30.0 mL of 4.0 M HNO_3, giving 93% and 91% ^{99}Tc recoveries, respectively. Mass analysis showed the chemical separation procedure removed 99% Mo and 99.6% Ru from the original sample concentrations. A method LOD of 1.1 dpm/L based on reagent blank analysis was obtained.

In order to evaluate thoroughly the removal of isobaric interferents ^{99}Ru and ^{99}Mo, Ihsanullah published two articles dealing with Ru and Mo decontamination.[25,26] Separation methods including precipitation, NaOH washings on anion exchange resin, cyclohexanone, chloroform, 5% TIOA-xylene, carbon tetrachloride, and tri-n-butyl phosphate solvent extractions, and cation exchange were evaluated for the removal of Ru. Decontamination factors ($X_{\text{Before Separation}}/X_{\text{After Separation}}$) for each separation method were calculated. ^{99}Tc recoveries (%) and decontamination factors (F) achieved included: precipitation = 83%, 345F; NaOH = 74.7%, 170F; cyclohexanone = 98%, 1000F; chloroform = 1F; 5% TIOA-xylene = 97%, 700F; carbon tetrachloride = 700F, tri-n-butyl phosphate = 99%, 4000F; cation exchange = 90%, 10F. Several separation methods such as MEK extraction, TEVA-Spec resin, and HNO_3/HCl rinses on anion exchange resin were not included in this study.

Due to the reported presence of Mo in ion exchange resin, the need for a good molybdenum separation from technetium was noted by Ihsanullah.[26] Excessive quantities of ^{98}Mo and ^{100}Mo in a sample may cause spectral interference with ^{99}Tc due

to peak overlap, especially when using a low resolution mass analyzer such as a quadrupole. 12.0 M and 8.0 M HNO_3 blank sample rinses from unconditioned Dowex 1-X8 resin were evaluated by ICP-MS at *m/z* 94 , 98 and 100. The rinse solution mass spectrum showed peaks in the Mo isotope regions at approximately ppb levels; however, countrate ratios were not evaluated to determine if Mo isotope ratios correlated with the countrate data. In order to evaluate the removal of Mo from the resin, several experiments were performed including elution of Mo using 4.0, 8.0, 12.0, and 16.0 M HNO_3, elution of Mo from different quantities of resin, elution of Mo with 1.0 M HCl, and elution of Mo with NaOH. From the data presented, a general decrease in countrate at ^{95}Mo occurred with each 10.0 mL fraction of acid rinse; however, the countrate of the first 20.0 mL 16.0 M rinse was twice the rate of the 4.0 M rinse, and the fifth 20.0 mL 16.0 M rinse was over three times the fifth 4.0 M rinse. In general, the trend was to obtain a higher countrate with higher acid concentrations and the rate remained elevated during the acid rinse. The possibility of a chemical interference suggested by Crain and Gallimore[22] for *m/z* 99 was not investigated.

CHAPTER III

ANALYTICAL INSTRUMENTATION

In order to evaluate the overall capability of ^{99}Tc analysis in urine by ICP-MS, the mass data were compared to data from an established radioanalytical method. ^{99}Tc detection by liquid scintillation was chosen as the comparative method. The study was conducted in water, artificial urine,[27] and composited real urine matrices by dividing split prepared samples and analyzing one portion by ICP-MS and the other by liquid scintillation.

A. Liquid Scintillation

Liquid scintillation analysis is a well established radioanalytical method of detection that has been in use since the early 1950's. [28] Liquid scintillation counting is based on the measurement of radioactivity from the rate of photons emitted in a liquid sample.

1. Liquid Scintillation Cocktail

When an imbalance in the neutron/ proton ratio of a nucleus occurs, the element becomes unstable and rearrangement occurs. In the case of ^{99}Tc, the rearrangement leads to the emission of a beta (β^-) particle and an antineutrino ($\bar{\nu}$). The two particles are released simultaneously and share the decay energy from the nucleus. In the case of ^{99}Tc, the β^- could theoretically carry off between 0 to 293.6 keV of kinetic energy. In a liquid medium, the energy will be dissipated causing heating, excitation, and/or ionization of the molecules within the media. In liquid scintillation counting, a scintillation cocktail is typically mixed with the sample to absorb excitation energy and transfer the energy to a scintillator or fluor. Scintillation cocktails are typically made up of an

organic solvent that is partially miscible with the sample matrix, fluors with conjugated pi bonds that directly or indirectly absorb β^- energy and de-excite by emission of visible light or UV light, wavelength shifters that absorb short wavelength UV light and re-emit light that is more efficiently detected by photomultiplier tubes, and emulsifiers to increase miscibility between organic and aqueous mixtures. In liquid scintillation counting it is extremely important to select a scintillation cocktail that efficiently and effectively converts the β^- energy into light energy for a given sample matrix.

2. Liquid Scintillation Counter

The liquid scintillation counter used in this research project was a Packard Canberra 2500TR Tri-Carb equipped with low-level coincidence counting and pulse-summing capabilities. A general diagram of photon detecting process in a liquid scintillation counter is illustrated in Figure 1.

In most liquid scintillation cocktails, a nuclear decay event typically produces approximately 10 photons per keV of energy that is dissipated over a period of 5 ns.[28] A true β^- event within a sample vial, when placed between two photomultiplier tubes (PMT), should be detected by both detectors within a given time period. When using coincidence counting, an event over a discriminated pulse height must be recorded by both PMTs to register the event as real, not background. If the linear PMT signal is registered, the summation circuit can produce an output signal with a pulse amplitude representing the keV of energy released in the scintillation solution. Typically a β^- particle will take a few nanoseconds to dissipate all of its energy, resulting in an analog pulse rising to a maximum amplitude then falling to zero. The amplitude of the analog

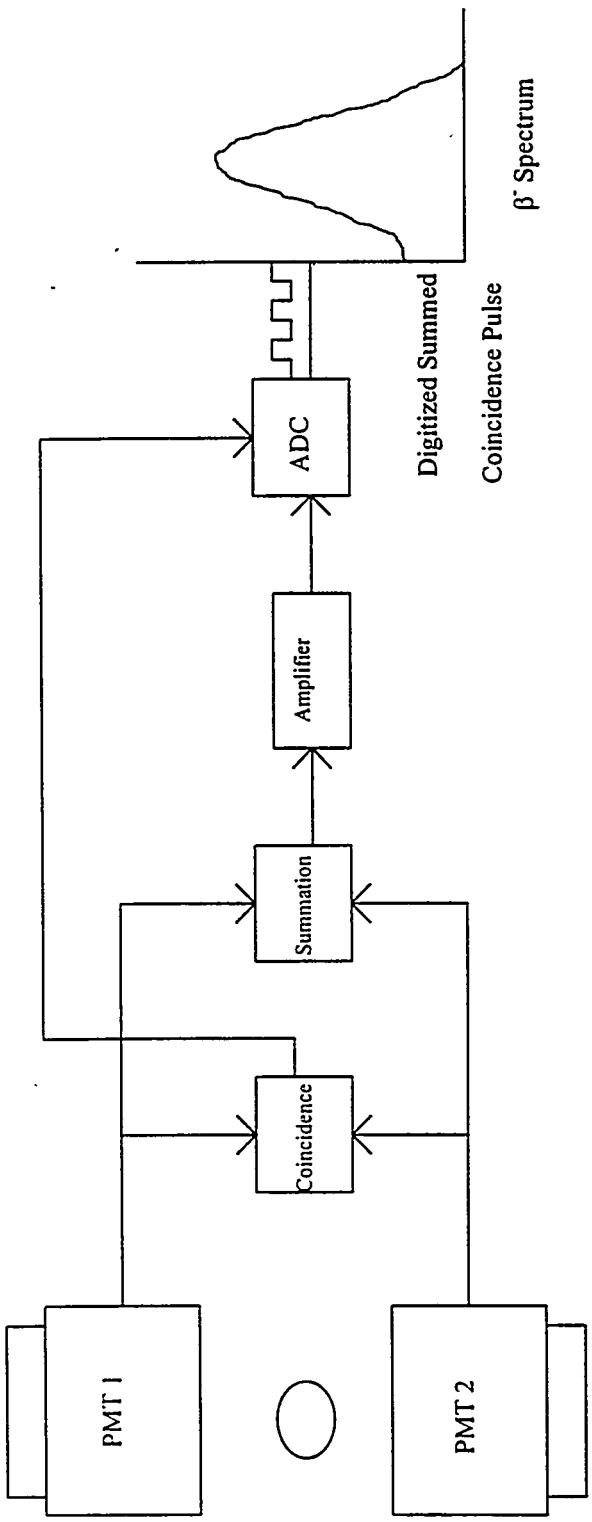


Figure 1. General liquid scintillation counter diagram.

pulse is converted into a digital value by a high speed analog to digital converter (ADC). The digital value is the address of a memory slot representing a channel within the energy range of 0 to 2000 keV.

The counting efficiency of a solvent-solute system can be affected by two factors, chemical and color quenching, that reduce the instrument detection efficiency. Chemical quenching occurs when chemical impurities in the sample interfere in the energy transfer from solvent to solute by absorbing the energy before it is converted into photons. All energy radiations are equally affected, and the net result is a skewed spectrum to lower apparent energies. Color quenching causes the attenuation of light photons in the cocktail. The resulting summed pulse heights may be the same as unquenched samples, but fewer in number. Color quenching will lead to a reduction in counts over the entire energy range. Illustrations of unquenched and quenched spectra are shown in Figures 2 and 3.

As a means of automatic quench correction, the Packard Canberra 2500TR Tri-Carb is equipped with the capability to perform transformed spectral index calculations (tSIE). In this technique, a sample is counted with and without the presence of a high activity ^{133}Ba gamma source. A mathematical technique is applied to the energy distribution of the ^{133}Ba-illuminated sample to correct for spectral distortions. In order to apply the quench correction, a series of uniformly spiked samples, each with increasing amounts of a quenching agent such as acetone, are counted in an appropriate liquid scintillation cocktail. The quenched standard activities and spectra are correlated with a tSIE value representing a %efficiency. An example of a quench correction calibration curve for ^{99}Tc is given in Figure 4.

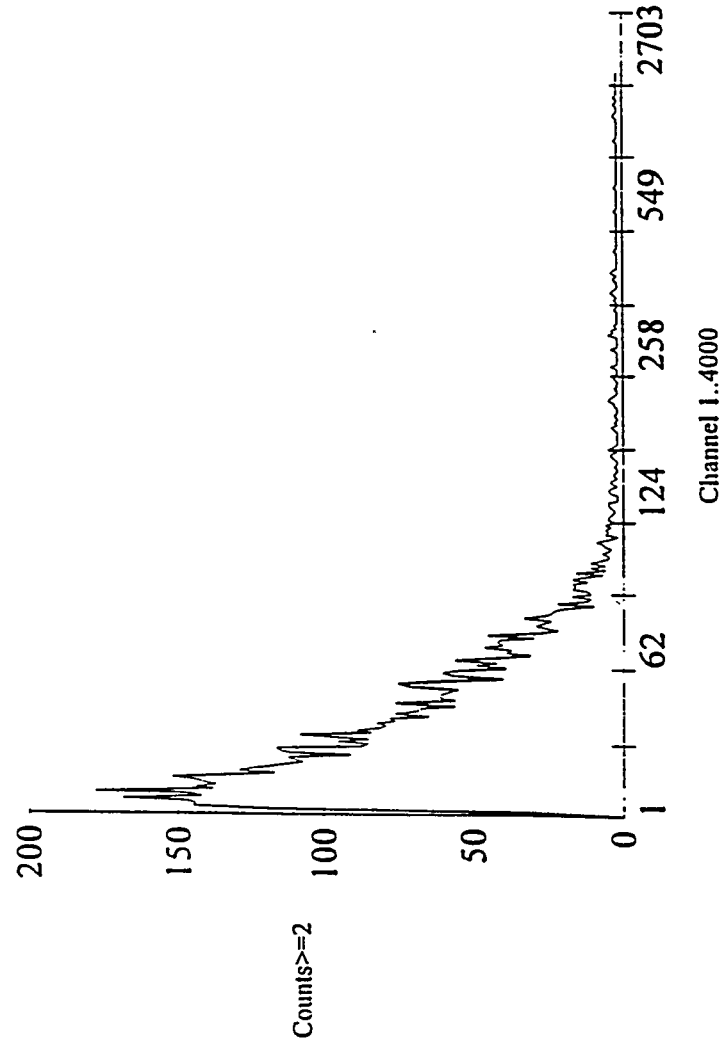


Figure 2. Liquid Scintillation unquenched urine sample spectrum.

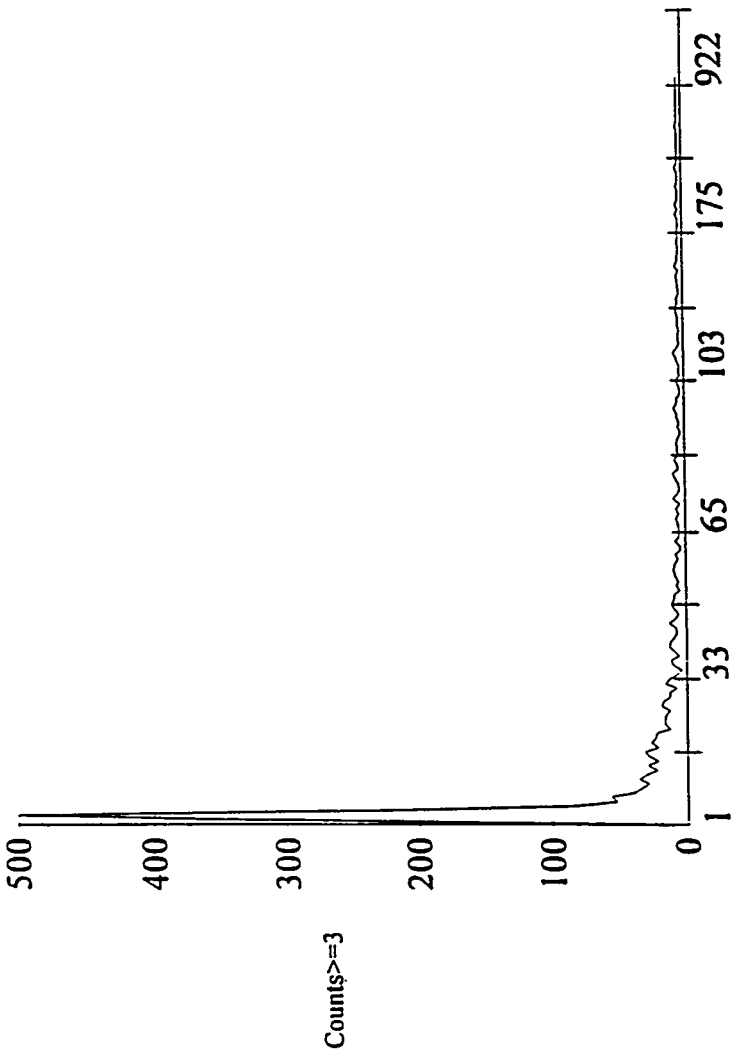
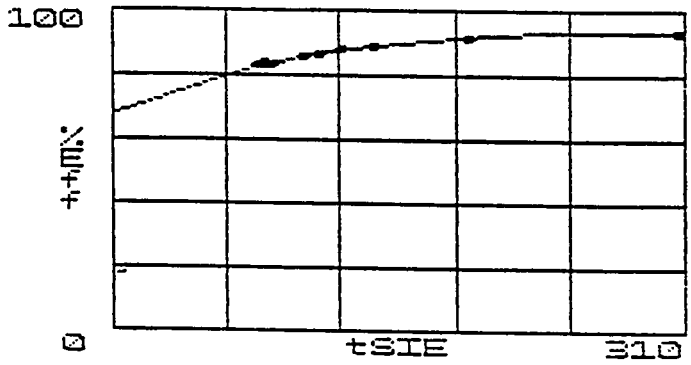


Figure 3. Liquid Scintillation quenched urine sample spectrum.

Data Mode: DPM
QIP Type: tSIE/AEC



tSIE	%Eff
305.70	93.49
194.63	91.91
143.36	89.13
124.61	87.96
113.06	86.98
103.74	85.87
85.78	83.39
84.97	83.70
83.22	83.86
78.61	82.97

Figure 4. Liquid Scintillation ^{99}Tc quench curve.

B. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ICP-MS system used in this research project was a Fissons PlasmaQuad +2 ICP-MS equipped with a standard cross-flow pneumonic nebulization sample introduction system. The PlasmaQuad +2 ICP-MS consists of six basic components: sample introduction, ICP, plasma sampling interface, ion optics, quadrupole mass filter, and ion detection systems. A general diagram of the basic ICP-MS components is given in Figure 5. Each of these systems, mass calibration, scan modes, and internal standards are briefly discussed in the following sections.

1. Sample Introduction

Pneumonic nebulization is based on the introduction of a sample that is disrupted by a high velocity gas flow causing the production of tiny droplets. A small positive pressure in the spray chamber propels the sample aerosol towards the torch. A cooled spray chamber is employed to ensure that only the smallest droplets (<10 μm) are carried to the plasma.[29] The introduction of only small droplets maintains an evenly loaded plasma that is not cooled by the larger droplets. Use of a spray chamber decreases the efficiency of the nebulization system to approximately one percent; however, use of a cooled spray chamber improves temperature stabilization promoting a rapid stabilization of instrument sensitivity.

2. ICP

Inductively coupled plasma is an electrodeless discharge in a gas at atmospheric pressure, maintained by an energy coupled RF generator.[30] Argon gas is used to create the plasma inside a quartz torch. The tourch is produced based on the Scott-Fassel

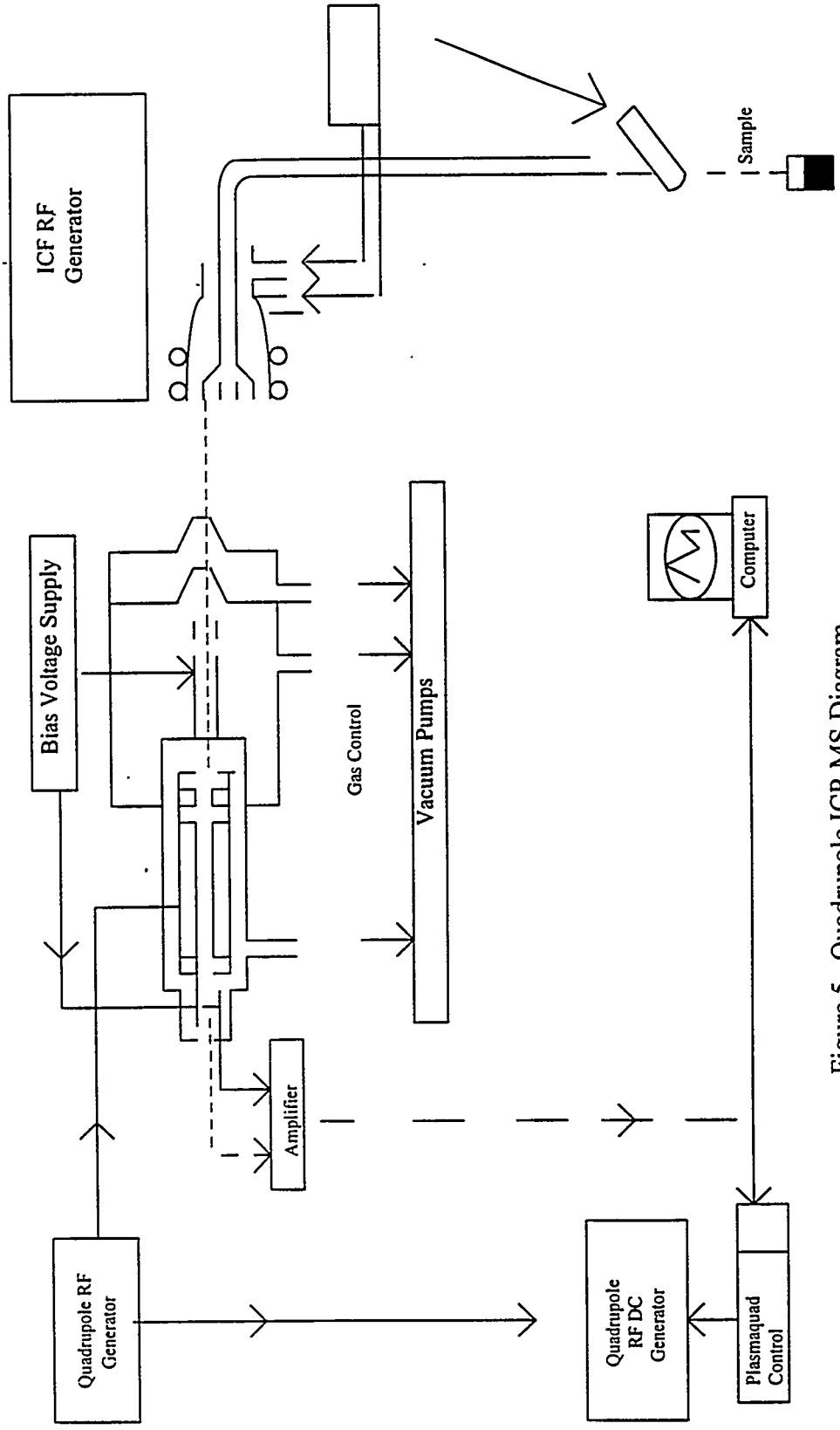


Figure 5. Quadrupole ICP-MS Diagram.

design. [31] The torch is made up of three different gas flow regions. Sample aerosol is introduced through the central region and carried by a nebulizer or carrier flow rate of about 1.0 L/min. The middle region contains the auxiliary gas flow that is primarily used to ensure the hot plasma is clear of the central tip. Gas flows between 0 and 1.5 L/min. are common.[30] The third region contains the outer coolant gas flow that protects the torch walls and supports the main plasma gas. Typical coolant flow rates are usually between 10 and 15 L/min.

An RF current is supplied by a generator that produces a magnetic field usually 27 to 40 MHz, along an axis. The plasma is initiated by a spark from a Tesla coil providing sufficient energy to overcome the dielectric resistance of the gas. The plasma is sustained by fluctuating magnetic and electric fields within the load coil. Free electrons are produced and couple with the fields. The electrons swirl in circular orbits causing the electrical energy to be converted to kinetic energy. Energy is transferred when free electrons collide with argon and other atoms in the plasma. At 10, 15 and 20 mm from the coil, approximate temperatures are cited as 8000, 6500, and 6200 K +/-10%, respectively.[29]

3. Sampling Interface

The purpose of the sampling interface is to transfer a sample of the plasma from near atmospheric pressure to a high vacuum chamber. The plasma is sampled by a water cooled metal orifice called the sampling cone, and directly behind the sampling cone is a second orifice called a skimmer cone. The expansion chamber is the partially evacuated region between the two cones.

The ICP-MS is designed to sample from the bulk plasma by ensuring a continuous flow into the vacuum system. This occurs when the ratio of the mean free path of gas species, λ, to the diameter of the sampling aperture is less than 0.01. Argon at 7500 K and $\lambda = 1.6\ \mu m$ requires an aperture of 0.16 mm or greater to ensure continuum flow.[29] Typical apertures are 1.0 mm for sample cones and 0.7 mm for skimmer cones.

A pressure ratio of 1 bar/1 mbar is established at the sampling interface which is sufficient to form a supersonic jet inside the first stage. The jet contains a zone of silence surrounded by shock waves called the Mach disc. To avoid ion loss due to scattering and collisions, the skimmer cone is positioned with its open tip within the disk causing the zone of silence to pass through the skimmer into the second vacuum stage.[30]

4. Ion Optics

Charged species are focused through a differential pumping aperture and into the mass filter by means of ion optics. The system is madeup of several symmetrical electrostatic lenses on the system axis and is powered by a lens power supply unit. A negative voltage on the extraction electrode extracts positive ions from the skimmer and directs them to the lens stack. Negatively charged species are repelled and neutral species diffuse away. Ions are directed to the collector electrode followed by an on-axis photon-stop mounted close to the collector to prevent light and neutral species from passing down the lens stack. Ions that are directed around the photon stop and through the differential pumping aperture are focused by lenses L1 and L2. Lenses L3 and L4 serve to refocus the ions emerging from the aperture into the quadrupole.[29]

5. Quadrupole Mass Filter

The role of the quadrupole mass filter is to transmit ions of a given *m/z* ratio. The mass resolving capability of the filter is based on the intrinsic stability/instability characteristics of an ion under a specific type of electric field. A high vacuum is essential for good performance because residual gas will disrupt ion trajectories.

A quadrupole is comprised of four electrically conducting molybdenum rods arranged in a square array with an internal circular (inscribed) radius $\mathbf{r_o}$. The rods are arranged to produce a time dependent oscillating electric field in good approximation to that of an ideal hyperbolic field. There is no field component along the axis of the quadrupole and the **x**, **y** components are independent of each other. Equal and opposite potentials, **+Vo** and **-Vo**, are applied to the **x** and **y** axis rod pairs. When a varying RF potential [$\mathbf{Vo = Vp}\cos(2\pi ft)$] and nonvarying potential (**U**) are applied, the overall sinusoidally varying field effect may be represented by the following equation:

$$Vo(t) = U + Vp\cos(2\pi ft) \qquad (1)$$

In the **x** axis, **+U** produces a potential valley that tends to stabilize trajectories of the higher mass ions that are less capable of following the swings of the RF component, producing a high pass filter. The opposite occurs in the **y** axis since **-U** creates a potential hill that defocuses all ions. Suitable frequencies may be selected that stabilize the lighter ions as they move down the potential hill producing a low pass filter. The overall consequence of the situation described by Equation 1 is a band pass mass filter in which the resolution is determined by the ratio of **U/Vp**.[29]

A rigorous analysis of the behavior of **Vo** was solved using the Mathieu differential equations, in which two types of regions, stable and unstable, were found.

Stable regions represented ion trajectories that pass along the quadrupole without hitting the rod surfaces, and unstable regions represented ion trajectories hitting the rod surfaces. When these areas are plotted graphically, a mass scan line representing a DC-to-RF ratio of 1/5.96 or smaller may be derived that passes through the **x**, **y** region of stability. To scan along the stability region of the mass scan line, **Vp** and **U** are varied within given limits.[30]

6. Ion Detection

A Channeltron electron multiplier is used in the PlasmaQuad +2 ICP-MS. The multiplier may be operated in either pulse counting mode for trace analysis or analog mode for higher level analysis. The interior of the Channeltron is coated with a lead oxide semiconducting material. For positive ion detection, a high negative potential (~ -3 kV) is applied to the cone, and the collector is maintained near ground. The resistance of the interior is varied continuously with position, setting-up a continuous potential gradient.[30] When a positive ion hits the multiplier, secondary electrons are ejected and amplified as the electrons move down the potential gradient toward ground. Approximately 10^8 electrons are collected as the result of one ion strike. The pulse is sensed and shaped by a fast pre-amp, and the output pulse is sent to a digital discriminator and counting circuit. Only pulses above a given amplitude are counted. When Channeltrons are operated in analog mode, the gain of the detector is lowered by reducing the applied voltage, and the ion current generated within the multiplier is monitored.

7. Mass Calibration

Mass calibrations are essential to the operation of an ICP-MS. During a

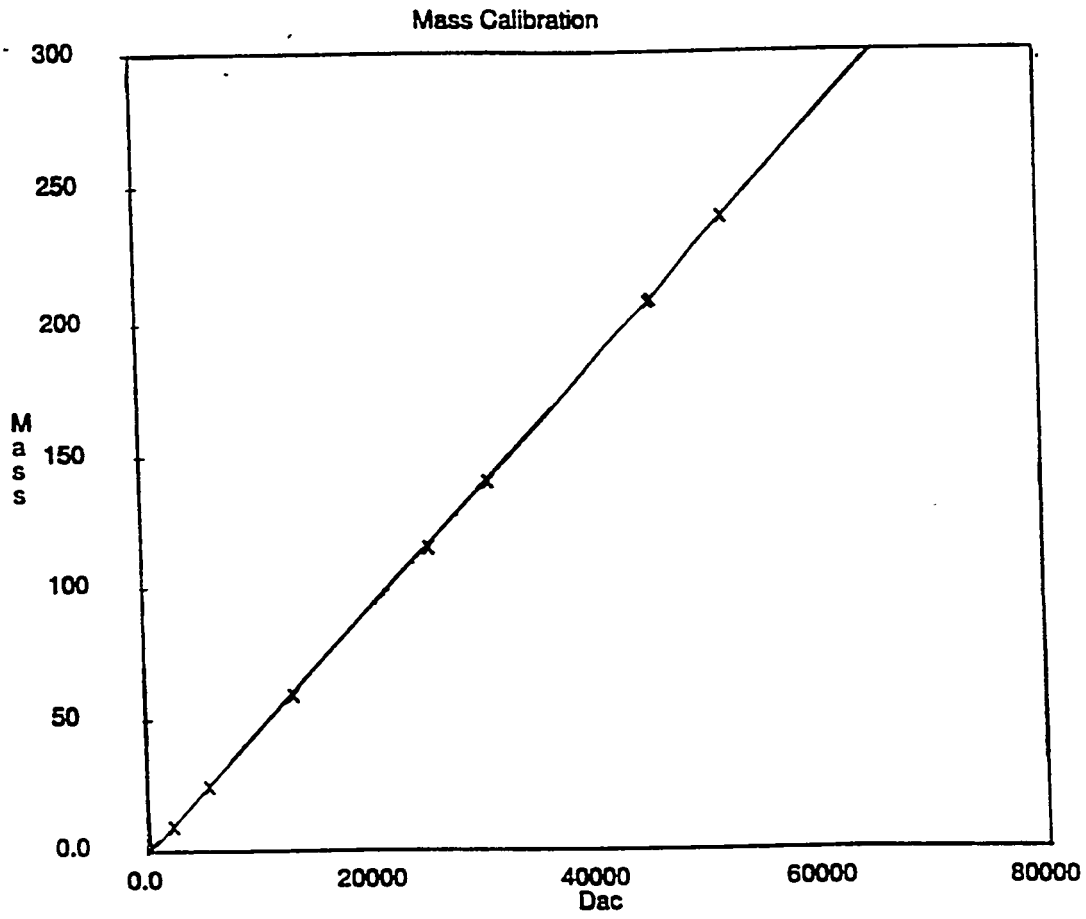
calibration, a solution containing approximately six elements (≈25 ppb) with masses covering the entire mass range is analyzed to determine the digital-to-analog conversion settings for the quadrupole control system. An example of a mass calibration plot is displayed in Figure 6.

8. Scanning Modes

Single ion monitoring, peak-jumping, and multichannel scanning are the three main scanning modes available with an ICP-MS. **U** and **V** remain unchanged at a selected *m/z* when using the single ion monitoring option, providing a 100% duty cycle. **U** and **V** can be changed rapidly under computer control to preselected discrete values in the peak-jumping mode. Alternatively, **U** and **V** can be scanned repetitively through values corresponding to a *m/z* region of interest with multichannel scanning.

9. Internal Standards

The correction of one element using a second element as a reference is the basis of internal standardization. Internal standards are employed to monitor and correct short or long term fluctuation in signals and correct for matrix effects. To be effective, internal standards must match the element of interest in both ionization potential (IP) and mass. ^{115}In was chosen as the internal standard for this research project due to its relative closeness in mass, 95.7% abundance, IP difference of 1.494 eV, and availability.[30]



Coefficients : Y = A0 + A1X + A2X^2 ... AnX^n

A0	A1	A2	A3	A4
-3.48500E-1	4.56456E-3	-6.44258E-12	0.00000E+0	0.00000E+0

Figure 6. ICP-MS mass calibration curve.

CHAPTER IV

METHOD DEVELOPMENT FOR THE ISOLATION OF ^{99}Tc FROM A URINE MATRIX FOR THE PURPOSE OF A COMPARISON STUDY BY LIQUID SCINTILLATION AND ICP-MS

As previously mentioned, a published analytical method for the analysis of ^{99}Tc in a urine matrix by ICP-MS was not located. In order to compare the ICP-MS detection capabilities and sensitivity to that of a radioanalytical technique, such as liquid scintillation, a method was developed that enabled samples to be analyzed by both methods. To accomplish this goal, a method was designed to remove both radioanalytical interferents (^{40}K and ^{99}Mo), as well as mass interferents (^{99}Mo, ^{99}Ru, and dissolved solids).

A. Chemicals

18 MΩ water was used in each stage of the research project. All nitric and hydrochloric acid solutions were prepared using J. T. Baker Ultrex concentrated acid. Biorad AG MP-1 anion exchange resin was used in the separation procedure and prepared by soaking in water for a minimum of 10 hours. Artificial urine[27] used in the method development and the comparison study was prepared according to the recipe described in the Appendix. All reagents used to prepare the artificial urine and the hydrogen peroxide were analytical grade supplied by VWR Scientific. Packard's Insta-gel XF® liquid scintillation cocktail was chosen for this project due to its ability to handle better the quenching characteristics of a prepared urine sample matrix. A ^{99}Tc standard was procured from the National Institute of Standards and Technology (NIST). Working solutions of the standard were prepared by mass, and secondary standard activities

were verified by liquid scintillation counting. Spectrometric standard solutions of Mo and Ru were obtained through VHG Labs, Inc., and Indium was obtained through High Purity Standards.

B. Sample Digestion

In order to digest properly the urine matrix, aliquots of sample blanks and spikes were transferred to covered beakers and heated on hot plates at temperatures between 150 and 200°C for approximately one hour. In order to convert technetium to the VII oxidation state and oxidize the organic matrix, an excess of H_2O_2 was added to the sample before digestion. To ensure that the addition of excessive amounts of peroxide did not interfere with ICP-MS analysis, a series of 50.0 mL real and artificial urine samples were spiked with ^{99}Tc and digested. Varying ratios of peroxide-to-sample volumes were used in the experiment. ^{99}Tc was separated from the dissolved solids and cations (including K^+) using anion exchange, eluted with 30.0 mL of 3.0 M HNO_3, diluted to 50.0 mL, and analyzed by ICP-MS in peak-jumping mode using ^{115}In as an internal standard. The results of the experiment are given in Table 1. The ratio of peroxide-to-sample volume did not appear to effect the total ^{99}Tc recovery. However, upon reviewing the calculated data, a discrepancy between the real and artificial urine recoveries was noted. When preparing this set of data, an omission of an artificial urine reagent blank was made. The calibration blank was used to blank correct the artificial urine values, while a real urine reagent blank was used to correct the real urine values. The value of the calibration blank was 0.0119 ppb, and that of the real urine blank was 0.0079 ppb. At this point, the necessity to matrix match the standards and samples as closely as possible was realized. Matrix matching will be covered further in Chapter V.

TABLE 1

DETERMINATION OF URINE SAMPLE-TO-PEROXIDE RATIO FOR DIGESTION

Sample ID	Matrix	Ratio Peroxide:Sample	^{99}Tc (ppb)	True Value (ppb)	% Recovery
R1-6	Real Urine	1:17	0.0071	0.0075	95
R2-6	Real Urine	1:17	0.0090	0.0075	120
R1-8	Real Urine	1:13	0.0073	0.0075	97
R2-8	Real Urine	1:13	0.0079	0.0075	110
R1-10	Real Urine	1:10	0.0082	0.0075	110
R2-10	Real Urine	1:10	0.0077	0.0075	100
R1-12	Real Urine	1:08	0.0078	0.0075	100
A1-2-10	Artificial Urine	1:10	0.0039	0.0075	52
A2-2-8	Artificial Urine	1:13	0.0021	0.0075	28
A1-7-10	Artificial Urine	1:10	0.0042	0.0075	56
A2-7-10	Artificial Urine	1:10	0.0043	0.0075	57
A3-7-8	Artificial Urine	1:13	0.0046	0.0075	61
A4-7-8	Artificial Urine	1:13	0.0050	0.0075	67

A peroxide-to-sample ratio of 1:10 was chosen for sample digestion.

C. ^{99}Tc Elution

The use of nickel sample and skimmer cones within an ICP-MS instrument limits acid concentrations that can be introduced into the instrument. Reported acid concentrations used to strip ^{99}Tc from anion exchange resin ranged from 4.0 to 16.0 M HNO_3. A decision was made to evaluate the ^{99}Tc extraction efficiency of less concentrated acids for subsequent ICP-MS analysis. Seven 150 mL solutions of artificial urine were spiked with 0.115 ppb ^{99}Tc and digested as described above. The solutions were poured over columns containing prepared 1.8 mL by volume AG MP-1 anion exchange resin (NO_3^--form) and rinsed with 0.50 M HNO_3 followed by 0.50 M HCl. ^{99}Tc was extracted from each column using a different molarity of nitric acid (1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 M). Columns containing a known amount of ^{99}Tc were extracted with a total of 40.0 mL of one of the above acids at room temperature. The column was extracted with 10 mL aliquots and each 10 mL fraction was collected, spiked with the internal standard, and analyzed by ICP-MS in peak-jumping mode. The experimental data obtained is displayed in Table 2. The 3.0 through 4.0 M HNO_3 concentrations appear to have extracted the majority of the ^{99}Tc in the first 30 mL. The 3.0 M acid extraction efficiency was comparable to that of 4.0 M. Fifteen samples, both real and artificial urine, were spiked with 0.1661 ppb ^{99}Tc, digested, and eluted with either 3.0 or 4.0 M HNO_3. The overall ^{99}Tc recovery was lower than desirable but consistent for both acid concentrations (Table 3).

In order to determine if the low recoveries were due to column loading failure, a series of real urine samples (50.0 mL) was digested and loaded onto prepared anion

TABLE 2

NITRIC ACID MOLARITY REQUIRED FOR ^{99}Tc ELUTION
FROM AG MP-1 RESIN

Nitric Acid Concentration M	% Recovery 1st 10 mL	% Recovery 2nd 10 mL	% Recovery 3rd 10 mL	% Recovery 4th 10 mL	% Recovery Total
4.0	75	12	0	0	87
3.5	61	29	3	1	94
3.0	37	35	5	1	78
2.5	38	37	8	1	84
2.0	26	29	18	5	78
1.5	16	25	30	23	94
1.0	9.1	10	10	11	40

TABLE 3

4.0 AND 3.0 M ELUTIONS OF ^{99}Tc
FROM AG MP-1 RESIN

Sample ID	Urine Matrix	Measured ^{99}Tc (ppb)	True Value ^{99}Tc (ppb)	% Recovery
4M1	Artificial	0.1394	0.1661	83.93
4M2	Artificial	0.1412	0.1661	85.01
4M3	Artificial	0.1268	0.1661	76.34
4M4	Artificial	0.1165	0.1661	70.14
3M1	Artificial	0.1151	0.1661	69.30
3M2	Artificial	0.1230	0.1661	74.05
4M1	Real	0.0898	0.1661	54.1
4M2	Real	0.1029	0.1661	61.95
4M3	Real	0.0840	0.1661	50.6
4M4	Real	0.1196	0.1661	72.00
3M1	Real	0.1180	0.1661	71.04
3M2	Real	0.1232	0.1661	74.17
3M3	Real	0.1322	0.1661	79.59
3M4	Real	0.1187	0.1661	71.46

exchange columns. The sample load solution and rinses were poured over a second column. Each column was extracted with 30.0 mL of 3.0 M HNO_3 and diluted to 50.0 mL. The solutions were spiked with internal standard and analyzed by ICP-MS in peak-jumping mode. The combined ^{99}Tc recoveries (Table 4) were consistent with previously obtained results. It appeared the anion exchange resin resulted in an incomplete release of ^{99}Tc into the aqueous phase (approximate flow rate of 1 mL/min). In an attempt to effect a complete release of ^{99}Tc into the aqueous phase, an experiment was carriedout in which the 3.0 M HNO_3 eluant was warmed to approximately 95°C before elution. The data obtained from this experiment (Table 5, Figure 7) were very promising; however, all recoveries were above 100%, suggesting the presence of a spectral interferent.

D. Evaluation Of Interferent Removal

When first evaluating the possibility of analyzing ^{99}Tc by ICP-MS, it was desirable to quantitate the levels using as little sample preparation as possible. It was thought that the high temperatures within the plasma could singly ionize all ^{99}Tc atoms and break down any undigested matrix complexes. Samples of raw urine were first digested with H_2O_2 and acidified with nitric acid to dissolve slightly soluble salts. Analysis by ICP-MS was attempted, however very few samples were analyzed before complete suppression of the signal occurred. When the sample cone was removed from the interface, long needle shaped salt crystals could be seen on the surface of the skimmer cone. At this point, it was obvious that the dissolved solid content of undiluted, digested urine was much too high for direct analysis by ICP-MS. Dilution of the digested urine prior to analysis would appear to be a possible solution. The amount of dilution

TABLE 4

EVALUATION OF COLUMN RINSE TO DETERMINE
SOURCE OF LOW RECOVERIES
ON AG MP-1 RESIN

Sample ID	True Value ^{99}Tc (ppb)	Column 1 ^{99}Tc (ppb)	Column 1 % Recovery	Column 2 ^{99}Tc (ppb)	Column 2 % Recover	Total Recovery
A-1	0.1069	0.0799	74.7	0.0094	8.8	84
A-2	0.1069	0.0760	71.1	0.0038	3.6	75
A-3	0.1069	0.0862	80.6	0.0039	3.6	84
A-4	0.1069	0.0994	93.0	0.0027	2.5	96
A-5	0.1069	0.0736	68.8	0.0058	5.4	74
A-6	0.1069	0.0591	55.3	0.0088	8.2	64
A-7	0.1069	0.0592	55.4	0.0098	9.2	65
B-1	0.0750	0.0505	67.3	0.0043	5.7	73
B-2	0.0750	0.0558	74.4	0.0057	7.6	82
B-3	0.0750	0.0502	66.9	0.0027	3.6	71
B-4	0.0750	0.0476	63.5	0.0059	7.9	71
B-5	0.0750	0.0533	71.1	0.0033	4.4	75
B-6	0.0750	0.0637	84.9	0.0046	6.1	91
C-1	0.0750	0.0512	68.2	0.0020	2.7	71
C-2	0.0750	0.0515	68.7	0.0035	4.7	73
C-3	0.0750	0.0481	64.1	0.0129	17.2	81
C-4	0.0750	0.0474	63.2	0.0093	12	76

TABLE 5

ELUTION OF ^{99}Tc USING 3.0 M NITRIC ACID AT 95 ^{o}C

Sample ID	1st 10 mL ^{99}Tc (ppb)	2nd 10 mL ^{99}Tc (ppb)	3rd 10 mL ^{99}Tc (ppb)	Total ^{99}Tc (ppb)	True value ^{99}Tc (ppb)	% Recovery
Sample 1	0.0790	0.0754	0.0074	0.1618	0.1490	110.0
Sample 2	0.0930	0.0626	0.0037	0.1593	0.1490	110.0
Sample 3	0.0918	0.0603	0.0033	0.1554	0.1490	100.0
Sample 4	0.0965	0.0611	0.0023	0.1599	0.1490	110.0
Sample 5	0.0855	0.0732	0.0033	0.1620	0.1490	110.0
Sample 6	0.0985	0.0647	0.0022	0.1654	0.1490	110.0
Sample 7	0.1039	0.0558	0.0016	0.1613	0.1490	110.0

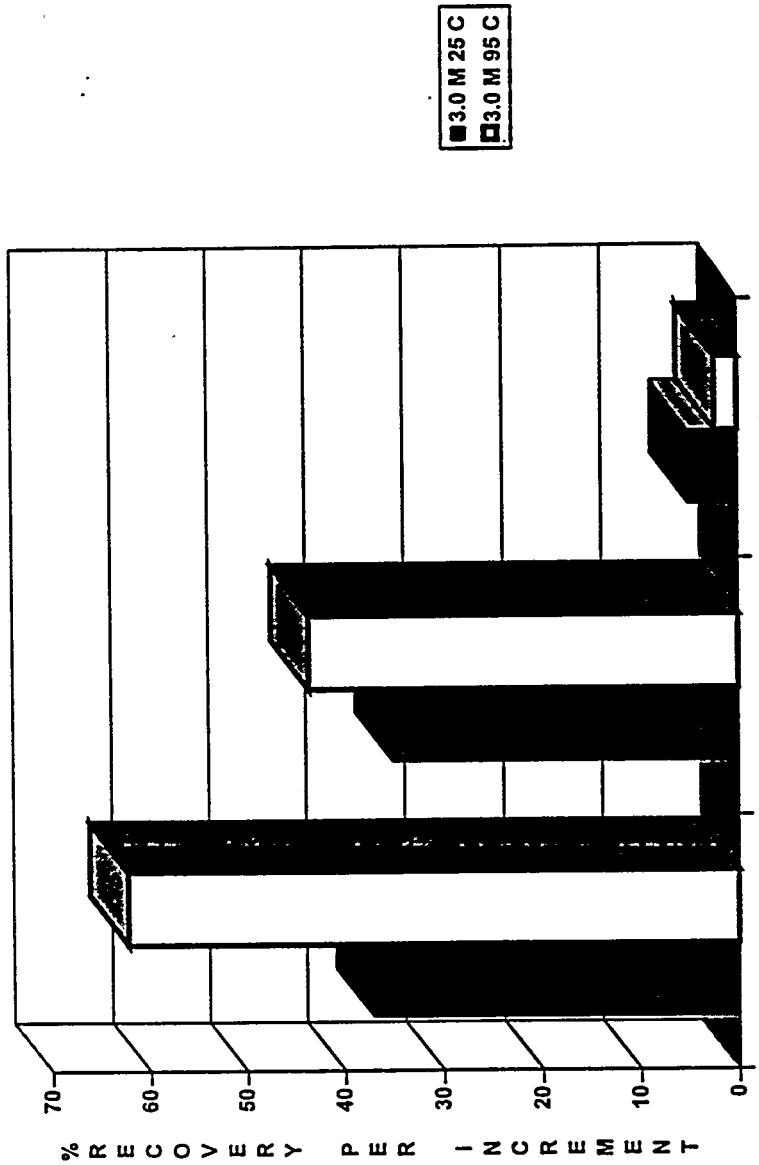


Figure 7. Tc-99 elution using 3.0 M nitric acid at 25 and 95 °C.

that would be required to analyze the urine sample, however, would yield an unacceptable MDC (Refer to Chapter V for MDC calculation) for radiation workers, and could dilute the ^{99}Tc concentration to a level below the MDC. At this point, it was obvious that a chemical separation procedure was necessary to reduce the total dissolved solid content.

The removal of isobaric Mo and Ru interferents was another incentive for the use of a chemical separation procedure to isolate ^{99}Tc. In order to evaluate the decontamination of Mo and Ru, three separate series of 30 mL water samples were spiked with four different levels of Mo and Ru: Blank, 0.0101, 0.0403, 0.0807, and 0.1518 ppb. Each level in a series was prepared in duplicate. Two blanks (NCB) were prepared for each series and taken through the sample digestion steps, but not the column separation steps. The final acid concentration of the NCB's was 0.50 M HNO_3 compared to 2.0 M for column separation samples. An individual series of samples was taken through the column separation procedure (digestion, acidification, column loading, and 0.5 M HNO_3 rinse), however a different concentration of the 30 mL HCl rinse was used for each series to remove Mo and Ru interferents. Acid rinse concentrations evaluated included 0.50, 0.70, and 1.0 M HCl. ^{99}Tc was eluted using 20 mL of hot (95°C) 3.0 M HNO_3 and diluted to 30 mL, resulting in a final acid concentration of 2.0 M. Both the acid rinse and samples were analyzed for Mo and Ru by ICP-MS in peak-jumping modes for mass regions 95, 97, 101, 102, and 104. Masses 95 and 97 represented Mo isotopes and masses 101, 102, and 104 represented Ru isotopes. Due to present software restrictions, only the total Mo and Ru concentration for each isotope was quantitated. ICP-MS calibration curves were generated using blank, 0.0506,

0.1009, and 0.2530 ppb Mo/Ru standards in 2.0 M HNO_3. The calibration slope for each of the masses evaluated was linear with a linear regression coefficient of 0.9993 or higher. The Mo and Ru decontamination results are given in Tables 6 - 8.

Close evaluation of the results revealed several interesting aspects. No apparent difference was noted between the calibration blank and the NCB Mo and Ru concentrations for the 0.50 and 1.0 M HCl rinses, nor in the Ru concentration for the 0.70 M HCl rinse; however, the 0.70 M NCB Mo concentrations were higher than the calibration blank concentration. In addition, the elevated total Mo concentrations in the chemically separated blanks were similar for both 95 and 97 *m/z*, suggesting the true presence of Mo.

The sample results displayed in Tables 6 - 8 were corrected with the appropriate column separated blanks for that series. Blank subtracted results for samples spiked between 0.0101 through 0.1518 ppb Mo and Ru were predominately less than 0.003 ppb for the 0.50 M rinse, but somewhat higher and more erratic for the 0.70 and 1.0 M rinses. As a result, the average percent removal for both Mo and Ru were higher for the 0.50 M HCl rinse.

In order to evaluate further the results from the decontamination experiments discussed above, the raw countrate data for each standard, blank, and sample were evaluated to ensure calibration abnormalities did not occur (Table 9). The 0.50 and 1.0 M series were prepared and analyzed together, and the 0.70 M series evaluation was conducted several days later. This time lapse may be noted in the blank and standard countrates. A decrease in sensitivity for the 0.70 M set was apparent, but the overall results did not appear to be affected. However, an approximate 40% lower than

TABLE 6

Ru AND Mo DECONTAMINATION USING
A 0.50 M HCl COLUMN RINSE

Sample ID	Blank Subtraction	^{95}Mo Mo (ppb)	^{97}Mo Mo (ppb)	^{101}Ru Ru (ppb)	^{102}Ru Ru (ppb)	^{104}Ru Ru (ppb)	True Value Mo-Ru (ppb)	%Removal Mo	%Removal Ru
Cal. B	None	0.0547	0.0617	0.0097	0.0085	0.0111	None	NA	NA
NCB1	None	0.0681	0.0727	0.0059	0.0069	0.0112	None	NA	NA
NCB2	None	0.0718	0.0834	0.0095	0.0073	0.0103	None	NA	NA
B1	None	0.1998	0.2135	0.0078	0.0073	0.0122	None	NA	NA
B2	None	0.1549	0.1662	0.0067	0.0075	0.0107	None	NA	NA
S1-1	B2	-0.0041	0.0048	0.0006	-0.0001	0.0012	0.0101	140	100
S1-2	B2	0.0006	-0.0022	0.0011	0.0002	0.0003	0.0101	90	100
S2-1	B2	-0.0098	-0.0091	0.0014	-0.0004	-0.0001	0.0403	100	100
S2-2	B2	-0.0048	-0.0038	0.0016	-0.0002	0.0012	0.0403	100	100
S3-1	B2	-0.0148	-0.0147	0.0024	0.0007	0.0013	0.0807	100	100
S3-2	B2	-0.0022	-0.0004	0.0020	0.0003	0.0019	0.0807	100	100
S4-1	B2	-0.0259	-0.0262	-0.0022	-0.0007	0.0007	0.1518	100	100
S4-2	B2	-0.0046	-0.0011	0.0032	-0.0003	0.0013	0.1518	100	100
	%Abundance:	15.9	9.5	17.0	31.0	18.4			

^{95}Mo and ^{102}Ru were used to determine %Removal of the Mo and Ru interference for ^{99}Tc analysis by ICP-MS.
NCB represents a blank that was taken through the procedure with the exception of the column step. B represents a blank that was taken through both the digestion and column steps.

TABLE 7

Ru AND Mo DECONTAMINATION USING
A 0.70 M HCl COLUMN RINSE

Sample ID	Blank Subtraction	^{95}Mo Mo (ppb)	^{97}Mo Mo (ppb)	^{101}Ru Ru (ppb)	^{102}Ru Ru (ppb)	^{104}Ru Ru (ppb)	True Value Mo-Ru (ppb)	%Removal Mo	%Removal Ru
Cal. B	None	0.0486	0.0543	0.0153	0.0054	0.0163	None	NA	NA
NCB1	None	0.1017	0.0982	0.0137	0.0038	0.0167	None	NA	NA
NCB2	None	0.0912	0.0954	0.0117	0.0061	0.0168	None	NA	NA
B1	None	0.0935	0.1119	0.0144	0.0055	0.0149	None	NA	NA
B2	None	0.1087	0.1152	0.0126	0.0042	0.0160	None	NA	NA
S1-1	B2	0.0174	0.0175	0.0015	0.0004	-0.0003	0.0101	70	100
S1-2	B2	-0.0091	-0.0077	0.0016	0.0018	0.0009	0.0101	200	80
S2-1	B2	-0.0101	-0.0086	0.0037	0.0017	-0.0012	0.0403	130	96
S2-2	B2	0.0037	0.0058	0.0037	0.0012	0.0001	0.0403	90	100
S3-1	B2	0.0198	0.0159	0.0018	0.0008	-0.0001	0.0807	80	100
S3-2	B2	-0.0061	-0.0039	0.0013	0.0007	0.0010	0.0807	100	100
S4-1	B2	-0.0107	-0.0106	0.0022	0.0005	-0.0003	0.1518	100	100
S4-2	B2	0.0026	0.0103	0.0018	0.0008	0.0004	0.1518	100	100
	%Abundance:	15.9	9.5	17.0	31.0	18.4			

^{95}Mo and ^{102}Ru were used to determine %Removal of the Mo and Ru interference for ^{99}Tc analysis by ICP-MS.
NCB represents a blank that was taken through the procedure with the exception of the column step. B represents a blank that was taken through the digestion and column steps.

TABLE 8

Ru AND Mo DECONTAMINATION USING
A 1.0 M HCl COLUMN RINSE

Sample ID	Blank Subtraction	^{95}Mo Mo (ppb)	^{97}Mo Mo (ppb)	^{101}Ru Ru (ppb)	^{102}Ru Ru (ppb)	^{104}Ru Ru (ppb)	True Value Mo-Ru (ppb)	%Removal Mo	%Removal Ru
Cal. B	None	0.0547	0.0617	0.0097	0.0085	0.0111	None	NA	NA
NCB1	None	0.0681	0.0727	0.0059	0.0069	0.0112	None	NA	NA
NCB2	None	0.0718	0.0834	0.0095	0.0073	0.0103	None	NA	NA
B1	None	0.1317	0.1350	0.0076	0.0076	0.0125	None	NA	NA
B2	None	0.1397	0.1599	0.0080	0.0070	0.0123	None	NA	NA
S1-1	B2	-0.0081	-0.0165	0.0006	-0.0001	0	0.0101	200	100
S1-2	B2	-0.0033	-0.0193	0.0012	0.0009	0.0005	0.0101	100	90
S2-1	B2	0.0087	-0.0007	0.0011	0.0009	-0.0004	0.0403	80	100
S2-2	B2	-0.0030	-0.0015	0.0003	0.0006	-0.0005	0.0403	100	100
S3-1	B2	0.0057	-0.0029	0.0023	0.0006	-0.0009	0.0807	90	100
S3-2	B2	0.0001	-0.0042	0.0006	0.0012	0.0003	0.0807	100	100
S4-1	B2	0.0168	0.0107	0.0009	0.0013	-0.0002	0.1518	90	100
S4-2	B2	-0.0159	-0.0197	0.0013	0.0010	0.0016	0.1518	110	99
	%Abundance	15.9	9.5	17.0	31.0	18.4			

^{95}Mo and ^{102}Ru were used to determine %Removal of the Mo and Ru interference for ^{99}Tc analysis by ICP-MS.
NCB represents a blank that was taken through the procedure with the exception of the column step. B represents a blank that was taken through the digestion and column steps.

TABLE 9

Mo AND Ru PEAK AREA COUNTS FOR SAMPLES RINSED WITH
0.50, 0.70, and 1.0 M HCl

Sample ID	Mass 95 (cps)	Mass 97 (cps)	Mass 99 (cps)	Mass 101 (cps)	Mass 102 (cps)	Mass 104 (cps)
Blank	121	88	36	35	43	52
Std1 (0.05ppb)	235	176	140	184	332	234
Std2 (0.10ppb)	352	241	243	337	598	405
Std3 (0.25ppb)	714	468	534	757	1460	927
NCB1	181	124	41	29	42	63
NCB2	180	134	40	39	42	56
0.50MB1	490	335	59	33	41	62
0.50MB2	384	264	47	30	43	57
0.50MS1-1	370	269	49	31	42	61
0.50MS1-2	381	257	46	32	43	57
0.50MS2-1	366	254	44	35	41	58
0.50MS2-2	366	254	50	34	41	61
0.50MS3-1	337	233	36	46	46	60
0.50MS3-2	364	253	45	34	43	62
0.50MS4-1	323	224	47	37	39	60
0.50MS4-2	370	260	46	40	41	61
1.0MB1	338	222	44	34	46	66
1.0MB2	351	258	48	34	40	64
1.0MS1-1	329	229	48	36	39	64
1.0MS1-2	331	218	45	36	44	64
1.0MS2-1	364	250	48	37	44	61
1.0MS2-2	345	234	47	35	44	62
1.0MS3-1	359	248	48	41	43	60
1.0MS3-2	341	243	48	35	46	63
1.0MS4-1	382	266	48	36	47	62
1.0MS4-2.	299	217	50	37	45	67

TABLE 9 (CONTINUED)

Mo AND Ru PEAK AREA COUNTS FOR SAMPLES RINSED WITH
0.50, 0.70, and 1.0 M HCl

Sample ID	Mass 95 (cps)	Mass 97 (cps)	Mass 99 (cps)	Mass 101 (cps)	Mass 102 (cps)	Mass 104 (cps)
Blank	107	79	39	34	42	50
Std1 (0.05ppb)	217	140	-	150	272	198
Std2 (0.10ppb)	325	221	-	274	518	344
Std3 (0.25ppb)	673	422	-	646	1224	804
NCB1	284	179	-	38	43	63
NCB2	260	178	-	32	58	65
0.70MB1	210	164	-	32	43	45
0.70MB2	250	172	-	28	37	50
0.70MS1-1	296	203	-	33	40	50
0.70MS1-2	235	165	-	33	47	54
0.70MS2-1	231	163	-	39	47	47
0.70MS2-2	266	186	-	38	44	51
0.70MS3-1	308	205	-	34	43	52
0.70MS3-2	242	171	-	32	41	54
0.70MS4-1	237	165	-	35	42	51
0.70MS4-2	270	198	-	35	43	54

expected countrate was observed for the 0.70 M column separated blanks. This percentage was based on the relationship between the column separated blank and the 0.1009 ppb Mo standard in the 0.50 and 1.0 M and the 0.70 M series analyses. In order to verify this observation, a difference between sample and column separated countrates was calculated for each sample in each series. The calculated results confirmed the noted decrease in the 0.70 M blank countrates (Table 10). A decision was made to evaporate the saved combined sample load/rinse waste solutions to 30 mL volumes (equivalent to the final sample volumes) and analyze the solutions by ICP-MS for Mo and Ru concentrations. The Mo countrate results obtained (Table 11) were unexpected. Mo waste countrates were approximately 125 times higher than the separated sample countrates. In an attempt to confirm that the actual counts were due to the presence of Mo, a ratio of the 95/97 masses was calculated (Table 12) and compared to the expected ratio based on Mo isotopic abundance. The expected 95/97 ratio was 1.67, and the measured average ratio was 1.60. Considering the results of this comparison, an assumption that chemical noise/interference was the root cause of the high Mo countrates could not be confirmed. In light of literature citation that stated a problem with Mo resin contamination and of decontamination results obtained,[28] a study was conducted using the 0.50 M HCl rinse to determine the exact volume necessary to completely and consistently remove all traces of Mo from the sample. A blank (B) and two water samples (F1, F2) were taken through the digestion, column loading, and extraction steps. Each sample was spiked with 0.0049 ppb ^{99}Tc and 0.15 ppb Mo/Ru. The column prerinse, eight 10 mL fractions of 0.50 M HCl wash, and the ^{99}Tc elutant were collected and analyzed by ICP-MS in peak-jumping mode (Table 13). Results

TABLE 10

EVALUATION OF THE DIFFERENCE IN 0.50, 0.70, and 1.0 M
SAMPLE PEAK AREAS AND AVERAGE
BLANK PEAK AREAS

Sample ID	Mass 95	Mass 97	Mass 99	Mass 101	Mass 102	Mass 104
0.50MS1-1	-67	-31	-4	-1	0	1
0.50MS1-2	-56	-43	-7	0	1	-3
0.50MS2-1	-71	-46	-9	3	-1	-2
0.50MS2-2	-71	-46	-3	2	-1	1
0.50MS3-1	-100	-67	-17	14	4	0
0.50MS3-2	-73	-47	-8	2	1	2
0.50MS4-1	-114	-76	-6	5	-3	0
0.50MS4-2	-67	-40	-7	8	-1	1
0.50M Mean	-77	-50	-8	4	0	0
1.0MS1-1	-16	-11	2	2	-4	-1
1.0MS1-2	-14	-22	-1	2	1	-1
1.0MS2-1	19	10	2	3	1	-4
1.0MS2-2	0	-6	1	1	1	-3
1.0MS3-1	14	8	2	7	0	-5
1.0MS3-2	-4	3	2	1	3	-2
1.0MS4-1	37	26	2	2	4	-3
1.0MS4-2	-46	-23	4	3	2	2
1.0M Mean	-1	-2	2	3	1	-2
0.70MS1-1	66	35	-	3	0	2
0.70MS1-2	5	-3	-	3	7	6
0.70MS2-1	1	-5	-	9	7	-3
0.70MS2-2	36	18	-	8	4	3
0.70MS3-1	78	37	-	4	3	4
0.70MS3-2	12	3	-	2	1	5
0.70MS4-1	7	-3	-	5	2	3
0.70MS4-2	40	30	-	5	3	5
0.7M Mean	31	14		5	3	3

The above values represent the difference in averaged sample and blank peak areas (cps).

TABLE 11

EVALUATION OF Mo AND Ru IN THE 0.50 AND
1.0 M HCl RINSE SOLUTIONS

Sample ID	Mass 95	Mass 97	Mass 99	Mass 101	Mass 102	Mass 104
Blank	19	23	14	29	25	23
Std1 (0.05ppb)	151	126	119	143	343	269
Std2 (0.10ppb)	301	209	196	256	491	343
Std3 (0.25ppb)	642	478	566	852	1414	956
0.50M BR1	32679	21000	98	27	19	34
0.50M BR2	39646	23286	74	27	12	29
0.50M SR1-1	33398	20840	87	38	76	74
0.50M SR1-2	36897	25356	119	57	76	53
0.50M SR2-1	47385	29625	217	111	155	96
0.50M SR2-2	37221	22343	181	89	243	187
0.50M SR3-1	38225	28387	348	247	407	217
0.50M SR3-2	35955	23894	311	207	516	322
0.50M SR4-1	55133	32507	399	322	576	401
0.50M SR4-2	49791	32060	478	393	694	412
1.0M BR1	36763	22568	117	38	34	40
1.0M BR2	55890	27225	0	0	0	0
1.0M SR1-1	43276	31251	234	42	66	87
1.0M SR1-2	41486	24432	106	42	32	123
1.0M SR2-1	43346	25902	134	85	153	177
1.0M SR2-2	36881	22472	192	93	181	151
1.0M SR3-1	42077	24191	200	153	373	224
1.0M SR3-2	67899	41892	0	0	0	0
1.0M SR4-1	51335	30158	0	0	0	0
1.0M SR4-2	53483	34753	472	324	632	399
% Abundance:	Mo 15.9	Mo 9.5	Ru 12.8	Ru 17.0	Ru 31.3	Ru 18.4

Samples 1.0M BR2, 1.0M SR3-2, and 1.0M SR4-1 contained Mo peak areas too high for detection in pulse counting mode and were analyzed in analog mode. Detecting Mo isotopes in analog mode precluded detection of Ru isotopes.

TABLE 12

EVALUATION OF Mo AND Ru ABUNDANCE RATIOS FROM THE 0.50 AND 1.0 M HCl RINSE SOLUTIONS

Sample ID	95/97	99/102	101/102	104/102
Blank	0.83	0.56	1.16	0.92
Std1 (0.05pp	1.20	0.35	0.42	0.78
Std2 (0.10pp	1.44	0.40	0.52	0.70
Std3 (0.25pp	1.34	0.40	0.60	0.68
0.50M BR1	1.56	5.16	1.42	1.79
0.50M BR2	1.70	6.17	2.25	2.42
0.50M SR1-	1.60	1.14	0.50	0.97
0.50M SR1-	1.46	1.57	0.75	0.70
0.50M SR2-	1.60	1.40	0.72	0.62
0.50M SR2-	1.67	0.74	0.37	0.77
0.50M SR3-	1.35	0.86	0.61	0.53
0.50M SR3-	1.50	0.60	0.40	0.62
0.50M SR4-	1.70	0.69	0.56	0.70
0.50M SR4-	1.55	0.69	0.57	0.59
1.0M BR1	1.63	3.44	1.12	1.18
1.0M BR2	2.05	0	0	0
1.0M SR1-1	1.38	3.55	0.64	1.32
1.0M SR1-2	1.70	3.31	1.31	3.84
1.0M SR2-1	1.67	0.88	0.56	1.16
1.0M SR2-2	1.64	1.06	0.51	0.83
1.0M SR3-1	1.74	0.54	0.41	0.60
1.0M SR3-2	1.62	0	0	0
1.0M SR4-1	1.70	0	0	0
1.0M SR4-2	1.54	0.75	0.51	0.63
Mass Ratio True Value:	1.67	0.41	0.54	0.59

TABLE 13

INTERFERENCE DECONTAMINATION FOR SAMPLES CONTAINING 0.15 ppb Mo AND Ru

Sample ID	Acid Wash	Mo (ppb)	Ru (ppb)	Tc (ppb)
Column Prerinse B	0.50 M HNO_3	41.96	0.0005	-
Column Prerinse F1	0.50 M HNO_3	47.13	0.0003	-
Column Prerinse F2	0.50 M HNO_3	46.83	0.0011	-
RB1	0.50 M HCl	0.1599	-0.0003	-
RF1-1	0.50 M HCl	0.1309	-0.0006	-
RF2-1	0.50 M HCl	0.0845	-0.0003	-
RB2	0.50 M HCl	0.2584	-0.0009	-
RF1-2	0.50 M HCl	0.1768	0.0002	-
RF2-2	0.50 M HCl	0.2015	0.0004	-
RB3	0.50 M HCl	0.2792	0.0003	-
RF1-3	0.50 M HCl	0.2328	0.0001	-
RF2-3	0.50 M HCl	0.2336	0.0002	-
RB4	0.50 M HCl	0.3246	0.0007	-
RF1-4	0.50 M HCl	0.2880	0.0006	-
RF2-4	0.50 M HCl	0.3678	0.0005	-
RB5	0.50 M HCl	0.4344	0.0003	-
RF1-5	0.50 M HCl	0.4295	0.0000	-
RF2-5	0.50 M HCl	0.5585	0.0006	-
RB6	0.50 M HCl	0.2405	0.0004	-
RF1-6	0.50 M HCl	0.2942	0.0000	-
RF2-6	0.50 M HCl	0.2447	-0.0001	-
RB7	0.50 M HCl	0.1686	0.0008	-
RF1-7	0.50 M HCl	0.1605	0.0007	-
RF2-7	0.50 M HCl	0.1721	0.0003	-
RB8	0.50 M HCl	0.1274	0.0004	-
RF1-8	0.50 M HCl	0.1272	0.0004	-
RF2-8	0.50 M HCl	0.1363	0.0000	-
B/Mo/Ru	3.0 M HCl	0.7095	0.0010	-
F1/Mo/Ru	3.0 M HCl	0.7170	0.0009	-
F2/Mo/Ru	3.0 M HCl	0.7048	0.0016	-
F1/Tc	3.0 M HCl	0.0348	0.0003	0.0043 (87%)
F2/Tc	3.0 M HCl	0.0091	0.0005	0.0047 (95%)

indicated Ru was either completely retained by the anion exchange resin during the rinse and elution steps, or not retained during sample load. The column prerinse and 0.50 M HCl rinse data confirmed the correct Mo abundance ratios at *m/z* 95 and 97. The average Mo concentration in the 50 mL prerinse solutions was 45.31 ppb. The eight 10 mL 0.50 M HCl fractions show an increasing level of Mo to a maximum of 0.47 ppb, then a drop to approximately 0.13 ppb. In each fraction set, the blank Mo results were within the same concentration range as the samples. Thus, the Mo from the sample as well as that in the resin was removed. The ^{99}Tc recovery for samples F1 and F2 was 86.72% and 95.05%, respectively.

In order to determine the Ru behavior on the anion exchange resin and to evaluate the effectiveness of storing the resin in 0.50 M HCl (presoaked), two blank and sample pairs were evaluated. A blank and sample pair were loaded onto columns containing presoaked anion exchange resin (NCLB, NCLS) that was not preconditioned with 0.50 M HNO_3. The resin for the second blank and sample pair (CLB, CLS) was preconditioned with 50 mL of 0.50 M HNO_3. Each sample was spiked with 0.0050 ppb ^{99}Tc and 0.12 ppb Mo and Ru. Sample load, rinse, and extraction data revealed that Ru was not retained on the anion exchange resin. In addition, the 0.50 M HCl presoaked resin contained Mo levels approximately six times higher than did the resin conditioned with 50 mL of 0.50 M HNO_3 (Table 14). The extraction data also indicate that a larger amount of Mo could be removed by preconditioning the column with a higher concentration of nitric acid followed with a more dilute acid solution prior to sample loading. The ^{99}Tc NCLS and CLS recoveries for this experiment were 90.80% and 97.97%, respectively.

TABLE 14

SAMPLE LOADING AND EXTRACTION BEHAVIOR OF Mo AND Ru ON AG MP-1 ANION EXCHANGE RESIN

Procedure Step	Ru (ppb) NCLB	Ru (ppb) NCLS	Ru (ppb) CLB	Ru (ppb) CLS	Mo (ppb) NCLB	Mo (ppb) NCLS	Mo (ppb) CLB	Mo (ppb) CLS
0.50 M HNO_3 Sample Load	0.0012	0.0967	0	0.0983	6.169	3.103	0.9653	0.7967
1^{st} 10 mL 0.50 M HNO_3 Rinse	0.0002	0.0003	0	0.0003	0.9719	0.6177	0.0939	0.0798
2^{nd} 10 mL 0.50 M HNO_3 Rinse	0.0001	0	0	0	0.3851	0.1362	0.0413	0.0565
3^{rd} 10 mL 0.50 M HNO_3 Rinse	0	0	0	0	0.1578	0.0485	0.0268	0.0099
20 mL 0.50 M HCl Rinse	0	0	0	0	0.7499	0.2732	0.1264	0.0493
30 mL 3.0 M HNO_3 Extraction	0.0008	0.0004	0.0003	0.0006	3.826	1.836	0.5817	0.3829
^{99}Tc %Recovery	-	91	-	98	-	91	-	98

^{99}Mo is not a naturally occurring isotope and considering its half-life of 62.02 hours, the potential for worker exposure during disassembly and decontamination activities is low. However, the removal of Mo is important to ensure peak-overlap interferences from *m/z* 98 and 100 does not occur. ^{99}Ru is naturally occurring with an abundance of 12.8%. In an attempt to determine the Ru removal efficiency in real radiological worker samples, an evaluation of the difference in real urine countrates and an averaged artificial urine countrate for *m/z* 101 (^{101}Ru) was made. Data from 18 individuals collected over a period of one month were evaluated (Table 15). The overall mean countrate difference of -3 cps was obtained, indicating effective Ru removal.

E. Comparison Study Procedure

After evaluating the collected experimental data, a ^{99}Tc separation method was devised that eliminated interferents in both liquid scintillation and ICP-MS analysis. Composite water, artificial urine, and real urine samples were spiked at three different levels with ^{99}Tc. Ten 50 mL samples of each level/matrix were pipetted into 250 mL beakers. The samples were digested with 5 mL H_2O_2 in a covered beaker on a hotplate between 150 to 175°C. After approximately one hour, the samples were removed from the hotplate and cooled. After cooling, the watch glass coverings were rinsed with 0.50 M HNO_3, and the samples were acidified with 2.5 mL of concentrated HNO_3 and diluted to 80 mL. The samples were warmed in order to aid in dissolving slightly soluble salts, cooled to room temperature, and poured over columns containing 1.8 mL of anion exchange resin that had been prepared by rinsing with 30 mL of 0.50 M HNO_3. The sample flow rate was approximately 1 mL/min. Samples were then washed

TABLE 15
COMPARISON OF RUTHENIUM IN REAL URINE SAMPLES
AND ARTIFICIAL URINE SAMPLES

Sample Number	^{101}Ru Value in Real Urine Samples (cps)	^{101}Ru Mean Value in Artificial Urine (cps)	^{101}Ru after Reagent Blank Subtraction
1	39	27	12
2	33	27	6
3	35	27	8
4	24	27	-3
5	26	27	-1
6	23	27	-4
7	18	27	-9
8	16	27	-11
9	21	27	-6
10	20	27	-7
11	24	27	-3
12	26	27	-1
13	22	27	-5
14	23	27	-4
15	20	27	-7
16	26	27	-1
17	22	27	-5
18	21	27	-6
Mean Difference Between Real Urine and the Artificial Urine Blank:			-3

The Artificial Urine Reagent Blank value (cps) was calculated from a population of nine blanks analyzed over a peroid of one month. The mean blank value was 27 +/- 9 cps.

sequentially with 30.0 mL volumes of 0.50 M HNO_3 and 0.50 M HCl, eluted with 30 mL hot 3.0 M HNO_3, and diluted to 50 mL. At this point, each sample was divided into two 25 mL portions. Samples to be analyzed by liquid scintillation were evaporated to approximately 1 mL volumes for acid removal, transferred to a polyethylene liquid scintillation vial, and diluted to an 8 mL mark. Liquid scintillation sample preparation was completed by the addition of 12.0 mL of Packard Insta-gel XF cocktail. Samples were well mixed and counted for a period of one hour. ICP-MS samples were transferred to 10 mL vials, spiked with a 0.2 ppb ^{115}In internal standard, and analyzed in peak-jumping mode.

The use of a yield monitor was not employed in this study due to the lack of an isotope that could be applied to the initial sample and not adversely affect one analysis method or the other. Direct %Bias was used to evaluate each method.

CHAPTER V

INSTRUMENTAL PARAMETERS AND STANDARD VALIDATION

Before analyzing ^{99}Tc by mass, instrumental parameters were established in order to quantitate accurately the isotope activity. Instrumental settings such as gas and sample flow rates, acquisition parameters, and resolution were evaluated. Calibration concerns such as scan mode, matrix matching, calibration linearity, internal standardization, instrument stability and analytical calculations were addressed. In addition autosampler uptake and rinse settings were optimized. For each of the three liquid scintillation counters used in the comparison study, the automatic quench corrections (quench curves) were evaluated and compared to manual external quench calculations. Finally, ^{99}Tc working solution activities were verified by liquid scintillation.

A. ICP-MS Operating Parameters

Initially ICP-MS operating parameters were optimized for the analysis of ^{99}Tc. The conditions that were chosen are listed in Table 16. Each week, or after an instrumental modification was made, a mass calibration was conducted as described in Chapter III. Prior to each analysis, a tuning standard containing 10 ppb each of Be, Mg, Co, Ni, In, Ce, Pb, and U was used to adjust detector sensitivity, focus the plasma, check mass calibration, and maximize resolution. Once instrumental operating conditions were established, a short term stability check was conducted. The stability check was carried out by observing 10 consecutive 30 s analyses of the tune solution. From mass countrates, the means, standard deviations, and relative standard deviations were determined. Less than 2% relative standard deviation was the goal for the higher mass elements In, Pb, and U. In order to determine if the ^{99}Tc response by

TABLE 16

INSTRUMENTAL OPERATING PARAMETERS

ICP-MS	
Forward Power/W	1350
Coolant Gas Flow Rate/L $min.^{-1}$	14.5
Auxiliary Gas Flow Rate/ L $min.^{-1}$	0.94
Nebulizer Gas Flow Rate/ L $min.^{-1}$	0.90
Flow-rate	0.01535 mL/s
Interface	
Sample Cone	Nickel
Skimmer Cone	Nickel
Acquisition Parameters	
Acquisition Time/s	45
Dwell Time/ms	10.24
Time per Sweep/s	0.60
Points per Peak	19
DAC per Step	9
Scan Mode	Peak-jumping
Signal Processing	Spectral Peaks Integrated
Counting Mode	Pulse Counting
Internal Standard	^{115}In
Vacuum Pressures	
Expansion/mbar	1.9×10^{0}
Interface/mbar	0.0×10^{-4}
Analyzer/mbar	1.9×10^{-6}

ICP-MS was linear in a column separated urine matrix, five real urine blanks were taken through a separation procedure, spiked with known amounts of ^{99}Tc, and analyzed in single ion monitoring mode. The blank samples were spiked after the column separation in order to evaluate the %Bias from the ^{99}Tc true value. Results of the analysis (Table 17) showed a discouraging -44% bias. After considering the possible cause of the negative bias, matrix matching was brought into question. A water matrix was then used to prepare the standards, and the final sample matrix was around 2.4 M HNO_3. In an attempt to determine if the lack of matrix matching was indeed the cause of the negative bias, a 1:1 sample dilution was made to reduce the acid concentration before the samples were analyzed. The overall bias of the diluted samples (Table 18) was -6.1%. A reduction in bias for the diluted samples indicates the necessity for matrix matching the calibration standards. Because sample dilution was undesirable, a decision was made to prepare the calibration standards in an acid concentration that matched that of the sample's final acid concentration. Once this modification was made, linear ^{99}Tc calibration curves (Figure 8) were obtained and control biases were reasonable.

As mentioned in Chapter IV, isobaric ^{99}Ru interference was a concern in radiation worker sample analysis. In order to monitor levels of ^{99}Ru, peak ^{101}Ru was monitored. Since masses 99, 101, and 115 were the only *m/z* values of interest, the mass scan mode chosen for ^{99}Tc analysis was peak-jumping. Examples of peak-jumping spectra are given in Figures 9 (Reagent Blank) and 10 (Sample).

The use of ^{115}In as an internal yield monitor was a concern because it has a mass corresponding to the formation of $^{99}TcO^+$. However in light of Crain and Gallimore's[22] finding that technetium does not readily form TcO^+, a verification was

TABLE 17

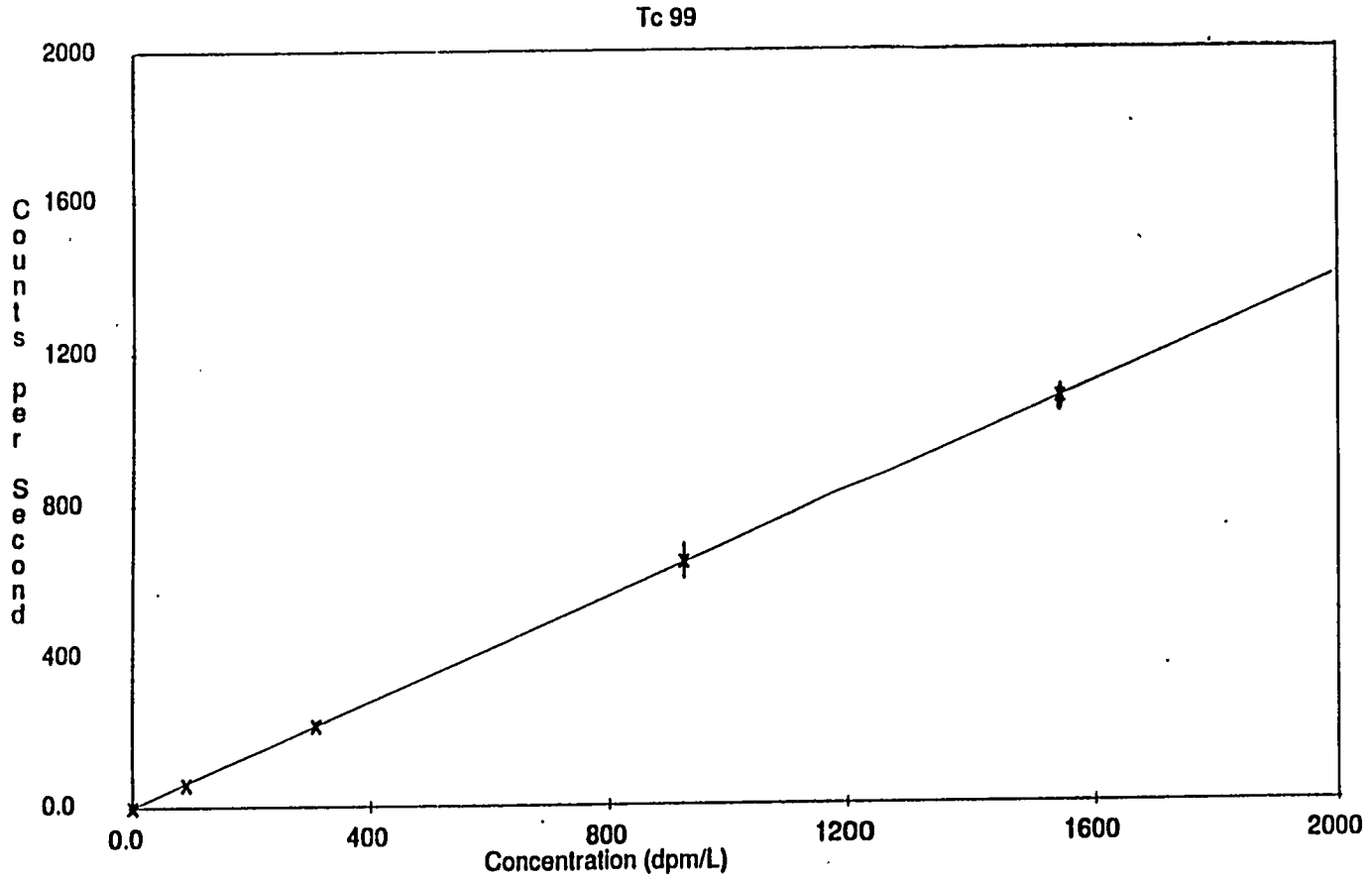
BLANK URINE SPIKED WITH ^{99}Tc AFTER COLUMN SEPARATION
USING AG MP-1

Sample ID	Run 1(ppb)	Run 2 (ppb)	Run 3 (ppb)	Mean (ppb)	True Value (ppb)	%Bias
Std. Blank	0.0009	0.0008	0.0009	0.0009	Blank	Blank
Std. 1	0.0379	0.0375	0.0376	0.0376	0.0370	2
Std. 2	0.0758	0.0779	0.0790	0.0775	0.0752	3.1
Std. 3	0.1477	0.1508	0.1514	0.1500	0.1503	-0.2
XXX Water	0.0000	-0.0001	-0.0002	-0.0001	Blank	Blank
Urine Blank	0.0002	0.0002	0.0002	0.0002	Blank	Blank
Sample 1	0.0863	0.0865	0.0871	0.0866	0.1478	-41.4
Sample 2	0.0421	0.0420	0.0416	0.0419	0.0739	-43.3
Sample 3	0.0093	0.0088	0.0088	0.0089	0.0149	-40
Sample 4	0.0039	0.0038	0.0037	0.0038	0.0074	-49

TABLE 18

BLANK URINE SPIKED WITH ^{99}Tc AFTER COLUMN SEPARATION
USING AG MP-1 WITH A 1:1 DILUTION

Sample ID	Run 1 (ppb)	Run 2 (ppb)	Mean	True Value	% Bias
Std. Blank	0.0008	0.0009	0.0009	Blank	Blank
Std. 1	0.0081	0.0079	0.0080	0.0077	4
Std. 2	0.0327	0.0382	0.0355	0.0370	-4.1
Std. 3	0.0719	0.0759	0.0739	0.0752	-1.7
Std. 4	0.1500	0.1499	0.1500	0.1503	-0.2
Sample 1	0.0710	0.0692	0.0701	0.0739	-5.1
Sample 2	0.0337	0.0343	0.0340	0.0370	-8.1
Sample 3	0.0069	0.0072	0.0071	0.0075	-5



Coefficients : Y = A0 + A1X + A2X^2 ... AnX^n

A0	A1	A2	A3	A4	Regression
-5.75533E-2	6.95410E-1	0.00000E+0	0.00000E+0	0.00000E+0	9.99985E-1

Figure 8. ICP-MS calibration curve for ^{99}Tc.

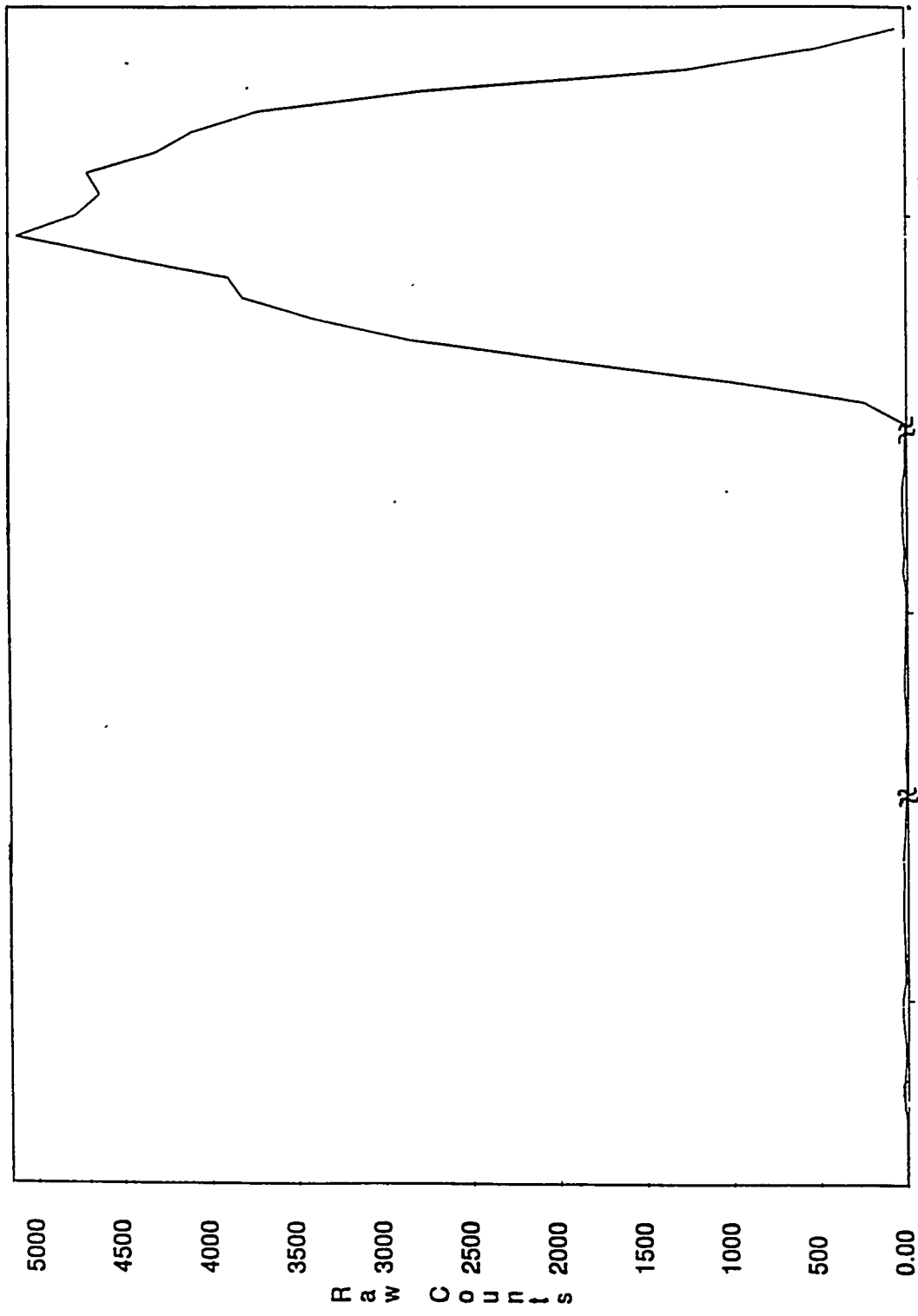


Figure 9. Mass spectrum of a blank urine sample collected in peak-jumping with ^{115}In internal standard.

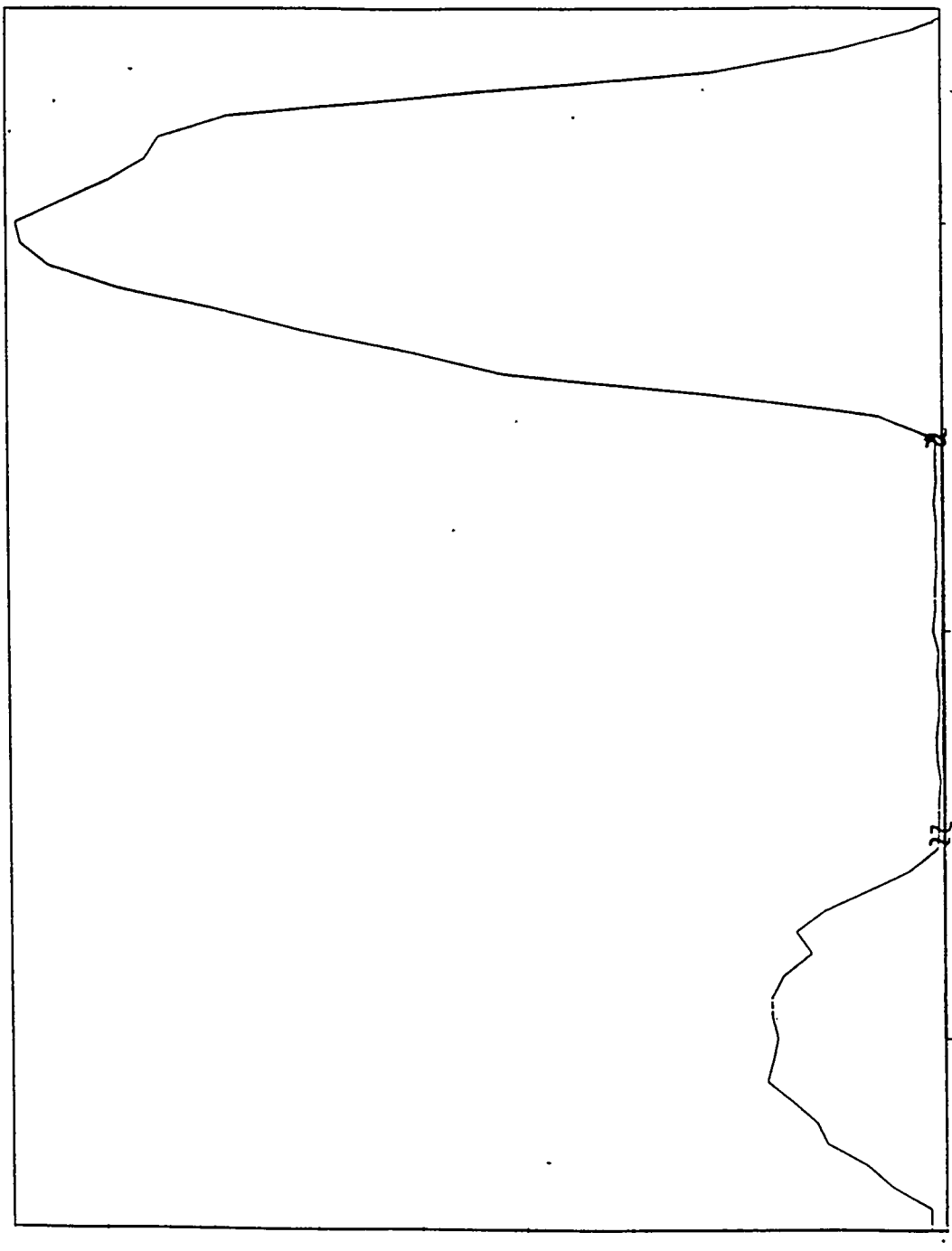


Figure 10. Mass spectrum of a urine control collected in peak-jumping with ^{115}In internal standard.

made. The relative percent intensity was monitored in a batch containing blank and ^{99}Tc-spiked real urine samples and standards in 2.0 M HNO_3 without the addition of ^{115}In. An interesting property was observed in the resulting data given in Table 19. The %Intensity for mass 115 was on average 6.3%. These data alone could possibly lead to the conclusion that technetium did form TcO^+. However, artificial urine reagent blank %Intensity averaged 6.1%. The %Intensity for Xchk standards in 2.0 M HNO_3 with ^{99}Tc activities between 303.3 and 1517 dpm/L averaged 1.7%. From the data obtained, the formation of TcO^+ did not appear to occur. Throughout the study, ^{115}In %Intensity was approximately 6 to 10% higher in both real and artificial urine matrices than in nitric acid solution. The consistency of this enhancement suggests that an acid matrix at the sample's acid concentration was not a perfect matrix match.

B. Liquid Scintillation Operating Parameters

In order to prepare liquid scintillation counters for automatic activity calculations, a quench curve must be established as discussed in Chapter III. Since radioanalytical counting techniques are direct methods, calibration curves, internal standards, and detector calibrations (other than quench curves) are not required. ^3H, ^{14}C, and background Instrument Performance Standards (IPA) are counted before each sample batch to monitor efficiency and background. When compared to a complex instrument such as ICP-MS, liquid scintillation counters are extremely simple. Samples in the comparison study were placed in the counters, dark adapted, and then counted sequentially for one hour.

C. Calculations

ICP-MS calibrations are based on linear relationships between countrate and

TABLE 19

EVALUATION OF %INTENSITY AT MASS 115

Sample ID	Original Matrix	%Intensity at Mass 115	^{99}Tc Activity (dpm/L)
R3-1	Real Urine	6.72	2122.2
R3-2	Real Urine	6.06	2122.2
R3-5	Real Urine	5.86	2122.2
R3-6	Real Urine	5.55	2122.2
R3-9	Real Urine	8.62	2122.2
R3-10	Real Urine	4.74	2122.2
RBlank1	Artificial Urine	6.12	None
RBlank2	Artificial Urine	5.98	None
Xchk2	2.0 M Nitric Acid	1.67	303.3
Xchk3	2.0 M Nitric Acid	1.66	910.0
Xchk4	2.0 M Nitric Acid	1.77	1516.7
XBlank	2.0 M Nitric Acid	1.2	None

concentration. The following formula is employed by the PlasmaQuad +2 ICP-MS:

$$y = a0 + a1x + a2x^2 + a3x^3 + a4x^4 \quad (2)$$

where y, x, a0, and a1 represents countrate, concentration, intercept, and slope, respectively. Higher order coefficients are represented by a3 and a4.

Internal standards were used in this study to correct for signal fluctuations and mass drift. The equation:

$$\text{Intensity Normalization Factor} = I_o/I_n \quad (3)$$

was employed. I_o represents the internal standard intensity on the first sample measured and I_n represents the internal standard intensity on the n^{th} sample.

Two detection limits were calculated in this study. A standard method limit of detection (LOD) was calculated from the standard deviation (s_B) of ten method blanks.

$$\text{LOD} = 3.29(s_B) \quad (4)$$

The minimum detectable concentration (MDC) was the second detection limit determined. A sample activity above the MDC represents a positive radiation dose within a 95% confidence level. MDC is based upon the lowest possible activity per unit volume of an analyte in urine which may be detected by a particular preparation and detection method. An MDC s_B represents a propagated value that incorporates the analytical blank and an unexposed person's activity concentration.[32] The unexposed person's blank activity s_B was assumed equivalent to the analytical blank due to a lack of ^{99}Tc population blank data. The result of this calculation is that the MDC was $\sqrt{2}$ higher than the LOD:

$$\text{MDC} = 4.65\ s_B \quad (5)$$

In this study, yield was not considered in the MDC equation because a direct comparison of ^{99}Tc activity between uncorrected mass and liquid scintillation results was made.

The activity per unit volume for samples counted by liquid scintillation was calculated using the following equation:

$$dpm/V = (S_{cnt} - B_{cnt})/ K \quad (6)$$

where S_{cnt} and B_{cnt} were the counts in the 2 to 294 keV regions for the sample and blank, and K represents e (efficiency), T (time), and V (volume). Normally yield (Y) is placed in the denominator to correct for tracer recovery. Efficiency was determined both automatically using a quench curve and manually using the following equation:

$$e = Q_s/s \quad (7)$$

Q_s was calculated by subtracting a samples quenched counts including background ($Q_U + Q_B$) from that sample's quenched counts and background after being exposed to a ^{133}Ba source ($Q_s + Q_U + Q_B$). The value s was determined by subtracting an unquenched blank (prepared using deionized water and cocktail) and background (b) from that unquenched blank and background after being exposed to the ^{133}Ba source (s + b).

The LOD for liquid scintillation counting was calculated using Equation (4), however, since s_B represents reagent blank counts, K was placed in the denominator. A modified equation was used to calculate MDC:

$$MDC = 4.65\ s_B/K + 3/K \quad (8)$$

This MDC equation was stated in the ANSI N13.30 Standard for radiobioassay[32] and was originally derived by Currie[33] for radioanalytical measurements.

Once the results were obtained, the %Bias was calculated from the measured (M) values and the known (T) values:

$$\%Bias = (M - T / T) * 100 \quad (9)$$

Results in the comparison study were evaluated based on %Bias.

D. Standard Validation

Using the liquid scintillation calculations stated above, the three working solution activities (14.08, 28.16, and 61.34 dpm/L) were verified on each of the three liquid scintillation counters used in this study. The average %Bias obtained on each of the instruments for each standard were within +/-5% with the exception of counter E using the automatic quench corrected values. All results that were obtained in this evaluation are given in Tables 20 and 21.

TABLE 20

INSTRUMENT PERFORMANCE EVALUATION USING THE
MANUAL QUENCH AND QUENCH CURVE
METHODS OF ANALYSIS

ID	Counter	Sample Qu + Qb (cpm)	External Std. Qs + Qu + Qb (cpm)	Unquenched b (cpm)	Unquenched s+b (cpm)	Qs (cpm)	s (cpm)	Manual Q e	Q Curve e	Manual Q (dpm)	Q Curve (dpm)
LS1-1	D	39.2	1944900	25.5	1925200	1944861	1925175	1.01	0.93	13.56	14.76
LS1-2	D	39.0	1922900	25.5	1925200	1922861	1925175	1.00	0.93	13.52	14.58
LS2-1	D	52.5	1805333	25.5	1925200	1805281	1925175	0.94	0.93	28.79	29.18
LS2-2	D	53.7	1935120	25.5	1925200	1935066	1925175	1.01	0.93	28.06	30.45
LS3-1	D	84.3	1927200	25.5	1925200	1927116	1925175	1.00	0.92	58.74	63.71
LS3-2	D	82.4	1918633	25.5	1925200	1918551	1925175	1.00	0.92	57.10	61.77
LS1-1	E	40.2	1948017	23.7	1930425	1947977	1930401	1.01	0.92	16.35	17.87
LS1-2	E	39.6	1952283	23.7	1930425	1952243	1930401	1.01	0.92	15.72	17.22
LS2-1	E	52.2	1947117	23.7	1930425	1947065	1930401	1.01	0.92	28.26	30.84
LS2-2	E	51.5	1919283	23.7	1930425	1919232	1930401	0.99	0.92	27.96	30.12
LS3-1	E	85.6	1934350	23.7	1930425	1934264	1930401	1.00	0.92	61.78	67.30
LS3-2	E	79.8	1905520	23.7	1930425	1905440	1930401	0.99	0.92	56.83	60.94
LS1-1	F	40.0	1995557	25.7	1998638	1995517	1998612	1.00	0.93	14.25	15.27
LS1-2	F	39.2	1977863	25.7	1998638	1977824	1998612	0.99	0.93	13.62	14.48
LS2-1	F	54.1	1999525	25.7	1998638	1999471	1998612	1.00	0.93	28.37	30.58
LS2-2	F	51.1	1968500	25.7	1998638	1968449	1998612	0.98	0.93	25.77	27.35
LS3-1	F	83.0	1986757	25.7	1998638	1986674	1998612	0.99	0.92	57.62	62.05
LS3-2	F	84.4	1978183	25.7	1998638	1978099	1998612	0.99	0.92	59.29	63.47

Evaluation samples were prepared by spiking 8 mL of 18.0 Mohm water with known amounts of ^{99}Tc. The spiked water was mixed with 12 mL of cocktail. The following activity levels were prepared: LS1 = 14.1 dpm, LS2 = 28.2 dpm, and LS3 = 61.3 dpm.

TABLE 21

STANDARD BIAS COMPARISON USING THE MANUAL QUENCH AND QUENCH CURVE METHODS OF ANALYSIS

ID	Counter	Standard True Value (dpm)	Manual Quench dpm	Manual Quench % Bias	Quench Curve dpm	Quench Curve % Bias
LS1-1	D	14.08	13.56	-3.7	14.76	4.8
LS1-2	D	14.08	13.52	-4.0	14.58	3.6
LS2-1	D	28.16	28.79	2.2	29.18	3.6
LS2-2	D	28.16	28.06	-0.4	30.45	8.1
LS3-1	D	61.34	58.74	-4.2	63.71	3.9
LS3-2	D	61.34	57.10	-6.9	61.77	0.7
		Average %Bias :		-2.8		4.1
LS1-1	E	14.08	16.35	16	17.87	27
LS1-2	E	14.08	15.72	12	17.22	22
LS2-1	E	28.16	28.26	0.36	30.84	9.5
LS2-2	E	28.16	27.96	-0.71	30.12	7.0
LS3-1	E	61.34	61.78	0.72	67.30	9.7
LS3-2	E	61.34	56.83	-7.4	60.94	-0.65
		Average %Bias :		3.5		12
LS1-1	F	14.08	14.25	1.2	15.27	8.5
LS1-2	F	14.08	13.62	-3.3	14.48	2.8
LS2-1	F	28.16	28.37	0.7	30.58	8.6
LS2-2	F	28.16	25.77	-8.5	27.35	-2.9
LS3-1	F	61.34	57.62	-6.1	62.05	1.2
LS3-2	F	61.34	59.29	-3.3	63.47	3.5
		Average %Bias :		-3.2		3.6

CHAPTER VI

RESULTS

Once the ^{99}Tc separation procedure was developed, two major studies were conducted in this research project. The first study involved a comparison of two methods capable of detecting ^{99}Tc, a radioanalytical measurement by liquid scintillation counting and a mass measurement by ICP-MS. Two liquid scintillation quench correction techniques, manual quench and quench curve, were evaluated and utilized to quantitate ^{99}Tc. The data generated by liquid scintillation counting and ICP-MS were evaluated and compared. The second study involved the determination of measurement sensitivities for both techniques as a function of radioactive decay and mass detection processes. The results from the first comparison study were then evaluated in light of the detection sensitivities.

Water, artificial urine, and real urine matrices spiked at three different levels, approximately 700, 1400, and 2200 dpm/L, were evaluated in the first study. Samples were labeled according to matrix and activity level, 1 lowest and 3 highest activity, using W1, W2, W3, A1, A2, A3, R1, R2, and R3 identifiers. Ten samples of each matrix and level were taken through the ^{99}Tc separation procedure as a group, and the final 50 mL solutions were divided into two aliquots, one for each analysis method. Sample results were not corrected for yield. The only applicable yield monitor capable of correcting both mass and liquid scintillation results without interferences by gamma counting is the tracer ^{95m}Tc, which was not available to this researcher at the time of this project. Because the samples were not corrected for yield, percent ^{99}Tc recovery was evaluated.

Aqueous solutions containing a known amount of ^{99}Tc were used to evaluate detection sensitivities for the two methods. Liquid scintillation water samples from the first study were employed to determine the detection sensitivities. The concentration range of 700 to 1400 dpm/L was well above the liquid scintillation detection limit. Calibration standards in 2.0 M HNO_3 with a range of 90 to 1400 dpm/L were used to determine ICP-MS detection sensitivity.

A. Liquid Scintillation Results

Tables 22 through 30 contain ^{99}Tc liquid scintillation results obtained during the first study. Parameters listed were those values required to determine activity using both manual quench and quench curve calculation methods. The original sample volumes were 0.025 L, and sample count times were 60 minutes. Final sample colors before counting were also noted.

When first evaluating the data, it appeared that a discrepancy existed between the efficiency values of the manual quench and quench curve methods for darkly colored samples. The manual quench efficiency appeared to be lower than the quench curve efficiency regardless of matrix and activity concentration. In order to assess thoroughly this observation, the difference in efficiency was recorded for each color class (clear, light yellow, yellow, and dark yellow). The average %efficiency difference for each class was determined : clear = 0.8%, light yellow = 6%, yellow = 11%, and dark yellow = 18%. From the average %efficiency difference values determined for each class, it appeared that the manual quench efficiencies were lower for colored samples than were the quench curve efficiencies, leading to higher calculated activities.

In order to evaluate rigorously the results obtained by the two quench correction

TABLE 22

LIQUID SCINTILLATION COMPARISON SET
WATER LEVEL 1: 712.2 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	20.80	22.16	1969400	-	1969379	-	-	-	-	-
W1-1	35.25	39.83	1669611	1669576	1969379	0.85	725.4	672.4	0.89	clear
W1-2	32.13	36.53	1601571	1601539	1969379	0.81	602.7	540.4	0.88	clear
W1-3	32.88	37.83	1564620	1564587	1969379	0.79	654.7	592.4	0.87	lt yellow
W1-4	33.67	38.67	1718189	1718155	1969379	0.87	632.4	626.0	0.87	lt yellow
W1-5	31.60	38.19	1259346	1259314	1969379	0.64	733.4	606.8	0.83	dk yellow
W1-6	33.67	39.01	1527600	1527566	1969379	0.78	711.3	639.6	0.86	lt yellow
W1-7	31.43	36.77	1470450	1470419	1969379	0.75	619.0	550.0	0.85	lt yellow
W1-8	34.62	39.63	1588800	1588765	1969379	0.81	731.0	664.4	0.87	clear
W1-9	31.78	37.43	1425920	1425888	1969379	0.72	657.7	576.4	0.85	lt yellow
W1-10	34.92	37.72	1872450	1872415	1969379	0.95	632.9	588.0	0.93	clear
WB1	21.6	25.13	1574640	1574618	1969379	0.80	40.02	118.8	0.86	lt yellow
WB2	18.05	21.09	1554238	1554220	1969379	0.79	-139.4	-42.80	0.86	lt yellow
WB3	21.03	24.08	1638075	1638054	1969379	0.83	11.06	76.80	0.87	clear
WB4	20.35	23.20	1692911	1692891	1969379	0.86	-20.94	41.60	0.88	lt yellow
WB5	18.35	21.59	1496250	1496232	1969379	0.76	-129.0	-22.80	0.85	lt yellow
WB Mean:	19.88	23.02								

Water was used to determine the unquench standard value. WB samples represent the reagent blanks.

TABLE 23

LIQUID SCINTILLATION COMPARISON SET
WATER LEVEL 2: 1422 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	26.02	28.14	1984600	-	1984574	-	-	-		
W2-1	52.45	61.29	1699011	1698959	1984574	0.86	1226	1200	0.86	clear
W2-2	51.33	61.31	1566870	1566819	1984574	0.79	1273	1201	0.84	dk yellow
W2-3	54.90	63.18	1714767	1714712	1984574	0.86	1329	1276	0.87	clear
W2-4	49.33	61.27	1473075	1473026	1984574	0.74	1246	1200	0.81	dk yellow
W2-5	48.15	60.72	1397656	1397608	1984574	0.70	1247	1178	0.79	dk yellow
W2-6	53.38	60.74	1763075	1763022	1984574	0.89	1224	1178	0.88	lt yellow
W2-7	50.08	58.68	1633020	1632970	1984574	0.82	1161	1096	0.85	lt yellow
W2-8	50.15	59.33	1633275	1633225	1984574	0.82	1164	1122	0.85	lt yellow
W2-9	49.48	61.47	1478675	1478626	1984574	0.75	1250	1208	0.80	dk yellow
W2-10	51.83	60.63	1650083	1650031	1984574	0.83	1233	1174	0.85	lt yellow
WB6	27.27	31.27	1791257	1791230	1984574	0.90	55.40	125.2	0.87	clear
WB7	26.15	33.06	1424546	1424520	1984574	0.72	7.24	196.8	0.79	dk yellow
WB8	26.73	33.11	1477856	1477829	1984574	0.74	38.14	198.8	0.81	dk yellow
WB9	24.13	27.53	1716000	1715976	1984574	0.86	-87.43	-24.40	0.88	lt yellow
WB10	26.77	31.46	1685017	1684990	1984574	0.85	35.33	132.8	0.85	clear
WB Mean:	26.21	31.29								

Water was used to determine the unquench standard value. WB samples represent the reagent blanks.

TABLE 24

LIQUID SCINTILLATION COMPARISON SET
WATER LEVEL 3: 2134 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	25.40	27.37	2035863	-	2035838	-	-	-		
W3-1	67.32	78.06	1954325	1954258	2035838	0.96	1715	1956	0.86	clear
W3-2	70.12	81.34	1732014	1731944	2035838	0.85	2066	2087	0.86	clear
W3-3	67.17	78.65	1701500	1701433	2035838	0.84	1962	1979	0.85	clear
W3-4	66.32	76.70	1734144	1734078	2035838	0.85	1885	1901	0.86	lt yellow
W3-5	69.55	80.90	1719322	1719252	2035838	0.84	2055	2069	0.86	clear
W3-6	68.12	79.15	1725889	1725821	2035838	0.85	1979	1999	0.86	clear
W3-7	61.55	72.84	1676414	1676352	2035838	0.82	1719	1747	0.85	clear
W3-8	68.68	76.00	1909433	1909364	2035838	0.94	1813	1873	0.90	clear
W3-9	72.18	83.72	1751900	1751828	2035838	0.86	2139	2182	0.86	clear
W3-10	69.02	81.66	1652533	1652464	2035838	0.81	2112	2100	0.85	clear
WB11	26.33	30.11	1801211	1801185	2035838	0.88	42.05	109.6	0.87	clear
WB12	25.22	27.86	1927486	1927461	2035838	0.95	-7.60	19.60	0.91	clear
WB13	26.40	29.38	1882943	1882917	2035838	0.92	43.25	80.40	0.90	clear
WB14	26.97	31.04	1804677	1804650	2035838	0.89	70.85	146.8	0.87	clear
WB15	25.95	30.14	1732444	1732418	2035838	0.85	25.85	110.8	0.86	clear
WB Mean:	26.17	29.71								

Water was used to determine the unquench standard value. WB samples represent the reagent blanks.

TABLE 25

LIQUID SCINTILLATION COMPARISON SET
ARTIFICIAL URINE LEVEL 1: 712.2 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	27.08	29.16	-	1844513	1844486	-	-	-		
A1-1	39.00	44.61	1688688	1688649	1844486	0.92	532.6	417.9	0.87	lt yellow
A1-2	40.75	46.11	1868467	1868426	1844486	1.01	550.5	477.9	0.88	lt yellow
A1-3	36.68	43.98	1511540	1511503	1844486	0.82	481.8	392.7	0.83	yellow
A1-4	40.27	45.73	1768750	1768710	1844486	0.96	561.5	462.7	0.88	lt yellow
A1-5	39.17	43.13	1693317	1693278	1844486	0.92	538.5	358.7	0.91	clear
A1-6	38.98	45.37	1813283	1813244	1844486	0.98	495.2	448.3	0.86	yellow
A1-7	34.30	46.99	567288	567253.7	1844486	0.31	974.2	513.1	0.73	dk yellow
A1-8	37.42	47.18	1276630	1276593	1844486	0.69	613.2	520.7	0.79	yellow
A1-9	21.05	28.22	22692.3	22671.25	1844486	0.01	-18740	-237.7	0.75	dk yellow
A1-10	36.25	47.52	1117836	1117800	1844486	0.61	623.1	534.3	0.76	dk yellow
AB1	27.13	35.09	1254500	1254473	1844486	0.68	2.941	237.20	0.77	yellow
AB2	26.78	34.81	1326667	1326640	1844486	0.72	-16.68	226.00	0.77	yellow
AB3	26.35	33.49	1233213	1233187	1844486	0.67	-43.67	173.20	0.79	yellow
AB4	26.32	30.80	1574645	1574619	1844486	0.85	-35.61	65.60	0.85	clear
AB5	27.57	36.62	1287433	1287405	1844486	0.70	28.08	298.40	0.75	yellow
AB Mean:	26.83	34.16								

Water was used to determine the unquench standard value. AB samples represent the reagent blanks.
Sample A1-9 was lost due to charring.

TABLE 26

LIQUID SCINTILLATION COMPARISON SET
ARTIFICIAL URINE LEVEL 2: 1422 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	25.75	27.82	-	2068671	2068645	-	-	-		
A2-1	45.23	61.60	989379	989334	2068645	0.48	1540	1170	0.73	clear
A2-2	48.20	55.31	1661933	1661885	2068645	0.80	1065	918	0.87	dk yellow
A2-3	51.85	62.75	1442550	1442498	2068645	0.70	1436	1216	0.83	clear
A2-4	47.48	63.28	1092422	1092375	2068645	0.53	1565	1237	0.75	dk yellow
A2-5	53.25	62.01	1626957	1626904	2068645	0.79	1344	1186	0.86	dk yellow
A2-6	53.78	62.15	1664400	1664346	2068645	0.80	1340	1192	0.87	lt yellow
A2-7	55.02	59.42	2069000	2068945	2068645	1.00	1128	1082	0.93	lt yellow
A2-8	46.75	60.90	1396450	1396403	2068645	0.68	1181	1142	0.77	lt yellow
A2-9	53.07	64.21	1890200	1890147	2068645	0.91	1149	1274	0.83	dk yellow
A2-10	52.47	61.72	1565757	1565705	2068645	0.76	1356	1174	0.85	lt yellow
AB6	25.22	30.54	1414109	1414084	2068645	0.68	-31.01	108.8	0.83	clear
AB7	25.97	32.19	1351036	1351010	2068645	0.65	13.47	174.8	0.81	dk yellow
AB8	27.40	33.59	1143400	1143373	2068645	0.55	119.4	230.8	0.82	dk yellow
AB9	27.55	34.33	1322080	1322052	2068645	0.64	112.7	260.4	0.80	lt yellow
AB10	27.95	31.16	1881688	1881660	2068645	0.91	96.74	133.6	0.90	clear
AB Mean:	26.82	32.36								

Water was used to determine the unquench standard value. AB samples represent the reagent blanks.

TABLE 27

LIQUID SCINTILLATION COMPARISON SET
ARTIFICIAL URINE LEVEL 3: 2134 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	26.27	28.80	-	2144829	2144803	-	-	-		
A3-1	69.78	80.26	1736586	1736516	2144803	0.81	2104	1967	0.87	lt yellow
A3-2	66.63	78.48	1661611	1661544	2144803	0.77	2036	1896	0.85	lt yellow
A3-3	68.75	80.19	1677378	1677309	2144803	0.78	2125	1964	0.86	lt yellow
A3-4	69.02	79.08	1739225	1739156	2144803	0.81	2063	1920	0.87	lt yellow
A3-5	70.65	80.60	1800200	1800129	2144803	0.84	2071	1980	0.88	clear
A3-6	69.53	79.05	1813500	1813430	2144803	0.85	2003	1918	0.88	clear
A3-7	65.63	77.24	1588620	1588554	2144803	0.74	2075	1846	0.85	lt yellow
A3-8	61.97	75.03	1520275	1520213	2144803	0.71	1962	1758	0.83	yellow
A3-9	69.18	77.18	1909817	1909748	2144803	0.89	1886	1844	0.90	clear
A3-10	67.52	78.92	1661744	1661676	2144803	0.77	2082	1913	0.86	lt yellow
AB11	26.85	29.93	1898388	1898361	2144803	0.89	26.21	45.20	0.90	clear
AB12	26.65	30.25	1814944	1814917	2144803	0.85	17.96	58.00	0.88	clear
AB13	27.12	32.04	1594533	1594506	2144803	0.74	45.73	129.6	0.85	lt yellow
AB14	27.37	30.73	1825825	1825798	2144803	0.85	51.69	77.20	0.89	lt yellow
AB15	28.03	32.48	1642414	1642386	2144803	0.77	91.94	147.2	0.86	lt yellow
AB Mean:	27.20	31.09								

Water was used to determine the unquench standard value. AB samples represent the reagent blanks.

TABLE 28

LIQUID SCINTILLATION COMPARISON SET
REAL URINE LEVEL 1: 703.5 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	24.42	26.33	-	2078086	2078062	-	-	-		
R1-1	38.98	44.33	1583271	1583232	2078062	0.76	627.9	526.2	0.88	lt yellow
R1-2	40.22	46.53	1484683	1484643	2078062	0.71	739.0	614.2	0.86	lt yellow
R1-3	39.25	43.69	1713333	1713294	2078062	0.82	593.4	500.6	0.90	clear
R1-4	39.13	43.45	1985500	1985461	2078062	0.96	507.0	491.0	0.90	clear
R1-5	41.32	46.24	2043360	2043319	2078062	0.98	581.7	602.6	0.89	clear
R1-6	38.12	42.63	1883500	1883462	2078062	0.91	489.9	458.2	0.89	clear
R1-7	40.36	45.21	1911188	1911148	2078062	0.92	580.2	561.4	0.89	clear
R1-8	41.08	48.31	1627938	1627897	2078062	0.78	717.9	685.4	0.85	lt yellow
R1-9	38.78	46.14	1524400	1524361	2078062	0.73	641.3	598.6	0.84	lt yellow
R1-10	40.57	49.54	1623100	1623059	2078062	0.78	693.9	734.6	0.82	yellow
RB1	26.60	29.87	1852833	1852806	2078062	0.89	97.80	141.6	0.89	clear
RB2	27.07	30.51	1811022	1810995	2078062	0.87	121.6	167.2	0.89	clear
RB3	27.40	32.06	1655829	1655802	2078062	0.80	149.6	229.2	0.85	clear
RB4	27.08	32.26	1791933	1791906	2078062	0.86	123.4	237.2	0.84	yellow
RB Mean:	27.04	31.18								

Water was used to determine the unquench standard value. RB samples represent the reagent blanks.

TABLE 29

LIQUID SCINTILLATION COMPARISON SET
REAL URINE LEVEL 2: 1419 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	26.05	28.14	-	2066900	2066874	-	-	-		
R2-1	49.13	62.72	1106085	1106036	2066874	0.54	1764	1308	0.78	dk yellow
R2-2	50.50	60.84	1441029	1440979	2066874	0.70	1433	1232	0.83	yellow
R2-3	52.70	64.21	1463538	1463485	2066874	0.71	1535	1367	0.82	yellow
R2-4	48.77	61.74	1237717	1237668	2066874	0.60	1552	1268	0.79	yellow
R2-5	53.23	60.10	1861856	1861803	2066874	0.90	1230	1203	0.89	clear
R2-6	52.13	63.42	1429390	1429338	2066874	0.69	1539	1336	0.82	yellow
R2-7	51.98	63.51	1387790	1387738	2066874	0.67	1576	1339	0.82	yellow
R2-8	53.35	62.65	1501150	1501097	2066874	0.73	1532	1305	0.85	yellow
R2-9	54.78	60.71	1869820	1869765	2066874	0.90	1293	1227	0.90	clear
R2-10	50.88	60.62	1481430	1481379	2066874	0.72	1415	1224	0.84	lt yellow
RB5	26.55	30.63	1680475	1680448	2066874	0.81	24.60	99.60	0.87	lt yellow
RB6	24.35	28.67	1564250	1564226	2066874	0.76	-89.85	21.20	0.85	lt yellow
RB7	25.68	30.79	1524478	1524452	2066874	0.74	-20.07	106.0	0.83	lt yellow
RB Mean:	25.53	30.03								

Water was used to determine the unquench standard value. RB samples represent the reagent blanks.

TABLE 30

LIQUID SCINTILLATION COMPARISON SET
REAL URINE LEVEL 3: 2123 dpm/L

Sample	Qu + Qb (cpm)	Instrument (dpm)	Qs + Qu +Qb (cpm)	Qs (cpm)	S (cpm)	Manual Q e	Manual Q (dpm/L)	Q Curve (dpm/L)	Q Curve e	Observed Color
Water	27.15	29.34	-	2111617	2111590	-	-	-		
R3-1	66.82	79.74	1514514	1514447	2111590	0.72	2239	1948	0.84	lt yellow
R3-2	65.07	74.38	1707600	1707535	2111590	0.81	1899	1733	0.87	lt yellow
R3-3	65.25	76.41	2068200	1578230	2111590	0.75	2065	1814	0.85	lt yellow
R3-4	68.02	78.64	1712100	1712032	2111590	0.81	2040	1904	0.86	lt yellow
R3-5	66.37	76.89	1658986	1658920	2111590	0.79	2021	1834	0.86	lt yellow
R3-6	66.65	81.34	1506900	1506833	2111590	0.71	2241	2012	0.82	yellow
R3-7	64.60	78.47	1432925	1432860	2111590	0.68	2236	1897	0.82	lt yellow
R3-8	59.02	74.50	1236000	1235941	2111590	0.59	2211	1738	0.79	yellow
R3-9	64.35	79.85	1304033	1303969	2111590	0.62	2441	1952	0.81	yellow
R3-10	68.65	81.71	1483825	1483756	2111590	0.70	2390	2026	0.84	yellow
RB8	26.53	32.80	1423138	1423111	2111590	0.67	-36.80	138.4	0.81	yellow
RB9	25.57	29.06	1852222	1852196	2111590	0.88	-72.05	-11.20	0.88	lt yellow
RB10	27.92	31.29	1895125	1895097	2111590	0.90	34.32	78.00	0.89	clear
RB Mean:	26.67	31.05								

Water was used to determine the unquench standard value. RB samples represent the reagent blanks.

methods, the %Bias, average %Efficiency, and absolute difference between bias values were recorded (Tables 31 through 33) for each sample. Examination of all data revealed several aspects concerning liquid scintillation counting using both quench correction methods. When comparing the mean %Bias values for each method, manual quench ranged between -16% to 4.9% and quench curve ranged between -36% to -6.8%. Upon examination of Tables 31 through 33, it is evident that the manual quench results were overall more accurate than the quench curve results. In light of the lower efficiencies obtained for colored samples using the manual quench calculations, it appears that the quench curve method does not adequately correct for color quench.

The standard deviation of %Bias for each set was equivalent with the exception of sets A1 and R2. The standard deviation of manual quench results for these two sets was over twice the value of quench curve results. For the manual quench method, $Q_u + Q_b + Q_s$ was not directly recorded by the instrument, but manually recorded when the value momentarily flashed upon the screen during the sample count. It is possible that the final updated value was not displayed causing an increased variability in the manual results.

A trend may also be observed in the absolute difference in %Bias values derived from manual quench and quench curve biases. The trend exists between low and high activity concentrations for a given matrix. For the water and artificial urine matrices, the %Bias difference was higher for the lower activity concentration and decreased with increasing activity concentrations. This trend was not noted for the real urine matrix, however for sets R2 and R3, a big discrepancy between manual quench and quench curve efficiencies exists resulting in a large %Bias difference. In each case, the manual

TABLE 31

COMPARISON OF %BIAS OF MANUAL AND AUTOMATIC QUENCH CORRECTED VALUES FOR THE WATER MATRIX

Control ID	Manual Quench %Bias	Automatic Quench %Bias	Difference Between %Bias Values
W1-1	1.9	-5.6	7.4
W1-2	-15	-24	8.8
W1-3	-8.1	-17	8.8
W1-4	-11	-12	0.91
W1-5	3.0	-15	18
W1-6	-0.11	-10	10
W1-7	-13	-23	9.7
W1-8	2.7	-6.7	9.4
W1-9	-7.7	-19	11
W1-10	-11	-17	6.3
Mean	-5.9	-15	9.0
s_B	7.1	6.3	4.2
Avg. %Efficiency	80	87	-
W2-1	-14	-16	1.8
W2-2	-10	-16	5.1
W2-3	-7	-10	3.7
W2-4	-12	-16	3.3
W2-5	-12	-17	4.9
W2-6	-14	-17	3.2
W2-7	-18	-23	4.6
W2-8	-18	-21	3.0
W2-9	-12	-15	3.0
W2-10	-13	-17	4.2
Mean	-13	-17	3.7
s_B	3.4	3.4	1.0
Avg. %Efficiency	81	84	-
W3-1	-20	-8.4	11
W3-2	-3.2	-2.2	0.95
W3-3	-8.1	-7.3	0.79
W3-4	-12	-11	0.74
W3-5	-3.7	-3.1	0.68
W3-6	-7.3	-6.3	0.93
W3-7	-19	-18	1.3
W3-8	-15	-12	2.8
W3-9	0.21	2.2	2.0
W3-10	-1.1	-1.6	0.57
Mean	-8.9	-6.8	2.2
s_B	7.3	6.0	3.3
Avg. %Efficiency	86	86	-

TABLE 32

COMPARISON OF %BIAS OF MANUAL AND AUTOMATIC QUENCH CORRECTED VALUES FOR THE ARTIFICIAL URINE MATRIX

Standard ID	Manual Quench %Bias	Automatic Quench %Bias	Difference Between %Bias Values
A1-1	-25	-41	16
A1-2	-23	-33	10
A1-3	-32	-45	13
A1-4	-21	-35	14
A1-5	-24	-50	25
A1-6	-30	-37	7
A1-7	37	-28	65
A1-8	-14	-27	13
A1-9	*	*	*
A1-10	-13	-25	12
Mean	-16	-36	19
s_B	21	8	18
Avg. %Efficiency	80	83	-
A2-1	8.3	-18	26
A2-2	-25	-35	10
A2-3	0.96	-15	15
A2-4	10	-13	23
A2-5	-5.5	-17	11
A2-6	-5.8	-16	10
A2-7	-21	-24	3.2
A2-8	-17	-20	2.8
A2-9	-19	-10	8.8
A2-10	-4.7	-17	13
Mean	-7.9	-19	12
s_B	12	7.0	7.5
Avg. %Efficiency	75	83	-
A3-1	-1.4	-7.9	6.4
A3-2	-4.6	-11	6.6
A3-3	-0.43	-8.0	7.6
A3-4	-3.3	-10	6.7
A3-5	-3.0	-7.2	4.2
A3-6	-6.2	-10	4.0
A3-7	-2.8	-14	11
A3-8	-8.1	-18	9.6
A3-9	-12	-14	2.0
A3-10	-2.5	-10	7.9
Mean	-4.4	-11	6.6
s_B	3.4	3.2	2.6
Avg. %Efficiency	80	87	-

* Chemical quench was so severe that the sample was an outlier.

TABLE 33

COMPARISON OF %BIAS OF MANUAL AND AUTOMATIC QUENCH CORRECTED VALUES FOR THE REAL URINE MATRIX

Standard ID	Manual Quench %Bias	Automatic Quench %Bias	Difference Between %Bias Values
R1-1	-11	-25	14
R1-2	5.1	-13	18
R1-3	-16	-29	13
R1-4	-28	-30	2.3
R1-5	-17	-14	3.0
R1-6	-30	-35	4.5
R1-7	-18	-20	2.7
R1-8	2.1	-2.6	4.6
R1-9	-8.9	-15	6.1
R1-10	-1.4	4.4	5.8
Mean	-12	-18	7.4
s_B	12	12	5.6
Avg. %Efficiency	83	87	-
R2-1	24	-7.9	32
R2-2	0.96	-13	14
R2-3	8.2	-3.7	12
R2-4	9.4	-11	20
R2-5	-13	-15	1.9
R2-6	8.4	-5.9	14
R2-7	11	-5.6	17
R2-8	8.0	-8.1	16
R2-9	-8.9	-14	4.7
R2-10	-0.30	-14	13
Mean	4.8	-9.7	15
s_B	11	4.1	8.3
Avg. %Efficiency	71	83	-
R3-1	5.5	-8.2	14
R3-2	-11	-18	7.8
R3-3	-2.7	-15	12
R3-4	-3.9	-10	6.4
R3-5	-4.8	-14	8.8
R3-6	5.6	-5.2	11
R3-7	5.3	-11	16
R3-8	4.2	-18	22
R3-9	15	-8.0	23
R3-10	13	-4.5	17
Mean	2.6	-11	14
s_B	8.0	4.9	5.8
Avg. %Efficiency	72	84	-

quench results were more accurate than the quench curve results at lower activity concentration. The larger absolute difference in %Bias, coupled with the less accurate results for lower activity concentrations, indicates that quench curve corrections are not as accurate at the lower activity levels.

B. ICP-MS Results

Results obtained by ICP-MS in the first study are given in Tables 34 through 42. One of the most notable differences in the ICP-MS ^{99}Tc results compared to the liquid scintillation results was a better precision for each matrix and activity concentration. The average %Bias values ranged from -17% to -7.9% and the standard deviation of the %Bias ranged from +/- 1.9 to 5.0%. When acquiring data by ICP-MS, it was very critical that instrument conditions were such that both accurate and precise results were obtained. Calibration standards were prepared by weight and verified against previously, well characterized standards. Check standards were periodically analyzed to ensure that accuracy and stability were maintained throughout the analysis. Since the samples were not corrected for yield, it was not possible to ensure that the values and associated 2σ error intersected the true values.

Due to the increased sensitivity of ^{115}In in both artificial urine and real urine matrices, a larger bias was expected due to internal standard overcorrection. However, no notable difference in %Bias between matrix or activity level appeared to exist. %Bias and standard deviations were very consistent between matrices and activity concentrations.

C. Liquid Scintillation and ICP-MS Comparison

In order to compare results from both liquid scintillation quench correction

TABLE 34

^{99}Tc WATER ICP-MS VALIDATION LEVEL 1
TRUE VALUE: 712.2 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
W1-1-1	585.6	82.2	-18
W1-1-2	581.3	81.6	-18
W1-2-1	618.7	86.9	-13
W1-2-2	634.5	89.1	-11
W1-3-1	583.5	81.9	-18
W1-3-2	595.6	83.6	-16
W1-4-1	647.3	90.9	-9.1
W1-4-2	658.0	92.4	-7.6
W1-5-1	648.9	91.1	-8.9
W1-5-2	656.8	92.2	-7.8
W1-6-1	647.6	90.9	-9.1
W1-6-2	651.0	91.4	-8.6
W1-7-1	619.1	86.9	-13
W1-7-2	630.8	88.6	-11
W1-8-1	656.7	92.2	-7.8
W1-8-2	647.2	90.9	-9.1
W1-9-1	657.7	92.3	-7.7
W1-9-2	646.9	90.8	-9.2
W1-10-1	660.5	92.8	-7.2
W1-10-2	615.7	86.5	-14
Mean	632.2	88.8	-11
s_b	27.1	3.81	3.8

TABLE 35

^{99}Tc WATER ICP-MS VALIDATION LEVEL 2
TRUE VALUE: 1422 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
W2-1-1	1199	84.4	-16
W2-1-2	1192	83.8	-16
W2-2-1	1244	87.5	-13
W2-2-2	1274	89.6	-10
W2-3-1	1264	88.9	-11
W2-3-2	1282	90.1	-9.9
W2-4-1	1275	89.7	-10
W2-4-2	1257	88.4	-12
W2-5-1	1224	86.1	-14
W2-5-2	1237	87.0	-13
W2-6-1	1261	88.7	-11
W2-6-2	1259	88.6	-11
W2-7-1	1206	84.8	-15
W2-7-2	1179	82.9	-17
W2-8-1	1195	84.0	-16
W2-8-2	1182	83.1	-17
W2-9-1	1197	84.2	-16
W2-9-2	1232	86.6	-13
W2-10-1	1280	90.0	-10
W2-10-2	1256	88.4	-12
Mean	1235	86.8	-13
s_b	35.2	2.47	2.5

TABLE 36

^{99}Tc WATER ICP-MS VALIDATION LEVEL 3
TRUE VALUE: 2134 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
W3-1-1	1861	87.2	-13
W3-1-2	1871	87.7	-12
W3-2-1	1952	91.5	-8.5
W3-2-2	2025	94.9	-5.1
W3-3-1	1971	92.3	-7.7
W3-3-2	1958	91.7	-8.3
W3-4-1	1903	89.2	-11
W3-4-2	1897	88.9	-11
W3-5-1	1833	85.9	-14
W3-5-2	1842	86.3	-14
W3-6-1	2000	93.7	-6.3
W3-6-2	2035	95.4	-4.6
W3-7-1	1641	76.9	-23
W3-7-2	1629	76.3	-24
W3-8-1	1929	90.4	-9.6
W3-8-2	1923	90.1	-9.9
W3-9-1	1982	92.9	-7.1
W3-9-2	1966	92.1	-7.9
W3-10-1	1932	90.5	-9.5
W3-10-2	1894	88.7	-11
Mean	1902	89.1	-11
s_b	107	5.03	5.0

TABLE 37

^{99}Tc ARTIFICIAL URINE ICP-MS VALIDATION LEVEL 1
TRUE VALUE: 712.2 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
A1-1-1	566.7	79.6	-20
A1-1-2	559.1	78.5	-21
A1-2-1	596.5	83.8	-16
A1-2-2	607.7	85.4	-15
A1-3-1	530.9	74.6	-25
A1-3-2	535.7	75.2	-25
A1-4-1	630.5	88.6	-11
A1-4-2	632.4	88.8	-11
A1-5-1	546.3	76.7	-23
A1-5-2	571.3	80.2	-20
A1-6-1	590.4	82.9	-17
A1-6-2	592.2	83.2	-17
A1-7-1	607.5	85.3	-15
A1-7-2	601.2	84.4	-16
A1-8-1	613.6	86.2	-14
A1-8-2	613.4	86.1	-14
A1-9-1	638.8	89.7	-10
A1-9-2	627.3	88.1	-12
A1-10-1	566.5	79.6	-20
A1-10-2	552.8	77.6	-22
Mean	589.0	82.7	-17
s_b	33.4	4.69	4.7

TABLE 38

^{99}Tc ARTIFICIAL URINE ICP-MS VALIDATION LEVEL 2
TRUE VALUE: 1422 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
A2-1-1	1265	89.0	-11
A2-1-2	1250	87.9	-12
A2-2-1	1328	93.4	-6.6
A2-2-2	1318	92.7	-7.3
A2-3-1	1293	90.9	-9.1
A2-3-2	1299	91.3	-8.7
A2-4-1	1326	93.2	-6.8
A2-4-2	1284	90.3	-9.7
A2-5-1	1327	93.3	-6.7
A2-5-2	1329	93.4	-6.6
A2-6-1	1294	91.0	-9.0
A2-6-2	1318	92.7	-7.3
A2-7-1	1293	90.9	-9.1
A2-7-2	1321	92.9	-7.1
A2-8-1	1363	95.9	-4.1
A2-8-2	1395	98.1	-1.9
A2-9-1	1362	95.8	-4.2
A2-9-2	1344	94.5	-5.5
A2-10-1	1226	86.2	-14
A2-10-2	1212	85.2	-15
Mean	1307	91.9	-8.1
s_b	45.4	3.20	3.2

TABLE 39

^{99}Tc ARTIFICIAL URINE ICP-MS VALIDATION LEVEL 3
TRUE VALUE: 2134 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
A3-1-1	1896	88.8	-11
A3-1-2	1910	89.5	-11
A3-2-1	1829	85.7	-14
A3-2-2	1843	86.4	-14
A3-3-1	1997	93.6	-6.4
A3-3-2	1941	90.9	-9.1
A3-4-1	1913	89.7	-10
A3-4-2	1912	89.6	-10
A3-5-1	1922	90.1	-9.9
A3-5-2	1941	90.9	-9.1
A3-6-1	1961	91.9	-8.1
A3-6-2	1942	91.0	-9.0
A3-7-1	1949	91.3	-8.7
A3-7-2	1923	90.1	-9.9
A3-8-1	2041	95.6	-4.4
A3-8-2	2025	94.9	-5.1
A3-9-1	1920	89.9	-10
A3-9-2	1898	88.9	-11
A3-10-1	1967	92.2	-7.8
A3-10-2	1933	90.6	-9.4
Mean	1933	90.6	-9.4
s_b	51.3	2.40	2.4

TABLE 40

^{99}Tc REAL URINE ICP-MS VALIDATION LEVEL 1
TRUE VALUE: 703.5 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
R1-1-1	631.3	89.7	-10
R1-1-2	629.3	89.5	-11
R1-2-1	614.0	87.3	-13
R1-2-2	611.5	86.9	-13
R1-3-1	584.4	83.1	-17
R1-3-2	589.6	83.8	-16
R1-4-1	613.0	87.1	-13
R1-4-2	615.2	87.4	-13
R1-5-1	603.8	85.8	-14
R1-5-2	605.8	86.1	-14
R1-6-1	598.4	85.1	-15
R1-6-2	598.7	85.1	-15
R1-7-1	602.2	85.6	-14
R1-7-2	620.4	88.2	-12
R1-8-1	617.1	87.7	-12
R1-8-2	617.9	87.8	-12
R1-9-1	631.0	89.7	-10
R1-9-2	621.7	88.4	-12
R1-10-1	624.3	88.7	-11
R1-10-2	618.7	88.0	-12
Mean	612.4	87.1	-13
s_b	13.2	1.87	1.9

TABLE 41

^{99}Tc REAL URINE ICP-MS VALIDATION LEVEL 2
TRUE VALUE: 1419 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
R2-1-1	1228	86.5	-13
R2-1-2	1249	88.1	-12
R2-2-1	1209	85.2	-15
R2-2-2	1190	83.9	-16
R2-3-1	1215	85.6	-14
R2-3-2	1231	86.7	-13
R2-4-1	1274	89.8	-10
R2-4-2	1271	89.6	-10
R2-5-1	1259	88.7	-11
R2-5-2	1272	89.7	-10
R2-6-1	1327	93.5	-6.5
R2-6-2	1331	93.8	-6.2
R2-7-1	1354	95.5	-4.5
R2-7-2	1369	96.4	-3.6
R2-8-1	1309	92.2	-7.8
R2-8-2	1323	93.2	-6.8
R2-9-1	1311	92.4	-7.6
R2-9-2	1321	93.1	-6.9
R2-10-1	1301	91.7	-8.3
R2-10-2	1317	92.8	-7.2
Mean	1283	90.4	-9.6
s_b	50.9	3.59	3.6

TABLE 42

^{99}Tc REAL URINE ICP-MS VALIDATION LEVEL 3
TRUE VALUE: 2123 dpm/L

Control ID	Result (dpm/L)	%Yield	%Bias
R3-1-1	1979	93.3	-6.7
R3-1-2	1990	93.8	-6.2
R3-2-1	1804	85.0	-15
R3-2-2	1801	84.8	-15
R3-3-1	1963	92.5	-7.5
R3-3-2	2001	94.3	-5.7
R3-4-1	1857	87.5	-12
R3-4-2	1866	87.9	-12
R3-5-1	1922	90.5	-9.5
R3-5-2	1899	89.5	-11
R3-6-1	2002	94.3	-5.7
R3-6-2	1952	92.0	-8.0
R3-7-1	2081	98.1	-1.9
R3-7-2	2085	98.3	-1.7
R3-8-1	1925	90.7	-9.3
R3-8-2	1947	91.7	-8.3
R3-9-1	1981	93.3	-6.7
R3-9-2	1961	92.4	-7.6
R3-10-1	2037	96.0	-4.0
R3-10-2	2053	96.7	-3.3
Mean	1955	92.1	-7.9
s_b	81.3	3.83	3.8

methods and ICP-MS, Tables 43 through 45 were assembled. Evaluation of the compiled data revealed that the liquid scintillation manual quench correction standard deviation tended to be 1.5 to 6.4 times higher than that from ICP-MS analysis. With the exception of the W3 set, the ICP-MS results were closer to the true value than the liquid scintillation quench curve results. The s_b values for liquid scintillation counting were too large to make a direct sample per sample comparison with ICP-MS values.

Reagent blanks were evaluated for each matrix and detection method (Tables 46 through 48) in order to determine the MDC and LOD detection limits. The larger standard deviation in total blank count values obtained by liquid scintillation had a detrimental effect on the calculated LOD and MDC values. MDC and LOD values were 3, 5, and 13 times higher for water, artificial urine, and real urine matrices, respectively, by liquid scintillation counting.

The overall %Recovery for each matrix was consistently higher for the manual correction method. The average recovery by liquid scintillation manual quench, liquid scintillation quench curve, and ICP-MS were: 91%, 87%, and 88% in water; 91%, 77%, and 88% in artificial urine; and 98%, 87%, and 90% in real urine.

D. ^{99}Tc ICP-MS and Liquid Scintillation Detection Sensitivity

ICP-MS quantitation of ^{99}Tc was based on the linear relationship between the countrate and concentration:

$$y = mx + b \tag{10}$$

$$cps_{analyte} = (\Delta cps/\ \Delta concentration)\ concentration + cps_{background} \tag{11}$$

The slope of this linear calibration curve was equivalent to the sensitivity k [cps/(g/vol)].

TABLE 43

^{99}Tc WATER COMPARISON

Control ID	Liquid Scintillation Manual Q (dpm/L)	Liquid Scintillation Q Curve (dpm/L)	ICP-MS (dpm/L)
W1-1	725.4	672.4	583.4
W1-2	602.7	540.4	625.6
W1-3	654.7	592.4	589.5
W1-4	632.4	626.0	652.6
W1-5	733.4	606.8	652.9
W1-6	711.3	639.6	649.3
W1-7	619.0	550.0	624.9
W1-8	731.1	664.4	652.0
W1-9	657.7	576.4	652.3
W1-10	632.9	588.0	638.1
Mean	670.1	605.6	632.1
s_b	50.4	44.9	26.4
%Bias	-5.9	-15	-11
W2-1	1226	1200	1196
W2-2	1273	1201	1259
W2-3	1329	1276	1273
W2-4	1246	1200	1266
W2-5	1247	1178	1231
W2-6	1224	1178	1260
W2-7	1161	1096	1193
W2-8	1164	1122	1189
W2-9	1250	1208	1214
W2-10	1233	1174	1268
Mean	1235	1183	1235
s_b	48.8	49.0	34.4
%Bias	-13	-17	-13
W3-1	1715	1956	1866
W3-2	2066	2087	1989
W3-3	1962	1979	1964
W3-4	1885	1901	1900
W3-5	2055	2069	1837
W3-6	1979	1999	2018
W3-7	1719	1747	1635
W3-8	1813	1873	1926
W3-9	2139	2182	1974
W3-10	2112	2100	1913
Mean	1945	1989	1902
s_b	156	128	109
%Bias	-8.9	-6.8	-11

TABLE 44

^{99}Tc ARTIFICIAL URINE COMPARISON

Control ID	Liquid Scintillation Manual Q (dpm/L)	Liquid Scintillation Q Curve (dpm/L)	ICP-MS (dpm/L)
A1-1	532.6	417.9	562.9
A1-2	550.5	477.9	602.1
A1-3	481.8	392.7	533.3
A1-4	561.5	462.7	631.5
A1-5	538.6	358.7	558.8
A1-6	495.2	448.3	591.3
A1-7	974.2	513.1	604.4
A1-8	613.2	520.7	613.5
A1-9	-	-	633.0
A1-10	623.1	534.3	559.6
Mean	596.7	458.5	589.0
s_b	149	60.2	33.8
%Bias	-16	-36	-17
A2-1	1540	1170	1258
A2-2	1065	918	1323
A2-3	1436	1216	1296
A2-4	1565	1237	1305
A2-5	1344	1186	1328
A2-6	1340	1192	1306
A2-7	1128	1082	1307
A2-8	1181	1142	1379
A2-9	1149	1274	1353
A2-10	1356	1174	1219
Mean	1310	1159	1307
s_b	174	99.4	45.2
%Bias	-7.9	-18	-8.1
A3-1	2104	1967	1903
A3-2	2036	1896	1836
A3-3	2125	1964	1969
A3-4	2063	1920	1913
A3-5	2071	1980	1932
A3-6	2003	1918	1951
A3-7	2075	1846	1936
A3-8	1962	1758	2033
A3-9	1886	1844	1909
A3-10	2082	1913	1950
Mean	2041	1901	1933
s_b	72.3	68.6	50.8
%Bias	-4.4	-11	-9.4

TABLE 45

^{99}Tc REAL URINE COMPARISON

Control ID	Liquid Scintillation Manual Q (dpm/L)	Liquid Scintillation Q Curve (dpm/L)	ICP-MS (dpm/L)
R1-1	627.9	526.2	630.3
R1-2	739.0	614.2	612.7
R1-3	593.4	500.6	587.0
R1-4	507.0	491.0	614.1
R1-5	581.7	602.6	604.8
R1-6	489.9	458.2	598.6
R1-7	580.2	561.4	611.3
R1-8	717.9	685.4	617.5
R1-9	641.3	598.6	626.4
R1-10	693.9	734.6	621.5
Mean	617.2	577.3	612.4
s_b	83.8	87.7	13.0
%Bias	-12	-18	-13
R2-1	1764	1308	1239
R2-2	1433	1232	1200
R2-3	1535	1367	1223
R2-4	1552	1268	1273
R2-5	1230	1203	1266
R2-6	1539	1336	1329
R2-7	1576	1339	1362
R2-8	1532	1305	1316
R2-9	1293	1227	1316
R2-10	1415	1224	1309
Mean	1487	1281	1283
s_b	152	57.6	51.8
%Bias	4.8	-9.7	-9.6
R3-1	2239	1948	1985
R3-2	1899	1733	1802
R3-3	2065	1814	1982
R3-4	2040	1904	1861
R3-5	2021	1834	1910
R3-6	2241	2012	1977
R3-7	2236	1897	2083
R3-8	2211	1738	1936
R3-9	2441	1952	1971
R3-10	2390	2026	2045
Mean	2178	1886	1955
s_b	170	104	82.5
%Bias	2.7	-11	-7.9

TABLE 46

^{99}TC DETECTION LIMITS IN WATER

Sample ID	ICP-MS (dpm/L)	Liquid Scintillation (Counts)
WB1	180.7	1628
WB2	151.6	1601
WB3	158.0	1581
WB4	152.6	1579
WB5	143.3	1654
WB6	214.3	1513
WB7	172.5	1558
WB8	177.8	1644
WB9	179.0	1653
WB10	177.3	1677
WB11	189.7	1580
WB12	169.3	1513
WB13	154.0	1584
WB14	157.0	1602
WB15	168.0	1557
s_b	18.10	49.43
MDC (dpm/L)	84.17	190.9
LOD (dpm/L)	59.54	162.6

Liquid Scintillation Parameters: e = 0.81, Volume = 0.025 mL, Time = 60 min.

TABLE 47

^{99}TC DETECTION LIMITS IN ARTIFICIAL URINE

Sample ID	ICP-MS (dpm/L)	Liquid Scintillation (Counts)
AB1	-	1628
AB2	112.1	1601
AB3	93.93	1581
AB4	84.19	1579
AB5	93.53	1654
AB6	106.1	1513
AB7	96.76	1558
AB8	87.86	1644
AB9	104.1	1653
AB10	90.25	1677
AB11	107.0	1611
AB12	94.47	1599
AB13	99.25	1627
AB14	93.88	1642
AB15	84.92	1682
s_b	8.49	47.70
MDC (dpm/L)	39.57	203.8
LOD (dpm/L)	28.00	156.9

Liquid Scintillation Parameters: e = 0.74, Volume = 0.025 mL, Time = 60 min.

TABLE 48

^{99}TC DETECTION LIMITS IN REAL URINE

Sample ID	ICP-MS (dpm/L)	Liquid Scintillation (Counts)
RB1	70.84	1596
RB2	68.07	1624
RB3	74.97	1644
RB4	66.20	1620
RB5	68.23	1593
RB6	70.38	1461
RB7	78.31	1541
RB8	70.12	1592
RB9	68.65	1534
RB10	79.15	1675
s_b	4.46	61.81
MDC (dpm/L)	20.74	263.3
LOD (dpm/L)	14.67	203.4

Liquid Scintillation Parameters: e= 0.74, Volume = 0.025 mL, Time = 60 min.

Assuming the flow rate of the nebulized solution was constant over time, and the sample volume introduced into the instrument for each measurement was a constant, g/vol was converted to atoms/s by the following relationship:

$$Atoms_{introduced}/s = g/vol * vol/s * mol/g * Atoms/mol \quad (12)$$

Since ^{99}Tc was analyzed in pulse counting mode, each pulse above background was assumed to be equivalent to one atom detected. Considering these facts, the instrument sensitivity and response were expressed as:

$$k = (Atoms_{Detected}/s)/(Atoms_{Introduced}/s) \quad (13)$$

$$Atoms_{Detected}/s = k\,(Atoms_{Introduced}/s) + cps_{Background} \quad (14)$$

Knowing the time the sample solution was observed at mass 99 and the flow rate of the sample being nebulized into the plasma, the total number of atoms entering the system was calculated. The sensitivity of the instrument, *k*, was determined from the data through the rearrangement of Equation 14:

$$k = [(Atoms_{Detected}/s) - cps_{Background}]/(Atoms_{Introduced}/s) \quad (15)$$

or

$$k = (Atoms_{Detected} - counts_{Background})/Atoms_{Introduced} \quad (16)$$

Once these parameters were determined, the sensitivity in units of atoms detected per atoms introduced was derived (A_D/A_P). When this value was obtained, the long-term stability of *k* over time for varying analysis times was evaluated. Four calibration standards at 0.0914, 0.3033, 0.9100, and 1.5167 dpm/mL were analyzed for 15, 30, 60, and 90 seconds at *m/z* 99 in single ion monitoring mode. For each analysis the ratio of A_D/A_P was calculated and listed in Table 49. The complete data acquisition was conducted over several hours, and the stability was surprisingly good. The mean value

TABLE 49

LONG-TERM STABILITY OF k
FOR ^{99}Tc BY ICP-MS

Sample ID	Count Time s	Atoms Introduced Per s A_P/s	Atoms Introduced A_P	Atoms Detected A_D	A_D/A_P
S1-1	15	2.276E+08	3.414E+09	750	2.197E-07
S1-2	15	2.276E+08	3.414E+09	780	2.284E-07
S2-1	15	7.559E+08	1.134E+10	2460	2.170E-07
S2-2	15	7.559E+08	1.134E+10	2415	2.130E-07
S3-1	15	2.268E+09	3.401E+10	7050	2.073E-07
S3-2	15	2.268E+09	3.401E+10	6990	2.055E-07
S4-1	15	3.779E+09	5.669E+10	11625	2.051E-07
S4-2	15	3.779E+09	5.669E+10	11970	2.111E-07
S1-1	30	2.276E+08	6.829E+09	1290	1.889E-07
S2-1	30	7.559E+08	2.268E+10	5010	2.209E-07
S2-2	30	7.559E+08	2.268E+10	4950	2.183E-07
S3-1	30	2.268E+09	6.803E+10	14970	2.201E-07
S3-2	30	2.268E+09	6.803E+10	14970	2.201E-07
S4-1	30	3.779E+09	1.134E+11	25050	2.209E-07
S4-2	30	3.779E+09	1.134E+11	24870	2.193E-07
S1	60	2.276E+08	1.366E+10	3060	2.241E-07
S2	60	7.559E+08	4.535E+10	10140	2.236E-07
S3	60	2.268E+09	1.361E+11	30240	2.223E-07
S4	60	3.779E+09	2.268E+11	50640	2.233E-07
S1	90	2.276E+08	2.049E+10	4680	2.284E-07
S2	90	7.559E+08	6.803E+10	15300	2.249E-07
S3	90	2.268E+09	2.041E+11	45270	2.218E-07
S4	90	3.779E+09	3.401E+11	74340	2.186E-07
				Mean	2.175E-07
				s_b	8.990E-09
				$\%s_b$	4.13

A_D represents atoms detected by the ICP-MS and A_P represents atoms introduced into the instrument.

for A_D/A_P was 2.18E-07 +/- 8.99E-9 and the percent deviation over the analysis time was +/- 4.13%. Thus, a little over 2 atoms were detected in every 10,000,000 atoms introduced.

In order to compare ICP-MS sensitivity to that of radioactive decay, the decay rate equation was evaluated:

$$-dN/dt = \lambda N \quad (17)$$

or

$$d/time = \lambda N \quad (18)$$

and

$$\lambda = \ln 2/\text{half-life } (t_{1/2}) \quad (19)$$

where d and N represent disintegrations and total atoms, respectively. Equation 17 refers to the decay rate, however during liquid scintillation counting, actual counts per minute (cpm) detected was a function of detector efficiency, quenching, background, and branching ratio. In order to compare instrument sensitivity *k* for ICP-MS with radioactive detection capabilities $\lambda_{Observed}$, Table 50 was constructed using the following relationship:

$$\lambda_{Observed} = (\beta^-_{Detected}/s - cps_{Background})/\text{Parent Atoms}_{Present} \quad (20)$$

Examination of radioanalytical ^{99}Tc detection sensitivities for liquid scintillation derived in Table 50, revealed a significant difference from sensitivities obtained by ICP-MS. The $\lambda_{Observed}$ mean value was 7.43E-14 +/- 7.46E-15 with a relative standard deviation of 10.0%. The detection sensitivity of liquid scintillation counting was almost 7 orders of magnitude lower than ICP-MS detection sensitivities. In addition, the relative error for liquid scintillation results was much greater between samples.

TABLE 50

BETA DECAY DETECTION SENSITIVITY
FOR ^{99}Tc

Sample	Sample cpm	Background cpm	dps A_D/s	Total Atoms A_P	λ_{Obs} A_D/A_Ps
W1-1	35.25	19.88	0.2562	2.890E+12	8.863E-14
W1-2	32.13	19.88	0.2042	2.890E+12	7.064E-14
W1-3	32.88	19.88	0.2167	2.890E+12	7.497E-14
W1-4	33.67	19.88	0.2298	2.890E+12	7.952E-14
W1-5	31.60	19.88	0.1953	2.890E+12	6.758E-14
W1-6	33.67	19.88	0.2298	2.890E+12	7.952E-14
W1-7	31.43	19.88	0.1925	2.890E+12	6.660E-14
W1-8	34.62	19.88	0.2457	2.890E+12	8.500E-14
W1-9	31.78	19.88	0.1983	2.890E+12	6.862E-14
W1-10	34.92	19.88	0.2507	2.890E+12	8.673E-14
W2-1	52.45	26.21	0.4373	5.772E+12	7.577E-14
W2-2	51.33	26.21	0.4187	5.772E+12	7.254E-14
W2-3	54.90	26.21	0.4782	5.772E+12	8.284E-14
W2-4	49.33	26.21	0.3853	5.772E+12	6.676E-14
W2-5	48.15	26.21	0.3657	5.772E+12	6.335E-14
W2-6	53.38	26.21	0.4528	5.772E+12	7.846E-14
W2-7	50.08	26.21	0.3978	5.772E+12	6.893E-14
W2-8	50.15	26.21	0.3990	5.772E+12	6.913E-14
W2-9	49.48	26.21	0.3878	5.772E+12	6.719E-14
W2-10	51.83	26.21	0.4270	5.772E+12	7.398E-14
				Mean	7.434E-14
				s_B	7.461E-15
				$\%s_B$	10.00%

A_D represents atoms detected by the liquid scintillation and A_P represents atoms present in the solution.

Results of detection sensitivities $\lambda_{Observed}$ vs. k for ^{99}Tc brought to light the premise behind the vast difference in count times (3600 s vs. 15 s) between liquid scintillation and ICP-MS. Even considering count times, the detection sensitivity of ICP-MS was far greater than liquid scintillation. In light of this evaluation, results from the liquid scintillation portion of the comparison study were reassessed. For each matrix and activity concentration, the manual quench corrected results were slightly higher than ICP-MS, however the standard deviations were much greater. The much lower detection sensitivity, even considering long count times, leads to reduced counting statistics compared to ICP-MS, ultimately producing an increase in the relative error and higher limits of detection for liquid scintillation counting.

CHAPTER VII

CONCLUSIONS AND FUTURE DIRECTIONS

As demonstrated in the previous chapter, the better precision of the ICP-MS data was a result of the increased detection sensitivity of detecting atoms rather than the β^- decay product. The ICP-MS quantitation was based upon comparing the acquired sample signal to a ^{99}Tc calibration curve and correcting for drift and signal attenuation using an ^{115}In internal standard. Even lower limits of detection for ^{99}Tc would be expected should the urine sample matrix contain the technetium standard and nebulization be accomplished ultrasonically. During this research project, ultrasonic nebulization was attempted because of the increased amounts of desolvated sample being carried into the plasma and resulting in an increased analyte signal. However, ultrasonic nebulization was not quantitative in this case, due to the difference between the ^{99}Tc standards in the 2.0 M HNO_3 matrix and in the prepared urine matrix. When ultrasonic nebulization was attempted, a linear calibration curve was produced, but the ^{99}Tc in the spiked real urine was not detected. In order for ultrasonic nebulization to be utilized, an isotope dilution technique must be employed. ^{97}Tc would be an ideal dilution isotope; however, this isotope is very rare and not readily available. A possible alternative would be ^{95m}Tc, but in order to utilize this isotope, *m/z* 95 must produce a stable countrate for blanks. As a result the anion exchange resin must be free of natural Mo or standardized to a constant level and the ^{95m}Tc daughter, ^{95}Mo, must be separated from the sample. As a result of this dissertation research project, additional research has been initiated in which ultrasonic nebulization isotope dilution ICP-MS will be used to determine ^{99}Tc with ^{95m}Tc as the isotope dilution standard.

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APPENDIX

APPENDIX

RECIPE FOR ARTIFICIAL URINE

Component	g/kg
Urea	16.0
NaCl	2.32
KCl	3.43
Creatinine	1.10
Na_2SO_4 (anhydrous)	4.31
Hippuric acid	0.63
NH_4Cl	1.06
Citric acid	0.54
$MgSO_4$ (anhydrous)	0.46
$NaH_2PO_4 . H_2O$	2.73
$CaCl_2 . 2H_2O$	0.63
Oxalic acid	0.02
Lactic acid	0.094
Glucose	0.48
$Na_2SiO_3 . 9H_2O$	0.071
Pepsin	0.029
Concentrated (70%) HNO_3	5.0

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

To the Graduate Council:

I am submitting herewith a dissertation written by Linda A. Lewis entitled "^{99}Tc Bioassay by inductively coupled plasma mass spectrometry (ICP-MS)." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

George K. Schweitzer, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School