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## Technetium and rhenium in volcanic soils by lcpms

Clifton Lee Jones

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# TECHNETIUM AND RHENIUM IN VOLCANIC SOILS BY ICPMS

by

Clifton Lee Jones

Bachelor of Science  
University of Nevada, Las Vegas  
1979

A thesis submitted in partial fulfillment  
of the requirements for the

**Master of Science Degree in Chemistry  
Department of Chemistry  
College of Sciences**

**Graduate College  
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## Thesis Approval

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Technetium and Rhenium in Volcanic Soils by ICPMS

is approved in partial fulfillment of the requirements for the degree of

Master of Science in Chemistry

Examination Committee Chair

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Graduate College Faculty Representative

## ABSTRACT

### **Technetium and Rhenium in Volcanic Soils by ICPMS**

by

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Technetium-99 ( $^{99}\text{Tc}$ ) and rhenium (Re) were determined in volcanic tuff muck rock, from the potential repository at Yucca Mountain and in nuclear bomb cavity samples from the Nevada Test Site (NTS). These analyses were performed in order to test the feasibility of using high resolution inductively couple plasma mass spectrometry (HR-ICPMS) for the determination of  $^{99}\text{Tc}$ . Six 20 gram tuff samples were analyzed in duplicate for  $^{99}\text{Tc}$  and Re following separation using an anion exchange resin to remove potential interferences. Four nuclear bomb cavity samples were analyzed using one gram samples. A  $^{99}\text{Tc}$  method detection limit (MDL) of 33 pg/kg (parts per quadrillion (ppq)) was achieved; however the tuff samples analyses results were all less than this concentration. The average Re concentration of the six tuff samples was 23 ng/kg (ppt) with an average relative standard deviation (RSD) of 7.5%. The nuclear bomb cavity samples  $^{99}\text{Tc}$  analyses results ranged from 330 to 11,800 pg/kg (ppq).

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## CHAPTER 1

### INTRODUCTION

#### Yucca Mountain Project

Yucca Mountain is located in southern Nevada approximately 160 kilometers North West of Las Vegas and immediately adjacent to the South West side of the Nevada Test Site (NTS). See Figures 1 and 2. Yucca Mountain is proposed as a repository for up to 70,000 metric tons of highly radioactive waste (USDOE, 2002). Ninety percent of the radioactive waste awaiting placement is derived from spent nuclear fuel rods from civilian nuclear reactors. The bulk of the remaining material will be derived from military and US Department of Energy reactors and from the generation and disposal of nuclear weapons.

In 1982, congress enacted the Nuclear Waste Policy Act (NWPAA) which charged the DOE with the responsibility for identifying an appropriate site and building a high-level radioactive waste repository (USDOE, 2002). The Nuclear Waste Policy Amendments Act (NWPAA) of 1987 identified Yucca Mountain for further primary investigation as a potential repository for high level nuclear wastes (USC, 2006). The President signed a Congressional Joint Resolution in July 2002 designating Yucca Mountain as the site for the nation's first High Level Waste Repository (HLWR) (USDOE YMPR-26, 2002). On July 19, 2006 the DOE presented a public letter indicating their intent to request licensure of the Yucca Mountain repository from the Nuclear Regulatory Commission no later than

June 2008 (USDOE, 2006). Creation of the 7.8 kilometer (5 mile) long Main Exploratory Studies Facility (ESF) tunnel at Yucca Mountain began in 1992, and was completed in 1997. A second 2.6 km tunnel off of the ESF tunnel, called the Enhanced Characterization of the Repository Block (ECRB) Cross-Drift tunnel, was completed in 1998 (USDOE, 2002). Figure 1 is an illustration of the underground layout of the proposed repository at Yucca Mountain.

Over the past 20 years, numerous studies of Yucca Mountain have been conducted. Government, state, and educational institutions conducting these studies include the University of Nevada, Las Vegas (UNLV) and Harry Reed Center (HRC), where this study was conducted. The results of these studies are currently being used to evaluate the radioactive waste long term storage feasibility, including possible radioactive waste containment failure modes over the next 10,000 to 1,000,000 years.

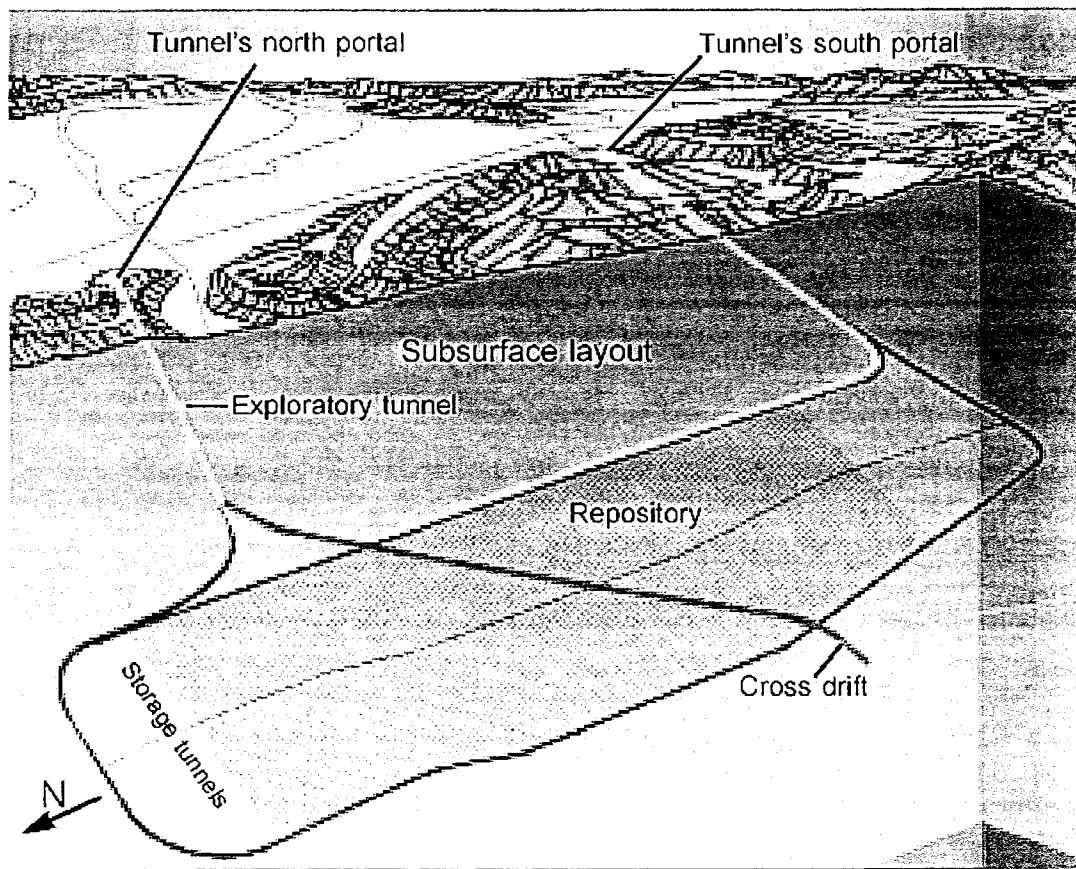


Figure 1. Underground layout of the proposed repository. The ESF tunnel from the north to south portal and the ECRB cross drift tunnel both have been completed (USDOE, 2002).

### Geologic Setting

Yucca Mountain is about 40 km (25mi) long and 6-10 km wide and about 650 meters higher than the surrounding washes (USDOE 1999). Yucca Mountain was formed from volcanic pyroclastic ash-flows that occurred approximately 13 to 7.5 million years ago during eruptions that gave rise to the Claim Canyon and Timber Mountain caldera complex (USDOE, 1999). These ash flows were deposited over underlying pre-existing

volcanic ash deposits from the Permian age. Below this, there are limestone/silt/sandstone sedimentary deposits from the Permian to the Cambrian derived from inland seas that once resided in the Great Basin region. The majority of Yucca Mountain was derived from volcanic ash flow eruptions that resulted in the formation of the Claim Canyon Caldera, which is located approximately 6 km north of Yucca Mountain. Figure 2 presents a graphic representation of the surface geology of the region around Yucca Mountain (USDOE, 1999). The ash-flows from the various eruptions formed several bedded layers of breccia (partially cemented volcanic rock and pumice), and welded and non-welded layers of tuff. Many of these layers of tuff have thicknesses exceeding 100 meters. The welded tuffs and non-welded tuffs are both derived from pyroclastic ash-flows and ash falls. The welded tuff formation differs, however, in that the volcanic ash particles and volcanic glass fragments remained hot enough (600-800°C) to, at least partially, melt and congeal into a cohesive rock layer. This welding usually occurs as the ash-flow is buried and thermally insulated by subsequent ash-flow layers. These highly siliceous ash-flows, with silica content greater than 65%, are generally termed rhyolitic ash-flows. Some of the ash-flows that have slightly lower silica content are more crystalline, and are given the term latite. The cooling of the welded tuff results in considerable fracturing of the tuff with typical fracture lengths of approximately 2 meters, but range in length from a few cm to 10 meters or more in the region of the potential repository (Mongano et al., 1999).

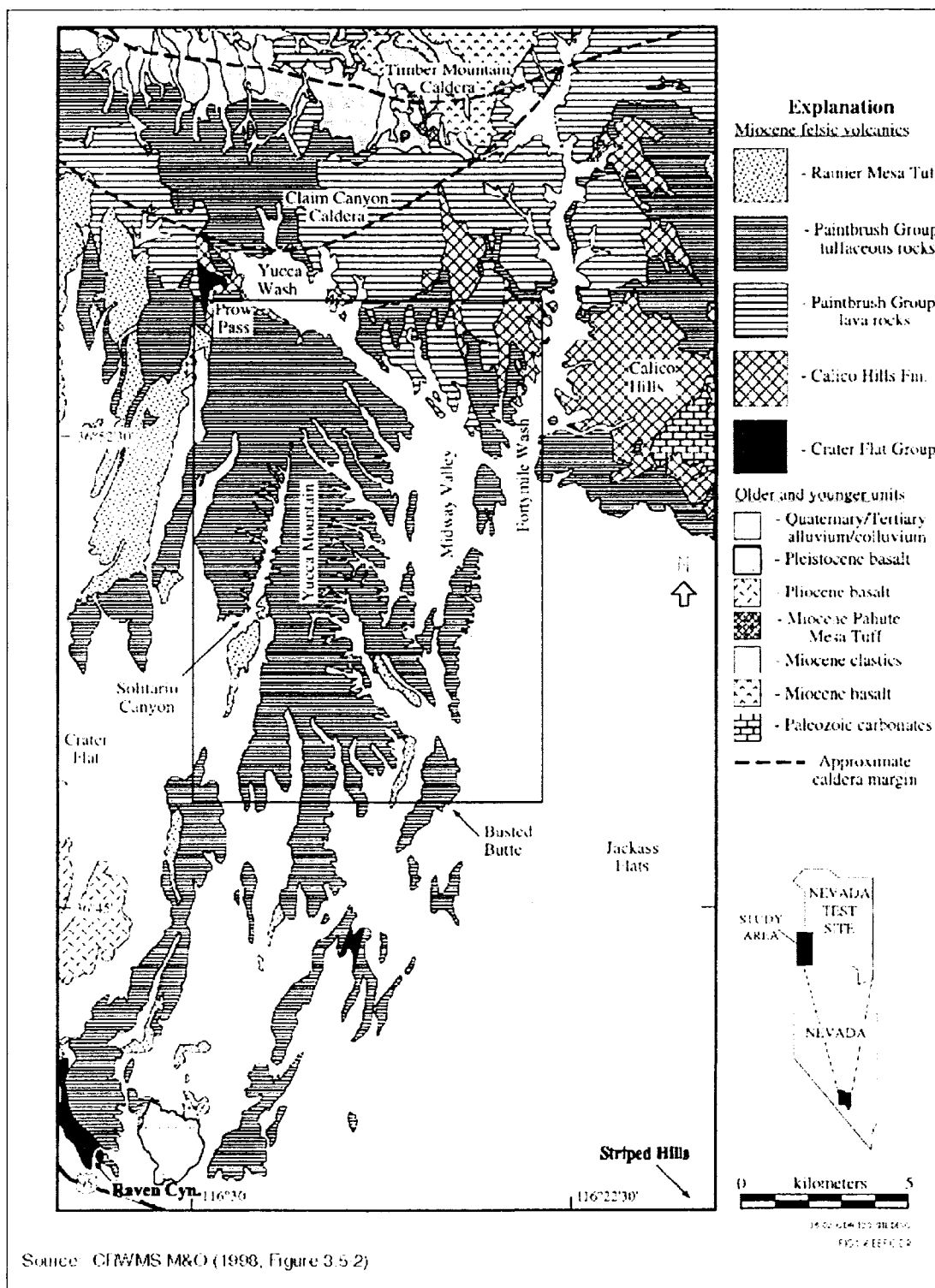


Figure 2. Geostratigraphy at Yucca Mountain (USDOE, 1999).

Since the initial deposition, the tuff at Yucca Mountain has been modified by rain and ground water flow through the tuff. The surface (meteoric) water percolation through the rhyolitic tuff induces chemical alteration producing various products including, clays, and open framework aluminosilicate zeolites. The meteoric water flow thorough the tuff also facilitates the deposition of calcite ( $\text{CaCO}_3$ ) and/or opal ( $\text{SiO}_2$ ) in the tuff fractures and in open cavities in the tuff called lithophysae (Marshall et al. Futa, 2001; Paces et al., 2001). The lithophysae in the tuff are originally derived from small air cavities formed from trapped air and steam in the original ash-flow, which were then quickly smashed into shallow ovate shapes under the weight of the subsequent ash-flows. Lithophysae at the level of the potential repository range in size from 1cm to 1m, although most are less than 50cm (USDOE, 2002). The presence or absence of lithophysae is one of two key characteristics in the defining and naming of the different layers of tuff at Yucca Mountain, the other being whether or not the tuff is welded (USDOE, 2002).

The repository is proposed to occupy the lowest member of the Paintbrush Group in a welded tuff geostratigraphic layer named Topopah Spring Tuff, which is immediately below the Pah Canyon tuff member. Figure 3 presents the Yucca Mountain vertical lithostratigraphy and geochronology at the area of the repository (USDOE, 1999). The Topopah Spring Tuff was formed approximately 12.8 million years ago and is approximately 290-360 meters thick at Yucca Mountain.

The Topopah Springs Tuff is divided into three main members, the upper crystal rich (latite) member and the middle and lower crystal poor members. The middle and lower crystal poor members are further subdivided into four sub-units based on the presence or absence of lithophysae. These four sub-units are the upper lithophysal, middle



lithophysal, lower non-lithophysal, and lower lithophysal (Mongano et al., 1999). The middle non-lithophysal unit has high rock content (85-95%), with 0-1% lithophysae ranging in size from 7-25cm. The remaining (6-14 %) of the tuff is composed of pumice, lithic, and mineral fragments. The lower lithophysal unit has a variable rock content of between 56-90%, with 5-30% lithophysae ranging in size from 5-100cm. Again, the remaining rock composition for this unit is made up of various amounts of pumice, lithic, and mineral fragments. The lower non-lithophysal zone rock matrix is 66-93% rock matrix, with 0-5% lithophysae ranging in size from 20-100cm (Hinds, 2000; Mongano et al., 1999).

If Yucca Mountain is granted license, the radioactive waste will be stored in specially designed canisters approximately 300 meters below the surface of Yucca Mountain, in the predominantly welded portion of Topopah Spring Tuff. The proposed repository would reside in the lower lithophysal (80%), and in the upper-lithophysal and middle non-lithophysal layers (20%). Figure 4 is a representation of Yucca Mountain and the potential repository horizon (USDOE ESS, 2002). The potential repository cannot completely reside in one layer because the tuff layers are slightly tilted, and the proposed repository will be horizontal. The potential repository layer is also approximately 300 meters above the water table.

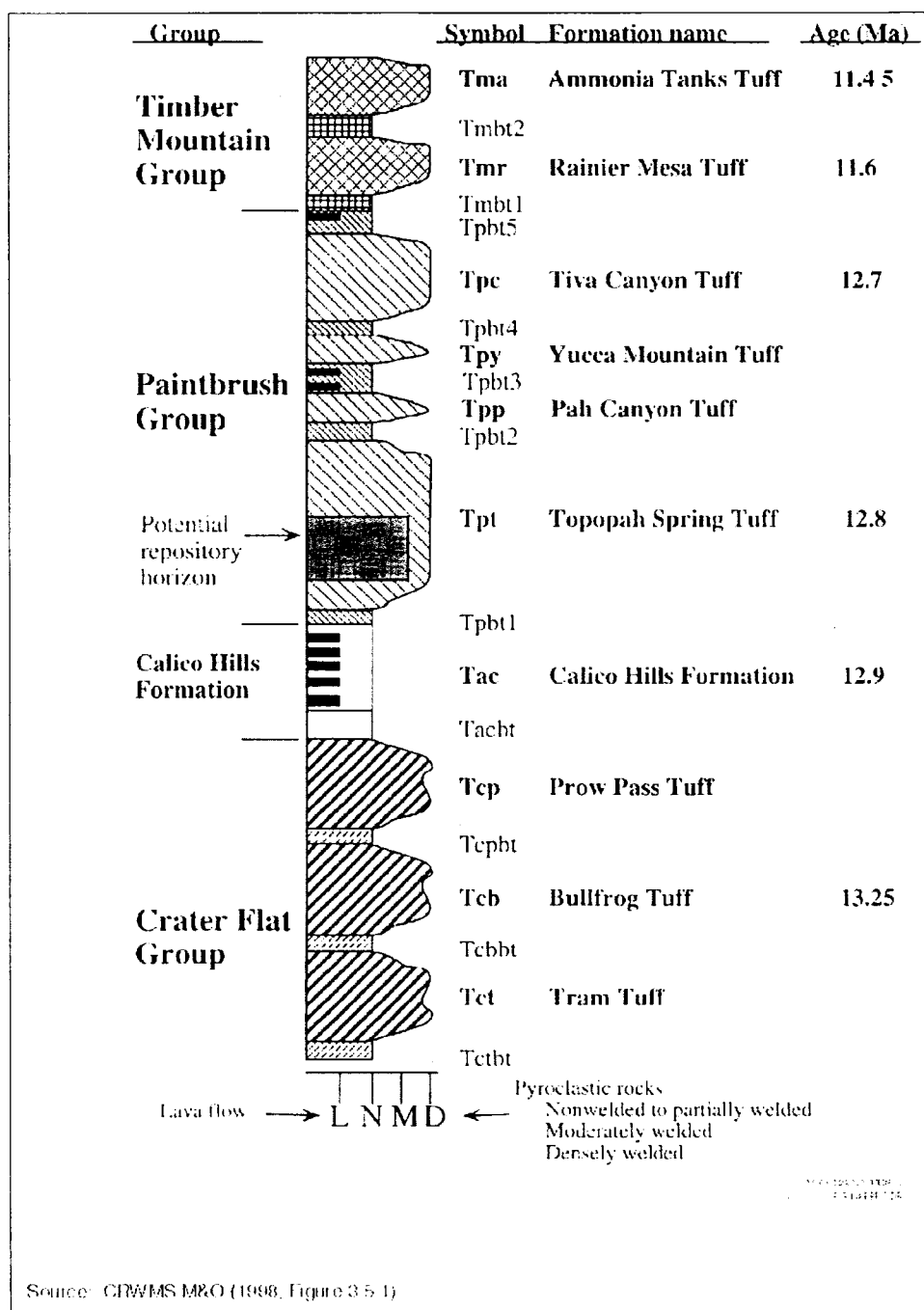


Figure 3 Vertical lithostratigraphy and geochronology of Yucca Mountain at the area of the repository (USDOE, 1999).

The average rain fall at Yucca Mountain is 15cm per year and it has been estimated that as much as 95% evaporates. (Eckhardt, 2000) The rate of infiltration into Yucca Mountain has been studied by several investigators and the estimate of infiltration rates vary from a net loss of moisture from the mountain due to evaporation, to a maximum infiltration of 13.4 mm per year. Most research indicates that the infiltration rate is probably between 1 to 10 mm per year (USDOE, 2000).

The tuff at Yucca Mountain is divided into two regions depending on the water content. The region above the water table is the unsaturated zone (UZ) and the region below is the saturated zone (SZ). The over-all the water content of the rock is depended on porosity, which is, in turn, related to the degree of welding. Table 1 presents the water content of the unsaturated zone at Yucca Mountain along with the percent distribution of water relative to the entire unsaturated zone column (USDOE 2001).

Table 1 Estimated Water Budget for the Unsaturated-Zone Rock Mass above the Level of the Emplacement Drifts (USDOE 2001)

Lithostratigraphic Unit	Thickness (ft)	H <sub>2</sub> O (%)	Saturation (%)	Distribution of H <sub>2</sub> O over Entire Column (%)
Tiva Canyon Tuff welded	213	5.52	75.8	11.4
Paintbrush Tuff Non-welded	85	16.33	51.6	13.5
Topopah Springs Tuff welded	954	8.11	78.2	75.1

It is estimated that the tuff has about 100 liters of water per cubic meter (Ewing & Long, 2004). Water infiltrating down from the surface generally travels through the becca and non-welded tuff rock through the matrix but when it arrives at welded tuff, it is thought, that the water flows preferentially along the rock fractures (USDOE, 2002).

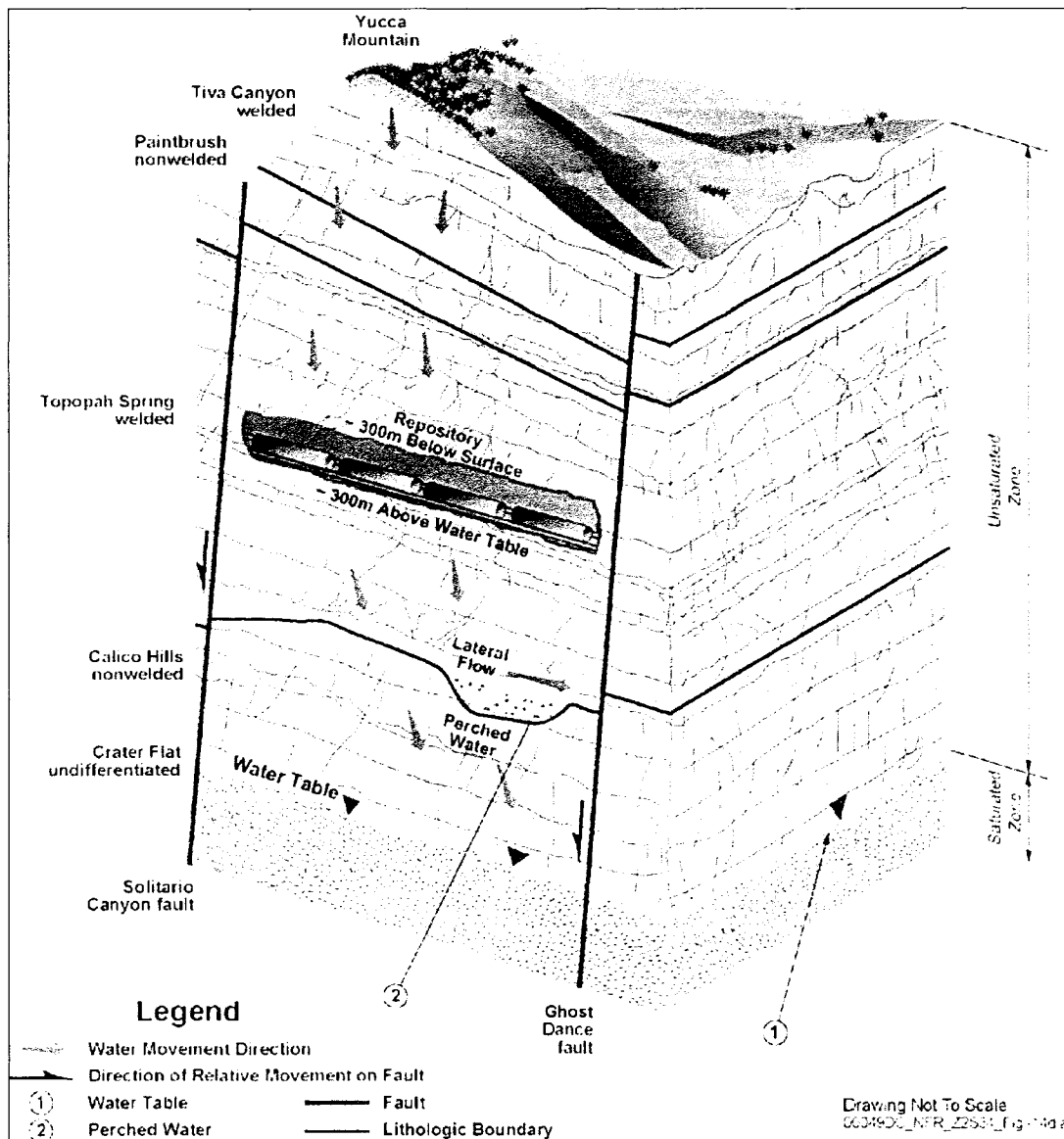


Figure 4. Representation of Yucca Mountain lithostratigraphy and potential repository horizon. Gray arrows indicate infiltrating water flow direction. (USDOE YMSSE, Fig. 23, 2002)

## Purpose of Study

Should the canisters containing highly radioactive material leak due to corrosion, volcanic event, etc., the waste would be released to the volcanic tuff and begin migration through the tuff and eventually arrive at the water table, called the saturated tuff, which is approximately 300 meters below the repository level. Therefore the rate of migration of the released radionuclides through the tuff and subsequently the water table is of great interest. Obviously, should a release occur, and if the radionuclides migrate quickly through the tuff, they might arrive at the water table in a short time relative to the congressionally mandated 10,000 year containment (Long & Ewing, 2004). It would follow in this scenario, that future populations could be exposed to the radionuclides and their ill health effects through drinking the water and eating plants and animals that have been exposed to the water. Alternatively, if studies show that none of many possible radionuclide species migrate through the tuff, or faults through the tuff, at a rate of any significance relative to the minimum of 10,000 year storage requirement, then concerns over simple release scenarios, such as short term (100-1000 year) canister failure due to corrosion, can be laid to rest. Other scenarios of repository and canister failure, such as, volcanic magma intrusion or significant hydrothermal events would still require further modeling and those investigations have been undertaken (USDOE, 2002).

Initial studies by DOE have shown that there are several radionuclides that warrant concern. Of these, there are at least five radionuclides; carbon-14, plutonium, neptunium, technetium, and iodine; that warrant special concern (Long & Ewing, 2004). These five radionuclides are a concern because they are all expected to be present in significant concentrations in the radioactive wastes, have significantly long half lives, and also may

be expected to migrate relatively quickly through the tuff. These radionuclides are all expected to be either anionic species, or form anionic species, or possibly form colloidal adducts under the conditions found in the interstitial spaces of the tuff. Since the tuff is primarily aluminosilicate, with predominantly negative charges on the surface of the mineral, it should show little attraction to dissolved anionic species. Under the current understanding of the interstitial conditions of the volcanic tuff, the iodine, carbon, and technetium are all expected to be anionic species,  $I^-$  or  $IO_3^-$ ,  $HCO_2^-$  or  $CO_3^{2-}$ , and  $TcO_4^-$ , respectively. The neptunium is expected to be at least partly in the form of the anionic species  $NpO_2CO_3^-$  (Eckhardt, 2000). The plutonium will quite likely be neutral  $PuO_2$ , which may form colloidal adducts that can diffuse through the tuff matrix at higher rates than typical cations (Eckhardt, 2000).

One means by which the rate of migration of these species in the tuff at Yucca Mountain might be ascertained is by determining the depth of infiltration and concentration of these, or similar radionuclides, in the tuff due to global and local radionuclide atmospheric deposition. The major source of terrestrial radionuclides is atmospheric nuclear weapon testing which occurred from 1945 to 1980 (Tagami, 2003). There are also relatively small contributions to global radionuclide deposition due to underground nuclear weapons testing venting, nuclear fuel reprocessing, nuclear power generation facilities operation, and accidents such as Chernobyl.

Studies have been performed in an effort to ascertain whether any of the surface deposited radionuclides have migrated down through the 300 meters of tuff to the layer of the potential repository horizon during the last 50 years. These studies have targeted both chlorine-36 ( $^{36}Cl$ ) and tritium ( $^3H$ ) (Fabryka-Martin 1996; Patterson, 2000).

Chlorine-36 is a beta emitter with a half-life of 301,000 years that is produced in the upper atmosphere with greater than 96% produced from cosmic ray induced spallation reactions with atmospheric argon-40,  $^{40}\text{Ar}(p,\alpha)^{36}\text{Cl}$  (Lazarev, 2003; USDOE LLNL, 2000). The cosmic ray is usually a proton (90%) or, less often, an alpha particle. The upper atmosphere  $^{36}\text{Ar}(n,p)^{36}\text{Cl}$  reaction accounts for less than 4% of the total natural produced  $^{36}\text{Cl}$ . Only a very small amount of the total natural Cl-36 is produced from the cosmic ray neutron activation reaction of the natural  $^{35}\text{Cl}$  isotope in the upper atmosphere, because there is little Cl in the upper atmosphere (Lazarev, 2003).

Chlorine-36 was generated in much larger than natural quantities during the period between 1946 and 1958 due to the approximately 67 atmospheric nuclear weapons tests that were performed near or slightly below sea level in the Pacific Proving Grounds (EED, 2006). The increase in radionuclides in the environment resulting due to the seaside and terrestrial atmospheric weapons testing releases during the period 1945-1980 has been given the generic term “bomb pulse” (USDOE LLNL, 2000). Bomb pulse  $^{36}\text{Cl}$  can be determined in a number of different matrices such as tree rings, animal and human bones. Bomb pulse  $^{36}\text{Cl}$  can also be determined in subterranean layers of soil or rock where the radionuclides are carried along a diffusion gradient resulting from surface deposition and infiltration from meteoric precipitation.

The normal background ratio of  $^{36}\text{Cl}/\text{Cl}$  is quite small and the average ratio for the last few thousand years is about  $500 \times 10^{-15}$ , which is based on the analysis of ice cores and pack rat middens (Frybrecka-Martin et al., 1993, 1996). Rain water samples collected from the 1950s and 1960 showed that the peak years of  $^{36}\text{Cl}$  radionuclide deposition were from 1953 through 1959 with the peak deposition occurring in 1957,



with a  $^{36}\text{Cl}/\text{Cl}$  ratio of  $217,000 \times 10^{-15}$ , which is approximately 400 times the normal background  $^{36}\text{Cl}/\text{Cl}$  ratio of  $500 \times 10^{-15}$  (Lu, et al., 2003). Figure 5 presents data from Greenland glacier ice core samples showing the  $^{36}\text{Cl}/\text{Cl}$  ratios for the period from 1945 to 1996, based on a study by Fabryka-Martin et al., (1996).

The occurrence of tuff samples with  $^{36}\text{Cl}/\text{Cl}$  ratios greater than  $1,250 \times 10^{-15}$  at the level of the potential repository have been considered significant and indicative of the infiltration of bomb pulse  $^{36}\text{Cl}$  to the level of the repository in less than 50 years (Fabryka-Martin, et al., 1996).

Chlorine-36 deposition from the atmospheric testing is still occurring today, but at a level barely above the normal level. The slight amount of  $^{36}\text{Cl}$  that maybe depositing today is perhaps due to  $^{36}\text{Cl}$  bioassimilation and reintroduction of chloromethane ( $^{36}\text{ClCH}_3$ ) (Lazarev, 2003).

Tuff rock samples collected from inside Yucca Mountain along the exploratory tunnel were initially determined to have considerably larger than the statistically significant  $1250 \times 10^{-15}$   $^{36}\text{Cl}/\text{Cl}$  ratio (Frybreca-Martin et.al, 1996). These large  $^{36}\text{Cl}$  ratios were, at first, considered to be evidence of fast travel, less than 50 years, of infiltrating water

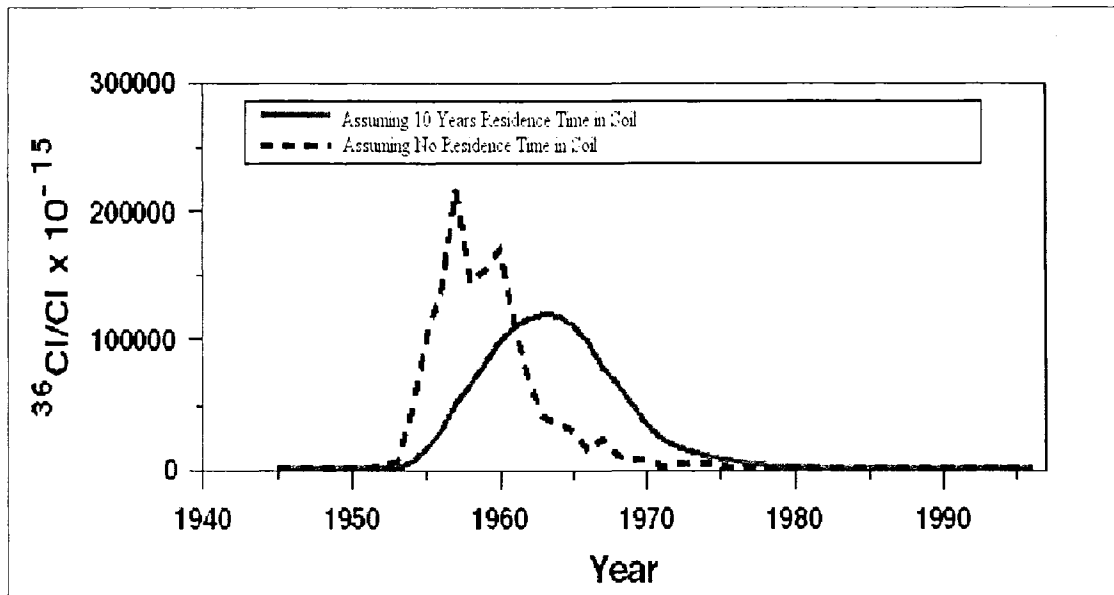


Figure 5. Bomb pulse of  $^{36}\text{Cl}$  measured in ice cores from Greenland based on a study by Fabryka-Martin et al., (1996). The dashed line is the initial data. The dark line represents simulated ten year residence time in the soil (USDOE Site Suitability, 2002).

carrying the bomb pulse  $^{36}\text{Cl}$  radionuclide through the tuff. Figure 6 presents the  $^{36}\text{Cl}/\text{Cl}$  ratios obtained by Frybreca-Martin et al. (1996) along the length of the ESF tunnel (USDOE 2002).

The  $^{36}\text{Cl}$  data seemed to indicate that the fast travel occurred mainly, but not always, along vertical fault lines leading to the surface at the middle and northern length of the ESF tunnel. Subsequent reviews of the data revealed puzzling incongruences that are yet to be explained. For example, in areas near some faults the data indicate that there is a local increase in the  $^{36}\text{Cl}/\text{Cl}$  ratio; however, this same increase in the  $^{36}\text{Cl}$  ratio was not echoed at other similar size vertical faults elsewhere in the ESF tunnel. The arrow in

Figure 6 points out the high  $^{36}\text{Cl}/\text{Cl}$  ratios for several samples taken from the Sundance fault. Also, the data indicate there are high ratios of  $^{36}\text{Cl}/\text{Cl}$  at areas along the exploratory tunnel where there appears to be no accompanying geological feature such a fault, or area of highly fractured tuff. Another perplexing feature of the sample data indicates high  $^{36}\text{Cl}/\text{Cl}$  ratios for the northern half of the ESF tunnel; however, the general trend of the thickness of the overlying tuff to the surface is the reverse, the south being the thinnest and the north significantly thicker.

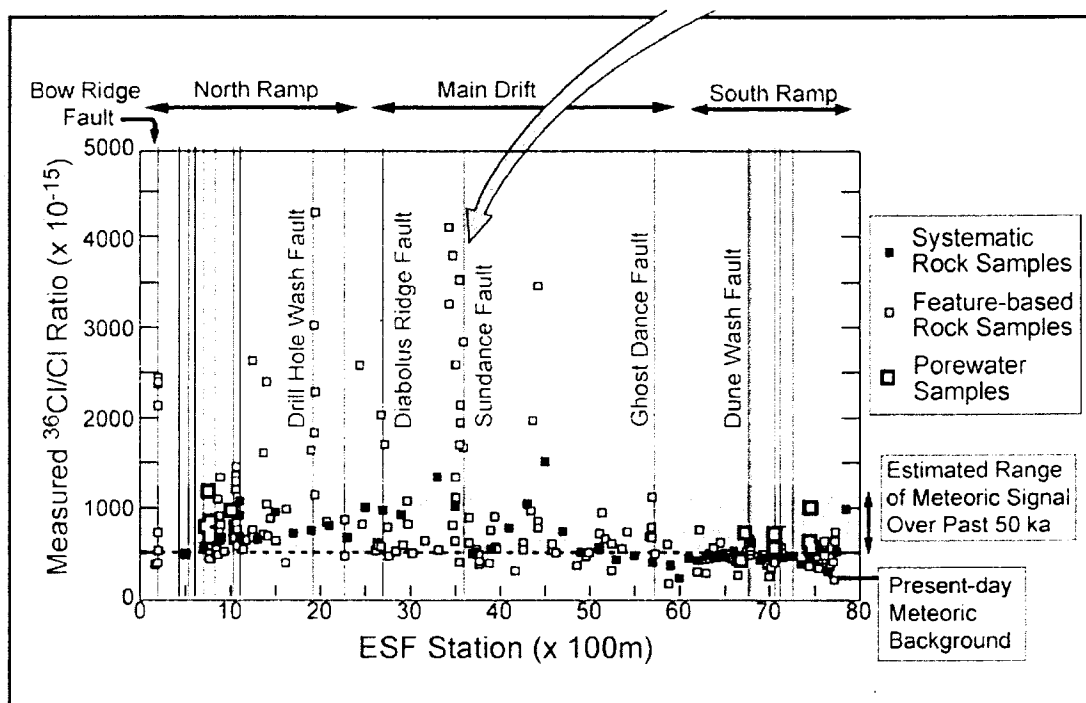


Figure 6. Graphic representation of Yucca Mountain ESF tunnel with overlay showing the ratios of  $^{36}\text{Cl}/\text{Cl}$  based on results from a report by Frybreca-Martin et al. (1996). The blue arrow shows indicates the Sundance fault where much higher than normal background ratios of  $^{36}\text{Cl}/\text{Cl}$  were determined in an initial analysis (USDOE, 2002).

To further complicate matters a re-sampling of the tuff at the Sundance fault within the ESF, which had initially showed much higher than expected ratios of  $^{36}\text{Cl}$ , were split and sent to two laboratories and the  $^{36}\text{Cl}/\text{Cl}$  results were mixed, one lab showing  $^{36}\text{Cl}/\text{Cl}$  ratios much greater than  $1250 \times 10^{-15}$  ratios, and the other laboratory showing normal background ratios (Paces et al., 2003; Lu et al., 2003). In a subsequent reanalysis of the samples taken from either the same bore holes or with a few meters, again sent to two laboratories, have shown  $^{36}\text{Cl}/\text{Cl}$  ratios that are less than the bomb pulse threshold ratio for all samples (USDOE Site Char. Prog. Rpt. 26 2002; Paces et al., 2003). A further re-sampling and analysis by two laboratories, including HRC-UNLV, showed sample  $^{36}\text{Cl}/\text{Cl}$  ratios that were less than the  $1250 \times 10^{-15}$  threshold ratio, with the exception of one sample (UNLV HRC Draft Rpt. TR-06-002, 2006). Because of the good precision of the data for this one sample, the investigators concluded that fast pathways do exist from the surface to the layer of the potential repository.

Tritium ( $^3\text{H}$ ) is another bomb pulse radionuclide, and like  $^{36}\text{Cl}$  it also has a natural complement which produced in the upper atmosphere due the cosmic ray spallation reactions in the atmosphere. Tritium has a comparatively short half-life of 12.4 years. The natural tritium concentration in rain water a Yucca Mountain has been estimated to be between 5 and 8 Tritium Units (TU). A TU is equal to one  $^3\text{H}$  atom per  $10^{18}$  hydrogen atoms. Given the short half-life it is thought that any tritium greater than 1 TU at the level of the potential repository must indicate that water that has infiltrated to the depth of the potential repository in the last 50 years (Patterson, 2000; Lu, et al., 2003). The

tritium analysis of samples from the Sundance fault, which had initially showed high  $^{36}\text{Cl}$  concentrations, did not show a  $^3\text{H}$  increase over the expected TU background (DOE 2000 Site Characterization Rpt. 22). However, several samples from the Southern and of the ESF tunnel did show higher than background tritium results. But, this is the exact opposite of the initial  $^{36}\text{Cl}$  data which did not show any sample with  $^{36}\text{Cl}/\text{Cl}$  ratios greater than the  $1250 \times 10^{-15}$  threshold in the southern end of the ESF tunnel. Complete resolution of these inconsistencies has yet to be made (Patterson, 2000; Lu, et al., 2003).

The pertechnetate anion is highly soluble and mobile and therefore, like  $^{36}\text{Cl}$  and  $^3\text{H}$ , may be carried by meteoric water downward to the level of the proposed repository. The main focus of this thesis research was to test the HR-ICPMS capability for determining  $^{99}\text{Tc}$  in Yucca Mountain tuff for the purpose of providing additional data that may help clarify previously collected  $^{36}\text{Cl}$  data, and also provide independent evidence as to whether or not surface water has migrated to the level of the potential repository during the last 50 years. Since Re is a chemical analog of Tc, we also analyzed for Re. The results of technetium analysis of volcanic tuff from Yucca Mountain could also provide indirect evidence, by inference, of the rate of migration of other highly mobile anionic (weakly bound) radionuclides through the volcanic tuff at Yucca Mountain, such as,  $^{36}\text{Cl}$ ,  $\text{I}^-$ ,  $\text{IO}_3^-$ , and  $\text{NpO}_2\text{CO}_3^-$ . Technetium has one analytical advantage over  $^{36}\text{Cl}$  and  $^3\text{H}$  in that the natural background of technetium is vanishingly small thus the only detectable Tc in most soils or rocks, must be derived from the man made nuclear sources (Desmet & Myttenaere, 1986; Colton, 1965). Natural technetium has only been detected in uranium ore, in the absorption spectra of giant stars, and possibly in columbite mineral in the

disputed initial claim of the discovery of technetium by Walter Noddack, Ida Tacke, and Otto Berg in 1925 (Colton, 1965; Armstrong, 2000).

The greatest portion of atmospheric technetium comes from uranium and plutonium fission in nuclear weapons (Tagami, 2003). Technetium from nuclear fission has a product yield of approximately 6% from either, uranium-235 ( $^{235}\text{U}$ ), or plutonium-239 ( $^{239}\text{Pu}$ ). The majority of technetium arriving at Yucca Mountain surface has been due to both global and local Nevada Test Site (NTS) atmospheric nuclear detonations. And, as mentioned earlier, there is also a relatively small component of  $^{99}\text{Tc}$  atmospheric deposition due to nuclear fuel reprocessing; venting of underground nuclear tests; and nuclear facility accidents, such as Chernobyl; however, these sources have contributed only slightly.

The simple presumption is that the deposition of radionuclides at Yucca Mountain from atmospheric testing would be predominately influenced by the local atmospheric testing that occurred at the Nevada Test Site from January 1951 through October 1958. During this period there were a total of 119 atmospheric tests with an average yield of 8.6 kiloton for a total yield of about 1 megaton (NCI, 2006; Simon & Bouville, et al., 2004). Actually only 5% of the total yield of the atmospheric tests worldwide were derived from NTS atmospheric tests (Simon & Bouville, et al., 2004). This is because the bulk, 150MT, of the larger atmospheric test occurred outside the continental US with only 1 MT total atmospheric detonations within the US. Therefore the majority (95%) of the atmospheric deposition of the radionuclides at Yucca Mountain is derived from global deposition (Simon & Bouville, et al., 2004). The deposition of long lived radionuclides

at Yucca Mountain will be about the same as for any similar elevation mountain with similar annual rain/snow fall in the region.

Obviously, the undisputable and reproducible detection of any of technetium at depth within Yucca Mountain would be irrefutable evidence of the fast infiltration of anionic species through hundreds of meters of volcanic tuff in less than 50 years. This finding would be of significance in the modeling of Yucca Mountain and has implications with regard to the overall suitability of Yucca Mountain as a repository.

Another means by which one could possibly ascertain the rate of migration of radionuclide in volcanic tuff is by analysis of the tuff and water adjacent to underground nuclear bomb cavities at the NTS. For example, if one could show that technetium is present in the detonation cavity at significant levels and is in a soluble form, but was not present in water saturated rock 100 meters away after fifty years, this would indicate a relatively slow migration of the technetium in the tuff matrix over the last fifty years. The idea that a nuclear bomb cavity might serve as an analog for a ruptured waste canister is not a new one, and has been discussed in detail by Thompson (1993).

Figure 7 show a graphic illustration of the sequence of events during a typical underground nuclear test. Initially the bomb cavity expands vaporizing the surrounding rock (USDOE LLNL, 2003). After a little as one half second, the vaporized rock gas that is super saturated with silica begins to condense into a glass puddle at the bottom of the newly formed bomb cavity. Often within 10 seconds the pressure has dissipated enough, the fractured ceiling begins to fall into the still molten glass at the bottom of the blast cavity. This broken rubble collapsing from the roof of the cavity generally, but not always, leads to a collapse of the bomb cavity which leads to the surface. The collapse of

the bomb cavity usually occurs within a few seconds but can take minutes or even weeks. The material filling the cavity contains some splashed glass fragments, especially at the bottom, and is generally termed chimney rubble. The rock material and gases at the bottom of the cavity are still quite hot for periods up to several minutes after the blast with temperature as high as 2000°C, and less refractory radionuclides are volatilized from the cavity and distributed to the cooler chimney rubble where they condense (USDOE LLNL, 2003).



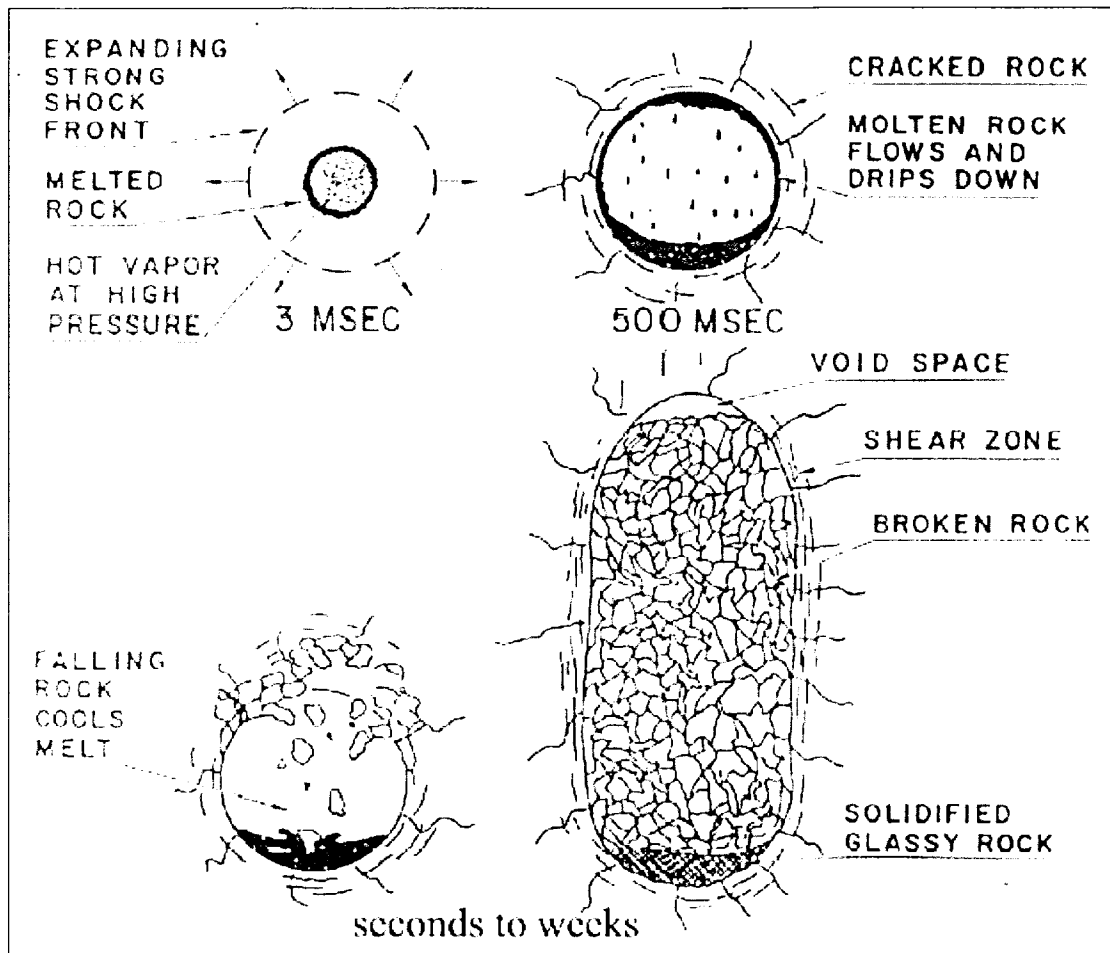


Figure 7. An illustration of the typical evolution of an underground nuclear cavity. The initial glass puddle may begin in as little as one-half second after the blast. Generally, after a few seconds, there is a reduction of initial pressure and the ceiling begins to collapse. Usually the ceiling collapse continues to the surface with in a few seconds or it may take as long as weeks (USDOE LLNL, 2003).

Figure 8 shows an illustration of a collapsed nuclear bomb cavity. The arrows in the illustration indicate the relative distribution of the refractory versus non refractory radionuclides (Daniels et al., 1993). It has been estimated that a least 700 tons of glass

are produced per kiloton yield, and at the NTS and as much as  $30 \times 10^6$  MT of glass have been produced due to the underground testing of the approximately 828 nuclear devices (Smith, et al., 2000).

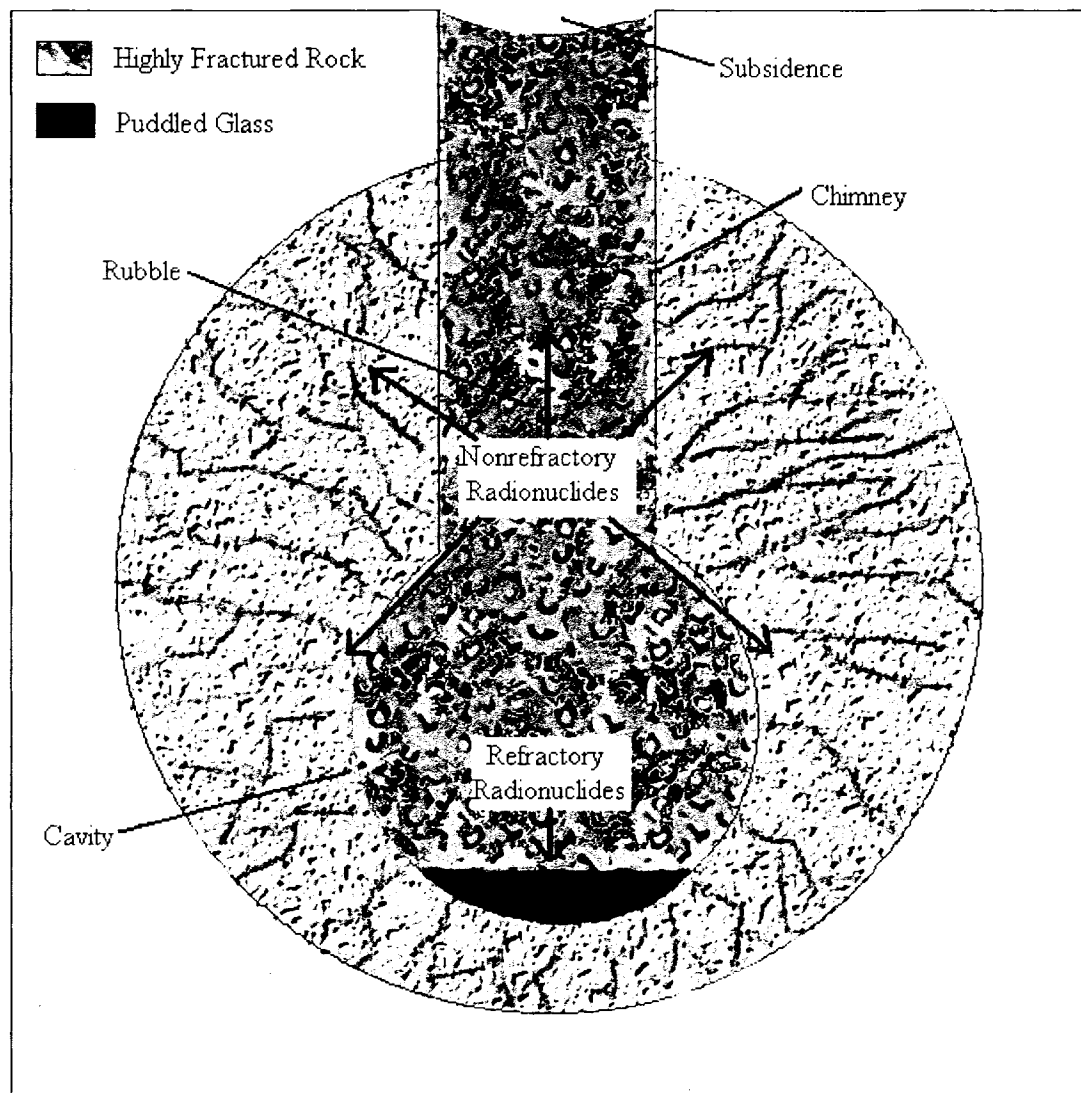


Figure 8. Figure showing the bomb cavity and rubble chimney after cavity subsidence. Arrows show the relative positions of refractory and non-refractory radionuclides. (Reproduced from Daniels, 1993)

Published data for technetium are rare, for both the detonation cavity and the immediately surrounding rock and water table (USDOE LLNL, 2003). The relative dearth of data for technetium is presumably due to the analytical difficulties encountered in the required ultra low level analysis methods as well as the relatively labor intensiveness of the analysis methods. This thesis research will also include results from the analysis of bomb cavity glass samples that have been acid leached to derive an indication of the amount of technetium present. The relative amount of  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ , to  $^{152}\text{Eu}$  present in the bomb cavity glass-rubble was also determined using gamma spectroscopy. The relative amount of  $^{99}\text{Tc}$  to  $^{137}\text{Cs}$  is important because  $^{99}\text{Tc}$ , which is probably in the form of the volatile (b.p.  $311^\circ\text{C}$ ) pertechnetate acid ( $\text{HTcO}_4$ ), is predominately incorporated into the condensing glass as it forms in the bomb blast cavity along with other more refractory radionuclides. It is believed that as much as 99.9% of the technetium is bound in the glass slag (USDOE LLNL, 2003). If this is correct, the technetium should therefore be present to a large degree in the glass slag at the bottom of the cavity, and present to a relatively minor degree in the cooler chimney rubble that usually forms within a few seconds to minutes after the blast during the collapse of the bomb blast cavity.

Given the volatility of the  $\text{Tc}_2\text{O}_7$ ,  $\text{HTcO}_4$ , or  $\text{CsTcO}_4$ , it is not unreasonable to expect that great deal of the  $^{99}\text{Tc}$  would be volatilized from the newly formed glass, or possibly never initially condense with the glass (USDOE LBNL 2003). Significant  $^{99}\text{Tc}$  losses have been measured from molten glass during the nuclear fuel rod waste vitrification studies (Bibler, et al., 1999; Darab & Smith, 1996). These studies indicate that as much

as 60% of the Tc and 10% of the Cs can be lost from the molten glass in small scale glass vitrification apparatuses.

Cesium is one of the fission yield radionuclides that is also somewhat non-refractory (b.p. 690°C) but, is found in very high amounts in the chimney rubble. This is because the precursor of  $^{137}\text{Cs}$  in the radioactive decay chain is the noble gas isotope xenon-137 ( $^{137}\text{Xe}$ ), which has a half-life of 3.8 minutes (USDOE LLNL, 2003). The noble gas xenon will not condense to a high degree in the glass. The 3.8 minute half-life gives just enough time for the chimney to form and the  $^{137}\text{Xe}$  to permeate the rubble and then decay into  $^{137}\text{Cs}$ . Table 2 presents the relative distribution of selected refractory and non-refractory radionuclides in the component features of a typical nuclear bomb test cavity (USDOE LLNL, 2003). The data in Table 2 indicate that as much as 90% of the cesium is present in the chimney rubble versus only 10% the cavity glass. The data presented in Table 2 are based partially on analysis results and is otherwise based on the applied chemistry and physics in consideration of parameters such as, nuclide boiling points, half-lives, and high temperature relative partitioning between the bomb-cavity-superheated atmosphere and glass.

If the bomb cavity technetium is present predominately in the chimney rubble, then migration with post blast steam and water, especially for bomb cavities below the water table, is very likely. However, if the preponderance of technetium is found in the relatively immobilizing glass slag, then investigations along the lines of determining the relative rate of technetium travel through the tuff surrounding of a bomb will require analytical diligence since the Tc concentration will be small and difficult to detect at 100 or more meters distance from the blast center. Environmental concerns over the leaching

of  $^{99}\text{Tc}$  from the bomb cavity can certainly be lessened if the highly mobile Tc species such as  $\text{HTcO}_4$  and  $\text{Tc}_2\text{O}_7$  are sequestered in glass and will be released relatively slowly over centuries or longer. Studies have been performed in an effort to estimate the rate of bomb glass degradation over time and the rates of radionuclide release (Smith, et al., 2000). The possible correlation of the concentration of volatile species such as  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$ , versus the more refractory species, such as,  $^{60}\text{Co}$ ,  $^{152}\text{Eu}$ , in bomb cavity glass-rubble samples were determined during the course of this thesis research and are presented in Chapter 4 Results and Discussion.

Table 2. Relative Distribution of Radionuclides in a Typical Nuclear Bomb Test Cavity. (USDOE LLNL, 2003)

Radionuclide	Glass (%)	Rubble (%)	Gas (%)	Water (%)
$^3\text{H}$			2	98
$^{36}\text{Cl}$	50	40		10
$^{60}\text{Co}$	90	10		
$^{90}\text{Sr}$	25	75		
$^{129}\text{I}$	50	40		10
$^{137}\text{Cs}$	10	90		
$^{155}\text{Eu}$	95	5		
$^{239}\text{Pu}$	95	5		
$^{241}\text{Am}$	95	5		

The Yucca Mountain tuff samples and bomb cavity samples were used in this preliminary study to elucidate possible method difficulties when employed on these matrices. More refined studies are planned based on the results of this study.

## Technetium

### Technetium Background

Technetium was formally discovered in 1937 by Emilio Segré and Carlo Perrier by the purification of a molybdenum target that had been bombarded with deuterons from a cyclotron at Berkeley, California by Ernest Lawrence. It was, at the time, touted as the first artificial element to be discovered. Technetium in Greek means artificial. Many believe however, that the initial discovery of technetium was made earlier, in 1925, by Walter and Ida Noddack and Otto Berg via the x-ray spectroscopy of columbite mineral ore who deduced that the element 43 was present. Their experiments, however, could not be repeated by their peers in the field. Their claim of discovery was substantiated much later by x-ray computer simulations at the Nation Institute of Standards and Technology (NIST) in 1998; however the discovery of element 43 is still dedicated to Segre and Perrier (Armstrong, 2000). There are at total of 25 Tc isotopes most of which have half lives of less than 1 hour. All isotopes of Tc are radioactive, with mass 97 the longest lived isotope, with a half-life of  $2.6 \times 10^6$  years, which is much smaller than the age of the earth. It was therefore initially assumed that any Tc present at the genesis of earth must have radioactively decayed long ago. A realization came with the understanding of nuclear fission of uranium, and that the fission products curves indicated a yield of approximately 6%  $^{99}\text{Tc}$ , that in fact there is technetium present everywhere due to the spontaneous fission of uranium. However, the amount of technetium present is extremely small due to, low crustal abundance of uranium, and the very long half-life of uranium-238 spontaneous fission of  $6.5 \times 10^{15}$  years (CRC, 1970). To date, the only natural technetium isotope that has been analytically detected is mass 99, with a half-life of

211,000 years, which has been found in only in uranium ore (0.2 ng/kg) and perhaps columbite ore of the disputed discovery in 1925 (Colton, (1965); Armstrong, (2000)). The extremely low natural technetium levels in most matrices makes technetium a good choice as an analyte for detection of a bomb pulse, since only the relatively high levels of technetium from anthropomorphic sources can be detected with current instrumental techniques. Of the 25 known isotopes only a few isotopes and meta-stable isotopes have half-lives long enough to be worthy of analytical consideration in the determination of Tc in environmental samples (Desmet & Myttenaere, 1986). These relatively long lived isotopes have been used for sample spiking or internal standards for isotope dilution mass-spectrometry. A selection of technetium isotopes that have significant half lives are presented in Table 3, along with the decay products, radioactive decay mode, and the decay energy for the major pathways of decay (CRC, 1970

Table 3 Selected Tc Isotopes and Modes of Radioactive Decay (CRC, 1970).

Isotope	NA	Half-life	DM	DE (MeV)	DP
<sup>95m</sup> Tc	-	61 d	ε	-	<sup>95</sup> Mo
			γ	0.204, 0.582, 0.835	-
			IT	0.0389, e	<sup>95</sup> Tc
<sup>96</sup> Tc	-	4.3 d	ε	-	<sup>96</sup> Mo
			γ	0.778, 0.850, 0.810	-
<sup>97m</sup> Tc	Trace	90 d	IT	0.0965, e	<sup>97</sup> Tc
<sup>97</sup> Tc	Trace	2.6×10 <sup>6</sup> y	ε	-	<sup>97</sup> Mo
<sup>98</sup> Tc	Trace	1.5×10 <sup>6</sup> y	β <sup>-</sup>	0.3	<sup>98</sup> Ru
			γ	0.770, 0.669	-
<sup>99m</sup> Tc	Trace	6.0 h	IT	0.142	<sup>99</sup> Tc
			γ	0.140	<sup>99</sup> Tc
<sup>99</sup> Tc	Trace	2.11×10 <sup>5</sup> y	β <sup>-</sup>	0.292	<sup>99</sup> Ru

NA = natural abundance, DM= decay mode, DE is decay energy, DP is decay product, ε is electron capture, IT is internal transition, β<sup>-</sup> is beta decay, γ is gamma decay.

### Technetium Sources

The major source of terrestrial Tc is from the atmospheric weapons testing that occurred from 1945 to 1980. As much as 140 TBq of technetium were released from atmospheric nuclear weapon testing (Tagami, 2003). A small amount of Tc is continually being released to the atmosphere from nuclear power plants, and from nuclear fuel refineries; however, these atmospheric releases are extremely minor in comparison with the atmospheric weapon testing. The nuclear fuel refinery releases of technetium to the ocean, conversely, have been quite large. It has been estimated that nuclear fuel refineries have released as much as 1000 TBq of  $^{99}\text{Tc}$  to the North Sea over the past 30 years, most of which came from the Windscale high level nuclear fuel refinery at Sellafield, England (Tagami, 2003). Technetium release to the atmosphere or ocean will usually be in the form of the chemical species pertechnetate ( $\text{TcO}_4^-$ ); however, subsequent reduction of  $\text{TcO}_4^-$  to the hydrous dioxide ( $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ ) may occur under reducing conditions, such as, estuaries, brackish tidal flats, and rice paddies (Lloyd & Macaskie, 1997; Lloyd et al., 2000; Keith-Roach et al., 2003; Tagami & Uchida, 2002; Tagami, 2003). The  $^{99}\text{Tc}$  removal under reducing conditions may be a function of the lower redox potential, or the formation of sulfide species, or the direct consequence of bacterial induced reduction. The large releases of Tc to the ocean over the past 30 years have had little effect, as yet, on the terrestrial levels of technetium, but over centuries, the terrestrial levels of  $^{99}\text{Tc}$  will increase due to wind (hurricane) blown sea mist and sea shore sand/dust which will be eventually deposited globally. Currently the vast majority of the technetium that has arrived terrestrially is derived from the atmospheric weapons testing that occurred from 1945 to 1980. On the order of 100 MBq of meta-stable



technetium-99 ( $^{99m}\text{Tc}$ ),  $t_{1/2} = 61$  days, are currently used annually world wide in the medical industry for radiological scanning. The introduction of atmospheric technetium from these medical procedures is considered insignificantly small (Tagami, 2003).

### Technetium Toxicity

Technetium-99 is a beta emitter with a long half-life of 211,000 years. The emitted electron has a relatively low energy of 0.292 MeV. Human technetium exposure in the environment will usually take place from drinking water or eating plants or animals containing technetium in the pertechnetate ( $\text{TcO}_4^-$ ) form (ANL, 2002). There is also an inhalation pathway of exposure to  $^{99}\text{Tc}$  from technetium fallout. We are currently being exposed to vanishing small amounts of  $^{99}\text{Tc}$  due to the fallout from the past atmospheric weapons test and current nuclear fuel reprocessing, but since the amount is small, the beta energy of decay is small, there is very little reason for concern. The ingestion pathway usually results in about 50% Tc absorption with about 10% of the absorbed Tc remaining in the stomach and GI tract (ANL, 2002). Absorbed Tc has a preferential attraction to the thyroid where it is absorbed to the degree of 4% relative to the rest of the body. The liver also absorbs about 3% of the ingested Tc, and the remainder is spread throughout the body including hair. Studies in rats have show that Tc crosses the rat placenta (Desmet & Myttenaere, 1986). Tc has also been found in the milk of lactating goats after their food was spike with  $\text{TcO}_4^-$  (Desmet & Myttenaere, 1986). The biological half-life of Tc in the body is highly dependent on which organ has absorbed it. Tc leaves the body through feces (65%) or urination (35%) (ANL, 2002). The removal of Tc is initially fast but with a significant tailing effect. The biological half-life the absorption of Tc in the thyroid is about 0.5 days. Fully 75% of the Tc leaves the body with a biological half-life of only

1.6 days. Approximately 20% of the absorbed Tc is removed from the body with a biological half-life of 3.7 days and the remaining 5% is eventually removed from the body with a biological half-life of 22 days (ANL, 2002). The hair of rats have shown the longest retention of the Tc and elimination would occur through shedding with presumably a month or more half-life (Desmet & Myttenaere, 1986).

The propensity for Tc to be absorbed quickly into the thyroid and then be evacuated quickly ( $t_{1/2} = 0.5$  days) has made Tc a very useful tool for radiological scanning of the thyroid. Metastable Technetium ( $^{99m}\text{Tc}$ ), which decays with a 140keV gamma emission, with half-life of 6.01 hr, is used in 80% of all radio nuclear medicine procedures, and is used in as many as 40,000 procedures a day worldwide (Boyd, 2006).

The USEPA maximum concentration level (MCL) in drinking water is 4 mrem per year in water based on an assumed water intake of 2 liters of water per day (CFR Part 141 section 61). In comparison a chest x-ray is about 5-10 mrem. The 4 mrem allowed dose translates to a  $^{99}\text{Tc}$  concentration of 33.3 Bq/L or 52.6 ng/L(ppt)

Since there is a slight propensity for Tc to accumulate in the thyroid and liver, then it follows that the low energy beta emission of  $^{99}\text{Tc}$ , after ingestion of significant amounts of  $^{99}\text{Tc}$ , will cause an increase occurrence of cancer in these organs. Tests performed on rats however; show that, at least over the short term of 30 days or so, the amount of Tc that must be consumed in order to cause noticeable degradation in organs, or overall decreased in health, would be quite high (Desmet & Myttenaere, 1986).

#### Technetium Chemistry

Technetium is in the VIIB family in the periodic table along with manganese, and rhenium. Technetium has several possible oxidation states from the -1 to 7 (Tagami,

2003). In soils or water under oxidative conditions Tc is in the plus 7 oxidation state pertechnetate  $\text{TcO}_4^-$ , regardless of pH. The word pertechnate should be considered synonymous with pertechnetic acid ( $\text{HTcO}_4$ ) under oxic conditions, at neutral or acidic pH. Pertechnetic acid has a  $\text{pK}_a$  of -0.12, which is similar to that of hydrobromic acid (Darab, & Smith, 1996). Under reducing conditions,  $\text{TcO}_4^-$  is reduced to the plus 4 oxidation state hydrous dioxide  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ , where  $n$  is considered to be approximately 1.6, but is often written rounded up to 2. The species of Tc present is dependent of the Eh-pH of the system. Figure 9 presents the aqueous Eh-pH diagram for Tc (Krupka & Serne, 2002).

The chemical behavior of Tc is mimicked to varying degrees by both manganese and rhenium (Colton, 1965; Darab, & Smith, 1996). Pertechnetate acid is fairly volatile with boiling point of  $311^\circ\text{C}$ . Drying the pertechnetate acid under oxidative conditions produces the heptoxide  $\text{Tc}_2\text{O}_7$ , which is also volatile with a boiling point of  $311^\circ\text{C}$ . It is estimated that at  $100^\circ\text{C}$  the vapor pressure of the pertechnetic acid is about 0.1 torr and is therefore easily volatilized from heated solutions. Pertechnetate is fairly easily, but slowly, reduced by ascorbic acid, hydroxyl amine, and  $\text{Sn(II)}$ , although these must be added in excess as the pertechnetate will slowly reform under oxic conditions. The hydrous oxide  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$  can be quickly oxidized by nitric acid-hydrogen peroxide mixtures, ammonia-hydrogen peroxide mixtures, or hydrogen peroxide alone (Anders, 1960).

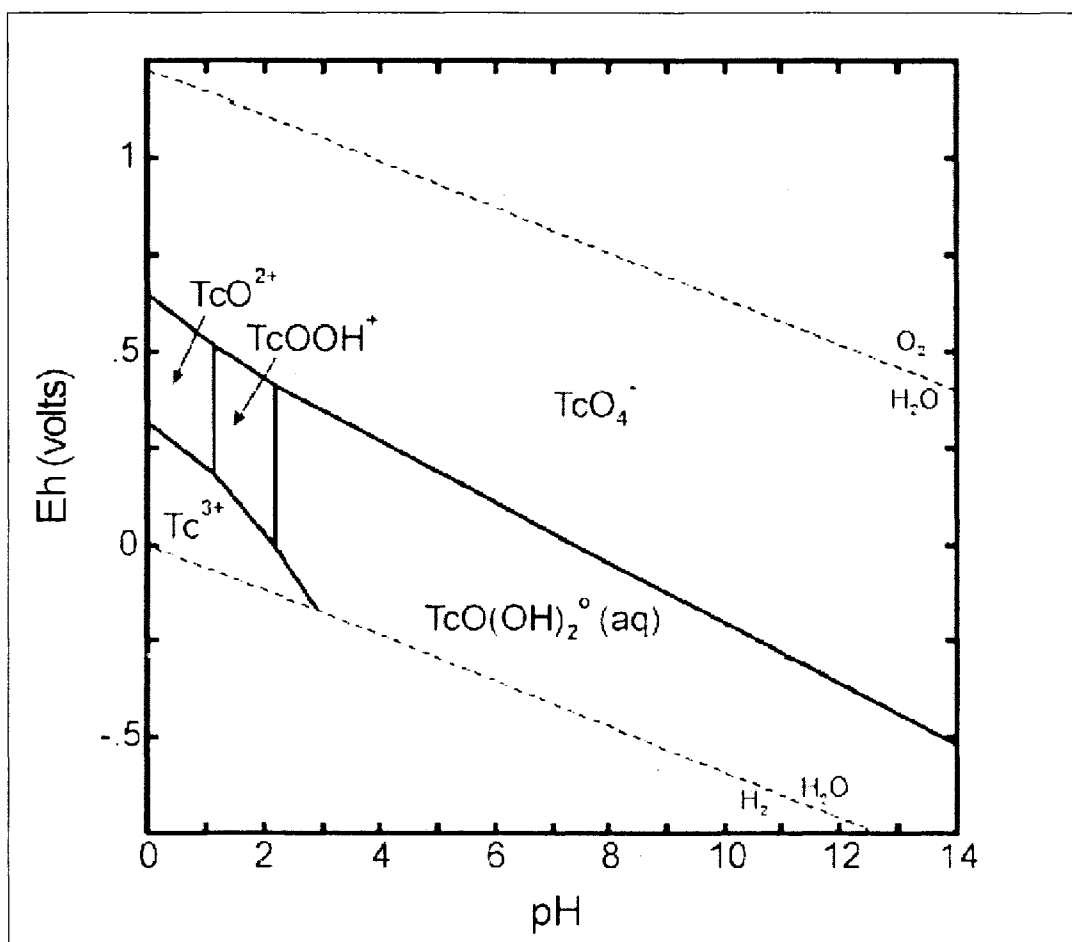


Figure 9. Eh-pH diagram showing dominant Aqueous species of technetium in the absence of dissolved carbonate. The diagram was collected at 25°C and a concentration of 53 ng/L dissolved  $^{99}\text{Tc}$  (Krupka & Serne, 2002).

In comparison to the other members of the group VIIB oxy-anions, permanganate  $\text{Mn(VII)}$  is more easily reduced to the hydrous dioxide (IV) state, and perrhenate  $\text{ReO}_4^-$  is less easily reduced than  $\text{TcO}_4^-$ . Under reducing conditions, with an Eh less than 100 mV, at neutral pH, the reduced Tc (IV) species  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$  is formed (Wildung et al., 2004; Darab, & Smith, 1996). Pertechnetate ( $\text{TcO}_4^-$ ) can also be precipitated by sulfide ( $\text{S}^{2-}$ ),

and forms  $\text{Tc}_2\text{S}_7$  (Colton, 1965). If  $\text{TcO}_4^-$  is added to mackinawite ( $\text{FeS}$ ) mineral, a reduction product  $\text{TcS}_2$ , with unknown hydration, is formed (Wildund, 2004; Bunker, 2000). The  $\text{TcO}_4^-$  species will form low solubility salts with K, Rb, and Cs (Krupka & Serne, 2002). Pertechnetate can be efficiently and quantitatively electrolytically reduced to  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$  in dilute sulfuric acid at the potential of -0.8 volts vs the saturated calomel electrode (SCE) (Anders, 1960).

## Rhenium

### Rhenium Background

Rhenium is also in the family (group) VIIB in the periodic table under technetium. Rhenium was discovered in 1925 by Walther Noddack, Ida Tacke (later Ms. Norddack), and Otto Berg, in platinum ore and columbite (ACS, 2006). They also claimed to have discovered technetium, but as discussed in the general technetium section above, their claim was dismissed. Rhenium is named after the river Rhine where it was first commercially produced. A total of 28 isotopes of Re have been identified; however, only a few have half-lives greater than a few days (ACS, 2006). There are four isotopes that are somewhat long lived or are considered stable and their half-lives and modes of radioactive decay are presented in Table 4. Rhenium isotope at mass 185 is considered stable and  $^{187}\text{Re}$  has a very long half-life of 43.5 billion years. The weakly radioactive  $^{187}\text{Re}$  decays with a beta emission to form osmium-187 ( $^{187}\text{Os}$ ). This relatively slow decay of  $^{187}\text{Re}$  has been used for geochronological dating. By determining the ratio of

$^{187}\text{Re}$  to  $^{187}\text{Os}$  isotope the age of rocks that are quite old relative to the earth's age can be determined (Selby & Creaser, 2004).

Like technetium, rhenium has a few relatively short lived radioisotopes that have been explored recently for medical diagnostic imaging and radiotherapy. The in vitro behavior of these rhenium isotopes is very similar to the widely used technetium radioisotopes showing the same preference for the thyroid tissue. The radioactive perrhenates,  $^{188}\text{ReO}_4^-$  and  $^{186}\text{ReO}_4^-$ , are often selected for nuclear medicine procedures.

Table 4. Rhenium Relatively Long Lived or Stable Isotopes (CRC, 1970).

Isotope	NA	Half-life	DM	DE (MeV)	DP
$^{185}\text{Re}$	37.4%	Stable			
$^{186}\text{Re}$	-	90 h	$\beta^-$	1.071	$^{186}\text{Os}$
$^{187}\text{Re}$	62.6%	$4.35 \times 10^{10}$ y	$\beta^-$	0.003	$^{187}\text{Os}$
$^{188\text{m}}\text{Re}$	-	18.7 m	$\gamma$	0.172	$^{188}\text{Re}$
$^{188}\text{Re}$	-	16.7 h	$\beta^-$	2.116	$^{188}\text{Os}$

NA = natural abundance, DM= decay mode, DE is decay energy, DP is decay product,  $\epsilon$  is electron capture, IT is internal transition,  $\beta^-$  is beta decay,  $\gamma$  is gamma decay.

#### Rhenium Sources

Rhenium is in general very rare in the earth's crust with an average abundance of only 1-2 ug/kg (Sun, & Arculus, et al. (2003). However, rhenium is found in concentrations up to 2000 mg/kg in a few minerals, such as, platinum ore, columbite, and molybdenite (CRC, 1970; Colton, 1965). Recently, there has been a find of a nearly pure rhenium sulfide mineral, rhenite, at sulfur rich volcano fumaroles (Korzhinsky, 2004). Rhenium is also found at concentration as high as 100 ug/L in organic-bearing black shale, which was originally derived from reducing anoxic organic rich black mud (Selby

& Creaser, 2004). Anoxic mud has been considered a sink for aqueous and marine Re, which is otherwise considered conservative, showing no chemical interaction, under all but significantly reducing conditions (Koide, Hodge, et al., 1987).

The rhenium industrial production source material is usually the byproduct molybdenum residues that form in the chimney flues of copper smelting plants. The United States production was 4.6 metric tons for 2003, and the world production was 33 metric tons (Magyar, J., 2004). In 2003, the United States imported 14.5 metric tons, and therefore, the apparent consumption of Re in the United States was 19.1 metric tons, which is about 58% of the world production. The uses and percent demand of Re include, petroleum catalysts (40%), and high temperature alloys for jet engine turbines (50%). Other uses of Re include high temperature thermal couples, electrical contacts, X-ray tube targets, vacuum tubes, mass spectrometer electron emitters, heating elements, and crucibles.

#### Rhenium Toxicity

Rhenium toxicity is unknown. Studies using mice using radioactive perrhenates such as,  $^{188}\text{ReO}_4^-$  and  $^{186}\text{ReO}_4^-$ , have shown that rhenium, once assimilated, behaves like technetium in that it is preferentially attracted to the thyroid (Zuckier et al., 2004). By inference, it can be assumed that long term exposure to high levels of stable rhenium will have disruptive effects on thyroid function; however, given the limited amount of rhenium in most minerals, and absence from general consumer products; the only people at risk of rhenium toxicity are metal workers that process and refine rhenium precursors, and workers that use concentrated rhenium metal or compounds.

## Rhenium Chemistry

Rhenium aqueous chemistry is quite similar to that of technetium as both are group VIIB elements (Darab, & Smith, 1996). Rhenium has possible oxidation states of -3 to 7, and like technetium the aqueous and soil chemistry the plus 4 and 7 oxidation states predominate. Under oxic conditions Re(VII) aqueous species predominate as perrhenate  $\text{ReO}_4^-$ , which is synonymous with perrhenic acid  $\text{HReO}_4$ , in both neutral and acid conditions. Figure 10 presents the aqueous Eh-pH diagram for Re (Darab, & Smith, 1996). Rhenium is considered an analog of technetium because, under oxic conditions, both form a tetrahedral oxy-anion, which is stable at any pH, and both have similar redox chemistry (Harvey et al., 1991; Darab, & Smith, 1996; Kim & Boulègue, 2003). Both  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$  generally form soluble salts with Na and ammonium ( $\text{NH}_4^+$ ) and generally less soluble salts with the larger aqueous cations, such as, potassium, rubidium, cesium, silver, and thallium (Darab, & Smith, 1996). When aqueous solutions containing  $\text{ReO}_4^-$  are evaporated to dryness, in the presence of oxygen,  $\text{Re}_2\text{O}_7$  forms, which is an analog of  $\text{Tc}_2\text{O}_7$ . Like  $\text{Tc}_2\text{O}_7$ ,  $\text{Re}_2\text{O}_7$  is fairly volatile, with a boiling point of approximately 360°C. Table 5 presents the melting and boiling points for both  $\text{Tc}_2\text{O}_7$  and  $\text{Re}_2\text{O}_7$ . Under reducing conditions, with an Eh less than 0 mV, and at neutral pH, the reduced Re (IV) species  $\text{ReO}_2$  is formed, but the specific degree of hydration has not been investigated (Darab, & Smith, 1996; Kim & Boulègue, 2003). There is a sparingly soluble  $\text{ReO}_2$  species, which is probably the analog of  $\text{TcO}(\text{OH})_2$ , but the formula also has not been rigorously investigated, but it is probably  $\text{ReO}(\text{OH})_2$  (Kim & Boulègue, 2003). Upon further reduction the oxide species (Re III)  $\text{Re}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  is formed, which does not have a corresponding Tc analog (Darab, & Smith, 1996).



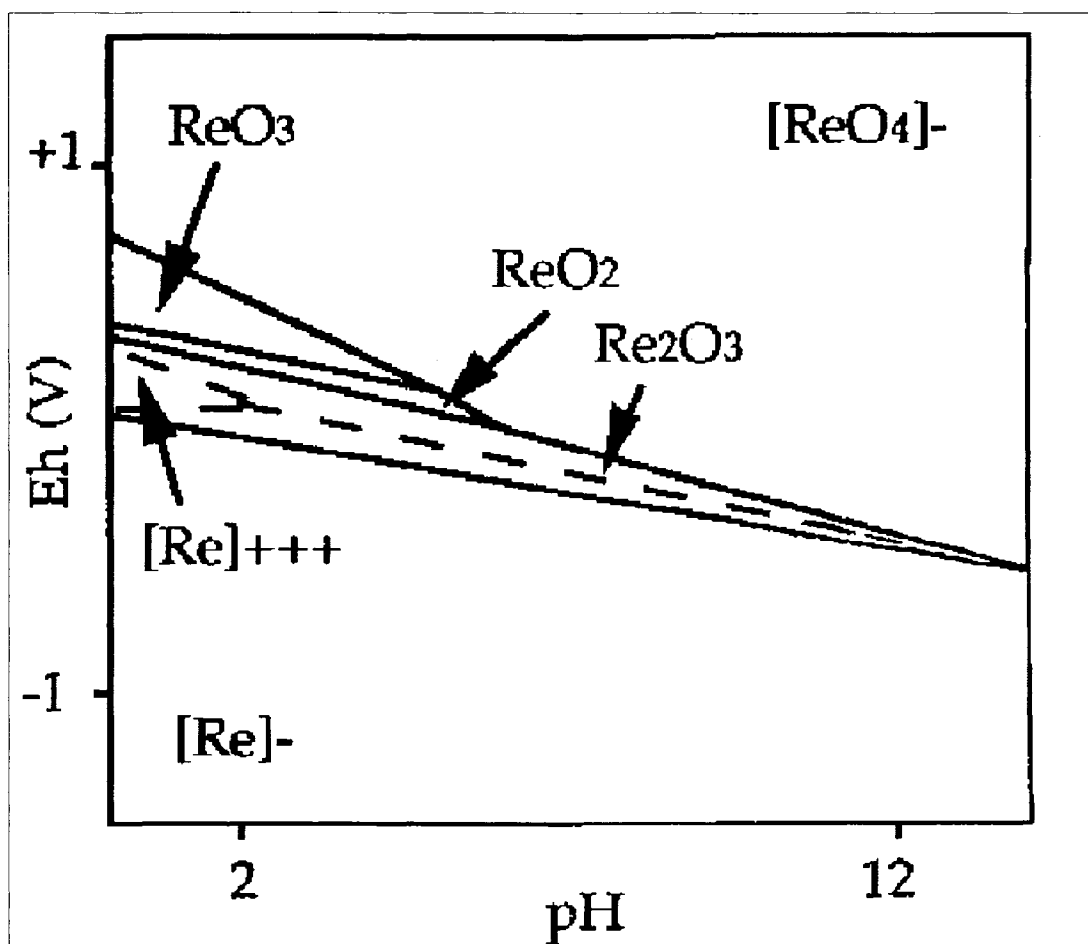


Figure 10. Eh-pH diagram for aqueous rhenium. Reduction of  $\text{ReO}_4^-$  to  $\text{ReO}_2 \cdot n\text{H}_2\text{O}$  apparently occurs at approximately 0 mV for pure water at pH 7 (Darab, & Smith, 1996).

Table 5. Tc and Re Species Melting and Boiling Points (Darab & Smith, 1996).

Species	Melting point	Boiling point
$\text{Tc}_2\text{O}_7$	119	311
$\text{Re}_2\text{O}_7$	~300	~360

## CHAPTER 2

### LITERATURE REVIEW

#### Background and Rationale

There are few data available for technetium or rhenium in the literature with regard to volcanic tuff or nuclear bomb cavities. The available data will be reviewed below. A literature review was performed in order to establish the expected concentrations of Tc and Re in to both volcanic tuff and nuclear bomb cavity glass. A literature search was also preformed to find relevant methodology that may be applied to the detection of low level Tc and Re in volcanic soil/tuff and nuclear bomb cavity glass.

#### Technetium Literature Review

##### Tc and Yucca Mt Tuff

Method development for the determination of the concentration of technetium in the Yucca Mountain Topopah Spring tuff is the object of this study. A literature search revealed only one determination of  $^{99}\text{Tc}$  from Yucca Mountain tuff, which was 0.11pg/kg, and was reported by Fabryka-Martin in a draft report (Fabryka-Martin, August Draft 1996). This value has not been confirmed. The concentration of  $^{99}\text{Tc}$  in the surface soil and immediate subsurface soil has been performed by several investigators (Tagami & Uschida, 2003). In one study by Tagami & Uschida, (2003),  $^{99}\text{Tc}$  was determined in the soil/sediment of rice patties in Japan at a concentration of ranging from 6-110

mBq/kg (9.5-174 pg/kg) (ppq). These same authors proposed that, based on the total amount of atmospheric Tc deposited by nuclear testing, that there should be approximately 6 mBq/kg (9.5 pg/kg (ppq)) of  $^{99}\text{Tc}$  in the top 25cm of top soil. In a separate set of analyses of soils from the NTS the concentration of  $^{99}\text{Tc}$  was determined to be 2 mBq/kg (3.2 pg/kg) at the surface, with 0.15 mBq/kg (0.24pg/kg (ppq)) at 50cm depth (USDOE LLNL, 1999). These authors indicate, based on their calculations, that 0.25 mBq (0.39 pg/kg (ppq)) of Tc can be expected in the first meter of top soil.

#### Tc Soil Species

At a pH of 7-8 and Eh greater than 100 mV versus the standard hydrogen electrode (SHE),  $\text{TcO}_4^-$  will be the dominate species (Wildung et al., 2004; Darab, & Smith, 1996). At pH between 7-8, and at an Eh slightly less than 100 mV vs SHE, Tc(VII) will slowly, over several hours, be reduced to Tc(IV) oxide species. The reduction reactions are reversible and the reduced species will slowly, over hours to weeks, re-oxidize to reform  $\text{TcO}_4^-$  due to dissolved oxygen (USEPA 2004, Tagami, 2003). The addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), however, will cause the rapid re-oxidation of reduced Tc species (USEPA 2004). Most of the Yucca Mountain pore water has an Eh of between 400-600 and a pH of between 6.5 and 7.5, although a pH as high as 8.3 may occur (Eckhart 2000; USDOE July 2000). At Yucca Mountain the Eh of well water is typically 350 mV, with a pH of approximately 7, and under these conditions Tc is presumed to be the  $\text{TcO}_4^-$  species. However, it is not known if reducing horizons exist in the Yucca Mountain strata that could cause the localized reduction of pertechnetate to the insoluble hydrous dioxide. Also, the presence of iron(II) oxides, magnetite, or the presence of reduced sulfide minerals, such as iron pyrite, for example, dispersed in the tuff may also cause localized

reduction of technetium, although these processes have not been shown to occur at Yucca Mountain (Krupka & Serne, 2002; Tagami & Uschida, 2002; Keith-Roach et al., 2003). Tests conducted on 1 meter columns of Topopah Spring Tuff from Yucca Mountain and near by Busted Butte have shown little, if any, reduction of  $\text{TcO}_4^-$  indicating little, if any, reduction to the hydrous oxide (Vandergraaf, et al., 2003; USNRC, 1987). These column experiments using Topopah Springs Tuff have actually shown that the  $\text{TcO}_4^-$  wave-front arrives ahead of the fluorescent dye marker and the tritium, indicating the possible exclusion of anionic  $\text{TcO}_4^-$  from the negatively charge aluminosilicate rock matrix, allowing it to pass quickly through the tuff columns. In a subsequent column experiment, using the same tuff, the investigators supposed that microbe activity, probably using the dye as food source, caused the decrease in the Eh of the column effluent to -500 mV. This low Eh resulted in the apparent reduction of  $\text{TcO}_4^-$  and complete retention of  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$  in the rock column. Other experiments using columns with reducing material added, such as, pyrite, magnetite, carbon, have shown marked increase in the retention of  $\text{TcO}_4^-$ . Again, it is assumed that  $\text{TcO}_2 \cdot \text{H}_2\text{O}$  formed and was retained on active sites in the matrix (USEPA 2004). Calculations indicate that  $\text{TcO}_4^-$ , at a pH of 6.9, an Eh of less than 100 mV, should result in the reduction of  $\text{TcO}_4^-$  to  $\text{TcO}(\text{OH})_2$ , but  $\text{TcO}(\text{OH})_2$  is still sparingly soluble up to 0.1 ng/L (ppt), therefore concentrations less than this might still be somewhat mobile in rock matrix, even under reducing conditions (Wildund, et al. 2004). Reduced Tc (IV) carbonate species, such as  $\text{TcCO}_3(\text{OH})_2$  and  $\text{TcCO}_3(\text{OH})_3^-$ , are probably more soluble and mobile in rock matrix than the  $\text{TcO}(\text{OH})_2$  species (Krupka & Serne, 2002). It is not known if the calcite that lines the fractures, which are the predominate water flow path through welded tuff, is sufficient to cause the

formation of the more soluble Tc(IV) carbonate species even if the  $\text{TcO}_4^-$  were to be reduced by conditions in the tuff matrix. As yet there are no experimental results that indicate the reduction of  $\text{TcO}_4^-$  to  $\text{TcO}_2 \cdot \text{H}_2\text{O}$  or the precipitation of  $\text{TcO}_4^-$ , such as, the formation of the sulfide  $\text{Tc}_2\text{S}_7$ , will occur in the tuff matrix. An experiment was performed on three core samples of Yucca Mountain tuff where  $\text{TcO}_4^-$  was spiked into synthetic well water. The core samples were then placed in the  $^{99}\text{Tc}$  spiked synthetic well water for 41 days (USDOE NNO, 1997). The results showed no  $\text{TcO}_4^-$  loss due to precipitation, reduction, or sorption due to interaction with the tuff matrix. In another investigation, approximately 60 gram samples of Topopah Spring Tuff (from the lower vitric zone), and Calico Hills Formation tuff were held in contact with pertechnetate spiked synthetic well water for 21 days, and again, there was no sorption of the pertechnetate by either of the tuff samples (Vandergraaf, et al., 2003).

#### Tc Bomb Cavity

As mentioned previously, reports of the concentration of technetium in underground test cavities are rare. The available results for well water from test cavities are present below in Table 6. These results indicate that range of  $^{99}\text{Tc}$  in the water of submerged nuclear cavities is from 13.4 to 4,100 pg/L. A  $^{99}\text{Tc}$  concentration value for nuclear cavity glass has not been located by the author.

Table 6. Technetium Concentrations in Water from Nuclear Test Cavities.

$^{99}\text{Tc}$ Concentration	Reference
(5.5 - 10.2 pCi/L) 320 - 600 pg/L (ppq)	USDOE NNSA (2004)
(2.6 Bq/L) 4,100 pg/L (ppq)	Daniels (1993), Bilby Test
2950 - 3970 pg/L (ppq)	Rokop (1990), Cheshire Test
13.4 pg/L (ppq)	Rokop (1990), Cambric Test

## Rhenium Literature Search

### Rhenium in Yucca Mt Tuff

The rhenium concentrations in rhyolite tuffs are quite low, less than 100 ng/kg (ppt), compared to the natural crustal abundance, which is about 1 ppb (Richter et al., 1998). Under the oxidizing conditions of a pyroclastic eruption, rhenium is in the volatile form of Re (VII),  $\text{Re}_2\text{O}_7$ , which has a boiling point of only 360°C. The typical pyroclastic flow has a temperature range of 600-800°C, so it has been recently surmised that rhenium is lost to the atmosphere on the explosive degassing of the pyroclastic eruptions (Sun, et al., 2003).

### Rhenium in Bomb Cavity Sample

No reports of rhenium content of Topopah Tuff, or other Yucca Mountain tuff were found in the literature. Richter, (1998) reported 36 ng/kg (ppt) for rhyolite. The only available certified rhyolite tuff material is from Geological Survey of Japan, which has a provisional Re value of 23 ng/kg (ppt).

The rhenium content of nuclear cavities is also unavailable. There is no evidence of Re from either  $^{235}\text{U}$  fission or tungsten activation. The activation of tungsten probably does occur, but the initial amount of W present in the southern Nevada volcanic tuff is probably quite low in the sub ug/kg range. However, there will certainly be some W present in the steel (as a hardener) that was used to house and lower the nuclear device into the underground test hole.

## Review of Analytical Methods

Technetium is a low energy beta emitter (292 keV), and until the last decade was primarily analyzed by liquid scintillation spectroscopy or gas proportional counting (Tagami, 2003). Advances during the last decade in ICPMS instrumentation and concentration and purification of  $^{99}\text{Tc}$  using ion exchange resins have produced much lower levels of detection which compare favorably with the radiochemistry techniques (Tagami, 2003).

The analysis for technetium at ultra low concentrations is difficult for several reasons. The most commonly employed methods and techniques for low level determination of Tc are presented below along with the major difficulties encountered for each. The detection limits for the analytical techniques are present in Table 7, which is derived from a table presented in a paper by Tagami (2003), unless otherwise indicated. These detection limits are based on the analysis analytical standards that are relatively free of physical/chemical matrix effects or isobaric interferences. Therefore, the detection limits listed in Table 7 may be somewhat lower than achievable for samples with complex matrices.

Table 7. Analytical Methods for  $^{99}\text{Tc}$  Determination (Tagami, 2003)

1-5 mBq	(1.6-7.9 pg) (ppq)	Anti coincidence Shielded Gas Flow Counting
3-5 mBq	(4.7-7.9 pg)	Neutron Activation (n, $\gamma$ )
1-25 mBq	(1.6-40 pg)	Liquid Scintillation Counting
0.002-4 mBq/mL	(3.2-6,300 pg/L)	Inductively Coupled Plasma Mass Spectrometry
3.8 mBq/mL	(6000 pg/L)	Q-ICPMS
1.1 mBq/mL	(1740 pg/L)	Q-ICPMS
0.03 mBq/mL	(47 pg/L)	Q-ICPMS
0.0021 mBq/mL	(3.3 pg/L)	Q-ICPMS with Ultrasonic Nebulizer
0.005 mBq/mL	(7.9 pg/L)	HR-ICPMS with Ultrasonic Nebulizer
0.003 mBq/mL	(4.7 pg/L)	HR-ICPMS Tagami (unpublished data)
0.012 mBq/mL	(19.2 pg/L)*	Isotope Dilution ICPMS
0.9mBq/mL	(1,400 pg/L)*	ETV-ICPMS
0.3 mBq	(0.5 pg)	Accelerator Mass Spectrometry (AMS)
$5 \times 10^6$ Atoms	$(8.2 \times 10^{-4} \text{ pg})^*$	Negative Thermal Ionization-MS (NTIMS)

Note. Q-ICPMS: quadrupole-ICPMS; HR-ICPMS: high resolution (or double focusing) ICPMS; ETV-ICPMS electrothermal vaporization-ICPMS; ID-MS. Those items mark with an asterisk “\*” have been added to the original table by author. The original Table in Tagami (2003) has references for the detection limits.

Anti coincidence shielded gas flow counting: This method uses relies on the detection of the 292 keV beta emissions from the decay of  $^{99}\text{Tc}$ . The final limitation of this method is the background radiation and instrumentation electronic noise. Normal ionizing radiation background is generally between 10-25 counts-per-minute due to cosmic rays and the radioactive decay of elements that make up the detection apparatus and sample container. The use of shielding and detector geometries allow for the detection of a little as of 1 count of  $^{99}\text{Tc}$  in 1000 seconds, i.e. one mBq. The use of beta decay for counting of rhenium is limited because of the few beta emissions given by  $^{187}\text{Re}$  due to the long half-life of  $42 \times 10^9$  years, which makes other analytical techniques, such as ICPMS, more sensitive.



Neutron activation: This method relies on the neutron activation of  $^{98}\text{Tc}$  to  $^{99\text{m}}\text{Tc}$  ( $t_{1/2}=6.0$  h) and monitoring for the gamma 140 keV decay of the  $^{99\text{m}}\text{Tc}$  to  $^{99}\text{Tc}$  based on neutron activation equation:  $^{98}\text{Tc}(n,\gamma)^{99\text{m}}\text{Tc} \rightarrow ^{99}\text{Tc}$  (Colton, 1965). Unfortunately, any  $^{99}\text{Tc}$  present may also be activated to  $^{99\text{m}}\text{Tc}$ , which interferes with the calculation of Tc concentration. Also, any  $^{98}\text{Mo}$  present in the sample would also be activated to  $^{99\text{m}}\text{Tc}$ , base on the neutron activation equation:  $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo} \rightarrow ^{99\text{m}}\text{Tc} \rightarrow ^{99}\text{Tc}$  (Colton, 1965). This limitation requires the complete removal of Mo from the sample before analyses. It is unlikely that there exists a technique such as selective precipitation, ion exchange, or preferential electro-reduction that would allow for the complete removal of Mo to less than a pg while leaving Tc undiminished. The detection limit is estimated between 3-5 mBq (4.7-7.9 pg) (Tagami, 2003).

Neutron activation analysis for the analysis of Re in soil relies on the neutron activation of  $^{187}\text{Re}$  based on the neuron activation equation  $^{187}\text{Re}(n,\gamma)^{188}\text{Re}$  (Samadi, et al., 1975). The activated  $^{188}\text{Re}$  is beta emitter with a  $t_{1/2}$  of 16.8hr (155 keV), which is, after separation from the matrix, counted by gas flow proportional counting or liquid scintillation. Unfortunately, any tungsten (W) in the sample will cause interference based on the neutron activation reaction  $^{186}\text{W}(n,\gamma)^{187}\text{W} \rightarrow ^{187}\text{Re}(n,\gamma)^{188}\text{Re}$ , where the  $^{187}\text{W}$  is a beta emitter with a  $t_{1/2}$  of 23.8 hours. The neutron activation determination of  $^{185}\text{Re}$  isotope has similar limitations to the  $^{187}\text{Re}$  isotope, due to activation of  $^{184}\text{W}$ . The detection limit for the neutron activation analysis of Re in soils, based on these limitations, is about 1 ng.

Liquid Scintillation Counting: The detection limit for this technique is about 1 mBq (1.6 pg). The limitations for this technique are the similar to that of the anti-coincidence

shielded gas flow counting. The reliable counting of less than 1 count per 1000 second from  $^{99}\text{Tc}$  decay is difficult because of background radiation and instrument electronic noise.

Inductively coupled plasma mass spectrometry ICPMS: The detection limit for this technique is dependent on the sample delivery technique and instrument mass analyzer configuration. Detection limits for the various ICPMS instrumental configurations are present in the paragraphs below.

Quadrupole Mass Spectrometer: A modern (2000) ICP using a typical concentric nebulizer with a quadrupole mass analyzer will deliver a  $^{99}\text{Tc}$  detection limit of a little as 47 pg/L (ppq), suitably long integration times are employed. The ion mass monitoring time, at the top of the peak, used to achieve this detection limit was 180 seconds for each analytical mass (Tagami, 2003). The detection limit for Re, employing the same instrumental configuration, is approximately 30-50 pg/L (ppq).

If an ultrasonic nebulizer is substituted for the concentric nebulizer, using the same quadrupole mass analyzer configuration, the detection limits can be reduced more than ten fold, to 3.3 pg/L (ppq) (Tagami, 2003). It should be pointed out that ultrasonic nebulizer can also lead to long wash out times due to memory effects, presumably due to  $\text{TcO}_4^-$  adherence to the inner wall of the transfer tube. The significant memory effects of the use of plastic tubing in  $^{99}\text{Tc}$  analysis by ICPMS have been reported by Richter et al. (1997) and Beals (1992). The later adopted a wash procedure that included alternate washing of the sample introduction system (tubing-nebulizer-spraychamber) with 10%  $\text{HNO}_3$ , followed by water, then 10% ammonium hydroxide, and final water rinse after each sample/standard solution.

High Resolution ICPMS: The detection limits compiled in Table 7 indicate the high resolution mass spectrometer, double focusing in low resolution mode, appears to give similar detection limits for either concentric or ultrasonic nebulizer sample introduction techniques. The detection limits for both configurations are in the range of 3-5 pg/L.

Electro-thermal Volatilization ICPMS (ETV-ICPMS): The detection limit presented for this technique is 1,400 pg./L, which is somewhat higher than the other ICPMS techniques; however, the authors report relatively fast sample throughput (Song, 2000).

The Accelerator Mass Spectrometer (AMS): The AMS has a  $^{99}\text{Tc}$  detection limit of less than 0.5 pg/L (0.3 mB) (Tagami, 2003). Work performed at LLNL using AMS has demonstrated a detection limit of 10  $\mu\text{Bq}$  ( $\sim 1 \times 10^8$  atoms), presumably based on clean water samples using a gas ionization detector (USDOE LLNL 1999). A reproducible result from a soil sample extract of 0.14 mB/kg (0.22 pg/kg) was obtained based on a 15 fg signal from 120 grams of soil (USDOE LLNL 1999). Presumably a similar detection limit could be shown for rhenium since the preparation chemistry would be identical and the interferences are less intense. An earlier study by the same group at LLNL reported an initial AMS  $^{99}\text{Tc}$  detection limit of 500 pg (LLNL, 1997). This study was interesting because the usual gas ionization detector was not used. Instead, a thin scandium foil was placed in the beam path and the induced characteristic L-shell x-rays produced by the  $^{99}\text{Tc}$  and  $^{99}\text{Ru}$  ion-electron recombination at the foil surface were detected by a high purity germanium (HPGe) x-ray detector. The authors indicated that the slightly different x-rays produced by  $^{99}\text{Tc}$  and  $^{99}\text{Ru}$  could be resolve to 1 part  $^{99}\text{Tc}$  part in 100 parts  $^{99}\text{Ru}$ . They estimated a detection limit of 10 fg of  $^{99}\text{Tc}$  (6 uBq, or  $6 \times 10^7$  atoms) was obtainable.

Negative Thermal Ionization Mass Spectrometry (NTIMS): This instrumental technique allows for the detection of less than 1 fg of Tc per sample. Rokop et al. (1990) indicate a detection limit of  $5 \times 10^6$  atoms ( $8.2 \times 10^{-4}$  pg) of  $^{99}\text{Tc}$ . Usually a rhenium filament is used for the sample source for NTIMS analysis. For the NTIMS analysis of  $^{99}\text{Tc}$  and Re, a platinum filament has been used (Dickin, 2002).

#### Mass Spectrometry $^{99}\text{Tc}$ and Re Interferences

The mass spectroscopy determinations of  $^{99}\text{Tc}$  and Re both suffer from isobaric interferences. Table 8 presents the percent mass abundances for selected isotopes around Re masses 185 and 187. A table of mass abundances for the mass region around  $^{99}\text{Tc}$ , 95-108 amu, and Re, 184-190 amu, are presented in Appendix I. The  $^{185}\text{Re}$  isotope has a relatively minor interference from tungsten hydride ion  $^{184}\text{WH}^+$ . There is also a direct spectral overlap of  $^{187}\text{Os}$  (1.6%) on  $^{187}\text{Re}$  (62.6%); however, this osmium interference is generally not a problem because most sample preparations usually involves heating the samples, at which point the osmium is lost as volatile osmium tetroxide ( $\text{OsO}_4$ ).

Table 8. Percent Mass Abundances Around Re Masses 185 and 187.

Ion	Percent Mass Abundance					
W	30.7		28.6			
Os		0.02	1.6	1.6	13.3	16.1
Re		34.4		62.6		
Mass>	184	185	186	187	188	189

All of the mass spectroscopy techniques for the determination of  $^{99}\text{Tc}$  have the same major limitation, which is the direct isobaric interference of  $^{99}\text{Ru}$ . The  $^{99}\text{Ru}$  mass is virtually identical to the  $^{99}\text{Tc}$  mass because  $^{99}\text{Ru}$  is formed from the beta decay of  $^{99}\text{Tc}$  and therefore the mass difference is equal to the mass of electron plus the energy of the decay ( $e=mc^2$ ), which is too small of a mass difference to be resolved by high resolution mass spectrometry. The  $^{99}\text{Tc}$  also has a relatively minor interference from the formation of  $^{98}\text{MoH}^+$  in the plasma. There also exists a potential interference for  $^{99}\text{Tc}$  determinations due the formation of krypton oxide ( $^{83}\text{Kr}^{16}\text{O}$ ) in the plasma. It is therefore prudent to monitor for the presences of high levels of Kr in the argon gas before initiating analyses. Table 9 presents the percent abundances of selected molecular ion species and isotopes near the  $^{99}\text{Tc}$  mass.

Ruthenium has 7 natural isotopes and the Ru at mass 99 has a natural abundance of 12.7% (CRC, 1970). The interference at  $^{99}\text{Tc}$  can be mathematically corrected by monitoring a near by Ru mass, such as mass 101, at 17% abundance, and then subtracting the natural isotopic abundance ratio amount of interference from mass 99, which has a Ru mass abundance of 12.7%. The precision with which the isobaric correction can be applied is dependent on the precision of the monitored mass measurement. The limitation arises when the imprecision of the Ru subtraction is significant relative to the  $^{99}\text{Tc}$  signal. The final limitation to accurate  $^{99}\text{Tc}$  determinations is that if there is significant amount of Ru in the sample and low levels of  $^{99}\text{Tc}$  in the sample then one can not be certain that it is actually  $^{99}\text{Tc}$  the is being detected and not  $^{99}\text{Ru}$ .

Several methods have been developed to separate the  $^{99}\text{Tc}$  and Re from these commonly encountered interferences. These methods include co-precipitation, selective

precipitation with, for example, tetraphenyl arsonium, and selective ion exchange using anion exchange resin (Anders, 1960). To date, the most promising methods for the decrease and possible removal of the  $^{99}\text{Ru}$  interference on  $^{99}\text{Tc}$  are based on the use of anion exchange resins.

Table 9. Percent Mass Abundances Around Mass  $^{99}\text{Tc}$  (CRC, 1970)

Ion	Percent Mass Abundance							
KrO	11.6	11.5	57.0		17.3	>1	>1	
Pd					1.0		11.1	22.3
Rh						100		
Mo	24.1		9.6					
Ru		12.7	12.6	17.0	31.6			
Tc		~100						
Mass>	98	99	100	101	102	103	104	105

The anion resins usually employed by investigators are the tetra alkyl amine resins such as, Amberlite IR 400 Cl form, Bio Rad AG 1-X8 Cl form, Bio Rad AG MP-1, and the Erichrom Teva-Spec resin. Each of these resins has shown excellent quantitative recoveries of both  $^{99}\text{Tc}$  and Re; however, none of the resins, regardless of specific procedure, have shown the complete separation of the  $^{99}\text{Tc}$  and  $^{99}\text{Ru}$ . Figure 11 shows a graph of the relative binding of  $\text{TcO}_4^-$  to anion exchange resin (TEVA) as the concentration of  $\text{HNO}_3$  is varied from 0.01 M to 10 M. The  $k'$  data, for  $^{99}\text{Tc}$  was derived from the number-of-free-column-volumes to peak maximum versus the molarity of  $\text{HNO}_3$  mobile phase. Figure 11 shows at low nitric acid concentration (0.1M), the  $\text{TcO}_4^-$  complexes to the resin giving rise to a large number of column volumes ( $k'$ ), more than 5000, to the peak maximum. As the nitric acid increases (and pH decreases) the  $\text{TcO}_4^-$  is

less strongly held by the resin. At a nitric acid concentration of 8 M, the graph indicates that  $\text{TcO}_4^-$  has a low  $k'$  (number of free column volumes), of less than 1, and therefore the  $\text{TcO}_4^-$ , under these conditions, is released from the resin into the 8 M  $\text{HNO}_3$  solution.

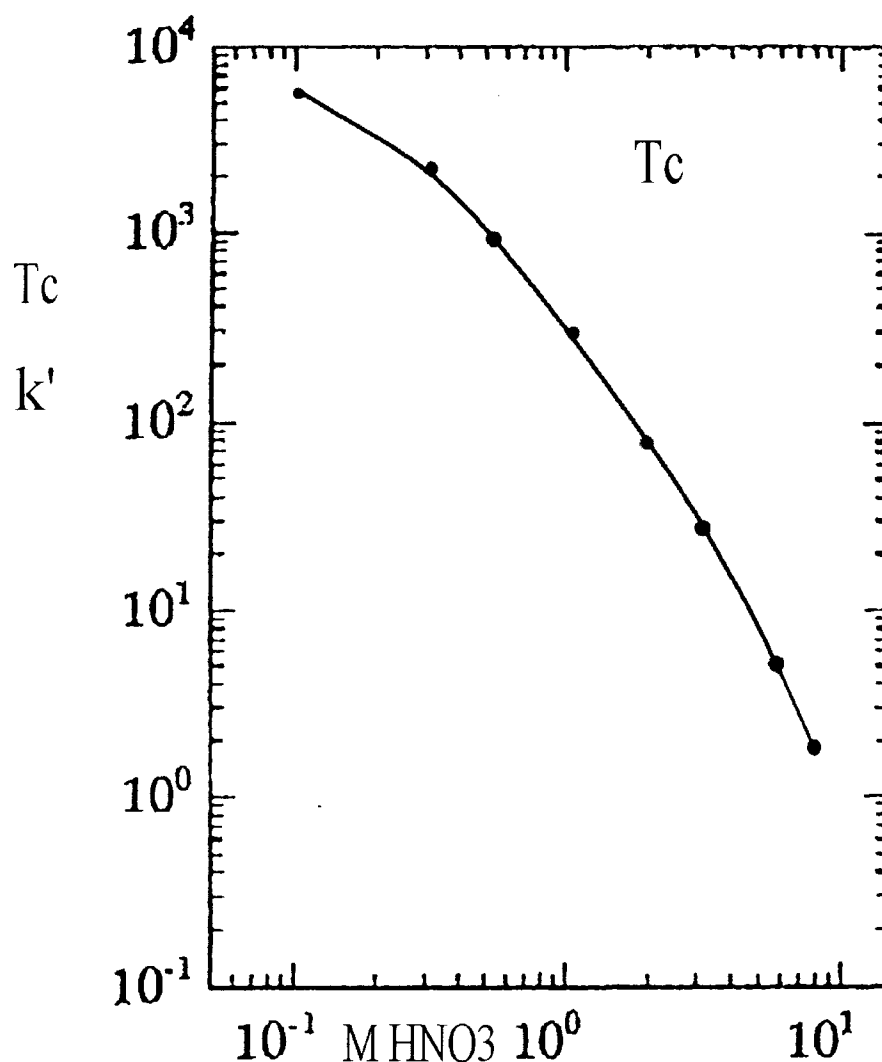


Figure 11. Graph showing the  $\log k'$  (number of column volumes to peak) for  $^{99}\text{Tc}$  vs the  $\log$  of the molarity of nitric acid concentration for Teva Spec resin. An explanation of the  $k'$  for the  $^{99}\text{Tc}$  data is provided in the text. Graph reproduced from Horwitz, (1993).

The equation for the  $k'$  follows:  $k' = D V_s/V_m$ . Where  $D$  is the distribution ratio,  $V_s$  is the volume of the stationary phase (resin beads), and  $V_m$  is the volume of the mobile phase  $\text{HNO}_3$  solution. The graph in Figure 11 and the equation were derived from Horwitz, (1993).

A typical aqueous sample preparation for ICPMS analysis of  $^{99}\text{Tc}$  and Re usually involves the oxidation of the sample by heating a sample aliquot solution in the presence of  $\text{HNO}_3$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), followed by the removal of the major matrix components, if necessary.

A soil sample preparation for ICPMS is generally more involved. If the soil has high organic content, the sample is heated to 400-450°C in to oxidize the organic components. Although, the boiling points of the  $\text{Tc}_2\text{O}_7$  and  $\text{Re}_2\text{O}_7$  are less than this, as presented previously in Table 5, the temperature at which the  $\text{Tc}_2\text{O}_7$  begins to be lost in most soil is usually greater than 450°C, as demonstrated using  $^{95\text{m}}\text{Tc}$  as a radiotracer. However some soil types showed losses of  $^{99}\text{Tc}$  up to 10% when heated to 450°C for 12 hrs (Tagami, 2003). Typically a soil sample is heated in solution of with 1-4 M  $\text{HNO}_3$  and 1-10 mL of 30%  $\text{H}_2\text{O}_2$ , the sample is centrifuged/filtered, and the sample major components are removed through various techniques.

Recently a technique for soil matrix separation for the  $^{99}\text{Tc}$  has been created that involves the heating of the soil sample, in multiple 50 gram aliquots, in a oxygen entrained furnace set at 1000°C (Uchida & Tagami, 2001; Tagami & Uchida, 2002). The effluent of the furnace is bubbled through 250 mL of slightly acidified ( $\text{HNO}_3$ ) or de-ionized water to collect the volatilized  $\text{HTcO}_4/\text{Tc}_2\text{O}_7$  and  $\text{HReO}_4/\text{Re}_2\text{O}_7$ . This technique is applicable to siliceous soils but poor recoveries were noted with carbonaceous soils



where the  $^{99}\text{Tc}$  recovery was significantly reduced (Tagami & Uchida, 2000). The investigators indicated that they believed that carbonate in the sample may have formed a liquid melt with in the furnace which limited the evolution of the  $^{99}\text{Tc}$ . The use of a oxygen furnace for the isolation of  $^{99}\text{Tc}$  and Re from the matrix would probably not work well for the highly carbonaceous surface soils of the NTS; however, it may be applicable to the volcanic tuff. Although, the carbonate deposits that usually (65%) line the tuff fractures may suppress the volatilization of  $^{99}\text{Tc}$ .

In-depth studies on the use of resin technology have focused on the amount and concentration of  $\text{HNO}_3$  that should be used to effectively wash through the interfering ions without removing the  $\text{TcO}_4^-$  or  $\text{ReO}_4^-$  as well (Uchida & Tagami, 1997, 2000; Tagami, 2003).

In a study performed by Suh, et al., (2003) using a AG MP-1 anion exchange resin, a 2 mL resin bed column was loaded with several elements including  $\text{TcO}_4^-$ , in a 0.5 M  $\text{HNO}_3$  carrier solution. They used a 10 mL aliquot of 1 M  $\text{HNO}_3$  for the wash solution. The elements that were loaded onto the column included;  $\text{TcO}_4^-$ , Mo(VI), Ru(III), Zr(IV), La(III), U(VI), Sr(II), and Ba(II). Their results indicated that the 1M  $\text{HNO}_3$  washed all of the potentially interfering elements through the column with a small amount of Ru as an exception. The Mo is generally easily washed through to levels that will not give rise to isobaric interference on  $^{99}\text{Tc}$ . Similarly, W is also easily washed through so that there will be little interference on either of the Re masses 185 or 187. They noted, that typically, a small (less than 1%), but significant amount of  $^{99}\text{Ru}$  remains on the column when using 1 M  $\text{HNO}_3$  wash, and is co-eluted with the higher concentration 10 M  $\text{HNO}_3$  stripping solution, along with the  $\text{TcO}_4^-$ . The species of Ru that remains on the column is

believed to be nitrosyl-ruthenium  $\text{Ru}(\text{NO})+3$  in the form of anionic species with a general formula  $[\text{RuNO}(\text{NO}_2)_m(\text{OH})_n]^{3-(m+n)}$  (Suh et al., 2003). These nitrosyl-ruthenium species, such as  $\text{RuNO}(\text{NO}_2)(\text{OH})_4^{-2}$  or  $\text{RuNO}(\text{NO}_3)(\text{OH})_4^{-2}$ , have a significant affinity for the resin, and are only removed with difficulty, with considerable amounts of  $\text{HNO}_3$  wash solution (Tagami, 1997). The amount and concentration of nitric acid wash solution that can be used as a column wash has limitations. This is because, at some point, the wash solution will cause the stripping of  $\text{ReO}_4^-$  and/or  $\text{TcO}_4^-$  from the resin.

Studies have been performed to identify the largest amount of 2 M  $\text{HNO}_3$  wash solution that can be used for washing off the matrix components (including Ru), without removing  $\text{TcO}_4^-$  or  $\text{ReO}_4^-$ . In one such column-wash-study, conducted by Uchida & Tagami, (1997), a 2 mL volume bed of Teva ion exchange resin was employed. In this study 2 M  $\text{HNO}_3$  was selected as the wash solution, and the wash was added to the column in sequential 20 mL aliquots. This study showed that the  $\text{TcO}_4^-$  is retained on the column with up to 40 mL of 2 M  $\text{HNO}_3$  wash solution, with only 1.8% loss of the initial  $^{99}\text{Tc}$  concentration. The study also showed that 99.2% Ru passed through the column during loading, and only 0.7 % was found in the first 20 mL of 2 M  $\text{HNO}_3$  wash solution. An addition, 0.1% of Ru was found in the second 20 mL wash of 8M  $\text{HNO}_3$ . Again, the  $\text{TcO}_4^-$  was retained on the column during the wash, with very little loss (1.8%), up to the addition of 40 mLs of 2 M  $\text{HNO}_3$  wash solution. The study also showed that all of the  $^{99}\text{Tc}$  was removed from the column with one 5 mL aliquot of 8 M  $\text{HNO}_3$ .

In a similar study by Uchida & Tagami (2000), a Teva anion exchange column was loaded with 250 mLs of pure water that was spiked with  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$ . In this study, 8 ml aliquots of 2 M  $\text{HNO}_3$  wash solutions were sequentially past through a 2 ml anion

exchange column. Their results indicate that  $\text{TcO}_4^-$  can be retained by the resin up, to 40 mL of 2 M  $\text{HNO}_3$ , as was indicated in the previously discussed study; however, the Re is eluted off the column, beginning with the third aliquot of 8 mLs of 2 M  $\text{HNO}_3$ . These results indicate that if Re is used as an analog spike for  $^{99}\text{Tc}$  recovery, then the wash solution should not exceed 16 mL of 2M  $\text{HNO}_3$ .

## CHAPTER 3

### METHODOLOGY

#### Research Approach

The method/techniques and instrument configurations selected for this thesis research included a soil sample preparation using Re as an analog spike for Tc with separation of Tc and Re from the solubilized sample matrix on a AG 1-X8 column with a 2 ml volume. The wash solution selected was 15 mL of 2 M HNO<sub>3</sub>, and the final column-stripping-solution selected was 5 mLs of 8 M HNO<sub>3</sub> followed by 10 mL of 1% (0.16M) HNO<sub>3</sub>. Since rhenium was selected as an analog spike for technetium, the use of more than 16 mL of 2 M HNO<sub>3</sub> would result in the loss of Re from the anion exchange resin during the washout step. A 15 mL volume of 2 M HNO<sub>3</sub> wash solution was selected, as the literature search revealed that this amount was the most wash solution that could be used without risk of the loss of ReO<sub>4</sub><sup>-</sup> from the column. Figure 12 presents a flow chart of the sample preparation method used in this thesis research. A HR ICPMS (VG-Axiom) in low-medium resolution mode was selected, as this was the most sensitive instrument available. A low flow rate (0.375 mL/min) concentric nebulizer sample introduction system was used. An ultrasonic nebulizer sample introduction technique was attempted, but the nebulized sample washout was very long and the tailing lead to a <sup>99</sup>Tc baseline significantly above the initial baseline. Attempts to wash out the Tc from sample introduction system with 3% HNO<sub>3</sub> for extended periods were unsuccessful, and

therefore a low flow concentric nebulizer, free flowing, using a short as possible length of Teflon tubing (no Tygon) was employed. The specifics of the sample preparation and analysis of the tuff samples and bomb cavity samples for  $^{99}\text{Tc}$  and Re are presented in the following sections.

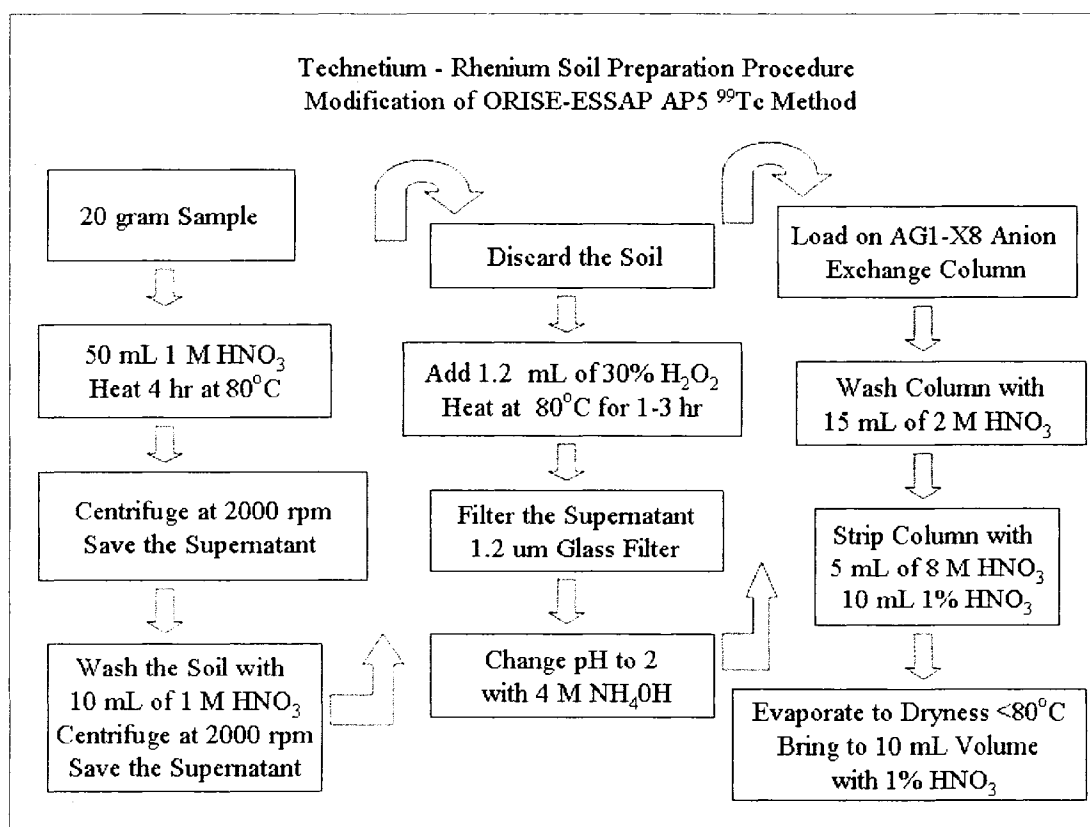


Figure 12. Flowchart of the sample preparation procedure modified from ORISE-ESSAP AP5 Tc-99 method (ORISE/ESSAP, 2003). See Appendix III for the sample preparation method, and Appendix II for the AP5 TC-99 method.

## Sample Preparation

### Sample Preparation Method

The sample preparation method selected originated in part from the ORISE/ESSAP AP5 method for analysis of Tc in soil and liquid samples by liquid scintillation, which is presented in Appendix II (ORISE/ESSAP, 2003). The method was modified based on information derived from the literature search. The method used for sample preparation is presented in Appendix III. The AP5 method was modified to use 20 grams of soil sample instead of 10 grams, to allow for the detection and quantification of lower levels of  $^{99}\text{Tc}$  and Re. Also, the original AP5 method column-wash-step employed a 0.05 M HF solution which was not used, as the use of HF would require the use of a HF resistant sample introduction system for the ICPMS. Based on the results of the literature search, a column wash solution of 2 M  $\text{HNO}_3$  was employed. An initial column wash solution of 10 mL of 2 M  $\text{HNO}_3$  was used for a preliminary analysis to check for reagent contamination and interferences. For all subsequent sample preparations, 15 ml of 2 M  $\text{HNO}_3$  was used as a column wash solution. The original method did not have a column final-elution-stripping step since the method was designed for liquid scintillation analysis whereby the entire resin bed of the resin column is placed in a liquid scintillation vial. The literature search indicated that a column-stripping solution, using 5 mLs of 8 M  $\text{HNO}_3$  followed by 10 mLs of 0.16M  $\text{HNO}_3$  (1% v/v  $\text{HNO}_3$ ), would be suitable, and was therefore used for all sample preparations. Again, a step by step procedure is presented Appendix III. The glass columns used had an internal diameter of 6 mm and were 100 mm in length, with bottom glass frit, which were filled approximately one-half full with a 2 ml volume of anion exchange resin beads Bio Rad, AG 1 - X8, 50-100 mesh.

The resin columns were initially washed with 5 mL of 8M HNO<sub>3</sub> followed by 10 mLs of 0.16M HNO<sub>3</sub> (1% v/v HNO<sub>3</sub>). This column washing procedure was performed twice before the column was used.

#### Tuff Sample Preparation

Six welded tuff samples, weighting 0.5 to 1.3 kg, were provided from the Yucca Mountain tunnel refuse rock enclosure, “muck rock” area. The “muck” rock area contains the tuff rock resulting from the tunneling of ES tunnel and cross drift tunnel through the Topopah Springs Tuff (approximately 90%, counting both the ESF and the cross drift tunnel), and some portion of the Tiva Canyon and Paintbrush tuff (approximately 10%). All the tuff samples were welded tuff. Four of the six tuff rocks were light gray to light pink or lavender. The remaining two tuff samples were a light orange color. The tuff rocks were individually photographed and weighted. The rocks were broken to less than 1cm by first wrapping the rock in household “saran” wrap, followed by several wrappings with 4 mil thick polyethylene plastic and then the rock was struck with a 2.5 pound sledge hammer while on cement. The plastic wrapping procedure was repeated after every few strikes with the hammer to avoid contamination of the rock with either the cement or the hammer. After the rocks were reduced to ca. 0.5cm, they were pulverized to less than 0.6 mm using a belt-drive Bruan pulverizer. The resulting powdered tuff rock was stored in double polyethylene bags until time for sub-sampling for analysis.

#### Physical Characteristics of Tuff Samples

One aliquot of powdered tuff sample was passed through two standard screens, 600µm and 150µm, to access the approximate range in particle size. The results of the

screening of one aliquot from pulverized tuff sample #5 showed 89% passing through a 600 um screen and 6% passing 150um; therefore, 83% of the particles were between 600 um and 150  $\mu\text{m}$ .

Five gram sub-samples of each of the six powdered tuff samples were dried in an oven at 103°C for 24 hrs, and the percent water was calculated for each using the weight difference from before and after drying. The percent moistures for the pulverized tuff samples were determined to be less than 0.1% for all six samples, and therefore no correction to the data for moisture content was made. This low moisture content is presumably due to the loss of water from the tuff samples due to the considerable frictional heat generated during pulverization. It should also be noted that the tuff rock samples were initially retrieved from the “muck rock” area at Yucca Mountain and had been exposed atmospheric conditions consisting of a low average humidity and annual rain/snow fall for perhaps three years or more.

A group digital picture of the samples before sample preparation is presented in Figure 13. A ruler has been included for size reference. The samples were designated 1 thru 6 based on this photo. A close up digital picture of the tuff sample #1 is presented in Figure 14.





Figure 13. The tuff samples left to right were 1698, 665, 664, 882, 703, 865 grams, and were designated samples 1 to 6, respectively, based on this digital photo.

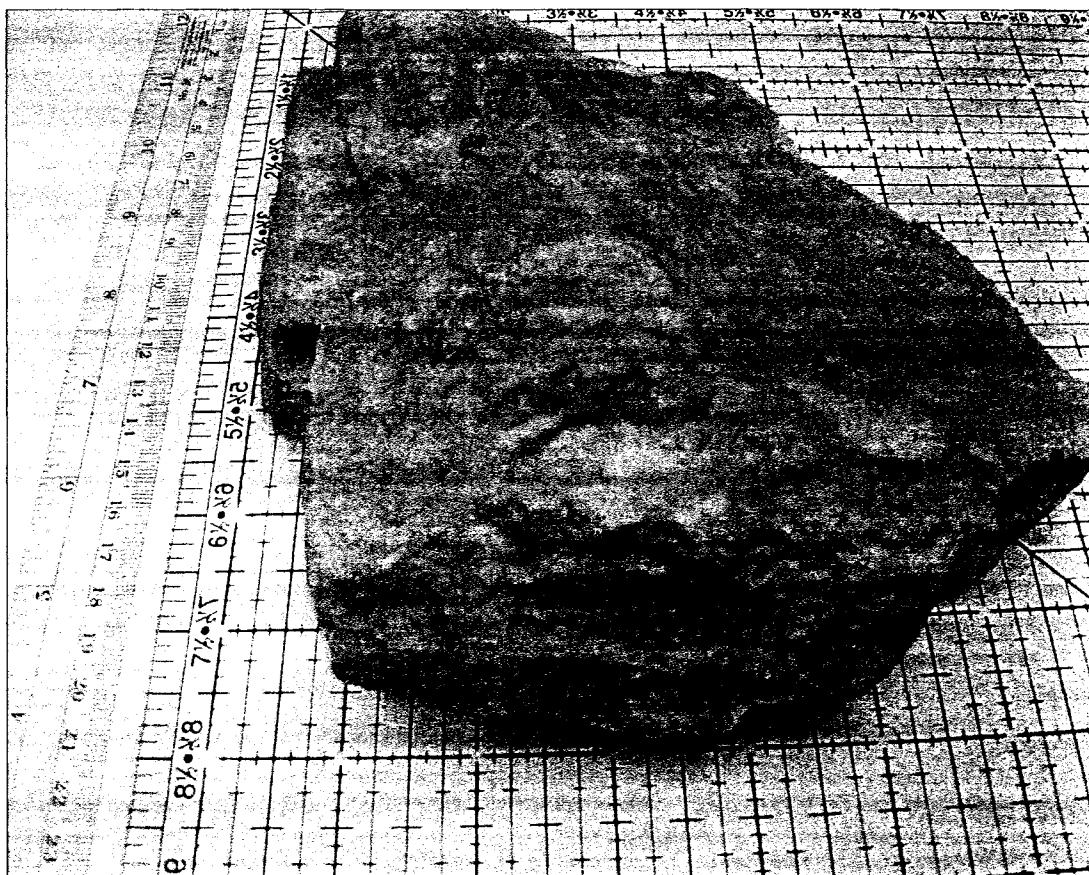


Figure 14. Close up digital photo of Tuff sample #1.

As a preliminary experiment, the first of six tuff samples was prepared in four replicates using 10 grams of sample and 10mLs of 2 M  $\text{HNO}_3$  column wash to check for reagent contamination and sample matrix interferences.

Each of six pulverized tuff samples were prepared, in duplicate, using the 20 gram sample size and the 15 mL  $\text{HNO}_3$  column wash, as described in the sample preparation procedure. Then they were each analyzed by HR-ICPMS. The duplicate preparation and analysis of each sample un-spiked was performed to remove the possibility of contamination of the samples with either Tc or Re spike from the spiking solutions. One of the tuff samples, prepared in the same preparation batch, was spiked with Tc at 100

pg/kg (ppq) and Re at 40 ng/kg (ppt). The  $^{99}\text{Tc}$  spike of 100 pg/kg (ppq) is considered a low level recovery spike, not a true analytical spike, given the detection limit of the HR-ICPMS (vide infra). The Re was spiked at 40 ng/L (ppt) based on the estimated concentration of Re in the tuff samples from an initial quadrupole-ICPMS scan. The Re spike was performed both for an assessment of Re recovery in the sample, as well as an analog spike for  $^{99}\text{Tc}$  recovery. All sample and standard analytical solutions were spiked with 1 ug/L Rh as an internal standard.

Two types of blank samples were prepared with each batch of tuff samples, a 20 gram blank sand sample and a reagent blank. The 20 gram blank sand sample was prepared and analyzed with each sample preparation batch because it is specified in the original AP5 Tc-99 method. The sand used was Ottawa sand (Ottawa, IL), that has a high silica content (99.8%), which was purchased from U.S. Silica Inc. as Flint Silica #16, with the highest particle fraction passing through a number 50 U.S. standard mesh, with a mean particle size of 300um.

#### Bomb Cavity Glass Sample Preparation

Four 60 mL polyethylene vials containing fragmented-tuff and glass fragments from undisclosed bomb cavities at the NTS were obtained. The weight of each bottle was recorded. Figure 15 presents a digital photograph of the contents of one of the bottles, with several glass fragments separated to the left side of the main pile. Figure 16 presents a digital photo of a single glass fragment. The hard beta and gamma originating from each bottle containing fragmented-tuff/glass fragments was measured with a Geiger counter with a pan head probe. The counts-per-min were recorded for the whole bottle at a distance of ~ 1cm. Approximately two grams of material were removed from each

bottle and ground (with difficulty) to a fine powder with a mortar and pestle, and then placed in a 30 mL polyethylene bottle until time for ICPMS sample preparation. Only one gram of each the powdered bomb cavity glass samples was used for ICPMS sample preparation and analysis, because the concentration levels of Tc were presumed to be easily measurable. Each of the four whole 30 mL bottles containing bomb cavity glass material were counted for  $^{137}\text{Cs}$ ,  $^{152}\text{Eu}$ , and  $^{60}\text{Co}$ , by gamma emission spectroscopy.

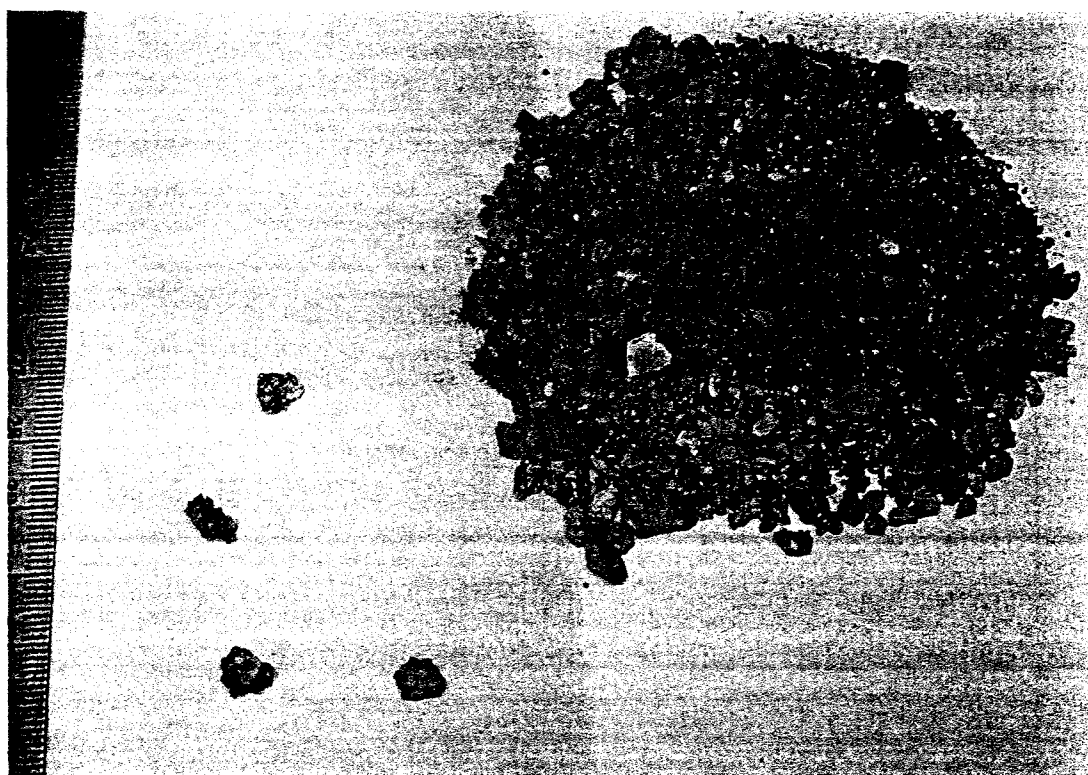


Figure 15. Contents of one of the sample bottles containing bomb cavity glass/rubble, with several glass fragments separated to the left side of the main pile. The ruler's smallest demarcations are millimeters.

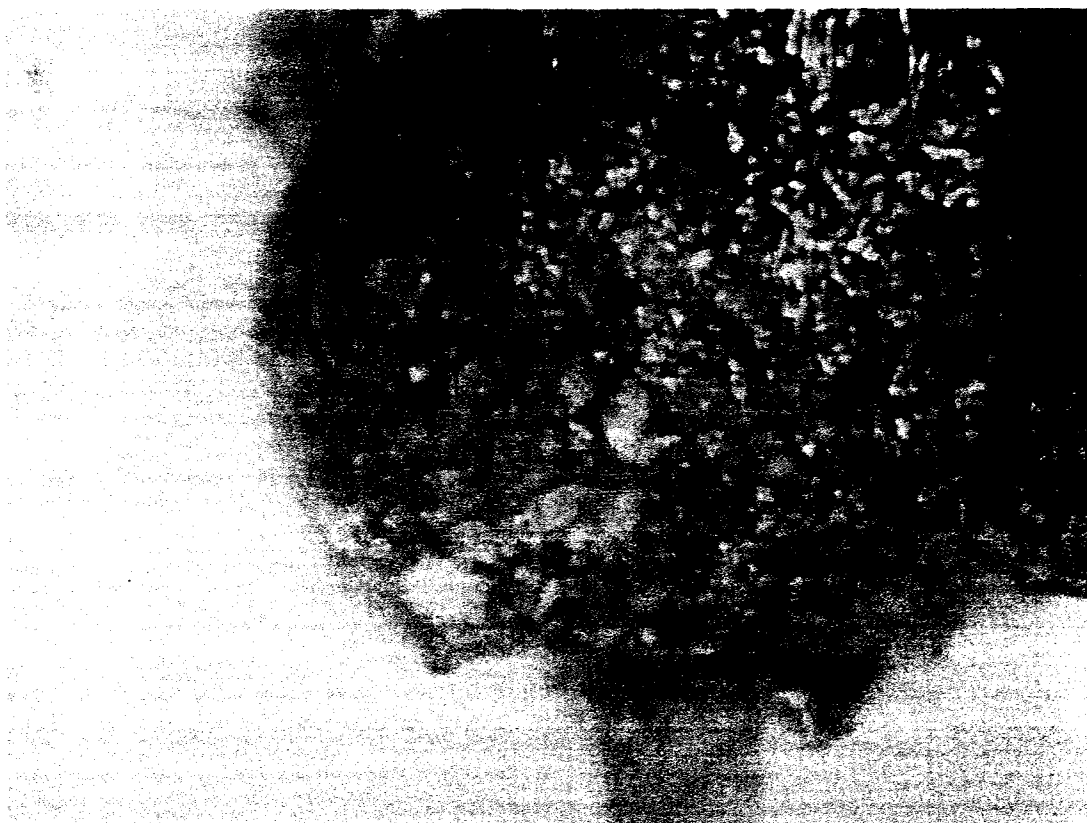


Figure 16. Single bomb cavity glass fragment. The width of region photographed is about 5 millimeters. The appearance was much like obsidian.

#### Summary of Sample Preparation and Analyses Performed

Table 10 presents a summary of the samples prepared, the samples analyzed, along with the sample weights used and the column wash conditions.

Table 10. Samples Analyzed, Sample Weights, and Column Wash Conditions

Sample Name	Number of Samples	Analysis Technique	Sample Weight	Column Wash
Pulverized Tuff Sample 1; four replicates and a sand blank	5	Quadrupole-ICPMS Analysis-Scan Only	10 grams	10 mL 2 M HNO <sub>3</sub>
Seven silica sand blanks run consecutively for detection limit determination (plus a blank)	8	HR-ICPMS	20 grams	15 mL 2 M HNO <sub>3</sub>
Pulverized Tuff Samples 1 to 6; (2 unspiked replicates each)	6 samples 12 replicates	HR-ICPMS	20 grams	15 mL 2 M HNO <sub>3</sub>
3 Spiked Pulverized Tuff Samples	3	HR-ICPMS	20 grams	15 mL 2 M HNO <sub>3</sub>
3 Batch silica sand blanks, 3 Reagent Blanks	6	HR-ICPMS	20 grams (for sand)	15 mL 2 M HNO <sub>3</sub>
Bomb Glass samples 1 to 4; plus 1 spiked sample; 1 silica sand and 1 reagent blank sample	7	HR-ICPMS	1 gram	15 mL 2 M HNO <sub>3</sub>
Re Ryolite Reference Sample JR-2	2	HR-ICPMS	20 gram	15 mL 2 M HNO <sub>3</sub>
Bomb Glass Samples 1 to 4	4	Gamma Spectroscopy	~ 20 Grams	No Sample Preparation

#### Sample Preparation and Analysis Reagents and Standards

The sample preparation/analysis reagents and standards used in the performance of this thesis research are presented in Tables 11 and 12, respectively.

Table 11. Sample Preparation and Analysis Reagents/Materials.

Ammonium hydroxide, NH <sub>4</sub> OH, 14.8 M, concentrated, ACS grade. Fisher Sci.
Hydrogen peroxide, H <sub>2</sub> O <sub>2</sub> , 30-35% (w/v). Fisher Sci.
Nitric acid, HNO <sub>3</sub> , 16 M, concentrated, double distilled grade. Seastar
AG-1 X8 Resin, packed 2 mL columns, 50-100 mesh size, chloride form, Bio-Rad

Table 12. Sample Preparation and Analysis Standards.

<sup>99</sup> Tc, standardized solution NIST SRM 4288a
Rhenium 1000 mg/L, Inorganic Ventures
Ruthenium 1000 mg/L, Spex Industries
Rhodium 1000 mg/L, Spex Industries

### Sample Analyses

#### Tuff Sample Analyses

Tables 13 and 14 provide the instrumental configuration and operational conditions used for the quadrupole-ICPMS and the HR-ICPMS analyses, respectively. Figure 17 presents a digital photo of the VG-Elemental Axiom HR-ICPMS, model 4600006, used in this thesis research. Calibration curves, from 0.01 to 200 ng/L, were generated for both <sup>99</sup>Tc and Re immediately prior to sample analysis. The internal standard Rh was monitored at mass 103, and Ru was monitored at mass 101. An intermediate standard and blank were analyzed after approximately every 8<sup>th</sup> sample analysis, to check for baseline and analytical sensitivity drift. A 20 ng/L (ppt) ruthenium standard, and a 1

ug/L (ppb) Mo standard were analyzed and the end of one analytical sequence in order to access their degree of interference on  $^{99}\text{Tc}$  mass during the HR-ICPMS analysis.

Table 13. ELAN 6100 Quadrapole ICPMS Configuration and Operational Conditions

Plasma forward power	1100 Watts
Plasma flow rate	0.8 L/min
Carrier flow rate	0.8 L/min
Nebulizer	Concentric- peristaltic pump 1 mL/min
Average of 15 scans, 400 us dwell, 10 points per amu.	
Detector	Electron Multiplier
Mode	Scanning
Masses	5-250

Table 14. VG-Axiom HR-ICPMS Configuration and Operational Conditions

Coolant gas flow rate	14
Auxiliary gas flow rate	0.92
Neb gas flow rate	0.92
RF Power	1300
Resolution Mode	Low resolution 400 all except Tc medium resolution 4180
Ion Energy	4977
Nebulizer	Concentric micro-flow nebulizer, Flow rate 0.375 mL/min
Spray Chamber(s)	Tandem, cyclonic- impact
Detector	Single Electron Multiplier
$4 \times 10^6$ counts for a 1 ug/L Indium std	
Masses/elements	( $^{99}\text{Tc}$ , $^{101}\text{Ru}$ , $^{103}\text{Rh}$ , $^{187}\text{Re}$ )
Scan-Dwell	25 points per peak, 0.250 ms dwell, 3 peak widths, 3 runs, 56.25 seconds per mass



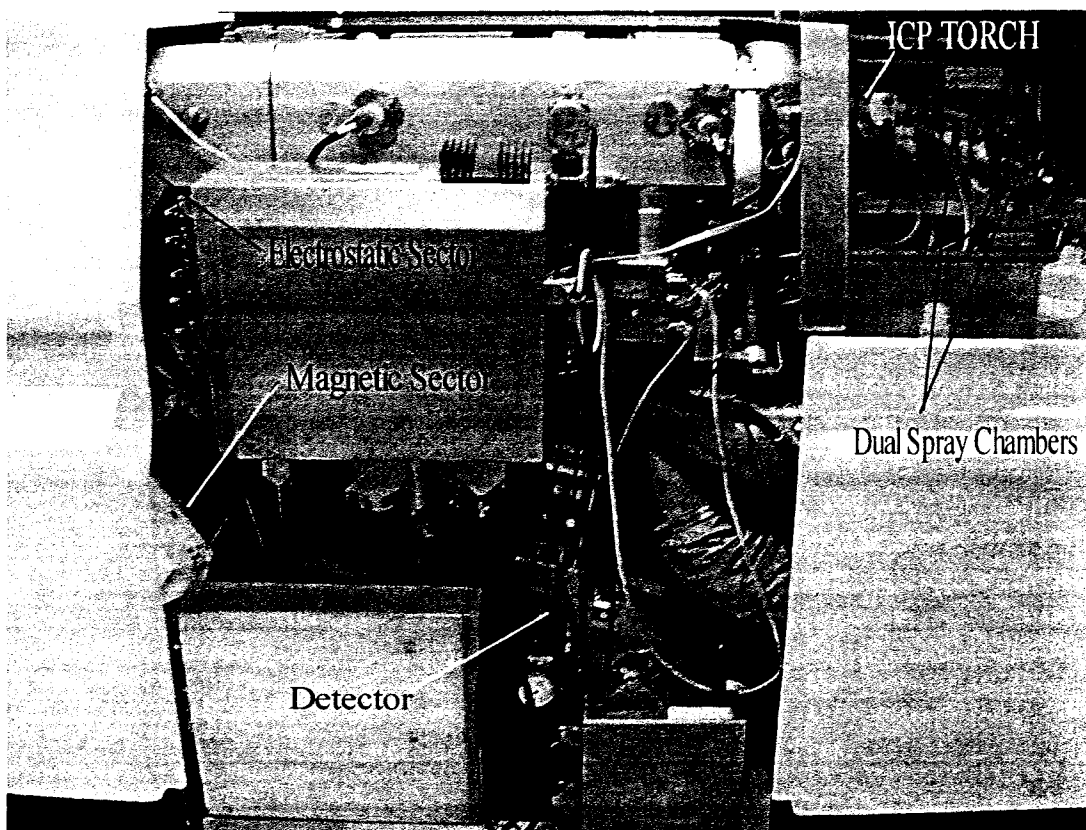


Figure 17. VG-Elemental Axiom HR-ICPMS, Model 4600006.

#### The Bomb Cavity Glass Sample Analyses

The bomb cavity sample were analysed by HR-ICPMS for  $^{99}\text{Tc}$  and Re at the end of a tuff sample analysis sequence to avoid sample cross contamination, since these samples were expected the have rather high concentrations of  $^{99}\text{Tc}$ .

The bomb-cavity-glass samples were also analyzed for  $^{137}\text{Cs}$ ,  $^{60}\text{Co}$ , and  $^{152}\text{Eu}$ , by gamma spectroscopy, without sample preparation, by placing the entire 30 mL polyethylene sample bottle in the detector cell. The analysis counting time was 960 minutes. Table 15 presents the instrumental configuration and operational conditions used for gamma analysis.

Table 15. Canberra Gamma Spectrometer Configurations and Operational Conditions

Detector Model	GX3519
Cryostat Model	7500SL
Liquid Nitrogen flow rate	1.8 L/min.
Detector geometry	HPG Extended range closed-end coaxial
Diameter	56 mm
Length	61 mm
Distance from window	5 mm
Depletion Voltage	2500
Bias Voltage	4000 V
Relative efficiency	35%
Resolution (FWHM)	1.9 keV at 1.33MeV
Peak/Compton ratio	56:1
Software Peak Locate Threshold	2.50
Peak Locate Range (in channels)	1 - 4096
Peak Area Range (in channels)	1 - 4096
Identification Energy Tolerance	1.000 keV
Sample Size	unit
Live Time	57564.3 seconds (959.4 minutes)
Real Time	57600.0 seconds (960 minutes)
Dead Time	0.06 %
Gamma measurement efficiency at 661.66 keV ( $^{137}\text{Cs}$ Gamma emission)	
Calculated efficiency	0.01299
Measured efficiency	0.01301
Measured error	3.41
Percent Deviation	-0.20

## CHAPTER 4

### RESULTS AND DISCUSSION

#### Tuff Samples Analyses Results

##### Quadrapole-ICPMS Analysis Results

As a preliminary experiment, the first of the six tuff samples was prepared in four replicates using 10 grams of sample and 10mLs of 2 M HNO<sub>3</sub> column wash to check for interferences. The samples were analyzed by Q-ICPMS using scanning mode. The resulting mass spectrum scan of the mass regions around <sup>99</sup>Tc, and <sup>185</sup>Re, <sup>187</sup>Re are presented in Figures, 18, 19, and 20. Tables 8 and 9, which were presented earlier, give the mass abundances for Tc and Re mass regions, and have been re-presented below for the reader's easy reference. Figure 18 shows the <sup>103</sup>Rh internal standard at 1 ug/L as well as the presence of Mo at about 1 ug/L (ppb) in the samples, and 0.1 ug/L (ppb) in the sand blank (lower line). Mo at this concentration is not expected form molybdenum hydride ion (MoH<sup>+</sup>) at mass-99 in concentrations high enough to cause positive interference with <sup>99</sup>Tc analyses. The samples prepared for the <sup>99</sup>Tc and Re analysis by HR-ICPMS used an increased column wash of 15 mL of 2 M HNO<sub>3</sub> which is expected to result in a lower Mo concentration in the final sample. The spectrum does not show the presents of any <sup>99</sup>Tc or Ru. The estimated detection limit for the Q-ICPMS scanning mode is about 10 ng/L (ppt), so <sup>99</sup>Tc and Ru concentrations less than this would not be evident in the scan.

Figure 19 shows the same scan around mass 99 as shown in Figure 18, but with the scale expanded. Again, the spectrum does not show the presence of Tc or Ru above noise levels. This spectrum does, however, show the apparent presence of  $^{104}\text{Pd}$  and  $^{105}\text{Pd}$  at an estimated concentration of 20 ng/L (ppt). The sample preparation procedure used for the  $^{99}\text{Tc}$  and Re analysis is quite similar to method used for platinum group metals (Jarvis, 1997). It is not certain if the signal at the Pd masses 104 and 105 are really Pd signal or an artifact, such as,  $^{88}\text{Sr}^{16}\text{O}$  or  $^{92}\text{Mo}^{12}\text{C}$  on mass 104, or  $^{89}\text{Y}^{16}\text{O}$  on mass 105. If the signals at masses 104 and 105 truly indicate Pd in the samples, it may not be derived from the tuff samples, but could be the result of ultra-trace contamination from either the sample preparation reagents or the Rh internal standard.

Figure 20 shows the Q-ICPMS scan mass spectrum around the  $^{185}\text{Re}$  and  $^{187}\text{Re}$  masses for four powdered tuff samples and sand blank. The tungsten concentration is estimated from the signal at masses 184 and 186 to be approximately 300 ng/L (ppt). Tungsten at this concentration is not expected to form tungsten hydride ion, ( $^{184}\text{WH}^+$ ) at Re mass-185 or  $^{186}\text{WH}^+$  at Re mass 187, in concentrations high enough to cause positive interference of the Re analyses. The Re concentration was estimated at 40 ng/L (ppt). No Os signal was evident above background noise. The presence of any osmium would be remarkable since this element forms the very volatile osmium tetroxide ( $\text{OsO}_4$ ) and should have been removed from the sample solution during the evaporation to dryness step. Based on this spectrum, the Re mass 187 was selected for quantitation on the HR-ICPMS. The Re mass 187 was selected because of the absence of the potential interferent Os, and because the  $^{187}\text{Re}$  mass has greater abundance (62.6%) and therefore increased sensitivity compared to the  $^{185}\text{Re}$  mass (34.4%).

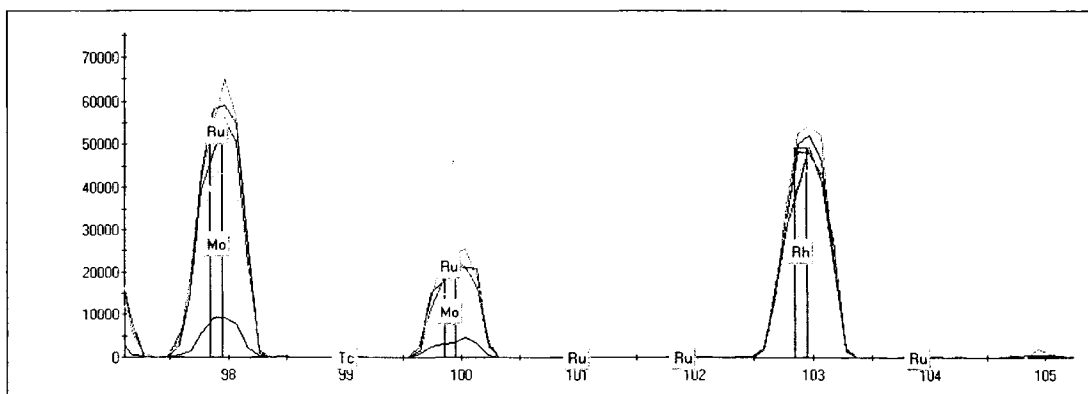


Figure 18. Q-ICPMS scan mass spectrum around the  $^{99}\text{Tc}$  mass for four powdered tuff samples and sand blank (lowest line) which are overlain in this one spectrum. Rh is a 1 ug/L (ppb) internal standard. The molybdenum concentration is estimated to be approximately 1 ug/L in the samples, and approximately 0.1 ug/L in the sand blank.

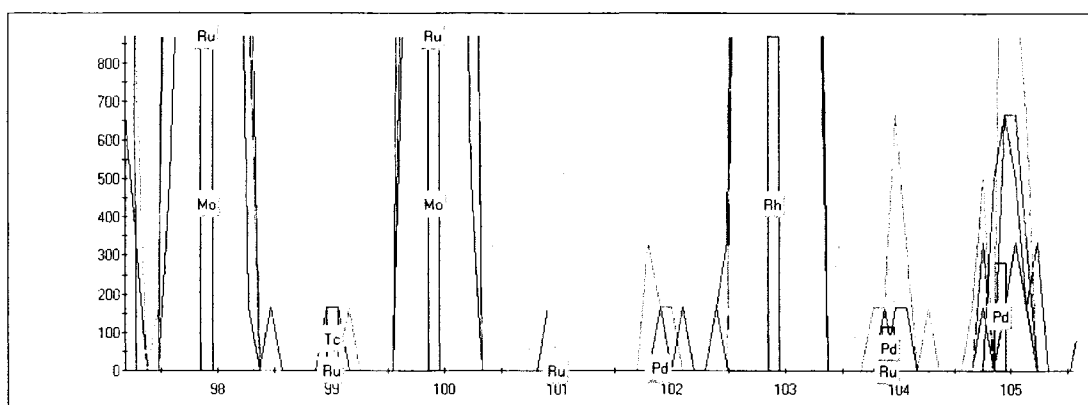


Figure 19. Same scan as Figure 18 with the scale expanded. Neither  $^{99}\text{Tc}$  nor Ru was evident above background noise; however, there appears to be Pd present at an estimated concentration of approximately 20 ng/L (ppt).

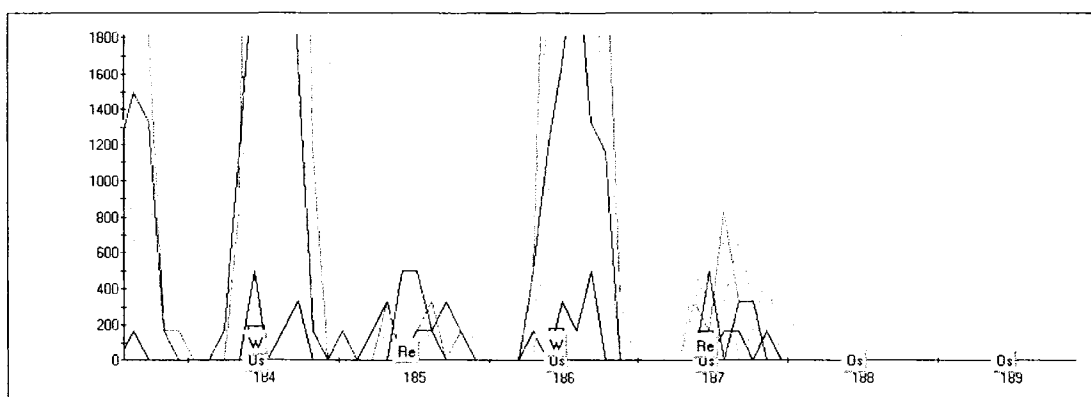


Figure 20. Q-ICPMS scan mass spectrum around the  $^{185}\text{Re}$  and  $^{187}\text{Re}$  masses for four powdered tuff samples and sand blank (lowest line) over lane in this one spectrum. The Re concentration was estimated at 40 ng/L (ppt). No Os was evident above background noise.

Table 8. Percent Mass Abundances Around Re Masses 185 and 187 (CRC, 1970).

Ion	Percent Mass Abundance					
W	30.7		28.6			
Os		0.02	1.6	1.6	13.3	16.1
Re		34.4		62.6		
Mass>	184	185	186	187	188	189

Table 9. Percent Mass Abundances Around Mass  $^{99}\text{Tc}$  (CRC, 1970)

Ion	Percent Mass Abundance							
KrO	11.6	11.5	57.0		17.3	>1	>1	
Pd					1.0		11.1	22.3
Rh						100		
Mo	24.1		9.6					
Ru		12.7	12.6	17.0	31.6			
Tc		~100						
Mass>	98	99	100	101	102	103	104	105

### HR-ICPMS Analyses Results

The HR-ICPMS was adjusted for maximum sensitivity using a 1 ug/L indium (In) standard. A calibration from 200 ng/L to 0.010 ng/L (ppt) typically had a linear 0.999 calibration coefficient for both  $^{99}\text{Tc}$  and  $^{187}\text{Re}$ . Figures 21 and 22 present typical calibration curves for  $^{99}\text{Tc}$  and  $^{187}\text{Re}$ , respectively. Dramatic memory effects were observed during initial sensitivity investigations using a peristaltic pump with Tygon type tubing, which is a phenomenon that has been reported and investigated in some detail by Richter et al., (1997), and Beals, (1992). The effect was significantly reduced by removing the peristaltic pump and Tygon tubing and employing the self aspiration of concentric micro-flow nebulizer (0.375 mL/min) using Teflon tubing. Also, the  $\text{HNO}_3$  wash solution concentration was increased from 1% to 3%  $\text{HNO}_3$  and the wash time was increased. This configuration was used for all HR-ICPMS sample analyses.

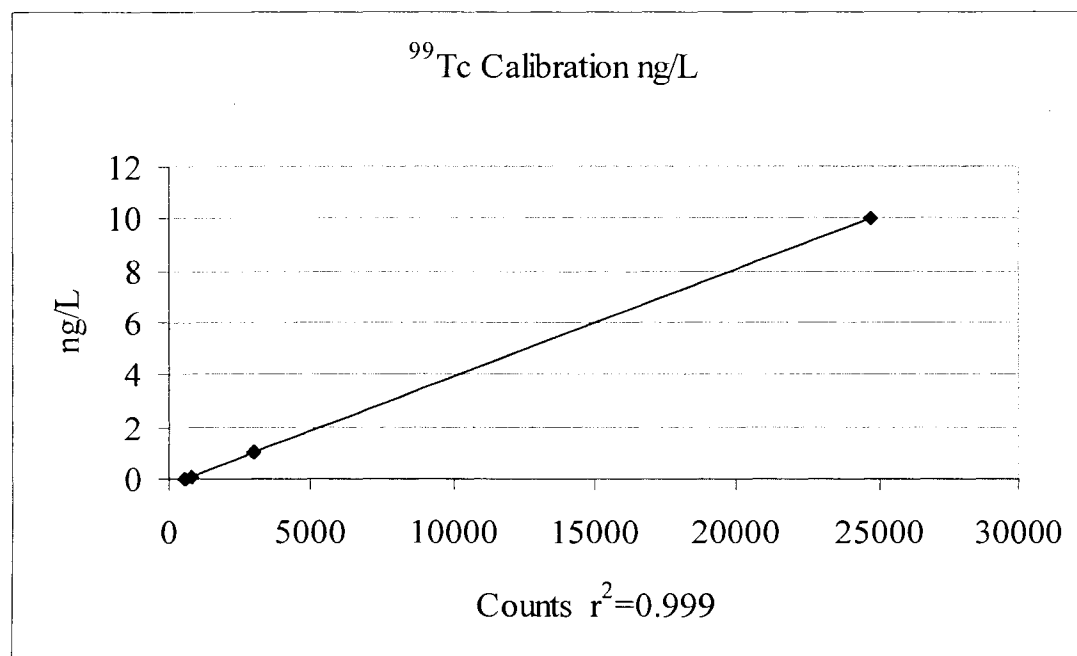


Figure 21. Typical calibration curve for  $^{99}\text{Tc}$ . The correlation coefficient is 0.999.

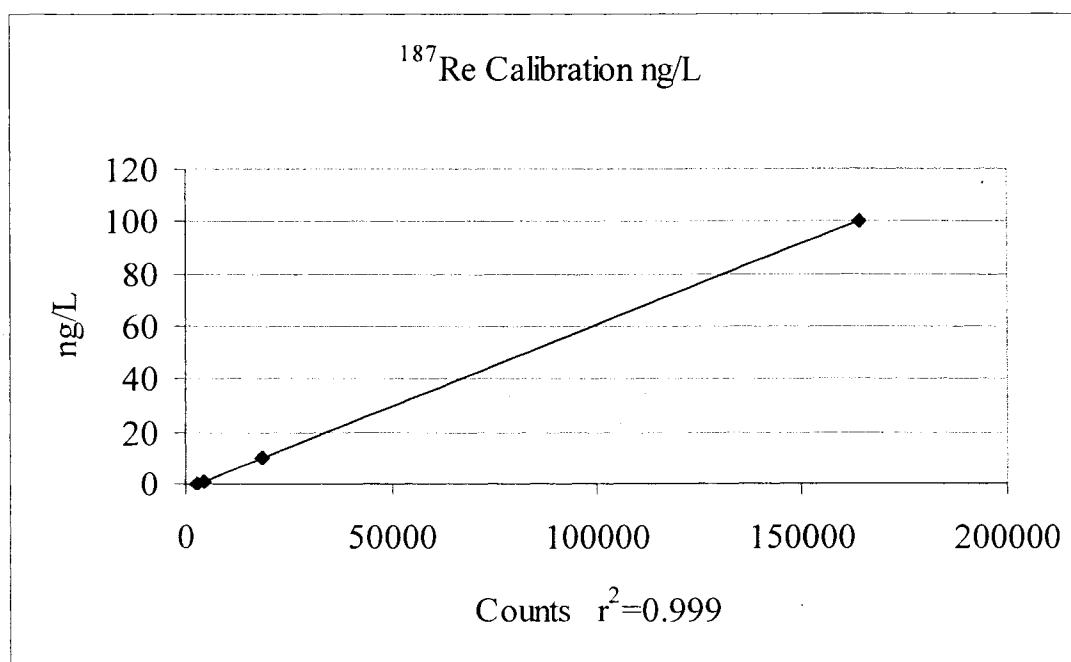


Figure 22. Typical calibration curve for <sup>187</sup>Re. The correlation coefficient is 0.999.

#### Method Detection Limits (MDL)

The MDL samples were prepared by spiking seven separate sand blanks with 50 pg/kg (ppq) <sup>99</sup>Tc and 5 ng/kg Re before sample preparation. The HR-ICPMS analysis results for the seven spiked sand blank replicates is present in Table 16. The first replicates of the seven replicates for <sup>99</sup>Tc were slightly higher than the subsequent replicates. This is due to the incomplete washout “memory” of the previous standards that were analyzed immediately prior to the MDL samples. This behavior was not mimicked by the <sup>187</sup>Re results or the Rh internal standard. The wash time was increased for subsequent analysis to minimize any <sup>99</sup>Tc memory effects. The wash solution was also changed from 1 to 3% HNO<sub>3</sub>. The standard deviation (n-1 weighting) of the seven replicates was performed and multiplied by Students’ *t* value of 3.143 to derive the



detection limit. The detection limit for  $^{99}\text{Tc}$  was also calculated using sequentially less replicates by step wise removal of the initial replicates from the calculation in order to eliminate the initial standards memory effect from the calculations. Table 16 presents the seven blank replicates as well as the subsequently calculated MDLs using fewer replicates. The percent recovery of the spike is presented in the second column, along with the average recovery. The average recovery for the seven replicates was 107%. The  $^{99}\text{Tc}$  detection limit of 33 pg/kg (ppq), calculated based on the latter five replicate sand samples, was used for reporting the sample data and is consistent with HR-ICPMS detection limits presented in Table 7 using a concentric nebulizer.

Table 16. Detection Limit Calculations for  $^{99}\text{Tc}$ , based on 50 pg/kg spiked silica sand.

Replicate	All 7 pg/kg (ppq)	Rec (%)	Last 6 pg/kg	Last 5 pg/kg	Last 4 pg/kg
1	91.8	184	-	-	-
2	67.8	136	67.8	-	-
3	58.2	116	58.2	58.2	-
4	45.4	91	45.4	45.4	45.4
5	42.2	84	42.2	42.2	42.2
6	37.3	75	37.3	37.3	37.3
7	30.4	61	30.4	30.4	30.4
SD	21.1	Avg 107	13.8	10.4	6.5
SD*3.143	66		43	33	21

Table 15 presents the MDL sample results for the seven replicate silica sand sample each spiked at 5 ng/kg. The sand was determined to contain an endogenous Re concentration of 6.5 ng/kg. The third column of Table 17 presents the MDL results corrected for the 6.5 ng/kg silica sand endogenous Re concentration. The forth column

gives the percent spike recovery for each replicate and the average MDL spike recovery. The Re MDL was determined to be 2.7 ng/kg (ppt) based on seven replicates. The average MDL spike recovery for the seven replicates was 100%. It should be noted a lower detection limit could probably be determined if another blank soil material could be selected that did not have an endogenous Re content.

Table 17. Detection Limit Calculation for  $^{187}\text{Re}$ , Based on a 5 ng/L Spike of Silica Sand.

Replicate	All 7 ng/kg (ppt)	Minus 6.5 ng/kg Sand Blank ng/kg	Spike Recovery (%)
1	12.8	6.3	126
2	11.9	5.4	109
3	12.4	6.0	119
4	10.8	4.3	86
5	11.0	4.5	91
6	10.7	4.2	84
7	10.8	4.4	88
SD	0.9	Avg 5.0	Avg 100
SD*3.143	2.7		

#### Yucca Mountain Tuff $^{99}\text{Tc}$ Sample Results

Each of the six tuff samples from Yucca Mountain muck rock area were analyzed in duplicate and the  $^{99}\text{Tc}$  results are presented in Table 18. None of the results show  $^{99}\text{Tc}$  at concentration levels greater than the detection limit of 33 pg/kg (ppq). The Ru concentration in the aqueous samples was estimated based on a single 20 ng/L (ppt) standard analyzed at the end of an analysis sequence. The Ru results for the tuff samples ranged from less than 100 pg/L to 1000 pg/L (ppq). The Ru concentration for the tuff samples 5 and 6, which were a slight orange-red color, were approximately twice that of

the lighter colored samples 1-4. Presumably the orange color of the rocks is due to iron oxides. The standard deviation of the Ru results was typically 2% RSD. Given the nature of  $\text{TcO}_4^-$  to reduce in the presence of mixed Fe(II)Fe(III) oxides makes these orange tuff samples good candidates for the possible detection of bomb pulse Tc. Unfortunately, these slightly orange tuff samples also have more Ru concentration which makes the possibility of accurate measurement of the  $^{99}\text{Tc}$  by ICPMS more difficult.

All Tc sample results were corrected for  $^{99}\text{Ru}$  interference based on the  $^{101}\text{Ru}$  signal using the ratio calculation for the correction of Ru interference on  $^{99}\text{Tc}$ , which is based on the relative mass abundance ratio of  $^{99}\text{Ru}$  (12.7%) to  $^{101}\text{Ru}$  (17.0%). No correction for Mo sample concentration was deemed necessary, because the 1 ug/L (ppb) Mo standard analyzed during an analytical sequence did not show any increase in the  $^{99}\text{Tc}$  signal.

Table 18.  $^{99}\text{Tc}$  concentrations of Powdered Yucca Mountain Tuff Samples.

	Sample pg/kg	Sample Duplicate pg/kg	Average pg/kg	RSD
Sample 1	< 33	< 33	< 33	NA
Sample 2	< 33	< 33	< 33	NA
Sample 3	< 33	< 33	< 33	NA
Sample 4	< 33	< 33	< 33	NA
Sample 5	< 33	< 33	< 33	NA
Sample 6	< 33	< 33	< 33	NA

### Yucca Mountain Tuff Re Sample Results

Each of the six tuff samples from Yucca Mountain muck rock area were analyzed for Re in duplicate and the results, along with the SD and RSD for each set of duplicate samples, are presented in Table 19. The Re results ranged from 18 to 42 ng/kg, based on the average of the duplicate samples, and the overall average result was 23 ng/L. The RSDs for the duplicate samples ranged from 0.6 to 13.2%, with an average overall RSD of 7.5%, indicating good analytical method precision between duplicate samples. The slight orange colored samples 5 and 6 showed higher Re concentrations than the lighter color samples 1-4.

Table 19. Re Concentrations of Powdered Yucca Mountain Tuff Samples.

Name	Sample ng/kg	Sample Duplicate ng/kg	Average ng/kg	SD	RSD
Sample 1	18	18	18	0.1	0.6
Sample 2	16	19	18	2.2	12.4
Sample 3	15	13	14	1.5	10.3
Sample 4	20	21	21	1.1	5.1
Sample 5	38	46	42	5.6	13.2
Sample 6	24	23	23	0.7	3.1
Average>	22	23	23	1.9	7.5

### Yucca Mt Tuff Samples Spike Recoveries for <sup>99</sup>Tc and Re

The <sup>99</sup>Tc spike recovery for the three tuff samples that were spiked are presented in Table 20. The <sup>99</sup>Tc spike recovery of the 100 pg/kg spike ranged from 32 to 54%, with an average spike recovery of 45 %. The Re spike results and percent recoveries are given

in Table 21. A 40 ng/kg Re spike was used as an analog for  $^{99}\text{Tc}$  recovery, and the recoveries ranged from 60 to 95%, with an average recovery of 77%.

Table 20.  $^{99}\text{Tc}$  Spike Recovery Results for Powdered Yucca Mountain Tuff Samples.

Sample Name	Tc Spike 100 pg/kg (ppq)	Sample pg/kg(ppq)	Difference pg/kg (ppq)	Recovery (%)
Tuff -1	130	76	54	54
Tuff -2	68	18	51	51
Tuff -5	94	62	32	32
Average				45

Table 21. Re Spike Recovery Results for Powdered Yucca Mountain Tuff Samples.

Sample Name	Re Spike 40 ng/kg (ppt)	Sample ng/kg(ppt)	Difference ng/kg (ppt)	Recovery (%)
Tuff -1	48.	18	30	76
Tuff -2	56	18	38	95
Tuff -5	66	42	24	60
Average				77

### Rhyolite SRM Results

Two 20 gram samples of Standard Reference Material (SRM) JR-2 were purchased from the Geological Survey of Japan. This SRM was selected because it is the only rhyolite reference material that has values for Re. The provisional Re concentration value supplied with the material was 23 ng/kg (ppt). The HR-ICPMS results from this study are presented in Table 22. The results yielded an average concentration of 5.4 ng/kg (ppt), with a RSD for the duplicate results of 0.2%. The average result is 23.5% of

the provisional value. The results are lower than the provisional value, but the sample preparation used in this thesis study involves heating of the sample with 1 M HNO<sub>3</sub>, and the provisional value may have been derive from a complete dissolution of the sample.

Table 22. Re HR-ICPMS Results for Geological Survey of Japan SRM JR-2 samples.

Sample Name	Sample ng/kg	Sample Duplicate ng/kg	Average ng/kg	SD	RSD
SRM JR-2	5.4	5.5	5.4	0.0	0.2

### Bomb Cavity Samples Analyses Results

#### Bomb Cavity HR-ICPMS Results

The HR-ICPMS analysis results for the four bomb cavity samples were derived from a one gram sample. The <sup>99</sup>Tc and Re results are present in Table 23. The spike recovery for the 40 ng/kg Re spike was 61.8 %, which is also a typical Re spike recovery of the powder tuff samples; however, the <sup>99</sup>Tc spike result was absent. The <sup>99</sup>Tc spike was small, at 1 ng/kg, relative to the un-spiked sample 11.8 ng/kg, and the apparent lack of recovery is probably the result of the method-instrumental variation as well as possible inhomogeneity the sample sub-portions used for the sample and spike sample.

Table 23. HR-ICPMS  $^{99}\text{Tc}$  and Re Results for Bomb Cavity Samples, units ng/kg (ppt).

Name	$^{99}\text{Tc}$ ng/kg	$^{187}\text{Re}$ ng/kg
CHE-6 T-2-A#2	9.6	2.2
CHE-3 T-4 #3	5.4	1.1
CHE-9 16-Tunnel	0.3	2.1
CHE-5 T-2-#2	11.8	1.5
CHE-5SPK	11.8	26.2

The  $^{99}\text{Tc}$  results are not inconsistent with the results for bomb cavity water samples taken from bomb cavities that were detonated below the water table and have subsequently refilled. The highest bomb cavity water results, presented in Table 6 in the Introduction section, were 3.9 ng/L and 4.1 ng/L (ppt). It should be pointed out that the bomb cavity samples were not pure glass fragments but, highly fragmented rubble that contained a significant amount of glass fragments. Also, the sample preparation involves heating the one gram of finely ground cavity sample with 50 mLs of 1 M  $\text{HNO}_3$  which is considered a leach of the material, and is not a complete dissolution of the sample or glass fragments.

#### Gamma Spectroscopy Results

The gamma spectroscopy of the four bomb cavity sample yielded results with high identification confidence ( $> 0.95\%$ ) for  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , and  $^{152}\text{Eu}$ . The gamma spectrum of the 16-tunnel sample is present below in Figure 19. The results the gamma spectroscopy were converted to activity in Bq/kg. The  $^{99}\text{Tc}$  HR-ICPMS analyses results were also converted to Bg/kg. The activity for these four analytes was then corrected for radioactive decay based on an estimate fifty years elapsed time since the bomb detonation. The results were then converted to the number of initial atoms of the

radioactive species present 50 years ago. The number of atoms of calculated initial radioactive species was divided the by the  $^{152}\text{Eu}$  number of atoms to derive the ratio. The resulting ratio of the number of atoms of  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , and  $^{152}\text{Eu}$  is presented in Table 24 and is also represented graphically in figures 24 - 27 for each of the four bomb cavity samples.

Cobalt-60 is a pure activation product of the stable  $^{59}\text{Co}$  present in the steel used to make the device. The  $^{152}\text{Eu}$  is derived from both fission and activation. Initially a small amount of  $^{152}\text{Eu}$  is produced as fission product of either,  $^{235}\text{U}$ ,  $^{238}\text{U}$ , or  $^{239}\text{Pu}$ . A small amount of  $^{151}\text{Eu}$  is also produced as a fission fragment. This  $^{151}\text{Eu}$  is then activated to  $^{152}\text{Eu}$  which adds to the small amount of  $^{152}\text{Eu}$  produced by fission (RRC, 2006).

Figure 24, tunnel-16 sample, shows the highest  $^{137}\text{Cs}/^{152}\text{Eu}$  ratio and at the same time shows the lowest  $^{99}\text{Tc}/^{152}\text{Eu}$  ratio of 0.2. This ratio is what might be expected if the sample were derived from the chimney rubble, according to the conventional thinking that from the blast is carried into the chimney rubble and  $^{137}\text{Xe}$  ( $t_{1/2}$  3.84 min) an then decays to  $^{137}\text{Cs}$ .



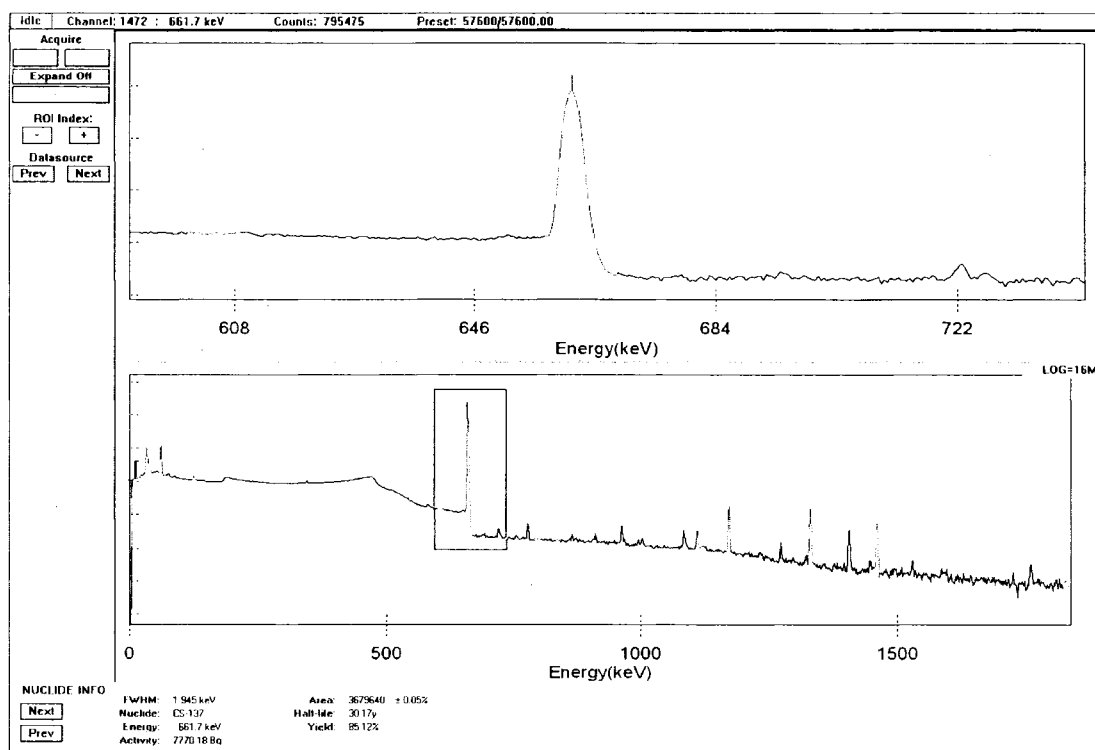


Figure 23. Gamma spectrum for 16-tunnel sample. The spectrum shows the large  $^{137}\text{Cs}$  peak, 7770 Bq, at 661.7 keV for a 21 gram sample size.

Table 24. Ratios of decay-corrected number-of-atoms ( $1 \times 10^{12}$ ) of  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ , and  $^{137}\text{Cs}$  to  $^{152}\text{Eu}$ .

Name>	16-Tunnel		T-2-A#2		T-2-#2		T-4 #3	
Geiger>	600 CPM		200 CPM		1200 CPM		CPM 600	
	# of Atoms	$^{152}\text{Eu}$ Ratio	# of Atoms	$^{152}\text{Eu}$ Ratio	# of Atoms	$^{152}\text{Eu}$ Ratio	# of Atoms	$^{152}\text{Eu}$ Ratio
$^{99}\text{Tc}$	1.5	0.2	51.5	0.9	41.8	68.0	23.5	0.7
$^{60}\text{Co}$	138.3	19.5	24.1	0.4	3.4	5.6	58.4	1.7
$^{137}\text{Cs}$	1149	162	84.0	1.5	38.4	62.4	195.0	5.7
$^{152}\text{Eu}$	7.1	1.0	56.7	1.0	0.6	1.0	34.4	1.0

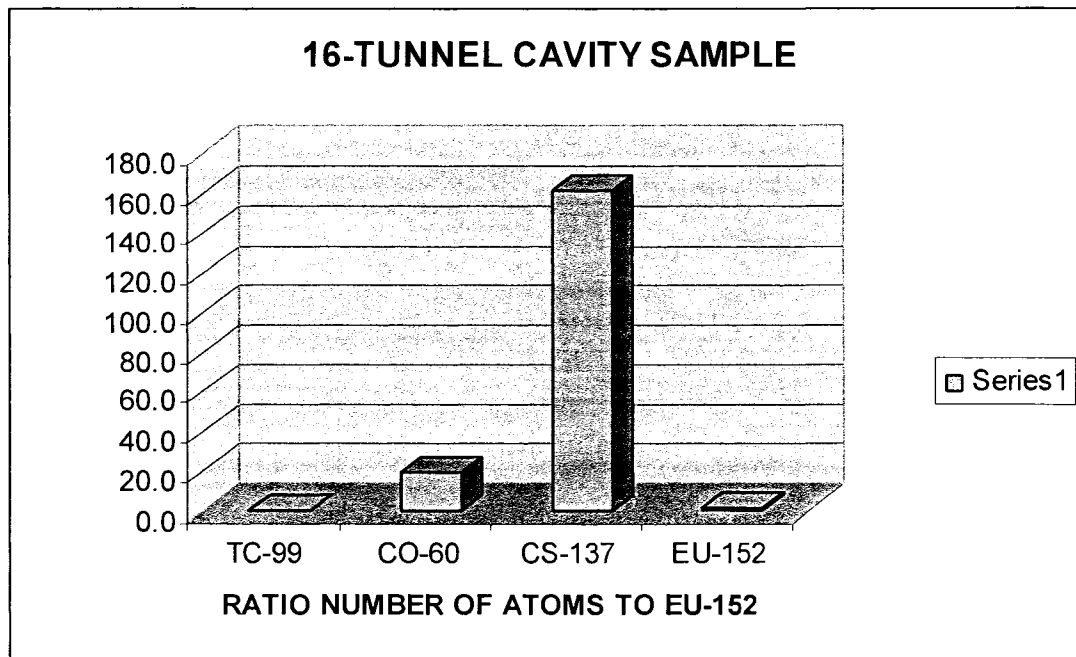


Figure 24. Ratios of  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , to  $^{152}\text{Eu}$  for 16-Tunnel bomb cavity sample.

The second bomb cavity sample T-2-A#2, Figure 25, shows similar ratios for the  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$ , in this sample the absolute amount of these radionuclides was lower and the gross counts per minute on a Geiger counter was the lowest of the four samples.

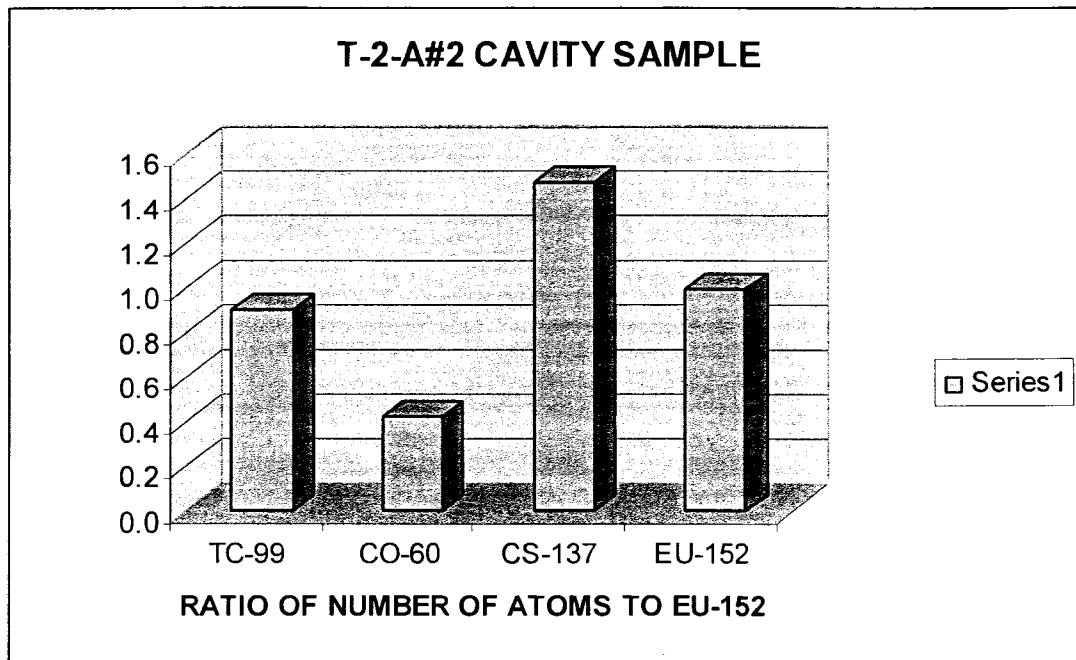


Figure 25. Ratios of  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , to  $^{152}\text{Eu}$  for T-2-A#2 bomb cavity sample.

The T-2-#2 cavity sample, Figure 26, had nearly equal  $^{152}\text{Eu}$  ratios for  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$ . This sample also had the highest gross Geiger reading of 1200 cpm. One could argue the point that the  $^{60}\text{Co}$  is rather low in this sample indicating that the sample was taken some distance from the source and  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  ratios are nearly equal. This might be the expected scenario where both  $^{137}\text{Cs}$  ( $^{137}\text{Xe}$ ), and  $^{99}\text{Tc}$ , have migrated to the chimney region.

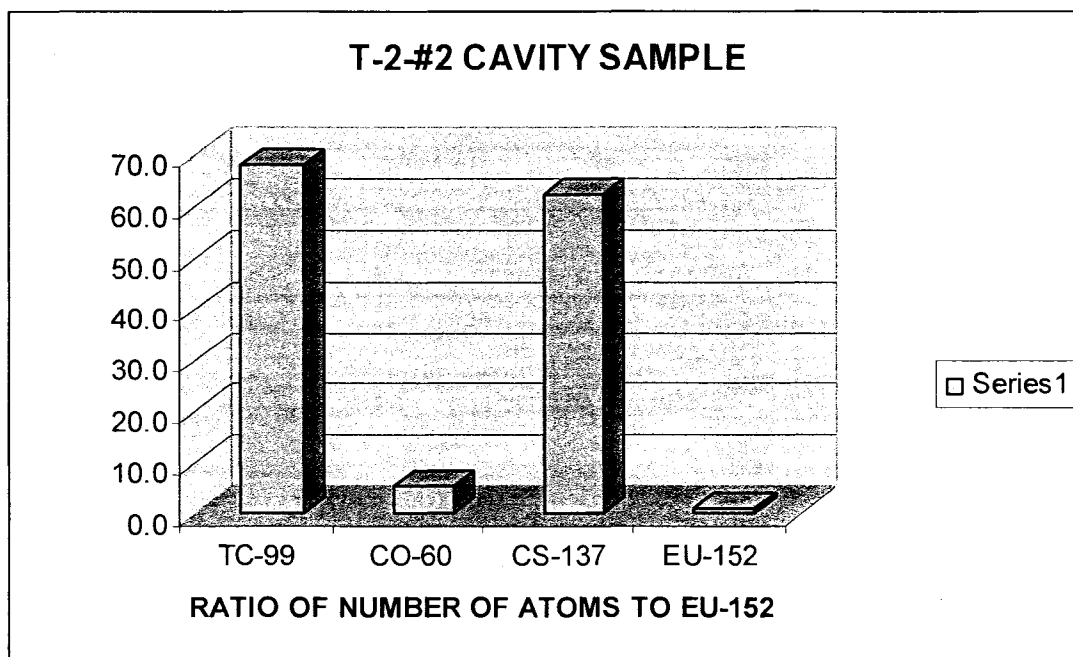


Figure 26. Ratios of  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , to  $^{152}\text{Eu}$  for T-2-#2 bomb cavity sample.

The last of four bomb cavity samples is T-4 #3, Figure 27, which shows similar  $^{152}\text{Eu}$  ratios for all the radionuclides with the  $^{99}\text{Tc}$  ratio of about 8. This sample seems to be near the bomb blast center given the number of atoms  $^{60}\text{Co}$  and  $^{152}\text{Eu}$ . This would seem to indicate that the  $^{99}\text{Tc}$  is well represented in the glass, as is the conventional thinking.

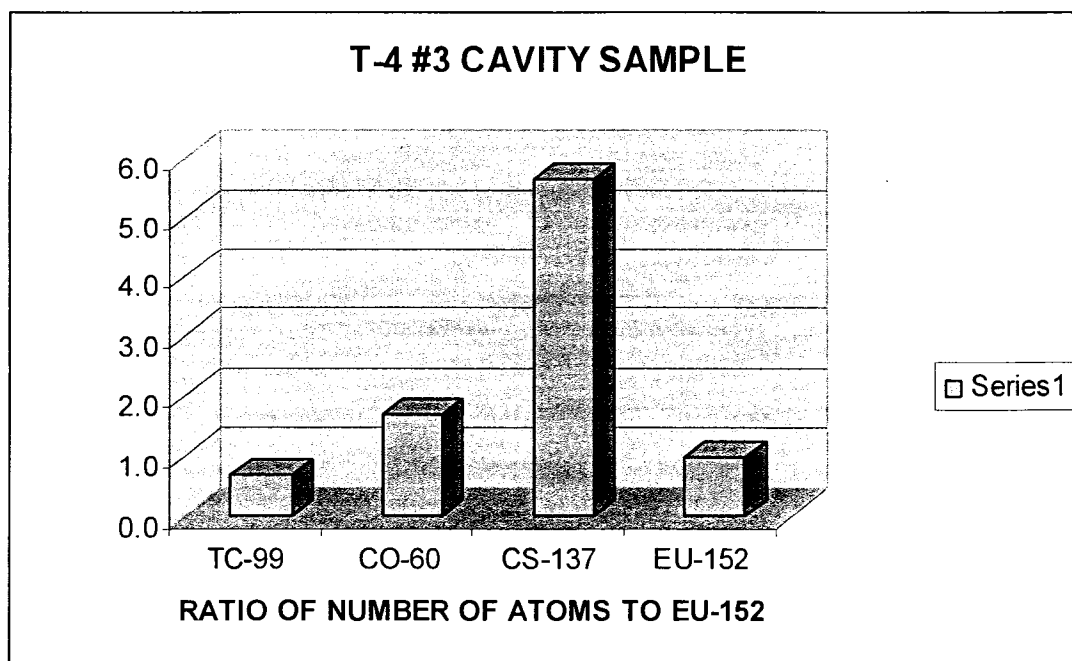


Figure 27. Ratios of  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , to  $^{152}\text{Eu}$  for T-4 #3 bomb cavity sample.

In a separate study, designated Radleg, by the International Science and Technology Center (Russia), the  $^{152}\text{Eu}$  activity ratios were determined for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  derived from gamma analysis of soil/glass fragments of an atmospheric bomb blast that occurred in Russia in 1949 (RRC, 2006). Their data shows a similar range of ratios for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  for the single site. The highest  $^{152}\text{Eu}$  ratio for  $^{137}\text{Cs}$  is about 26, which also correlates well with the highest  $^{60}\text{Co}$  ratio. This difference between the highest  $^{137}\text{Cs}$  ratio for 16-tunnel sample of 162 and the highest ratio of 26 for the Russian blast may well be due to the escape of  $^{137}\text{Xe}$  from the atmospheric fragments; whereas the  $^{137}\text{Xe}$  in an underground blast is trapped until it decays to  $^{137}\text{Cs}$ .

The highest  $^{137}\text{Cs}$  ratio for the four bomb samples analyze during the course of this thesis study was 162 for the 16-tunnel sample, which also had the highest  $^{60}\text{Co}$  ratio

indicating a relative nearness to the blast center, however there is virtually no  $^{99}\text{Tc}$  in this sample. These results might indicate the loss of  $^{99}\text{Tc}$  from the molten glass.

It is possible that  $^{99}\text{Tc}$  may, under certain conditions, become fugitive from the molten glass and migrate in to the chimney rubble. The few samples analyzed here are interesting to ponder, but inconclusive as to whether  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  may co-locate in the chimney rubble where they maybe more available to ground water leaching when compare to the glass fragments at the bottom of the bomb detonation cavity.

## CHAPTER 5

### CONCLUSION

The primary purpose of this thesis study was the investigation of the analysis of Yucca Mountain tuff samples for technetium by HR-ICPMS and secondarily the investigation of the concentration of  $^{99}\text{Tc}$  in bomb cavity samples. These studies were conducted to assist in the understanding of the Yucca Mountain tuff geochemical behavior with respect to sample preparation and analysis for  $^{99}\text{Tc}$  using HR-ICPMS. The analysis for  $^{99}\text{Tc}$  and its analog Re in tuff samples from Yucca Mountain and from rock and water samples near nuclear blast cavities is an important means of obtaining the long term transit time for anionic radionuclides through volcanic tuff. The certain determination of  $^{99}\text{Tc}$  at the level of the potential repository at Yucca would be significant in that it would indicate the fast transit time of the  $^{99}\text{Tc}$  bomb pulse through 300 meters of tuff in only fifty years. This result would have implications for the radioactive waste storage modeling and overall suitability of Yucca Mountain as a repository.

In this study the Orise/Essap AP5 method (APPENDIX II) was modified by doubling the initial starting material and adding a variation of the resin column matrix separation step based on recent studies by Tagami (2000). The AP5 method originally finished with a  $^{99}\text{Tc}$  determination using a liquid scintillation technique, which was replaced in this study by the HR-ICPMS technique. The average recovery of the 40 ng/kg Re analog

spike of 77% indicated that the modification and addition to the procedure allows for reasonable Re recoveries. The  $^{99}\text{Tc}$  spike recovery was 45.4 %; however, the spike was 100pg/kg (ppq) which is only ~3 times the MDL of 33 pg/kg (ppq), and therefore a spike at this level was not expected to be highly quantitative for a soil sample.

### Future Work

The analysis of tuff samples obtained from the Yucca Mountain muck area for  $^{99}\text{Tc}$  and this analog Re by HR-ICPMS was performed during this thesis study. Although  $^{99}\text{Tc}$  was not detected in the Yucca Mountain tuff sample, several observation were made that may prove useful to others investigating the low level determination of  $^{99}\text{Tc}$  in Yucca Mountain tuff sample or similar material. The signal for  $^{99}\text{Ru}$  during the ICPMS analysis proves to be the most difficult problem in the accurate determination of  $^{99}\text{Tc}$  by ICPMS. The second difficulty is obtaining a concentrated enough sample to allow the  $^{99}\text{Tc}$  detection by HR-ICPMS.

Information available indicates that the nominal concentration of  $^{99}\text{Tc}$  on the soil surface and immediate sub-surface maybe between 2 and 6 pg/kg. The  $^{99}\text{Tc}$  MDL achieved in this study was 33 pg/kg (ppq), therefore, at a minimum, a 12 fold concentrated sample would be required to have a signal for the hypothetical 6 pg/kg sample at two times the MDL, or 66 pg/kg (ppq). Given that the starting aliquot was 20 grams in this study with a 10 mL final volume, a 240 gram sample would require sample processing with a final volume of 10 mLs to allow for the detection of surface  $^{99}\text{Tc}$ . The use of a one kilogram sample would be better. Even further sample concentration would be required for the detection of  $^{99}\text{Tc}$  bomb pulse samples taken a depth.



The complete removal of  $^{99}\text{Ru}$  from the analytical solution containing  $^{99}\text{Tc}$  is made difficult by the formation of nitrosyl-ruthinate anion species that bind strongly to the anion exchange resin and are washed out in the final stripping solution with the  $^{99}\text{Tc}$ . Several anion exchange resin studies have been conducted in an effort to remove the  $^{99}\text{Ru}$  while still retaining the  $^{99}\text{Tc}$  (Tagami, 1997; Suh et al., 2003). The important understanding gleaned from these studies is that for samples that contain significant amounts of Ru relative to the Tc concentration, then Re is not appropriate as an analog for  $^{99}\text{Tc}$ . The data presented by (Tagami, 1997), indicates that in order to significantly reduce the amount of  $^{99}\text{Ru}$  in the sample solution, as much as 40 mLs of 2 M  $\text{HNO}_3$  wash solution must be used, and unfortunately other studies have indicated that Re will begin to be removed from the column after only 16 mL of 2 M  $\text{HNO}_3$  (Tagami, 2000). The meta stable  $^{95\text{m}}\text{Tc}$  should be used as the recovery monitor for all further studies of Yucca Mountain tuff samples, because of the extremely low amount of  $^{99}\text{Tc}$  present, if any, and the presence of a small but significant amount Ru in the tuff. The  $^{95\text{m}}\text{Tc}$  isotope unfortunately has a short half-life (61 days), and is rather expensive, as it is produced by alpha bombardment in a cyclotron, and has a significantly higher activity relative to  $^{99}\text{Tc}$ . It is important to obtain  $^{95\text{m}}\text{Tc}$  from alpha bombardment of  $^{93}\text{Nb}$  yielding  $^{95\text{m}}\text{Tc}$  through the nuclear reaction  $^{93}\text{Nb}(\alpha, 2n)^{95\text{m}}\text{Tc}$ , as this material is unlikely to have  $^{99}\text{Tc}$  contamination (Harvey, 1991, Sekine, et al., 1999; Tagami, 2003).

The use of high resolution anion exchange chromatography with fractional collection may allow for a more complete separation of  $^{99}\text{Tc}$  from  $^{99}\text{Ru}$ . Column flow conditions using 4 M  $\text{HNO}_3$  may allow for the Ru(III) species to proceed through the column first,

followed by  $\text{TcO}_4^-$  and then the nitrosyl-ruthenate species. This anion chromatography technique may warrant investigation.

In another study, the investigators (Suh et al., 2003) added potassium periodate ( $\text{KIO}_4$ ) to the sample to oxidize the nitrosyl-ruthenate species to the volatile ruthenium tetraoxide. Ethanol is then added to the solution to reduce the  $\text{Ru(IV)}$  to the plus 3 oxidation state. The sample is then separated on an anion exchange column and the  $\text{TcO}_4^-$  is retained and the  $\text{Ru(III)}$  species pass through with the column wash. This technique may allow for the complete separation of  $^{99}\text{Tc}$  from  $^{99}\text{Ru}$ , and warrants further investigation.

Several investigations using thermal chromatography have been conducted that indicate that Tc can be completely separated from Ru in the gaseous phase (Steffen & Bachmann, 1978). In one experiment using a 1 meter long, 1 cm diameter, glass column packed with quartz crystals, the column was heated at  $20^\circ\text{C}$  per min to  $900^\circ\text{C}$ , with a column flow of 3 cc min of 10%  $\text{O}_2$  ( $\text{N}_2$  90%), the  $\text{TcO}_3$  gas was separated from the Ru oxide species (Steffen & Bachmann, 1978). In a similar experiment, 150mm partial pressure of  $\text{H}_2\text{O}$  was added to the 10% oxygen gas and the  $\text{HTcO}_4$  species was conducted through the column, while the ruthenate species were reduced to a non-volatile form. In another experiment, using a quartz tube (no quartz crystals) and 10%  $\text{O}_2$ , and a much faster flow rate of 1.3 liters a minute, the volatilized  $\text{TcO}_3$  and ruthenium oxides were conducted along the column then a saturated HCL mixture was added and the column temperature reduced to  $150^\circ\text{C}$ , the  $\text{TcO}_3$  was converted to the volatile  $\text{TcO}_3\text{Cl}$  and the ruthenate species were reduced (Matschob & Bachmann, 1979). The interesting fact about the later experiment is the flow rates are very similar to the ICPMS carrier flow

rates, making the concept of direct coupling of the techniques an intriguing possibility. The column effluent could be condensed onto an aluminum (or stainless steel) plates that could later be electrothermally heated in an entrained argon-O<sub>2</sub> carrier flow connected to the ICPMS torch injector. The thermal chromatography separation of <sup>99</sup>Tc from Ru for environmental samples should be considered for future work.

The tuff sample analysis for <sup>99</sup>Tc requires only leaching with HNO<sub>3</sub> acid, not a digestion. The method employed in this study used a 1 M HNO<sub>3</sub> leach, followed by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) treatment of the supernatant solution after centrifugation and removal of the sediment/soil. In an effort to leave as much of the matrix elements behind as possible, while still extracting the <sup>99</sup>Tc, the sample, after addition of sufficient H<sub>2</sub>O to make a slurry, might be acidified to pH 2 with HNO<sub>3</sub>, and then H<sub>2</sub>O<sub>2</sub> added to the slurried sample in as little as 1 mL of 30% H<sub>2</sub>O<sub>2</sub> per 100 grams of soil. This same procedure could also be investigated using only water and 1 mL of 30% H<sub>2</sub>O<sub>2</sub> per 100 grams of soil, for samples as large as one kilogram, or perhaps even larger.

## APPENDIX I

### PERCENT MASS ABUNDENCES FOR TC AND RE REGIONS

Source: Perkin Elmer Sciex Mass Abundance Sheet March 1998, Values Verified

Against (CRC, 1970) Table of Isotopes.

The Relative Mass Abundances for the Mass Region 97 to 106.

Mass	EL	% AB	EL	% AB	EL	%AB
97			Mo	9.55		
98			Mo	24.13		
99	Tc	--			Ru	12.7
100			Mo	9.63	Ru	12.6
101					Ru	17.0
102	Pd	1.02			Ru	31.6
103			Rh	100		
104	Pd	11.14			Ru	18.7
105	Pd	22.33				
106	Pd	27.33	Cd	1.25		

The Relative Mass Abundances for the Mass Region 182 to 191.

Mass	EL	% AB	EL	% AB	EL	%AB
182			W	26.3		
183			W	14.3		
184	Os	0.02	W	30.67		
185					Re	37.4
186	Os	1.58	W	28.6		
187	Os	1.6			Re	62.6
188	Os	13.3				
189	Os	16.1				
190	Os	26.4			Pt	0.01
191			Ir	37.3		

## APPENDIX II

### ORISE/ESSAP AP5 DETERMINATION OF TECHNETIUM-99

#### PART A

#### PRINCIPLE

Solid samples are leached with dilute nitric acid. The leachates are passed through an extraction chromatographic column containing a resin (TEVA resin) which is highly specific for technetium in the pertechnetate form. The technetium is absorbed onto the extraction resin. The resin is added to a scintillation vial containing an appropriate cocktail and counted using a liquid scintillation analyzer. Water samples are treated as leachates and carried through the same procedure. All beta emitting radionuclides are effectively removed (including C-14, P-32, S-35, Sr-90, Y-90, and H-231) using TEVA resin under the conditions in this procedure. Tritium may follow technetium due to the absorption of some tritium-labeled compounds by the resin. Possible tritium interferences are eliminated by setting the technetium counting window above the maximum energy for tritium beta particles.

#### REFERENCES

1. Eichrom Industries, Inc., Analytical Procedures, "Technetium-99 in Soil", April 29, 2002.
2. L.O. Hoffman et al, Sampling of Technetium-99 in Vegetation and Soils in the Vicinity of Operating Gaseous Diffusion Plants, ORNL/TM-7386.
3. DOE Methods Compendium RP550, "Technetium-99 Analysis Using Extraction Chromatography".
4. Sullivan, L., et al., "Determination of Technetium-99 in Borehole Waters Using an Extraction Chromatographic resin", 37th Annual conference on Bioassay, Analytical and Environmental Radiochemistry, Ottawa, Canada, 1991.
5. Wyse, L.J. and Fadelil, S.K., "Alternative Techniques for the Determination of Technetium-99 in Groundwater: ICP MS and Extraction Resin", To be submitted for publication.
6. Eichrom Industries, Inc., Analytical Procedures, "Technetium-99 in Water", April 2, 2002.

## Certification Record for

### PROCEDURE AP5

#### DETERMINATION OF TECHNETIUM-99

##### CHECKPOINTS

1.	JOB HAZARD ANALYSIS (JHA)	_____	_____
2.	MSDS/HAZARDS DISCUSSED	_____	_____
3.	SAMPLE PREPARATION	_____	_____
4.	Tc LEACHING	_____	_____
5.	COLUMN PREPARATION	_____	_____
6.	EXTRUSION OF RESIN	_____	_____
7.	COUNTING PREPARATION	_____	_____
8.	FINAL CALCULATIONS	_____	_____

ANALYST SIGNATURE: \_\_\_\_\_

CERTIFIED BY: \_\_\_\_\_

DATE: \_\_\_\_\_

ANALYSIS VALUE: \_\_\_\_\_

KNOWN VALUE: \_\_\_\_\_

MEASURED/KNOWN RATIO: \_\_\_\_\_

COMMENTS: \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

## PART B

### 1.0 PURPOSE AND SCOPE

This is a procedure for the determination of technetium-99 in sediment, soil, smears, and water at environmental levels.

### 2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP5 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , 14.8 M, concentrated, reagent grade.

Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , 4 M, slowly add 135 mL 14.8 M  $\text{NH}_4\text{OH}$  to 300 mL reagent water. Dilute to 500 mL with reagent water. Mix well.

Hydrofluoric acid,  $\text{HF}$ , 28 M, concentrated, reagent grade.

Hydrofluoric acid,  $\text{HF}$ , 1 M, slowly add 18 mL 28 M  $\text{HF}$  to 400 mL water. Dilute to 500 mL with water and mix.

Hydrogen peroxide,  $\text{H}_2\text{O}_2$ , 30-35% (w/v).

Nitric acid,  $\text{HNO}_3$ , 0.01 M, slowly add 10 mL 1 M  $\text{HNO}_3$  to 900 mL water. Dilute to 1 L with reagent water and mix.

Nitric acid,  $\text{HNO}_3$ , 1 M, slowly add 64 mL 16 M  $\text{HNO}_3$  to 900 mL water. Dilute to 1 L with reagent water and mix.

Nitric acid,  $\text{HNO}_3$ , 16 M, concentrated, reagent grade.

Nitric acid (0.02 M) - Hydrofluoric acid (0.05 M) solution: Add 100 mL 1 M  $\text{HNO}_3$  to 250 mL 1 M  $\text{HF}$ . Dilute solution to 500 mL with water and mix well.

Liquid Scintillation Cocktail, Ultima Gold-XR or equivalent

HVA Resin, prepacked 2 mL columns, 100-150  $\mu\text{m}$  size.

Technetium-99, standardized solution



### 3.0 APPARATUS

Balance  
Beakers, appropriate for sample matrix  
Centrifuge  
Centrifuge tubes  
Column rack  
Column strips  
Extension funnels, 25 mL  
Filters, DM-150, 25mm, or equivalent  
Hotplate  
Liquid Scintillation Analyzer  
pH paper  
Scintillation Vials  
Watch glasses

### 4.0 PROCEDURE

#### 4.1 General Requirements

Before proceeding, you must be certified as indicated in QCPI of this manual and Section 3 of the QA Manual. See page two for a copy of the certification record.

A matrix spike must be run with each batch to determine chemical recovery for the batch (see section 6.0 for calculation). This is not a QC sample; two QC samples must be run with each batch.

#### 4.2 Water Samples

For water, measure 0.05 to 0.25 L, using a volumetric flask and pour into an appropriate size beaker. Use reagent water for a method blank. Adjust samples, blank, batch yield sample, and standard to pH of 2 using either 1 M  $\text{HNO}_3$  or 1 M  $\text{HClO}_4$ . Go to step 4.3.8. **See step 4.2 of AP5 JHA.**

#### 4.3 Soil, sediment, and smear samples

4.3.1 Weigh up to 10 g of soil, sediment, or solid material in an appropriate size beaker. Use clean sand for a method blank. Place smear in a beaker. Use a clean smear for method blank. **See step 4.3.1 of AP5 JHA.**

4.3.2 Add 50 mL of 1 M  $\text{HNO}_3$  to each beaker. **See step 4.3.2 of AP5 JHA.**

- 4.3.3 Place a watch glass on each beaker on a hot plate and heat to 80°C for 4 hours, while stirring. Add 1 M HNO<sub>3</sub> as needed to keep volume at 50 mL. **See step 4.3.3 of AP5 JHA.**
- 4.3.4 Remove each beaker from the hotplate and allow to cool.
- 4.3.5 Transfer the solution and solids to a centrifuge tube and centrifuge for approximately 10 minutes at 2000 rpm. **See step 4.3.5 of AP5 JHA.**
- 4.3.6 Decant supernatant into a 150 mL beaker.
- 4.3.7 Add 10 mL of 1 M HNO<sub>3</sub> to the centrifuge tube. Vortex, and centrifuge for 5 minutes at 2000 rpm. Add supernate to the 150 mL beaker. Discard solids to the appropriate waste stream. **See step 4.3.7 of AP5 JHA.**
- 4.3.8 Add 1-5 mL of 30% H<sub>2</sub>O<sub>2</sub> (use 1 mL per 50 mL of solution). Heat to 80°C with stirring until the effervescence and the yellow color disappears (for soils). **See step 4.3.8 of AP5 JHA.**  
  
**Note: It is imperative that all the H<sub>2</sub>O<sub>2</sub> is decomposed. If any H<sub>2</sub>O<sub>2</sub> remains, the TEVA column flow rate will decrease or even stop.**
- 4.3.9 If a dark color persists, repeat step 4.3.8, otherwise go to step 4.3.10.
- 4.3.10 Allow beakers to cool to room temperature.
- 4.3.11 Filter samples with visible solids using DM-150 filter paper. **See step 4.3.11 of AP5 JHA.**
- 4.3.12 For solid samples, adjust pH to 2 using 1 M NH<sub>4</sub>OH. **See step 4.3.12 of AP5 JHA.**

#### 4.4 Column Preparation

- 4.4.1 Place the TEVA Resin column in a column rack.
- 4.4.2 Place a beaker below each column, remove the bottom plug from each column, allowing each column to drain. **See step 4.4.2 of AP5 JHA.**
- 4.4.3 Pipette 5 mL of 0.01 M HNO<sub>3</sub> into each TEVA Resin column to condition the resin and allow to drain. **See step 4.4.2 of AP5 JHA.**

## 4.5 Te-99 column separation

4.5.1 Transfer each sample leachate from step 4.3.10 (water samples) or 4.3.12 (solid samples) to a labeled column, allow the eluent to drain, and discard to the appropriate waste stream. **See 4.5.1 of AP5 JHA.**

4.5.2 Rinse beaker with 5 mL 0.01 M  $\text{HNO}_3$ . Transfer rinse to column and allow to drain. **See 4.5.1 of AP5 JHA.**

4.5.3 Pipette 25 mL 0.02 M  $\text{HNO}_3$  - 0.05 M  $\text{HF}$  solution directly into each column, allow to drain, and discard to the appropriate waste stream. **See 4.5.3 of AP5 JHA.**

**Note: If greater sample cleanup is needed (i.e. samples which may contain high levels of natural uranium or Th-234), add up to 25 mL of 0.02 M  $\text{HNO}_3$  - 0.05 M  $\text{HF}$  solution to enhance the Te-99 purification.**

4.5.4 Pipette 5 mL 0.01 M  $\text{HNO}_3$  into each column and allow to drain. **See 4.5.4 of AP5 JHA.**

4.5.5 Transfer the resin to a liquid scintillation vial by carefully cutting the plastic column with the column snips near the bottom and pushing the resin into the vial. **See step 4.5.5 of AP5 JHA.**

4.5.6 Add 10 mL of the desired scintillation cocktail to each vial, cap, shake well, and allow the resin to settle for at least one hour before submitting for counting. **See step 4.5.6 of AP5 JHA.**

**Note: It is important to shake the vial well to completely strip all the Te from the resin.**

## 5.0 CALIBRATION

5.1 Transfer the resin from a new TEVA column to a liquid scintillation vial by carefully cutting the plastic column with the column snips near the bottom and pushing the resin into the vial. **See step 5.1 of AP5 JHA.** (JHA will be revised once the procedure is complete.)

5.2 Using a NIST traceable Te-99 standard add approximately 2000 pCi directly to the resin from the previous step. **See step 5.2 of AP5 JHA.**

- 5.3 Add 10 mL of the desired scintillation cocktail to each vial, cap, shake well, allow the resin to settle for at least one hour before submitting for counting. **See step 5.3 of AP5 JHA.**

**Note: It is important to shake the vial well to completely strip all the Tc from the resin.**

- 5.4 This efficiency standard is counted with each sample batch. The calculated efficiency and the quench indicating parameter (tSIE) are monitored to ensure that the efficiency standard does not deteriorate. If the calculated efficiency does not agree with the established value, a new efficiency standard is prepared. If the tSIE value does not agree within 20 percent of the established value, a new efficiency standard is prepared.

## 6.0 CALCULATIONS

Critical data values will be documented on standard forms maintained as critical records. The following equations define the critical data values. All data will be recorded and reduced according to these calculations.

**NOTE: The analyst and reviewer must ensure that the tSIE values for all samples in a batch agree within  $\pm 20\%$  of the tSIE values for the detector background and the efficiency standard.**

$$\text{Concentration} = \frac{G - B}{(Q \cdot I + E \cdot I)} = \text{pCi/mL}$$

$$2\sigma \text{ Error} = \frac{1.96\sqrt{(G + B) \cdot I}}{(Q \cdot I + E \cdot I)} = \text{pCi/mL}$$

$$2\sigma \text{ TPI} = \pm 1.96 \sqrt{\frac{(G + B) \cdot I}{(Q \cdot I + E \cdot I)^2} + RP^2 + RE^2 + RQ^2} = \text{pCi/mL}$$

$$\text{MDC} = \frac{3 + 1.65\sqrt{B \cdot I}}{(Q \cdot I + E \cdot I)} = \text{pCi/mL}$$

Efficiency: 
$$E = \frac{G_s - B}{E_{ACT}} = \text{cpm/pCi}$$

Yield: 
$$Y = \frac{G_{BY} - B}{E \cdot BY_{ACT}}$$

where:	B	background cpm beta
	BY <sub>ACT</sub>	pCi of Te-99 added to batch yield sample
	C	concentration in pCi/unit
	E	counting efficiency cpm/pCi
	E <sub>ACT</sub>	pCi of Te-99 added to efficiency standard
	G	sample gross cpm beta
	G <sub>s</sub>	efficiency standard gross cpm beta
	G <sub>BY</sub>	batch yield gross cpm beta
	MDC	minimum detectable concentration
	Q	quantity
	RE	1 • relative uncertainty of the efficiency
	RY	1 • relative uncertainty of the yield
	RQ	1 • relative uncertainty of the quantity
	T	time minutes
	TPI	total propagated uncertainty
	Y	chemical yield

## 7.0 RECORDS

- 7.1 Reference QA Manual for general record requirements.
- 7.2 The raw count data is saved during the weekly backup of the Liquid Scintillation Analyzer to the ORISE network disks.
- 7.3 Hard copies of assignment and calculation sheets are maintained in the archived site file. Electronic copies of assignment and calculation sheets are saved during the daily incremental backup of the network system. The following data sheets should be completed and retained:
  - Te-99 Analysis Assignment Form
  - Te-99 Lab Data Sheet
  - Te-99 Concentration and Uncertainty Report

## AP5(Rev 15) - Tc-99 ANALYSIS ASSIGNMENT FORM

Assigned To: \_\_\_\_\_ Date: \_\_\_\_\_ Batch: \_\_\_\_\_

Task #: \_\_\_\_\_ LWR #: \_\_\_\_\_ Activity Lev.: \_\_\_\_\_

Sample #'s: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

### QC REQUIRED:

BLANK	<input type="checkbox"/>			
REPLICATE	<input type="checkbox"/>	SAMPLE # _____	# Repl cates _____	
LCS	<input type="checkbox"/>	Tc99 STD # _____	QUANTITY: _____	INITIALS <input type="checkbox"/>
		Pipet: # _____	Volume (mL) _____	UNITS: _____
			Weight (g) _____	
MATRIX SPK	<input type="checkbox"/>	SAMPLE # _____		
		Tc99 STD # _____	QUANTITY: _____	<input type="checkbox"/>
			UNITS: _____	
BATCH YIELD	<input type="checkbox"/>	SAMPLE # _____		
		Tc99 STD # _____	QUANTITY: _____	<input type="checkbox"/>
			UNITS: _____	

SPECIAL INSTRUCTIONS: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

\* If Activity Level is indicated as Moderate or High perform area survey.

COMMENTS: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

## AP5(Rev 15) - Tc-99 LAB DATA SHEET

	BATCH YIELD	SAMPLE				
Sample #						
Quantity						
Units						

Sample #						
Quantity						
Units						

Sample #						
Quantity						
Units						

Sample #		
Quantity		
Units		

# AP5(Rev 15) - Technetium-99 (by batch yield) Concentration and Uncertainty Report

INPUT BY:	<div style="border: 1px solid black; padding: 2px;"> <b>Batch Yield (BY) Calculation</b>  <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY sample ID</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY sample cpm</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY Sample Quantity (SQ)</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY SQ error</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">Sample cpm</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">SQ</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">SQ error</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY pCi added</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">By pCi added error</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY Error</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">BY Relative Error</div> </div>	<div style="border: 1px solid black; padding: 2px;"> <b>Efficiency (Eff) Calculation</b>  <div style="border-bottom: 1px solid black; margin-bottom: 2px;">Eff spike cpm</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">Background cpm</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">pCi added</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">pCi added error</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">Eff (cpm/pCi)</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">Eff Error (cpm/pCi)</div> <div style="border-bottom: 1px solid black; margin-bottom: 2px;">Eff Relative Error</div> </div>
	Counting time for Eff and BY calculations (min)	

Position #	SAMPLE ID	GROSS cpm	SQ	SQ ERROR	UNITS	TIME (min)	CONC.	TPU	4.65 sigma MDC
1									
2									
3									
4									
BY									
BY Sample									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

<b>Te-99</b> Known Activity	Meas. Known      Unc.
-----------------------------------	--------------------------

QA SAMPLES CORRECT? YES [ ] NO [ ]  
 IF NO, SPECIFY REASON:

INIT \_\_\_\_\_

ANALYST REVIEW: _____	DATE: _____
REVIEWED BY: _____	DATE: _____
GIVEN TO: _____	DATE: _____



## APPENDIX III

### SAMPLE PREPARATION PROCEDURE

#### Reagents:

Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , 14.8 M, concentrated, reagent grade.

Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , 4 M, slowly add 135 mL 14.8 M  $\text{NH}_4\text{OH}$  to 300 mL reagent water. Dilute to 500 mL with reagent water. Mix well.

Hydrogen peroxide,  $\text{H}_2\text{O}_2$ , 30-35% (w/v).

Nitric acid,  $\text{HNO}_3$ , 0.16 M (1%  $\text{HNO}_3$ ), slowly add 10 mL 16 M  $\text{HNO}_3$  to 900 mL water. Dilute to 1 L

Nitric acid,  $\text{HNO}_3$ , 1 M, slowly add 64 mL 16 M  $\text{HNO}_3$  to 900 mL water. Dilute to 1 L

Nitric acid,  $\text{HNO}_3$ , 16 M, concentrated, double distilled grade.

Nitric acid (8 M) – Add 500 mL of 16 M  $\text{HNO}_3$  to 400 mL water. Dilute to 1 L

AG-1 X8 Resin, 50-100um mesh size, 2 mL columns,

#### Standards:

Technetium-99, Standard Solution NIST SRM 4288a

Rhenium

Rhodium

#### Procedure:

- 1) Weigh 20 g of soil, sediment, or solid material in a 200 mL TEFLON beaker. Use clean sand for a method blank. Also use a reagent blank without sand.
- 2) Add 50 mL of 1M  $\text{HNO}_3$  to each beaker
- 3) Place a TEFLON watch glass on each beaker on a hot plate and heat to 80°C for 4 hours, while stirring. Add 1 M  $\text{HNO}_3$  as needed to keep volume at 50 mL.
- 4) Remove each beaker from the hotplate and allow to cool.
- 5) Transfer the solution and solids to a centrifuge tube and centrifuge for approximately 10 minutes at 2000 rpm. Use 1%  $\text{HNO}_3$  to assist in all solid or liquid transfer.
- 6) Decant supernatant into a 200 mL beaker.

- 7) Add 10 mL of 1 M  $\text{HNO}_3$  to the centrifuge tube. Vortex, and centrifuge for 5 minutes at 2000 rpm. Add supernatant to the 200 mL beaker. Discard solids to the appropriate waste stream.
- 8) Add 2 mL of 30%  $\text{H}_2\text{O}_2$  (1 mL per 10 grams of soil). Heat to 80°C with stirring until the effervescence and the yellow color disappears. Note: It is imperative that all the  $\text{H}_2\text{O}_2$  is decomposed. If any  $\text{H}_2\text{O}_2$  remains, the resin column flow rate will decrease or even stop.
- 9) If a dark color persists, repeat previous  $\text{H}_2\text{O}_2$  addition step, otherwise go to following step.
- 10) Allow beakers to cool to room temperature.
- 11) Filter samples using 45mm diameter, 1  $\mu\text{m}$  pore size, glass filter.
- 12) For solid samples, adjust pH to 2 using 4 M  $\text{NH}_4\text{OH}$ , using a well rinsed pH probe.
- 13) Prepare 2 ml resin bed column, Pre-treat column by adding 5 mLs of 8 M  $\text{HNO}_3$  followed by 10 mLs of 1%  $\text{HNO}_3$ . With column stopcock, adjust column flow rate to 1 mL per minute, which is approximately 1 drop every 4 seconds. Repeat this step once.
- 14) Pass sample through column at a flow rate 1 mL per minute, wash column reservoir with 10 mLs of 1 %  $\text{HNO}_3$ . Discard column eluent.
- 15) Wash out column with 15 mLs of 2 M  $\text{HNO}_3$  followed by 10 mLs of 1%  $\text{HNO}_3$ . Discard column eluent.
- 16) Place appropriate receiving vessel under column, such as a wide mouth 30 mL polyethylene bottle. Add 5 mL of 8 M  $\text{HNO}_3$  to column, adjust flow rate to 1 mL per minute. Add 10 mL of 1%  $\text{HNO}_3$  to column. Place lid on bottle.
- 17) Transfer bottle contents to a 50 mL flat bottom beaker using 10 mL of 1%  $\text{HNO}_3$ . Heat beaker on hot plate at 80 until one drop, approximately 200  $\mu\text{L}$  remains. Do not evaporate to dryness.
- 18) Allow beaker to cool.
- 19) Add 10 mL of 1%  $\text{HNO}_3$  to beaker, wash down the sides of the beaker while doing so. Transfer beaker contents directly to a 30 mL polyethylene bottle or other suitable vessel without dilution.
- 20) Add a 0.1 mL spike of a rhodium standard to the 10 mL sample in the vessel such that the final concentration is 1  $\mu\text{g/L}$  Rh. Mix contents.

- 21) The sample is ready for analysis by ICPMS. The sample results will be 2 fold concentrated. Obtain the dry weight of the sample from a separate portion of the soil sample.

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