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Department of Energy Radioactive Waste**

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APPLICATION OF ICP-MS RADIONUCLIDE ANALYSIS TO "REAL WORLD" SAMPLES OF DEPARTMENT OF ENERGY RADIOACTIVE WASTE

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Disposal of Department of Energy (DOE) radioactive waste into repositories such as the Waste Isolation Pilot Plant (WIPP) and the Nevada Test Site (NTS) requires characterization to ensure regulatory and transportation requirements are met. Characterization is also used to collect information regarding chemistry of the waste for processing concerns. The range of characterization typically includes radionuclide activity, RCRA metals and organic compounds, process metals, and risk assessment. Recent addition of an inductively coupled plasma quadrupole mass spectrometer in a radioactive contaminated laboratory at the Oak Ridge National Laboratory (ORNL) has provided cost savings, time savings, reduced personnel exposure to radiation, and in some cases, improved accuracy over the traditional techniques for radionuclides, risk assessment and metals analysis. Application of ICP-MS to ORNL waste tank characterization has also provided the opportunity to estimate never-before-measured radionuclides and metals without increased cost. Data from analyses of ORNL waste tank sludges and supernates indicate the benefit of using this technique over counting techniques and Thermal Ionization Mass Spectrometry (TIMS) for analysis of fission products and U isotopics as well as the ability to estimate certain radionuclides and metals for the first time in these tanks.

INTRODUCTION

Oak Ridge National Laboratory radioactive waste storage tanks, like many radioactive waste storage tanks throughout the DOE complex, contain both aqueous liquids and solids in the form of an inorganic sludge. The liquid phase is primarily concentrated sodium/potassium nitrate solutions at high pH (12-13) with high beta-gamma activity from caustic soluble fission products, mostly ^{137}Cs . The sludge is typically a combination of hydroxides, carbonates, mixed- and hydrous- oxides, and various nitrate salts (the nitrates are mostly present in the interstitial liquid

associated with the solids). The radioactivity present in the sludge includes caustic insoluble fission products (mostly lanthanides and strontium), ^{137}Cs adsorbed on the solids and present in the interstitial liquid and the actinides, which account for most of the alpha activity present in the waste tanks. Tanks often contain high levels of uranium and thorium which are either added for criticality control or are from various processing projects.

Disposal of the ORNL tank waste requires processing and packaging of the sludge and supernate separately and disposal of the sludge at the WIPP and the supernate at the NTS or similar facility. Before these activities can be performed, waste characterization is needed to address waste processing options, address concerns of the performance assessment for the WIPP, evaluate characteristics with respect to the waste acceptance criteria for WIPP and NTS, address criticality concerns, and to meet DOT requirements for transporting waste. Characterization typically includes the measurement of selected fission products and actinides (selection is based upon process knowledge and waste acceptance criteria), Th, U and Pu isotopes (risk assessment), RCRA and process metals, RCRA organic compounds, selected anions, and physical measurements.

Recently, ORNL has installed an inductively coupled plasma quadrupole mass spectrometer in a radioactive contaminated laboratory and applied this setup to analysis of ORNL radioactive waste storage tank samples. Application has included the estimation of metals which have not routinely been measured (Li, Ti, rare earths, etc.) and the measurement of long-lived fission products (^{99}Tc and ^{135}Cs), rare shorter-lived fission products (^{151}Sm), and U isotopes. The use of ICP-MS for these analyses has shown advantages over traditional techniques such as counting and thermal ionization mass spectrometry (TIMS).

The challenge in applying ICP-MS to ORNL radioactive waste tank characterization is the

complexity of the samples. Unlike environmental samples or fuel process waste, the ORNL radioactive waste tanks contain a wide variety of naturally abundant and non-naturally abundant elements. Waste stored in the ORNL tanks results from the liquid low level waste system which processes waste from reactor and laboratory operations. Non-naturally abundant elements are generated from reactor operations while naturally abundant elements are generated from materials used in reactors and laboratories and from evaporation/concentration of process water. Other challenges include high salt content primarily from sodium and potassium nitrate (approximately 10^5 ppm) in the supernates and sludges and high concentrations of thorium and uranium (approximately 10^3 - 10^4 ppm) in the sludges¹. Obviously, consideration must also be given to the radiation levels of the samples during sample handling. Laboratory dose rate studies of dried sludge samples from 5 different underground storage tanks have shown beta and gamma dose rates to average 39.0 and 0.02 Rad/h/g, respectively².

This report presents the methods and resulting data from application of ICP-MS to estimation of metals, measurement of long-lived fission products and measurement of U isotopics in ORNL radioactive waste storage tanks. Emphasis will be placed on how the unique sample matrix challenges are overcome and how the data compares with traditional techniques.

PROCEDURE

Instrumentation

The ICP quadrupole mass spectrometer system is a VG Elemental Plasma Quad II Plus Turbo partially enclosed in a radiochemical hood within a radiochemical laboratory. The radiochemical hood is interfaced with the instrument at the slide valve such that only the torchbox area is enclosed within the hood and the remaining instrument electronics are separated out of the hood. This hood

design was chosen to minimize contamination of the instrument and maintain the contaminated sections of the instrument and sample preparation safely within a hood. Recent contamination surveys have shown detectable beta activity only within the torchbox area. Surveys of the electronics indicate no removable beta contamination.

An ultra high sensitivity interface was installed with the system to increase sensitivity in the mid and high mass range. This interface, known as the S-option, is an additional rotary vane pump connected to the expansion vacuum stage and upgrades the vacuum from 1.5 mbar to 0.8 mbar on this system. The S-option includes a manual switch which allows it to be turned on or off and is used to increase sensitivity and reduce noise at the mass range above 50.

Sample Dissolution

Sample dissolution for the waste tank sludges and supernates typically involves closed vessel microwave digestion using nitric acid. This sample preparation follows the SW-846 methodology and is considered to be a total digestion for most metals by regulatory agencies and yields good results for most radionuclides of interest³. A total digestion for ⁹⁹Tc analysis of sludge samples is typically not performed. Instead, a water leach of the sludge provides accurate results with less dilution of the sample as presented later in this report. Depending upon the requested analyses, samples are either submitted to further sample preparation methods (i.e. radiochemical separations, sample clean-up, etc.) or further sample dilutions for ICP-MS analysis. Typically, ICP-MS analysis dilutions performed directly after sample dissolution require a 1000-10,000 fold dilution of the supernates and 100-1000 fold dilution of the sludges to reduce the levels of sodium, uranium, and thorium to 10² ppm range. Analyses of samples with sodium, uranium, and thorium concentrations greater than 10² ppm range result in the ¹¹⁵In internal standard drift dropping below the 70% recovery

quality control limit specified by SW-846 methodology. It is suspected that this internal standard drift is due to signal suppression.

Estimation of Metals

Application of semiquantitative analysis by ICP-MS to ORNL waste tank samples has led to increased information about tank chemistry with minimal cost. Semiquantitative analysis quantifies elements based upon an instrument response curve which describes the relationship between mass and detectability using a single standard of a few elements. The advantage of this technique is that it allows quantification of elements without the need for a standard containing each element of interest. Instead, the instrument is calibrated daily using a single standard of at least 5 elements selected across the mass range (i.e. Be, Co, In, Pb, U) at a known concentration of 10-25 ppb. A response curve is generated and verified by analyzing a mixed calibration standard. Samples are then scanned for the full mass range (skipping masses 12-23, 28-40, and 80) and related to the response curve by means of an internal standard. This technique is dependent upon isotopic abundances and ionization of the elements; therefore, when using this technique to quantify an element of non-natural abundance, interference equations should be applied to sum individual isotopes of the element, or quantification of individual isotopes should be performed. Of course, the typical polyatomic interferences must also be incorporated. Quality control checks include analyzing laboratory control samples, pre-digestion matrix spike samples and method blanks, although the checks do not always contain every element of interest.

Measurement of Fission Products

The advantage of using ICP-MS over traditional counting techniques for long-lived beta emitters (half lives > 100 years) has been proven and documented in literature both experimentally

and in direct application to sample analysis^{4,6}. Table 1 presents a list of long-lived fission products of interest in waste characterization along with ⁹⁰Sr and ¹³⁷Cs for comparison. The last two columns in Table 1 give the percent of activity for each isotope relative to ⁹⁰Sr or ¹³⁷Cs. These relative percents only take into account the specific activity and the fission yield with no decay time included, but emphasize the difficulty in obtaining measurements of long-lived beta emitters in radioactive waste by counting techniques. The fission products currently being analyzed in ORNL waste tank samples by ICP-MS include ⁹⁹Tc, ¹³⁵Cs, and ¹⁵¹Sm with development underway to determine other isotopes. Where possible, radiochemical separations and sample clean-up are minimized to reduce cost and personnel exposure to radiation.

Analysis of ⁹⁹Tc in the waste tank samples rarely requires radiochemical separation. Waste supernate samples are microwave digested, sludge samples are water leached, and both are diluted 100-1000 fold for ICP-MS analysis using 2% nitric acid. After scanning the samples to ensure no interference from Ru, the samples are fully quantitated using two independent lots of Amersham ⁹⁹Tc standardized solutions following SW-846 method 6020 guidelines³. Typically, the S-option is utilized during ⁹⁹Tc analysis of the waste tank samples. Detection limits can be lowered from 0.010 Bq/mL in regular operation to 0.003 Bq/mL in S-option operation, calculating detection limits according to SW-846 methodology.

Analysis of ¹³⁵Cs requires a clean-up step prior to analysis to remove the bulk of natural barium typically present in the waste samples. This clean-up step basically involves precipitation of Ba(OH)₂ by adding concentrated ammonium hydroxide to the digested samples and removal of the precipitate via centrifugation. With the bulk of the barium precipitated, isotopes of Cs (133, 135, and 137) can be individually quantified using barium interference equations and

semiquantitative analysis. ^{135}Cs results are then verified using two methods: 1) by comparing the concentration of ^{137}Cs calculated by ICP-MS to the ^{137}Cs concentration calculated by gamma spectrometry and 2) by comparing the total Cs concentration calculated by ICP-MS to the total Cs concentration calculated by graphite furnace atomic absorption analysis. The detection limit for ^{135}Cs is 0.67 Bq/L based upon the mass detection limit for ^{133}Cs of 0.02 ug/L

The direct analysis of ^{151}Sm is complicated by the presence of non-natural Eu (151 and 153) which results from the enrichment of natural europium materials used in reactors. Because the abundances of ^{151}Eu and ^{153}Eu are unknown, correction of the ^{151}Sm results is not easily achievable, and a separation procedure is required. The separation of rare earths has long been studied using ion exchangers⁷. This philosophy is being applied at ORNL using a strong cation exchange resin prepacked in a plastic cartridge of 1mL volume. This cartridge is commercially available by Varian Sample Preparation Products (Harbor City, CA) and attaches to a 2mL syringe. The pre-packaging and design of the cartridge provides a quick and simple method for separating rare earths in radioactive samples. The resin retains rare earth elements in an ammonium nitrate/dilute nitric acid matrix, while eluting them sequentially with dilute alpha-hydroxyisobutyric acid adjusted to pH 4. Europium is eluted before samarium. The samarium fraction is then analyzed by ICP-MS using semi-quantitative analysis.

Measurement of U isotopics

Traditionally, uranium isotopic analysis of ORNL waste tanks samples has been performed by Thermal Ionization Mass Spectrometry (TIMS). However, due to the cost and time involved with the TIMS technique, ICP-MS is being implemented for this analysis. The need for isotopics analysis results from requirement to assess critically risk of the tanks as well as to know the radioactivity .

of the uranium isotopes in the tanks. Currently, U isotopic analysis on ORNL waste tank samples is being performed by both TIMS and ICP-MS to gain comparison data and to validate the use of ICP-MS on these types of samples. Sample preparation for U isotopic analysis of waste tank samples requires a chemical separation of U from Pu and the complex sample matrix. This separation is achieved using anion exchange resin and varying concentrations of nitric acid and hydrochloric acid. Analysis of the samples requires measurement of the relative amounts of ^{233}U , ^{234}U , ^{235}U , ^{236}U , and ^{238}U isotopes in the sample by both TIMS and ICP-MS. Uranium isotopic standards used for quality control checks and mass bias corrections are obtained from the New Brunswick Laboratory, U.S. DOE, Chicago Operations Office, Argonne, IL.

RESULTS AND DISCUSSION

Estimated Metals Data

Table 2 includes the list of metals that are routinely fully quantitated in the ORNL waste tank samples by a combination of ICP atomic absorption spectroscopy (ICP-AES), graphite furnace atomic absorption (GFAA), and cold vapor atomic absorption (CVAA). Also included in the table is the additional list of metals that have been reported on the ORNL waste tanks using semiquantitative analysis by ICP-MS. The selected metals reported by semiquantitative analysis are reported with $\pm 30\text{-}50\%$ error and are only included if they are not fully quantitated by another method and after careful interpretation of the results and spectra. This interpretation requires that the metals be present in the sample at 10 times the method blank concentration after subtraction of the instrument blank and are not subjected to significant interference by polyatomic elements or do not have ionization energies drastically different from those corresponding to the elements used for response calibration. This methodology is acceptable for waste characterization because it is used

as information in determining if tank chemistry will be significantly impacted by high concentrations of certain metals. Knowledge of tank chemistry is important in designing waste treatment options. The cost in obtaining the semiquantitative analysis is relatively inexpensive due to the fact that only a single scan of the sample is required without full instrument calibration. Typically, this analysis is in addition to other requested analyses of the sample, and therefore only adds an additional 1-2 hours per sample in which the majority of the time results from data interpretation.

Further data obtained by semiquantitative analysis includes a comparison between metals measured by ICP-MS semiquantitative analysis to results obtained by quantitative analysis by ICP-AES and GFAA. This comparison is shown in Figure 1 and indicates the precision of semiquantitative analysis for the metals identified. The figure shows the average percentage of ICP-MS semiquantitative results on several metals from sludge samples from six ORNL Melton Valley Storage Tanks relative to either GFAA or ICP-AES fully quantitative results which have been normalized to 100%. As seen in Figure 1, Be, Ni and Sb exceed the $\pm 50\%$ error range. The large deviation of Be may be due to the high levels of B in the waste which causes trailing of the peak and biases the Be results. Because Be is used in the response calibration, differences in ionization potential are not the likely cause of the biased result. The suspected problem with biased Ni results is the potential for removal of Ni from the Ni cones caused by pitting of the sample cone orifice by the high solid content of the sludge samples. The cause for the low recovery of Sb is likely due to a combination of the ionization potential of the element being lower than the elements used for response calibration and the fact that Sb is unstable in the matrix used for sample dilution. This comparison emphasizes the need for careful interpretation of semiquantitative analysis data and for ensuring its proper use in waste characterization.

Fission Product Data

⁹⁹Tc: Table 3 and Figure 2 show useful and interesting data obtained from analyzing ⁹⁹Tc by ICP-MS in several different ORNL waste tank samples. Table 3 shows a comparison between data obtained from a water leach of waste tank sludge samples and a microwave digestion of the samples followed by radiochemical separation using an Eichrom TEVA-Spec® column. Because of the high concentration of U and salts in the microwave digested samples, pre-concentration of ⁹⁹Tc in microwave digested samples is required using the TEVA-Spec column. Water leaching of the sludge does not result in this problem. As can be seen in Table 3, the results of the water leach compare closely with the results from the digested and pre-concentrated samples. Therefore, water leaching has been implemented as the sample dissolution step for ⁹⁹Tc analysis by ICP-MS because it allows the samples to be analyzed without separation. Ruthenium has not been observed in the mass spectra of the waste tank samples and molybdenum hydride had not shown significant effect on ⁹⁹Tc results.

Figure 2 shows the relative activities of ⁹⁹Tc measured in the sludges of several ORNL waste tanks compared to the expected activity of ⁹⁹Tc in the tanks. The expected activities are determined by using the ¹³⁷Cs activities in the waste tank samples measured by gamma spectrometry to calculate the expected activity of ⁹⁹Tc based upon the ²³⁵U mass fission yield ratio of ¹³⁷Cs to ⁹⁹Tc. With the exceptions of tank W-24, the results show that the measured activities of ⁹⁹Tc are comparable to the expected activities.

¹³⁵Cs: The ¹³⁵Cs isotope data is confirmed by also measuring ¹³⁷Cs and total Cs. Table 4 shows an example of how the ¹³⁵Cs result is validated using the calculated concentration from the measurement of ¹³⁷Cs by gamma spectrometry and the total cesium concentration measured by

GFAA. Validation of the ^{135}Cs result requires that comparison between the ^{137}Cs results and total cesium results be within $\pm 30\%$ deviation between measurement techniques, although an error of $\pm 50\%$ is associated to the ^{135}Cs result due to the fact that it is performed semiquantitatively by ICP-MS. Due to the low amounts of ^{135}Cs in the waste tank samples, $\pm 50\%$ error can still ensure that the upper limits of waste acceptance criteria are met.

^{151}Sm : Figure 3 is a spectrum of an ORNL Melton Valley Tank sludge sample showing the Sm and Eu isotope mass region. It is apparent from the spectrum that the ^{153}Eu is enriched. Natural Eu is used as a neutron absorber in the control plates within reactors and is enriched over time due to reactor processes. This enrichment amount is unknown and therefore does not allow the correction of ^{151}Sm for ^{151}Eu during ICP-MS analysis. Without correction from ^{151}Eu interference, direct measurement of mass 151 results in calculated activities for ^{151}Sm as high as 10^9 Bq/g after incorporating analysis dilutions. This value is too high to report to ensure waste acceptance criteria are met. Alternatively, the separation of Sm from Eu using the Varian cation resin cartridge can reduce this interference. Using this cartridge and 0.1M alpha-hydroxyisobutyric acid at pH 4.4, approximately 90% of the Eu is eluted with 2-3.5mL of eluent while the Sm is eluted with 3.5-5 mL of eluent, indicating incomplete separation of Eu from Sm. However, it is expected that this separation can be further improved by using two cartridges stacked in series or by pH adjustment.

U isotopic data

Uranium isotopic analysis data obtained from TIMS and ICP-MS analysis is used to calculate atom% and weight% with mass bias correction applied. Typically, total U is measured by ICP-AES because the measurement does not require the radiochemical separations and large analysis dilutions involved with ICP-MS and TIMS. Therefore, the weight % results obtained by TIMS and ICP-MS

is used with the total U result for ICP-AES to determine activities of ^{233}U , ^{234}U , ^{235}U , ^{236}U and ^{238}U . Criticality risk assessment involves the calculation of denature ratios (i.e. $^{238}\text{U}/^{235}\text{U}$ fissile equivalent mass). These ratios are calculated in various ways at ORNL, however, the standard equation requires that: $^{238}\text{U}/(1.35 * ^{233}\text{U} + ^{235}\text{U})$ must be < 110 . This equation utilizes the weight percent of the isotopes.

Figures 4 and 5 show the comparison between ICP-MS and TIMS data for atom percent measurements of ^{233}U and ^{235}U on samples from five ORNL Old Hydrofracture Storage Tanks. With the exception of one tank, the results compare within 2% deviation. Both techniques are currently being employed at ORNL to obtain historically consistent U isotopic data between TIMS and ICP-MS. Relative cost and time per waste tank sample is \$1700 and 14 hours for TIMS and \$700 and 6 hours for ICP-MS. Due to the cost and time comparison, ICP-MS is expected to become the sole technique for U isotopics of ORNL waste tank samples in the near future.

CONCLUSIONS

Application of ICP-MS to ORNL waste tank samples has demonstrated the ability of this technique to perform analyses of fission products and uranium isotopics with reliability, lower cost, and quicker turn-around time in comparison to traditional techniques. In addition, the use of ICP-MS for estimation of non-routinely requested elements has provided more information on tank chemistry useful in waste processing design without a significant increase in cost. Other applications of ICP-MS to ORNL waste tank samples are in development and include other actinide analyses (^{237}Np , ^{252}Cf and isotopes of Am, Cm, Pu), additional fission product measurements (^{129}I , ^{107}Pd , etc.), and the addition of ion chromatography to the instrument for speciation measurements.

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Table 1 Long-Lived Fission Products

fission product	$t_{1/2}$ (year)	β^- max. (KeV)	σ_f (barns)	^{235}U fission yield (%)	% of ^{137}Cs	% of ^{90}Sr
^{90}Sr	29.1	546	0.014	5.8	97.1	-
^{137}Cs	30.2	514	0.11	6.19	-	103
^{79}Se	65000	160	unknown	0.044	0.00033	0.00034
^{91}Zr	1500000	60	1	6.37	0.00207	0.00213
^{94}Nb	20000	473	130	6.5	0.158	0.163
^{99}Tc	213000	292	20	6.1	0.0139	0.0144
^{107}Pd	6500000	40	unknown	0.145	0.00001	0.00001
^{129}I	15700000	150	20	0.75	0.00002	0.00002
^{134}Cs	2300000	210	8.7	6.32	0.00134	0.00138
^{151}Sm	90	76	15200	0.417	2.26	2.32

Table 2 Reported Metals List

Metals by ICP-AES	Metals by GFAA/CVAA	Metals by ICP-MS
Be B Na Mg Al Si P K Ca V Cr Mn Fe Co Ni Cu Zn Sr Ag Cd Ba Th U	As Se Sb Hg Tl Pb	Li Ti Ga Rb Sr Nb Mo Tc Sn Te I Cs W Bi

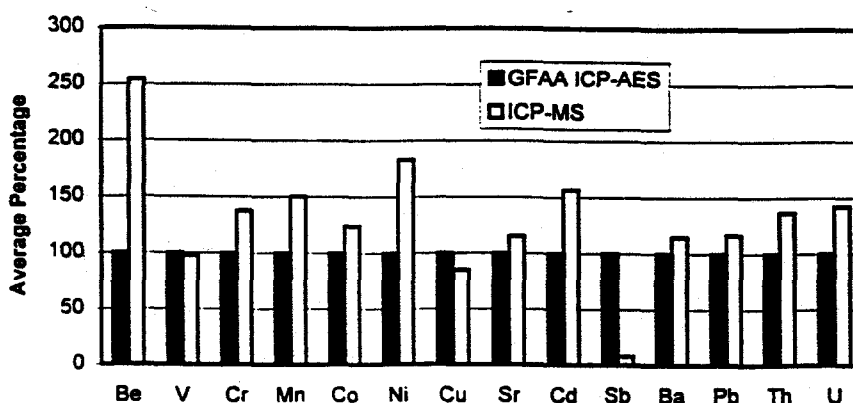
Table 3 ⁹⁹Tc Water Leach Vs. Microwave Digestion/TEVA Method

Tank	Activity (Bq/g)		Difference (%)
	Water leaches	Acid digestions	
W-28	123	121	2
W-24	448	464	3
W-25	102	101	0
W-26	1161	1087	7
W-27	87	83	5

Table 4 Example of ¹³⁵Cs ICP-MS Analysis Confirmation Using Gamma Spectrometry and GFAA

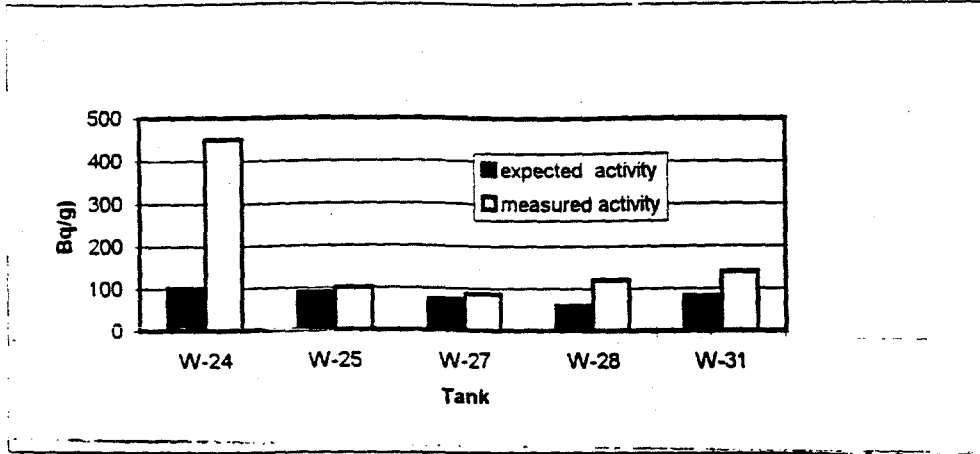
Tank	¹³⁵ Cs (ICP-MS)	¹³⁷ Cs (ICP-MS)	¹³⁷ Cs (gamma spectrometry)	% Diff.	Total Cs (ICP-MS)	Total Cs (GFAA)	% Diff.
W-24 sludge	<0.02	0.171	0.165	4%	0.777	0.900	-15%
W-26 sludge	0.082	0.258	0.276	-7%	1.26	1.53	-19%
W-23 supernate	0.172	0.264	0.340	-25%	1.41	NA	NA

Figure 1: Comparison of ICP-MS Semiquantitative Results to ICP-AES/GFAA Results



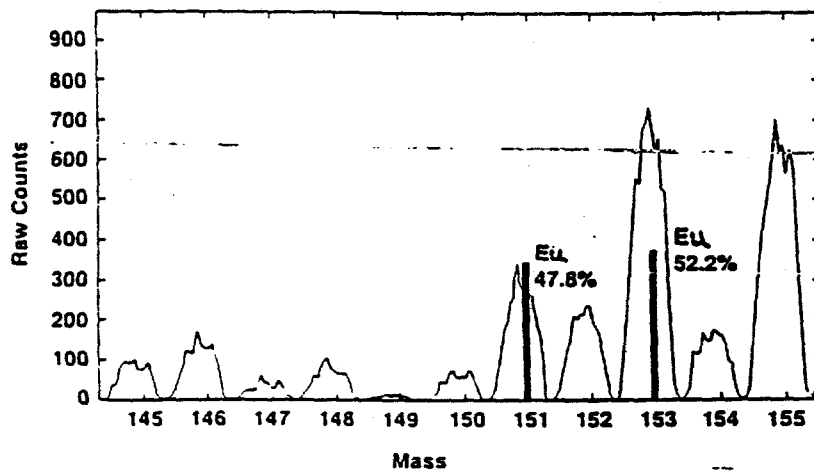
Average Percentage based upon results from 6 ORNL Melton Valley Storage Tank sludge samples, normalizing ICP-AES and GFAA results to 100.

Figure 2: Expected Vs. Measured Tc-99 activity in Melton Valley Storage Tank Sludges



*Based upon mass fission yield ratio of Cs-137 to Tc-99

Figure 3: ICP-MS Spectrum of ORNL Melton Valley Storage Tank Sludge



Spectrum shows the presence of non-naturally abundant Eu which interferes with the measurement of ¹⁵¹Sm

Figure 4: Comparison of U-233 ICP-MS results to TIMS results in ORNL Old Hydrofracture Tank Supernate

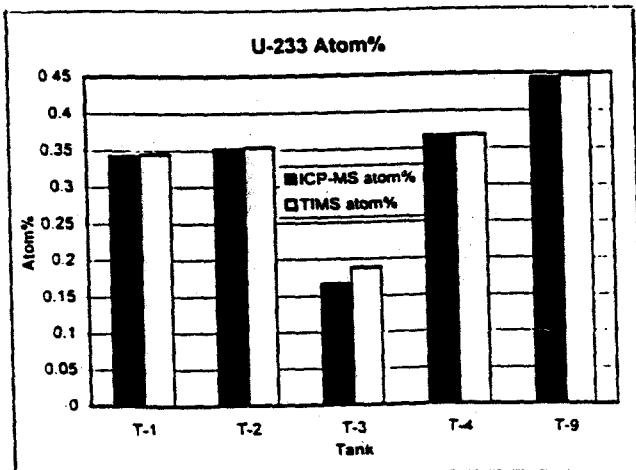


Figure 5: Comparison of U-235 ICP-MS results to TIMS in ORNL Old Hydrofracture Tank Supernate

