

Characterization of Selected Waste Tanks from the Active LLLW System

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Sampling Radioactive Waste Tanks

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ACRONYMS AND INITIALISMS

ALARA	As Low As Reasonably Achievable
CAO	Carlsbad Area Office
CASD	Chemical and Analytical Sciences Division
CVAA	Cold Vapor Atomic Absorption
DQO	Data Quality Objective
EPA	Environmental Protection Agency
GC/MS	Gas Chromatography/Mass Spectrometry
GC	Gas Chromatography
GFAA	Graphite Furnace Atomic Absorption
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IDL	Instrument Detection Limit
LCS	Laboratory Control Sample
LLLW	Liquid Low-Level Waste
LMER	Lockheed Martin Energy Research, Inc.
LMES	Lockheed Martin Energy Systems, Inc.
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MVST	Melton Valley Storage Tanks
NHVOA	Nonhalogenated Volatile Organic Analysis
NTS	Nevada Test Site
ORNL	Oak Ridge National Laboratory
PCB	Polychlorinated Biphenyls
QA	Quality Assurance
QAPP	Quality Assurance Program Plan for Waste Isolation Pilot Plant
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RMAL	Radioactive Materials Analytical Laboratory (Building 2026)
SVOA	Semivolatile Organic Analysis
TC	Total Carbon
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
TIC	Tentatively Identified Compounds
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TRU	Transuranic
TWCP	Transuranic Waste Characterization Program
VOA	Volatile Organic Analysis
WIPP	Waste Isolation Pilot Plant

ABSTRACT

From September 1989 through January of 1990, there was a major effort to sample and analyze the Active Liquid Low-Level Waste (LLLW) tanks at ORNL which include the Melton Valley Storage Tanks (MVST) and the Bethel Valley Evaporator Service Tanks (BVEST). The purpose of this report is to summarize additional analytical data collected from some of the active waste tanks from November 1993 through February 1996. The analytical data for this report were collected for several unrelated projects which had different data requirements. The overall analyte list was similar for these projects and the level of quality assurance was the same for all work reported. The new data includes isotopic ratios for uranium and plutonium and an evaluation of the denature ratios to address criticality concerns. Also, radionuclides not previously measured in these waste tanks, including ^{99}Tc and ^{237}Np , are provided in this report.

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1.0 INTRODUCTION

The Active Liquid Low Level Waste (LLLW) system consists of the waste tanks summarized in Table 1.1. From September 1989 through January of 1990 there was a major effort to sample and analyze these waste tanks which is described by Sears¹ et.al. Some earlier work, in 1985 by Peretz² et.al., discussed mostly radiochemical data and provided some very limited inorganic data. The purpose of this report is to summarize new analytical data collected from some of the active waste tanks from November 1993 through February 1996. The supernate and sludge from BVEST tank W-22 was sampled in the fall of 1994 and characterized by the Radioactive Materials Analytical Laboratory (RMAL) at ORNL. The data from tank W-22 are well documented in a recent Sears³ report and not discussed here. The samples analyzed and reported in this document were not taken as part of a planned comprehensive characterization of the LLLW system. The samples were collected at different times with different analytical requirements. Therefore, the set of measured parameters may vary some from tank to tank. The level of quality assurance approximates that required for regulatory measurements with the understanding that sample size requirements are reduced and modifications to reduce sample handling are required for radiation dose considerations (ALARA). Also, some procedure modifications are required to handle matrix interference problems. Deviations from procedures or other sample problems are documented in the data files located in the RMAL. The regulatory holding time requirements for mercury and organic analyses were complied with unless noted differently in the data tables.

The previous analytical work done on the liquid and sludge samples listed in Table 1.1 did not specifically address criticality concerns. There was limited radiochemical data on ²³³U, ²³⁵U and ²³⁹Pu; the data reported was taken from gross screening measurements. The past data for fissile actinides in these waste tanks had relatively large analytical errors and should be used with caution. The new analytical data for fissile isotopes in this report are based on more precise and accurate techniques. The uranium and

plutonium were

Table 1.1. Summary of Active LLLW System

Tank	Previous Data Available for Supernatant	Previous Data Available for Sludge	Data Presented in this report	
			Liquid	Sludge
C-1 (HLW)	none	none		
C-2 (HLW)	none	none		
W-21 (PWTP)	Ref. 1	Ref. 1,2		✓
W-22 (BVST)	Ref. 3	Ref. 2,3		
W-23 (LLW)	Ref. 1,2	Ref. 1,2		✓
W-24	Ref. 1,2	Ref. 1,2	✓	
W-25	Ref. 1,2	Ref. 1,2	✓	✓
W-26	Ref. 1,2	Ref. 1,2	✓	
W-27	Ref. 1,2	Ref. 1,2	✓	
W-28	Ref. 1,2	Ref. 1,2	✓	
W-29	Ref. 1,2	Ref. 2		
W-30	Ref. 1,2	Ref. 2		
W-31	Ref. 1	Ref. 1,2	✓	

each chemically separated from the waste matrix and isotopic ratios were determined by mass spectrometry. The mass spectrometry data gives detailed and accurate information on the major fissile isotopes present. However, these isotopic ratio measurements on the sludge do not represent the average isotopic ratios across the complete waste tank sludge present. The isotopic data for each liquid sample should be more representative of the overall supernate present than comparable measurements for the sludge. Based upon physical observations, the tank sludge tends to be segregated into vertical layers which indicates minimal mixing of the sludge material as it was added to the tank. Due to limited access to the tanks, there is no analytical data available to evaluate segregation horizontally across the tank.

An inventory of radioactive liquid wastes and sludges in the tanks is shown in Table 1.2 and includes the liquid volume estimates through March 1996. The volume data⁴ is based on estimates by the Chemical Technology Division (CTD).

Table 1.2. Inventory of Radioactive Liquid Wastes and Sludges in Storage Tanks

Tank	Total Waste Volume		Sludge Volume		Supernate Volume	
	(gal)	(L)	(gal)	(L)	(gal)	(L)
W-21	21150	80100	6100	23100	15100	57100
W-22	15390	58300	6800	25700	8590	32500
W-23	20190	76400	16400	62100	3790	14300
W-24	22330	84500	13200	50000	9130	34600
W-25	44130	167000	23400	88600	20730	78500
W-26	44100	167000	15100	57200	29000	110000
W-27	44630	168000	17700	67000	26900	102000
W-28	43810	166000	3800	14400	40000	151000
W-29	41600	157000	11000	41600	30600	116000
W-30	23380	88500	11000	41600	12400	46900
W-31	43860	166000	6400	24200	37500	142000

2.0 SAMPLING AND ANALYSIS

2.1 Sample Collection Activities

A detailed description on the background, operation of the LLLW system, and the sample collection techniques has been presented in past reports and will not be discussed here (see Sections 2 and 3 of Reference 1). The staff from the Liquid and Gaseous Waste Operations (LGWO) provided all sample collection support and delivered the samples to the analytical laboratory. A good description of the sampling procedures is provided in Appendix E of Reference 1; a current copy of these procedures is available from the LGWO group. The paperwork for chain-of-custody was prepared and maintained for each sample collected.

2.2 Analytical Methodology

The information and data collected from these studies are used to support various activities. The activities include demonstration of regulatory compliance, measurements to support future processing options, and to meet data needs for risk assessments and other safety related assessments such as criticality. Standardized analytical procedures are used to the extent possible to ensure broad acceptance of the data generated. Unless stated otherwise, the U. S. Environmental Protection Agency (EPA) methods are used for the analyses for constituents listed as hazardous under the Resource Conservation and Recovery Act (RCRA), which includes all the inorganic and organic measurements presented in this report. In general the EPA Guidance Manual, *Test Methods for Evaluating Solid Waste*⁵ (SW-846), is used for inorganic and organic methods. Some modifications of the standard procedures are necessary to handle the high radiation levels and high salt/solids content. Frequently, procedure modifications are required to generate valid data, these changes were usually needed to correct for matrix related interferences. All deviations from the standard procedures are documented in the raw data files and can be provided upon request to data users.

2.21 Sample Preparation

The aqueous supernate samples from the MVSTs were filtered or centrifuged to remove suspended particles. The clarified liquids were then digested by the SW-846 Method 3015, *Microwave Assisted Acid Digestion of Aqueous Samples and Extracts*. This sample preparation for aqueous samples was then used for all subsequent metal analyses by ICP-AES and GFAA, and most of the radiochemical analyses. Based

upon results from a collaborative study⁶ with Argonne National Laboratory - East (ANL-E), Method 3015/3051 demonstrated excellent recovery for mercury. The Method 3015 was also used to prepare tank samples for mercury determination.

The primary method for digesting the MVST sludge samples was SW-846 Method 3051, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*. This sample preparation is considered to be a total digestion for metals and radionuclides by regulatory agencies and is good for most metals and radionuclides of interest. This digestion gave poor performance on two of the metals of interest, silver and silicon. Although nitric acid is excellent for dissolving silver compounds, there is usually enough chloride present in waste samples to form an insoluble silver chloride (AgCl) precipitate. If the chloride concentration is increased sufficiently, a silver chloride complex (AgCl_3^{-2}) forms which is soluble in an aqueous environment. Good matrix spike recovery and valid data for silver was obtained using a separate sample digestion as discussed below.

If the total silicon content in the sludge must be known to develop waste treatment options such as vitrification, another sample digestion is required. A simple nitric acid treatment will not dissolve most siliceous materials. The SW-846 Method 3052, *Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices*, provides the necessary digestion chemistry to yield good silicon data. Sludge samples were prepared for measurement of total silicon, by taking approximately 0.5 g of sludge and mixing with 7 mL of concentrated nitric acid and 3 mL of hydrofluoric acid in a fluorocarbon microwave vessel. The samples were digested for 10 minutes at 95% full power (570 watts) and then cooled to room temperature. The acid solution was then treated with excess boric acid and heated to 80°C for ten minutes to complex any free fluoride. This digestion mixture is cooled, filtered into a 50 mL volumetric flask, and diluted to volume with ASTM Type II water. Care must be exercised to ensure the digestion solution is cooled to room temperature prior to opening the sealed microwave vessel or there may be a significant loss of the volatile SiF_4 . The free fluoride must be removed to protect the sample introduction system to the ICP-AES. This sample digestion with hydrofluoric acid should not be used for radiochemical measurements, especially for measurement of lanthanides or actinides.

The metal and radionuclide data presented in this report under the heading “ HNO_3 ” is based upon a Method

3051 digestion with approximately a 0.5 gram sludge sample and 10 mL of concentrated nitric acid. After the microwave digestion is completed and the solution cooled to room temperature, the sample is filtered into a volumetric flask and diluted to 50 mL with ASTM Type II water or better. For data listed under the heading “HNO₃-HCl”, samples were digested in a similar manner except the 10 mL of nitric acid is replaced with 6 mL of concentrated nitric acid plus 4 mL of concentrated hydrochloric acid. Any residue remaining after the nitric acid or nitric-hydrochloric acid digestion is mostly SiO₂. Both the acid digestion methods along with a water wash of the sludge are presented in the data tables for comparison of the metal and selected radiochemical results.

2.22 Metal Analysis

Three analytical methods were used to determine all of the metals included in this report. Most of the metals are first determined by SW-846 Method 6010A, *Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)*. There are several elements of interest for which the ICP-AES has insufficient detection limits, and these elements must be determined by Method 7000A, *Atomic Absorption Methods*. For the RMAL, a Graphite Furnace Atomic Absorption (GFAA) Spectrometer was used for elements that require better sensitivity. The elements that usually required GFAA were antimony (Method 7041), arsenic (Method 7060A), lead (Method 7421), selenium (Method 7740), and thallium (Method 7841). All the mercury measurements are done by either Method 7470A, *Mercury in Liquid Waste (Manual Cold-Vapor Technique)*, or Method 7471A, *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)*. The samples, discussed in this report, were prepared for mercury analysis by the microwave technique discussed in section 2.21, the sample preparation specified in the mercury methods (7470A and 7471A) were not used.

The level of radioactivity in most LLLW tank samples required that the analytical systems used for metal measurements be modified for operation in a chemical hood or glove box. These custom instrument configurations are necessary for contamination control and worker safety. Both an ICP-AES system and a GFAA system can generate dry, dusty particles which are difficult to contain and are highly hazardous when radioactive. A detailed description of the RMAL setup for these instruments are given in Appendix B of Reference 1.

The instrument detection limits (IDL) for various metals with undiluted aqueous samples are listed in Tables 3.1 and 3.2. For sludge samples these detection limits must be increased by a factor that represents the dilution that results from the sample preparation. For most sludge samples, a 0.5 g sample was diluted to 50 mL, which results in a 100 fold dilution.

The analytical error for the metal measurements depends upon the analytical method, the concentration level, and the chemical matrix. ICP-AES is a multi-element measurement technique that is designed for the best average performance for all elements analyzed, but the technique is not optimized for any single element. The sample introduction system for ICP instruments adds additional variability due to changes in sample density, viscosity, and solids content between samples and/or calibration standards. Overall, the expected analytical error for ICP measurements range from $\pm 4-6\%$ at concentrations above 10 times the detection limit to $\pm 20-50\%$ near the detection limit. These error estimates are typical for both ICP-AES and ICP-MS measurements.

For GFAA measurements the system is optimized on a per element basis and usually gives lower detection limits and better precision. The expected analytical error for GFAA measurements range from 3-5% for concentrations greater than 10 times the detection limit to 20-40% near the detection limit. One advantage of GFAA analysis is that the measurements are normally well above the method's detection limits. The mercury measurements were done by Cold Vapor Atomic Absorption (CVAA), which is very selective and sensitive for mercury. The analytical errors for CVAA measurements are similar to GFAA work.

2.23 Anion Analysis

The determination of anions was needed for the development of process treatment options, provided information needed to explain the distribution and chemical behaviors observed in the waste tanks, and was needed to calculate the mass and charge balance which helps ensure the major chemical constituents have been identified in the waste. The common inorganic anions; including fluoride, chloride, bromide, phosphate, nitrate, nitrite, and sulfate; are measured by ion chromatography (IC) with a Dionex Model 4500i system. The ion chromatography system was configured such that the components that come into contact with radioactivity were isolated in a radiochemical hood for contamination control.

From past observations, the anionic contribution to both the mass and charge balance is dominated by the nitrate in the supernate and sludge found in the active LLLW system. There are many other anions present in the waste, some which are measured directly by ion chromatography and others which can be estimated from the metal data such as chromate, dichromate, permanganate, and others. The carbonate is estimated from the total inorganic carbon measurement.

The supernatant samples were analyzed directly by ion chromatography after an appropriate dilution with ASTM Type II water. Accounting for the mass and charge balance with aqueous samples requires less assumptions about the solution chemistry than the precipitation chemistry in the sludge samples. For aqueous samples the balance checks should agree within the analytical error (approximately $\pm 10\%$) of the measurements. A large fraction of the sludge found in the LLLW system consists of mixed oxides and hydrated hydroxides (heavy metals and actinides) along with insoluble carbonates (calcium carbonate, etc.). The precipitation chemistry of the sludge complicates the measurements of total anions and makes estimates for the mass and charge balance more difficult. The preferable anion measurements are done on aqueous solutions with little sample pretreatment. Analytical techniques such as x-ray fluorescence (XRF) and x-ray diffraction (XRD) are useful for solid samples but are limited to total element measurements (total sulfur vs. sulfate, total phosphorous vs. phosphate) or only provide qualitative information (identification by crystal structure). For this report, the sludge anion data represents the sum of the anions in the interstitial liquid and the water soluble anions from the solids. The sludge samples were prepared by adding approximately 1 gram of sludge to 10 mL of ASTM Type II water, mixing for several minutes at room temperature on a vortex mixer, and separating the solids. The resulting solution was analyzed by ion chromatography and the anion concentration was normalized back to the wet weight of the sludge.

For simple water samples, without complex chemical matrix problems, the expected analytical error for ion chromatography measurements ranges from 3-5% for concentration above 10 times the detection limits to 20-40% near the detection limit. The measurement of anions present at concentration much lower ($< 1/25$) than other anionic species present may increase the overall error of the measurement.

2.24 Radiochemical Analysis

The only standard radiochemical methods useful for radioactive waste characterization are EPA Method 600/900.0, *Gross Alpha and Beta Radioactivity in Drinking Water*, and EPA Method 600/901.1: *Gamma Emitting Radionuclides in Drinking Water*. The EPA Method 600/905.0, *Radioactive Strontium in Drinking Water*, gave poor performance with the chemical matrix found in ORNL LLLW supernatant and sludge samples. Other than the gross alpha/beta and the gamma spectral measurements, all of the radionuclide measurements were done with in-house procedures. The method detection limits for radiochemical measurements are dependent on both sample matrix and count time and are not listed here. In general, the radiochemical measurements used count times to yield at least 1% (10,000 counts) counting statistics. The expected errors for the radiochemical data range from ± 5 -10 % for gross alpha/beta and gamma emitter measurements to ± 10 -20 % for radionuclides that require complex separations before counting (i.e. ^{99}Tc , ^{90}Sr , ^{129}I , and ^{237}Np). The data user should note that the gross beta efficiency is based on ^{90}Sr with ^{90}Y in secular equilibrium, and only gives the beta activity relative to this calibration. For aged fission product waste this beta activity is very close to the true total beta activity.

Table 2.1. Long-Lived Fission Products

fission product	$t_{1/2}$ (year)	β^- max. (KeV)	σ_γ (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
^{93}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
^{135}Cs	2300000	210	8.7	6.32	0.00134	0.00138
^{151}Sm	90	76	15200	0.417	2.26	2.32

There has been considerable discussion about the need to measure long-lived fission products and other

radionuclides with low fission yields. Most of these radionuclides are listed in Table 2.1 along with ^{90}Sr and ^{137}Cs for comparison. With the exception of ^{151}Sm , the long-lived fission products will be present in the waste long after the ^{90}Sr and ^{137}Cs have decayed away in 300-500 years. Most of the fission product containing waste found throughout the DOE sites has been aged more than five years, and the overall activity is dominated by the ^{137}Cs plus the ^{90}Sr in secular equilibrium with ^{90}Y . In the near future (< 100 years), the long-lived fission products will be a small fraction of the overall activity.

The data presented in Table 2.1 are based on simple estimates to indicate the relative activity present for each radionuclide and is not intended to account for all sources of the radionuclides. The last two columns in Table 2.1 give the percent of activity for each isotope relative to either ^{137}Cs or ^{90}Sr . These relative percents only take into account the specific activity and the fission yield with no decay time included. The (percent ^{137}Cs)/100 multiplied times the actual ^{137}Cs activity observed in the mixed fission product waste gives an estimate of the upper limit for the radionuclide listed (a similar calculation can be done with ^{90}Sr). Excluding ^{151}Sm , the sum of the remaining long-lived fission products listed in Table 2.1 is less than 0.2% of either the ^{137}Cs or ^{90}Sr activity.

All of the long-lived fission products are typically more difficult and expensive to measure than short lived fission products. These radionuclides are either pure beta emitters or have weak, low energy, and/or low yield gamma-rays which are not very useful for accurate analytical measurements. In general, good radiochemical data requires that each of these isotopes be chemically separated from all other radioactivity prior to measurement. These chemical separations and measurements are currently being done routinely for ^{99}Tc and ^{129}I because both exist as anionic species (TcO_4^- , I^- , and IO_3^-) in the waste and are highly mobile in the environment. The ^{99}Tc is currently being separated by extraction chromatography and measured by ICP-MS which is much more sensitive than counting techniques. The ^{129}I is first extracted into carbon tetrachloride as iodine (I_2), then reduced to iodide (I^-), back-extracted into an aqueous matrix, and loaded onto an anion exchange resin. The ^{129}I is then determined by neutron activation analysis. Typically the level of ^{99}Tc and ^{129}I in the waste is lower than expected from the fission yields, and one possible explanation is that both isotopes form volatile species (HTcO_4 , HI , and I_2) when exposed to either acid and/or heat.

The thermal neutron (n,γ) cross sections (σ_γ) are listed in Table 2.1 to show the relative loss of fission products exposed to a high neutron dose (i.e. reactor core). It should be noted that the high cross section for ^{151}Sm indicates a high rate of transmutation to ^{152}Sm , which is not radioactive. The activity of ^{135}Cs present is also strongly influenced by the historical neutron dose but the mechanism is not apparent from the data in Table 2.1. The ^{135}Xe precursor to ^{135}Cs has such a large neutron cross section ($2.6\text{e}+06$ barns) that a large fraction of the ^{135}Xe is transmuted to non-radioactive ^{136}Xe before the isotope can beta decay to ^{135}Cs .

The remaining long-lived fission products, listed in Table 2.1, are present at very small fractions of the overall activity and there has been little interest in the measurement of these radionuclides. The determination of these isotopes are less routine, require labor extensive separation techniques, and are generally expensive measurements. The judgement of many waste characterization teams has been that the measurement of these radionuclides would be interesting but there was insufficient risk to justify the analytical cost.

There are also some long-lived and/or pure beta emitting neutron activation products that are difficult to measure and have not been routinely determined in ORNL waste streams. Two of the radionuclides that fall into this category, and are likely to be present in ORNL waste include ^{59}Ni and ^{63}Ni . The ^{59}Ni has a 75000 year half life, decays by electron capture, and only emits weak x-rays and auger electrons. The ^{63}Ni has a half life of 100 years and is a pure beta emitter. In typical ORNL fission product waste, these nickel radionuclides result from activation of stainless steel components and would only be expected to be present at levels less than 1% of the total activity.

2.25 Criticality Controls

The current ORNL waste acceptance criteria (WAC) for liquid-low level waste requires that the fissile isotopes of uranium and plutonium be isotopically diluted with ^{238}U and ^{232}Th , respectively. These administrative controls require that the ratio of the ^{238}U mass divided by the fissile equivalent mass (FEM) for uranium be greater than 100. The FEM is a useful scale, for criticality calculations, that normalizes the fission probability for each fissile isotope to ^{235}U . These FEM factors are discussed and listed in the Appendix A, Table 1 of ORNL Procedure NCS-1.0, *Nuclear Criticality Safety Program*.

The major fissile isotopes of concern in the ORNL waste tanks are ^{233}U , ^{235}U , and ^{239}Pu . The fissile isotope ^{241}Pu is also present in the waste but the mass is usually several orders of magnitude lower and below a level that would influence the isotopic dilution ratio for plutonium. Other fissile isotopes present in the ORNL waste include isotope of neptunium, americium, and curium, but the actual mass present in the waste has been too low for major concern, and would be difficult to measure by mass spectrometry.

The data presented in this report for isotopic dilution ratios (also referred to as denature ratios) reflects the past ORNL standard practices for disposal of fissile isotopes of uranium and plutonium. These administrative controls required that the ^{233}U and ^{235}U be diluted with depleted uranium such that the following condition was true,

$$\frac{(^{238}\text{U})}{(1.35)(^{233}\text{U})+(^{235}\text{U})} \geq 100$$

Because of differences in uranium and plutonium chemistry, the administrative procedures required that the ^{239}Pu be diluted with ^{232}Th as follows,

$$\frac{(^{232}\text{Th})}{(^{239}\text{Pu})} \geq 100$$

All of the isotopic ratios dealing with isotopic dilution for criticality safety are based on isotope mass and must not be confused with activity ratios. For any data discussed in this report that uses ^{232}Th relative to isotopic mass ratios, the total thorium and the ^{232}Th are the same value. There has been discussions of raising the dilution ratios limits, and some of the suggested ratios include $^{238}\text{U}/^{235}\text{U} > 104$, $^{238}\text{U}/^{233}\text{U} > 140$, and $^{232}\text{Th}/^{239}\text{Pu} > 200$.

2.26 Organic Analysis

The sample preparation and analysis methods were EPA SW-846 methods which had been adapted for radioactive samples and whose performance had been demonstrated according to the Transuranic Waste Characterization Program (TWCP) Quality Assurance Program Plan (QAPP)⁷ requirements. The amounts of sample which were extracted and analyzed were limited by the ALARA principle because of their radioactivity. However, the sensitivity of only the semivolatile organic compound analysis (SVOA)

was reduced by a factor of 2. The sensitivities of the volatile organic compound analysis (VOA), the non-halogenated volatile organic compound analysis (NHVOA), and the polychlorinated biphenyls (PCBs) analysis were not reduced.

NHVOA: SW-846 method 8015 was used. One gram of sludge was extracted by shaking with 1 mL of water. This extraction was reduced two-fold from the method used in the TWCP, but it retained the same method detection limit (MDL) because the relative proportions of sample and solvent were not changed. One μL of the extract was injected onto each of two gas chromatography columns, and the analytes were detected by flame ionization and quantitated using the method of external standards. A surrogate standard was added to all samples and quality control samples. The latter included a laboratory blank, matrix spike (MS) and spike duplicate (MSD) samples, and a laboratory control sample (LCS).

VOA: SW-846 method 8260 was used. One gram of sludge was extracted by shaking with 1 mL of methanol. This extraction was reduced two-fold from the method used in the TWCP, but it retained the same MDL because the relative proportions of sample and solvent were not changed. A 50 μL aliquot of the extract was added to 5 mL of water and was subjected to purge and trap gas chromatography-mass spectrometry (GC-MS). Quantitation was by the method of internal standards. Surrogate standards were added to all samples and quality control samples. The latter included a laboratory blank, MS and MSD, and a LCS.

SVOA: SW-846 methods 3550 and 8270 were used. Five grams of sludge were mixed with 40 grams of sodium sulfate, and extracted with 100 mL of methylene chloride using an ultrasonic bath. After concentration to 1 mL, the extract was analyzed by GC-MS, using the method of internal standards. This method was a two-fold reduction in scale from the method used in the TWCP, and the MDL was increased two-fold. Surrogate standards were added to all samples and quality control samples. The latter included a laboratory blank, MS and MSD, and a LCS.

PCBs: SW-846 methods 3550, 3665, and 8080 were used. Two grams of sludge were mixed with 16 grams of sodium sulfate, extracted three times with 15 mL portions of methylene chloride. The extract was concentrated and solvent-exchanged into hexane, washed with sulfuric acid until the acid washes were colorless and did not contain precipitates, washed with water to remove acid, combined with a hexane

back-extract of the acid washes, and then were concentrated to 1 mL. Analysis was conducted on a dual capillary column GC equipped with dual electron capture detectors using the method of external standards. A surrogate standard was added to all samples and quality control samples. The latter included a laboratory blank, MS and MSD, and a LCS.

2.3 Quality Assurance

Both the inorganic and organic chemical characterization of the sludges followed the method requirements and Data Quality Objectives (DQO) of the TWCP QAPP. The RMAL implements the TWCP QAPP with a flow down RMAL Quality Assurance Project Plan (QAPjP)⁸. The list of metals determined was expanded from the TWCP requirements to meet ORNL needs. Although the organic target analytes were those listed in the TWCP QAPP, the full set of semivolatile and volatile organic analytes on the EPA Contract Laboratory Program Target Compound List would have been reported as Tentatively Identified Compounds (TICs) if they were detected in the samples.

Quality assurance during the sampling activities was primarily addressed by the use of approved procedures for sampling both the liquid and sludge phase found in each waste tanks. These procedures provide detailed instructions for the collection, labeling, and shipping of each sample. Chain-of-custody forms were used to track individual samples from their collection point to the analytical laboratory.

The RMAL also operates under a Radioactive Waste Characterization QA Plan⁹ which, in conjunction with the TWCP QAPjP, defines the basis for quality assurance and quality control used for the analysis of the waste tank samples. The QA plans discusses staff qualification requirements, laboratory participation in performance demonstration programs, quality control acceptance criteria for analytical methods, sample management, and most other laboratory operations. The set of QA plans in place for RMAL work also meet the Nevada Test Site (NTS) QA requirements for inorganic, organic, and radiochemical measurements.

3.0 SUMMARY OF INORGANIC, PHYSICAL, AND RADIOCHEMICAL RESULTS

3.1 Description of Data Tables

A summary of the inorganic, physical, and radiochemical analytical results are presented in Table 3.1 and Table 3.2 for the MVST supernatant samples; the BVEST (W-21 and W-23) sludge samples are presented in Table 3.3 and Table 3.4, and MVST tank W-25 is given in Table 3.5. These tables are arranged in a similar format to facilitate comparing data from different tanks and to group information into useful units. The analytical data presented in these tables is the consolidation of data from several projects which had different analytical requirements. Therefore, the list of analytical parameters presented from tank to tank may vary. Any parameter reported with a dash (“-”) indicates that the data was not measured for that sample.

The first section, “Physical properties and miscellaneous data”, includes unrelated information that does not fit well into other table groups. The first parameters entered in a column include the RMAL request and sample numbers, which are laboratory filing codes used to track sample information. The next set of data includes information on the moisture or water content and the solids content of the sample. The group is completed with data on the inorganic and organic carbon content. For waste tank samples the inorganic carbon can be assumed to be all carbonate and bicarbonate. The Total Organic Carbon (TOC) provides an upper limit on the organic content in the tank waste but does not include volatile organic compounds. Most of the liquid waste in the active system has been through an evaporator and the highly volatile organics have already been removed.

The next two sections include groups of metals, the “RCRA metals” are separated out for quick reference, The regulatory limit for the concentration are listed in parentheses next to each RCRA metal. For the liquid samples the RCRA regulatory limits are used directly, since the supernatant would be defined as the TCLP leachate in the determination of characteristics for hazardous waste. The RCRA metal sludge data represents total metal measurements, as defined by EPA. Exceeding the RCRA regulatory limits listed for the sludge samples only indicates that the waste has the potential to be classified as hazardous. The sludge waste should only be classified as RCRA waste if the final form, ready for disposal, fails the TCLP leaching test.

The remaining metals are grouped under “Process metals”, which includes the common Group I & II metals along with elements that could effect chemical processing, criticality concerns, and stabilization techniques such as grouting or vitrification. For the sludge data, all the metals are reported on a “as received” (wet weight) basis.

The “Alkalinity” and the “Anions by ion chromatography” sections are separate for the supernatant samples, but are combined for the sludge samples. For supernatant samples the pH is measured directly, and the anions are determined on the liquid samples after dilution with water. The pH and anions reported for the sludge samples are based on a water wash of the sludge, as discussed in section 2.23.

The “Beta/gamma emitters” section summarizes the radionuclides that emit gamma-rays and beta particles. This section includes the gross beta activity, radionuclides identified by gamma spectrometry, and several “pure” beta emitters of interest. The “pure” beta emitters (^3H , ^{14}C , ^{90}Sr , and ^{99}Tc), require radiochemical separations prior to measurement by either liquid scintillation or gas-flow proportional counting.

The “Alpha emitters by alpha spectrometry” section for the supernatants, and the “Alpha emitters” section for the sludge data, summarize the actinides in the waste. These sections includes the gross alpha activity, an estimate of the activity for each alpha emitter identified in a gross alpha spectrum, and plutonium isotopes determined by alpha spectrometry after a radiochemical separation. For supernatant samples, an estimate of the $^{232}\text{Th}/^{239}\text{Pu}$ mass ratio is included in this section to address criticality concerns. For the sludge samples, this mass ratio is included with the plutonium mass spectrometry data.

The remaining sections include “Uranium isotopes by TIMS” and Plutonium isotopes by TIMS”. These sections summarize the uranium and plutonium data measured by thermal ionization mass spectrometry. Also, included in these sections are the isotopic mass dilution or “denature” ratios for uranium and plutonium. The plutonium section for the sludge samples includes the activity for each plutonium isotope, which is calculated from the mass spectrometry data.

Table 3.1. Supernatant Data from MVSTs W-24, W-25, and W-26

Characteristic (Analysis)	W-24	W-25	W-26	IDL ^g
Physical properties and miscellaneous data				
Request number	7302	7302	7302	-
Sample number	941219-084	941219-085	941219-086	-
TSS ^a (mg/mL)	32	33	38	-
TDS ^b (mg/mL)	269	320	385	-
Density (g/mL)	1.191	1.220	1.255	-
TIC ^c (mg/L)	1131	374	< 15	15
TC ^d (mg/L)	1756	1223	938	15
TOC ^e (mg/L)	625	849	938	15
RCRA Metals				
Ag (5) ^f (mg/L)	< 0.063	< 0.069	< 0.069	0.005
As (5) (mg/L)	< 0.25	< 0.25	< 0.25	0.005
Ba (100) (mg/L)	0.178	0.859	3.47	0.001
Cd (1) (mg/L)	0.824	0.674	0.653	0.006
Cr (5) (mg/L)	1.46	3.24	1.52	0.004
Hg (0.2) (mg/L)	0.0475	0.125	0.085	0.0002
Ni (50) (mg/L)	0.825	1.12	6.99	0.009
Pb (5) (mg/L)	< 2.0	2.71	< 2.2	0.005
Se (1) (mg/L)	< 0.50	< 0.50	< 0.50	0.005
Tl (0.9) (mg/L)	< 18	< 19	< 19	0.005
Process metals				
Al (mg/L)	32.5	1.36	< 0.32	0.02
B (mg/L)	1.45	1.71	0.859	0.012
Be (mg/L)	0.040	< 0.003	< 0.003	0.0009
Ca (mg/L)	5.54	6.97	1590	0.01
Co (mg/L)	< 0.14	< 0.15	< 0.15	0.007
Cs (mg/L)	0.485	0.540	0.485	0.005
Cu (mg/L)	0.229	0.117	0.232	0.002
Fe (mg/L)	< 0.04	< 0.04	< 0.04	0.003
K (mg/L)	20600	19100	40900	0.08
Mg (mg/L)	< 0.34	< 0.37	145	0.020
Mn (mg/L)	< 0.006	< 0.007	< 0.007	0.0009
Na (mg/L)	74800	81600	79900	0.02
Sb (mg/L)	< 2.5	< 2.8	< 2.8	0.13
Si (mg/L)	53.1	69.0	20.6	0.013
Sr (mg/L)	0.604	1.71	42.8	0.0003
Th (mg/L)	< 0.62	< 0.68	< 0.68	0.04
U (mg/L)	5.79	2.98	< 1.3	0.07
V (mg/L)	0.065	0.083	< 0.07	0.02
Zn (mg/L)	24.1	0.688	0.549	0.02
Alkalinity				

Characteristic (Analysis)		W-24	W-25	W-26	IDL ^g
pH	(pH)	13.0	13.0	9.3	-
Hydroxide	(<u>M</u>)	< 0.1	< 0.1	< 0.1	0.1
Carbonate	(<u>M</u>)	< 0.1	< 0.1	< 0.1	0.1
Bicarbonate	(<u>M</u>)	< 0.1	< 0.1	< 0.1	0.1

Characteristic (Analysis)		W-24	W-25	W-26	IDL ^g
Anions by ion chromatography					
Bromide (mg/L)		11	665	690	0.05
Chloride (mg/L)		4380	4730	4800	0.05
Cyanide (mg/L)		0.1	< 0.01	0.028	0.01
Fluoride (mg/L)		1080	1100	1040	0.05
Nitrate (mg/L)		197000	239000	299000	0.10
Phosphate (mg/L)		11	< 10	< 10	0.20
Sulphate (mg/L)		1720	1950	2940	0.10
Beta/gamma emitters					
Gross beta (Bq/mL)		1.3e+06	1.4e+06	1.7e+06	-
²⁴¹ Am (Bq/mL)		< 2.8e+03	< 3.0e+03	< 3.1e+03	-
⁶⁰ Co (Bq/mL)		3.2e+02	3.1e+02	2.7e+03	-
¹³⁴ Cs (Bq/mL)		7.1e+04	8.2e+04	3.6e+04	-
¹³⁷ Cs/ ^{137m} Ba (Bq/mL)		1.1e+06	1.2e+06	1.4e+06	-
¹⁵² Eu (Bq/mL)		< 2.3e+03	< 2.4e+03	< 2.5e+03	-
¹⁵⁴ Eu (Bq/mL)		< 8.9e+02	< 9.5e+02	< 9.9e+02	-
¹⁵⁵ Eu (Bq/mL)		< 1.4e+03	< 1.5e+03	< 1.6e+03	-
⁹⁰ Sr/ ⁹⁰ Y (Bq/mL)		6.5e+02	1.1e+03	1.7e+04	-
¹⁴ C (Bq/mL)		-	-	-	-
³ H (Bq/mL)		1.9e+02	1.9e+02	2.0e+02	-
⁹⁹ Tc (Bq/mL)		6.7e+02	7.2e+02	1.9e+03	-
Alpha emitters by alpha spectrometry					
Gross alpha (Bq/mL)		< 45	< 20	82	-
²⁴⁴ Cm (%)		-	-	-	-
²³⁹ Pu/ ²⁴⁰ Pu (%)		-	-	-	-
²³⁸ Pu/ ²⁴¹ Am (%)		-	-	-	-
Total Pu alpha (Bq/mL)		0.31	0.68	< 0.6	-
²³⁸ Pu (%)		-	-	-	-
²³⁹ Pu/ ²⁴⁰ Pu (%)		-	-	-	-
²⁴² Pu (%)		-	-	-	-
[²³⁹ Pu] (ng/mL)		0.14	0.30	< 0.26	-
²³² Th/ ²³⁹ Pu (200)		-	-	-	-
Uranium isotopics by TIMS					
²³³ U (atom %)		0.12	0.11	0.13	0.01
²³⁴ U (atom %)		< 0.01	< 0.01	< 0.01	0.01
²³⁵ U (atom %)		0.27	0.35	0.30	0.01
²³⁶ U (atom %)		< 0.01	< 0.01	< 0.01	0.01
²³⁸ U (atom %)		99.60	99.53	99.57	0.01
²³⁸ U/ ²³⁵ U FEM		231	200	209	-
²³⁵ U/MS (mg/L)		0.015	0.010	< 0.004	-
²³⁵ U/NAA (mg/L)		0.026	0.014	0.002	-

(a) Total suspended solids, (b) Total dissolved solids, (c) Inorganic carbon, (d) Total carbon, (e) Total organic carbon, (f) RCRA regulatory limits, (g) Instrument detection limits.

Table 3.2. Supernatant Data from MVSTs W-27, W-28, and W-31

Characteristic (Analysis)	W-27	W-28	W-31	IDL ^g
Physical properties and miscellaneous data				
Request number	7302	7302	7302	-
Sample number	941219-087	941219-088	941219-089	-
TSS ^a (mg/mL)	48	46	38	-
TDS ^b (mg/mL)	407	524	391	-
Density (g/mL)	1.279	1.334	1.264	-
TIC ^c (mg/L)	90	44	489	15
TC ^d (mg/L)	500	779	1230	15
TOC ^e (mg/L)	407	735	741	15
RCRA Metals				
Ag (5) ^f (mg/L)	< 0.069	0.072	< 0.069	0.005
As (5) (mg/L)	< 0.25	< 0.25	< 0.25	0.005
Ba (100) (mg/L)	12.7	7.91	0.954	0.001
Cd (1) (mg/L)	0.311	0.311	0.813	0.006
Cr (5) (mg/L)	1.03	1.03	11.8	0.004
Hg (0.2) (mg/L)	0.638	0.143	0.713	0.0002
Ni (50) (mg/L)	3.18	2.84	0.947	0.009
Pb (5) (mg/L)	< 2.2	< 2.2	< 2.2	0.005
Se (1) (mg/L)	< 0.50	< 0.50	< 0.50	0.005
Tl (0.9) (mg/L)	< 19	< 19	< 19	0.005
Process metals				
Al (mg/L)	< 0.32	< 0.32	2.56	0.02
B (mg/L)	0.722	0.554	0.806	0.012
Be (mg/L)	< 0.003	< 0.003	< 0.003	0.0009
Ca (mg/L)	10400	10300	153	0.01
Co (mg/L)	0.183	0.183	< 0.15	0.007
Cs (mg/L)	0.280	0.500	0.365	0.005
Cu (mg/L)	0.696	0.696	0.237	0.002
Fe (mg/L)	< 0.04	< 0.04	0.092	0.003
K (mg/L)	11500	30100	16500	0.08
Mg (mg/L)	1090	1870	< 0.37	0.020
Mn (mg/L)	0.294	0.030	< 0.007	0.0009
Na (mg/L)	95100	110000	99200	0.02
Sb (mg/L)	< 2.8	< 2.8	< 2.8	0.13
Si (mg/L)	24.5	20.8	40.8	0.013
Sr (mg/L)	69.1	80.9	1.44	0.0003
Th (mg/L)	11.9	4.67	< 0.68	0.04
U (mg/L)	503	234	2.28	0.07
V (mg/L)	< 0.07	< 0.07	< 0.07	0.02
Zn (mg/L)	1.90	1.03	0.961	0.02
Alkalinity				
pH (pH)	7.2	7.2	11.9	-
Hydroxide (M)	< 0.1	< 0.1	< 0.1	0.1
Carbonate (M)	< 0.1	< 0.1	< 0.1	0.1
Bicarbonate (M)	< 0.1	< 0.1	< 0.1	0.1

Characteristic (Analysis)		W-27	W-28	W-31	IDL ^g
Anions by ion chromatography					
Bromide (mg/L)		343	395	425	0.05
Chloride (mg/L)		3800	5950	4370	0.05
Cyanide (mg/L)		0.025	< 0.01	0.22	0.01
Fluoride (mg/L)		975	1070	1050	0.05
Nitrate (mg/L)		342000	425000	311000	0.10
Phosphate (mg/L)		< 10	< 10	< 10	0.20
Sulphate (mg/L)		1570	1750	1670	0.10
Beta/gamma emitters					
Gross beta (Bq/mL)		5.3e+05	1.0e+06	6.0e+05	-
²⁴¹ Am (Bq/mL)		< 1.5e+03	< 2.1e+03	< 1.9e+03	-
⁶⁰ Co (Bq/mL)		2.0e+03	4.9e+03	3.5e+02	-
¹³⁴ Cs (Bq/mL)		1.4e+03	4.2e+03	1.6e+04	-
¹³⁷ Cs/ ^{137m} Ba (Bq/mL)		3.3e+05	6.2e+05	4.8e+05	-
¹⁵² Eu (Bq/mL)		< 1.2e+03	< 1.7e+03	< 1.5e+03	-
¹⁵⁴ Eu (Bq/mL)		< 4.7e+02	< 6.5e+02	< 5.8e+02	-
¹⁵⁵ Eu (Bq/mL)		< 7.4e+02	< 1.1e+03	< 9.0e+02	-
⁹⁰ Sr/ ⁹⁰ Y (Bq/mL)		6.6e+04	1.2e+05	8.7e+03	-
¹⁴ C (Bq/mL)		-	-	-	-
³ H (Bq/mL)		1.3e+02	6.8e+01	1.0e+02	-
⁹⁹ Tc (Bq/mL)		2.6e+02	4.0e+02	5.7e+02	-
Alpha emitters by alpha spectrometry					
Gross alpha (Bq/mL)		300	180	< 29	-
²⁴⁴ Cm (%)		-	-	-	-
²³⁹ Pu/ ²⁴⁰ Pu (%)		-	-	-	-
²³⁸ Pu/ ²⁴¹ Am (%)		-	-	-	-
Total Pu alpha (Bq/mL)		0.49	0.18	0.12	-
²³⁸ Pu (%)		-	-	-	-
²³⁹ Pu/ ²⁴⁰ Pu (%)		-	-	-	-
²⁴² Pu (%)		-	-	-	-
[²³⁹ Pu] (ng/mL)		0.21	0.08	0.05	-
²³² Th/ ²³⁹ Pu (200)		55700	59600	-	-
Uranium isotopics by TIMS					
²³³ U (atom %)		0.12	0.12	0.12	0.01
²³⁴ U (atom %)		< 0.01	< 0.01	< 0.01	0.01
²³⁵ U (atom %)		0.25	0.25	0.30	0.01
²³⁶ U (atom %)		< 0.01	< 0.01	< 0.01	0.01
²³⁸ U (atom %)		99.62	99.62	99.57	0.01
²³⁸ U/ ²³⁵ U FEM		242	242	216	-
²³⁵ U/MS (mg/L)		1.24	0.58	< 0.01	-
²³⁵ U/NAA (mg/L)		1.7	0.76	0.10	-

(a) Total suspended solids, (b) Total dissolved solids, (c) Inorganic carbon, (d) Total carbon, (e) Total organic carbon, (f) RCRA regulatory limits, (g) Instrument detection limits.

Table 3.3. Sludge from Tank W-21: Collects Concentrate from Process Waste Evaporator

Characteristic (Analysis)	W-21 S (HNO ₃)	W-21 S (HNO ₃ - HCl)	W-21 S (H ₂ O)	W-21 S (Sears)
Physical properties and miscellaneous data				
Request number	7603B	7603C	7603D	6282
Sample number	960212-178	960305-012	960311-012	900131-107
Water ^a (%)	49.8	-	-	48.9
Bulk density (g/mL)	1.46	-	-	1.40
TIC ^b (mg/kg)	28000	-	-	12000
TC ^c (mg/kg)	28000	-	-	18500
TOC ^d (mg/kg)	< 100	-	-	6480
RCRA Metals				
Ag (100) ^e (mg/kg)	< 2.8	< 3.3	< 1.2	50
As (100) (mg/kg)	< 5.1	< 1.3	-	42
Ba (2000) (mg/kg)	48.4	45.5	3.40	78
Cd (20) (mg/kg)	39.0	29.0	5.14	27
Cr (100) (mg/kg)	248	274	3.03	160
Hg (4) (mg/kg)	11.3	14.7	-	56
Ni (1000) (mg/kg)	98.5	96.0	10.8	75
Pb (100) (mg/kg)	302	339	-	290
Se (20) (mg/kg)	< 5	< 1.3	-	< 25
Tl (18) (mg/kg)	75.2	< 1.3	-	< 10
Process metals				
Al (mg/kg)	852	904	2.94	1000
B (mg/kg)	7.89	< 2.5	5.05	< 6.6
Be (mg/kg)	< 0.15	< 0.4	< 0.15	-
Ca (mg/kg)	83900	73000	58200	45000
Co (mg/kg)	< 1.3	< 3.6	< 1.3	-
Cu (mg/kg)	77.4	61.7	2.29	-
Cs (mg/kg)	2.57	< 7.4	-	-
Fe (mg/kg)	4040	3600	3.49	2300
K (mg/kg)	10300	9840	9490	8500
Mg (mg/kg)	8630	7620	5610	9600
Mn (mg/kg)	114	125	25.9	-
Na (mg/kg)	42400	38100	38700	48000
P (mg/kg)	-	16000	-	-
Sb (mg/kg)	< 20	< 55	< 20	-
Si (HF) (mg/kg)	3360	356	404	-
Sr (mg/kg)	295	276	171	200
Th (mg/kg)	7460	7010	9.36	14000
U (mg/kg)	25300	26500	5040	31000
V (mg/kg)	< 0.38	< 1.0	0.918	-
Zn (mg/kg)	756	851	58.0	-

Characteristic (Analysis)		W-21 S (HNO ₃)	W-21 S (HNO ₃ - HCl)	W-21 S (H ₂ O)	W-21 S (Sears)
Anions by ion chromatography					
pH		-	-	8.3	-
Bromide	(mg/kg)	-	-	89	-
Chloride	(mg/kg)	-	-	1120	-
Fluoride	(mg/kg)	-	-	157	-
Nitrate	(mg/kg)	-	-	166000	-
Phosphate	(mg/kg)	-	48000	< 210	-
Sulphate	(mg/kg)	-	-	8030	-
Beta/gamma emitters					
<u>Gross beta</u>	(Bq/g)	3.0e+06	3.0e+06	5.3e+05	3.4e+06
¹⁴ C	(Bq/g)	-	-	-	1.8e+02
⁶⁰ Co	(Bq/g)	5.5e+04	5.9e+04	6.4e+03	8.1e+04
⁹⁰ Sr/ ⁹⁰ Y	(Bq/g)	4.4e+05	3.6e+05	2.3e+05	7.8e+05
⁹⁹ Tc	(Bq/g)	8.1e+02	-	-	-
¹³⁴ Cs	(Bq/g)	< 2.6e+03	< 2.3e+03	1.3e+03	7.0e+03
¹³⁷ Cs/ ^{137m} Ba	(Bq/g)	1.3e+05	1.4e+05	1.3e+05	2.5e+05
¹⁵² Eu	(Bq/g)	9.8e+05	1.1e+06	1.4e+04	1.3e+06
¹⁵⁴ Eu	(Bq/g)	4.2e+05	4.5e+05	5.3e+03	4.8e+05
¹⁵⁵ Eu	(Bq/g)	9.9e+04	9.6e+04	1.8e+03	1.3e+05
²⁴¹ Pu	(Bq/g)	4.1e+04	-	-	-
Alpha emitters					
<u>Gross alpha</u>	(Bq/g)	150000	150000	2900	130000
²³² Th	(Bq/g)	30	-	-	-
²³³ U	(Bq/g)	9700	-	-	8100
²³⁴ U	(Bq/g)	< 570	-	-	-
²³⁵ U	(Bq/g)	4.3	-	-	-
²³⁸ U	(Bq/g)	310	-	-	-
²³⁷ Np	(Bq/g)	6.1	-	-	-
²⁴¹ Am	(Bq/g)	17000	-	-	51000
²⁴⁴ Cm	(Bq/g)	99000	-	-	45000
<u>Total Pu alpha</u>	(Bq/g)	20000	-	-	-
²³⁸ Pu	(Bq/g)	13000	-	-	-
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)	7400	-	-	25000
Uranium isotopics by TIMS					
²³³ U	(atom %)	0.11	-	-	-
²³⁴ U	(atom %)	< 0.01	-	-	-
²³⁵ U	(atom %)	0.24	-	-	-
²³⁶ U	(atom %)	0.01	-	-	-
²³⁸ U	(atom %)	99.64	-	-	-
²³⁸ U/ ²³⁵ U FEM		256	-	-	-
²³⁵ U/MS ^h	(mg/kg)	60.0	-	-	-
²³⁵ U/NAA ⁱ	(mg/kg)	75.8	-	-	-

Characteristic (Analysis)		W-21 S (HNO ₃)	W-21 S (HNO ₃ - HCl)	W-21 S (H ₂ O)	W-21 S (Sears)
Plutonium isotopics by mass spectrometry					
²³⁸ Pu	(atom %)	1.24	-	-	-
²³⁹ Pu	(atom %)	78.55	-	-	-
²⁴⁰ Pu	(atom %)	18.79	-	-	-
²⁴¹ Pu	(atom %)	0.60	-	-	-
²⁴² Pu	(atom %)	0.82	-	-	-
²⁴⁴ Pu	(atom %)	< 0.01	-	-	-
Pu activity^j					
²³⁸ Pu	(Bq/g)	1.4e+04	-	-	-
²³⁹ Pu	(Bq/g)	3.2e+03	-	-	-
²⁴⁰ Pu	(Bq/g)	2.8e+03	-	-	-
²⁴¹ Pu	(Bq/g)	4.1e+04	-	-	-
²⁴² Pu	(Bq/g)	2.2e+00	-	-	-
²⁴⁴ Pu	(Bq/g)	< 1.0e+00	-	-	-
(²³⁹ Pu)	(ng/g)	1.4e+03	-	-	-
²³² Th/ ²³⁹ Pu ^k		5280	-	-	-

(a) % Water, (b) Total inorganic carbon, (c) Total carbon, (d) Total organic carbon, (e) RCRA regulatory limits, (f) Instrument detection limit, (g) Denature ratios for uranium, ²³⁸U/²³⁵U FEM, (h) Concentration of ²³⁵U calculated from the MS and ICP data, (i) Gross fissile content by delayed neutron counting, units are ²³⁵U equivalent, (j) Calculated from mass spec. and total Pu alpha data, (k) Denature ratio for plutonium, ²³²Th/²³⁹Pu.

Table 3.4. Sludge from Tank W-23: Collects Concentrate from LLW Evaporator

Characteristic (Analysis)		W-23 S (HNO ₃)	W-23 S (HNO ₃ - HCl)	W-23 S (H ₂ O)	W-23 S (Sears)
Physical properties and miscellaneous data					
Request number		7603A	7603C	7603D	6282
Sample number		960118-141	960305-011	960311-011	900131-108
Water ^a	(%)	42.3	-	-	45.6
Bulk density	(g/mL)	1.46	-	-	1.34
TIC ^b	(mg/kg)	32000	-	-	18100
TC ^c	(mg/kg)	32000	-	-	22200
TOC ^d	(mg/kg)	< 100	-	-	4120
RCRA Metals					
Ag	(100) ^e (mg/kg)	3.15	< 3.3	< 1.1	28
As	(100) (mg/kg)	< 4.7	< 1.3	-	< 50
Ba	(2000) (mg/kg)	55.4	42.2	< 0.12	63
Cd	(20) (mg/kg)	16.1	< 5.6	< 1.8	32
Cr	(100) (mg/kg)	152	141	9.69	190
Hg	(4) (mg/kg)	8.44	10.8	-	19
Ni	(1000) (mg/kg)	69.6	58.0	3.04	110
Pb	(100) (mg/kg)	380	392	-	450
Se	(20) (mg/kg)	< 4.7	< 1.3	-	< 39
Tl	(18) (mg/kg)	< 17	< 1.3	-	< 16
Process metals					
Al	(mg/kg)	2330	2510	60.4	2800
B	(mg/kg)	5.03	< 2.6	3.20	< 10
Be	(mg/kg)	3.66	< 0.41	< 0.13	-
Ca	(mg/kg)	55500	62500	478	55000
Co	(mg/kg)	5.20	< 3.7	< 1.2	-
Cu	(mg/kg)	37.9	11.2	1.40	-
Cs	(mg/kg)	2.81	8.18	-	-
Fe	(mg/kg)	1930	1870	< 0.28	1900
K	(mg/kg)	25200	27500	25300	18000
Mg	(mg/kg)	14500	16200	807	16000
Mn	(mg/kg)	275	292	< 0.13	-
Na	(mg/kg)	66500	66500	65300	82000
P	(mg/kg)	-	13700	-	-
Sb	(mg/kg)	< 19	< 56	< 18	-
Si (HF)	(mg/kg)	2660	330	158	-
Sr	(mg/kg)	275	289	1.81	290
Th	(mg/kg)	7520	7550	6.41	13000
U	(mg/kg)	39700	36600	1220	17000
V	(mg/kg)	5.37	< 1.1	0.657	-
Zn	(mg/kg)	997	1080	12.6	-

Characteristic (Analysis)	W-23 S (HNO ₃)	W-23 S (HNO ₃ - HCl)	W-23 S (H ₂ O)	W-23 S (Sears)
Anions by ion chromatography				
pH	-	-	12.4	-
Bromide (mg/kg)	-	-	470	-
Chloride (mg/kg)	-	-	3170	-
Fluoride (mg/kg)	-	-	185	-
Nitrate (mg/kg)	-	-	126000	-
Phosphate (mg/kg)	-	41100	< 200	-
Sulphate (mg/kg)	-	-	3540	-
Beta/gamma emitters				
<u>Gross beta</u> (Bq/g)	4.2e+06	4.4e+06	5.7e+05	6.7e+06
¹⁴ C (Bq/g)	-	-	-	3.7e+02
⁶⁰ Co (Bq/g)	1.8e+05	2.2e+05	5.0e+03	2.5e+05
⁹⁰ Sr/ ⁹⁰ Y (Bq/g)	5.8e+05	6.2e+05	7.1e+03	2.3e+06
⁹⁹ Tc (Bq/g)	3.8e+02	-	-	-
¹³⁴ Cs (Bq/g)	9.8e+03	8.0e+03	9.0e+03	< 6.5e+03
¹³⁷ Cs/ ^{137m} Ba (Bq/g)	4.1e+05	4.5e+05	4.5e+03	5.0e+05
¹⁵² Eu (Bq/g)	1.1e+06	1.2e+06	7.5e+03	7.2e+05
¹⁵⁴ Eu (Bq/g)	6.4e+05	6.5e+05	4.3e+03	5.1e+05
¹⁵⁵ Eu (Bq/g)	1.3e+05	1.3e+05	1.6e+03	1.2e+05
²⁴¹ Pu (Bq/g)	3.7e+04	-	-	-
Alpha emitters				
<u>Gross alpha</u> (Bq/g)	120000	100000	1100	220000
²³² Th (Bq/g)	31	-	-	-
²³³ U (Bq/g)	19000	-	-	12000
²³⁴ U (Bq/g)	< 900	-	-	-
²³⁵ U (Bq/g)	6.4	-	-	-
²³⁸ U (Bq/g)	490	-	-	-
²³⁷ Np (Bq/g)	6.1	-	-	-
²⁴¹ Am (Bq/g)	15000	-	-	32000
²⁴⁴ Cm (Bq/g)	68000	-	-	170000
<u>Total Pu alpha</u> (Bq/g)	12000	-	-	-
²³⁸ Pu (Bq/g)	7200	-	-	-
²³⁹ Pu/ ²⁴⁰ Pu	4800	-	-	12000
Uranium isotopics by TIMS				
²³³ U (atom %)	0.14	-	-	-
²³⁴ U (atom %)	< 0.01	-	-	-
²³⁵ U (atom %)	0.23	-	-	-
²³⁶ U (atom %)	0.01	-	-	-
²³⁸ U (atom %)	99.62	-	-	-
²³⁸ U/ ²³⁵ U FEM ^g	238	-	-	-
²³⁵ U/M ^h (mg/kg)	90	-	-	-
²³⁵ U/NAA ⁱ (mg/kg)	125	-	-	-

Characteristic (Analysis)		W-23 S (HNO ₃)	W-23 S (HNO ₃ - HCl)	W-23 S (H ₂ O)	W-23 S (Sears)
Plutonium isotopics by mass spectrometry					
²³⁸ Pu	(atom %)	0.80	-	-	-
²³⁹ Pu	(atom %)	78.77	-	-	-
²⁴⁰ Pu	(atom %)	18.82	-	-	-
²⁴¹ Pu	(atom %)	0.67	-	-	-
²⁴² Pu	(atom %)	0.94	-	-	-
²⁴⁴ Pu	(atom %)	< 0.01	-	-	-
Pu activity^j					
²³⁸ Pu	(Bq/g)	7.2e+03	-	-	-
²³⁹ Pu	(Bq/g)	2.6e+03	-	-	-
²⁴⁰ Pu	(Bq/g)	2.3e+03	-	-	-
²⁴¹ Pu	(Bq/g)	3.7e+04	-	-	-
²⁴² Pu	(Bq/g)	2.0e+00	-	-	-
²⁴⁴ Pu	(Bq/g)	< 1.0e+00	-	-	-
(²³⁹ Pu)	(ng/g)	1120	-	-	-
²³² Th/ ²³⁹ Pu ^k		6717	-	-	-

(a) % Water, (b) Total inorganic carbon, (c) Total carbon, (d) Total organic carbon, (e) RCRA regulatory limits, (f) Instrument detection limit, (g) Denature ratios for uranium, ²³⁸U/²³⁵U FEM, (h) Concentration of ²³⁵U calculated from the MS and ICP data, (i) Gross fissile content by delayed neutron counting, units are ²³⁵U equivalent, (j) Calculated from mass spec. and total Pu alpha data, (k) Denature ratio for plutonium, ²³²Th/²³⁹Pu.

Table 3.5. Sludge from Melton Valley Storage Tank W-25

Characteristic (Analysis)	W-25 S (HNO ₃)	W-25 S (HNO ₃ /HF-H ₃ BO ₃)	W-25 S (HNO ₃ /HF-H ₃ BO ₃)+heat	W-25 S (H ₂ O)	W-25 S (Sears)
Physical properties and miscellaneous data					
Request number	7018	7018B	7018D	7018A	6223
Sample number	931103-018	940222-019	940505-077	940222-017	890925-209
Water ^a (%)	40.99	-	-	-	46.9
Bulk density (g/mL)	-	-	-	-	1.32
TIC ^b (mg/kg)	25600	-	-	-	3920
TC ^c (mg/kg)	55000	-	-	-	6250
TOC ^d (mg/kg)	29400	-	-	-	2330
RCRA Metals					
Ag (100) ^e (mg/kg)	< 0.85	< 0.80	20.9	-	< 7.6
As (100) (mg/kg)	< 2	-	< 2	-	< 41
Ba (2000) (mg/kg)	411	437	496	-	59
Cd (20) (mg/kg)	50.2	52.3	63.4	-	11
Cr (100) (mg/kg)	583	584	479	-	59
Hg (4) (mg/kg)	224	-	244	-	37
Ni (1000) (mg/kg)	358	365	335	-	34
Pb (100) (mg/kg)	1980	1980	2010	-	220
Se (20) (mg/kg)	< 2	-	< 2	-	< 51
Tl (18) (mg/kg)	< 790	< 750	413	-	< 16
Process metals					
Al (mg/kg)	25800	23300	20000	-	2800
B (mg/kg)	7.78	-	-	-	< 1.5
Be (mg/kg)	59.1	30.8	46.3	-	-
Ca (mg/kg)	91500	96100	94800	-	38000
Co (mg/kg)	38.8	38.9	32.3	-	-
Cu (mg/kg)	277	212	189	-	-
Cs (mg/kg)	-	-	-	-	< 1.3
Fe (mg/kg)	8550	8410	7560	-	940
K (mg/kg)	14000	14400	12500	-	9200
Mg (mg/kg)	13500	13000	4340	-	5900
Mn (mg/kg)	733	758	780	-	-
Na (mg/kg)	110000	104000	72100	-	66000
Sb (mg/kg)	< 5.8	< 5.5	< 51	-	-
Si (mg/kg)	< 5.1	-	15300	-	-
Sr (mg/kg)	558	555	-	-	150
Th (mg/kg)	57400	10600	36800	-	3860
U (mg/kg)	21100	21100	27600	-	4800
V (mg/kg)	32.7	< 0.45	29.0	-	-
Zn (mg/kg)	765	753	655	-	-

Characteristic (Analysis)	W-25 S (HNO ₃)	W-25 S (HNO ₃ /HF-H ₃ BO ₃)	W-25 S (HNO ₃ /HF-H ₃ BO ₃)+heat	W-25 S (H ₂ O)	W-25 S (Sears)
Anions by ion chromatography					
pH	-	-	-	-	-
Bromide (mg/kg)	-	-	-	737	-
Chloride (mg/kg)	-	-	-	3740	-
Fluoride (mg/kg)	-	-	-	1890	-
Nitrate (mg/kg)	-	-	-	176000	-
Phosphate (mg/kg)	6710	-	29400	< 12	-
Sulphate (mg/kg)	-	-	-	2270	-
Beta/gamma emitters					
<u>Gross beta</u> (Bq/g)	3.9e+07	3.4e+07	3.9e+07	1.1e+05	4.0e+06
¹⁴ C (Bq/g)	-	-	-	-	1.7e+02
⁶⁰ Co (Bq/g)	1.5e+05	1.5e+05	1.3e+05	3.8e+02	4.0e+04
⁹⁰ Sr/ ⁹⁰ Y (Bq/g)	1.4e+07	1.5e+07	1.9e+07	4.0e+04	1.7e+06
⁹⁹ Tc (Bq/g)	-	-	-	-	-
¹³⁴ Cs (Bq/g)	< 3.2e+03	< 1.1e+03	< 4.6e+03	< 3.7e+01	7.1e+02
¹³⁷ Cs/ ^{137m} Ba (Bq/g)	1.1e+06	1.1e+06	1.1e+06	3.1e+04	2.2e+05
¹⁵² Eu (Bq/g)	2.3e+05	2.2e+05	1.9e+05	5.8e+02	8.1e+04
¹⁵⁴ Eu (Bq/g)	1.4e+05	1.3e+05	1.1e+05	2.9e+02	5.1e+04
¹⁵⁵ Eu (Bq/g)	2.9e+04	2.6e+04	< 2.0e+04	< 1.2e+02	1.6e+04
²⁴¹ Am (Bq/g)	2.6e+04	-	< 3.8e+04	-	-
Alpha emitters by alpha spectrometry					
<u>Gross alpha</u> (Bq/g)	4.2e+05	2.1e+05	3.6e+05	< 2.0e+03	4.7e+04
²³³ U (Bq/g)	8.8e+03	1.1e+04	-	-	8.4e+02
²³⁸ Pu/ ²⁴¹ Am (Bq/g)	2.4e+04	2.4e+04	3.2e+04	-	7.4e+03
²³⁹ Pu/ ²⁴⁰ Pu (Bq/g)	7.5e+04	-	1.0e+04	-	2.9e+03
²⁴⁴ Cm (Bq/g)	3.2e+05	1.7e+05	3.1e+05	-	3.3e+04
<u>Total Pu alpha</u> (Bq/g)	4.2e+04	2.8e+04	4.6e+04	-	-
²³⁸ Pu (Bq/g)	2.7e+04	1.8e+04	3.1e+04	-	-
²³⁹ Pu/ ²⁴⁰ Pu (Bq/g)	1.6e+04	9.9e+03	1.5e+04	-	-
²⁴² Pu (Bq/g)	-	-	-	-	-
(²³⁹ Pu) (ng/g)	18300	12200	-	-	-
²³² Th/ ²³⁹ Pu ^k (200)	3137	869	-	-	-

Characteristic (Analysis)	W-25 S (HNO ₃)	W-25 S (HNO ₃ /HF-H ₃ BO ₃)	W-25 S (HNO ₃ /HF-H ₃ BO ₃)+heat	W-25 S (H ₂ O)	W-25 S (Sears)
Uranium isotopics by ICP/MS					
²³³ U (mg/kg)	27.4	36.1	-	-	-
²³⁴ U (mg/kg)	1.33	1.88	-	-	-
²³⁵ U (mg/kg)	128	135	-	-	-
²³⁶ U (mg/kg)	-	-	-	-	-
²³⁸ U (mg/kg)	23200	24800	-	-	-
²³⁸ U/ ²³⁵ U FEM	141	135	-	-	-
²³⁵ U/MS ^h (mg/kg)	116	114	-	-	-
²³³ U (wt. %)	0.1173	0.1446	-	-	-
²³⁴ U (wt. %)	0.0057	0.0075	-	-	-
²³⁵ U (wt. %)	0.5480	0.5406	-	-	-
²³⁶ U (wt. %)	< 0.0010	< 0.0010	-	-	-
²³⁸ U (wt. %)	99.3290	99.3073	-	-	-

(a) % Water, (b) Total inorganic carbon, (c) Total carbon, (d) Total organic carbon, (e) RCRA regulatory limits, (f) Instrument detection limit, (g) Denature ratios for uranium, ²³⁸U/²³⁵U, (h) Concentration of ²³⁵U calculated from the MS and ICP data, (j) Calculated from mass spec. and total Pu alpha data, (k) Denature ratio for plutonium, ²³²Th/²³⁹Pu.

3.2 MVST Supernatant Characteristics

The analytical data for the MVST supernatants are presented in Tables 3.1 and 3.2. This data is based on samples that were first clarified by centrifugation and then stabilized with nitric acid. Although extra care was taken to remove suspended particles from the liquid, some trace amounts of the undissolved solids were present. The evidence of suspended particles is apparent from the TSS measurements and the uranium concentration in the high pH tanks W-24 and W-25. At a pH above 11-12, most compounds of uranium and other actinides in the ORNL waste tanks form an insoluble precipitate. This chemical behavior is apparent with the supernatant data when the pH is compared to the uranium concentration and the alpha activity. When the pH is down to 7.2, in W-27 and W-28, the uranium jumps up to a few hundred parts per million in concentration, but at pH = 13, in W-24 and W-25, the uranium concentration is less than 10 parts per million.

The Group I elements, sodium and potassium, are very soluble in the supernatant at any pH. The concentration of Group II metals, calcium and strontium, increase in the supernatant as the pH decreases. These Group II metals remain somewhat soluble in the liquid phase, even at high pH. As expected, the concentration of silicon compounds increases in the supernatant as the pH increases. Many of the other common metals found in the waste, such as iron and magnesium, are less soluble as the pH increases. In general, as the pH decreases, the total dissolved solids in the supernatant increases.

The sludge layer in the ORNL waste tanks are typically high in several RCRA metals, including chromium, mercury, and lead. At high pH these RCRA metals are below the hazard limits in the supernatant, but as the pH decreases the concentration of these RCRA metals can increase to the point where the regulatory limits are exceeded.

A good check for data completeness is the mass and charge balance, which are summarized in Table 3.6 for the MVST supernatant samples. The mass balance check is based on the summation of cation and anion concentrations divided by the total solids concentration. The total solids concentration is measured directly by weighing a known volume of sample that has been dried to a constant weight. The mass balance data shows excellent agreement, within $\pm 3\%$, for all MVST supernatant samples. The charge balance checks are less accurate than the mass balance check because one must make an assumption about the chemical form and oxidation state for each species present in solution. The charge balance data is based on the

summation of the molar cation charge divided by the summation of the molar anion charge. The charge balance data shows good agreement, within $\pm 14\%$, for all MVST supernatant samples. The charge balance looks especially good considering the assumptions required for the calculation. For both the mass and charge balance checks on the supernatant samples, the calculations were dominated by the sodium, potassium, and nitrate concentration.

Table 3.6. Summary of Mass/Charge Balance and Beta Recovery for MVST Supernatant

Tank	Mass Balance ($TS_{\text{calc.}}/TS_{\text{meas.}}$)	Charge Balance (M^+/A^-)	pH	% ^{137}Cs	% $^{90}\text{Sr}/^{90}\text{Y}$	Beta Recovery (%)
W-24	0.999	0.907	13.0	93.5	0.12	85.7
W-25	0.987	1.017	13.0	93.1	0.18	87.2
W-26	1.019	1.102	9.3	94.8	2.43	82.3
W-27	1.027	1.133	7.2	69.8	29.5	84.6
W-28	1.029	1.144	7.2	70.2	28.7	83.6
W-31	1.014	1.107	11.9	93.1	3.57	81.4

The beta recovery listed in Table 3.6 is based on the summation of the activity for the known beta emitters divided by the gross beta activity. Considering the typical analytical errors associated with radiochemical measurements, the beta recoveries listed in Table 3.6 are excellent. The gross beta data reported is based on a calibration with ^{90}Sr and ^{90}Y in equilibrium, and when applied to a mixture of radionuclides the beta activity, is by definition, the strontium equivalent activity. The beta activity can have a significant error ($\pm 10\text{-}15\%$) when applied to a mixture of radionuclides, and care must be exercised when using any gross beta data to account for all radionuclides in a sample. Also, one must take into account the large effect the analytical error for the radioactive strontium activity can have on the beta recovery result. Since the ^{90}Sr is in secular equilibrium with the ^{90}Y , and only the radioactive strontium is measured directly, any error on the ^{90}Sr result would be doubled when calculating the beta recovery.

Another point of interest in Table 3.6 is the distribution of ^{137}Cs and ^{90}Sr as a function of pH. At the highest pH, almost all the ^{90}Sr is precipitated into the sludge. As the pH decreases the ^{90}Sr slowly increases

until somewhere between pH=9.3 and pH=7.2, there is a significant jump in the relative amount of ^{90}Sr present in the supernatant.

In general, the beta/gamma emitters found in the supernatant represent what would be expected for fission product waste that had been aged for several years. The relative distribution of the beta activity in the MVST supernatant is summarized in Table 3.7. The distribution of the activity in these MVST supernatant samples is typical of ORNL liquid waste. The ORNL liquid waste is normally stored at a caustic pH and the radioactive cesium dominates the activity. The pH in tanks W-27 and W-28 are lower than what is usually observed and there is a corresponding increase in the strontium and uranium in the liquid phase.

Table 3.7. Distribution of Beta Activity in Supernatant

Tank	pH	Percent of Total Beta Activity				Uranium (mg/L)
		$^{90}\text{Sr}/^{90}\text{Y}$ (%)	^{99}Tc (%)	^{134}Cs (%)	^{137}Cs (%)	
W-24	13.0	0.12	0.06	6.4	93.4	5.8
W-25	13.0	0.18	0.06	6.7	93.0	3.0
W-26	9.3	2.4	0.14	2.6	94.7	1.3
W-27	7.2	29.5	0.06	0.31	69.7	503
W-28	7.2	28.7	0.05	0.50	70.2	234
W-31	11.9	3.6	0.12	3.3	93.0	2.3

The ^{134}Cs , with a half life of 2.07 years, is the shortest lived radionuclide observed in the liquid waste, which indicates that some of the mixed fission products were produced in the last ten years. The ^{134}Cs is a poor indicator for the waste decay time because of its relatively low fission yield, which is due to the ^{134}Cs being a shielded fission product. A shielded nuclide is one that has a stable isobar one unit lower in atomic number (Z) so that it can not be formed as a daughter product in a beta-decay chain. The total fission yield for ^{134}Cs is due to its direct formation as a fission product plus the (n, γ) reaction with ^{133}Cs , and is much lower than the fission yield for ^{137}Cs , which is not a shielded fission product.

The alpha activity in the supernatant is low, as would be expected with a caustic pH. The small amount of alpha activity that is observed in the liquid phase can not be accounted for with the uranium present, however, the mass of the uranium present is much higher than the other actinides. Below pH = 12, the uranium forms a complex with the carbonate present and becomes more soluble as the pH decreases. As can be seen in Table 3.4, at the higher pH the uranium is present below 10 mg/L, and when the pH drops to 7.2 the uranium concentration increases significantly.

The alpha content in the MVST supernatant is usually very low, but can increase if the pH is allowed to decrease below 10. The gross alpha for the supernatant samples varies from < 20 to 300 Bq/mL. Based on past experience, the alpha activity is likely due to suspended particles which are usually dominated by the ^{244}Cm alpha activity present. The uranium contribution to the total alpha activity is typically minor relative to the ^{244}Cm activity present in ORNL waste.

3.3 BVEST and MVST Sludge Characteristics

Determination of the mass and charge balance for the sludge samples are more difficult than for the supernatant samples. Not only are there assumptions required about the chemical form and the oxidation state of the species present in the sludge, but many of the compounds in the sludge are mixed oxides which are not directly measured. Also, the sludge is actually a slurry with a high water content. The interstitial liquid is in close contact with the sludge, and there are many ionic solubility equilibria. The anion data for the sludge samples are based on the water soluble anions that would be available to a water wash. The water wash would not account for the insoluble hydroxides, carbonates, and mixed oxides present. The insoluble species do not contribute to the charge balance, and the cation charge is not used in the calculation, as indicated in Table 3.8. Most of the nitrate reported for the sludge is due to the interstitial liquid. Considering these limitations, the compounds listed in Table 3.8 were used to estimate the mass and charge balance

Table 3.9 summarizes the mass and charge balance for the two BVEST (W-21 and W-23) tank sludge samples and the MVST sludge from W-25. Considering the limitations of these calculations, the mass

balance is within the analytical error ($\pm 20\%$) for these sludge samples. The charge balance is more influenced by the chemical form assumptions, and the results have a larger corresponding error range. The low charge balance for W-21 results from the assumption that most of the actinide elements are present as insoluble hydroxides or oxides. The low pH and the low charge balance ratio for W-21 indicates that much of the uranium may be present as soluble uranyl nitrate.

Table 3.8. Assumption Used for Major Compounds in LLLW Sludge

Cation	Chemical Form	Cation Charge Used	Gravimetric Factors
Al ³⁺	Al ₂ O ₃	0	1.890
Ca ²⁺	CaCO ₃	0	2.497
Fe ³⁺	Fe ₂ O ₃	0	1.430
K ⁺	K ⁺ NO ₃ ⁻	+1	2.586
Mg ²⁺	Mg(OH) ₂	0	2.399
Mn ²⁺	Mn(OH) ₂	0	1.619
Na ⁺	Na ⁺ NO ₃ ⁻	+1	3.697
Th ⁴⁺	Th(OH) ₄	0	1.293
UO ₂ ²⁺	UO ₂ ((OH) ₂ -H ₂ O	0	1.353

Table 3.9. Summary of Mass/Charge Balance and Beta Recovery for LLLW Sludge

Tank	Mass Balance (TS _{calc.} /TS _{meas.})	Charge Balance (M ⁺ /A ⁻)	pH	% ¹³⁷ Cs	% ⁹⁰ Sr	Beta Recovery (%)
W-21	0.877	0.552	8.3	4.1	29.5	105
W-23	0.802	1.079	12.4	9.6	28.7	100
W-25	0.963	1.301	-	3.5	94.3	77

The beta recovery results are listed in Table 3.9, and most of the discussion for the supernatant samples also apply to the sludge samples. As discussed before, the low beta recovery for W-25 is probably due to the analytical error on the ^{90}Sr measurement. A 10% error for the ^{90}Sr activity would result in a 20% error for the beta recovery calculation.

The distribution of the beta emitters are summarized in Table 3.10, and the observed distributions are shown to be dependent upon both the pH and the age of the radioactive waste. The major difference in the beta distribution between the supernatant and the sludge is that the distribution of the longer lived fission products (^{90}Sr and ^{137}Cs) are reversed due to the differences in solubility. The Group I metals (^{134}Cs and ^{137}Cs) and the radionuclides that form anionic species ($^{99}\text{TcO}_4^-$, $^{129}\text{I}^-$, and $^{129}\text{IO}_3^-$) are more soluble in the supernatant. Most of the other metals, lanthanides, and actinides form insoluble hydroxides and mixed oxides, and are found in the sludge. The ^{99}Tc activity is 2-14 times higher in the supernatant than the sludge, and most of the ^{99}Tc in the sludge sample comes from the interstitial liquid. Both W-21 and W-23 collect the most recently generated radioactive waste and the beta activity is more weighted towards the radionuclides with a shorter half-life. The shorter lived radionuclides observed include the europium (^{152}Eu , ^{154}Eu , and ^{155}Eu) isotopes and to some extent ^{134}Cs . The waste stored in the MVST tank W-25 has been aged longer and the beta activity is dominated by the $^{90}\text{Sr}/^{90}\text{Y}$ equilibrium pair.

Table 3.10. Distribution of Beta Activity in Sludge

Tank	pH	Percent of Total Beta Activity					
		$^{90}\text{Sr}/^{90}\text{Y}$ (%)	$^{134}\text{Cs}+^{137}\text{Cs}$ (%)	^{60}Co (%)	^{99}Tc (%)	$^{152,154,155}\text{Eu}$ (%)	^{241}Pu (%)
W-21	8.3	29.5	4.2	1.8	0.03	63.0	1.4
W-23	12.4	28.5	9.5	4.4	0.01	56.4	0.9
W-25	-	94.3	3.5	0.5	-	1.7	-

The distribution of the alpha activity is summarized in Table 3.11, which includes both the activity and the percent alpha for each tank sludge sample. In general, the alpha activity in the LLLW system is strongly weighted by the ^{244}Cm , which has a high specific activity.

Table 3.11. Summary of Actinides Found in Sludge Samples

Actinide	W-21		W-23		W-25	
	(Bq/g)	(%)	(Bq/g)	(%)	(Bq/g)	(%)
²³² Th	30	0.02	31	0.03	230	0.06
²³³ U	9700	6.6	19000	16.6	8800	2.2
²³⁴ U	< 570	< 0.4	< 900	< 0.8	280	0.07
²³⁵ U	4.3	0.00	6.4	0.00	8.2	0.00
²³⁸ U	310	0.21	490	0.43	260	0.07
²³⁷ Np	6.1	0.00	6.1	0.00	-	-
²³⁸ Pu	14000	9.6	7200	6.3	27000	6.8
²³⁹ Pu ^a	3200	2.2	2600	2.3	16000	4.0
²⁴⁰ Pu	2800	1.9	2300	2.0	-	-
²⁴¹ Pu (β ⁻)	41000	na	37000	na	-	-
²⁴¹ Am ^b	17000	11.6	15000	13.1	26000	6.5
²⁴⁴ Cm	99000	67.8	68000	59.3	320000	80.3
	146050	na	114634	na	398578	na
Gross	150000	na	120000	na	420000	na

^a For the W-25 data the ²³⁹Pu is actually the sum of the ²³⁹Pu and the ²⁴⁰Pu.

^b For the W-21 and W-23 samples, the ²⁴¹Am data is based on subtracting the ²³⁸Pu by TIMS from the alpha peak measured at 5.15 MeV (²³⁸Pu + ²⁴¹Am) in the alpha spectrum. The ²⁴¹Am for the W-25 sample is based on a gamma spectral measurement of the 59 KeV gamma-ray.

The list of actinides in Table 3.11 required several radiochemical and inorganic analytical measurements to generate the best estimates for each of the alpha activities. The ²³²Th activity is calculated from the total thorium measured by ICP-AES. The other thorium isotopes (²²⁸Th, ²²⁹Th, and ²³⁰Th) are present in the ORNL sludge waste at such low mass, their presence would not effect the ICP-AES measurement. The uranium isotopes are measured by TIMS. The atom % results are converted to weight %, which is used to calculate the concentration of each uranium isotope from the total uranium results obtained by ICP-

AES. The activity for each uranium radionuclide is then calculated from the specific activity for each isotope. The plutonium isotopes are first measured by TIMS, and the total plutonium alpha activity, measured after a chemical separation, is used to calculate the activity for each isotope. The ^{244}Cm was measured directly by alpha spectrometry without any chemical separation. The ^{241}Am activity is determined by subtracting the ^{238}Pu activity from the sum of the $^{238}\text{Pu} + ^{241}\text{Am}$ measured by alpha spectrometry. Both ^{238}Pu and ^{241}Am have an alpha energy of about 5.50 MeV and can not be resolved by alpha spectrometry. Future work will include a chemical separation of tri-valent actinides (Am, Cm, ...) prior to measurement by alpha spectrometry.

The RMAL has recently acquired an inductively coupled plasma - mass spectrometer (ICP-MS), which has been installed in a radiochemical hood for contamination control. The ICP-MS will allow the direct measurement of most of the actinide elements and is more sensitive than alpha counting for radionuclides with a half life greater than about 300 years. This ICP-MS was not available for analysis of the waste samples discussed in this report, but the system will make a significant contribution to future characterization projects. The ICP-MS will also enhance the measurement of long-lived fission products that are difficult to determine by counting techniques.

3.4 RCRA Characteristics for LLLW System

The RCRA regulatory limits are listed in Table 3.12, which also includes the limits for the EPA Toxicity Characteristic Leaching Protocol (TCLP) extract and the functional total metal limits for a solid or sludge waste. The total metal limits are a factor of twenty times higher than the TCLP extraction limits and are based on the 1:20 dilution used for the TCLP extraction procedure. If the RCRA metal concentrations are below the total metal limits, the solid waste can not fail the TCLP leach test. If the RCRA metal concentrations exceed the total metal limits, the TCLP leach test must be done to determine if the solid waste is hazardous. For solid samples, the TCLP leach test is only defined for a final waste form ready for disposal. The total metal concentration data can be used as acceptable process knowledge if the final waste form only results in a dilution of the RCRA metal concentrations. Examples of waste forms that results in a dilution of a solid waste includes grouting (2 fold dilution) and vitrification (3 fold dilution). If the total metal limit are exceeded after stabilizing the waste, the TCLP leach test would be required for only the metals that had the potential to exceed the regulatory limits.

Table 3.12. Summary of RCRA Regulatory Limits

Metals		TCLP Extract and Liquids (mg/L)	Solid/Sludge Total Metal (mg/Kg)
Silver	(Ag)	5	100
Arsenic	(As)	5	100
Barium	(Ba)	100	2000
Cadmium	(Cd)	1	20
Chromium	(Cr)	5	100
Mercury	(Hg)	0.2	4
Nickel	(Ni)	50	1000
Lead	(Pb)	5	100
Selenium	(Se)	1	20
Thallium	(Tl)	0.9	18

Several of the supernatant samples from the MVST tanks exceed the RCRA regulatory limits. These tanks include W-27 for mercury, and W-31 for both mercury and chromium. Waste tanks W-24 and W-31 come close to exceeding the limits for cadmium and could be considered over the limit depending on the confidence limits used. The current technology used for long term storage of the liquid waste is a solidification process that results in a final waste form that passes the TCLP leach test. The nickel and thallium are proposed RCRA metals and are include in the data for future waste management decisions.

Both the BVEST tank sludge samples (W-21 and W-23) and the MVST tank sludge from W-25 exceed the total metal limits for chromium, lead, and mercury. Most of the ORNL radioactive waste sludge samples, characterized to date, have exceeded the total metal limits for these three RCRA metals. The total metal limits for cadmium and thallium are also exceeded in the W-21 sludge, and the cadmium limit is exceeded in the W-25 sludge. Based on past experience, it is expected that solidification of the ORNL LLLW sludge would fix these RCRA metals such that the final waste form would pass the TCLP leach test.

3.5 TRU Classifications for LLLW System

The DOE definition for Transuranic (TRU) Waste includes the following conditions,

- TRU activity ≥ 3700 Bq/g (100 nCi/g),
- TRU isotopes must be alpha emitting actinides with $Z > 92$ (uranium),
- TRU isotopes must have a half life ≥ 20 years.

This definition excludes all thorium and uranium isotopes. The short lived actinide ^{244}Cm ($t_{1/2} = 18.1$ years), which is common to ORNL waste, falls outside the TRU definition. Also, the plutonium isotope, ^{241}Pu , would be excluded from calculation of the TRU activity because it is a pure beta emitter. The primary actinide elements common to ORNL waste, that are present at sufficient levels to meet the TRU definition, include ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Am . There is some current work at the Radiochemical Engineering Development Center (Mark-42 fuel assembly processing) that could generate enough ^{243}Am so that the waste could be classified as TRU. The remaining actinides are not normally available at high enough activity in ORNL waste to meet the TRU definition.

If the pH of the LLLW supernatant is kept above seven it is unlikely that any of the liquid waste would ever be classified as TRU. None of the MVST supernatant samples discussed in this report had enough alpha activity to be considered as TRU waste. All of the active LLLW sludge that has been characterized to date has been classified as TRU waste. From Table 3.11, it is apparent that W-21, W-23, and W-25 are all transuranic, even with the alpha activity dominated by the ^{244}Cm activity. The alpha activity reported is based on wet weight, if adjusted for dry weight the activity would almost double. These three sludge samples contained enough plutonium and americium activity to easily satisfy the WIPP waste acceptance criteria¹⁰ for transuranic waste. Based on the TRU activity, a dilution of the sludge activity that would result from a solidification process such as grouting or vitrification would not effect the TRU classification.

3.6 Distribution of Fissile Material in LLLW System

As discussed in section 2.25, the ORNL LLLW waste acceptance criteria requires the fissile isotopes of uranium and plutonium to be diluted with ^{238}U and ^{232}Th , respectively. Table 3.13 summarizes the dilution or “denature” ratios for the MVST supernatant samples. All the dilution ratios for the MVST liquid phase exceed the required factor of 100. Only two of the supernatant samples, W-27 and W-28, had a pH low enough to allow estimates for the plutonium ratios. The solubility of the actinide elements above uranium are very low at pH levels above neutral.

Table 3.13. Summary of Dilution Ratios for MVST Supernatant

Tank	$^{238}\text{U}/^{235}\text{U}$ FEM	$^{232}\text{Th}/^{239}\text{Pu}$	pH
W-24	231	na ^a	13.0
W-25	200	na	13.0
W-26	209	na	9.3
W-27	242	55700	7.2
W-28	242	59600	7.2
W-31	216	na	11.9

^a Concentration of thorium and plutonium too low to calculate ratio.

A summary of the dilution ratios for fissile material in the sludge samples is provided in Table 3.14. All the dilution ratios for the sludge samples exceed the required factor of 100 for the fissile isotopes of uranium and plutonium.

Table 3.14. Summary of Dilution Ratios for LLLW Sludge

Tank	²³⁸ U/ ²³⁵ U FEM	²³² Th/ ²³⁹ Pu	pH
W-21	256	5280	8.3
W-23	238	6717	12.4
W-25	141	3137	-

There is a small difference between atom %, reported for the uranium and plutonium, and weight %, which is needed for many calculations performed with the analytical data. To convert from atom % to weight %, we used the following equation,

$$W_i = \frac{a_i M_i}{\sum_i^n a_i M_i} \times 100\%$$

where, W_i = weight %,
 M_i = isotopic mass
 a_i = atom %.

An example of this calculation is provided in Table 3.15. As can be seen from the example calculation there is not much difference between the atom % and the weight %.

Table 3.15. Example of Converting Atom % to Weight % for W-21 Sludge

Isotope	Isotope mass (g/mol)	atom %	($a_i M_i$)	weight %
²³³ U	233.039629	0.11	25.6344	0.1077
²³⁴ U	234.040947	0.01	2.3404	0.0098
²³⁵ U	235.043924	0.24	56.4105	0.2370
²³⁶ U	236.045563	0.01	2.3605	0.0098
²³⁸ U	238.050785	99.64	23719.3802	99.6356
Total		100.01	23806.1260	99.9999

3.7 Miscellaneous Comments

In the presence of low concentrations of chloride the RCRA metal silver cannot be determined accurately in a sample that has been digested with only nitric acid. This sample matrix effect is due to the formation of an insoluble silver chloride. If the sample is digested in a nitric-hydrochloric acid mixture, the high chloride forms a soluble silver chloride complex which then allows the determination of valid silver concentrations. The high chloride has also been observed to improve the recovery of antimony. Since a sample preparation with a nitric-hydrochloric acid digestion was available from the silver measurements, and the analytical instruments were already calibrated, the cost to measure the full set of metals was relatively low. Therefore, the metals, gross alpha/beta, and the gamma emitters were determined to evaluate the general effect of chloride on these measurements.

The sludge samples from W-21 and W-23 were taken through a water wash to determine the water soluble anions and measure the effect of the sludge on pH. For the same reason discussed for the nitric-hydrochloric acid sample digestion, the metals, gross alpha, and gamma emitters were measured on the wash to evaluate the relative solubility of the sludge in water.

This report provides the first accurate data for uranium and plutonium isotopic ratios in the active LLLW system. This isotopic ratio data is needed to address criticality safety concerns for the BVEST and MVST waste tanks. Also, some of the first radiochemical data for ⁹⁹Tc, ²³⁷Np, and ²⁴¹Pu activities in the active LLLW system, are provided in this data summary. Although, we are confident that greater than 99% of the radioactivity has been accounted for in these waste samples, there remains some interest in the

measurement of radionuclides for nickel (^{59}Ni and ^{63}Ni) and samarium (^{151}Sm). These additional radionuclides need to be considered for future waste characterization projects.

There is a new sampling campaign planned for late summer of 1996 to provide additional analytical data on the BVEST and MVST systems. The new analytical data for the waste tanks will help address new QA requirements, provide additional measurements to support waste processing options and risk assessments, and improve the confidence level on existing data. There has been new methodology developed, since the characterization work on this project was completed, for the measurement of water soluble chelators by ion chromatography. Analytical data is needed for water soluble chelators for additional evaluation of the mobility of metals and radionuclides in the environment. The presence of significant amounts of complexing agents could change the outcome of risk assessments or influence the expected behavior of fissile elements in the waste.

4.0 SUMMARY OF ORGANIC ANALYSIS ON TANKS W-21 AND W-23 SLUDGE

The organic compound content of these two sludges was very low, and consisted mainly of compounds expected from the Purex and other transuranics separation processes. The TWCP target compound hits and the tentatively identified compounds (TICs) from the GC-MS analyses are listed in Table 4.1. In the following discussions the J qualifier signifies that the result is an estimated value and the B indicates the analyte also was found in the blank. There were no hits on the TWCP target compounds in any of the analyses, with method detection limits of 10 mg/kg for the NHVOA, 1 mg/kg for the VOA, 0.6 - 10 mg/kg for the SVOA, and 0.025 - 0.05 mg/kg for the PCB analysis. Several TICs were estimated in the volatile and the semivolatile organics analyses. In the VOA, the W-21 sludge was found to contain two C₄-benzene isomers (probably diethyl benzenes at 0.38 J and 0.19 J mg/kg each), a C₆-benzene (0.19 J mg/kg), dodecane (0.1 J mg/kg), tridecane (0.18 J mg/kg), tetradecane (0.11 J mg/kg), and heptanone (0.13 J mg/kg), while W-23 was not different from the blank. In the semivolatile organics analysis, W-21 and W-23 were both found to contain tributylphosphate (25 J and 1 J mg/kg, respectively), tris(ethylhexyl)phosphate (17 BJ and 3.8 J mg/kg, respectively), and dodecane (14 J and 3.3 J mg/kg, respectively), tridecane (43 J and 5.7 J mg/kg, respectively), and tetradecane (29 J and 4.9 J mg/kg, respectively). The concentrations of the alkanes measured in the semivolatile organics analysis were higher than in the volatile organics analysis because of the greater efficiency of solvent extraction versus purge and trap for these compounds. The phthalates were also detected in the blanks and cannot be attributed to the sludges. A trace of tris(ethylhexyl)phosphate also was detected in the blank processed with sludge W-21, but its concentration was much lower than what was found in the sludge (0.83 J versus 17 BJ mg/kg, respectively).

4.1 Organic Quality Control

The surrogate standard recoveries for the four analyses are listed in Tables 4.2-4.5. The surrogate standard on column 1 of the NHVOA was low, but this did not affect data quality because the surrogate standard recovery on column 2 was in control. One of the VOA surrogate standards (1,2-dichloroethane-d₄) was slightly high in one blank and in the W-23 MSD. There was no adverse effect on data quality because there were no target compound hits. Any hits could be biased slightly high. The recovery of the PCB surrogate standard was very low for sludge W-21, and low for sludge W-23 and the two blanks. This

indicates a low bias to the results, but, because of the very low reporting limits for the PCBs (0.025 - 0.05 mg/kg) versus the LMES limit for PCB concentration (2 mg/kg), the sludges most likely do not exceed the LMER limit and certainly not the EPA limit of 50 mg/kg.

MS and MSD spike recoveries and relative percent differences (RPD) for the four analyses are listed in Tables 4.5-4.7. All of the NHVOA and the PCB MS and MSD data were in control. The recoveries of 4 of the 5 compounds in the VOA MSD were low, and contributed to the high RPD. This result indicates a low bias to the analytical results. In the SVOA, the two cresols and pentachlorophenol were low in both the MS and MSD. This most likely is a matrix effect of the alkaline sludge sample upon acidic analytes and it indicates that data for such compounds are biased low. The recovery of hexachloroethane also was slightly low in the MS.

LCS analyte recoveries are shown in Tables 4.8-4.10. The LCS analytes were all in control for the NHVOA, SVOA and PCB analysis. However, recoveries of 21 of the analytes in the VOA LCS were higher than the DQO, as opposed to the MSD, where recoveries were low. The latter suggests that matrix effects may cause a low bias to results, while the former suggests that the analytical system should be yielding results with a high bias. The cause of this disparity is not clear. The net effect on data quality is negligible, because there were no target compound hits.

Table 4.1. Organic Results of Analysis for Sludges from Tanks W-21 and W-23

Target Compound	Concentration in Sludge, mg/Kg			
	W-21	Blank	W-23	Blank
Non-halogenated Volatile Organic Compounds				
Methanol	10 U	10 U	10 U	10 U
Acetone	10 U	10 U	10 U	10 U
Methyl Ethyl Ketone	10 U	10 U	10 U	10 U
Isobutanol	10 U	10 U	10 U	10 U
Butanol	10 U	10 U	10 U	10 U
Pyridine	10 U	10 U	10 U	10 U
Volatile Organic Compounds				
Vinyl Chloride	1 U	1 U	1 U	1 U
Trichlorofluoromethane	1 U	1 U	1 U	1 U
Ethyl Ether	1 U	1 U	1 U	1 U
1,1,2-Trichloro-1,2,2-trifluoroethane	1 U	1 U	1 U	1 U
1,2-Dichloroethylene	1 U	1 U	1 U	1 U
Methylene Chloride	1 U	1 U	1 U	1 U
Chloroform	1 U	1 U	1 U	1 U
1,2-Dichloroethane	1 U	1 U	1 U	1 U
1,1,1-Trichloroethane	1 U	1 U	1 U	1 U
Carbon Tetrachloride	1 U	1 U	1 U	1 U
Benzene	1 U	1 U	1 U	1 U
Trichloroethylene	1 U	1 U	1 U	1 U
1,1,2-Trichloroethane	1 U	1 U	1 U	1 U
Bromoform	1 U	1 U	1 U	1 U
Toluene	1 U	1 U	1 U	1 U
Tetrachloroethylene	1 U	1 U	1 U	1 U

Target Compound	Concentration in Sludge, mg/Kg			
	W-21	Blank	W-23	Blank
Chlorobenzene	1 U	1 U	1 U	1 U
Ethylbenzene	1 U	1 U	1 U	1 U
m&p-Xylenes	1 U	1 U	1 U	1 U
o-Xylene	1 U	1 U	1 U	1 U
1,1,2,2-Tetrachloroethane	1 U	1 U	1 U	1 U
1,4-Dichlorobenzene	1 U	1 U	1 U	1 U
Ortho-Dichlorobenzene	1 U	1 U	1 U	1 U
Tentatively Identified Volatile Organic Compounds				
Bromomethane	1 U	1 U	0.17 J	0.16 J
Heptanone	0.13 J	1 U	1 U	1 U
C ₄ -Benzene Isomer	0.38 J	1 U	1 U	1 U
C ₄ -Benzene Isomer	0.19 J	1 U	1 U	1 U
C ₆ -Benzene Isomer	0.19 J	1 U	1 U	1 U
Dodecane	0.1 J	1 U	1 U	1 U
C ₆ -Benzene Isomer	0.11 J	1 U	1 U	1 U
Tridecane	0.18 J	1 U	1 U	1 U
Tetradecane	0.11 J	1 U	1 U	1 U
Unknown	1 U	0.34 J (1) ^a	0.28 JB (1) ^a	0.22 J (1) ^a
Semivolatile Organic Compounds				
2-Methyl Phenol	10 U	10 U	10 U	10 U
Hexachloroethane	10 U	10 U	10 U	10 U
4-Methyl Phenol	10 U	10 U	10 U	10 U
Nitrobenzene	10 U	10 U	10 U	10 U
2,4-Dinitrotoluene	0.6 U	0.6 U	0.6 U	0.6 U
2,4-Dinitrophenol	10 U	10 U	10 U	10 U
Hexachlorobenzene	0.6 U	0.6 U	0.6 U	0.6 U

Target Compound	Concentration in Sludge, mg/Kg			
	W-21	Blank	W-23	Blank
Pentachlorophenol	10 U	10 U	10 U	10 U
Tentatively Identified Semivolatile Organic Compounds				
Dodecane	14 J	10 U	3.3 J	10 U
Tridecane	43 J	10 U	5.7 J	10 U
Tetradecane	29 J	10 U	4.9 J	10 U
Dibutylphthalate	3.1 BJ	14 J	5.9 J	8.2 J
Tributylphosphate	25 J	10 U	1.0 J	10 U
Tris(ethylhexyl)phosphate	17 BJ	0.83 J	3.8 U	10 U
Unknown	180 J (12) ^a	3.2 J (2) ^a	27 (14) ^a	13 J (2) ^a
Ethylphenylethanone	18 (2) ^a	10 U	10 U	10 U
Bis(2-ethylhexyl)phthalate	10 U	10 U	10 U	0.2 U
PCB Analysis				
Aroclor-1016	0.025 U	0.025 U	0.025 U	0.025 U
Aroclor-1221	0.050 U	0.050 U	0.050 U	0.050 U
Aroclor-1232	0.025 U	0.025 U	0.025 U	0.025 U
Aroclor-1248	0.025 U	0.025 U	0.025 U	0.025 U
Aroclor-1254	0.025 U	0.025 U	0.025 U	0.025 U
Aroclor-1260	0.025 U	0.025 U	0.025 U	0.025 U

^a Number of compounds listed in parenthesis.

Table 4.2. Surrogate Standard Recoveries for Nonhalogenated Volatile Organics Analysis

Sample	Recovery for Propanol Surrogate Standard, %	
	Column 1 (65-138)	Column 2 (49-127)
LCS 212	111	102
Blank 213	111	111
W-21	99	96
LCS 123	73	93
Blank 126	89	86
W-23	17	61
W-23 MS	79	75
W-23 MSD	102	83

Table 4.3. Surrogate Standard Recoveries for Volatile Organics Analysis

Sample	Recovery for Surrogate, %		
	1,2-Dichloroethane-d ₄ (QC Limits: 67-131)	Toluene-d ₈ (QC Limits: 95-118)	4-Bromofluorobenzene (QC Limits: 90-107)
Blank 212	135	101	103
WC-21	124	105	101
Blank 129	113	107	99
LCS129	98	107	105
W-23	131	106	107
W-23 MS	125	105	105
W-23 MSD	136	105	102

Table 4.4. Surrogate Standard Recoveries for Semivolatile Organics Analysis

Sample	Recovery for Surrogate ^a , %					
	2FP (D-107)	P-d ₅ (8-142)	NBZ-d ₅ (28-117)	2FBP (24-145)	TBP (D-156)	TPH-d ₁₄ (D-226)
Blank 213	42	51	68	76	89	86
W-21	35	46	55	60	3	67
Blank126	48	62	67	68	68	120
LCS126	49	64	67	70	76	109
W-23	2	12	67	70	8	96
W-23 MS	10	22	68	74	16	110
W-23 MSD	3	14	71	74	9	105

^a 2FP= 2-fluorophenol, P-d₅= phenol-d₅, NBZ-d₅= nitrobenzene-d₅, 2FBP= 2-fluorobiphenyl, TBP= tribromophenol, TPH-d₁₄= terphenyl-d₁₄. QC Limits listed in parenthesis.

Table 4.5. Surrogate Standard Recoveries for PCB Analysis.

Sample	Recovery of Decachlorobiphenyl, % (QC Limits 60-150)	
	Column 1	Column 2
Blank 213	58	60
W-21	1	1
Blank 126	39	40
LCS 126	82	75
W-23	32	32
W-23 MS	75	72
W-23 MSD	77	75

Table 4.6. Matrix Spike Recoveries for Nonhalogenated Volatiles Analysis

Column 1

Compound	Recovery, %			RPD ^a , %	
	MS	MSD	QC Limits	MS&MSD	QC Limits
Methanol	86	107	60-150	22	≤50
Acetone	73	94	60-150	25	≤50
Methyl Ethyl Ketone	68	84	60-150	21	≤50
Isobutanol	72	88	60-150	20	≤50
Butanol	74	92	60-150	22	≤50
Pyridine	77	97	60-150	23	≤50

^aRPD= relative percent difference.

Column 2

Compound	Recovery, %			RPD ^a , %	
	MS	MSD	QC Limits	MS&MSD	QC Limits
Methanol	75	80	60-150	6	≤50
Acetone	71	77	60-150	8	≤50
Methyl Ethyl Ketone	74	76	60-150	3	≤50
Isobutanol	71	75	60-150	5	≤50
Butanol	70	76	60-150	8	≤50
Pyridine	66	75	60-150	13	≤50

^aRPD= relative percent difference.

Table 4.7. Matrix Spike Recoveries for Volatile Organics Analysis

Compound	Recovery, %			RPD ^a , %	
	MS	MSD	QC Limits	MS&MSD	QC Limits
1,1-Dichloroethylene	41	12	D-234	108	≤250
Benzene	79	16	37-151	133	≤45
Trichloroethylene	62	13	71-157	131	≤36
Toluene	91	23	47-150	119	≤29
Chlorobenzene	111	35	37-160	104	≤38

^aRPD= relative percent difference.

Table 4.8. Matrix Spike Recoveries for Semivolatile Organics Analysis

Compound	Recovery, %			RPD ^a , %	
	MS	MSD	QC Limits	MS&MSD	QC Limits
Semivolatile Organics Analysis					
2-Methyl Phenol	39	41	60-150	5	≤50
Hexachloroethane	39	40	40-113	3	≤44
4-Methyl Phenol	44	42	60-150	5	≤50
Nitrobenzene	64	67	35-180	5	≤72
2,4-Dinitrotoluene	62	63	39-139	2	≤46
Hexachlorobenzene	54	56	D-152	4	≤319
Pentachlorophenol	3	2	14-176	23	≤128
PCB Analysis					
Aroclor-1248	123	130	60-150	5	≤150

^aRPD= relative percent difference.

Table 4.9. Laboratory Control Sample Recovery for Nonhalogenated Volatiles Analysis

LCS 123

Compound	Recovery, %		
	Column 1	Column 2	QC Limits
Methanol	70	92	49-145
Acetone	72	92	61-136
Methyl Ethyl Ketone	71	89	62-134
Isobutanol	71	89	52-126
Butanol	70	88	50-110
Pyridine	63	84	64-122

LCS 212

Compound	Recovery, %		
	Column 1	Column 2	QC Limits
Methanol	124	111	49-145
Acetone	112	109	61-136
Methyl Ethyl Ketone	105	107	62-134
Isobutanol	105	106	52-126
Butanol	107	104	50-110
Pyridine	115	107	64-122

Table 4.10. Laboratory Control Sample Recovery for Volatile Organics Analysis

Compound	Recovery, %	
	LCS 129	QC Limits
Vinyl Chloride	84	34-100
Trichlorofluoromethane	113	43-100
Ethyl Ether	135	51-100
1,1,2-Trichloro- 1,2,2trifluoroethane	137	46-100
1,1-Dichloroethylene	116	39-100
Methylene Chloride	152	65-101
Carbon Disulfide	96	32-100
Chloroform	172	69-105
1,2-Dichloroethane	175	72-107
1,1,1-Trichloroethane	169	72-100
Carbon Tetrachloride	166	47-108
Benzene	166	70-101
Trichloroethylene	176	81-100
1,1,2-Trichloroethane	181	75-107
Bromoform	171	52-114
Toluene	178	80-120
Tetrachloroethylene	188	80-120
Chlorobenzene	184	80-120
Ethylbenzene	184	80-120
m&p-Xylenes	37	80-120
o-Xylene	185	80-120
1,1,2,2-Tetrachloroethane	184	58-116
1,4-Dichlorobenzene	180	80-120
ortho-Dichlorobenzene	170	80-120

Table 4.11. Laboratory Control Sample Recovery for SVOA and PCB Analyses

Compound	Recovery, %	
	LCS 126	QC Limits
Semivolatile Organics Analysis		
2-Methyl Phenol	63	46-104
Hexachloroethane	60	38-100
4-Methyl Phenol	66	46-114
Nitrobenzene	63	49-100
2,4-Dinitrotoluene	79	54-146
Hexachlorobenzene	74	52-115
2,4-Dinitrophenol	51	47-100
Pentachlorophenol	55	54-130
PCB Analysis		
Aroclor-1248	82	60-150

5.0 REFERENCES

1. M. B. Sears, J. L. Botts, R. N. Ceo, J.J. Ferrada, W. H. Griest, J. M. Keller, and R. L. Schenley, *Sampling and Analysis of Radioactive Liquid Wastes and Sludges in the Melton Valley and Evaporator Facility Storage Tanks at ORNL*, ORNL/TM-11652, September 1990.
2. F. J. Peretz, B. R. Clark, C. B. Scott, and J. B. Berry, *Characterization of Low-Level Liquid Wastes at the Oak Ridge National Laboratory*, ORNL/TM-10218, December 1986.
3. M. B. Sears, *Results of Sampling the Contents of the Liquid Low-Level Waste Vaporator Feed Tank W-22*, ORNL/TM (in preparation).
4. S. M. DePaoli, Oak Ridge National Laboratory, personal communication to J. M Keller, June 25, 1996.
5. U. S. Environmental Protection Agency, *Test Methods for Evaluating Soild Waste*, SW-846, 3rd ed, Office of Soild Waste and Emergency Response, Washington, D.C., November 1986; Update I, July 1992; and Final Update II, September 1994.
6. J. M. Giaquinto, A. M. Essling, and J. M. Keller, *Comparison of SW-846 Method 3051 and SW-846 Method 7471A for the Preparation of Soild Waste Samples for Mercury Determination*, ORNL/TM-13236, July 1996.
7. *Transuranic Waste Characterization Quality Assurance Program Plan*, Rev. 0, CAO-94-1010, April 30, 1995
8. *Radioactive Materials Analysis Laboratory - Oak Ridge National Laboratory (RMAL-ORNL) Quality Assurance Project Plan (QAPjP) for the Transuranic Waste Characterization Program (TWCP)*, Rev. 1, QAP-X-CASD/RML-002, January 1996.
9. *Radioactive Materials Analysis Laboratory Quality Assurance Plan for the Characterzation of Radioactive Waste*, QAP-X-CASD/RML-001, Rev. 1, June 1996
10. *Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, WIPP-DOE-069, Rev. 5.0, April 1996.