ORNL/TM--11652

DE91 001021

Chemical Technology Division

SAMPLING AND ANALYSIS OF RADIOACTIVE LIQUID WASTES AND SLUDGES IN THE MELTON VALLEY AND EVAPORATOR FACILITY STORAGE TANKS AT ORNL

M. B. Sears
J. L. Botts*
R. N. Ceo†
J. J. Ferrada
W. H. Griest*
J. M. Keller*
R. L. Schenley*

*Analytical Chemistry Division
†Currently employed by the Y-12 Plant, Oak Ridge, Tennessee

Date Published - September 1990

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

The authors wish to express appreciation to the many staff members of the ORNL Analytical Chemistry Division who made important contributions to this work:

Inorganic and Radiochemical Analytical Support

C. J. Baggett
D. A. Caquelin
L. R. Hall
H. J. Hall
K. O. Jeter
R. A. Jones
B. K. Larkins
M. G. McClung
R. T. Pack
R. F. Peacher
J. M. Peele
C. W. Scott
J. E. Sutherland
L. C. Tabor

Organic Chemical Characterization

G. S. Fleming
S. H. Harmon
L. J. Wachter
J. E. Caton
M. P. Maskarinec

The authors are also indebted to several staff members of the Liquid and Gaseous Waste Operations Department of the Office of Waste Management and Remedial Actions for tank sampling services and field sampling data and to the Radiation Protection Department of the Office of Environmental and Health Protection. Special thanks go to the following individuals:

Sampling Radioactive Waste Tanks

J. D. Brewer
C. B. Scott
D. R. Anderson
D. T. Lewis
M. D. Nelson
K. Seeber

ACRONYMS AND INITIALISMS

AA	Atomic Absorption
ACD	Analytical Chemistry Division
ALARA	As Low As Reasonably Achievable
ASTM	America Society for Testing Materials
CB	Calibration Blank
CCS	Calibration Check Standard
CLP	(EPA) Contract Laboratory Program
CPA	Chemical and Physical Analysis (Group)
DAIGC	Direct Aqueous Injection Gas Chromatography
EASC	Emergency Avoidance Solidification Campaign
EPA	Environmental Protection Agency
EP-TOX	Extraction Procedure for Toxic Materials
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAA	Graphite Furnace Atomic Absorption
HEPA	High Efficiency Particulate Air
HP	Health Physicist
HRLAL	High Radiation Level Analytical Laboratory
IC	Inorganic Carbon
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ID	Internal Diameter
IDL	Instrument Detection Limit
IPA	Inorganic and Physical Analysis (Group)
IR	Infrared Light
LLLW	Liquid Low-Level Waste
LLW	Low-Level Waste
MVST	Melton Valley Storage Tank
MSA	Method of Standard Addition
OD	Outer Diameter
ORNL	Oak Ridge National Laboratory
PHA	Pulse-Height Analysis
PRD	Percent Relative Difference
PVC	Polyvinyl Chloride (polymer)
PWTP	Process Waste Treatment Plant
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RSD	Relative Standard Deviation
SVOA	Semivolatile Organic Compound Analysis
TAL	Transuranium Analytical Laboratory
TC	Total Carbon
TCL	Target Compound List

ACRONYMS AND INITIALISMS (continued)

TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
TIC	Tentatively Identified Compound
TOC	Total Organic Carbon
TRU	Transuranic
TS	Total Solids
VOA	Volatile Organics Analysis
WHPP	Waste Handling and Packaging Plant
WIPP	Waste Isolation Pilot Plant

ABSTRACT

The sampling and analysis of the radioactive liquid wastes and sludges in the Melton Valley Storage Tanks (MVSTs), as well as two of the evaporator service facility storage tanks at ORNL, are described. Aqueous samples of the supernatant liquid and composite samples of the sludges were analyzed for major constituents, radionuclides, total organic carbon, and metals listed as hazardous under the Resource Conservation and Recovery Act (RCRA). Liquid samples from five tanks and sludge samples from three tanks were analyzed for organic compounds on the Environmental Protection Agency (EPA) Target Compound List. Estimates were made of the inventory of liquid and sludge phases in the tanks. Descriptions of the sampling and analytical activities and tabulations of the results are included.

The report provides data in support of (1) the design of the proposed Waste Handling and Packaging Plant, (2) the Liquid Low-Level Waste Solidification Project, and (3) research and development activities (R&D) activities in developing waste management alternatives.

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1. INTRODUCTION AND OVERVIEW

Purpose and scope. The purpose of this study was to determine the characteristics of the radioactive liquid wastes and sludges stored at the Oak Ridge National Laboratory (ORNL). This project is a preliminary step in planning the processing of these wastes for disposal. Objectives include providing data in support of (1) the design of the proposed Waste Handling and Packaging Plant (WHPP), (2) the Liquid Low-Level Waste Solidification Project, and (3) research and development (R&D) activities in developing waste management alternatives. This report presents the results of an effort to sample and analyze the contents of the liquid radioactive waste storage tanks. A related report on physical properties tests (e.g., viscosity, sedimentation rate) of four of these samples is in preparation.[1]

Liquid low-level wastes (LLLWs) are generated by various R&D activities at ORNL. These wastes are collected, made basic, and concentrated by processing in the low-level waste (LLW) evaporator. The resulting concentrates are stored in eight tanks at the Melton Valley Storage Tank (MVST) facility (Building 7830) and four tanks at the evaporator facility (Building 2531) in Bethel Valley.

Samples of the supernatant liquid and sludge were collected from six of the MVSTs (tanks W-24 through W-28 and W-31) and from two of the storage tanks at the evaporator service facility (W-21 and W-23). These samples were analyzed for major chemical constituents, radionuclides, total organic carbon, metals listed as hazardous under the Resource Conservation and Recovery Act (RCRA), and general waste characteristics. A scoping survey was made for volatile and semivolatile organic constituents. Because of limited access into the tanks and the relatively high radiation levels of the waste, only one location in each tank was sampled (i.e., under the access pipe). Full characterization of the wastes under RCRA will be conducted when the wastes are processed for disposal and more representative samples can be collected.

The supernatant liquids in tanks W-29 and W-30 were sampled and analyzed in preparation for a campaign to remove the supernate from the tanks and immobilize it in a cement matrix. This project, the Liquid Low-Level Waste Solidification Project, is being planned to increase the available storage capacity for LLLW and improve operating flexibility. The process will be similar to the Emergency Avoidance Solidification Campaign (EASC) conducted in 1988. Tanks W-29 and W-30 were modified at the time of the EASC to serve as feed tanks to the solidification equipment in addition to their storage function. Liquid samples were analyzed for major chemical constituents, radionuclides, total organic carbon, RCRA metals, volatile and semivolatile organic components, and general waste characteristics. Because of the tank modifications, it is not possible to gain access to sample the sludge in these particular tanks.

The two remaining storage tanks (C-1 and C-2) were not sampled because the tank design did not include sample access ports.

Background information on the LLLW system is given in Sect. 2, and an overview of the field sampling and analytical activities in Sect. 3. The results of the waste characterization studies are summarized in Sect. 4. Details of the work are presented in the appendixes, including field sampling data (Appendix A), Analytical Chemistry Division support (Appendixes B-D), and the sampling procedures (Appendixes E and F).

General characteristics of the waste samples. The liquid samples appeared to be single phase and ranged from pale to deep yellow. Dose rates (field survey) on contact with the full 250-mL sample jars ranged from 0.1 to 0.5 R/h except for the samples from tank W-26, which measured 1.2 R/h.

The sludges are not homogeneous. Soft sludges after sonication varied in consistency from "similar to prepared mustard" to "like peanut butter with gritty particles." Tanks W-27 and W-31 contained layers of "hard" sludge in addition to soft sludge. Dose rates (field survey) for the wet sludge samples ranged from 1 to 2.8 R/h for a 250-mL sample. Dose rates of up to 50 R per hour per gram were observed for dried sludge subsamples.

Major components. The supernatant liquid wastes in the storage tanks, except tank W-21, are essentially high-pH (typically 11 to 13), sodium/potassium nitrate salt solutions. The nitrate concentration varies from 3 to 5 M, with the average being about 4 M. The waste solutions are about 0.08 M in chloride; five tank solutions contain dissolved carbonate. The concentrations of the heavy metals (e.g., U, Th, RCRA metals), as well as the iron and aluminum, are generally in the low-ppm range. Tank W-21 was found to be acidic when it was sampled for this study and contained higher levels of heavy metals than the basic wastes.

The principal metals found in the sludges were sodium, potassium, calcium, magnesium, uranium, and thorium.

Alpha emitters (TRU waste) and beta-gamma emitters. All of the composite sludge samples except the soft sludge in tank W-31 were identified as transuranic (TRU) wastes. If the tank W-31 sludge were dried, then the solid residue would also be classified as a TRU waste.

In general, little or no alpha activity was observed in the basic liquid phases in the tanks. The liquid samples were all non-TRU solutions; their salt residues, if dried, would also be non-TRU.

The most abundant beta-gamma emitters observed were ^{137}Cs and ^{90}Sr and their short-lived daughters ^{137}Ba and ^{90}Y, respectively. Gamma-active europium isotopes were observed in the sludges but were not detected in the liquid phase of any tanks that were basic.

RCRA characteristics. This study included some preliminary screening tests for RCRA hazardous characteristics. The full RCRA characterization was not performed due to budget limitations. The liquid phases in eight tanks were corrosive and/or contained a toxic metal at a concentration high enough to classify the waste as RCRA hazardous. The classifications of the sludge samples are preliminary, based on the total metal contents obtained with a nitric acid leach, and are not the EP-toxicity or the Toxicity Characteristic Leaching Procedure (TCLP) results. All sludge samples exceeded the EP-toxicity equivalent limits for mercury and lead and are potentially RCRA hazardous. That is, the metals content would result in the classification of the sample as RCRA hazardous if the sludge dissolved completely in the acetate buffer used in the regulatory test. Several sludge samples were also potentially RCRA hazardous with respect to chromium and cadmium.

Selected samples from the waste tanks were analyzed for the Environmental Protection Agency (EPA) Target Compound List (TCL) volatile and semivolatile organic compounds. Very few TCL compounds were found in the waste samples.

1.1 REFERENCE

1. R. N. Ceo and J. T. Shor, Physical Characterization of Radioactive Sludges in Selected Melton Valley and Evaporator Facility Storage Tanks, ORNL/TM-11653, in preparation.

2. BACKGROUND AND SAMPLING CONSIDERATIONS

2.1 LIQUID LOW-LEVEL WASTE SYSTEM

The LLLW system receives wastes from a variety of source facilities, including reactors, radioactive fuel and target processing areas, radioisotope processing areas, decontamination operations, hot cells, and radiochemical laboratories. A simplified schematic of the LLLW system is shown in Fig. 2.1.1. The wastes are gathered in collection tanks and transferred to the LLW evaporator feed tank (W-22 and formerly W-21).* Many of the source facilities generate acidic wastes. The wastes are made basic with sodium hydroxide in the collection tanks or in the evaporator feed tank, which precipitates most of the TRU and heavy metals.

The wastes are concentrated by processing in the LLW evaporator. This is a batch operation with the volume of the waste reduced until a predetermined specific gravity (currently about 1.25) is reached. The final temperature is approximately 135-140°C. The evaporator bottoms are discharged into tank W-23 and from there are pumped to other storage tanks. Concentrations of dissolved solids in the wastes in the MVSTs are somewhat lower than in the evaporator discharge because of dilution by the water used to rinse the transfer line. The waste stream has a relatively high activity level and is processed/stored in shielded facilities. The evaporator overheads are condensed and treated by the Process Waste Treatment Plant (PWTP).

The Process Waste Treatment Plant (PWTP) also generates LLLW. Process wastewater is waste that is slightly or potentially contaminated (steam condensate from heating coils, process cooling water, leakage, and miscellaneous waste from building sinks, floor drains, etc.). It is treated by ion exchange, and the effluent is routed to the Nonradiological Wastewater Treatment Plant for further treatment and is released. The discharge point is permitted under the National Pollution Discharge Elimination System (NPDES). The PWTP ion exchange columns are regenerated with nitric acid. A portion

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*Some (or all) of the Bethel Valley and Melton Valley collection tanks may be shut down under the pending Federal Facilities Agreement, with wastes handled by bottling and/or treatment at the source and an unloading station at the LLW evaporator complex.

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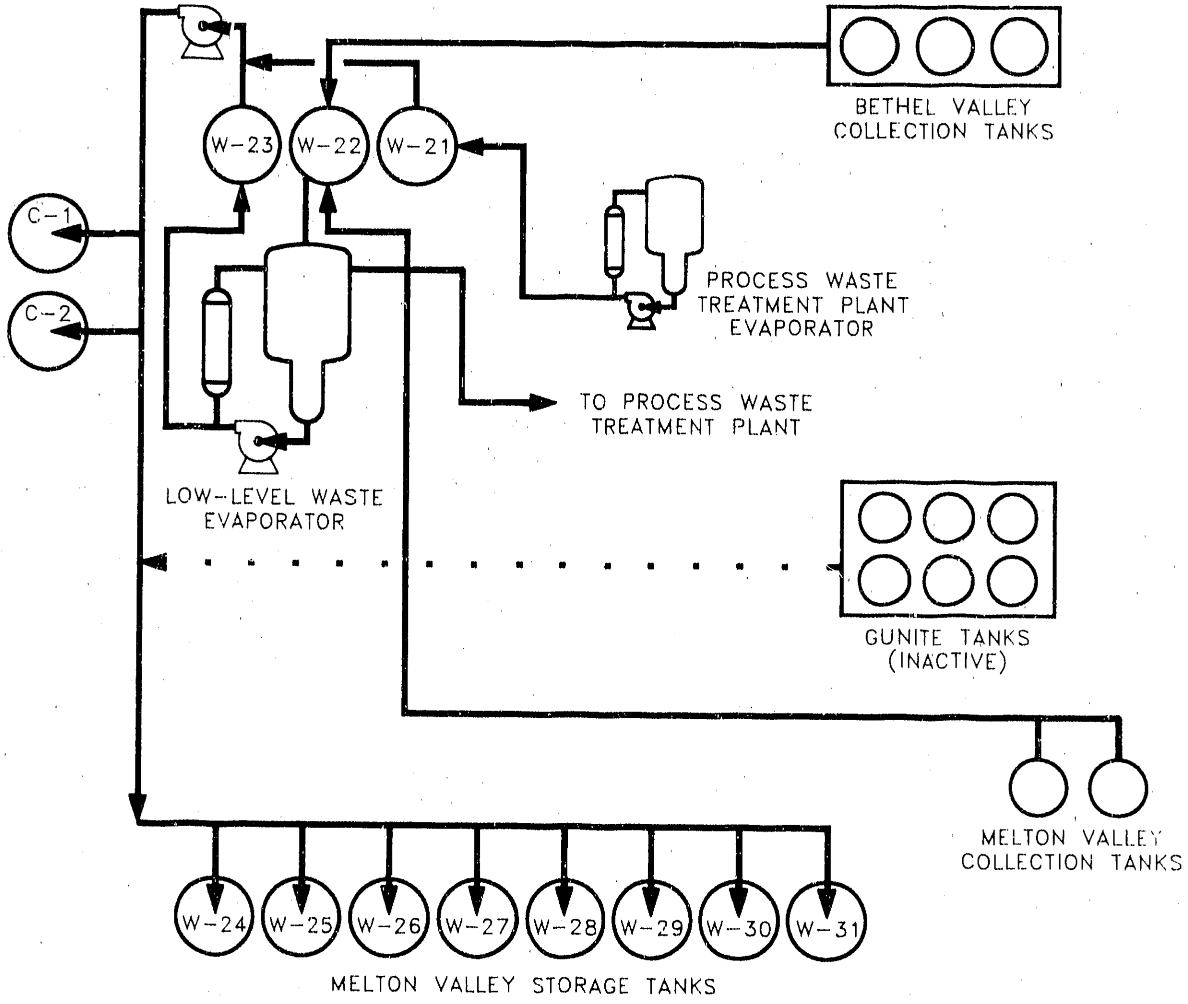

Fig. 2.1.1. Schematic of the liquid low-level waste system.

of the resulting eluate is processed at the PWTP evaporator to recover nitric acid. The evaporator bottoms are transferred to the LLLW storage tanks. The remainder of the eluate is neutralized and routed to the LLW evaporator. Both PWTP concentrates and LLW concentrates are stored in tank W-21.

Through 1984, the waste concentrates were disposed of as a cement-waste mixture (grout) by injection into shale formations located 800 to 1100 ft (250 to 335 m) below the ground surface using hydrofracture. The MVSTs served both for interim storage and as feed tanks for the hydrofracture facility. Hydrofracture was terminated after 1984 and is not presently considered to be an acceptable disposal option.

The gunite tanks (now inactive) received LLLW during the period 1943-1978 and over the years accumulated a large quantity of sludge. Most of these sludges were resuspended, transferred from the gunite tanks to the MVSTs, and then disposed of by hydrofracture. However, some of the sludges settled out in the MVSTs.

The radioactive waste concentrates have been accumulated in tanks since the termination of hydrofracture, and the system is nearing capacity. These are primarily wastes generated since 1984 plus some heels from hydrofracture. Wastes are currently stored in eight 50,000-gal tanks (W-24 through W-31) in the MVST facility and four 50,000-gal tanks (W-21, W-23, C-1, and C-2) at the LLW evaporator service facility in Bethel Valley. To free some storage capacity, in 1988 about 48,000 gal of supernate were removed from tanks W-29 and W-30 and immobilized in a cement matrix in the EASC. The solidified waste (non-transuranic) has been stored on-site pending resolution of waste form performance criteria and disposal requirements.

Waste minimization efforts have reduced the quantity of LLLW generated. The more recently generated waste is more concentrated in radioactive materials (i.e. "hotter") than the older wastes.

Solidification campaigns or additional concentration of the liquid waste by evaporation will be used to maintain safe-fill conditions in the system until a permanent disposal method can be implemented. The longer-range plan is to remove the wastes from the tanks and process them in the proposed Waste Handling and Packaging Plant (WHPP). It is expected that the solidified TRU waste will be shipped for disposal to the Waste Isolation Pilot Plant (WIPP) in New Mexico, which is under construction.

2.2 EARLIER SAMPLING CAMPAIGNS

The MVSTs were sampled previously: (1) in 1985 by Peretz et. al,[1] and (2) the supernates in tanks W-29 and W-30 in 1988 to plan the EASC.[2] The 1985 data are primarily radiochemical, although there are some chemical composition data for the liquid phase. An extensive series of analyses was performed on the EASC samples.[2] No sludge samples were taken at that time. Samples were collected from tank W-26 in March 1989 for a related study on physical properties of the sludge.[3]

2.3 INTERIM WASTE TRANSFERS

Since these earlier sampling projects there have been waste transfers at the MVSTs including:[4,5]

(1) Tank W-28 emptied (except a small heel) with contents transferred to the other MVSTs; W-28 refilled with waste from Bethel Valley tanks (July 1987),

(2) About 48,000 gal of waste removed from tanks W-29 and W-30 in the EASC (September-December 1988). Tanks refilled by transfers from W-25 and W-26 (May 1989),

(3) Tanks W-25 and W-26 refilled by transfers from Bethel Valley tanks in May and August 1989. Tank W-26 received principally waste from W-23.

At the time of the sampling for this study, the MVSTs were essentially filled to their working capacity, tank W-23 was the LLW evaporator catch tank, and W-21 was the PWTP evaporator catch tank. Tank W-21 also contained some LLW concentrates and historical sludges from its service as an evaporator feed tank. The air spargers at the MVSTs had been turned "off" before the EASC campaign and left off until after sampling was completed in December 1989, except brief periods when waste transfers were made. Following the August 1989 transfers, tanks W-25 and W-26 were air sparged for 24 h to mix the liquid – the disturbed solids were then allowed to settle before sampling.

2.4 CONSIDERATIONS IN SAMPLING

The number, size, and type of samples collected was limited by the need to keep personnel radiation exposures to a minimum, and the limitations imposed by the tank configurations.

The tanks contain large quantities of radioactive materials that produce relatively high radiation fields. In the 1985 sampling of the MVSTs, the radiation levels of "core" sludge samples ranged from 200 mR/h at 6 in. to 4 R/h at 4 in.[1] Any operation that brings the tank contents outside the shielded vaults will expose people to the radiation fields. The exposure could be to the workers actually sampling the tanks, the laboratory workers analyzing the samples, or people who work in surrounding areas.

The storage system is designed to handle radioactive wastes. The tanks are stainless steel, 12-ft diam. by 60-ft long and are located in below-grade, reinforced concrete vaults with stainless steel liners that provide radiation shielding and secondary containment. Waste transfers are handled remotely. The tanks are equipped with air spargers and an off-gas sweep and are vented through a demister and HEPA filter system to a stack. Access to the tank contents is very limited, generally consisting of one pipe, 3-in. diam. by about 9-ft long, that protrudes through the vault roof. A representative tank configuration is shown in Fig. 2.4.1. Samples can only be collected directly below the access port because the pipe is long and narrow. Tanks C-1 and C-2 are of a different design and do not have an access port; therefore, these tanks were not sampled in this campaign.

Tanks W-29 and W-30 at the MVST were modified to serve as the feed tanks to the EASC processing system. The tank penetrations were used for the pump module suction legs. Liquid samples can be pulled from the end of the suction leg using the pump module sampler. There is no access to tanks W-29 and W-30 for sampling the sludge.

2.5 REFERENCES

1. 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.

2. R. M. Schultz, Oak Ridge National Laboratory, personal communication, June 30, 1988.

3. R. N. Ceo, A. J. Mattus, and J. T. Shor, Oak Ridge National Laboratory, personal communication, September 28, 1989.

4. J. J. Maddox, Oak Ridge National Laboratory, personal communication, October 26, 1989.

5. S. M. DePaoli, Oak Ridge National Laboratory, personal communication to M. B. Sears, March 20, 1990.

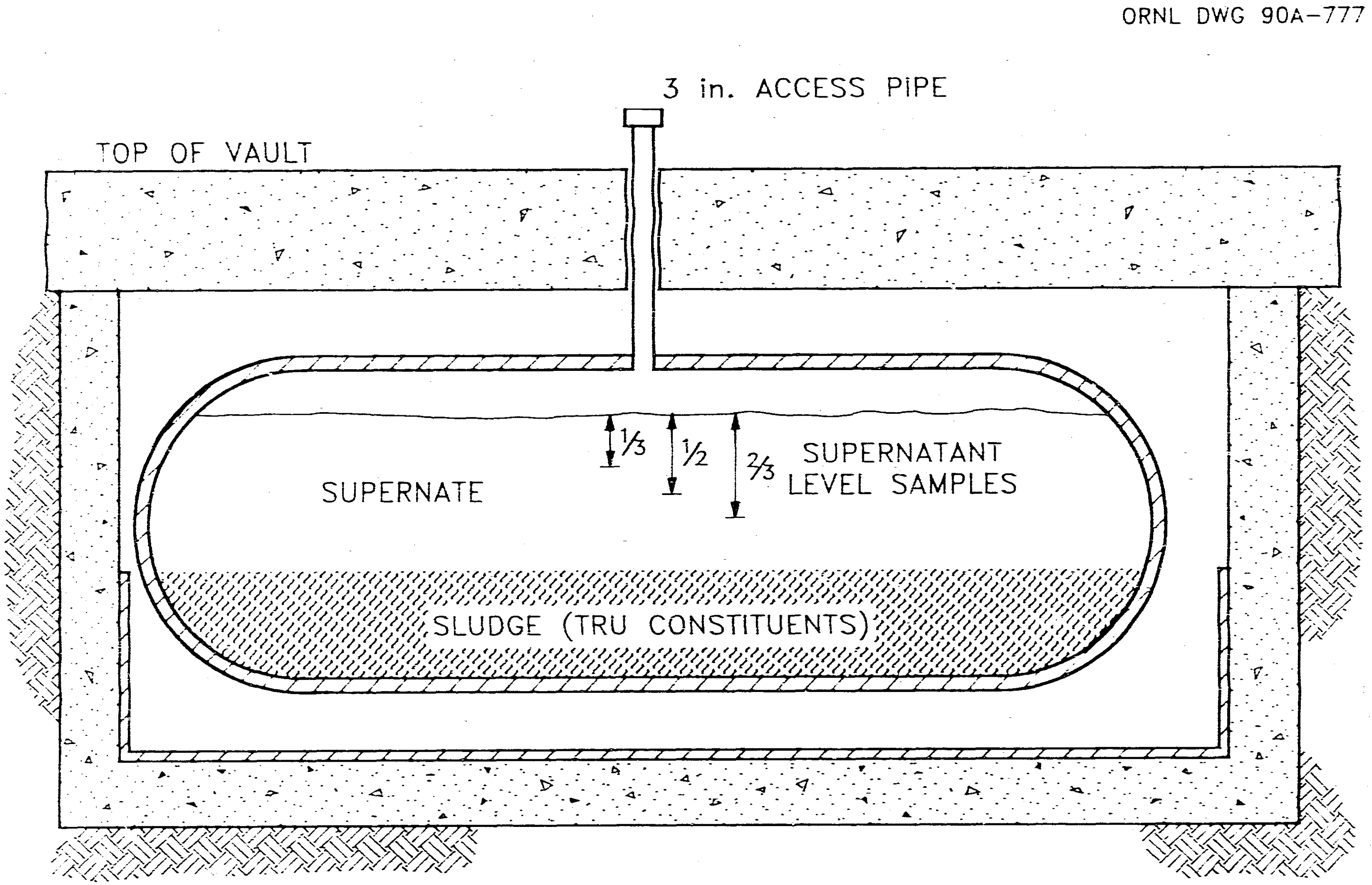

Fig. 2.4.1. Tank configuration with sampling locations.

3. SAMPLING AND ANALYTICAL ACTIVITIES

3.1 SAMPLING ACTIVITIES

The sampling plan provides information concerning the supernatant liquid and sludges for six of the MVSTs (tanks W-24 through W-28 and tank W-31) and two of the concentrate storage tanks (W-21 and W-23) at the evaporator complex in Bethel Valley. Samples were drawn through the penetration used to house the liquid level instrumentation. The access is a 3-in.-diam. pipe that penetrates the tank from the vault roof. Liquid samples were taken at three levels — one-third, one-half, and two-thirds depth of the aqueous supernate (see Fig. 2.4.1). A sludge-level detector was used to determine the depth of the supernate and sludge. Samples representative of a vertical "core" of sludge were collected to pick up layering in the waste. Because only sludge directly under the access port can be sampled, the samples may not be representative of other locations in the tank and should be considered merely an indicator of the tank contents. The air-liquid interface was checked for the presence of any immiscible (e.g., organic) layer.

Samples of the aqueous supernates in tanks W-29 and W-30 were collected using the pump module (Isolock) sampler. There is no access to sample the sludge in these tanks.

Sampling was conducted by trained chemical operators in protective clothing. Sampling activities were continuously monitored by the Health Physics (HP) representative.

A general description of the sample collection is presented in this section. Detailed, task-specific procedures are given in Appendixes E and F. These include general sampling procedures, instructions for the different types of samplers, precleaning and decontamination of equipment, sample custody, and field log records.

Samples were collected at the MVSTs during the period September 19 - December 5, 1989, and from tanks W-21 and W-23 at the evaporator service facility on January 30-31, 1990. There were no waste additions or transfers at the MVSTs during the period September 1, 1989 - January 31, 1990 while sampling was in progress. The air spargers for the MVSTs had been off since before the 1988 EASC, except when tanks W-25 and W-26 were sparged for about 24 h to mix the liquid contents after the August 1989 waste transfers.

3.1.1 Presampling Survey

A presampling survey was conducted before collecting the samples. At this time, the air-liquid and the liquid-sludge interfaces were located using the Markland Model 10 sludge gun, thus establishing the depth of the supernatant liquid in the tank. This instrument measures the amount of light transmitted across a fixed gap in a probe. As the probe detects a phase change or enters the sludge, the operator logs the depth from the tank access point (i.e., the flange on the access pipe). This information was used in making final plans for sample collection, and in estimating the volume of waste in the tank.

The presampling survey of the MVSTs was conducted about 2 weeks prior to collecting the samples. The liquid samples from tanks W-21 and W-23 were collected the same morning as the Markland measurements were taken.

The Markland instrument is capable of detecting immiscible liquid layers (e.g., an organic layer over the aqueous layer) if the layers are deep enough to give a reading with the probe, which is about 2 in. across vertically. No immiscible or stratified liquid layers were detected in the tanks with the Markland instrument.

3.1.2 Collection of Liquid Samples with the Vacuum Pump System

Samples of the supernatant liquid were collected from tanks W-21, W-23 to W-28, and W-31 using a vacuum pump sampling system. Samples were taken at one-third, one-half, and two-thirds the supernatant liquid level depth (see Fig. 2.4.1), except tank W-21 where the liquid layer was only 8-in. deep (Markland) and only one level was sampled. A schematic of the sampling system is shown in Fig. 3.1.1. The sample was pulled by vacuum from the specified level in the tank through Teflon tubing into the sample jar. The pump was arranged with a safety surge bottle as a back-up. The depth of the liquid phase and sampling locations were determined from the Markland measurements. Teflon tubing was cut to length, premeasured, and marked with tape to indicate when the end of the tubing had been lowered below the access pipe flange to the appropriate level in the tank liquid. A stainless steel weight was attached to the lower end to keep the tubing vertical. The upper end of the tubing was plugged while the tubing was lowered to restrict entry of liquid until the desired depth was reached. After the sample was taken, the liquid remaining in the tubing was drained back into the tank, and the tubing was removed. New tubing was used at each sampling location to avoid cross contamination of the samples.

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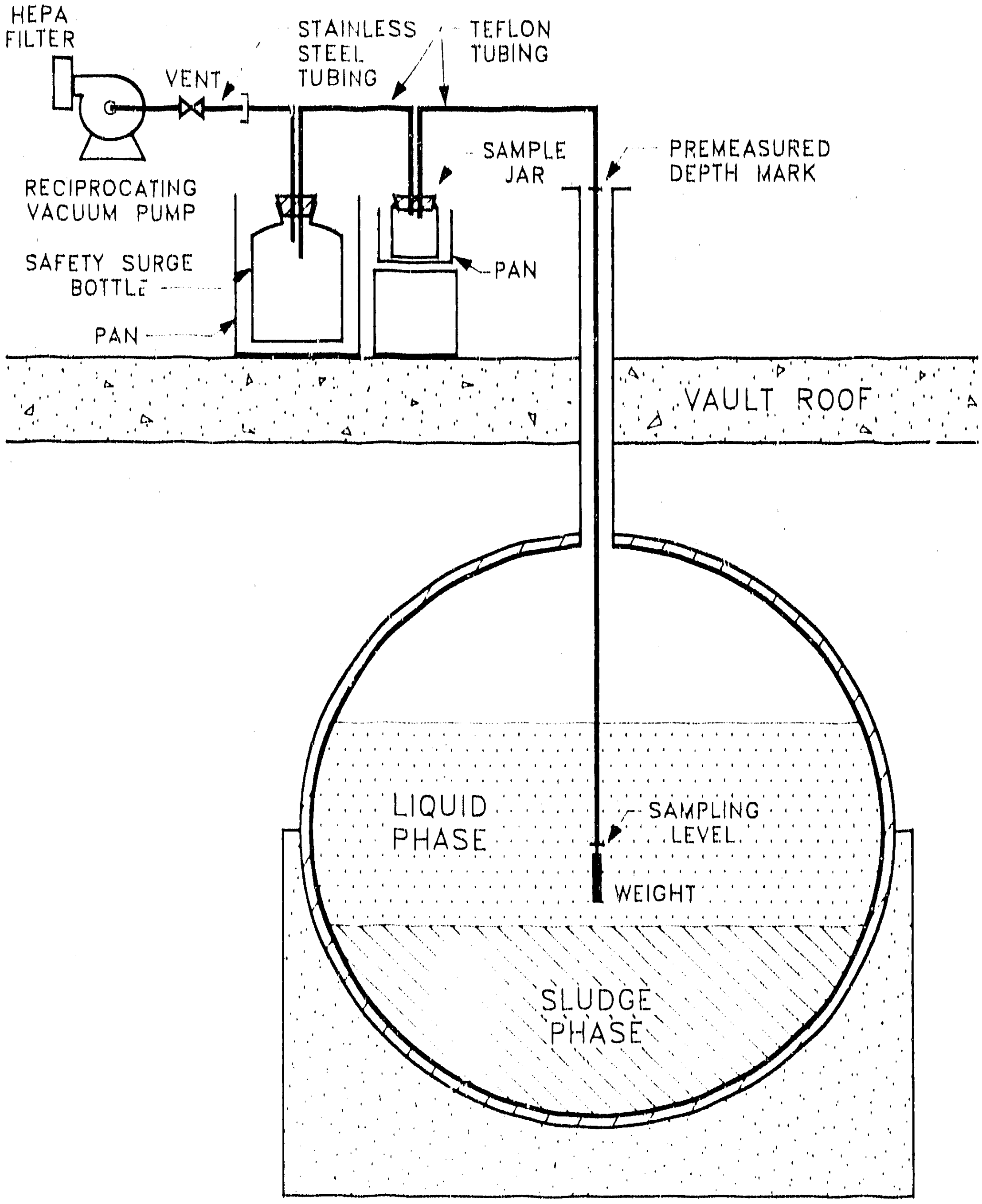

Fig. 3.1.1. Liquid sample collection system.

Liquid samples were collected in 250-mL glass sample jars and sealed with Teflon-lined caps. The radiation level of the unshielded sample was measured by the HP. The sample was then placed in a lead pig, and the outer surface of the pig was monitored by the HP. If the radiation level at the surface of the pig was 100 mrem/h or less, the sample was transported in the pig. Most of the liquid samples were below this level and were transported to the analytical laboratory in the pigs. The dose rates for the liquid samples from tank W-26 were higher than the others (about 280 mrem/h at the outer surface of the pig). These samples were placed in a shielded stainless steel carrier for transport.

The use of a pump to collect the liquid samples rather than a dip-type sampler or a Coliwasa minimized radiation exposure to personnel and was simple to operate. The liquid is pumped directly into the sample container, which reduces the handling time and the potential for drips or spills. The use of a vacuum pump to collect samples potentially might impact volatile organics; however, it seems unlikely that easily vaporized organics would be present in the waste following concentration in the evaporator.

3.1.3 Air-Liquid Interface

Wastes are segregated as much as possible, and in general the LLLW system is not used for the disposal of organic solvents.[1,2] However, the waste acceptance criteria are based on the primary hazard.[2] Small quantities of organics may be discharged to the LLLW system when the primary hazard of concern is the radioactivity. The air-liquid interface was checked for the possible presence of an organic layer floating on the aqueous supernate. The bottom-opening soft sludge sampler (see Sect. 3.1.4.1) was used to collect a "column" of liquid at the interface. The location of this interface was determined with the Markland detector during the presampling survey. Before sampling, the appropriate length was measured on the handle of the sampling device, and the handle was marked with tape to show how deep to lower the sampler into the tank. The sample was pulled and examined visually in the field for the possible presence of immiscible liquid layers.

Samples from the air-liquid interface were drawn from the following tanks: W-21, W-23 through W-28, and W-31. The interface was clear in all the samples with no immiscible phases. No organic layer was observed in any of these tanks. The interface sample was returned to the tank and the sampler was then used to collect a soft sludge sample.

While the bottom-opening sampler worked well as a method of checking the interface, it might not pick up a sufficient quantity of sample to do the chemical analyses. A top-opening sampler was developed for this project, which was designed to collect a larger sample of the organic phase if a relatively shallow organic layer were found. This device is described in Appendix E, Procedure SC-007. As noted above, no layer was found and the organic sampler was never used. It was constructed of PVC and was designed to be capped and serve as the sample transport container to the analytical laboratory. A leach test (48 h) of the device was performed using hexane as the solvent to check for organics that might leach from the PVC into an organic matrix sample (see Appendix D, Sects. D.2.5 and D.3.5). No detectable quantities of substances of concern were observed, which indicates that PVC is a satisfactory construction material for short contact times.

3.1.4 Collection of Sludge Samples

Most sludge samples were collected with the soft-sludge sampler. If the consolidated sample could not be obtained with the soft-sludge sampler, a "hard" sludge sampler with a sharper tip was used. Two tanks, W-27 and W-31, contained layers of "hard" sludge.

3.1.4.1 Soft-Sludge Sampling

A bottom-opening, soft-sludge sampler was used to collect a core of sludge up to 20-in. deep. The device consists of a detachable handle assembly and a hollow probe of clear PVC pipe with a bottom closure that can be controlled from above by the operator (Fig. 3.1.2). The design is a modification of the device developed for sampling the inactive tanks.[3] The sludge was usually more than 20-in. deep in the tanks. Samples were collected at successively lower layers to obtain a vertical profile.* Because the sample collector is a clear material, visual measurements of sludge depth can be made and other properties observed. This examination was performed in a hot cell at the High Radiation Level Analytical Laboratory (HRLAL).

Sampling at different depths to provide "cores" representative of a vertical profile of the sludge is illustrated schematically in Fig. 3.1.3. The locations (depths) for collecting the sludge samples were developed from the Markland data on the location of the liquid-

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*The length of the sampler is limited to about 22 in. overall (20.25 in. below the vent hole) by the remote handling capabilities at the analytical laboratory.

ORNL DWG 90-146

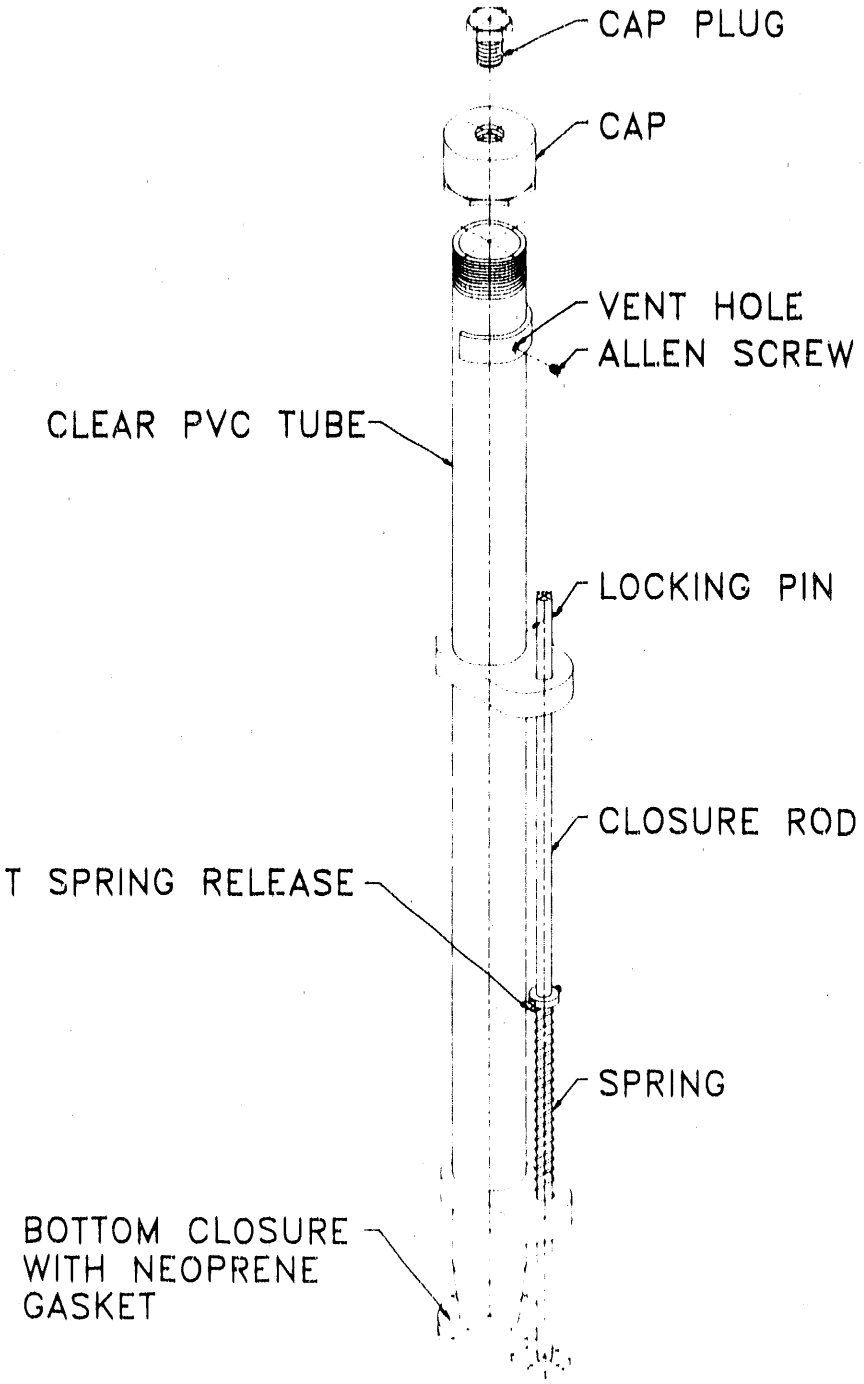

Fig. 3.1.2. Soft-sludge sampler.

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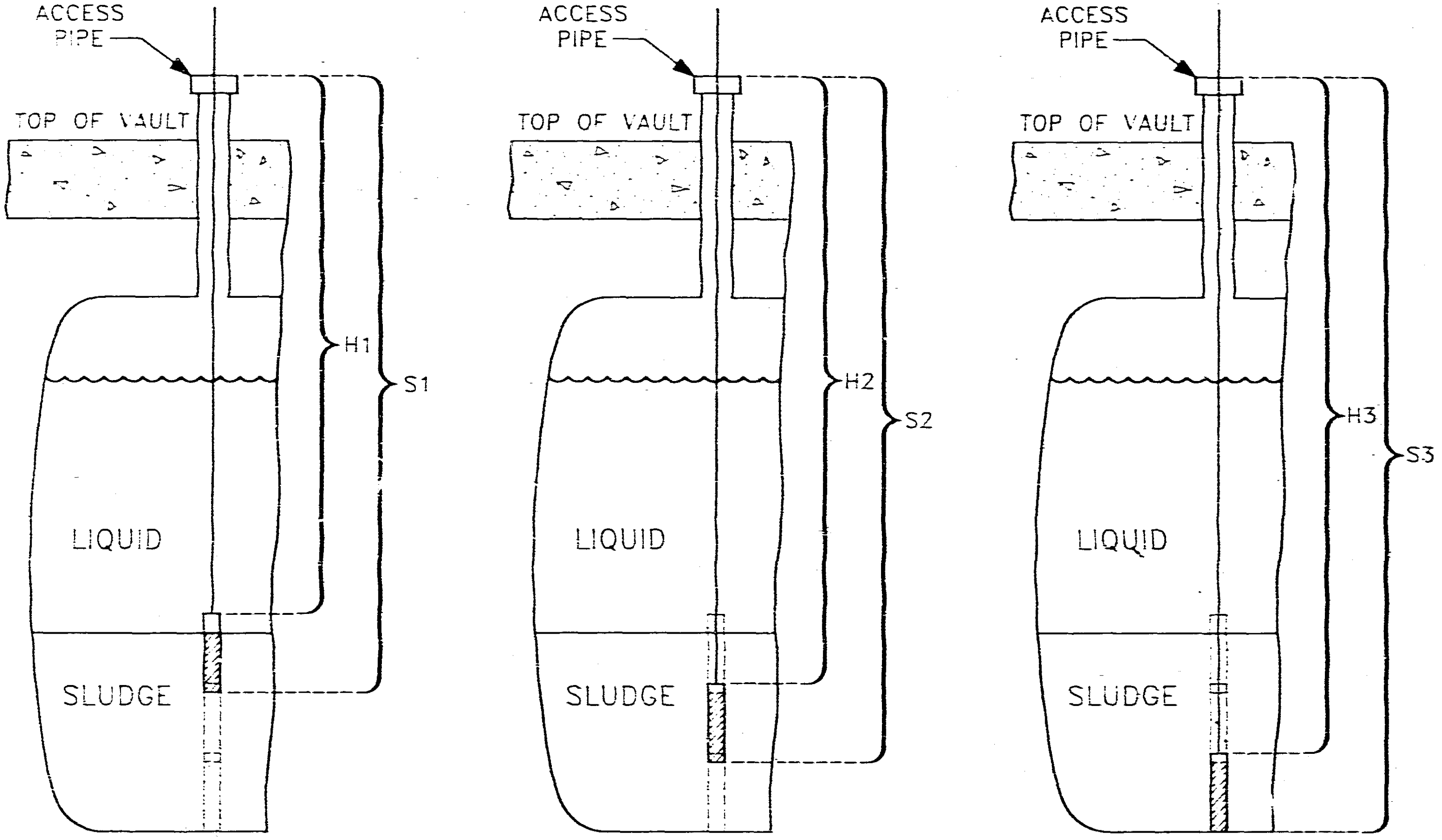

FIRST SLUDGE SAMPLE SECOND SLUDGE SAMPLE THIRD SLUDGE SAMPLE

Fig. 3.1.3. Schematic of sampling sludge layers.

sludge interface and the available information on the distance from the access point to the bottom of the tank. Specific depths were defined for collecting the upper samples. Before sampling the appropriate lengths were measured on the handle (e.g., H1, H2, ...) and marked with tape to show when the sampler had been lowered to the specified depth in the tank. The bottom sample was collected by pushing the sampler to the bottom of the tank. The depth to the tank bottom was recorded on the log sheet. In sampling lower layers, the sampler was closed until the bottom tip of the sampler was approximately 1 in. above the lowest point previously sampled. The sampler was then opened, lowered to the specified depth, and the sludge sample collected.

After a sludge sample was collected, the outside of the sampling device was rinsed with deionized water and wiped. The handle was removed, the PVC sample tube was capped, and the vent hole was plugged. The sampler was sealed in two layers of plastic bags and in a can, and the packaged sample was then placed in a shielded, stainless steel transport carrier. The radiation level of the unshielded sample was measured by the HP in the field. This information was used by the analytical laboratory in planning sample handling.

In collecting the first batch of sludge samples, the samplers were rinsed while they were held in the access pipe to remove the sludge on the outside. There were some problems in sampling tank W-31 with the sludge dripping and spattering. To improve the confinement of radioactive materials, a large stainless steel funnel (2-ft. diam.) was custom fabricated before collecting the next batch of samples. This funnel was temporarily attached to the flange on the access pipe as each tank was sampled. The funnel served to contain drips or spills, facilitated rinsing the excess sludge from the outside of the sampler, and directed the rinse water back into the tank.

The samples were removed from the PVC sampling tubes and transferred to glass sample jars with Teflon-lined caps at the analytical laboratory using remote handling in a hot cell. A leach test (aqueous matrix) was performed to check for volatile or semivolatile organics that might leach from the PVC into the sample for the inactive tanks project. No detectable quantities of any substances of concern were observed.

The field sampling measurements of the depths to the tank bottoms from the access points are listed in Appendix A, Table A.1. For the MVSTs the depths generally were in the range 21 ft 3 in. to 21 ft 6 in., while for tanks W-21 and W-23 at the evaporator facility they were about 19 ft. The distances to the bottoms of the MVSTs were deeper than expected. There was an error in measuring the depth when tank W-26 at the MVST was sampled in March 1989 for a preliminary study of the physical properties of the sludge.[4] [The depths from the tank access points are not given on the drawings.] Because of this discrepancy in the tank dimensions, there is a gap in the cores from tanks W-24 and W-25. The missing segment is the layer that lies about 20 to 30 in. above the tank bottom. The sludge sampling plan was revised before sampling the other tanks.

An obstruction of unknown size and shape, which does not show on the drawings, was found in the access pipe to each of the MVSTs and to tanks W-21 and W-23 at the evaporator service facility, so that the access opening is less than the nominal 3-in. diam. pipe. Because of the obstruction, it was necessary to make modifications to the sampling equipment after the sampling activities had begun. It was also necessary to "snake" the equipment past the obstruction. The original plan had been to use the handle comprised of 5-ft sections that was used in the inactive tank sampling project. This handle was tried in tanks W-23, W-24, and W-25, but would not clear the obstruction. A handle comprised of two 12-ft sections, which was more rigid, but less convenient, was used successfully.* It is thought that the obstruction is at the flange, where the access pipe is connected to the tank.

3.1.4.2 Hard-Sludge Sampling

Commercial Hard Sludge Sampler. The earlier work by Peretz et al.[5] had indicated the presence of a hard crusty layer in tank W-27 that might require cutting blades to take a sample. A commercial hard-sludge sampler with an auger type bit was used for this layer. This sampler consists of a stainless steel pipe (barrel) about 1.4- ID by 10-in. long, sharpened blades at the bottom, a gate valve to hold the sample in place, a vented cap, and handle sections. A schematic of a sampler similar to the one used is shown in Appendix E, Procedure SC-004. (The stainless steel sampler was used without the plastic liner shown on the figure.) A cross handle was used to apply a turning pressure to cut the

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*There is only one handle comprised of two 12-ft sections. For future tank sampling, it is recommended that a spare handle(s), especially the bottom section, which gets contaminated with sludge, be procured.

sludge. After the sample had been taken, the sampler was rinsed with deionized water, wiped (except the blades), detached from the handle, and placed in a PVC container with a quick release, O-ring seal cap. The PVC container was put into a can and then into the transport carrier. The auger bit cut through the hard layers, but the hard sludge plugged the sampler and a sample of the underlying soft layers was not obtained (see Sect. 3.1.4.3).

Alternate Hard-Sludge Sampler. The hard-sludge sampler developed for the inactive tanks sampling project[3] was used to sample the thick material near the bottom of tank W-31. This device consists of a stainless steel pipe (7.25 in. long) that has a sharp, machine-bevel cutting edge on one end and is threaded at the other end so that it can be attached to a handle. This sampler is suitable only for very thick, sticky sludges. The cores are stored in a specially designed stainless steel sample container.

On the first attempt to sample the sludge, the sampler was empty when it was pulled from the tanks. On the second try, the sampler was pushed into the bottom layer three times to force the sample in. After the sample had been collected, the sampling device was very quickly transferred to the sample container. The sample container was sealed in a paint can and placed in the transport carrier.

3.1.4.3 Sampling sludges in tank W-27

In the first sampling effort of tank W-27, a soft-sludge sample was collected at the supernate-sludge interface (sample W27-S1). When the effort was made to sample the next layer of sludge, a very hard layer that felt like concrete was encountered about 38 in. above the tank bottom. This layer was hard enough to bend the stainless steel closure plate on the sampler and, thus, no sample was collected. A sample of the upper soft sludge layer (W27-S2) was collected later in the second sampling effort. This core overlaps the solids phase of sample W27-S1.

The auger bit sampler was used to cut through the hard layer. It was estimated that the hard layer was about 1-ft thick. The sampler was then pushed through an underlying soft sludge layer (no cutting force needed) to the bottom of the tank. Upon examination of the sampler (W27-H1) at the analytical laboratory, it was found that the hard sludge had plugged the lower part of the sampler (i.e. the cutting bit end between the blades and immediately above the gate valve). The "barrel" section of the sampler contained soft sludge from the upper layer. At the analytical laboratory, the soft sludge was poured into one jar (W27-H1-S) and the hard sludge was scraped with a spatula into a second jar (W27-H1-H). A sample of the soft sludge that lies under the hard sludge was not obtained.

3.1.5 Sampling Tanks W-29 and W-30 with the Pump Module (Isolock) Sampler

Tanks W-29 and W-30 were modified to serve as feed tanks to the EASC system. The tank penetrations were used for the pump module suction legs. Samples of the aqueous supernate were collected from these tanks using the pump module (Isolock) sampler (Fig. 3.1.4). It is not possible to gain access through the penetrations to sample the tanks by the methods described in Sects. 3.1.1-3.1.4. No sludge samples were taken from tanks W-29 and W-30 and no checks were made for an organic layer.

A general description of the sample collection is presented in this section. The detailed procedure for using the pump module sampler is given in Appendix F. The transfer pump was used to pull liquid waste through the suction leg from one tank and circulate it through the sampler valve. The liquid loop discharges to the other tank. When the sampler is activated, the sampler valve cycles between the circulating liquid loop and the nozzle that drains to the sample collection jar. The collection jar, a standard "Mason" jar, screws into a fixed stainless steel cap on the sampler. This jar is too large to place in a lead pig, and the lid of the jar does not meet EPA specifications. The sample was transferred to an I-Chem sample jar and capped with a Teflon-lined lid immediately after it was collected. After the samples were pulled from the first tank, the module piping was flushed with water. Liquid waste from the second tank was then circulated for a period before sampling the second tank.

Four samples were collected from each tank. The first, second, and fourth samples were transported to the laboratory for analysis. These are in essence triplicate samples since only one point in each tank, i.e., the end of the pump module suction leg, can be sampled. The third sample was placed in the archive storage area.

The equipment had not been operated since the EASC. Some maintenance was required to make the system operational. This included disassembly and cleaning of the solenoid for the air operated control valves for the sampler. The sampler operated slower than designed, probably because of corrosion.

3.1.6 Transport

The samples collected from the tanks were transported to the High Radiation Level Analytical Laboratory (Building 2026) in shielded containers. The routes connecting the

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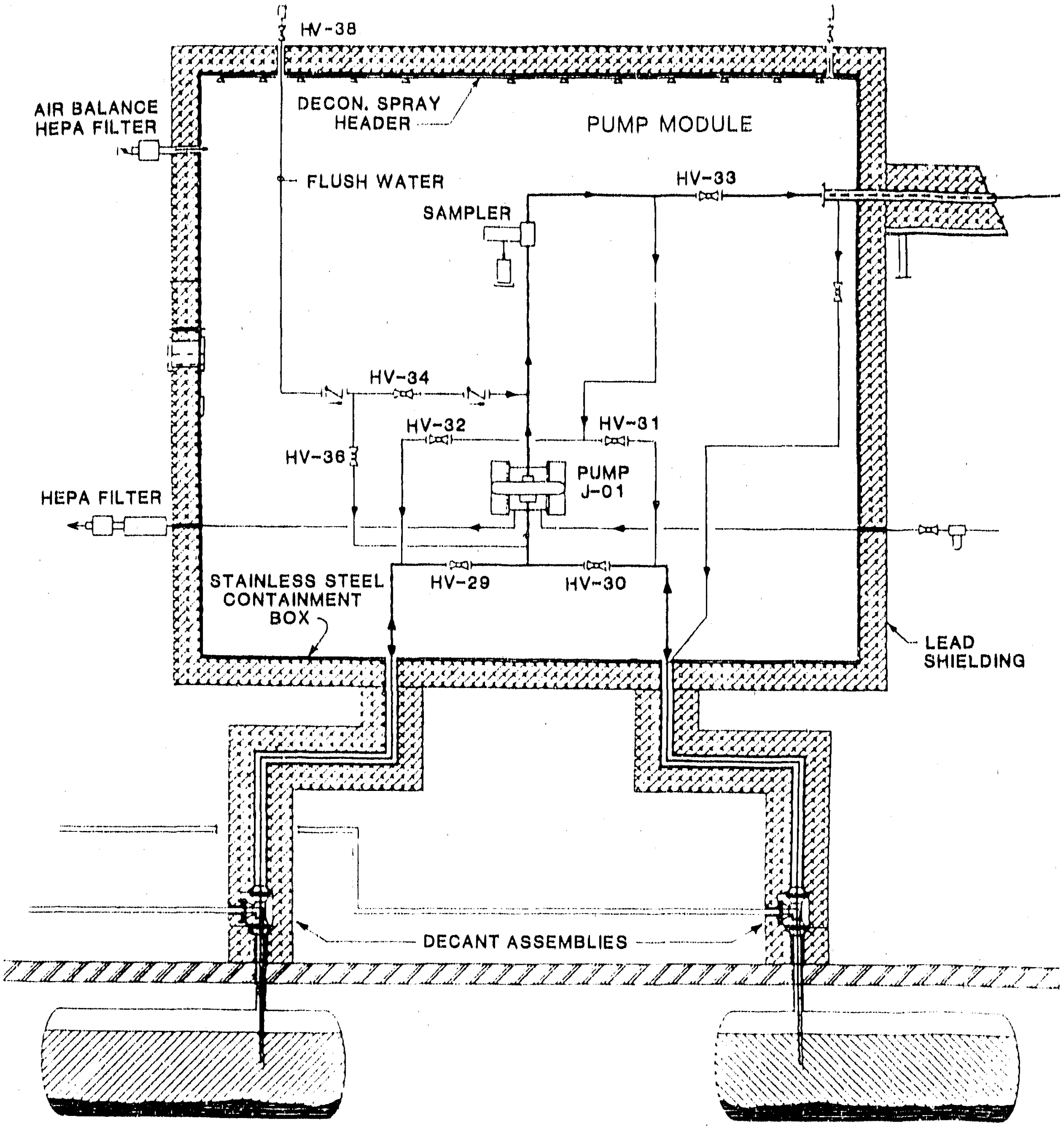

Fig. 3.1.4. Schematic of pump-module sampling system for tanks W-29 and W-30.

tank areas and the analytical laboratory are within the controlled access areas of ORNL. Transport was carried out according to Health Physics Manual, Procedures 4.1, "Handling and Transfer of Radioactive Materials Within the Laboratory," and 5.1, "Segregation and Management of Solid Radioactive Waste Materials," which are standard ORNL practices for the transport of contaminated materials.[2] These procedures call for decontaminating and/or shielding the sample containers, as necessary, to maintain radiation levels at 200 mrem/h or less at the outer surfaces of the transport packages.

Liquid samples, except those from tank W-26, were transported in lead pigs. Sludge samples and the liquid samples from W-26 were transported in a shielded, stainless steel carrier. Samples were delivered to the analytical laboratory the day they were collected, except the liquid samples from W-26 which were too hot to handle in lead pigs. These samples were held overnight in a locked building and delivered the next day in the carrier along with a batch of sludge samples.

3.2 SAMPLE ANALYSIS

The purpose of the sampling was to obtain data that are meaningful and useful in support of the program for the solidification and disposal of the liquid low-level wastes and sludges. The wastes were analyzed to determine (1) the major chemical constituents, (2) the principal radionuclides, (3) the total organic carbon, (4) any metals listed as hazardous under RCRA, and (5) some physical properties. A scoping survey was made of volatile and semivolatile organic compounds which are on the EPA Target Compound List (TCL).

The overall scheme used for the characterization of the waste tank contents is shown in Fig. 3.2.1. Liquid samples were examined visually. No immiscible layers (i.e., no organic layers) were observed. The aqueous sample drawn from the one-half level of the supernate was analyzed for metals, anions, radionuclides, and total organic carbon. The aqueous samples from the one-third and two-thirds levels were screened to check the uniformity of the supernate.

The sludge column in the sampling tube(s) was inspected visually. The sludge was allowed to settle and the height of solids was measured. Any excess liquid was removed and the solids were transferred to a sample jar. Composite sludge samples were made up for each tank in proportions representative of a complete vertical core. Composite samples were sonicated to ensure complete mixing. The remaining portion of the sludge was

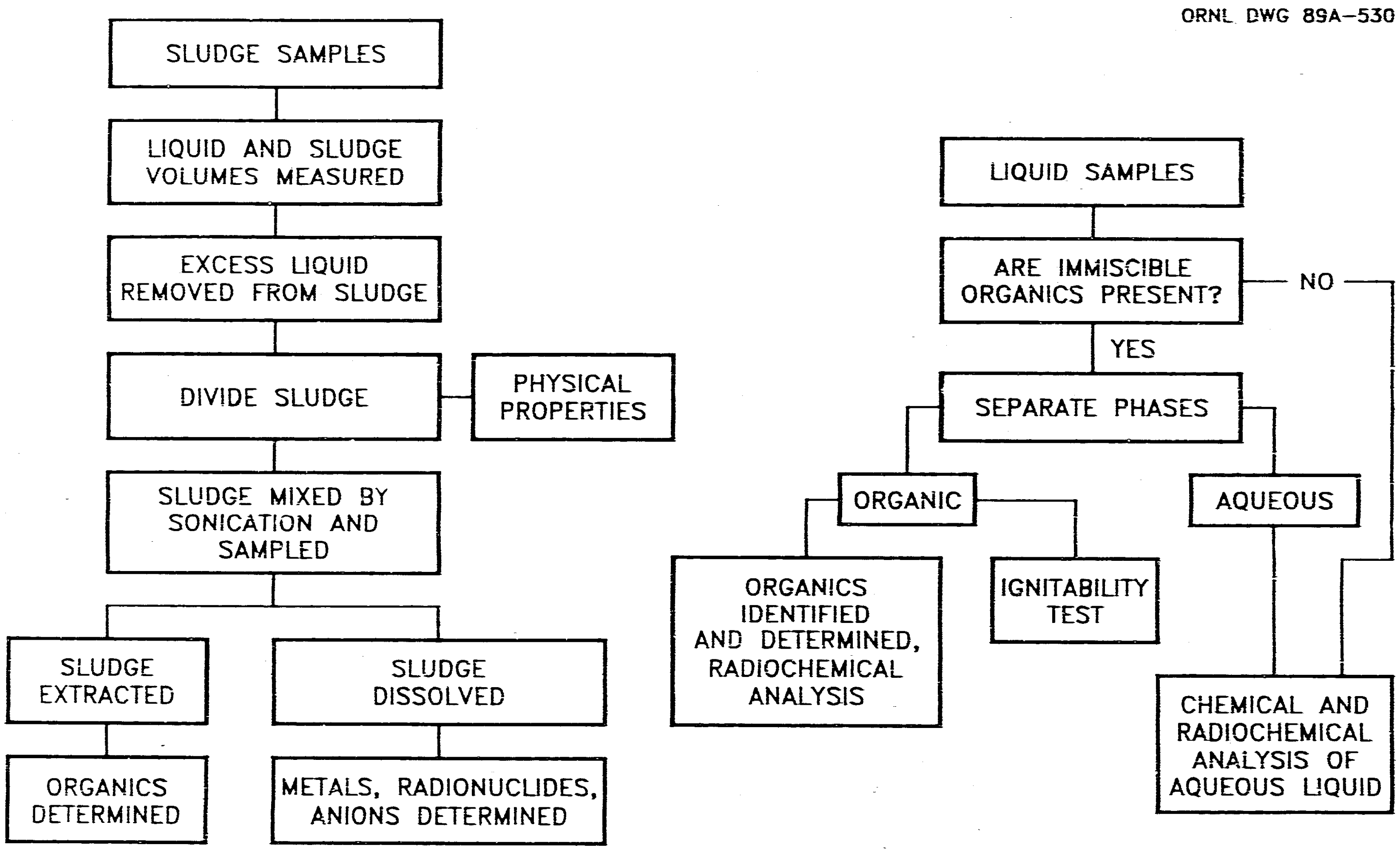

Fig. 3.2.1. Overall analysis scheme for contents of ORNL liquid low-level waste storage tanks.

retained for possible future use. Metals, radionuclides, and total organic carbon were determined on aliquots or extracts of the sonicated sludge. Sludge samples from three tanks were analyzed for organic compounds.

Details of the analytical procedures are presented in Appendix B. The EPA-approved analytical procedures were followed, as much as possible, in analyses for RCRA and organic compounds. Generally, modifications of procedures from the EPA guide, Test Methods for Evaluating Solid Waste (SW-846) were used.[6] Some modifications to the standard procedures are necessary because of the high radiation levels, high salt content, and generally complex chemical matrices in the samples. Procedures for the other analyses were selected from the ORNL Analytical Chemistry Division methods or modified EPA methods[6,7] based on the sample characteristics and type of information needed.

3.3 QUALITY ASSURANCE

Quality assurance during tank sampling activities was maintained primarily through the use of specific procedures for the sampling crew to follow. These procedures provided step-by-step instructions for the collection, labeling, and shipping of each sample. All field data, such as liquid and sludge depths, sample identification numbers, and field surveys were recorded on data forms to ensure an accurate account of the sampling activities. Chain-of-custody forms were used to track individual samples from their collection point to the analytical laboratory. An independent surveillance by the Quality Assurance Specialist verified that sampling procedures, chain-of-custody criteria, radiation protection, and operator training were in compliance with all written procedures.

Quality assurance during sample analyses is more fully described in Appendix B of this report. A traveler composed of a chain-of-custody form and a request for analytical services form accompanied every sample, subsample, or extract when transferred between analytical laboratories.

3.4 REFERENCES

1. ORNL Environmental Protection Manual, Procedure EPM-18.0, "Liquid Waste Disposal," staff of the Department of Environmental Management, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

2. Procedures and Practices for Radiation Protection, Health Physics Manual, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

3. L. D. Kaiser, Oak Ridge National Laboratory, personal communications, April 29 and May 24, 1988.

4. R. N. Ceo, A. J. Mattus, and J. T. Shor, Oak Ridge National Laboratory, personal communication, September 28, 1989.

5. 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.

6. U.S. Environmental Protection Agency, Test Materials for Evaluating Solid Waste, SW-846, 3rd ed., Office of Waste and Emergency Response, Washington, D.C., November 1986.

7. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

4. SUMMARY OF RESULTS

4.1 SAMPLE COLLECTION AND GENERAL CHARACTERISTICS

4.1.1 Sample Collection

Liquid and sludge samples were collected from six of the MVSTs (tanks W-24 through W-28 and W-31) and two of the concentrate storage tanks (W-21 and W-23) at the evaporator service facility by the methods described in Sect. 3.1 and Appendix E. The access is a 3-in.-diam pipe that penetrates the tank from the roof of the vault which houses the tanks and provides radiation shielding. A Markland sludge level detector was used to locate the air-liquid and liquid-sludge interfaces. Liquid samples were collected at three levels – one-third, one-half, and two-thirds of the depth of the supernate, except in the case of tank W-23 where the liquid layer was shallow and only the one-half level sample was collected. Samples representative of a "core" of sludge were collected from seven of the tanks. Tank W-27 contained a layer of hard sludge which plugged the sampling device: a sample of the underlying soft sludge was not obtained. Because only sludge directly under the access port can be sampled, the sludge samples may not be representative of other locations in the tank and should be considered merely an indicator of the tank contents.

Liquid samples were collected from tanks W-29 and W-30 using the pump module (Isolock) sampler (see Sect. 3.1.5 and Appendix F). These tanks were modified for the Emergency Avoidance Solidification Campaign and cannot be accessed by the general procedure used for the other tanks. Because of the modifications, it is not possible to sample the sludge in these tanks.

A total of 28 liquid samples and 21 sludge samples were collected and transported to the High Radiation Level Analytical Laboratory (Building 2026). One sample each from tanks W-29 and W-30 was archived, since the sampling of these wastes was in support of a second solidification campaign which is being planned for FY 1991.

Field sampling data, including the profile of the tank contents and a comprehensive listing of the samples collected (date of collection, sampling location, and radiation level) are given in Appendix A. The field data are from the perspective of the sampling crew standing on the pad over the tank, with distances measured from the flange on the access pipe down into the tank. The estimated radiation doses to personnel from field sampling activities are presented in Table A.4.

4.1.2 General Characteristics

General characteristics of the samples are summarized in Table 4.1.1. All of the liquid samples appeared to be single phase and ranged from pale to deep yellow with little, if any, turbidity. Dose rates (field survey) on contact with the full 250-mL sample jars ranged from 0.1 to 0.5 R/h except for the samples from tank W-26, which measured 1.2 R/h. Most of the liquid samples could be transported and stored in lead pigs. However, the samples from W-26 were transported in a shielded carrier and unloaded into a hot cell at the analytical laboratory. Tank W-26 contains some more recently generated liquid waste, which was transferred from the evaporator service facility in the summer of 1989.

Most of the sludges could be sampled with the soft-sludge sampler. Tanks W-27 and W-31 contained layers of "hard" sludge; samplers with hard cutting edges were used to collect these samples. Dose rates (field survey) for the wet sludge samples ranged from 1 to 2.8 R/h for a ~250-mL sample. Radiation fields were considerably higher near small samples dried in the laboratory. Dose rates of up to 50 R per hour per gram were observed for dried samples. The increased dose rate was primarily due to beta particles from ^{90}Sr and ^{90}Y, which had been attenuated by the wet sludges. Sludge samples were transported in a shielded carrier and unloaded into a hot cell; small subsamples were removed for analysis in radiochemical hoods and glove boxes. Every effort was made to avoid handling dried samples in order to reduce both exposure and spread of contamination.

The sludges are not homogeneous and vary in consistency and color. Subjective observations by the sampling crew (e.g., the effort required to push the sampler into the sludge) and by the analysts who worked with the samples in the laboratory are given in Table 4.1.1. For example, the sampling crew thought that most of the sludge in tanks W-24 and W-25, except for the thin layer of "mud" at the bottom, could probably be pumped with a peristaltic pump. The consistency of soft sludges that had been sonicated ranged from "similar to prepared mustard" to "like peanut butter with gritty particles" (sample W26-S). The "hard" sludge from tank W-27 had the consistency of a hard mud and the appearance of concrete pieces mixed with mud or clay; it was too stiff to sonicate. The hard sludge from tank W-31 has the appearance of mud or clay with a little grit.

In a separate study, physical properties tests were conducted on aliquots of four of the soft sludge samples collected in this campaign.[1] The sludge from the bottom of tank W-26 had the highest viscosity of the four samples that were tested.

Table 4.1.1. General characteristics of waste samples

Tank	Liquid samples: radiation level[a] (R/h)	Organic layer	Sludge samples		
			Number/type	Radiation level[a] (R/h)	Comments
W-21	0.300	No	2/soft sludge	1.0-1.5	Sonicated sludge: consistency of prepared mustard; medium yellow with dark flecks
W-23	0.120	No	3/soft sludge	1.0-2.5	Top sample (W23-S1): smooth, brownish-yellow paste; 2.5 R/h
					Sonicated sludge: consistency of prepared mustard, medium brown with dark flecks
W-24	0.180	No	2/soft sludge	1.2	Could probably pump with a peristaltic pump, except for the thin layer of "mud" on bottom
					Sonicated sludge: light yellow tan; very fine particles with a few coarser particles
W-25	0.260	No	3/soft sludge	1.3	Thicker sludge than in tank W-24
					Could probably pump with a peristaltic pump, except for the thin layer of "mud" on bottom
					Sonicated sludge: light tan; very fine particles with a few coarser particles
W-26	1.200	No	3/soft sludge	0.8-2.0	Top sample (W26-S1): highest radiation level
					Bottom sample[b] (W26-S3): highest viscosity of the tank samples studied by Ceo and Shor
					Sonicated sludge: dense and plastic with the consistency of peanut butter; gritty particles

Table 4.1.1 (continued)

Tank	Liquid samples: radiation level[a] (R/h)	Organic layer	Sludge samples: Number/type	Sludge samples: Radiation level (R/h)	Sludge samples: Comments
W-27	0.160-0.200	No	2/soft sludge	0.2	Sample W27-S2: appearance of small pieces of concrete in a softer sludge
			1/auger bit (soft and hard sludge)	0.3	Soft sludge in auger-bit sampler: (a) Unsonicated: appearance of small pieces of concrete in a softer sludge (b) Sonicated sludge (W27-H1-S): gray and gritty; consistency of cooked oatmeal Hard sludge: (a) Felt like hitting concrete during sampling; on first attempt to collect sample W27-S2, bent closure plate of soft sludge sampler when hit hard layer (b) Consistency like a hard mud; no free liquid; appearance of concrete pieces mixed with mud or clay; too stiff to sonicate General: soft sludge over hard layer; had to cut hard layer with auger-bit sampler; estimated 1 ft thick; below hard layer, about 2-ft thick layer of soft sludge; hard sludge plugged sampler; no sample of underlying soft layer
W-28	0.480	No	1/soft sludge to the bottom; took second sample for more material	1.2	Fluid (weight of handle carried sampler to the bottom of the tank) Sludge (W28-S1): deep yellow; seems homogeneous Sonicated sludge: very finely divided with a few dark flakes
W-29	0.110	NA[c]	NA	NA	
W-30	0.110	NA	NA	NA	

Table 4.1.1 (continued)

Tank	Liquid samples: radiation level[a] (R/h)	Organic layer	Sludge samples		
			Number/type	Radiation level (R/h)	Comments
W-31	0.180	No	2/soft sludge	1.5-2.2	Sonicated soft sludge: medium tan, watery sludge; fine and very fine particles separated during centrifugation
			1/hard sludge	2.8	Hard sludge: appearance of clay or mud with a little grit

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[a] Field survey.

[b] R. N. Ceo and J. T. Shor, Physical Characterization of Radioactive Sludges in Selected Melton Valley and Evaporator Facility Storage Tanks, ORNL/TM-11653, in preparation.

[c] NA = not applicable because of no access to tanks W-29 and W-30 for sampling.

4.1.3 Checks for Water-Insoluble Organic Liquids

There was no indication of organic liquids/solvents that are immiscible with the aqueous liquid in any of the tanks or samples. A column of liquid was collected at the air-liquid interface and examined visually in the field. The interface was clear in all cases. No organic layer lighter than the aqueous phase was observed in any of the tanks, and no immiscible or stratified liquid layers were detected with the Markland instrument. There was also no indication of any water-insoluble organic liquids in the sludge samples. No immiscible liquid phases were observed when sludge samples were centrifuged as a step in determining bulk densities. No "oily" droplets were seen on the walls of the PVC tubes or funnels when the sludge samples were transferred to jars, or on the walls of the analytical glassware/plastic ware.

4.1.4 Inventory of Radioactive Liquid Wastes and Sludges

Profiles of the tank contents are presented in Table 4.1.2. The dimensions are measured from the tank bottom and are derived from the sampling data presented in Appendix A. A typical MVST contains a bottom layer of sludge solids, which is about 4 ft deep in the center of the tank below the access pipe, and a top layer of supernatant liquid about 6.5 ft deep (see Fig. 4.1.1). Sludge depths in the tanks ranged from about 19 to 68 in. The MVSTs are filled essentially to their working capacity; tanks W-21 and W-23 at the evaporator service facility are about half full. Tank W-27, which has a somewhat different profile, contains (1) a layer of soft sludge on the bottom; (2) a layer of hard sludge, estimated to be 1 ft thick, immediately above the bottom layer; and (3) a layer of soft sludge over the hard sludge (Fig. 4.1.1).

The location of the top of the sludge solids layer was determined from the height of the settled solids phase in the sample collected at the liquid-sludge interface (measured in the analytical laboratory) and the location in the tank where the sample was collected. Some samples had a slightly cloudy layer over the sludge which was detectable by the Markland instrument (see Appendix A), but visually the amount of suspended solids was very small. This layer is included in the liquid inventory in this discussion.

Estimates of the quantities of radioactive liquid wastes and sludges stored in six of the MVSTs (tanks W-24 through W-28 and W-31) and two evaporator storage tanks (W-21 and W-23) are given in Table 4.1.3. The calculations assume horizontal tanks with ellipsoidal heads that coincide with the drawings and American Society for Testing and

Table 4.1.2. Profiles of tank contents[a,b]
(measured from tank bottom)

Tank	Height of waste (in.)		
	Total waste (liquid and sludge)	Top of sludge solids layer[c]	Top of hard sludge
W-21	65	26	-
W-23	62	52	-
W-24	127	44	-
W-25	127	68	-
W-26	120	49	-
W-27	125	54	38[d]
W-28	131	19	-
W-31	122	27	5

[a] Inventory in MVSTs as of December 5, 1989; inventory in tanks W-21 and W-23 as of Janaury 31, 1990. No waste transfers at MVSTs during period September 1, 1989 - January 31, 1990.

[b] Derived from sampling data in Appendix A, Table A.1.

[c] Based on height of settled sludge solids phase in the PVC sampling tube; sample collected at the supernate/sludge interface.

[d] Hard-sludge layer estimated to be about 1 ft thick. Underlying layer of soft sludge about 2 ft thick.

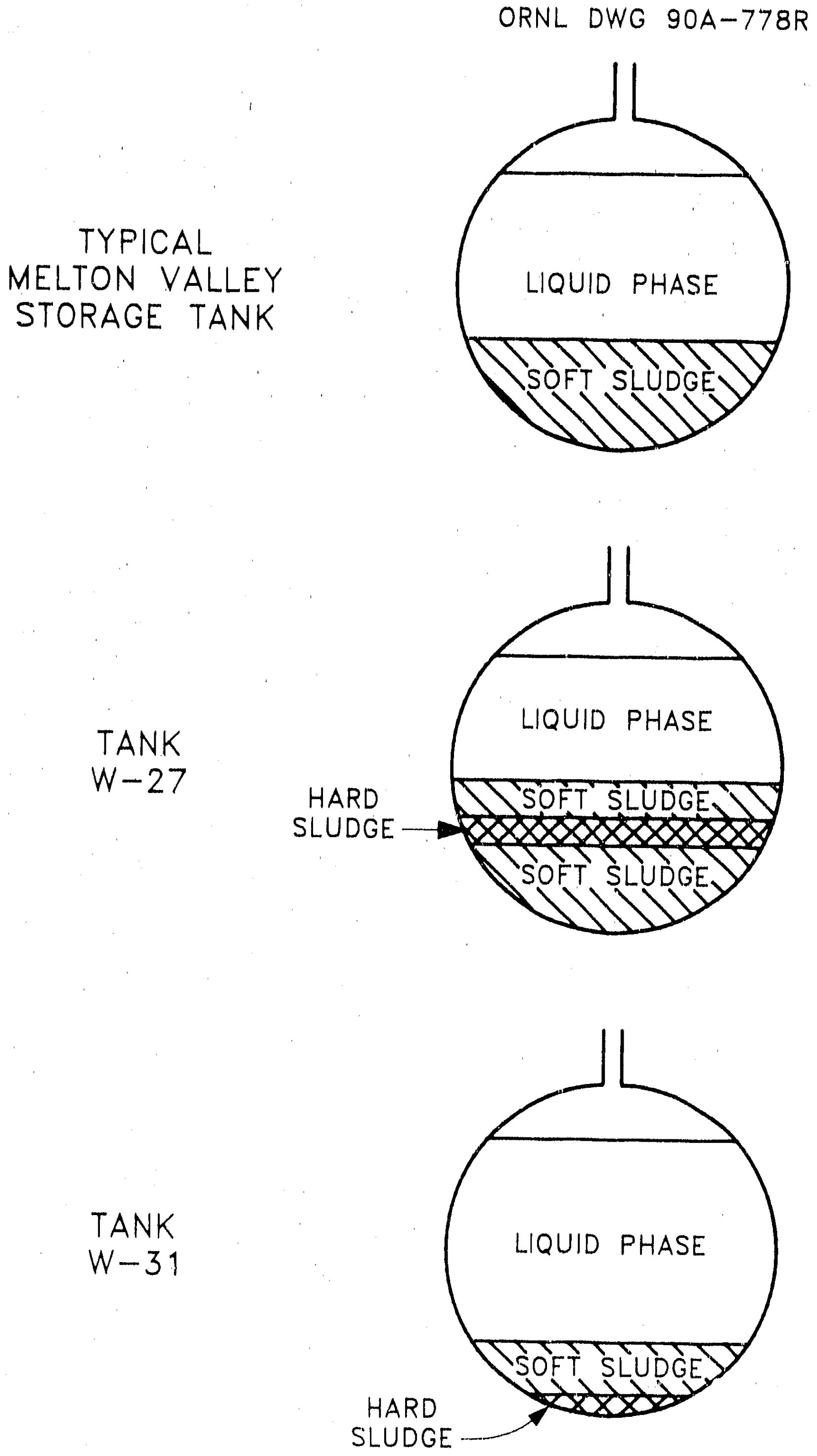

Fig. 4.1.1. Profile of wastes in the Melton Valley Storage Tanks.

Table 4.1.3. Inventory of radioactive liquid wastes and sludges in storage tanks[a,b,c]

	Total waste			Sludge				Supernate		
	Volume			Volume				Volume		
Tank	(gal)	(L)	Solids content[d] (kg)	(gal)	(L)	Mass (kg)	Solids content[d] (kg)	(gal)	(L)	Solids content[d] (kg)
W-21	22,100	83,700	42,100	6,100	23,200	32,500	16,600	16,000	60,500	25,500
W-23	20,800	78,800	51,600	16,400	61,900	83,000	45,200	4,400	16,800	6,400
W-24	47,400	179,500	80,300	13,200	50,100	63,200	30,800	34,200	129,400	49,600
W-25	47,400	179,500	92,500	23,400	88,600	116,900	62,100	24,000	90,900	30,400
W-26	45,200	171,200	81,300	15,100	57,200	88,100	39,600	30,100	113,900	41,700
W-27	46,900	177,600	71,800[e]	17,700	67,100	84,500[e]	32,600[e]	29,200	110,500	39,200
W-28	47,400[f]	179,500	90,300	3,800	14,400	21,400	11,400	43,600	165,100	78,900
W-31	46,000	174,200	63,600[e]	6,400	24,300	30,700[e]	11,300[e]	39,600	149,900	52,300

[a] Inventory in MVSTs as of December 5, 1990; inventory in tanks W-21 and W-23 as of January 31, 1990. No waste transfers made at MVSTs during period September 1, 1989 - January 31, 1990.

[b] Calculations assume horizontal tanks with ellipsoidal heads that coincide with the drawings and ASTM norms. Depths of wastes in tanks derived from sampling data. Location of the top of the settled sludge layer based on sample collected at the liquid-sludge interface.

[c] Densities and solids contents based on experimental data in Tables 4.2.1 and 4.2.4.

[d] Dried at 115°C.

[e] Sludge mass and solids content were estimated from analyses of soft sludge and have not been adjusted for the hard sludge.

[f] Estimate based on tank level detector (C. B. Scott, Oak Ridge National Laboratory, personal communication to M. B. Sears, Aug. 22, 1990.)

Materials (ASTM) norms. The heights of the sludge and liquid phases are based on the sampling data (Table 4.1.2), and the densities and solids contents used in the calculations are derived from the experimental data in Sect. 4.2, Table 4.2.1, and Table 4.2.4. The solids contents were determined for waste samples dried at 115°C.

4.2 INORGANIC, PHYSICAL, AND RADIOCHEMICAL CHARACTERISTICS

4.2.1 Analytical Results

Samples of the supernatant liquids and composite samples of the sludges in the waste tanks were analyzed for major constituents, radionuclides, total organic carbon, metals listed as hazardous under RCRA, and general waste characteristics. Details of the analytical work, including sample preparation, analytical methods, and quality control, are described in Appendixes B and C.

The analytical data for the liquid and sludge samples are presented in Tables 4.2.1-4.2.3 and 4.2.4, respectively. The sample identification code includes the tank identification (e.g., W21, W23, etc.) followed by a hyphen and a phase identification (L = liquid; S = soft sludge; H = hard sludge). The code may contain an additional number to identify the location/depth in the tank at which the sample was collected. (The location/depth information is given in Appendix A.) The less than symbol (<) in Tables 4.2.1-4.2.4 means that the constituent was not detected and the limit of detection is reported. Data in parentheses (e.g., Ag in the sludges) are of questionable quality due to poor spike recovery. The initialisms used in the tables are defined as follows:

TDS - total dissolved solids,
TS - total solids,
IC - inorganic carbon,
TC - total carbon,
TOC - total organic carbon.

4.2.2 Overall Trends and Solubility

The supernatant liquid wastes in the storage tanks (except tank W-21) are high-pH (typically 11 to 13) sodium/potassium nitrate salt solutions. The sludges contain significant levels of carbonate, and some tank solutions contain dissolved carbonate ions. While the alkali metals (Na, K, Cs) are soluble, most of the other metals present in the wastes are precipitated to the sludge phase. With the exception of the alkali metals and

Table 4.2.1 (continued)

Characteristic		W26-L2	W27-L2	W28-L2	W31-L2
Physical properties and miscellaneous data					
TDS	(mg/mL)	369	358	485	351
TS	(mg/mL)	366	355	478	349
Density	(g/mL)	1.2177	1.2118	1.2852	1.2075
IC	(mg/L)	2580	4.7	7.0	18.9
TC	(mg/L)	3860	364	581	464
TOC	(mg/L)	1280	359	574	445
RCRA metals					
Ag	(mg/L)	1.2	<0.69	<0.69	<0.69
As	(mg/L)	<3.7	<3.7	<3.7	<3.7
Ba	(mg/L)	0.20	4.1	5.8	3.5
Cd	(mg/L)	4.5	0.12	0.51	<0.12
Cr	(mg/L)	1.8	2.8	0.38	6.0
Hg	(mg/L)	<0.08	<0.048	0.14	0.15
Ni	(mg/L)	8.2	<0.38	1.4	<0.38
Pb	(mg/L)	3.2	<2.1	<2.1	<2.1
Se	(mg/L)	<4.7	<4.7	<4.7	<4.7
Tl	(mg/L)	<1.4	<1.4	<1.4	<1.4
Process metals					
Al	(mg/L)	4.8	<4.2	5.2	4.2
B	(mg/L)	3.9	0.67	0.35	0.20
Ca	(mg/L)	20	2600	7800	79
Co	(mg/L)	<0.57	<0.57	<0.57	<0.57
Fe	(mg/L)	<2.6	<2.6	<2.6	<2.6
K	(mg/L)	51000	8500	26000	9500
Mg	(mg/L)	3.5	<1.3	1600	<1.3
Na	(mg/L)	68000	90000	96000	94000
Si	(mg/L)	11.9	<1.0	<1.0	8.57
Sr	(mg/L)	<0.74	18	65	12
Th	(mg/L)	10	<2.2	<2.2	<2.2
U	(mg/L)	1130	<0.1	<0.1	0.25
Anions					
Chloride	(M)	0.099	0.071	0.14	0.073
Fluoride	(M)	<0.026	<0.026	<0.026	<0.026
Nitrate	(M)	3.29	4.52	5.97	4.52
Phosphate	(M)	<0.053	<0.053	<0.053	<0.053
Sulfate	(M)	<0.052	<0.052	<0.052	<0.052
Alkalinity					
pH		11.2	11.8	9.1	11.7
OH^-	(M)	<0.01	0.01	<0.01	0.01
CO_3^{2-}	(M)	0.20	<0.01	<0.01	<0.01
HCO_3^-	(M)	0.02	<0.01	<0.01	<0.01
Beta/gamma emitters					
Gross alpha	(Bq/mL)	1.03e+03	<1.0e+00	4.40e+01	<1.0e+00
Gross beta	(Bq/mL)	2.20e+06	3.30e+05	9.80e+05	3.58e+05
^{14}C	(Bq/mL)	1.23e+02	1.81e+02	1.67e+02	1.12e+02
^{144}Ce	(Bq/mL)	<2.3e+03	<7.5e+02	<1.8e+03	<7.8e+02
^{60}Co	(Bq/mL)	1.22e+04	3.09e+02	8.72e+03	3.23e+02
^{134}Cs	(Bq/mL)	1.31e+04	1.61e+03	1.06e+04	5.01e+03
^{137}Cs	(Bq/mL)	2.07e+06	2.16e+05	5.66e+05	2.29e+05
^{152}Eu	(Bq/mL)	<2.1e+02	<1.1e+02	1.67e+03	<9.3e+01
^{154}Eu	(Bq/mL)	<2.4e+02	<6.6e+01	7.37e+02	<6.7e+01
^{155}Eu	(Bq/mL)	<1.2e+03	<4.0e+02	<9.3e+02	<4.2e+02
^{3}H	(Bq/mL)	6.18e+02	2.09e+02	1.19e+02	1.56e+02
^{95}Nb	(Bq/mL)	<1.4e+02	<3.0e+01	<1.2e+02	<3.3e+01
^{106}Ru	(Bq/mL)	<2.8e+03	<1.1e+03	3.02e+03	<1.1e+03
^{90}Sr	(Bq/mL)	4.90e+02	5.57e+04	1.75e+05	7.38e+04
^{95}Zr	(Bq/mL)	<2.7e+02	<5.2e+01	<2.2e+02	<5.7e+01
Alpha emitters					
^{232}U	(Bq/mL)	3.60e+01	-	-	-
^{233}U	(Bq/mL)	9.20e+02	-	-	-
^{238}U	(Bq/mL)	1.00e+01	-	-	-
^{239}Pu/^{240}Pu	(Bq/mL)	1.00e+01	-	-	-
^{238}Pu/^{241}Am	(Bq/mL)	<1.5e+01	-	-	-

Table 4.2.1. Analytical data for liquid samples

Characteristic		W21-L2	W23-L1	W24-L2	W25-L2
Physical properties and miscellaneous data					
TDS	(mg/mL)	393	381	377	348
TS	(mg/mL)	421	383	383	334
Density	(g/mL)	1.2391	1.2423	1.2348	1.2018
IC	(mg/L)	<1.0	8340	1910	15.8
TC	(mg/L)	571	9500	2400	478
TOC	(mg/L)	571	1160	489	462
RCRA metals					
Ag	(mg/L)	1.2	<0.44	<0.69	<0.69
As	(mg/L)	3.8	<3.0	<3.7	<3.7
Ba	(mg/L)	25	<0.19	0.29	3.2
Cd	(mg/L)	2.0	1.7	0.22	<0.12
Cr	(mg/L)	27	0.42	3.1	1.9
Hg	(mg/L)	0.92	0.07	0.046	0.054
Ni	(mg/L)	15	3.0	<0.38	0.45
Pb	(mg/L)	7.1	2.7	6.7	<2.1
Se	(mg/L)	<2.3	<2.3	<4.7	<4.7
Tl	(mg/L)	<0.94	<0.94	<1.4	<1.4
Process metals					
Al	(mg/L)	<1.2	1.8	46	<4.2
B	(mg/L)	1.0	10	0.95	0.60
Ca	(mg/L)	23000	18	7.2	280
Co	(mg/L)	-	-	<0.57	<0.57
Fe	(mg/L)	240	0.70	<2.6	<2.6
K	(mg/L)	20000	78000	11000	17000
Mg	(mg/L)	5600	3.4	<1.3	<1.3
Na	(mg/L)	61000	82000	100000	78000
Si	(mg/L)	<1	<1	245	<1
Sr	(mg/L)	160	0.40	<0.74	23
Th	(mg/L)	95.1	15.8	<2.2	<2.2
U	(mg/L)	750	17	9.4	<0.10
Anions					
Chloride	(M)	0.059	0.10	0.073	0.071
Fluoride	(M)	<0.053	<0.053	<0.026	<0.026
Nitrate	(M)	5.0	3.23	4.19	4.19
Phosphate	(M)	<0.053	<0.053	<0.053	<0.053
Sulfate	(M)	<0.052	0.081	<0.052	<0.052
Alkalinity					
pH		0.56	12.8	13.1	12.5
H^+	(M)	0.085	-	-	-
OH^-	(M)	-	0.15	0.29	0.06
CO_3^{2-}	(M)	-	0.70	0.15	<0.01
HCO_3^-	(M)	-	-	<0.01	<0.01
Beta/gamma emitters					
Gross alpha	(Bq/mL)	2.14e+03	8.20e+01	5.00e+00	2.00e+00
Gross beta	(Bq/mL)	4.99e+05	4.62e+05	2.30e+05	3.92e+05
^{14}C	(Bq/mL)	<1.0e+00	6.35e+01	7.87e+02	3.29e+02
^{144}Ce	(Bq/mL)	<1.5e+03	<1.6e+03	<7.4e+02	<1.3e+03
^{60}Co	(Bq/mL)	8.50e+03	6.21e+02	3.29e+02	1.88e+03
^{134}Cs	(Bq/mL)	5.12e+03	4.63e+03	1.34e+03	3.77e+03
^{137}Cs	(Bq/mL)	3.19e+05	4.36e+05	2.21e+05	3.27e+05
^{152}Eu	(Bq/mL)	3.31e+04	<2.1e+02	<3.2e+02	<1.6e+02
^{154}Eu	(Bq/mL)	1.66e+04	<1.6e+02	<6.0e+01	<1.2e+02
^{155}Eu	(Bq/mL)	5.22e+03	<8.5e+02	<4.0e+02	<6.9e+02
^{3}H	(Bq/mL)	3.50e+02	1.19e+02	3.08e+02	3.45e+02
^{95}Nb	(Bq/mL)	<1.5e+02	<1.0e+02	<2.8e+02	<6.3e+01
^{106}Ru	(Bq/mL)	1.95e+03	3.78e+03	<1.1e+03	<1.9e+03
^{90}Sr	(Bq/mL)	7.46e+04	4.12e+02	9.13e+02	1.95e+04
^{95}Zr	(Bq/mL)	<7.1e+03	<1.0e+02	<5.0e+02	<1.2e+02
Alpha emitters					
^{233}U	(Bq/mL)	6.80e+01	4.00e+00	-	-
^{235}U	(Bq/mL)	3.96e+02	6.00e+00	-	-
$^{239}Pu/^{240}Pu$	(Bq/mL)	6.20e+01	6.00e+00	-	-
$^{238}Pu/^{241}Am$	(Bq/mL)	2.61e+02	3.90e+01	-	-
^{244}Cm	(Bq/mL)	1.15e+03	4.00e+00	-	-

Table 4.2.2. Analytical data for liquid samples from tanks W-29 and W-30

Characteristic		W29-1.1	W29-1.2	W29-1.4	W30-1.1	W30-1.2	W30-1.4
Physical properties and miscellaneous data							
TDS	(mg/mL)	375	376	375	371	377	370
TS	(mg/mL)	377	379	382	396	391	374
Density	(g/mL)	1.2251	1.2277	1.2254	1.2225	1.2218	1.2211
IC	(mg/L)	478	477	456	602	596	600
TC	(mg/L)	985	1040	833	805	695	799
TOC	(mg/L)	507	563	377	203	99	199
RCRA metals							
Ag	(mg/L)	<0.69	<0.69	<0.69	<0.69	<0.69	<0.69
As	(mg/L)	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7
Ba	(mg/L)	1.0	1.1	1.0	0.80	0.84	0.79
Cd	(mg/L)	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Cr	(mg/L)	2.4	2.4	2.3	3.0	2.9	2.9
Hg	(mg/L)	0.09	0.08	0.09	0.10	0.10	0.10
Ni	(mg/L)	<0.38	<0.38	<0.38	<0.38	<0.38	<0.38
Pb	(mg/L)	<2.1	<2.1	2.3	3.0	2.9	2.3
Se	(mg/L)	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7
Tl	(mg/L)	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4
Process metals							
Al	(mg/L)	18	18	17	34	33	34
B	(mg/L)	0.50	0.47	0.36	0.49	0.42	0.42
Ca	(mg/L)	4.1	5.5	3.6	10	9.4	11
Fe	(mg/L)	<2.6	<2.6	<2.6	<2.6	<2.6	<2.6
K	(mg/L)	10000	10000	10000	9200	9300	9400
Mg	(mg/L)	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Na	(mg/L)	110000	110000	110000	100000	100000	110000
Si	(mg/L)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	(mg/L)	1.9	2.1	1.9	1.7	1.8	1.9
Th	(mg/L)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
U	(mg/L)	4.5	4.3	4.3	5.5	5.8	5.9
Anions							
Chloride	(M)	0.082	0.078	0.082	0.078	0.082	0.078
Fluoride	(M)	<0.026	<0.026	<0.026	<0.026	<0.026	<0.026
Nitrate	(M)	4.52	4.52	4.52	4.35	4.35	4.35
Phosphate	(M)	<0.053	<0.053	<0.053	<0.053	<0.053	<0.053
Sulfate	(M)	<0.052	<0.052	<0.052	<0.052	<0.052	<0.052
Alkalinity							
pH		13.0	13.0	13.0	13.2	13.3	13.3
OH^-	(M)	0.064	0.069	0.074	0.13	0.13	0.13
CO_3^{2-}	(M)	0.043	0.040	0.054	0.054	0.052	0.052
HCO_3^-	(M)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Beta/gamma emitters							
Gross alpha	(Bq/mL)	<1.0e+01	<1.0e+01	<1.0e+01	<1.0e+01	<1.0e+01	<1.0e+01
Gross beta	(Bq/mL)	2.11e+05	1.98e+05	2.09e+05	1.97e+05	1.93e+05	1.92e+05
^{14}C	(Bq/mL)	1.43e+02	7.3e+01	5.6e+01	6.8e+01	8.6e+01	1.10e+02
^{144}Ce	(Bq/mL)	<1.4e+03	<1.3e+03	<1.3e+03	<1.2e+03	<1.2e+03	<1.3e+03
^{60}Co	(Bq/mL)	6.44e+02	5.99e+02	6.26e+02	4.93e+02	4.83e+02	4.91e+02
^{134}Cs	(Bq/mL)	2.51e+03	2.57e+03	2.53e+03	2.05e+03	2.03e+03	1.96e+03
^{137}Cs	(Bq/mL)	2.21e+05	2.22e+05	2.16e+05	1.86e+05	1.87e+05	1.90e+05
^{152}Eu	(Bq/mL)	<1.6e+02	<2.0e+02	<2.7e+02	<1.7e+02	<2.2e+02	<2.1e+02
^{154}Eu	(Bq/mL)	<1.5e+02	<1.6e+02	<1.2e+02	<1.5e+02	<1.1e+02	<1.0e+02
^{155}Eu	(Bq/mL)	<7.2e+02	<7.1e+02	<7.2e+02	<6.7e+02	<6.6e+02	<6.6e+02
^{3}H	(Bq/mL)	2.01e+02	2.01e+02	2.01e+02	2.04e+02	2.01e+02	2.01e+02
^{95}Nb	(Bq/mL)	<6.4e+01	<6.2e+01	<6.3e+02	<5.1e+01	<5.5e+01	<5.8e+01
^{106}Ru	(Bq/mL)	<2.1e+03	<2.0e+03	<2.0e+03	<1.9e+03	<1.9e+03	<1.9e+03
^{90}Sr	(Bq/mL)	7.13e+03	7.00e+03	7.11e+03	6.75e+03	6.70e+03	6.70e+03
^{95}Zr	(Bq/mL)	<9.3e+01	<1.1e+02	<1.0e+02	<9.5e+01	<1.1e+02	<9.3e+01

Table 4.2.3. Uniformity of waste tank supernate

Sample[a]	pH	^{60}Co (Bq/mL)	^{134}Cs (Bq/mL)	^{137}Cs (Bq/mL)	Cr (mg/L)	U (mg/L)
W21-L1		8640	5240	3.24e+05	25.0	690
W21-L2	0.56	8620	5220	3.21e+05	27.0	750
W21-L3		8390	4920	3.19e+05	24.0	710
W24-L1		<300	1250	2.22e+05	3.3	10.3
W24-L2	13.1	406	1130	2.24e+05	3.1	9.4
W24-L3		338	1450	2.28e+05	3.5	10.5
W25-L1		1670	3440	3.32e+05	2.0	<0.1
W25-L2	12.5	1840	3600	3.26e+05	1.9	<0.1
W25-L3		1710	3790	3.43e+05	2.0	<0.1
W26-L1		14300	12100	2.21e+06	1.8	912
W26-L2	11.2	10700	10200	2.08e+06	1.8	1130
W26-L3		12000	11700	2.09e+06	1.7	808
W27-L1		346	1560	2.26e+05	2.5	<0.1
W27-L2	11.8	253	1510	2.18e+05	2.8	<0.1
W27-L3		<300	1400	2.26e+05	2.6	<0.1
W28-L1		8730	10100	5.85e+05	0.30	0.20
W28-L2	9.1	8640	10800	5.85e+05	0.38	<0.1
W28-L3		8290	9550	5.84e+05	0.33	<0.1
W31-L1		<200	4560	2.31e+05	5.4	0.20
W31-L2	11.7	<200	4580	2.23e+05	6.0	0.25
W31-L3		<200	4590	2.33e+05	5.6	0.30

[a] Sample identification code: -L1 = 1/3 supernatant level; -L2 = 1/2 supernatant level, -L3 = 2/3 supernatant level.

Table 4.2.4. Analytical data for sludge samples

Characteristic		W21-S	W23-S	W24-S	W25-S	W26-S
Physical properties and miscellaneous data						
TS	(mg/g)	511	544	487	531	449
Density	(g/mL)	1.40	1.34	1.26	1.32	1.54
IC	(mg/kg)	12000	18100	6630	3920	12000
TC	(mg/kg)	18500	22200	9570	6250	18200
TOC	(mg/kg)	6480	4120	2940	2330	6220
RCRA metals						
Ag	(mg/kg)	(50)	(28)	(<7.7)	(<7.6)	(30)
As	(mg/kg)	(42)	(<50)	<42	<41	65
Ba	(mg/kg)	78	63	44	59	87
Cd	(mg/kg)	27	32	6.1	11	4.2
Cr	(mg/kg)	160	190	36	59	170
Hg	(mg/kg)	56	19	26	37	64
Ni	(mg/kg)	75	110	22	34	92
Pb	(mg/kg)	290	(450)	150	220	470
Se	(mg/kg)	<25	<39	<52	<51	<55
Tl	(mg/kg)	<10	<16	<16	<16	<17
Process metals						
Al	(mg/kg)	1000	2800	1600	2800	7500
B	(mg/kg)	<6.6	<10	3.1	<1.5	<7.3
Ca	(mg/kg)	45000	55000	29000	38000	36000
Cs	(mg/kg)	-	-	<1.3	<1.3	-
Fe	(mg/kg)	2300	1900	600	940	2300
K	(mg/kg)	8500	18000	7600	9200	15000
Mg	(mg/kg)	9600	16000	5600	5900	11000
Na	(mg/kg)	48000	82000	69000	66000	51000
Sr	(mg/kg)	200	290	110	150	120
Th	(mg/kg)	13700	12000	1480	3860	9360
U	(mg/kg)	31000	17000	3700	4800	24100
Beta/gamma emitters						
Gross alpha	(Bq/g)	1.29e+05	2.23e+05	2.34e+04	4.65e+04	9.13e+04
Gross beta	(Bq/g)	3.36e+06	6.67e+06	2.62e+06	4.00e+06	5.70e+06
^{14}C	(Bq/g)	1.80e+02	3.65e+02	8.43e+02	1.71e+02	2.13e+02
^{144}Ce	(Bq/g)	<2.8e+04	<2.7e+04	<3.9e+03	<4.2e+03	<1.2e+04
^{60}Co	(Bq/g)	8.07e+04	2.52e+05	3.39e+04	4.03e+04	1.03e+05
^{134}Cs	(Bq/g)	6.99e+03	<6.5e+03	<6.2e+02	7.07e+02	2.97e+03
^{137}Cs	(Bq/g)	2.49e+05	4.95e+05	1.96e+05	2.21e+05	6.84e+05
^{152}Eu	(Bq/g)	1.30e+06	7.22e+05	6.20e+04	8.14e+04	4.92e+05
^{154}Eu	(Bq/g)	4.77e+05	5.14e+05	3.60e+04	5.06e+04	3.19e+05
^{155}Eu	(Bq/g)	1.33e+05	1.21e+05	1.03e+04	1.63e+04	7.51e+04
^{95}Nb	(Bq/g)	<4.7e+03	<7.0e+03	<5.6e+02	<5.9e+02	<2.6e+03
^{106}Ru	(Bq/g)	<4.4e+04	<6.2e+04	<5.7e+03	<5.9e+03	<2.5e+04
^{90}Sr	(Bq/g)	7.52e+05	2.28e+06	1.05e+06	1.65e+06	2.03e+06
^{95}Zr	(Bq/g)	<3.9e+04	<4.5e+04	<2.8e+03	<4.6e+03	<1.3e+05
Alpha emitters						
^{232}U	(Bq/g)	-	-	-	-	-
^{233}U	(Bq/g)	8.13e+03	1.18e+04	5.15e+02	8.37e+02	6.66e+03
^{235}U	(Bq/g)	<2.8e+04	<2.8e+04	<3.7e+03	<4.2e+03	<1.2e+04
^{239}Pu/^{240}Pu	(Bq/g)	2.49e+04	1.18e+04	1.54e+03	2.93e+03	5.11e+03
^{238}Pu/^{241}Am	(Bq/g)	5.13e+04	3.21e+04	3.74e+03	7.35e+03	1.48e+04
^{243}Cm	(Bq/g)	<2.5e+04	<2.6e+04	<3.6e+03	<3.9e+03	<1.3e+04
^{244}Cm	(Bq/g)	4.46e+04	1.67e+05	1.63e+04	3.32e+04	6.14e+04

Table 4.2.4 (continued)

Characteristic		W27-H1-S	W27-H1-H	W28-S	W31-S	W31-H
Physical properties and miscellaneous data						
TS	(mg/g)	386	471	533	369	964
Density	(g/mL)	1.26	1.33	1.49	1.26	-
IC	(mg/kg)	5250	12700	3620	1410	21900
TC	(mg/kg)	7690	16500	6120	1820	30400
TOC	(mg/kg)	2440	3830	2500	410	8530
RCRA metals						
Ag	(mg/kg)	(<7.2)	(<13.)	(17.)	(<6.1)	(<5.4)
As	(mg/kg)	<39	<69	27	<33	<29
Ba	(mg/kg)	49	72	39	17	180
Cd	(mg/kg)	13	17	26	1.7	1.5
Cr	(mg/kg)	65	90	55	27	75
Hg	(mg/kg)	11	18	12	14	39
Ni	(mg/kg)	27	40	62	17	52
Pb	(mg/kg)	120	200	190	170	360
Se	(mg/kg)	<49	<86	<29	<41	<37
Tl	(mg/kg)	20	<27	<9	<13	<11
Process metals						
Al	(mg/kg)	4300	6800	830	1400	16000
B	(mg/kg)	<6.4	<11	4.9	<1.2	22
Ca	(mg/kg)	38000	54000	57000	5600	62000
Cs	(mg/kg)	-	-	<0.8	<1.1	2.4
Fe	(mg/kg)	1400	2500	630	420	7700
K	(mg/kg)	6100	6700	11000	7900	6700
Mg	(mg/kg)	4800	5900	15000	870	3100
Na	(mg/kg)	71000	66000	66000	69000	48000
Sr	(mg/kg)	120	150	130	30	170
Th	(mg/kg)	1890	3040	1370	2790	11800
U	(mg/kg)	2710	1960	17000	3000	9200
Beta/gamma emitters						
Gross alpha	(Bq/g)	2.25e+04	3.10e+04	5.39e+04	2.31e+04	8.95e+04
Gross beta	(Bq/g)	1.44e+06	2.02e+06	2.40e+06	3.18e+06	1.10e+07
^{14}C	(Bq/g)	1.89e+02	4.86e+02	7.60e+01	3.14e+02	1.05e+03
^{144}Ce	(Bq/g)	<5.6e+03	<7.7e+03	<1.7e+04	<9.4e+03	<1.4e+04
^{60}Co	(Bq/g)	1.61e+04	2.50e+04	7.91e+04	8.10e+03	3.01e+04
^{134}Cs	(Bq/g)	<1.2e+03	<1.8e+03	<4.6e+03	3.64e+03	2.07e+03
^{137}Cs	(Bq/g)	3.75e+05	5.71e+05	1.94e+05	2.35e+05	5.52e+05
^{152}Eu	(Bq/g)	1.99e+04	2.42e+04	7.18e+05	<1.7e+04	2.72e+04
^{154}Eu	(Bq/g)	1.26e+04	1.51e+04	3.20e+05	5.86e+03	2.07e+04
^{155}Eu	(Bq/g)	<3.4e+03	3.26e+03	9.70e+04	<5.9e+03	<8.7e+03
^{95}Nb	(Bq/g)	<7.3e+02	<1.4e+03	<2.9e+03	<9.2e+02	<1.2e+03
^{106}Ru	(Bq/g)	<1.1e+04	<1.6e+04	<2.8e+04	<1.4e+04	<1.7e+04
^{90}Sr	(Bq/g)	4.55e+05	5.51e+05	5.57e+05	1.42e+06	5.17e+06
^{95}Zr	(Bq/g)	<1.7e+03	<2.6e+03	<2.4e+04	<4.7e+03	<6.6e+03
Alpha emitters						
^{232}U	(Bq/g)	-	-	1.46e+03	-	-
^{233}U	(Bq/g)	5.18e+02	6.20e+02	3.56e+03	5.08e+02	2.05e+03
^{235}U	(Bq/g)	<5.8e+03	<8.3e+03	<1.7e+04	<9.7e+03	<1.4e+04
^{239}Pu/^{240}Pu	(Bq/g)	1.04e+03	1.86e+03	1.51e+03	8.78e+02	3.22e+03
^{238}Pu/^{241}Am	(Bq/g)	4.41e+03	6.73e+03	5.28e+03	2.43e+03	1.12e+04
^{243}Cm	(Bq/g)	<6.5e+03	<1.0e+04	<1.4e+04	<8.4e+03	<1.3e+04
^{244}Cm	(Bq/g)	1.60e+04	2.15e+04	3.83e+04	1.71e+04	6.89e+04

some alkaline earth metals (Ca, Sr), most metals form hydroxides that have very low solubilities in basic solutions. Many metal carbonates, including those of calcium and strontium also have low solubilities. The insolubilities of the metal hydroxides and carbonates largely account for the concentration of the heavy metals (e.g., U, Th, RCRA metals, and TRU and rare-earth radioisotopes), as well as the calcium and magnesium in the sludge phase. Solubility products in water for many species of interest are presented in Appendix B, Table B.1. These provide a qualitative indication of general trends. (The solubility products apply quantitatively only in dilute solutions with a low ionic strength.)

4.2.3 Inorganic and Physical Characteristics of Liquid Samples

4.2.3.1 Major Inorganic Components in Liquid Samples

The supernatant liquid wastes in the storage tanks, except tank W-21, are essentially high-pH (typically 11 to 13), sodium/potassium nitrate salt solutions. The nitrate concentration varies from 3 to 5 M, with the average being about 4 M. The sodium concentration varies from 61 to 110 g/L and the potassium concentration from 8 to 78 g/L. The potassium levels are higher in the more recently generated LLW evaporator concentrates than in the older wastes. The K/Na mass ratios are 0.8 and 1.0 for the supernates in tanks W-26 and W-23, respectively, compared with 0.1 to 0.3 in the other tanks. The waste solutions are about 0.08 M in chloride. The supernates in five tanks contain dissolved carbonate at concentrations high enough that it could be determined by potentiometric titration.

The supernate in tank W-21 (the PWTP evaporator catch tank) was found to be acidic (pH of 0.6) when the tank was sampled for this study.* It contained higher concentrations of calcium, magnesium, and heavy metals than did the basic waste solutions. Carbonate and bicarbonate ions are not stable in acidic solutions; they react with hydronium ions to form CO_2 (gas) and water.

The concentrations of the major inorganic constituents in g-equivalents/L (N) are given in Table 4.2.5. The cation-anion balance is good, considering that these are radioactive samples with a high salt matrix.

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*After the tanks were sampled for this study, 5,200 gal of waste was transferred from tank W-23 to W-21 to neutralize the low pH waste concentrate in tank W-21.[2] The pH of the liquid sample collected from tank W-21 in June 1990 was 6.9 (neutral).

Table 4.2.5. Major inorganic constituents of liquid samples

Characteristic		W21-L2	W23-L1	W24-L2	W25-L2	W26-L2	W27-L2	W28-L2	W29-L2	W30-L2	W31-L2
pH		0.6	12.8	13.1	12.5	11.2	11.8	9.1	13.0	13.3	11.7
Cations											
Ca^{2+}	(N)	1.15			0.01		0.13	0.39			
K^+	(N)	0.51	1.99	0.28	0.43	1.30	0.22	0.66	0.26	0.24	0.24
Mg^{2+}	(N)	0.46						0.13			
Na^+	(N)	2.65	3.57	4.35	3.39	2.96	3.91	4.18	4.78	4.35	4.09
H^+	(N)	0.08									
Cation total	(N)	4.85	5.56	4.63	3.83	4.26	4.26	5.36	5.04	4.59	4.33
Anions											
NO_3^-	(N)	5.00	3.23	4.19	4.19	3.29	4.52	5.97	4.52	4.35	4.52
Cl^-	(N)	0.06	0.10	0.07	0.07	0.10	0.07	0.14	0.08	0.08	0.07
OH^-	(N)		0.15	0.29	0.06		0.01		0.07	0.13	
CO_3^{2-}	(N)		1.40	0.30		0.40			0.08	0.10	
HCO_3^-	(N)					0.02					
SO_4^{2-}	(N)		0.16								
Anion total	(N)	5.06	5.04	4.85	4.32	3.81	4.59	6.11	4.75	4.66	4.59

4.2.3.2 Process Metals in Liquid Samples

Basic supernates. The alkali metals (Na, K) are the primary cations present in basic supernates. The concentrations of the heavy metals (e.g., U, Th, RCRA metals), as well as the iron and aluminum, in such wastes are in the low-ppm range as would be expected from the insolubilities of the hydroxides and carbonates. The concentrations of calcium and strontium in liquid wastes containing carbonate were low (<20 and <2 ppm, respectively), largely because of the limited solubility of $CaCO_3$ and $SrCO_3$. By comparison, the levels in tank solutions with <0.01 M carbonate were 79 to 7800 ppm and 12 to 65 ppm, respectively. The pH of tank W-28 is a little lower than that of the others. The liquid waste in this tank contains a higher level of magnesium than the other tanks (1600 ppm at a pH of 9 compared with <4 ppm at a pH of 11 to 13), as would be expected from the solubility of $Mg(OH)_2$. At a higher pH, the common-ion effect suppresses the ionization and, hence, the dissolution of $Mg(OH)_2$. Cobalt was not detected in the six tank samples that were analyzed (limit of detection, 0.57 mg/L).

The uranium concentration in the tank W-26 waste solution is higher (1130 ppm) than in the other basic tanks. This may be due to the formation of a uranyl tricarbonate complex $[UO_2(CO_3)_3^{4-}]$ that is stable in basic carbonate/bicarbonate solutions.[3] The uranium can be precipitated at a pH of about 12 or above.[3]

The boron and soluble silica concentrations in the liquid wastes were low (typically <4 and <12 ppm, respectively). The soluble silica concentration was slightly higher in tank W-24 (i.e., 245 ppm).

Basic solutions tend to dissolve atmospheric carbon dioxide and accumulate increasing amounts of carbonate with time. The end result, then, may be the precipitation of carbonates from tank solutions that presently contain dissolved calcium and strontium (including ^{90}Sr) and other shifts in the equilibrium state of the solutions related to pH changes.

Tank W-21. The supernate in tank W-21 was acidic (pH of 0.6) at the time the tank was sampled. This aqueous waste contained significantly higher levels of calcium, magnesium, and heavy metals than did waste in the other tanks and was not in equilibrium with the interstitial liquid (pH of 7) in the sludge phase.

4.2.3.3 Anions in Liquid Samples

The principal anions were nitrate (3 to 5 M), carbonate (in some tanks), and chloride (0.06 to 0.14 M). Sulfate was detected in tank W-23 (0.08 M). Fluoride and phosphate were not detected at the reporting limits, which were 0.026 to 0.053 and 0.053 M, respectively. The reporting limit for sulfate was 0.052 M. As discussed in Appendix B, Sect. B.4.3, a new ion chromatograph is currently being installed for analyses of radioactive waste samples. Following some methods development work, more-detailed anion data should be obtainable for future waste tank samples.

4.2.3.4 Inorganic and Total Organic Carbon in Liquid Samples

Inorganic carbon (IC) in the liquid samples varied from low ppm to 8340 ppm. It can be accounted for by the carbonate in the solution. The ratio of inorganic carbon to carbonate carbon varied from 96 to 106%. The total organic carbon (TOC) concentrations in the aqueous liquid wastes were typically 400 to 600 ppm, although the levels for tanks W-23 and W-26 were higher (1160 and 1280 ppm, respectively). The organic carbon characterization is discussed in Sect. 4.3 and Appendix D.

4.2.3.5 Physical Measurements of Liquid Samples

The total solids (TS) content, based on the weight of residue after drying a measured volume of sample overnight at 115°C, ranged from 334 to 478 mg/mL. The results for the total dissolved solids (TDS), where the sample was filtered before drying, are similar to the total solids measurements. The analyses for metals and other constituents were conducted on unfiltered samples. Good agreement was found between the mass of the cations and anions determined in the study and the total solids (accounted for 90 to 111% of the total solids).

The density measurements for the liquid wastes were typically in the range 1.21 to 1.24 g/mL. However, the density of one tank, W-28, was somewhat higher (1.28 g/mL). These measurements corresponded with the dissolved solids contents of the samples.

4.2.3.6 Uniformity of Supernate in Waste Tanks

The aqueous samples from the one-third and two-thirds levels in the tanks (see Fig. 2.4.1) were screened to check the uniformity of the supernate. The supernate in the tanks appears to be uniform (see Table 4.2.3).

4.2.4 Inorganic and Physical Characteristics of the Sludges

4.2.4.1 Physical Measurements of the Sludges

The total solids (TS) contents of the sludges, based on the weight of residue after drying a measured volume of sample overnight at 115°C, were about 400 to 500 mg/g, except for the hard sludge in tank W-31, which had a higher concentration (see Table 4.2.4). The sludges contain 50 to 60% water; however, this does not include any water of crystallization that might be associated with the precipitated solids.

The bulk density measurements of the wet sludges (i.e., the precipitated solids plus the interstitial liquid) were in the range 1.3 to 1.5 g/mL. These are the densities of the composite sludge samples that were used in both the chemical and the radiochemical analyses.

Results of physical properties tests (e.g., viscosity, sedimentation rate) on four of the sludge samples are described in a separate report by Ceo and Shor.[1]

4.2.4.2 Process Metals in the Sludges

The principal metals found in the sludges were sodium, potassium, calcium, magnesium, uranium, and thorium. Based on the total metals determined, the sodium and potassium combined are typically 40 to 60 wt %; the calcium plus magnesium, 30 to 40%; and the uranium plus thorium, 4 to 20%. The uranium plus thorium account for 28% of the metals determined in tank W-21 sludges. The more recently generated soft sludges (W-21, W-23, and W-26) have higher uranium-plus-thorium concentrations than do the older wastes. Most alkali metals are soluble. While a small amount of sodium may be present in the sludge solids (e.g., $Na_2U_2O_7$ may be precipitated), it is expected, based on solubility, that most of the sodium and potassium are present as dissolved salts in the interstitial sludge liquid. Most of the other metals are probably precipitated to the sludge solids, based on their low solubilities in the tank liquids (Sect. 4.2.2). The sludges also contain low levels of aluminum (0.1 to 0.8%) and iron (0.1 to 0.25%). The levels are higher in the hard sludge in the bottom of tank W-31. The boron concentrations in the sludges were very low (<11 ppm).* The sludges were not analyzed for silica.

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*The boron data for the sludges in the report by Peretz et al.[4] have no meaning because a lithium borate fusion was used to dissolve the samples.[5]

4.2.4.3 Inorganic Carbon and Total Organic Carbon in the Sludges

The sludges typically contain 0.4 to 2 wt % inorganic carbon (IC), as carbonate. On a mole basis, this amounts to 0.3 to 1.8 mol of carbonate per kilogram. The inorganic carbon concentration was lower in the tank W-31 soft (watery) sludge, which has a high sodium content but a relatively low calcium content. The total organic carbon (TOC) was typically in the range 0.2 to 0.6 wt % (0.8% in W-31). The organic carbon characterization is discussed in Sect. 4.3 and Appendix D.

4.2.4.4 Anions

The determination of anions within the sludge phase has been a problem. Ion chromatography may not be appropriate for anion determination in sludge samples since the solid phase must first be dissolved with a strong acid. The use of a strong acid places severe limitations on the anions that can be determined by ion chromatography. Therefore, considerable development work may be required to obtain useful anion data for the sludge phase of the waste tanks.

Tests are being planned to wash a few sludge samples with water (to remove the interstitial liquid) and with dilute acid. The new ion chromatograph which is currently being installed for analyses of radioactive samples, could be used to examine the leachate.

4.2.5 Radioactive Materials

4.2.5.1 Alpha Emitters (TRU Waste)

Wastes that are contaminated with transuranium (TRU) alpha emitters with half-lives greater than 20 years and activities greater than 3700 Bq/g (100 nCi/g) at the time of assay are classified as TRU wastes.[6] All of the composite sludge samples except the soft sludge in tank W-31 exceeded the 3700 Bq/g threshold and, therefore, were identified as TRU wastes (see Table 4.2.6). If the tank W-31 sludge were dried, the solid residue would then also be classifed as a TRU waste. The ^{244}Cm isotope has a half-life of 18 years and is excluded from the TRU-waste definition. However, it is included in Table 4.2.6 because of its high specific activity in the wastes. The ^{244}Cm and TRU-waste isotopes contribute, on the average, 72 and 20%, respectively, of the gross alpha in the sludge (excluding tank W-21); the uranium isotopes contribute only a few percent. The TRU-waste alpha in tank W-21 sludge was considerably higher than in the other sludges. Also included in Table 4.2.6 are the checks on the alpha balance obtained by a ratio of the sum of the alpha

Table 4.2.6. TRU-waste classification for sludge samples

Sample	Gross alpha (Bq/g)	TRU-waste status[a]	TRU[a] (Bq/g)	TRU[a] (%)[b]	^{244}Cm (Bq/g)	^{244}Cm (%)[b]	Sum of alpha emitters (%)[b]
W21-S	129,000	TRU	76,200	59	44,600	35	100
W23-S	223,000	TRU	43,900	20	167,000	75	100
W24-S	23,400	TRU	5,280	23	16,300	70	94
W25-S	46,500	TRU	10,280	22	33,200	71	95
W26-S	91,300	TRU	19,910	22	61,400	67	96
W27-H1-S	22,500	TRU	5,450	24	16,000	71	98
W27-H1-H	31,000	TRU	8,590	28	21,500	69	99
W28-S	53,900	TRU	6,790	13	38,300	71	93
W31-S	23,100	c	3,310	14	17,100	74	90
W31-H	89,500	TRU	14,420	16	68,900	77	95

[a] Transuranic alpha emitters with half-lives greater than 20 years and activities in excess of 3700 Bq/g are classified as TRU waste.

[b] The percent columns denote percent of gross alpha.

[c] The wet sludge is not much below the threshold for TRU waste. If the sludge were dried or dewatered, the solid residues would be TRU waste.

emitters identified by alpha spectroscopy to the gross alpha. The alpha balance varied from 90 to 100% (average, 96%).

In general, little or no alpha activity was observed in the basic liquid phases in the tanks (see Tables 4.2.1 and 4.2.2). Low levels of alpha activity were observed in the liquid samples from tanks W-21 and W-26. Tank W-21 supernate was acidic when the tank was sampled for this study. Ninety-six percent of the gross alpha in the tank W-26 liquid can be accounted for as uranium isotopes. This is consistent with the above-average uranium metal content determined by fluorometric analysis (Sect. 4.2.3.2). The liquid samples were all non-TRU solutions; their salt residues, if dried at 115°C, would also be non-TRU. Individual alpha emitters were determined if the results of the gross alpha analysis were high enough that meaningful results could be obtained by pulse-height analysis. If the gross alpha content was low, individual alpha emitters were not determined.

4.2.5.2 Beta-Gamma Emitters

The most abundant radionuclides observed in the sludges were ^{137}Cs and ^{90}Sr and their short-lived daughters ^{137}Ba and ^{90}Y, respectively. Most of the beta activity in tank solutions containing carbonate resulted from ^{137}Cs, which was higher than ^{90}Sr and other beta emitters by a factor of $\geq$30 . The ^{90}Sr was more soluble in supernates containing little or no carbonate and, together with its ^{90}Y daughter, contributed approximately one-third of the beta activity in those solutions. Gamma-active europium isotopes were observed in the sludges. They were not detected in the liquid phase of any of the tanks that were basic but were present in the acidic supernate in tank W-21. This observation is not surprising, considering the low solubility of europium hydroxide (see Appendix B, Table B.1). Because of the age of the waste, ^{95}Zr, ^{95}Nb, and ^{144}Ce (half-lives of 64, 35, and 284 d, respectively) were not expected to be present. "Less-than" values for these radionuclides are included in the Tables 4.2.1, 4.2.2, and 4.2.4 for completeness.

Little tritium was found in the liquid samples; the ^{14}C concentration was also low in both the liquid and the sludge phases.

The gross beta balances were obtained by ratioing the sum of the individual beta emitters, including the ^{90}Y daughter of ^{90}Sr, to the gross beta determination. For liquid samples, the gross beta balances varied from 95 to 115% (average, 101%) and the sludge samples from 86 to 109% (average, 98%).

4.2.5.3 Nuclear Materials

Estimates were made of the concentrations of nuclear materials in the wastes based on the radiochemical analyses (Table 4.2.7). It should be noted that the values given here are less than values and do not signify that these quantities are present in the wastes. The ^{235}U and ^{243}Cm concentrations are based on the limit of detection by gamma spectroscopy. The ^{239}Pu and ^{241}Am were calculated by assuming that all the ^{239}Pu/^{240}Pu was ^{239}Pu and all the ^{238}Pu/^{241}Am was ^{241}Am. The ^{241}Pu cannot be determined accurately by radiochemical analysis; mass spectroscopic analysis is required for quantitative determination. The ratio of the nuclear material to the total uranium, was <2 wt % for wastes containing 4800 to 31,000 ppm (0.5 to 3%) uranium.

4.2.6 RCRA Evaluation for Inorganic Species

A waste tank is classified as hazardous if the contents exhibit any of the following characteristics: (1) ignitability, (2) reactivity, (3) corrosivity, or (4) toxicity, according to specified procedures. Preliminary screening tests for RCRA characteristics, principally the hazardous metals, were included in the analysis plan. The RCRA metal limits and results of the screening tests are presented in Tables 4.2.8 and 4.2.9, respectively.

The waste tanks contain only aqueous-liquid phases. None of the tanks contained a RCRA ignitable waste. The liquid wastes in six tanks were corrosive with a pH $\leq$2 (W-21) or $\geq$12.5 (W-23, W-24, W-25, W-29, and W-30). (The waste in tank W-21 has been neutralized since the tank was sampled for this study.[2])

The liquid phases in four of the basic tanks (W-23, W-24, W-26, and W-31) contain one toxic metal each at a concentration that is high enough to classify the waste as RCRA hazardous (Table 4.2.9). The levels are in the low-ppm range and are only slightly above the threshold that defines a waste as RCRA. The supernatant liquid in tank W-21 was acidic and contained higher levels of dissolved heavy metals than the other tanks. It exhibited the characteristic of "Extraction Procedure (EP) - toxicity" with respect to cadmium, chromium, lead, and mercury. Arsenic, selenium, thallium (a proposed RCRA metal), and silver (except tank W-26) were not detected at quantitative levels in the basic waste tank liquids.

The classification of the sludges is preliminary. The measurements listed are the total metal contents obtained with a nitric acid leach and are not the EP-toxicity or Toxicity

Table 4.2.7 Estimates of nuclear materials in the sludges based on radiochemical analyses[a]

	Concentrations in waste (mg/kg)						Ratio of nuclear material to total U[a]
Sample	^{233}U	^{235}U	^{239}Pu[b]	^{241}Am[c]	^{243}Cm	Total U	(wt %)
W21-S	23.1	<350	<22.6	<0.44	<0.013	31,000	<1.2
W23-S	33.5	<350	<14.2	<0.27	<0.014	17,000	<2.1
W24-S	1.5	<46	<0.7	<0.03	<0.002	3,700	<1.2
W25-S	2.4	<53	<1.3	<0.06	<0.002	4,800	<1.1
W26-S	18.9	<150	<2.2	<0.13	<0.007	24,100	<0.6
W27-H1-S	1.5	<73	<0.5	<0.04	<0.003	2,710	<2.7
W27-H1-H	1.8	<100	<0.8	<0.06	<0.005	1,960	<5.1
W28-S	10.1	<210	<0.7	<0.04	<0.007	17,000	<1.2
W31-S	1.4	<120	<0.4	<0.02	<0.004	3,000	<4.0
W31-H	5.8	<180	<1.4	<0.10	<0.007	9,200	<2.0

[a] ^{241}Pu cannot be determined accurately by radiochemical analysis; mass spectroscopic analysis is required for quantitation.

[b] Calculated by assuming that ^{239}Pu/^{240}Pu is all ^{239}Pu.

[c] Calculated by assuming that ^{238}Pu/^{241}Am is all ^{241}Am.

Table 4.2.8. Regulatory limits for RCRA metals in solid waste

Element	(Liquid) Regulatory limit (mg/L)	(Sludge) EP-toxicity equivalent (mg/kg)
As	5.0	100
Ba	100	2000
Cd	1.0	20
Cr	5.0	100
Pb	5.0	100
Hg	0.2	4
Se	1.0	20
Ag	5.0	100
Ni (proposed)	50	1000
T1 (proposed)	0.9	18
pH	≤ 2 or ≥ 12.5	

Table 4.2.9. Preliminary screening for RCRA hazardous characteristics

	RCRA-waste status		Comments		
			Liquid		Sludge
Tank	Liquid	Sludge[a]	Corrosive	Hazardous metals above regulatory limit (mg/L)	Hazardous metals[a] above EP-toxicity equivalent (mg/kg)
W-21	RCRA	RCRA	Yes (pH = 0.56)	Cd(2.0), Cr(27), Pb(7.1), Hg(9.2)	Cd(27), Cr(160), Hg(56), Pb(290)
W-23	RCRA	RCRA	Yes (pH = 12.8)	Cd(1.7)	Cd(32), Cr(190), Hg(19), Pb(450)
W-24	RCRA	RCRA	Yes (pH = 13.1)	Pb(6.7)	Hg(26), Pb(150)
W-25	RCRA	RCRA	Yes (pH = 12.5)		Hg(37), Pb(220)
W-26	RCRA	RCRA		Cd(4.5)	Cd(42), Cr(170), Hg(64), Pb(470)
W-27		RCRA			Soft sludge: Hg(11), Pb(120) Hard sludge: Hg(18), Pb(200)
W-28		RCRA			Cd(26), Hg(12), Pb(190)
W-29	RCRA	NA[b]	Yes (pH = 13.0)		NA[b]
W-30	RCRA	NA[b]	Yes (pH = 13.3)		NA[b]
W-31		RCRA		Cr(6.0)	Soft sludge: Hg(14), Pb(170) Hard sludge: Hg(39), Pb(360)

[a] Preliminary screening based on nitric acid dissolution; status only if sludge dissolves completely in the EP-toxicity acetate buffer.

[b] NA = not applicable because of no access to tanks W-29 and W-30 for sampling.

Characteristic Leaching Procedure (TCLP) results. Classification is based on an EP-toxicity/TCLP equivalent. This is a value that accounts for the 20-fold dilution of the EP-toxicity or TCLP procedures and represents the concentration that would result in classification of the sample as RCRA hazardous waste if the sludge dissolved completely in the acetate buffers used in these tests.

All sludge samples exceeded the EP-toxicity equivalent limits for mercury and lead. Samples from four tanks exceeded the EP-toxicity equivalent limit for cadmium; three of them also exceeded the criterion for chromium. In general, arsenic, silver, selenium, and thallium were not found at quantitative levels in the sludge. In the few exceptions, the values were very close to the reporting limits for the instrument.

Because of the high salt contents of these wastes, it was not possible to measure selenium at the required levels by inductively coupled plasma spectrometry (ICP, SW-846 Method 6010).[7] An effort was made to determine selenium in the liquid samples from tanks W-29 and W-30 by graphite furnace atomic absorption (GFAA). The high sodium nitrate levels were very corrosive to the graphite tube furnaces, and fewer than 20 sample injections could be completed before complete destruction of the graphite was observed. These difficulties are discussed in Appendix B, Sect. B.4.9.

Liquid samples from tanks W-29 and W-30 were analyzed for total cyanide using EPA Method 9010 modified for small samples. A substance in the waste interfered with the analysis (see Appendix B, Sect. B.4.5). A new ion chromatograph, which is currently being installed, may resolve these questions for future waste samples.

4.3 SUMMARY OF ORGANIC CHEMICAL CHARACTERIZATION

A subset of samples from the waste tanks (W-24, -25, -29, -30, and -31) were analyzed for EPA Target Compound List (TCL) volatile and semivolatile organic compounds using modified EPA SW-846 methodologies (see Tables 4.3.1 and 4.3.2 for TCL constituents and reporting limits). Decontaminated organic extracts were prepared by modifications of SW-846 Methods 5030 (volatiles in aqueous liquids) and 3510 (semivolatiles in aqueous liquids) or 3550 (semivolatiles in sludges) in radioactive contamination-zoned facilities. The extracts were analyzed by Contract Laboratory Program (CLP) methods equivalent to SW-846 gas chromatography with mass spectrometry (GC/MS) Methods 8240 (volatiles) or 8270 (semivolatiles) in a conventional analytical laboratory. These analyses

Table 4.3.1. Target Compound List volatile organics and reporting limits

Compound	Reporting limit (μg/L)
Chloromethane	10
Bromomethane	10
Vinyl chloride	10
Chloroethane	10
Methylene chloride	10
Acetone	10
Carbon disulfide	5
1,1-Dichloroethene	5
1,1-Dichloroethane	5
1,2-Dichloroethene (total)	5
Chloroform	5
1,2-Dichloroethane	5
2-Butanone	10
1,1,1-Trichloroethane	5
Carbon tetrachloride	5
Vinyl acetate	10
Bromodichloromethane	5
1,2-Dichloropropane	5
Cis-1,3-dichloropropene	5
Trichloroethene	5
Dibromochloromethane	5
1,1,2-Trichloroethane	5
Benzene	5
Trans-1,3-dichloropropene	5
Bromoform	5
4-Methyl-2-pentanone	10
2-Hexanone	10
Tetrachloroethene	5
1,1,2,2-Tetrachloroethane	5
Toluene	5
Chlorobenzene	5
Ethylbenzene	5
Styrene	5
Xylene (total)	5

Table 4.3.2. Target Compound List semivolatile organics and reporting limits

	Reporting limits		
		Sludge sample	
Compound	Aqueous sample (μg/L)	3-g extract (μg/kg)	4-g extract (μg/kg)
Phenol	250	3300	2500
Bis(2-chloroethyl)ether	250	3300	2500
2-Chlorophenol	250	3300	2500
1,3-Dichlorobenzene	250	3300	2500
1,4-Dichlorobenzene	250	3300	2500
Benzyl alcohol	250	3300	2500
1,2-Dichlorobenzene	250	3300	2500
2-Methylphenol	250	3300	2500
Bis(2-chloroisopropyl)ether	250	3300	2500
4-Methylphenol	250	3300	2500
N-Nitroso-di-N-propylamine	250	3300	2500
Hexachloroethane	250	3300	2500
Nitrobenzene	250	3300	2500
Isophorone	250	3300	2500
2-Nitrophenol	250	3300	2500
2,4-Dimethylphenol	250	3300	2500
Benzoic acid	1300	17000	13000
Bis(2-chloroethoxy)methane	250	3300	2500
2,4-Dichlorophenol	250	3300	2500
1,2,4-Trichlorobenzene	250	3300	2500
Naphthalene	250	3300	2500
4-Chloroaniline	250	3300	2500
Hexachlorobutadiene	250	3300	2500
4-Chloro-3-methylphenol	250	3300	2500
2-Methylnaphthalene	250	3300	2500
Hexachlorocyclopentadiene	250	3300	2500
2,4,6-Trichlorophenol	250	3300	2500
2,4,5-Trichlorophenol	1300	17000	13000
2-Chloronaphthalene	250	3300	2500
2-Nitroaniline	1300	17000	13000
Dimethylphthalate	250	3300	2500
Acenaphthylene	250	3300	2500

Table 4.3.2 (continued)

	Reporting limits		
		Sludge sample	
Compound	Aqueous sample (μg/L)	3-g extract (μg/kg)	4-g extract (μg/kg)
2,6-Dinitrotoluene	250	3300	2500
3-Nitroaniline	1300	1700	13000
Acenaphthene	250	3300	2500
2,4-Dinitrophenol	1300	17000	13000
4-Nitrophenol	1300	1700	13000
Dibenzofuran	250	3300	2500
2,4-Dinitrotoluene	250	3300	2500
Diethylphthalate	250	3300	2500
4-Chlorophenylphenylether	250	3300	2500
Fluorene	250	3300	2500
4-Nitroaniline	1300	17000	13000
4,6-Dinitro-2-methylphenol	1300	17000	13000
N-Nitrosodiphenylamine[a]	250	3300	2500
4-Bromophenylphenylether	250	3300	2500
Hexachlorobenzene	250	3300	2500
Pentachlorophenol	1300	17000	13000
Phenanthrene	250	3300	2500
Anthracene	250	3300	2500
Di-n-butylphthalate	250	3300	2500
Fluoranthene	250	3300	2500
Pyrene	250	3300	2500
Butylbenzylphthalate	250	3300	2500
3,3-Dichlorobenzidine	500	6700	5000
Benzo(a)anthracene	250	3300	2500
Chrysene	250	3300	2500
Bis(2-ethylhexyl)phthalate	250	3300	2500
Di-n-octylphthalate	250	3300	2500
Benzo(b)fluoranthene	250	3300	2500
Benzo(k)fluoranthene	250	3300	2500
Benzo(a)pyrene	250	3300	2500
Indeno(1,2,3-cd)pyrene	250	3300	2500
Dibenz(a,h)anthracene	2500	3300	2500
Benzo(g,h,i)perylene	250	3300	2500

[a] Cannot be resolved from diphenylamine.

were supplemented by a modification of SW-846 Method 8015 permitting direct aqueous injection gas chromatographic (DAIGC) determination of major water-soluble organic compounds that are not amenable to purge-and-trap GC/MS.

Very few EPA TCL compounds were found in the waste samples. Results are shown in Tables 4.3.3 and 4.3.4 for the volatile and semivolatile organic compounds, respectively. These tables list only compounds whose possible presence was indicated by the analysis. No volatile organics attributable to the samples were determined by the purge-and-trap GC/MS or by DAIGC procedures with reporting limits of 5 to 10 μg/L and 1 to 2 mg/L, respectively. The volatile compounds methylene chloride, acetone, and toluene were found in each of the tank samples but were also observed in blanks at similar concentrations and thus cannot be attributed to the aqueous samples. Semivolatile phthalates, which are almost ubiquitous in nature, were present in the sludge samples and some liquid samples. Phthalates were also present in relatively high concentrations in the water and sand blanks. The main TCL hit was the semivolatile organic compound benzoic acid (40 to 3500 μg/L). Naphthalene and phenanthrene were found (400 to 520 μg/kg) in two sludges. Most of the organic matter was found as Tentatively Identified Compounds (TICs). The main TICs were not identifiable, but 2,6-dibromo-4-nitrophenol was estimated at 600 to 2000 μg/L. Tributyl phosphate was only found in the soft sludge (1900 μg/kg) and the hard sludge (12,000 μg/kg) of tank W-31. Dimethylbenzene and diethylbenzene also were detected in a few samples. Polychlorinated biphenyls were not specifically determined, but they would have been estimated as TICs. Reporting limits for individual polychlorinated biphenyl cogeners (not Aroclor mixtures) were each 2.5 mg/L for aqueous liquids and 13 to 17 mg/kg for sludges. Recoveries of surrogate standards and matrix spikes were generally good and consistent with previous experiences with nuclear wastes.

Very little (4 to 14%) of the organic matter suggested to be present by total organic carbon analyses was accounted for by the regulatory organics determinations. The remainder may consist of highly polar, water-soluble, and possibly polymeric compounds arising from the radiolysis and degradation of chelators, extractants, or other compounds originally present in the wastes. Identification of these compounds would require further development and application of the analytical methods.

Table 4.3.3. Results for volatile organic compound analysis of waste samples[a]

	Tank identification and concentration									
			W29-			W30-				
	W24-L2 (μg/L)	W25-L2 (μg/L)	L1 (μg/L)	L2 (μg/L)	L4 (μg/L)	L1 (μg/L)	L2 (μg/L)	L4 (μg/L)	W31-L2 (μg/L)	Water blank[b] (μg/L)
Target Compound List										
Methylene chloride	30	37	7	10	7	17	6	10	30	52
Acetone	12	12	27	15	11	11	16	18	18	19
Toluene			9	6	6	7	18	19		9
Tentative ID compounds										
Unknown		6 (2)[c]	13 (2)			7 (1)		5 (1)		
Trichlorofluoromethane	36		29			31		20	6	10

[a] Only compounds whose possible presence was indicated by the analysis are listed. See Table 4.3.1 for Target Compound List of volatile organics and reporting limits.

[b] Representative blank.

[c] Number of TICs are given in parentheses.

Table 4.3.4. Results from semivolatile organic compound analysis of waste samples[a]

	Tank identification and concentration						
	W24-		W25-		W29-		
	L2 (μg/L)	Sludge (μg/kg)	L2 (μg/L)	Sludge (μg/kg)	L1 (μg/L)	L2 (μg/L)	L4 (μg/L)
Target Compound List							
Benzoic acid	40		2500		3500	3000	2300
Diethylphthalate			63				
Di-n-butylphthalate		9800		4000			
Bis(2-ethylhexyl)phthalate		17000		2400			
Di-n-octylphthalate		18000		15000	250	430	69
Naphthalene				460			
2-Nitrophenol							
Phenanthrene				480			
Tentative ID compounds							
Unknown	6066 (20)[c]	187830 (4)	34280 (20)	145900 (2)	17030 (19)	19810 (19)	11940 (19)
Unknown hydrocarbon		22260 (4)		110100 (11)			
Unknown phthalate		69300 (12)		55400 (6)			
Unknown phenol							
Dibromonitrophenol							
Diethylbenzene				9900			
Dimethylbenzene							
2.6-Dibromo-4-nitrophenol					1800	2000	1600
Tributyl phosphate							

Table 4.3.4 (continued)

	Tank identification and concentration							
	W30-			W31-				
	L1 (μg/L)	L2 (μg/L)	L4 (μg/L)	L2 (μg/L)	Soft sludge (μg/kg)	Hard sludge (μg/kg)	Water blank[b] (μg/L)	Sand blank[b] (μg/kg)
Target Compound List								
Benzoic acid	1300	2300	1400	2400				
Diethylphthalate								
Di-n-butylphthalate					19000	2000		19000
Bis(2-ethylhexyl)phthalate					1300	1800	110	2700
Di-n-octylphthalate		290					4800	22000
Naphthalene						440		
2-Nitrophenol			1400					
Phenanthrene						520		
Tentative ID compounds								
Unknown	6188 (19)	7603 (18)	5449 (20)	38480 (19)	143200 (3)	149700 (3)		166900 (7)
Unknown hydrocarbon					48200 (15)	175700 (14)	540 (1)	
Unknown phthalate							19080 (19)	93200 (13)
Unknown phenol		420						
Dibromonitrophenol				2400				
Diethylbenzene								
Dimethylbenzene						5500		
2,6-Dibromo-4-nitrophenol		600						
Tributyl phosphate					1900	120000		

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[a] Only compounds whose possible presence was indicated by the analysis are listed. See Table 4.3.2 for Target Compound List of semivolatile organics and reporting limits.

[b] Representative blank.

[c] Number of TICs are given in parentheses.

Additional information on the organic chemical characterization is presented in Appendix D; a brief description of the analytical methods and a more extensive discussion of the results are also included.

4.4 DISCUSSION AND RECOMMENDATIONS

This study provides a relatively extensive characterization of the liquid wastes in the tanks in the winter of 1989-1990. The in-tank-evaporation project using air sparging of the MVSTs, which was started shortly after the samples had been taken, may cause shifts in equilibrium related to pH and carbonate as carbon dioxide is absorbed from the air, in addition to concentrating the wastes. The general properties of the supernates will probably continue to be similar, but some changes in composition should be expected with time.

In this study, sludge samples could be collected at only one location in each tank (i.e., directly under the access pipe); remote equipment was not available to examine other locations. Therefore, the sludge data should be regarded as merely an indicator of the tank contents. Statistical sampling of these tanks, as defined by EPA SW-846, is not possible because of the high radiation levels and limited access. Results of the study provide a relatively extensive characterization of the metals and radioactive materials in the sludge samples. Although not determined in this study, it is recommended that both ^{99}Tc ($t_{1/2}$ = 2.13 x 10^5 y) and ^{129}I ($t_{1/2}$ = 1.6 x 10^7 y) be determined on selected samples. However, the determination of anions within the sludge phase of the waste tanks is a problem area. Some preliminary washing tests and dilute acid leaching of the sludge are planned. This might provide some information about anions which are soluble in water or dilute acid (e.g., the anions in the interstitial liquid). Considerable development work may be required to obtain useful anion data.

About 90% of the organic carbon compounds determined by the total organic carbon analysis were not accounted for by the EPA regulatory procedures. The application of high-performance liquid chromatography might yield information about the possible presence of low-molecular-weight organic acids/salts (e.g., oxalates, acetates, butyrates). This would require a special column for the new ion chromatograph as well as methods development. Considerable additional development and application of analytical methods would be required to identify other types of organic compounds such as radiolytical and chemical degradation products.

This study was primarily focused on support for WHPP design and included only a preliminary RCRA characterization. The full RCRA characterization will be needed in the future.

The EPA regulatory procedures for solid wastes were not designed for radioactive wastes or the types of chemical matrices found in the waste tanks. There is a need for greater flexibility and modifications in the regulatory procedures to give a high priority to worker health and safety [e.g., As Low As Reasonably Achievable (ALARA)]. This is especially true in cases where the spirit and intent of environmental regulations can be satisfied technically using alternative procedures. With the current visibility that DOE facilities are receiving on health and safety practices, it is becoming increasingly difficult, if not impossible, to satisfy some of the EPA regulatory procedures. In this study, modifications were made in the EPA procedures to reduce worker exposure; however, there has been no agreement that these modifications will be acceptable for compliance purposes. Many of these modifications involved reduced sample size, which also reduces the amount of contaminated waste requiring disposal from sampling and laboratory activities.

Some additional issues must be considered along with ALARA requirements. Some holding time requirements (e.g., mercury, volatile organics, and cyanide) are unrealistic since radiological data must be obtained on all samples prior to other measurements to ensure that activity limits are maintained in various laboratories. The volumes (sample sizes) required and/or suggested for various analytical measurements (volatile and semivolatile organic compounds, EP-TOX, TCLP, cyanide and sulfide distillations) are unacceptable for the levels of activity involved. On-site filtration and acid preservation are unacceptable for field operations with radioactive samples since these operations would result in unnecessary radiation exposures to personnel. Required measurements on undiluted samples are unacceptable for the levels of activity involved. The drying of samples for dissolved solid determinations creates an extreme hazard due to possible dusting. The QA/QC requirements (duplicates, spikes, etc.) for nonautomated procedures result in additional radiation exposure to personnel.

Some of the EPA regulatory procedures do not work on the chemical matrices found in the waste tank samples. For example, GFAA for metals and the EPA cyanide procedure do not work.

There is a need for specialized analytical instrumentation (capital equipment) to meet the needs for regulatory characterization of radioactive samples. The analytical equipment includes items such as an inductively coupled plasma-mass spectrometer (ICP-MS) for more efficient and sensitive measurement of metals and isotopes, a gas chromatograph-mass spectrometer (GC-MS) for volatile and semivolatile organics determination on radioactive samples, and a liquid chromatograph-mass spectrometer (LC-MS) for identification and measurement of polar organic compounds.

4.5 REFERENCES

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APPENDIX A

FIELD SAMPLING DATA

INTRODUCTION

Field sampling data are presented in this appendix. The data are from the perspective of the sampling crew standing on the pad over the tank, with distances measured from the flange on the access pipe down into the tanks. Profiles of the tank contents are presented in Table A.1. The parameters were determined as follows:

1. locations of the air-liquid and liquid-sludge interfaces as measured with the Markland detector;
2. location of the tank bottom measured by pushing a rod (i.e., the sampling equipment) down into the tank and measuring the length on the rod;
3. location of the top of the settled sludge solids layer derived from the height of the sludge solids phase in the sample collected at the liquid-sludge interface (measured in the analytical laboratory, see Appendix B, Table B.3, "S1" code samples) and the location where the sample was collected (Table A.3);
4. location of any hard-sludge layer measured by pushing the soft-sludge sampler into the tank until a consolidated layer was reached; and
5. calculated values for the one-third, one-half, and two-thirds liquid levels in the tanks, based on the presampling survey with the Markland detector.

A comprehensive listing of the samples collected, dates of collection, sampling locations in the tanks, and field survey radiation levels is presented for the liquid and sludge samples in Tables A.2 and A.3, respectively.

The estimated personnel exposures (pocket-meter readings) from field sampling activities are given in Table A.4. The doses received during the collection of 18 liquid samples (0.1 to 1.2 R/h) at the MVSTs using the vacuum pump sampling system were about the same as those received during collection of 8 liquid samples (0.1 R/h) using the pump module (Isolock) system, including the maintenance to make the system operational. The doses from sampling tanks at the evaporator service facility are higher than those from sampling the MVSTs because "hot" piping/ductwork near the access to tank W-21 makes the work-area radiation levels higher around that tank (and also tank W-22, which was not part of this study). The doses to the hand (finger ring dosimeters) were about the same as those from handling MVSTs samples. Tank W-23, also located at the evaporator facility, is in a different vault.

Table A.1. Profiles of tank contents

(depth from tank access point[a])

Tank	Top of liquid[b]	Liquid zone[c]			Top of sludge layer (Markland detector)[b]	Top of sludge solids layer (sample)[d]	Top of hard sludge	Tank bottom
		One-third	One-half	Two-thirds				
W-21[e]	13 ft 6 in.	14 ft 2 in.	14 ft 10 in.	15 ft 6 in.	16 ft 2 in.	16 ft 9 in.	-	18 ft 11 in.
W-23[e]	14 ft 0 in.	-	14 ft 4 in.	-	14 ft 8 in.	14 ft 10 in.	-	19 ft 2 in.
W-24	10 ft 11 in.	13 ft 3 in.	14 ft 6 in.	15 ft 8 in.	18 ft 0 in.	17 ft 10 in.	-	21 ft 6 in.
W-25	10 ft 11 in.	12 ft 7 in.	13 ft 6 in.	14 ft 4 in.	16 ft 0 in.	15 ft 10 in.	-	21 ft 6 in.
W-26	11 ft 3 in.	13 ft 1 in.	14 ft 1 in.	15 ft 0 in.	16 ft 10 in.	17 ft 2 in.	-	21 ft 3 in.
W-27	11 ft 0 in.	12 ft 10 in.	13 ft 10 in.	14 ft 9 in.	16 ft 7 in.	16 ft 11 in.	18 ft 3 in.[f]	21 ft 5 in.
W-28	10 ft 5 in.	13 ft 4 in.	14 ft 9 in.	16 ft 2 in.	19 ft 1 in.	19 ft 9 in.	-	21 ft 4 in.
W-31	10 ft 6 in.	12 ft 9 in.	13 ft 11 in.	15 ft 0 in.	17 ft 3 in.	18 ft 5 in.	20 ft 3 in.	20 ft 8 in.

[a] Depth measured from the top of the flange on the access pipe.

[b] Located with Markland Model 10 sludge gun.

[c] Based on presampling survey with the Markland detector.

[d] Based on the height of the sludge solids phase in the PVC sampling tube; sample collected at the supernate-sludge interface; phase height measurements made in a hot cell at the analytical laboratory.

[e] Air-liquid and liquid-sludge interfaces measured with the Markland detector on January 30, 1990.

[f] Hard sludge layer estimated to be about 1 ft thick; underlying layer of soft sludge, about 2 ft thick.

Table A.2. Field information for liquid samples

Tank	Sample	Date collected	Liquid level sampled	Sampling depth from tank access point[a]	Radiation level of 250-mL sample[b] (R/h)
W-21	W21-L1	1/30/90	One-third	14 ft 2 in.	0.310
	W21-L2	1/30/90	One-half	14 ft 10 in.	0.300
	W21-L3	1/30/90	Two-thirds	15 ft 6 in.	0.300
W-23	W23-L1 [c]	1/30/90	One-half	14 ft 4 in.	0.120
W-24	W24-L1	9/19/89	One-third	13 ft 3 in.	0.120
	W24-L2	9/19/89	One-half	14 ft 6 in.	0.180
	W24-L3	9/19/89	Two-thirds	15 ft 8 in.	0.180
W-25	W25-L1	9/19/89	One-third	12 ft 7 in.	0.190
	W25-L2	9/19/89	One-half	13 ft 6 in.	0.280
	W25-L3	9/19/89	Two-thirds	14 ft 4 in.	0.260
W-26	W26-L1	9/19/89	One-third	13 ft 1 in.	1.200
	W26-L2	9/19/89	One-half	14 ft 1 in.	1.200
	W26-L3	9/19/89	Two-thirds	15 ft 0 in.	1.200
W-27	W27-L1	9/19/89	One-third	12 ft 10 in.	0.160
	W27-L2	9/19/89	One-half	13 ft 10 in.	0.200
	W27-L3	9/19/89	Two-thirds	14 ft 9 in.	0.100
W-28	W28-L1	9/19/89	One-third	13 ft 4 in.	0.500
	W28-L2	9/19/89	One-half	14 ft 9 in.	0.480
	W28-L3	9/19/89	Two-thirds	16 ft 2 in.	0.480
W-29	W29-L1	11/30/89	-	d	0.110
	W29-L2	11/30/89	-	d	0.110
	W29-L3	11/30/89	-	d	0.110
	W29-L4	11/30/89	-	d	0.110
W-30	W30-L1	11/30/89	-	d	0.110
	W30-L2	11/30/89	-	d	0.110
	W30-L3	11/30/89	-	d	0.110
	W30-L4	11/30/89	-	d	0.110
W-31	W31-L1	9/19/89	One-third	12 ft 9 in.	0.190
	W31-L2	9/19/89	One-half	13 ft 11 in.	0.180
	W31-L3	9/19/89	Two-thirds	15 ft 0 in.	0.180

[a] Depth measured from the top of the flange on the access pipe.

[b] Field survey.

[c] Liquid layer about 8 in. deep (Markland detector) in tank W-23. Therefore, only one sample, the midpoint sample, was collected.

[d] Sample collected using the pump module sampler. Pump pickup is at one-half the tank depth. There is no access to tanks W-29 and W-30 for measuring sludge depth.

Table A.3. Field information for sludge samples

Tank	Sample/layer	Date sample collected	Type of sample	Depth from tank access point[a,b,c]	Radiation level of sample[d] (R/h)	Comments
W-21	Top of soft sludge			16 ft 2 in.		
	W21-S1	1/31/90	Soft sludge	17 ft 10 in.	1.5	
	W21-S2	1/31/90	Soft sludge	18 ft 11 in. (tank bottom)	1.0	e
W-23	Top of soft sludge			14 ft 8 in.		
	W23-S1	1/31/90	Soft sludge	16 ft 4 in.	2.5	
	W23-S2	1/31/90	Soft sludge	18 ft 0 in.	2.0	
	W23-S3	1/31/90	Soft sludge	19 ft 2 in. (tank bottom)	1.0	
W-24	Top of soft sludge			18 ft 0 in.		
	W24-S1	9/21/89	Soft sludge	18 ft 10 in.	0.100	
	W24-S2	9/21/89	Soft sludge	21 ft 6 in. (tank bottom)	1.2	
W-25	Top of soft sludge			16 ft 0 in.		
	W25-S1	9/21/89	Soft sludge	17 ft 4 in.	0.500	
	W25-S2	9/21/89	Soft sludge	18 ft 9 in.	0.500	
	W25-S3	9/21/89	Soft sludge	21 ft 6 in. (tank bottom)	1.3	
W-26	Top of soft sludge			16 ft 10 in.		
	W26-S1	12/5/89	Soft sludge	18 ft 6 in.	2.0	
	W26-S2	12/5/89	Soft sludge	20 ft 0 in.	0.8	
	W26-S3	12/5/89	Soft sludge	21 ft 3 in. (tank bottom)	1.2	
W-27	Top of soft sludge			16 ft 7 in.		
	W27-S1	9/21/89	Soft sludge	17 ft 6 in.	0.100	
	W27-S2	12/5/89	Soft sludge	To hard sludge	0.2	f
	Top of hard sludge	9/21/89		18 ft 3 in.		
	W27-H1	12/5/89	Hard sludge	21 ft 6 in. (tank bottom)	0.3	g
W-28	Top of soft sludge			19 ft 1 in.		
	W28-S1	9/21/89	Soft sludge	21 ft 4 in. (tank bottom)	1.2	
	W28-S2	9/21/89	Soft sludge	21 ft 4 in. (tank bottom)	0.8	h

Table A.3 (continued)

Tank	Sample/layer	Date sample collected	Type of sample	Depth from tank access point[a,b,c]	Radiation level of sample[d] (R/h)	Comments
W-31	Top of soft sludge			17 ft 3 in.		
	W31-S1	9/27/89	Soft sludge	18 ft 10 in.	1.5	
	W31-S2	9/27/89	Soft sludge	20 ft 3 in.	2.2	
	W31-H1	9/27/89	Hard sludge	20 ft 8 in. (tank bottom)	2.8	

[a] Depth measured from the top of the flange on the access pipe.

[b] Liquid-sludge interface located with the Markland detector.

[c] Sampling depth is the distance to the bottom of the sampler from the access point (i.e., distance S1, S2, . . . shown in Fig. 3.1.3).

[d] Field survey.

[e] An older design sampler used which collected a shorter core (15 in.) than the others.

[f] Encountered hard sludge layer, which bent the closure on the sampler on first attempt to collect sample W27-S2 (9/21/89); no sample was collected at that time. Went back 12/5/89 to sample this tank. Sample W27-S2 overlaps the solids layer of sample W27-S1.

[g] Auger bit cut through an estimated 1-ft-thick layer of hard sludge, then pushed sampler through underlying soft layer to tank bottom. Hard sludge plugged the sampler; a sample of the underlying soft layer was not obtained.

[h] Collected a second sample at same location to obtain more material.

APPENDIX B

INORGANIC AND RADIOCHEMICAL ANALYTICAL SUPPORT

APPENDIX B CONTENTS

INORGANIC AND RADIOCHEMICAL ANALYTICAL SUPPORT

B.1 INTRODUCTION

The objective of this project was to characterize the concentrates from the liquid low-level wastes (LLLW) generated at the Oak Ridge National Laboratory (ORNL). The historical information and the various sources of waste are discussed in Sect. 2 of this report. Since information obtained from these studies will be used in support of various activities, standardized analytical procedures were used as much as possible for all measurements.[1-3] Some modifications to the standard procedures were necessary because of the high radiation level, high salt content, and generally complex chemical matrix in the samples. Deviations from standard procedures were documented in the raw data files for these measurements. This project has involved the cooperation and participation of groups from all sections of the Analytical Chemistry Division (ACD) at ORNL. The organization, sample preparation, sample distribution, and many analyses were performed by the Inorganic and Physical Analysis (IPA) Group. An example of a sample flow diagram is shown in Fig. B.1.

All of the waste tank solutions analyzed for this project had a high dissolved solid content and high ionic strength. The high ionic strength has a significant effect on both the solution chemistry and various chemical measurements. For example, a potentiometric pH measurement is not based upon the hydronium ion concentration but is a function of the hydronium ion activity, which can vary significantly at high ion strength. The pH measurements on the waste samples discussed in this report can only be considered as apparent pH values. In addition, the ionic strength affects the kinetics of reactions involving ionic species and can shift the solubility behavior of many species. In general, the waste tank solution chemistry is far from ideal, and expected behavior for many species may not be observed.

The complex chemical composition of the waste tank samples is compounded by the effects of radiolysis.[4] Within the liquid and sludge phases, the sample matrix experienced very high dose rates due to the intimate contact of the radioactive species. A majority of the radiation effects on the matrix is due to the alpha activity, which is primarily present in the sludge phase. The alpha radiation can result in decomposition of water to generate hydrogen peroxide and interactions with solute molecules to generate free radicals. The free radicals can interact with other solute species, including initiating the polymerization of organic materials.

The formation of the sludge phase is due to the insolubility of many of the species present at high pH. A list of solubility products for many of the species of interest is included in Table B.1 for the convenience of the reader.

Several miscellaneous deviations, not discussed under procedures, involve the initial handling of samples. Frequently the analytical methodology, as written by the U. S. Environmental Protection Agency (EPA) for regulatory measurements, was not appropriate for characterizing the contents of radioactive waste tanks. It was then necessary to modify the regulatory procedures to (1) reduce radiation exposure to personnel to meet the policy of maintaining radiation exposure As Low As Reasonably Achievable (ALARA), (2) accommodate the

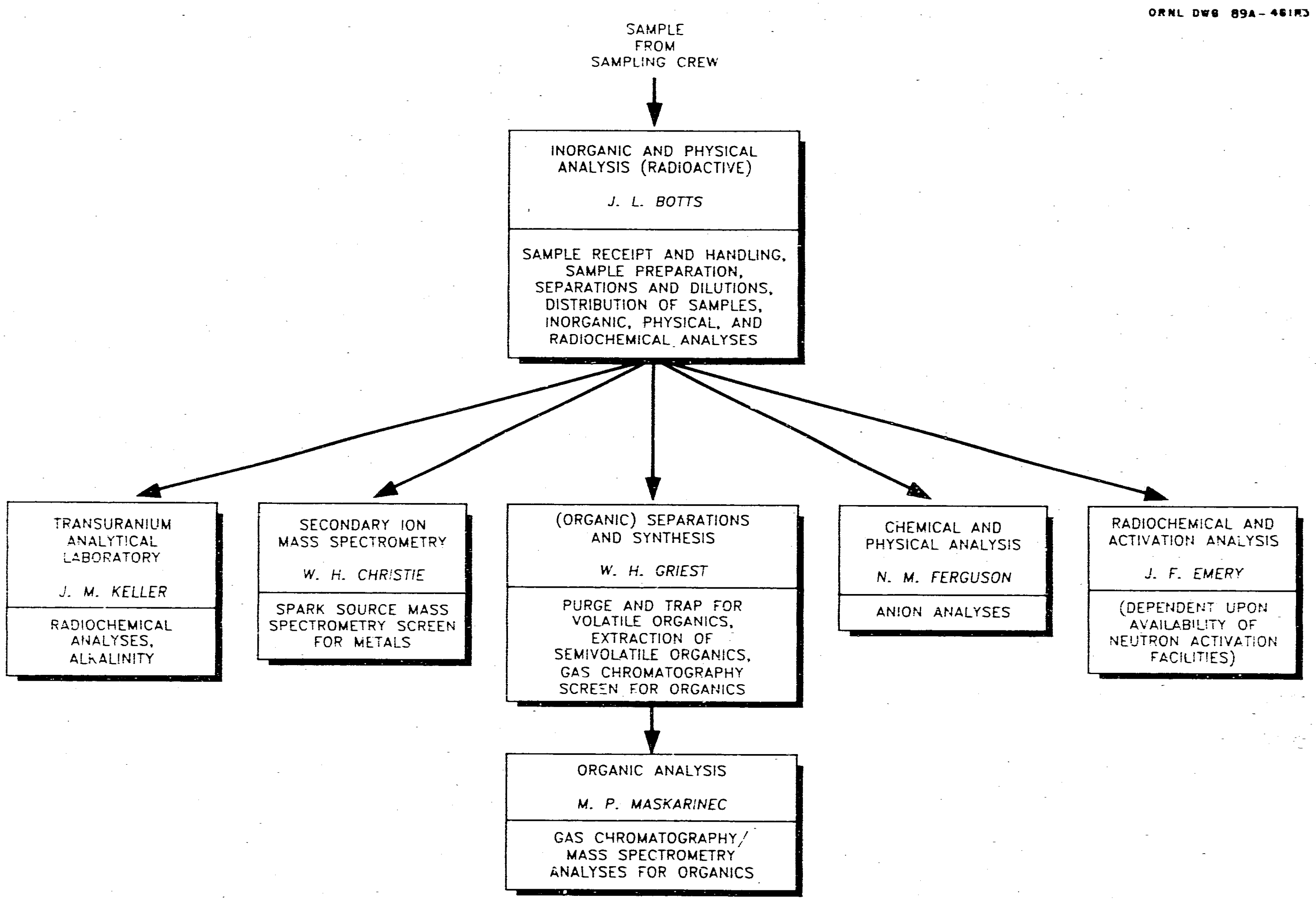

Fig. B.1. Example of a sample flow diagram.

Table B.1. Solubility products for RCRA metals and TRU metals

Compound	Formula	pK_{sp}[a]
RCRA Metals		
Barium carbonate	$BaCO_3$	8.29
Barium chromate	$BaCrO_4$	9.93
Barium fluoride	BaF_2	5.98
Barium hydroxide	$Ba(OH)_2$	2.30
Barium hydrogen phosphate	$BaHPO_4$	6.50
Barium phosphate	$Ba_3(PO_4)_2$	22.47
Barium nitrate	$Ba(NO_3)_2$	2.35
Barium sulfate	$BaSO_4$	9.96
Cadmium carbonate	$CdCO_3$	11.28
Cadmium fluoride	CdF_2	2.19
Cadmium hydroxide	$Cd(OH)_2$	13.60
Cadmium phosphate	$Cd_3(PO_4)_2$	32.60
Cadmium sulfide	CdS	26.10
Chromium(III) fluoride	CrF_3	10.18
Chromium(II) hydroxide	$Cr(OH)_2$	15.70
Chromium(III) hydroxide	$Cr(OH)_3$	30.20
Chromium(III) phosphate (green)	$CrPO_4 \cdot 4H_2O$	22.62
Chromium(III) phosphate (violet)	$CrPO_4 \cdot 4H_2O$	17.00
Lead carbonate	$PbCO_3$	13.13
Lead chromate	$PbCrO_4$	12.55
Lead chloride	$PbCl_2$	4.79
Lead fluoride	PbF_2	7.57
Lead chloride fluoride	$PbClF$	8.62
Lead hydroxide	$Pb(OH)_2$	14.93
Lead(IV) hydroxide	$Pb(OH)_4$	65.50
Lead hydroxide chloride	$PbOHCl$	13.70
Lead hydroxide nitrate	$PbOHNO_3$	3.55
Lead hydrogen phosphate	$PbHPO_4$	6.24
Lead phosphate	$Pb_3(PO_4)_2$	42.10
Lead sulfate	$PbSO_4$	7.79
Lead sulfide	PbS	27.90
Mercury(I) carbonate	Hg_2CO_3	16.05
Mercury(I) chloride	Hg_2Cl_2	17.88
Mercury(I) chromate	Hg_2CrO_4	8.70
Mercury(I) hydroxide	$Hg_2(OH)_2$	23.70
Mercury(II) hydroxide	$Hg(OH)_2$	25.52
Mercury(I) hydrogen phosphate	Hg_2HPO_4	12.40
Mercury(I) sulfide	Hg_2S	47.00
Mercury(II) sulfide (black)	HgS	51.80
Mercury(II) sulfide (red)	HgS	52.40
Nickel(II) carbonate	$NiCO_3$	8.18
Nickel(II) hydroxide	$Ni(OH)_2$	14.70
Nickel(II) phosphate	$Ni_3(PO_4)_2$	30.30
Nickel(II) sulfide (alpha)	NiS	18.50
Nickel(II) sulfide (beta)	NiS	24.00
Nickel(II) sulfide (gamma)	NiS	25.70
Silver carbonate	Ag_2CO_3	11.09
Silver chloride	$AgCl$	9.75
Silver chromate	Ag_2CrO_4	11.95
Silver hydroxide	$AgOH$	7.71
Silver phosphate	Ag_3PO_4	15.84
Silver sulfate	Ag_2SO_4	4.84
Silver sulfide (alpha)	Ag_2S	49.18
Silver sulfide (beta)	Ag_2S	49.00
Thallium(I) chloride	$TlCl$	3.76
Thallium(I) chromate	Tl_2CrO_4	12.00
Thallium(I) sulfide	Tl_2S	20.30
Thallium(III) hydroxide	$Tl(OH)_3$	45.20
TRU and Other Elements of Interest		
Americium(III) hydroxide	$Am(OH)_3$	19.57
Americium(IV) hydroxide	$Am(OH)_4$	56.00
Calcium carbonate[b]	$CaCO_3$	8.03
Calcium hydroxide[b]	$Ca(OH)_2$	5.10
Europium hydroxide	$Eu(OH)_3$	23.05
Magnesium carbonate[b]	$MgCO_3$	4.40
Magnesium hydroxide[b]	$Mg(OH)_2$	10.92
Neptunyl hydroxide	$NpO_2(OH)_2$	21.60
Plutonium(III) hydroxide	$Pu(OH)_3$	19.70
Plutonium(IV) hydroxide	$Pu(OH)_4$	55.00
Plutonyl(IV) hydroxide	$PuO_2(OH)_2$	24.70
Plutonium hydrogen phosphate	$Pu(HPO_4)_2$	27.70
Scandium fluoride	ScF_3	17.37
Scandium hydroxide	$Sc(OH)_3$	30.10
Strontium carbonate	$SrCO_3$	9.96
Strontium chromate	$SrCrO_4$	4.65
Strontium fluoride	SrF_2	8.61
Strontium phosphate	$Sr_3(PO_4)_2$	27.39
Strontium sulfate	$SrSO_4$	6.49
Thorium hydroxide	$Th(OH)_4$	44.40
Thorium phosphate	$Th_3(PO_4)_4$	78.60
Thorium hydrogen phosphate	$Th(HPO_4)_2$	20.00
Uranyl carbonate	UO_2CO_3	11.73
Uranyl hydroxide	$UO_2(OH)_2$	21.95
Uranyl phosphate	$(UO_2)_3(PO_4)_2$	46.70
Uranyl hydrogen phosphate	UO_2HPO_4	10.67
Yttrium fluoride	YF_3	12.14
Yttrium hydroxide	$Y(OH)_3$	22.10

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[a] Solubility product data taken from Lange's Handbook of Chemistry, 12th Ed., edited by J. A. Dean. McGraw-Hill Book Co. (1979)

[b] W. B. Meldrum and A. F. Daggett, A Textbook of Qualitative Analysis, American Book Company, p. 138, (1946).

limitations of the instrumentation and facilities available, and (3) handle the complex nature of the sample composition (e.g. high levels of salt, dissolved solids, uranium, and thorium) to obtain valid data. To reduce radiation exposure, sample-size requirements were reduced significantly for numerous measurements. The reduced sample sizes and instrumental limitations resulted in reduced sensitivities and other conflicts with some of the regulatory quality assurance/quality control (QA/QC) procedures that were too stringent to accommodate these problems. The deviations from regulatory QA/QC practices will be discussed for individual procedures under the topic of Analytical Methods.

First, the EPA sample-preservation procedures that involve maintenance of samples at 4°C were avoided because of the lack of refrigeration facilities for radioactive samples and to prevent shifts in the equilibrium states of solutions with elevated levels of both pH and dissolved solids. In addition, the on-site filtration, upon collection, and the on-site acid preservation of metals in aqueous samples were not performed because of the danger of handling radioactive materials. The EPA requirement, which states that all samples must initially be run undiluted, was not met for samples with high radiation levels or for techniques in which high-salt content interfered with the measurement.

B.2 INITIAL SAMPLING HANDLING

The request numbers and the ACD numbers for all samples from this project are summarized in Table B.2. This information is useful for retrieval of data from the ACD data management system.

The waste samples were inspected by a health physics representative, and a field survey was performed on each sample before it was packaged and delivered to the High Radiation Level Analytical Laboratory (HRLAL). Based upon the field survey, all liquid samples except those from tank W-26 were handled in radiochemical laboratories (classified as radiation contamination zones). The sludge samples required remote handling for dissolution and dilution before their removal from the hot cell and distribution to various laboratories. The liquid samples from tank W-26 also required remote handling in the hot cell with subsamples removed for analysis. Sample volumes or weights were adjusted to comply with Appendix 7 of the ORNL Health Physics Manual.

B.2.1 Liquid Samples

Liquid samples, designated with "L" in the sample identification number, were decanted into 250-mL glass "I-CHEM" jars at the sampling point. Some minor leakage problems were experienced with these jars. The jars, which had previously been cleaned according to EPA protocol, were labeled and capped using lids with Teflon seals. Each jar was enclosed in a plastic bag and shielded in a lead pig before delivery to Building 2026. Dose rates on contact with full jars were on the order of a few hundred mR/h, except the "W26-L" code samples where the dose rate was about 1.2 R/h. The sample liquids all appeared to be single-phase and ranged from pale to deep yellow with little, if any, turbidity. Upon delivery, liquid samples were photographed in plastic bags on the benchtop using ambient light, returned to their lead pigs, then secured in the sample storage room.

B.2.2 Sludge Samples

Each sludge sample was delivered to Building 2026 contained in its original sampler and sealed in two 6-mil plastic sleeves. The completed package was delivered in a metal can inside a stainless steel (SS) carrier. Samplers were placed in a hot cell on arrival, then removed from the SS carrier and inner can. The samples were allowed to stand overnight in the PVC samplers to allow the solids to settle. The heights of the sludge (solids) and liquid layers were then measured. Each sludge sample was transferred to one or more "I-CHEM" jars within about three days of sampling except request IPA6282, which was transferred after seven days. After the sludges were transferred to I-CHEM jars, they were photographed through the cell window. The resulting pictures had poor resolution, and a strong yellow cast from light filtered through the zinc bromide-filled window. Sludges were designated either as "-H" (hard sludge) or "-S" (soft sludge); this designation was made at the sampling point and refers to the type of sampler used to collect the sludge.

The dimensional characteristics of the sludge samples as received are listed in Table B.3. The original sampling plan called for removal of the liquid layer before a transfer of sludge to its receiving jar. All tanks except W-28 contained thick sludge blankets that required more than one sampler to obtain a full vertical core. These sludges were to be divided in the hot cell

Table B.2. ACD Sample Codes (Request Number / Sample Code)

Sample	IPA (2026)	CPA (4500S)	TAL (7920)
W21-L1	IPA6279/900130-092		
W21-L2	IPA6279/900130-093	CPA10585/900307-075	TRU9024/900312-227
W21-L3	IPA6279/900130-094		
W23-L1	IPA6279/900130-095	CPA10585/900307-076	TRU9024/900312-228
W24-L1	IPA6222/890925-166		
W24-L2	IPA6222/890925-167	CPA10231/891121-047	TRU8742/891023-021
W24-L3	IPA6222/890925-168		
W25-L1	IPA6222/890925-169		
W25-L2	IPA6222/890925-170	CPA10231/891121-048	TRU8742/891023-022
W25-L3	IPA6222/890925-171		
W26-L1	IPA6222/890925-197		
W26-L2	IPA6222/890925-198	CPA10231/891121-049	TRU8742/891023-023
W26-L3	IPA6222/890925-199		
W27-L1	IPA6222/890925-172		
W27-L2	IPA6222/890925-173	CPA10231/891121-050	TRU8742/891023-024
W27-L3	IPA6222/890925-174		
W28-L1	IPA6222/890925-175		
W28-L2	IPA6222/890925-176	CPA10231/891121-051	TRU8742/891023-025
W28-L3	IPA6222/890925-177		
W31-L1	IPA6222/890925-178		
W31-L2	IPA6222/890925-179	CPA10231/891121-052	TRU8742/891023-026
W31-L3	IPA6222/890925-180		
W29-L1	IPA6255/891204-048	CPA10367/900110-012	TRU8875/900102-056
W29-L2	IPA6255/891204-049	CPA10367/900110-013	TRU8875/900102-057
W29-L4	IPA6255/891204-050	CPA10367/900110-014	TRU8875/900102-058
W30-L1	IPA6255/891204-051	CPA10367/900110-015	TRU8875/900102-059
W30-L2	IPA6255/891204-052	CPA10367/900110-016	TRU8875/900102-060
W30-L4	IPA6255/891204-053	CPA10367/900110-017	TRU8875/900102-061
W21-S	IPA6282/900131-107		TRU9023/900312-210
W23-S	IPA6282/900131-108		TRU9023/900312-211
W24-S	IPA6223/890925-205		TRU8880/900104-019
W25-S	IPA6223/890925-209		TRU8880/900104-020
W28-S	IPA6223/890925-217		TRU8880/900104-021
W31-S	IPA6229/891009-019		TRU8880/900104-022
W31-H	IPA6229/891009-020		TRU8880/900104-023
W26-S	IPA6257/891205-051		TRU8944/900130-168
W26S-D	IPA6257/891205-051		TRU8944/900130-169
W27-H1-S	IPA6257/891205-052		TRU8944/900130-170
W27-H1-H	IPA6257/891205-053		TRU8944/900130-171
W27-H1-H-D	IPA6257/891205-053		TRU8944/900130-172

Table B.3. Dimensional characteristics of sludge sample

Sample	Sludge		Liquid	
	(cm)	(in.)	(cm)	(in.)
W21-S1	33.0	13	15.2	6
W21-S2	38.1[a]	15		
W23-S1	48.2	19	2.54	1
W23-S2	45.7	18	5.08	2
W23-S3	45.7	18	2.54	1
W24-S1	29.8	11.75	15.9	6.25
W24-S2	48.3	19		
W25-S1	45.1	17.75	7.0	2.75
W25-S2	51.4	20.25		
W25-S3	48.9	19.25		
W26-S1	40.6	16	8.9	3.5
W26-S2	43.2	17	5.1	2
W26-S3	47.0	18.5	3.8	1.5
W27-S1	16.5	6.5	>22[b]	>8.75[b]
W27-S2	16.5	6.5	25.4	10
W27-H1	d			
W28-S1	48.9[c]	19.25	2.9	1.125
W28-S2				
W31-S1	12.7	5	38.7	15.25
W31-S2	19.1	7.5	30.5	12
W31-H1	d			

[a] Sample W21-S2 was taken with an older design sampler that collected a shorter core (38.1 cm) than the other samplers.

[b] Estimated. Sampler W27-S1 leaked a small amount. Exact liquid height was not measured.

[c] Sampler W28-S1 contained a full vertical core of the sludge in the tank.

[d] Could not measure the vertical core thickness with the hard sludge sampler.

so that one-fourth of the solids from each related sampler were mixed together and sonicated. Physical and chemical analysis would be performed on the sonicated composite sludge, and the remaining liquid and solids fractions would be reserved.

During the project, there were some variations in sludge handling procedures. The first batch of samples were transferred from samplers to jars without removal of excess liquid, including sample W27-S1 and all soft sludges from tanks W24, W25, W28, and W31. All other sludge samples had excess liquid decanted before transfer to jars. Funnels were used in transferring soft, fluid sludges, but denser, more viscous sludges were transferred directly to avoid sample loss.

Sludge sample W25-S2 was noticeably stratified, so it was split into two components using two jars— the lower layer was thick and brown with hard gritty particles, and the upper layer was soft and yellow.

Composite sludge samples were made up for each tank in proportions representative of the complete vertical core (see Table B.4). "Soft" sludges and "hard" sludges were analyzed separately. The first batch of samples were split without any mixing, but samples from the second batch were gently stirred with SS spatulas in their receiving jars before separating. All samples were recombined in representative proportions for inorganic and radiochemical analyses. Portions were taken from each jar using the spatula— each portion consisting of approximately 25% of the total from that jar.

Composite sludges were sonicated for about 1 min each to ensure complete mixing. Sonicated sludges appeared to be well-mixed, but often contained hard particles suspended in the body of sludge. No practical amount of mixing will completely homogenize these samples.

The W27-H1 sampler contained both liquid and hard sludge. Liquid was poured into one jar and the sludge was scraped out into another jar using a SS spatula. Since the hard sludge sampler was opaque, liquid and solids depths could not be measured. The hard fraction of W27-H1 was too stiff to sonicate.

Jar lids did not always seal properly, especially if any sludge got smeared on the jar lip. Sludge liquid would evaporate from poorly sealed jars, leaving a crust of dried salts between jar and lid. The W27-S1 sampler was leaky, and an indeterminate amount (<13 cm) of the liquid was lost through seepage.

Table B.4. Components of composite sludge samples

Composite sample	Constituents
W21-S	W21-S1, W21-S2
W23-S	W23-S1, W23-S2, W23-S3
W24-S	W24-S1, W24-S2
W25-S	W25-S1, W25-S2, W25-S3
W26-S	W26-S1, W26-S2, W26-S3
W27-H1-S	W27-H1 soft sludge
W27-H1-H[a]	W27-H1 hard sludge
W28-S	W28-S1
W31-S	W31-S1, W31-S2, W31-S3
W31-H	W31-H1

[a] Sample W27-H1-H contained no free liquid and was not sonicated.

B.3 ANALYTICAL METHODOLOGY

The analytical procedures are listed in Table B.5, which includes a brief summary for each procedure and detection limits for most measurements. Additional discussion on selected procedures and techniques is provided to document deviations from procedures or problems encountered.

B.4 INORGANIC AND PHYSICAL MEASUREMENTS

B.4.1 Sample Preparation for Metal Analysis

Liquid samples were prepared by a 5.0 mL/50.0 mL dilution with 5% nitric acid. A 0.5-mL aliquot of a 1.0 mg/mL scandium standard was added prior to dilution to serve as an internal standard for Inductively-Coupled Plasma (ICP) analyses.

Sludge samples were prepared by microwave digestion with a CEM MDS-81D microwave instrument. The digestion procedure is similar to the proposed SW-846 Method 3051, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*. Approximately 1.0 g of sludge sample was placed in a Teflon vessel (120 mL size) with 10 mL of nitric acid. After heating for 2.5 min at 100% power and 10 min at 80% power, the sample was allowed to cool to room temperature. After cooling, 2-5 mL of 30% hydrogen peroxide was added dropwise to the solution. On the completion of effervescence, the samples were filtered through a #541 Whatman filter and diluted to 100 mL with ASTM Type II water. A 1.0-mL aliquot of a 1.0 mg/mL scandium standard was added prior to the dilution. The scandium serves as an internal standard to account for matrix interferences with ICP analyses.

B.4.2 Sludge Density

The densities of the wet sludges (including the interstitial liquid) were measured using graduated 15- mL centrifuge tubes. Portions of sludge were packed into thin Teflon tubing, then extruded from the tubing into the bottoms of tared centrifuge tubes using a glass stirring rod as a plunger. Care was taken not to smear sludge on the inside wall of the centrifuge tubes. Samples were capped and centrifuged at high speed (>4000 G) for 15 min to displace any air, then total (both liquid and solids) and compacted solids volumes were recorded and the loaded tubes were reweighed. Densities were computed as net mass/total volume.

Sample W27-H1 was dry and contained lumps and fines. A modification of the above technique was used to determine this sample's density. 1.00 mL of liquid from the same tank (liquid sample W27-L3) was placed in a centrifuge tube and weighed. The solid sludge was added to the liquid and centrifuged to compact the solids and displace any air. Sludge volume was computed as the difference between liquid volume and total volume after centrifugation, and sludge mass was computed as the difference between total mass and the mass of tube plus liquid. Density was computed as net mass/net volume.

Table B.5. Analytical methods

Parameter	Reference	Method Summary	Approximate Detection Limit
Radiochemical Procedures			
Gross alpha	ACD 9 002301, EPA-600-900.0 ACD 9 0733005	Sample is dissolved, if necessary, then samples are diluted, if needed, to reduce dissolved solids; a small volume of sample (usually 0.1 mL) is evaporated on a stainless steel planchet that is alpha counted with a gas-flow proportional counter in 2-pi geometry.	2 pCi/L
Gross beta	ACD 9 0733005 ACD 9 002302	Sample is dissolved, if necessary, then samples are diluted, if needed, to reduce dissolved solids; a small volume of sample (usually 0.1 mL) is evaporated on a stainless steel planchet that is beta counted with a gas-flow proportional counter.	4 pCi/L
Gamma Spectroscopy	ACD 2 21996 ACD 2 00376 EPA-600-901.1	Sample is dissolved, if necessary, and a 10-mL aliquot is analyzed by gamma spectroscopy. If the dead time exceeds 5%, the sample is diluted or mounted in a less efficient geometry and re-analyzed.	varies with energy
Alpha Spectroscopy (Americium-241 Curium-244 Uranium-232, -233, -235, -238 Plutonium-238, -239, -240)	ACD 2 21996 ACD 1 003115	Sample is dissolved, if necessary, co-precipitated with ferric hydroxide to separate actinides from complex matrix; a small volume of sample is then evaporated on a stainless steel plate that is counted with a surface barrier detector.	50 pCi/mL
Strontium-90	EPA-600-905.0 ACD 2 21807	Sample is dissolved, if necessary; strontium carrier is added, and the sample is processed through several purification steps; final purification is made by precipitation of the strontium as the carbonate. The precipitate is mounted for beta counting with a gas-flow proportional counter.	4 pCi/L
Tritium	ACD 2 0950	Tritium is distilled from aqueous samples and a portion of the distillate is analyzed by liquid scintillation counting.	5 pCi/mL
Carbon-14		Samples were heated to 900°C to volatilize organic species and decompose carbonates. Organics were converted to CO_2 in an oxidizing bed. Off-gases were collected in a basic solution and counted by liquid scintillation.	5 pCi/mL
Technetium-99	ACD 5 11873	Technetium is first separated from other fission products by an oxidation step followed by extraction of the pertechnetate anion. The ^{99}Tc is then stripped into water and loaded onto an anion exchange resin. The ^{99}Tc content is determined by neutron activation analysis of the resin column.	
Iodine-129	ACD 2 21393	Iodine activity is separated from other fission products by oxidation to periodate with sodium hypochlorite in basic solution, followed by reduction to iodine with hydroxylamine hydrochloride and extraction of iodine into carbon tetrachloride. The iodine is stripped into an aqueous solution of potassium metabisulfate which reduces the iodine to iodide.	

Table B.5, continued

Parameter	Reference	Method Summary	Approximate Detection Limit
		The iodide is loaded onto an anion exchange resin that is dried and analyzed by neutron activation. The induced ^{130}I activity is measured along with added ^{131}I activity for yield corrections.	
<u>Inorganic Analytical Procedures</u>			
<u>Metals by ICP</u>	EPA 200.7/ SW-846-6010	Liquid samples or dissolved sludges are nebulized and the aerosol that is produced is transported to a argon plasma torch where excitation occurs. Characteristic atomic-line spectra are produced by an inductively coupled plasma (ICP); the intensity of the emission lines from the excited elements is measured with a computer controlled scanning monochromator (Perkin-Elmer 6500 ICP). The measured intensity is compared to stored calibration curves for quantitation.	
		<u>Wavelength (nm)</u>	
Silver (Ag)		328.068	69 ng/mL
Arsenic (As)		197.197	265 ng/mL
Barium (Ba)		233.527	13 ng/mL
Cadmium (Cd)		226.502	19 ng/mL
Chromium (Cr)		205.552	35 ng/mL
Nickel (Ni)		231.604	56 ng/mL
Lead (Pb)		220.353	144 ng/mL
Selenium (Se)		196.026	312 ng/mL
Thallium (Tl)		190.864	177 ng/mL
Aluminium (Al)		309.271	420 ng/mL
(Al)		396.152	120 ng/mL
Boron (B)		249.773	5 ng/mL
(B)		208.959	
Calcium (Ca)		393.366	-
Cobalt (Co)		228.616	57 ng/mL
Iron (Fe)		275.574	260 ng/mL
Potassium (K)		766.491	-
Magnesium (Mg)		279.553	130 ng/mL
Sodium (Na)		589.592	29 ng/mL
Strontium (Sr)		407.771	13 ng/mL
(Sr)		216.596	74 ng/mL
Thorium (Th)		283.730	220 ng/mL
Uranium (U)		367.007	
Zinc (Zn)		213.856	2 ng/mL
<u>Metals by GFAA</u>	SW-846-7000	Graphite Furnace Atomic Absorption (GFAA) is based upon the attenuation of characteristic radiation from a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL), by ground state atoms in a vapor phase. An aliquot of sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. A monochromator and a photomultiplier tube (PMT) are used to measure the attenuated transmitted radiation as it passes through the vapor containing ground-state atoms of the element to be measured. The absorption of the characteristic radiation increases in proportion to the amount of ground-state element in the vapor. The measured absorption is compared to stored calibration curves for quantitation.	

Table B.5. continued

Parameter	Reference	Method Summary			Approximate Detection Limit
		<u>Wavelength (nm)</u>	<u>Pyrolysis</u>	<u>Atomization</u>	
Silver (Ag)	EPA 272.2	328.1	650	1600	0.16 ng/mL
Arsenic (As)	EPA 206.2	193.7	1300	2300	11.4 ng/mL
Barium (Ba)	EPA 208.2	553.6	1200	2550	15.6 ng/mL
Cadmium (Cd)	EPA 213.2	228.8	700	1600	0.13 ng/mL
Chromium (Cr)	EPA 218.2	357.9	1650	2500	1.32 ng/mL
Nickel (Ni)	EPA 249.2	232.0	1400	2500	3.55 ng/mL
Lead (Pb)	EPA 239.2	283.3	850	1800	1.24 ng/mL
Selenium (Se)	EPA 270.2	196.0	900	2100	8.80 ng/mL
Thallium (Tl)	EPA 279.2	276.8	600	1300	9.40 ng/mL
Cesium (Cs)	none	852.1	900	1900	
Metals by Spark Source Mass Spectrometry	ACD 4 0200	Approximately 50 elements are determined simultaneously by sparking a sample, which was dried on a graphite electrode, in the source of a mass spectrometer. This technique was not used to report data, but to provide screening for ICP and GFAA analysis.			Depends on the metal, but is generally in the ppm range; precision is about a factor of ten.
Mercury (Hg) by Cold Vapor Technique	CLP-M 245.1	The flameless AA procedure is a physical method based upon the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state with stannous chloride and aerated from the solution. The mercury vapor passes through a cell positioned in the light path of an AA spectrometer. The absorbance (peak area) is measured as a function of concentration.			1-2 ng/mL for a 1 mL sample size
Soluble Silica (Si)	ASTM-426C	The silica in a filtered sample is converted to molybdosilicic acid, which is reduced by 1-amino-2-naphthol-4-sulfonic acid to hetropoly blue. The color is measured at 815 nm or 650 nm and the signal compared to a calibration curve for quantitation.			1 mg/L for a 1 mL sample size
Total Uranium (U)	ACD 1 219240	Uranium is extracted from 3 *M* HNO_3 solutions with tri-octylphosphine oxide (TOPO); an aliquot of the organic extractant is pipetted onto pellets of sodium fluoride, which is dried and sintered. The fluorescence due to the measured uranium is measured on a fluorophotometer.			
Total Thorium (Th)	ACD 1 218710-1	Thorium forms a red complex with Thoron, 2-(2-hydroxy-3, 6-disulfo-1-napthylazo) benzenearsonic acid. The Thorium-Thoron complex absorbance was measured at 545 nm and the concentration calculated from a calibration curve.			1 mg/L
Anions by Ion <u>Chromatography</u>		Samples, diluted if necessary, are injected directly into an ion chromatograph, and the resultant chromatogram is analyzed to identify anions and determine concentration.			
F^-	EPA300.0				
Cl^-	EPA300.0				
PO_4^{-2}	EPA300.0				
NO_3^-	EPA300.0				
SO_4^{-2}	EPA300.0				

Table B.5. continued

Parameter	Reference	Method Summary	Approximate Detection Limit
pH	ACD 1 230041 SW-846-9040	The pH of the sample was determined electrometrically using combination electrodes. The measuring device is calibrated using a series of standard solutions of known pH.	not applicable
Hydroxide (OH^-) Acid (H^+) Carbonate (CO_3^{-2}) Bicarbonate (HCO_3^-)	ACD 1 003105	The OH^-, CO_3^{-2}, HCO_3^-, and H^+ were all determined by potentiometric titration with either 0.1 *N* HCl or 0.1 *N* NaOH. The change in potential as a function of reagent consumption was recorded with an automatic potentiograph.	0.01 *N*
Cyanide (CN^-)	SW-846-9010	The cyanide is released by refluxing the sample with a strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then manually determined colorimetrically.	0.5 mg/L for a 10 mL sample size
Sulfide (S^{-2})	SW-846-9030	An aliquot of the absorbing solution from the cyanide analysis is treated with iodine to oxidize the sulfide to sulfur under acidic conditions. The excess iodine is back-titrated with phenylarsine oxide.	2 mg/L for a 10 mL sample size
Total Organic Carbon (TOC)	SW-846-9060	The organic carbon in a sample is converted to carbon dioxide (CO_2) by a catalytic combustion. The CO_2 is then measured directly by an infrared detector.	
Total Carbon (TC)		See text, Sect. B.4.4.	
Inorganic Carbon (IC)		See text, Sect. B.4.4.	
<u>**Physical Measurement Procedures**</u>			
Total Solids	EPA-600/160.3	A well mixed aliquot of the sample is quantitatively transferred to a pre-weighted evaporating dish and evaporate to dryness at 115°C for 16 h.	10 mg/L
Dissolved Solids	EPA-600/160.2	A well-mixed sample is filtered, and the filtrate quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 115°C for 16 h.	4 mg/L
Suspended Solids	EPA 600/160.2	The suspended solids were calculated by subtracting the dissolved solids from the total solids.	4 mg/L
Density (liquids)	ACD 1 1011	A measured volume of sample is weighed at ambient temperature.	
Density (sludge)		See text, Sect. 4.4.2.	

B.4.3 Common Anions

The determination of anions was primarily for developing process flow sheets, but the anion data were also useful in understanding the distribution of various metals between the liquid and solid phases. Liquid samples were analyzed by ion chromatography (Dionex, Model 16 instrument) for nitrate, chloride, fluoride, sulfate, and phosphate. Because of the high nitrate concentration, it was necessary to dilute the samples so that the nitrate peak would not overlap the other peaks. This resulted in some loss of sensitivity relative to the original solution. The detection limits for these high nitrate samples were 5,000 ppm for sulfate and phosphate, and 500 ppm for fluoride. Hydroxide, carbonate, and bicarbonate (if present) were determined by potentiometric titration.

A basic limitation of ion chromatography is that the relative concentration of all anions must be within a factor of about 100, or the predominate species behaves as an eluant for the other anionic species, which results in all anions eluting in a single band. High levels of certain anions can be tolerated by the use of special precolumns to reduce the level of a predominate species, however, these precolumns were not available for this project. A new ion chromatograph is currently being installed for radioactive samples. Following some methods development work, much more detailed anion data should be obtainable for future waste-tank type samples.

The determination of anions within the sludge phase of the waste tanks is a problem area. Ion chromatography may not be appropriate for anion determination in sludge samples since the solid phase must first be placed into solution with a strong acid. The use of a strong acid to dissolve the sludge samples places severe limitations on the anions that can be determined by ion chromatography. Considerable development work may be required to obtain useful anion data for the sludge phase of the waste tanks.

B.4.4 Carbon Analysis

Liquids were assayed for total carbon (TC) and inorganic carbon (IC) on the Dohrmann DC-90 carbon analyzer. The TC was measured by direct sample injection into a combustion tube packed with cobalt oxide at 900 °C. The furnace was continually sparged with oxygen, which converted all carbon to carbon dioxide and transported the off-gases through a detector chamber. The carbon dioxide was detected by a nondispersive infrared (IR) detector. Liquids were assayed for IC by sample injection into a phosphoric acid bath that converted carbonates to carbon dioxide. The phosphoric acid bath was continually sparged with oxygen, which transported the evolved carbon dioxide to the IR detector.

An optional solids adapter for the Dohrmann DC-90 carbon analyzer was employed for the measurement of total carbon and total organic carbon (TOC) on the sludge samples. Sludges were assayed for TC by placing the sample in a platinum boat, then heating it to 900 °C to oxidize organic species and decompose carbonates. The furnace was continually sparged with oxygen, which passed through a combustion bed packed with cobalt oxide for conversion of carbon-bearing species to carbon dioxide. The evolved carbon dioxide was transported to the IR detector. Sludges were assayed for organic carbon after pretreatment with concentrated nitric acid. The sample was weighed, acidified, and dried before placement in the same furnace used for total carbon determination.

B.4.5 Cyanides

Liquid samples from tanks W29 and W30 were analyzed for total cyanide using EPA method 9010 modified for small samples. Sample size was reduced from 500 to 10 mL in order to reduce the radiation hazard to the analyst and to conserve the limited sample. Trap solutions were reduced from 50 to 40 mL, and the scrubber bottles were modified to maintain collection efficiency using smaller trap solution volumes. Volumes and concentrations of colorimetric reagents were adjusted so that final concentrations were the same as they would have been using the unmodified EPA procedure.

Although good results were obtained from an external control solution, no color developed in either spiked or unspiked samples. An additional 2 μg of cyanide was added directly to a leftover trap solution from sample W29-L4 and then reanalyzed; still no color was observed. The failure of color to develop in the sample with post-distillation spike added indicates that an interfering substance was distilled from the samples and absorbed in the trap solutions.

Two types of interference are possible. The interfering substance could destroy any cyanide present, or it could prevent color formation between cyanides and pyridine/barbituric acid. This question will be resolved using either an ion-selective electrode for cyanide or by ion chromatography.

B.4.6 Metal Analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

A Perkin-Elmer XR 6500 ICP was modified for use with radioactive samples by isolating the ICP torch box in a SS enclosure for containment of radioactivity. The enclosure is provided with sliding glass doors and ports that may be gloved if higher levels of radioactivity must be handled. The performance of the system with the separation of the torch box and monochromator was evaluated and found to be comparable with normal operation.

The Perkin-Elmer ICP, employed for the analysis of the tank samples, has a poor dynamic range relative to most other ICP systems. The poor dynamic range translates into a narrow calibration range, which resulted in numerous measurements exceeding the high standard of the calibration curve. When a measurement exceeded the calibration range, several dilutions were usually required to obtain a valid result. The additional dilutions and sample handling resulted in a significant increase in the analysis time and radiation exposure to the analyst.

A Perkin-Elmer Cross-Flow, a Hildebrand Grid, and a Meinhard Type C nebulizer were evaluated for operation and effectiveness with samples containing high dissolved solids content while maintaining acceptable standard deviations. The Meinhard Type C nebulizer was chosen for measurements on the waste tank samples. This nebulizer is similar to a standard glass concentric type, but has the inner capillary recessed from tip to improve performance with samples containing high solids. In addition, a mass flow controller was added to the nebulizer gas flow to improve the precision of the ICP measurements.

Quality control (QC) was applied to batches of tank samples, where a batch was defined by grouping samples with similar matrices. All samples were analyzed with an internal standard (scandium) to compensate for matrix differences on the nebulization of the sample.

Batch acceptance criteria for the ICP measurements were based upon several factors. The percent relative difference (PRD) for the calibration check standard (CCS) was required to be within ± 20% of the known standard value. The PRD for duplicates and serial dilutions were required to be between ± 20% for analytes at 10 times the instrument detection limit (IDL), or higher. Spike recoveries were required to be within the range of 75-125%. If an analyte spike recovery was outside this range, the analytical line employed was inspected graphically, and a hardcopy of the original sample data was saved. The PRD for an interference check standard was required to be within ± 25% of the known standard concentration. The relative errors for analytes at or near the IDL were not employed for batch acceptance. The calibration blank and reagent blanks were monitored to check for contamination of the reagent and/or the sample introduction system. It was up to the discretion of the analyst to determine if there was a problem with the blank measurements and take the necessary action for correction.

B.4.7 Sample Preparation for Mercury Analysis

In addition to inorganic forms of mercury, the EPA procedures suggest that organo-mercury compounds may be present which will not respond to the cold vapor technique unless they are first broken down to the mercuric ions. Due to biological activity this expectation is reasonable for environmental or sewage-type samples, but is questionable for the type of waste found in the storage tank samples. Based upon the operations and processes that are employed by the waste storage system, only elemental or inorganic mercury is likely to be present. As a result of the harsh environment (high pH, high salt, and radioactivity), it is unlikely that sufficient biological activity is present in the waste storage tanks to convert inorganic mercury to organo-mercury compounds. Therefore, to reduce sample handling and radiation exposure to personnel, the sample digestion steps to oxidize organo-mercury compounds to mercuric ions was not used.

Hydrogen peroxide, which results from radiolytic decomposition of water[4] in aqueous solutions, is probably present in the waste storage tanks. Hydrogen peroxide is a strong oxidizing agent in alkaline solutions that tends to stabilize the mercury in the high pH waste tanks. Potassium permanganate was used to evaluate the reducing power of the waste tank samples prior to mercury measurements. The samples were tested by observing the decolorization following the addition of several drops of 5% potassium permanganate. The sludge samples, which were prepared for ICP spectrochemical analysis (Sec. B.4.1), were employed for the mercury measurements. The liquid samples were diluted with 5% nitric acid prior to mercury analysis.

B.4.8 Mercury Analysis by Cold Vapor Technique

The instrumentation for the mercury cold vapor technique was a MHS-20 (Mercury-Hydride System) attachment for the Perkin-Elmer 5100 Atomic Absorption (AA) system. The MHS-20 includes a heated 10-cm quartz cell which is placed in the flame AA light path of the 5100 system, sample handling system, and a system controller for programing the addition of reductant and reaction times. The signal from the spectrometer is then processed by the 5100 system computer and peak areas are employed for quantitation. A listing of the quality control data for mercury analyses is included in Table B.6.

B.4.9 Metal Analyses by Graphite Furnace Atomic Absorption (GFAA)

The instrumentation employed for the GFAA measurements was a Perkin-Elmer 5100 AA system with the HGA-600 furnace option with Zeeman-effect background correction. The spectrometer was placed in a SS enclosure, similar to the ICP system, to permit measurements on radioactive samples. The technique used for all GFAA samples was an approach referred to as the stabilized temperature platform furnace (STPF)[5] concept, which was developed by Perkin-Elmer Corporation. The STPF approach is based on the use of the L'vov platform, fast electronics, quantitation by peak area, matrix modifiers, pyrolytically coated graphite tubes, fast heating of furnace, no flow of support gas during the atomization step, and Zeeman-effect background correction. Based on recent literature, an additional step was added to the typical furnace temperature program that consists of a cool-down step.[6] It was reported that, in some instances, better results were obtained if the furnace was allowed to cool down to ambient temperature before the atomization step. Also reported was that, for some real samples, the use of a cool-down step reduced or completely eliminated interferences that could not be controlled otherwise. Therefore, the furnace temperature program for all GFAA measurements included a cool-down step before atomization.

The analytical approach developed for GFAA measurements provided adequate QA/QC and followed the ALARA principle by minimizing the radiation exposure to the analyst. Instrument calibration consisted of constructing calibration curves from the average absorbance values, which were obtained with double injections of a blank and 3-4 standards, vs the known concentrations. The concentration of the standards were chosen to be within the optimum range, as listed by the EPA GFAA procedures.[1] Calibration verification, which followed the generation of the calibration curve, consisted of measurements for a calibration blank (CB) and a calibration check standard (CCS). The tolerance limits for CB and CCS have not been set at this time due to a lack of sufficient data to statistically define the limits. Additional QC data was obtained for CB and CCS at a frequency such that no more than five samples were analyzed between calibration verification samples. For each batch of samples (4-5 samples), an additional divisional QC sample was measured for the elements of interest.

The analysis of samples, which followed the initial calibration verification, included sample and spike measurements, each with double injections from which the average concentrations were reported or employed for spike recovery calculations. With the double injection for samples and spikes, the analysis of five samples implied twenty furnace injections between QC samples. For concentrations greater than 5 times the Instrument Detection Limit (IDL), the duplicate sample measurement should have agreed within a 30% relative standard deviation (RSD), or the sample was rerun once. If the RSD still exceeded 30%, the sample was flagged. If the spike recoveries were within the range of 75-125%, the data were quantified directly from the calibration curve and reported to the IDL. If spike recoveries were outside the range, the sample was flagged for a more detailed examination at a later date. Up to this point in the analysis scheme, details are similar to CLP procedures with the exception of the broader spike recovery range and duplicate RSD. The CLP procedure specifies analysis by Method of Standard Addition (MSA) when spike recoveries are poor. However, for this work, the MSA technique was not used due to increased sample handling that would increase the radiation exposure to the analyst.

The high sodium nitrate levels found in the active waste tanks was very corrosive to the graphite tube furnaces employed for GFAA. Even with a 5-10 fold dilution of the sample, fewer than 20 sample injections could be completed before complete destruction of the graphite was observed. Since replacement of the graphite furnace requires recalibration, it was difficult to complete the QA/QC batch certification specified by SW-846 with these samples. Although the batch certification discussed above involves more than twenty sample injections, many of the measurements are on standards that do not contain the high sodium nitrate. This problem not only increases the sample analysis time but also involves extensive handling of contaminated equipment and much more radiation exposure time to the analyst.

B.4.10 QA/QC Data and Comments for Metal Analyses

In general, the QA requirements from SW-846 were employed for all regulatory type measurements. In addition, ACD's blind quality control samples were analyzed with each batch of waste tank samples.

As discussed above, the QC data were obtained on batches of samples. The spike recoveries for the RCRA metals and mercury are listed in Table B.6. The comments on each request are discussed below.

REQUEST IPA6222 (samples: W24-L2, W25-L2, W26-L2, W27-L2, W28-L2, W31-L2)

- The mercury results on samples W24-L2, W25-L2, and W28-L2 are suspect due to spike recovery values less than 75%.
- Thallium results are suspect due to spike recovery value less than 75%.
- The duplicate sample on cadmium has a 25% relative percent error, however, the error bars overlap.
- Cadmium analysis on W26-L2 was repeated and samples W26-L1 and W26-L3 were analyzed in order to verify the initial findings.
- Although no unusual occurrences were observed with sample W26-L2 in the analyses for potassium and sodium by ICP, the samples were rechecked for sodium and potassium.
- The samples were analyzed for thorium by ICP. No thorium was observed above the IDL except on W26-L2, and this observance seems to be a spectral interference. Sample W26-L2 was rerun by colormetric thorium analysis (Thoron procedure).

Table B.6. RCRA element percent spike recovery table

Element	IPA6222	IPA6223&29	IPA6257	IPA6279	IPA6282	IPA6255
Tl	70	90	95	91	86	70
Se	119	89	109	102	97	97
As	104	99	84	103	138	115
Cr	96	94	92	oc[a]	75	98
Pb	86	oc	40	82	oc	104
Cd	91	76	62	88	94	105
Ni	87	84	92	95	95	97
Ba	89	93	99	87	101	95
Ag	86	3	3	-20	1	12
Hg (W24-L2)	74					
Hg (W25-L2)	71					
Hg (W26-L2)	86					
Hg (W27-L2)	90					
Hg (W28-L2)	67					
Hg (W31-L2)	104					
Hg (W24-S)		114				
Hg (W25-S)		117				
Hg (W28-S)		107				
Hg (W31-S)		116				
Hg (W31-H)		84				
Matrix spike		111				
Hg (W26-S)			87			
Hg (W27-H1-H)			121			
Hg (W27-H1-S)			104			
Matrix spike			167			
Hg (W21-L2)				89		
Hg (W23-L1)				80		
Hg (W21-S)					77	
Hg (W23-S)					97	
Matrix spike					100	
Hg (W29-L1)						82
Hg (W29-L2)						86
Hg (W29-L4)						75
Hg (W30-L1)						84
Hg (W30-L2)						79
Hg (W30-L4)						81

[a] oc = over calibration.

REQUEST IPA6223 and IPA6229 (samples: W24-S, W25-S, W28-S, W31-S, W31-H)

- The mercury analysis for sample W28-S was inadvertently skipped and analyzed after the hold time had expired. (Sample W28-S was held 27 d.)

- The aliquots for mercury analysis on samples W24-S and W25-S were found to reduce the 5% $KMnO_4$ in the reaction vessel. This action is probably due to an excess amount of unreacted hydrogen peroxide from the sample preparation.

- The ICP external control sample was out of control for selenium.

- All of the silver results are suspect due to poor spike recovery (3%).

- Some of the magnesium and aluminum values were over calibration initially and had to be diluted and reanalyzed. Upon reanalysis, the magnesium external control was out of control.

- Precision was poor for the boron analysis by ICP; however, these measurements were done near the detection limit.

- Cesium analysis by GFAA was difficult as expected. High (>125%) spike recovery values encountered on the first analysis attempt. A second analysis attempt produced acceptable spike recoveries, but out-of-control results on the calibration verification standards. It is interesting to note that the sample results on both runs were virtually identical.

- Density was not measured on W31-H because the sample had dried to hard lumps and, thus, meaningful data could not be obtained.

REQUEST IPA6255 (samples: W29-L1, -L2, -L4, W30-L1, -L2, -L4)

- Spike recovery on W29-L1, for mercury analysis, was initially 73% but analysis was repeated at a later date with acceptable results (82%).

- The thallium results by ICP are suspect due to low spike recovery (70%).

- A difference exists between original analysis and serial dilution for chromium; however, the serial dilution has a large error bar associated with it (Results are: original 2.4 $\pm$ 0.6 μg/ml, vs serial dilution 1.2 $\pm$ 1.0 μg/ml.)

- The silver results are suspect due to poor spike recoveries (12%).
- Initial spike recovery of magnesium was 136%, but the entire magnesium analysis was repeated and the second analysis yielded an acceptable spike recovery (90%).
- Two external controls were analyzed for sodium, one being outside the control limits. The other control sample was acceptable.

<u>REQUEST IPA6257 (samples: W26-S, W27-H1-H, W27-H1-S)</u>

- Samples were composited (when appropriate) and sonicated in the hot cells. Sample W27-H1-H could not be sonicated due to its consistency (no interstitial liquid). After digestion, the samples from tank W27 had visual residue left. This residue was light gray in color.
- Matrix-spiked sample for mercury yielded a higher result than expected (167% recovery, 150% recovery on recheck).
- The mercury analysis for samples W27-H1-H and W27-H1-S were completed after the hold time had expired. This delay was the result of environmental problems in the laboratory (ie. elevated radon levels in laboratory). (The samples were held for 28 d.)
- Spike recoveries for lead and cadmium were 40% and 62%, respectively.
- The lead analysis was initially over calibration and had to be reanalyzed on a second calibration curve.
- The duplicate samples for this batch checked well.
- The boron was measured at the 208.959-nm emission line. The 249.773-nm line was not employed due to a spectral interference at that wavelength.
- Initially, there was a variation in the sample handling, and the samples were not sonicated prior to sample dissolution. Upon attempting the mercury analysis, great differences were observed between the original sample and duplicate. This discrepancy demonstrates that the sludge samples lack homogeneity. The attempt to analyze these preps was aborted, and the samples were composited and reprepared for analysis.

REQUEST IPA6279 (samples: W21-L2, W23-L1)

- Arsenic value on W21-L2 is suspect. This value is very close to the IDL, and the large error bar indicates that the value is probably due to excessive baseline noise (As result = 3.8 ± 7.3 μg/ml).
- No chromium spike recovery was calculated since the spiked sample was over calibration.
- There was a discrepancy between the original and duplicate sample for thallium analysis; however, there was a large error bar on the duplicate, and the values were close to the IDL.
- The presence of cadmium and nickel were verified at alternate wavelengths in the graphics spectrum mode.
- The aluminum emission line at 309.271 nm could not be used due to spectral interferences, so the 396.152-nm line was employed instead.

REQUEST IPA6282 (samples: W21-S, W23-S)

- The holding time for mercury on these samples had expired due to hardware problems with the Perkin-Elmer 5100 spectrometer. The samples were held for 22 d.
- The arsenic values are suspect due to a spike recovery of 138%. Also, there was a large error bar associated with arsenic analysis of sample W21-S.
- No spike recovery was calculated for lead as this result was over calibration.
- Duplicate sample on the Pb analysis had a 32% Relative Percent Difference (RPD) value, but there was a large error bar on the duplicate (i.e. original Pb=450 ± 60 μg/ml vs duplicate Pb=620 ± 250 μg/ml).
- The aluminum emission line at 309.271 nm could not be used due to spectral interferences, so the 396.152-nm line was employed instead.
- The boron emission line at 249.773 nm could not be used due to spectral interferences, so the 208.959-nm line was employed instead.

B.5 RADIOCHEMICAL MEASUREMENTS

The radiochemical characterization of the waste tanks included gross alpha, gross beta, gamma spectrometry, strontium-90, and actinides by alpha spectrometry. To ensure valid data, all of the above radiochemical measurements except the alpha spectrometry were duplicated by two separate laboratories. A brief description of the radiochemical methods are listed in Table B.5, along with typical detection limits. In addition, carbon-14 and tritium were determined by liquid scintillation on all liquid samples, and carbon-14 was determined for all sludge samples. Although not measured for this project, it is recommended that both technetium-99 ($t_{1/2}$ = 2.13 x 10^5 y) and iodine-129 ($t_{1/2}$ = 1.6 x 10^7 y) be determined on selected samples from this project.

Most of the radiochemcial data presented in the summary tables in Sect. 4 are from the Transuranium Analytical Laboratory (TAL) to provide a consistent data package from one laboratory. The ^{90}Sr data are from the IPA because of the experience of the analyst performing the testing. Tritium and ^{14}C data are also from the IPA. Results that were duplicated by two separate laboratories are presented in Appendix C.

B.5.1 Sample Preparation for Alpha Counting

A rapid and reliable method was needed to prepare clean alpha plates from samples of the LLLW concentrates. Excessive solid materials on alpha plates led to self absorption, flaking, and poor alpha spectrometry for isotopic determination. The method used to clean up these samples is based on a double precipitation with ferric iron. Ferric nitrate is first added to the sample solution, which is then heated to boiling, followed by dropwise addition of NH_4OH to precipitate what is best described as hydrous ferric oxide (Fe_2O_3-nH_2O, but is commonly called ferric hydroxide). Yields in excess of 97% for uranium and the transuranic actinides have been reported for coprecipitation with ferric hydroxide.[7] A test solution was prepared with three isotopes found in waste tank samples.

Table B.7. Composition of alpha test solution

Isotope	Energy (MeV)	Activity Ratio	Activity (Bq/mL)
^{233}U	4.82	34.0%	659.6
^{240}Pu	5.15	44.6%	865.2
^{241}Am	5.50	21.4%	415.2
		Total:	1940 Bq/mL

Results on 2 aliquots of the above solution with double ferric hydroxide precipitations to separate and recover the actinides are given in Table B.8.

Table B.8. Recovery of actinides from test solution

Gross Alpha (Bq/mL)	^{233}U (%)	^{240}Pu (%)	^{241}Am (%)	Recovery (%)
1900	31.9	45.3	22.8	98
1960	33.9	44.2	21.9	103

Four dissolved sludge samples were analyzed for alpha concentration and isotopic composition. The alpha concentration was determined with no precipitation, a single ferric hydroxide precipitation, and a double ferric hydroxide precipitation. Results were as follows:

Table B.9. Alpha recovery for actual sludge samples

Sludge sample	No ppt. (Bq/g)	Single Fe ppt. (Bq/g)	Double Fe ppt. (Bq/g)	% Lost No ppt.
1	17,100	18,400	22,300	23
2	62,000	67,300	83,800	26
3	84,900	105,000	99,700	15
4	147,000	165,000	204,000	28

Due to excessive solids, the isotopic composition could not be determined on the waste tank samples that were plated directly. There was no significant difference in the pulse-height analysis (PHA) of the single and double iron precipitates. This method is reliable, rapid, and generates very little waste. It can easily be carried out on samples with low alpha activity and results in minimal dilution of the sample (dilution factor less than 5).

Table B.10. Typical gross alpha spike recoveries for liquid samples

IPA 6222		IPA 6255		IPA 6279	
Sample	Spike recovery (%)	Sample	Spike recovery (%)	Sample	Spike recovery (%)
W24-L2	77	W29-L1	87	W21-L2	85
W25-L2	75	W29-L2	83	W23-L1	83
W26-L2	75	W29-L4	86		
W27-L2	78	W30-L1	89		
W28-L2	77	W30-L2	88		
W31-L2	77	W30-L4	86		

B.5.2 Instrumentation

The gross alpha and gross beta measurements were done on 2-pi gas-flow proportional counters. Also, a Ludlum alpha scintillation counter was employed for gross alpha measurements. All the gross alpha data reported in the summary tables were taken from the alpha scintillation counter because of its superior performance in the presence of a high beta background. Several Tenneled high purity germanium (HPGe) detectors, with a nominal efficiency of 25%, were employed for all gamma spectroscopy measurements — all spectral data was processed with Nuclear Data software. The alpha spectroscopy was done on both Tennelec TC-256 alpha spectrometers or a Canberra Quad Four alpha spectrometer, using surface barrier detectors which had active areas that ranged from 300-1000 mm^2. Carbon-14 and tritium measurements were done on a Packard 2500TR liquid scintillation system.

B.5.3 Carbon-14

The Dohrmann DC-90 carbon analyzer is equipped with a combustion tube for solids analysis that was adapted to the analysis of ^{14}C. In this procedure, samples were heated to 900°C to volatilize organic compounds and decompose carbonates. The furnace was continually sparged with oxygen and all off-gases passed through an oxidizing bed (cobalt oxide) to convert organic species to carbon dioxide. Samples were collected in gas washing bottles filled with a carbon dioxide-absorbent solution. Aliquots of the carbon dioxide absorber solutions were pipetted into a compatible liquid scintillation cocktail and counted.

B.5.4 Quality Control

As mentioned earlier, many of the radiochemical measurements were duplicated by two separate laboratories. The duplicated measurements included gross alpha, gross beta, gamma spectroscopy, and strontium-90 measurements. Also, duplicate measurements were done for most radiochemical measurements by each laboratory. Finally, both laboratories participate in the ACD QC that involves the measurement of blind QC samples.

B.6 REFERENCES

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APPENDIX C

COMPREHENSIVE LISTING OF PHYSICAL, INORGANIC, AND RADIOCHEMICAL ANALYTICAL DATA

Sample: W21-L2		IPA[a]	TAL[b]
Physical properties and miscellaneous data			
TDS[c]	(mg/mL)	393	-
TS[d]	(mg/mL)	421	-
Density	(g/mL)	1.2391	-
IC[e]	(mg/L)	<1.0	-
TC[f]	(mg/L)	571	-
TOC[g]	(mg/L)	571	-
RCRA metals			
Ag	(mg/L)	1.2	-
As	(mg/L)	3.8	-
Ba	(mg/L)	25	-
Cd	(mg/L)	2.0	-
Cr	(mg/L)	27	-
Hg	(mg/L)	0.92	-
Ni	(mg/L)	15	-
Pb	(mg/L)	7.1	-
Se	(mg/L)	<2.3	-
Tl	(mg/L)	<0.94	-
Process metals			
Al	(mg/L)	<1.2	-
B	(mg/L)	1.0	-
Ca	(mg/L)	23000	-
Fe	(mg/L)	240	-
K	(mg/L)	20000	-
Mg	(mg/L)	5600	-
Na	(mg/L)	61000	-
Si (color)	(mg/L)	<1.0	-
Sr	(mg/L)	160	-
Th (color)	(mg/L)	-	95.1
U (fluor)	(mg/L)	750	-

Sample: W21-L2		IPA	TAL
Anions (analyzed by CPA Lab.)[h]			
Chloride	(mg/L)	2.10e+03[i]	-
Fluoride	(mg/L)	<1.0e+03	-
Nitrate	(mg/L)	3.10e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		0.75	0.56
H^+	(M)	-	0.085
OH^-	(M)	-	-
CO_3^{2-}	(M)	-	-
HCO_3^-	(M)	-	-
Beta/gamma emitters			
Gross alpha	(Bq/mL)	1.67e+03	2.14e+03
Gross beta	(Bq/mL)	4.24e+05	4.99e+05
^{14}C	(Bq/mL)	<1.0e+00	-
^{144}Ce	(Bq/mL)	-	<1.5e+03
^{60}Co	(Bq/mL)	8.62e+03	8.50e+03
^{134}Cs	(Bq/mL)	5.22e+03	5.12e+03
^{137}Cs	(Bq/mL)	3.21e+05	3.19e+05
^{152}Eu	(Bq/mL)	3.58e+04	3.31e+04
^{154}Eu	(Bq/mL)	1.63e+04	1.66e+04
^{155}Eu	(Bq/mL)	4.77e+03	5.22e+03
^{3}H	(Bq/mL)	3.50e+02	-
^{95}Nb	(Bq/mL)	-	<1.5e+02
^{106}Ru	(Bq/mL)	-	1.95e+03
^{90}Sr	(Bq/mL)	7.46e+04	7.64E+04
^{95}Zr	(Bq/mL)	-	<7.1e+03
Alpha emitters			
^{232}U	(Bq/mL)	-	6.80e+01
^{233}U	(Bq/mL)	-	3.96e+02
^{239}Pu/^{240}Pu	(Bq/mL)	-	6.20e+01
^{238}Pu/^{241}Am	(Bq/mL)	-	2.61e+02
^{244}Cm	(Bq/mL)	-	1.15e+03

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[a] IPA = Inorganic and Physical Analysis.
[b] TAL = Transuranium Analytical Laboratory.
[c] TDS = total dissolved solids.
[d] TS = total solids.
[e] IC = inorganic carbon.
[f] TC = total carbon.
[g] TOC = total organic carbon.
[h] CPA = Chemical and Physical Analysis.
[i] Read as 2.10×10^3.

Sample: W23-L1		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	381	-
TS	(mg/mL)	383	-
Density	(g/mL)	1.2423	-
IC	(mg/L)	8340	-
TC	(mg/L)	9500	-
TOC	(mg/L)	1160	-
RCRA metals			
Ag	(mg/L)	<0.44	-
As	(mg/L)	<3.0	-
Ba	(mg/L)	<0.19	-
Cd	(mg/L)	1.7	-
Cr	(mg/L)	0.42	-
Hg	(mg/L)	0.07	-
Ni	(mg/L)	3.0	-
Pb	(mg/L)	2.7	-
Se	(mg/L)	<2.3	-
Tl	(mg/L)	<0.94	-
Process metals			
Al	(mg/L)	1.8	-
B	(mg/L)	10	-
Ca	(mg/L)	18	-
Fe	(mg/L)	0.70	-
K	(mg/L)	78000	-
Mg	(mg/L)	3.4	-
Na	(mg/L)	82000	-
Si (color)	(mg/L)	<1.0	-
Sr	(mg/L)	0.40	-
Th (color)	(mg/L)	-	15.8
U (fluor)	(mg/L)	17	-

Sample: W23-L1		IPA	TAL
<u>**Anions (analyzed by CPA Lab.)**</u>			
Chloride	(mg/L)	3.60e+03	-
Fluoride	(mg/L)	<1.0e+03	-
Nitrate	(mg/L)	2.00e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	7.80e+03	-
<u>**Alkalinity**</u>			
pH		12.8	12.8
OH^-	(<u>M</u>)	-	0.15
CO_3^{2-}	(<u>M</u>)	-	0.70
HCO_3^-	(<u>M</u>)	-	-
<u>**Beta/gamma emitters**</u>			
Gross alpha	(Bq/mL)	6.80e+01	8.20e+01
Gross beta	(Bq/mL)	4.15e+05	4.62e+05
^{14}C	(Bq/mL)	6.35e+01	-
^{144}Ce	(Bq/mL)	-	<1.6e+03
^{60}Co	(Bq/mL)	5.97e+02	6.21e+02
^{134}Cs	(Bq/mL)	4.48e+03	4.63e+03
^{137}Cs	(Bq/mL)	4.52e+05	4.36e+05
^{152}Eu	(Bq/mL)	<8.8e+02	<2.1e+02
^{154}Eu	(Bq/mL)	<2.2e+02	<1.6e+02
^{155}Eu	(Bq/mL)	<7.7e+02	<8.5e+02
^{3}H	(Bq/mL)	1.19e+02	-
^{95}Nb	(Bq/mL)	-	<1.0e+02
^{106}Ru	(Bq/mL)	-	3.78e+03
^{90}Sr	(Bq/mL)	4.12e+02	4.36e+02
^{95}Zr	(Bq/mL)	-	<1.0e+02
<u>**Alpha emitters**</u>			
^{232}U	(Bq/mL)	-	4.00e+00
^{233}U	(Bq/mL)	-	6.00e+00
$^{239}Pu/^{240}Pu$	(Bq/mL)	-	6.00e+00
$^{238}Pu/^{241}Am$	(Bq/mL)	-	3.90e+01
^{244}Cm	(Bq/mL)	-	4.00e+00

Sample: W24-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	377	-
TS	(mg/mL)	383	-
Density	(g/mL)	1.2348	-
IC	(mg/L)	1910	-
TC	(mg/L)	2400	-
TOC	(mg/L)	489	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	0.29	-
Cd	(mg/L)	0.22	-
Cr	(mg/L)	3.1	-
Hg	(mg/L)	0.046	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	6.7	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	46	-
B	(mg/L)	0.95	-
Ca	(mg/L)	7.2	-
Co	(mg/L)	<0.57	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	11000	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	100000	-
Si (color)	(mg/L)	245	-
Sr	(mg/L)	<0.74	-
Th (ICP)	(mg/L)	<2.2	
U (fluor)	(mg/L)	9.4	-

Sample: W24-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.60e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.60e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		-	13.1
OH^-	($\underline{M}$)	-	0.29
CO_3^{2-}	($\underline{M}$)	-	0.15
HCO_3^-	($\underline{M}$)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	1.05e+01	5.00e+00
Gross beta	(Bq/mL)	2.05e+05	2.30e+05
^{14}C	(Bq/mL)	7.87e+02	-
^{144}Ce	(Bq/mL)	-	<7.4e+02
^{60}Co	(Bq/mL)	4.06e+02	3.29e+02
^{134}Cs	(Bq/mL)	1.13e+03	1.34e+03
^{137}Cs	(Bq/mL)	2.24e+05	2.21e+05
^{152}Eu	(Bq/mL)	-	<3.2e+02
^{154}Eu	(Bq/mL)	-	<6.0e+01
^{155}Eu	(Bq/mL)	-	<4.0e+02
^{3}H	(Bq/mL)	3.08e+02[a]	-
^{95}Nb	(Bq/mL)	-	<2.8e+02
^{106}Ru	(Bq/mL)	-	<1.1e+03
^{90}Sr	(Bq/mL)	9.13e+02	8.86e+02
^{95}Zr	(Bq/mL)	-	<5.0e+02

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[a] Tritium determined on sample W24-L1.

Sample: W25-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	348	-
TS	(mg/mL)	334	-
Density	(g/mL)	1.2018	-
IC	(mg/L)	15.8	-
TC	(mg/L)	478	-
TOC	(mg/L)	462	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	3.2	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	1.9	-
Hg	(mg/L)	0.054	-
Ni	(mg/L)	0.45	-
Pb	(mg/L)	<2.1	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	<4.2	-
B	(mg/L)	0.60	-
Ca	(mg/L)	280	-
Co	(mg/L)	<0.57	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	17000	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	78000	-
Si	(mg/L)	<1.0	-
Sr	(mg/L)	23	-
Th (ICP)	(mg/L)	<2.2	
U (fluor)	(mg/L)	<0.10	-

Sample: W25-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.50e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.60e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		-	12.5
OH^-	(M)	-	0.06
CO_3^{2-}	(M)	-	<0.01
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	2.71e+01	2.00e+00
Gross beta	(Bq/mL)	3.21e+05	3.92e+05
^{14}C	(Bq/mL)	3.29e+02	-
^{144}Ce	(Bq/mL)	-	<1.3e+03
^{60}Co	(Bq/mL)	1.84e+03	1.88e+03
^{134}Cs	(Bq/mL)	3.60e+03	3.77e+03
^{137}Cs	(Bq/mL)	3.26e+05	3.27e+05
^{152}Eu	(Bq/mL)	-	<1.6e+02
^{154}Eu	(Bq/mL)	-	<1.2e+02
^{155}Eu	(Bq/mL)	-	<6.9e+02
^{3}H	(Bq/mL)	3.45e+02[a]	-
^{95}Nb	(Bq/mL)	-	<6.3e+01
^{106}Ru	(Bq/mL)	-	<1.9e+03
^{90}Sr	(Bq/mL)	1.95e+04	1.94e+04
^{95}Zr	(Bq/mL)	-	<1.2e+02

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[a] Tritium determined on sample W25-L1.

Sample: W26-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	369	-
TS	(mg/mL)	366	-
Density	(g/mL)	1.2177	-
IC	(mg/L)	2580	-
TC	(mg/L)	3860	-
TOC	(mg/L)	1280	-
RCRA metals			
Ag	(mg/L)	1.2	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	0.20	-
Cd	(mg/L)	4.5[a]	-
Cr	(mg/L)	1.8	-
Hg	(mg/L)	<0.08	-
Ni	(mg/L)	8.2	-
Pb	(mg/L)	3.2	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	4.8	-
B	(mg/L)	3.9	-
Ca	(mg/L)	20	-
Co	(mg/L)	<0.57	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	51000[b]	-
Mg	(mg/L)	3.5	-
Na	(mg/L)	68000[b]	-
Si	(mg/L)	11.9	-
Sr	(mg/L)	<0.74	-
Th (color)	(mg/L)	-	10
U (fluor)	(mg/L)	1130[c]	-

Sample: W26-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	3.50e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.04e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		-	11.2
OH^-	(M)	-	<0.01
CO_3^{2-}	(M)	-	0.20
HCO_3^-	(M)	-	0.02
Beta/gamma emitters			
Gross alpha	(Bq/mL)	1.10e+03	1.03e+03
Gross beta	(Bq/mL)	2.10e+06	2.20e+06
^{14}C	(Bq/mL)	1.23e+02	-
^{144}Ce	(Bq/mL)	-	<2.3e+03
^{60}Co	(Bq/mL)	1.07e+04	1.22e+04
^{134}Cs	(Bq/mL)	1.02e+04	1.31e+04
^{137}Cs	(Bq/mL)	2.08e+06	2.07e+06
^{152}Eu	(Bq/mL)	-	<2.1e+02
^{154}Eu	(Bq/mL)	-	<2.4e+02
^{155}Eu	(Bq/mL)	-	<1.2e+03
^{3}H	(Bq/mL)	6.18e+02[d]	-
^{95}Nb	(Bq/mL)	-	<1.4e+02
^{106}Ru	(Bq/mL)	-	<2.8e+03
^{90}Sr	(Bq/mL)	4.90e+02	2.51e+02
^{95}Zr	(Bq/mL)	-	<2.7e+02
Alpha emitters			
^{232}U	(Bq/mL)	-	3.60e+01
^{233}U	(Bq/mL)	-	9.20e+02
^{238}U	(Bq/mL)	-	1.00e+01
^{238}Pu/^{241}Am	(Bq/mL)	-	<1.5e+01
^{239}Pu/^{240}Pu	(Bq/mL)	-	1.00e+01

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[a] Recheck: Cd, 5.0 mg/L. Cd in other samples from same tank: W26-L1, 4.3 mg/L; W26-L3, 4.3 mg/L.

[b] Recheck: K, 56000 mg/L; Na, 75000 mg/L.

[c] Uranium was confirmed by other peaks in ICP spectrum.

[d] Tritium was determined on sample W26-L1.

Sample: W27-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	358	-
TS	(mg/mL)	355	-
Density	(g/mL)	1.2118	-
IC	(mg/L)	4.7	-
TC	(mg/L)	364	-
TOC	(mg/L)	359	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	4.1	-
Cd	(mg/L)	0.12	-
Cr	(mg/L)	2.8	-
Hg	(mg/L)	<0.048	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	<2.1	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	<4.2	-
B	(mg/L)	0.67	-
Ca	(mg/L)	2600	-
Co	(mg/L)	<0.57	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	8500	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	90000	-
Si (color)	(mg/L)	<1.0	-
Sr	(mg/L)	18	-
Th (ICP)	(mg/L)	<2.2	
U (fluor)	(mg/L)	<0.1	-

Sample: W27-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.50e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.80e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		-	11.8
OH^-	(M)	-	0.01
CO_3^{2-}	(M)	-	<0.01
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	1.89e+01	<1.0e+00
Gross beta	(Bq/mL)	3.02e+05	3.30e+05
^{14}C	(Bq/mL)	1.81e+02	-
^{144}Ce	(Bq/mL)	-	<7.5e+02
^{60}Co	(Bq/mL)	2.53e+02	3.09e+02
^{134}Cs	(Bq/mL)	1.51e+03	1.61e+03
^{137}Cs	(Bq/mL)	2.18e+05	2.16e+05
^{152}Eu	(Bq/mL)	-	<1.1e+02
^{154}Eu	(Bq/mL)	-	<6.6e+01
^{155}Eu	(Bq/mL)	-	<4.0e+02
^{3}H	(Bq/mL)	2.09e+02[a]	-
^{95}Nb	(Bq/mL)	-	<3.0e+01
^{106}Ru	(Bq/mL)	-	<1.1e+03
^{90}Sr	(Bq/mL)	5.57e+04	5.24e+04
^{95}Zr	(Bq/mL)	-	<5.2e+01

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[a] Tritium determined on sample W27-L1.

Sample: W28-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	485	-
TS	(mg/mL)	478	-
Density	(g/mL)	1.2852	-
IC	(mg/L)	7.0	-
TC	(mg/L)	581	-
TOC	(mg/L)	574	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	5.8	-
Cd	(mg/L)	0.51	-
Cr	(mg/L)	0.38	-
Hg	(mg/L)	0.14	-
Ni	(mg/L)	1.4	-
Pb	(mg/L)	<2.1	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	5.2	-
B	(mg/L)	0.35	-
Ca	(mg/L)	7800	-
Co	(mg/L)	<0.57	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	26000	-
Mg	(mg/L)	1600	-
Na	(mg/L)	96000	-
Si (color)	(mg/L)	<1.0	-
Sr	(mg/L)	65	-
Th (ICP)	(mg/L)	<2.2	
U (fluor)	(mg/L)	<0.10	-

Sample: W28-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	4.80e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	3.70e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		-	9.1
OH^-	(M)	-	<0.01
CO_3^{2-}	(M)	-	<0.01
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	2.14e+02	4.40e+01
Gross beta	(Bq/mL)	9.35e+05	9.80e+05
^{14}C	(Bq/mL)	1.67e+02	-
^{144}Ce	(Bq/mL)	-	<1.8e+03
^{60}Co	(Bq/mL)	8.64e+03	8.72e+03
^{134}Cs	(Bq/mL)	1.08e+04	1.06e+04
^{137}Cs	(Bq/mL)	5.85e+05	5.66e+05
^{152}Eu	(Bq/mL)	-	1.67e+03
^{154}Eu	(Bq/mL)	-	7.37e+02
^{155}Eu	(Bq/mL)	-	<9.3e+02
^{3}H	(Bq/mL)	1.19e+02[a]	-
^{95}Nb	(Bq/mL)	-	<1.2e+02
^{106}Ru	(Bq/mL)	-	3.02e+03
^{90}Sr	(Bq/mL)	1.75e+05	1.22e+05
^{95}Zr	(Bq/mL)	-	<2.2e+02

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[a] Tritium determined on sample W28-L1.

Sample: W29-L1		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	375	-
TS	(mg/mL)	377	-
Density	(g/mL)	1.2251	-
IC	(mg/L)	478	-
TC	(mg/L)	985	-
TOC	(mg/L)	507	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	1.0	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	2.4	-
Hg	(mg/L)	0.09	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	<2.1	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	18	-
B	(mg/L)	0.50	-
Ca	(mg/L)	4.1	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	10000	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	110000	-
Si	(mg/L)	<1	-
Sr	(mg/L)	1.9	-
Th (color)	(mg/L)	-	<1.0
U (fluor)	(mg/L)	4.5	-

Sample: W29-L1		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.9e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.8e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		12.7	13.0
OH^-	(M)	-	0.064
CO_3^{2-}	(M)	-	0.043
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	8.62e+00	<1.0e+01
Gross beta	(Bq/mL)	1.77e+05	2.11e+05
^{14}C	(Bq/mL)	1.43e+02	-
^{144}Ce	(Bq/mL)	-	<1.4e+03
^{60}Co	(Bq/mL)	5.78e+02	6.44e+02
^{134}Cs	(Bq/mL)	2.43e+03	2.51e+03
^{137}Cs	(Bq/mL)	2.18e+05	2.21e+05
^{152}Eu	(Bq/mL)	-	<1.6e+02
^{154}Eu	(Bq/mL)	-	<1.5e+02
^{155}Eu	(Bq/mL)	-	<7.2e+02
^{3}H	(Bq/mL)	2.01e+02	-
^{95}Nb	(Bq/mL)	-	<6.4e+01
^{106}Ru	(Bq/mL)	-	<2.1e+03
^{90}Sr	(Bq/mL)	7.13e+03	6.98e+03
^{95}Zr	(Bq/mL)	-	<9.3e+01

Sample: W29-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	376	-
TS	(mg/mL)	379	-
Density	(g/mL)	1.2277	-
IC	(mg/L)	477	-
TC	(mg/L)	1040	-
TOC	(mg/L)	563	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	1.1	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	2.4	-
Hg	(mg/L)	0.08	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	<2.1	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	18	-
B	(mg/L)	0.47	-
Ca	(mg/L)	5.5	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	10000	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	110000	-
Si	(mg/L)	<1	-
Sr	(mg/L)	2.1	-
Th (color)	(mg/L)	-	<1.0
U (fluor)	(mg/L)	4.3	-

Sample: W29-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.8e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.8e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		12.8	13.0
OH^-	(M)	-	0.069
CO_3^{2-}	(M)	-	0.04
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	1.24e+01	<1.0e+01
Gross beta	(Bq/mL)	1.82e+05	1.98e+05
^{14}C	(Bq/mL)	7.3e+01	-
^{144}Ce	(Bq/mL)	-	<1.3e+03
^{60}Co	(Bq/mL)	6.06e+02	5.99e+02
^{134}Cs	(Bq/mL)	2.37e+03	2.57e+03
^{137}Cs	(Bq/mL)	2.17e+05	2.22e+05
^{152}Eu	(Bq/mL)	-	<2.0e+02
^{154}Eu	(Bq/mL)	-	<1.6e+02
^{155}Eu	(Bq/mL)	-	<7.1e+02
^{3}H	(Bq/mL)	2.01e+02	-
^{95}Nb	(Bq/mL)	-	<6.2e+01
^{106}Ru	(Bq/mL)	-	<2.0e+03
^{90}Sr	(Bq/mL)	7.00e+03	7.08e+03
^{95}Zr	(Bq/mL)	-	<1.1e+02

Sample: W29-L4		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	375	-
TS	(mg/mL)	382	-
Density	(g/mL)	1.2254	-
IC	(mg/L)	456	-
TC	(mg/L)	833	-
TOC	(mg/L)	377	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	1.0	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	2.3	-
Hg	(mg/L)	0.09	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	2.3	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	17	-
B	(mg/L)	0.36	-
Ca	(mg/L)	3.6	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	10000	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	110000	-
Si	(mg/L)	<1	-
Sr	(mg/L)	1.9	-
Th (color)	(mg/L)	-	<1.0
U (fluor)	(mg/L)	4.3	-

Sample: W29-L4		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.9e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.8e+05	-
Phosphate	(mg/L)	5.0e+03	-
Sulfate	(mg/L)	5.0e+03	-
Alkalinity			
pH		12.7	13.0
OH^-	(M)	-	0.074
CO_3^{2-}	(M)	-	0.054
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	8.49e+00	<1.0e+01
Gross beta	(Bq/mL)	1.84e+05	2.09e+05
^{14}C	(Bq/mL)	5.6e+01	-
^{144}Ce	(Bq/mL)	-	<1.3e+03
^{60}Co	(Bq/mL)	6.41e+02	6.26e+02
^{134}Cs	(Bq/mL)	2.67e+03	2.53e+03
^{137}Cs	(Bq/mL)	2.18e+05	2.16e+05
^{152}Eu	(Bq/mL)	-	<2.7e+02
^{154}Eu	(Bq/mL)	-	<1.2e+02
^{155}Eu	(Bq/mL)	-	<7.2e+02
^{3}H	(Bq/mL)	2.01e+02	-
^{95}Nb	(Bq/mL)	-	<6.3e+02
^{106}Ru	(Bq/mL)	-	<2.0e+03
^{90}Sr	(Bq/mL)	7.11e+03	6.73e+03
^{95}Zr	(Bq/mL)	-	<1.0e+02

Sample: W30-L1		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	371	-
TS	(mg/mL)	396	-
Density	(g/mL)	1.2225	-
IC	(mg/L)	602	-
TC	(mg/L)	805	-
TOC	(mg/L)	203	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	0.80	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	3.0	-
Hg	(mg/L)	0.10	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	3.0	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	34	-
B	(mg/L)	0.49	-
Ca	(mg/L)	10	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	9200	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	100000	-
Si	(mg/L)	<1	-
Sr	(mg/L)	1.7	-
Th (color)	(mg/L)	-	<1.0
U (fluor)	(mg/L)	5.5	-

Sample: W30-L1		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.8e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.7e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		12.8	13.2
OH^-	(M)	-	0.13
CO_3^{2-}	(M)	-	0.054
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	8.36e+00	<1.0e+01
Gross beta	(Bq/mL)	1.68e+05	1.97e+05
^{14}C	(Bq/mL)	6.8e+01	-
^{144}Ce	(Bq/mL)	-	<1.2e+03
^{60}Co	(Bq/mL)	5.01e+02	4.93e+02
^{134}Cs	(Bq/mL)	1.82e+03	2.05e+03
^{137}Cs	(Bq/mL)	1.95e+05	1.86e+05
^{152}Eu	(Bq/mL)	-	<1.7e+02
^{154}Eu	(Bq/mL)	-	<1.5e+02
^{155}Eu	(Bq/mL)	-	<6.7e+02
^{3}H	(Bq/mL)	2.04e+02	-
^{95}Nb	(Bq/mL)	-	<5.1e+01
^{106}Ru	(Bq/mL)	-	<1.9e+03
^{90}Sr	(Bq/mL)	6.75e+03	6.24e+03
^{95}Zr	(Bq/mL)	-	<9.5e+01

Sample: W30-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	377	-
TS	(mg/mL)	391	-
Density	(g/mL)	1.2218	-
IC	(mg/L)	596	-
TC	(mg/L)	695	-
TOC	(mg/L)	99	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	0.84	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	2.9	-
Hg	(mg/L)	0.10	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	2.9	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	33	-
B	(mg/L)	0.42	-
Ca	(mg/L)	9.4	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	9300	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	100000	-
Si	(mg/L)	<1	-
Sr	(mg/L)	1.8	-
Th (color)	(mg/L)	-	<1.0
U (fluor)	(mg/L)	5.8	-

Sample: W30-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.9e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.7e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		12.9	13.3
OH^-	(M)	-	0.13
CO_3^{2-}	(M)	-	0.052
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	7.76e+00	<1.0e+01
Gross beta	(Bq/mL)	1.90e+05	1.93e+05
^{14}C	(Bq/mL)	8.6e+01	-
^{144}Ce	(Bq/mL)	-	<1.2e+03
^{60}Co	(Bq/mL)	4.04e+02	4.83e+02
^{134}Cs	(Bq/mL)	2.02e+03	2.03e+03
^{137}Cs	(Bq/mL)	1.90e+05	1.87e+05
^{152}Eu	(Bq/mL)	-	<2.2e+02
^{154}Eu	(Bq/mL)	-	<1.1e+02
^{155}Eu	(Bq/mL)	-	<6.6e+02
^{3}H	(Bq/mL)	2.01e+02	-
^{95}Nb	(Bq/mL)	-	<5.5e+01
^{106}Ru	(Bq/mL)	-	<1.9e+03
^{90}Sr	(Bq/mL)	6.70e+03	6.55e+03
^{95}Zr	(Bq/mL)	-	<1.1e+02

Sample: W30-L4		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	370	-
TS	(mg/mL)	374	-
Density	(g/mL)	1.2211	-
IC	(mg/L)	600	-
TC	(mg/L)	799	-
TOC	(mg/L)	199	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	0.79	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	2.9	-
Hg	(mg/L)	0.10	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	2.3	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	34	-
B	(mg/L)	0.42	-
Ca	(mg/L)	11	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	9400	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	110000	-
Si	(mg/L)	<1	-
Sr	(mg/L)	1.9	-
Th (color)	(mg/L)	-	<1.0
U (fluor)	(mg/L)	5.9	-

Sample: W30-L4		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.8e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.7e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		12.8	13.3
OH^-	(M)	-	0.13
CO_3^{2-}	(M)	-	0.052
HCO_3^-	(M)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	7.17e+00	<1.0e+01
Gross beta	(Bq/mL)	1.84e+05	1.92e+05
^{14}C	(Bq/mL)	1.10e+02	-
^{144}Ce	(Bq/mL)	-	<1.3e+03
^{60}Co	(Bq/mL)	4.78e+02	4.91e+02
^{134}Cs	(Bq/mL)	1.99e+03	1.96e+03
^{137}Cs	(Bq/mL)	1.89e+05	1.90e+05
^{152}Eu	(Bq/mL)	-	<2.1e+02
^{154}Eu	(Bq/mL)	-	<1.0e+02
^{155}Eu	(Bq/mL)	-	<6.6e+02
^{3}H	(Bq/mL)	2.01e+02	-
^{95}Nb	(Bq/mL)	-	<5.8e+01
^{106}Ru	(Bq/mL)	-	<1.9e+03
^{90}Sr	(Bq/mL)	6.70e+03	6.57e+03
^{95}Zr	(Bq/mL)	-	<9.3e+01

Sample: W31-L2		IPA	TAL
Physical properties and miscellaneous data			
TDS	(mg/mL)	351	-
TS	(mg/mL)	349	-
Density	(g/mL)	1.2075	-
IC	(mg/L)	18.9	-
TC	(mg/L)	464	-
TOC	(mg/L)	445	-
RCRA metals			
Ag	(mg/L)	<0.69	-
As	(mg/L)	<3.7	-
Ba	(mg/L)	3.5	-
Cd	(mg/L)	<0.12	-
Cr	(mg/L)	6.0	-
Hg	(mg/L)	0.15	-
Ni	(mg/L)	<0.38	-
Pb	(mg/L)	<2.1	-
Se	(mg/L)	<4.7	-
Tl	(mg/L)	<1.4	-
Process metals			
Al	(mg/L)	4.2	-
B	(mg/L)	0.20	-
Ca	(mg/L)	79	-
Co	(mg/L)	<0.57	-
Fe	(mg/L)	<2.6	-
K	(mg/L)	9500	-
Mg	(mg/L)	<1.3	-
Na	(mg/L)	94000	-
Si	(mg/L)	8.57	-
Sr	(mg/L)	12	-
Th (ICP)	(mg/L)	<2.2	
U (fluor)	(mg/L)	0.25	-

Sample: W31-L2		IPA	TAL
Anions (analyzed by CPA Lab.)			
Chloride	(mg/L)	2.60e+03	-
Fluoride	(mg/L)	<5.0e+02	-
Nitrate	(mg/L)	2.80e+05	-
Phosphate	(mg/L)	<5.0e+03	-
Sulfate	(mg/L)	<5.0e+03	-
Alkalinity			
pH		-	11.7
OH^-	($\underline{M}$)	-	0.01
CO_3^{2-}	($\underline{M}$)	-	<0.01
HCO_3^-	($\underline{M}$)	-	<0.01
Beta/gamma emitters			
Gross alpha	(Bq/mL)	1.24e+02	<1.0e+00
Gross beta	(Bq/mL)	3.47e+05	3.58e+05
^{14}C	(Bq/mL)	1.12e+02	-
^{144}Ce	(Bq/mL)	-	<7.8e+02
^{60}Co	(Bq/mL)	<2.0e+02	3.23e+02
^{134}Cs	(Bq/mL)	4.58e+03	5.01e+03
^{137}Cs	(Bq/mL)	2.23e+05	2.29e+05
^{152}Eu	(Bq/mL)	-	<9.3e+01
^{154}Eu	(Bq/mL)	-	<6.7e+01
^{155}Eu	(Bq/mL)	-	<4.2e+02
^{3}H	(Bq/mL)	1.56e+02[a]	-
^{95}Nb	(Bq/mL)	-	<3.3e+01
^{106}Ru	(Bq/mL)	-	<1.1e+03
^{90}Sr	(Bq/mL)	7.38e+04	6.32e+04
^{95}Zr	(Bq/mL)	-	<5.7e+01

[a] Tritium determined on sample W31-L1.

Sample: W21-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	511	-
Density	(g/mL)	1.40	-
IC	(mg/kg)	12000	-
TC	(mg/kg)	18500	-
TOC	(mg/kg)	6480	-
RCRA metals			
Ag	(mg/kg)	(50)	-
As	(mg/kg)	(42)	-
Ba	(mg/kg)	78	-
Cd	(mg/kg)	27	-
Cr	(mg/kg)	160	-
Hg	(mg/kg)	56	-
Ni	(mg/kg)	75	-
Pb	(mg/kg)	290	-
Se	(mg/kg)	<25	-
Tl	(mg/kg)	<10	-
Process metals			
Al	(mg/kg)	1000	-
B	(mg/kg)	<6.6	-
Ca	(mg/kg)	45000	-
Cs	(mg/kg)	-	-
Fe	(mg/kg)	2300	-
K	(mg/kg)	8500	-
Mg	(mg/kg)	9600	-
Na	(mg/kg)	48000	-
Sr	(mg/kg)	200	-
Th	(mg/kg)	14000[a]	13700[b]
U (ICP)	(mg/kg)	31000	-

Sample: W21-S		IPA	TAL
<u>Beta/gamma emitters</u>			
Gross alpha	(Bq/g)	1.34e+05	1.29e+05
Gross beta	(Bq/g)	3.50e+06	3.36e+06
^{14}C	(Bq/g)	1.80e+02	-
^{144}Ce	(Bq/g)	-	<2.8e+04
^{60}Co	(Bq/g)	7.04e+04	8.07e+04
^{134}Cs	(Bq/g)	-	6.99e+03
^{137}Cs	(Bq/g)	2.28e+05	2.49e+05
^{152}Eu	(Bq/g)	1.30e+06	1.30e+06
^{154}Eu	(Bq/g)	3.93e+05	4.77e+05
^{155}Eu	(Bq/g)	1.17e+05	1.33e+05
^{95}Nb	(Bq/g)	-	<4.7e+03
^{106}Ru	(Bq/g)	-	<4.4e+04
^{90}Sr	(Bq/g)	7.52e+05	7.83e+05
^{95}Zr	(Bq/g)	-	<3.9e+04
<u>Alpha emitters</u>			
^{233}U	(Bq/g)	-	8.13e+03
^{235}U	(Bq/g)	-	<2.8e+04
^{239}Pu/^{240}Pu	(Bq/g)	-	2.49e+04
^{238}Pu/^{241}Am	(Bq/g)	-	5.13e+04
^{233}Cm	(Bq/g)	-	<2.5e+04
^{244}Cm	(Bq/g)	-	4.46e+04

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[a] Thorium by ICP.
[b] Thorium by colorimetric.

Sample: W23-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	544	-
Density	(g/mL)	1.34	-
IC	(mg/kg)	18100	-
TC	(mg/kg)	22200	-
TOC	(mg/kg)	4120	-
RCRA metals			
Ag	(mg/kg)	(28)	-
As	(mg/kg)	(<50)	-
Ba	(mg/kg)	63	-
Cd	(mg/kg)	32	-
Cr	(mg/kg)	190	-
Hg	(mg/kg)	19	-
Ni	(mg/kg)	110	-
Pb	(mg/kg)	(450)	-
Se	(mg/kg)	<39	-
Tl	(mg/kg)	<16	-
Process metals			
Al	(mg/kg)	2800	-
B	(mg/kg)	<10	-
Ca	(mg/kg)	55000	-
Cs	(mg/kg)	-	-
Fe	(mg/kg)	1900	-
K	(mg/kg)	18000	-
Mg	(mg/kg)	16000	-
Na	(mg/kg)	82000	-
Sr	(mg/kg)	290	-
Th	(mg/kg)	13000[a]	12000[b]
U (ICP)	(mg/kg)	17000	-

Sample: W23-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	2.23e+05	2.23e+05
Gross beta	(Bq/g)	6.90e+06	6.67e+06
^{14}C	(Bq/g)	3.65e+02	-
^{144}Ce	(Bq/g)	-	<2.7e+04
^{60}Co	(Bq/g)	2.41e+05	2.52e+05
^{134}Cs	(Bq/g)	-	<6.5e+03
^{137}Cs	(Bq/g)	4.81e+05	4.95e+05
^{152}Eu	(Bq/g)	7.81e+05	7.22e+05
^{154}Eu	(Bq/g)	5.00e+05	5.14e+05
^{155}Eu	(Bq/g)	1.16e+05	1.21e+05
^{95}Nb	(Bq/g)	-	<7.0e+03
^{106}Ru	(Bq/g)	-	<6.2e+04
^{90}Sr	(Bq/g)	2.28e+06	2.33e+06
^{95}Zr	(Bq/g)	-	<4.5e+04
Alpha emitters			
^{233}U	(Bq/g)	-	1.18e+04
^{235}U	(Bq/g)	-	<2.8e+04
^{239}Pu/^{240}Pu	(Bq/g)	-	1.18e+04
^{238}Pu/^{241}Am	(Bq/g)	-	3.21e+04
^{243}Cm	(Bq/g)	-	<2.6e+04
^{244}Cm	(Bq/g)	-	1.67e+05

[a] Thorium by ICP.

[b] Thorium by colorimetric.

Sample: W24-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	487	-
Density	(g/mL)	1.26	-
IC	(mg/kg)	6630	-
TC	(mg/kg)	9570	-
TOC	(mg/kg)	2940	-
RCRA metals			
Ag	(mg/kg)	(<7.7)	-
As	(mg/kg)	<42	-
Ba	(mg/kg)	44	-
Cd	(mg/kg)	6.1	-
Cr	(mg/kg)	36	-
Hg	(mg/kg)	26	-
Ni	(mg/kg)	22	-
Pb	(mg/kg)	150	-
Se	(mg/kg)	<52	-
Tl	(mg/kg)	<16	-
Process metals			
Al	(mg/kg)	1600	-
B	(mg/kg)	3.1	-
Ca	(mg/kg)	29000	-
Cs	(mg/kg)	(<1.3)	-
Fe	(mg/kg)	600	-
K	(mg/kg)	7600	-
Mg	(mg/kg)	5600	-
Na	(mg/kg)	69000	-
Sr	(mg/kg)	110	-
Th (color)	(mg/kg)	-	1480
U (ICP)	(mg/kg)	3700	-

Sample: W24-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	2.03e+04	2.34e+04
Gross beta	(Bq/g)	2.73e+06	2.62e+06
^{14}C	(Bq/g)	8.43e+02	-
^{144}Ce	(Bq/g)	-	<3.9e+03
^{60}Co	(Bq/g)	3.51e+04	3.39e+04
^{134}Cs	(Bq/g)	-	<6.2e+02
^{137}Cs	(Bq/g)	1.94e+05	1.96e+05
^{152}Eu	(Bq/g)	6.44e+04	6.20e+04
^{154}Eu	(Bq/g)	3.24e+04	3.60e+04
^{155}Eu	(Bq/g)	-	1.03e+04
^{95}Nb	(Bq/g)	-	<5.6e+02
^{106}Ru	(Bq/g)	-	<5.7e+03
^{90}Sr	(Bq/g)	1.05e+06	1.15e+06
^{95}Zr	(Bq/g)	-	<2.8e+03
Alpha emitters			
^{233}U	(Bq/g)	-	5.15e+02
^{235}U	(Bq/g)	-	<3.7e+03
^{239}Pu/^{240}Pu	(Bq/g)	-	1.54e+03
^{238}Pu/^{241}Am	(Bq/g)	-	3.74e+03
^{243}Cm	(Bq/g)	-	<3.6e+03
^{244}Cm	(Bq/g)	-	1.63e+04

Sample: W25-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	531	-
Density	(g/mL)	1.32	-
IC	(mg/kg)	3920	-
TC	(mg/kg)	6250	-
TOC	(mg/kg)	2330	-
RCRA metals			
Ag	(mg/kg)	(<7.6)	-
As	(mg/kg)	<41	-
Ba	(mg/kg)	59	-
Cd	(mg/kg)	11	-
Cr	(mg/kg)	59	-
Hg	(mg/kg)	37	-
Ni	(mg/kg)	34	-
Pb	(mg/kg)	220	-
Se	(mg/kg)	<51	-
Tl	(mg/kg)	<16	-
Process metals			
Al	(mg/kg)	2800	-
B	(mg/kg)	<1.5	-
Ca	(mg/kg)	38000	-
Cs	(mg/kg)	(<1.3)	-
Fe	(mg/kg)	940	-
K	(mg/kg)	9200	-
Mg	(mg/kg)	5900	-
Na	(mg/kg)	66000	-
Sr	(mg/kg)	150	-
Th (color)	(mg/kg)	-	3860
U (ICP)	(mg/kg)	4800	-

Sample: W25-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	3.74e+04	4.65e+04
Gross beta	(Bq/g)	4.16e+06	4.00e+06
^{14}C	(Bq/g)	1.71e+02	-
^{144}Ce	(Bq/g)	-	<4.2e+03
^{60}Co	(Bq/g)	3.94e+04	4.03e+04
^{134}Cs	(Bq/g)	-	7.07e+02
^{137}Cs	(Bq/g)	2.14e+05	2.21e+05
^{152}Eu	(Bq/g)	8.54e+04	8.14e+04
^{154}Eu	(Bq/g)	4.96e+04	5.06e+04
^{155}Eu	(Bq/g)	1.59e+04	1.63e+04
^{95}Nb	(Bq/g)	-	<5.9e+02
^{106}Ru	(Bq/g)	-	<5.9e+03
^{90}Sr	(Bq/g)	1.65e+06	1.73e+06
^{95}Zr	(Bq/g)	-	<4.6e+03
Alpha emitters			
^{233}U	(Bq/g)	-	8.37e+02
^{235}U	(Bq/g)	-	<4.2e+03
^{239}Pu/^{240}Pu	(Bq/g)	-	2.93e+03
^{238}Pu/^{241}Am	(Bq/g)	-	7.35e+03
^{243}Cm	(Bq/g)	-	<3.9e+03
^{244}Cm	(Bq/g)	-	3.32e+04

Sample: W26-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	449	-
Density	(g/mL)	1.54	-
IC	(mg/kg)	12000	-
TC	(mg/kg)	18200	-
TOC	(mg/kg)	6220	-
RCRA metals			
Ag	(mg/kg)	(30)	-
As	(mg/kg)	6[illegible]	-
Ba	(mg/kg)	87	-
Cd	(mg/kg)	42	-
Cr	(mg/kg)	170	-
Hg	(mg/kg)	64	-
Ni	(mg/kg)	92	-
Pb	(mg/kg)	470	-
Se	(mg/kg)	<55	-
Tl	(mg/kg)	<17	-
Process metals			
Al	(mg/kg)	7500	-
B	(mg/kg)	<7.3	-
Ca	(mg/kg)	36000	-
Fe	(mg/kg)	2300	-
K	(mg/kg)	15000	-
Mg	(mg/kg)	11000	-
Na	(mg/kg)	51000	-
Sr	(mg/kg)	120	-
Th (color)	(mg/kg)	-	9360
U (fluor)	(mg/kg)	24100	-

Sample: W26-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	8.14e+04	9.13e+04
Gross beta	(Bq/g)	5.60e+06	5.70e+06
^{14}C	(Bq/g)	2.13e+02	-
^{144}Ce	(Bq/g)	-	<1.2e+04
^{60}Co	(Bq/g)	1.03e+05	1.03e+05
^{134}Cs	(Bq/g)	2.38e+03	2.97e+03
^{137}Cs	(Bq/g)	7.03e+05	6.84e+05
^{152}Eu	(Bq/g)	5.53e+05	4.92e+05
^{154}Eu	(Bq/g)	3.00e+05	3.19e+05
^{155}Eu	(Bq/g)	7.32e+04	7.51e+04
^{95}Nb	(Bq/g)	-	<2.6e+03
^{106}Ru	(Bq/g)	-	<2.5e+04
^{90}Sr	(Bq/g)	2.03e+06	1.84e+06
^{95}Zr	(Bq/g)	-	<1.3e+05
Alpha emitters			
^{233}U	(Bq/g)	-	6.66e+03
^{235}U	(Bq/g)	-	<1.2e+04
^{239}Pu/^{240}Pu	(Bq/g)	-	5.11e+03
^{238}Pu/^{241}Am	(Bq/g)	-	1.48e+04
^{243}Cm	(Bq/g)	-	<1.3e+04
^{244}Cm	(Bq/g)	-	6.14e+04

Sample: W27-H1-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	386	-
Density	(g/mL)	1.26	-
IC	(mg/kg)	5250	-
TC	(mg/kg)	7690	-
TOC	(mg/kg)	2440	-
RCRA metals			
Ag	(mg/kg)	(<7.2)	-
As	(mg/kg)	<39	-
Ba	(mg/kg)	49	-
Cd	(mg/kg)	13	-
Cr	(mg/kg)	65	-
Hg	(mg/kg)	11	-
Ni	(mg/kg)	27	-
Pb	(mg/kg)	120	-
Se	(mg/kg)	<49	-
Tl	(mg/kg)	20	-
Process metals			
Al	(mg/kg)	4300	-
B	(mg/kg)	<6.4	-
Ca	(mg/kg)	38000	-
Fe	(mg/kg)	1400	-
K	(mg/kg)	6100	-
Mg	(mg/kg)	4800	-
Na	(mg/kg)	71000	-
Sr	(mg/kg)	120	-
Th (color)	(mg/kg)	-	1890
U (fluor)	(mg/kg)	2710	-

Sample: W27-H1-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	1.85e+04	2.25e+04
Gross beta	(Bq/g)	1.50e+06	1.44e+06
^{14}C	(Bq/g)	1.89e+02	-
^{144}Ce	(Bq/g)	-	<5.6e+03
^{60}Co	(Bq/g)	1.55e+04	1.61e+04
^{134}Cs	(Bq/g)	-	<1.2e+03
^{137}Cs	(Bq/g)	4.26e+05	3.75e+05
^{152}Eu	(Bq/g)	2.16e+04	1.99e+04
^{154}Eu	(Bq/g)	1.28e+04	1.26e+04
^{155}Eu	(Bq/g)	2.72e+03	<3.4e+03
^{95}Nb	(Bq/g)	-	<7.3e+02
^{106}Ru	(Bq/g)	-	<1.1e+04
^{90}Sr	(Bq/g)	4.55e+05	4.21e+05
^{95}Zr	(Bq/g)	-	<1.7e+03
Alpha emitters			
^{233}U	(Bq/g)	-	5.18e+02
^{235}U	(Bq/g)	-	<5.8e+03
^{239}Pu/^{240}Pu	(Bq/g)	-	1.04e+03
^{238}Pu/^{241}Am	(Bq/g)	-	4.41e+03
^{243}Cm	(Bq/g)	-	<6.5e+03
^{244}Cm	(Bq/g)	-	1.60e+04

Sample: W27-H1-H[a]		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	471	-
Density	(g/mL)	1.33	-
IC	(mg/kg)	12700	-
TC	(mg/kg)	16500	-
TOC	(mg/kg)	3830	-
RCRA metals			
Ag	(mg/kg)	(<13)	-
As	(mg/kg)	<69	-
Ba	(mg/kg)	72	-
Cd	(mg/kg)	17	-
Cr	(mg/kg)	90	-
Hg	(mg/kg)	18	-
Ni	(mg/kg)	40	-
Pb	(mg/kg)	200	-
Se	(mg/kg)	<86	-
Tl	(mg/kg)	<27	-
Process metals			
Al	(mg/kg)	6800	-
B	(mg/kg)	<11	-
Ca	(mg/kg)	54000	-
Fe	(mg/kg)	2500	-
K	(mg/kg)	6700	-
Mg	(mg/kg)	5900	-
Na	(mg/kg)	66000	-
Sr	(mg/kg)	150	-
Th (color)	(mg/kg)	-	3040
U (fluor)	(mg/kg)	1960	-

Sample: W27-H1-H[a]		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	2.59e+04	3.10e+04
Gross beta	(Bq/g)	1.88e+06	2.02e+06
^{14}C	(Bq/g)	4.86e+02	-
^{144}Ce	(Bq/g)	-	<7.7e+03
^{60}Co	(Bq/g)	1.83e+04	2.50e+04
^{134}Cs	(Bq/g)	7.36e+02	<1.8e+03
^{137}Cs	(Bq/g)	5.40e+05	5.71e+05
^{152}Eu	(Bq/g)	2.86e+04	2.42e+04
^{154}Eu	(Bq/g)	1.42e+04	1.51e+04
^{155}Eu	(Bq/g)	4.19e+03	3.26e+03
^{95}Nb	(Bq/g)	-	<1.4e+03
^{106}Ru	(Bq/g)	-	<1.6e+04
^{90}Sr	(Bq/g)	5.51e+05	6.15e+05
^{95}Zr	(Bq/g)	-	<2.6e+03
Alpha emitters			
^{233}U	(Bq/g)	-	6.20e+02
^{235}U	(Bq/g)	-	<8.3e+03
^{239}Pu/^{240}Pu	(Bq/g)	-	1.86e+03
^{238}Pu/^{241}Am	(Bq/g)	-	6.73e+03
^{243}Cm	(Bq/g)	-	<1.0e+04
^{244}Cm	(Bq/g)	-	2.15e+04

[a] Sample W27-H1-H contained no free liquid and was not sonicated.

Sample: W28-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	533	-
Density	(g/mL)	1.49	-
IC	(mg/kg)	3620	-
TC	(mg/kg)	6120	-
TOC	(mg/kg)	2500	-
RCRA metals			
Ag	(mg/kg)	(17)	-
As	(mg/kg)	27	-
Ba	(mg/kg)	39	-
Cd	(mg/kg)	26	-
Cr	(mg/kg)	55	-
Hg	(mg/kg)	12	-
Ni	(mg/kg)	62	-
Pb	(mg/kg)	190	-
Se	(mg/kg)	<29	-
Tl	(mg/kg)	<9	-
Process metals			
Al	(mg/kg)	830	-
B	(mg/kg)	4.9	-
Ca	(mg/kg)	57000	-
Cs	(mg/kg)	(<0.8)	-
Fe	(mg/kg)	630	-
K	(mg/kg)	11000	-
Mg	(mg/kg)	15000	-
Na	(mg/kg)	66000	-
Sr	(mg/kg)	130	-
Th (color)	(mg/kg)	-	1370
U (ICP)	(mg/kg)	17000	-

Sample: W28-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	4.66e+04	5.39e+04
Gross beta	(Bq/g)	2.39e+06	2.40e+06
^{14}C	(Bq/g)	7.60e+01	-
^{144}Ce	(Bq/g)	-	<1.7e+04
^{60}Co	(Bq/g)	7.48e+04	7.91e+04
^{134}Cs	(Bq/g)	3.38e+03	<4.6e+03
^{137}Cs	(Bq/g)	1.84e+05	1.94e+05
^{152}Eu	(Bq/g)	7.08e+05	7.18e+05
^{154}Eu	(Bq/g)	2.84e+05	3.20e+05
^{155}Eu	(Bq/g)	8.87e+04	9.70e+04
^{95}Nb	(Bq/g)	-	<2.9e+03
^{106}Ru	(Bq/g)	1.92e+04	<2.8e+04
^{90}Sr	(Bq/g)	5.57e+05	6.06e+05
^{95}Zr	(Bq/g)	-	<2.4e+04
Alpha emitters			
^{232}U	(Bq/g)	-	1.46e+03
^{233}U	(Bq/g)	-	3.56e+03
^{235}U	(Bq/g)	-	<1.7e+04
^{239}Pu/^{240}Pu	(Bq/g)	-	1.51e+03
^{238}Pu/^{241}Am	(Bq/g)	-	5.28e+03
^{243}Cm	(Bq/g)	-	<1.4e+04
^{244}Cm	(Bq/g)	-	3.83e+04

Sample: W31-S		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	369	-
Density	(g/mL)	1.26	-
IC	(mg/kg)	1410	-
TC	(mg/kg)	1820	-
TOC	(mg/kg)	410	-
RCRA metals			
Ag	(mg/kg)	(6.1)	-
As	(mg/kg)	<33	-
Ba	(mg/kg)	17	-
Cd	(mg/kg)	1.7	-
Cr	(mg/kg)	27	-
Hg	(mg/kg)	14	-
Ni	(mg/kg)	17	-
Pb	(mg/kg)	170	-
Se	(mg/kg)	<41	-
Tl	(mg/kg)	<13	-
Process metals			
Al	(mg/kg)	1400	-
B	(mg/kg)	<1.2	-
Ca	(mg/kg)	5600	-
Cs	(mg/kg)	(<1.1)	-
Fe	(mg/kg)	420	-
K	(mg/kg)	7900	-
Mg	(mg/kg)	870	-
Na	(mg/kg)	69000	-
Sr	(mg/kg)	30	-
Th (color)	(mg/kg)	-	2790
U (ICP)	(mg/kg)	3000	-

Sample: W31-S		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	2.12e+04	2.31e+04
Gross beta	(Bq/g)	3.35e+06	3.18e+06
^{14}C	(Bq/g)	3.14e+02	-
^{144}Ce	(Bq/g)	-	<9.4e+03
^{60}Co	(Bq/g)	7.26e+03	8.10e+03
^{134}Cs	(Bq/g)	3.52e+03	3.64e+03
^{137}Cs	(Bq/g)	2.35e+05	2.35e+05
^{152}Eu	(Bq/g)	8.73e+03	<1.7e+04
^{154}Eu	(Bq/g)	5.66e+03	5.86e+03
^{155}Eu	(Bq/g)	-	<5.9e+03
^{95}Nb	(Bq/g)	-	<9.2e+02
^{106}Ru	(Bq/g)	-	<1.4e+04
^{90}Sr	(Bq/g)	1.42e+06	1.43e+06
^{95}Zr	(Bq/g)	-	<4.7e+03
Alpha emitters			
^{233}U	(Bq/g)	-	5.08e+02
^{235}U	(Bq/g)	-	<9.7e+03
^{239}Pu/^{240}Pu	(Bq/g)	-	8.78e+02
^{238}Pu/^{241}Am	(Bq/g)	-	2.43e+03
^{243}Cm	(Bq/g)	-	<8.4e+03
^{244}Cm	(Bq/g)	-	1.71e+04

Sample: W31-H		IPA	TAL
Physical properties and miscellaneous data			
TS	(mg/g)	964	-
Density	(g/mL)	a	-
IC	(mg/kg)	21900	-
TC	(mg/kg)	30400	-
TOC	(mg/kg)	8530	-
RCRA metals			
Ag	(mg/kg)	(5.4)	-
As	(mg/kg)	<29	-
Ba	(mg/kg)	180	-
Cd	(mg/kg)	1.5	-
Cr	(mg/kg)	75	-
Hg	(mg/kg)	39	-
Ni	(mg/kg)	52	-
Pb	(mg/kg)	360	-
Se	(mg/kg)	<37	-
Tl	(mg/kg)	<11	-
Process metals			
Al	(mg/kg)	16000	-
B	(mg/kg)	22	-
Ca	(mg/kg)	62000	-
Cs	(mg/kg)	(2.4)	-
Fe	(mg/kg)	7700	-
K	(mg/kg)	6700	-
Mg	(mg/kg)	3100	-
Na	(mg/kg)	48000	-
Sr	(mg/kg)	170	-
Th (color)	(mg/kg)	-	11800
U (ICP)	(mg/kg)	9200	-

Sample: W31-H		IPA	TAL
Beta/gamma emitters			
Gross alpha	(Bq/g)	8.52e+04	8.95e+04
Gross beta	(Bq/g)	1.17e+07	1.10e+07
^{14}C	(Bq/g)	1.05e+03	-
^{144}Ce	(Bq/g)	-	<1.4e+04
^{60}Co	(Bq/g)	2.83e+04	3.01e+04
^{134}Cs	(Bq/g)	3.25e+03	2.07e+03
^{137}Cs	(Bq/g)	5.64e+05	5.52e+05
^{152}Eu	(Bq/g)	2.16e+04	2.72e+04
^{154}Eu	(Bq/g)	1.62e+04	2.07e+04
^{155}Eu	(Bq/g)	-	<8.7e+03
^{95}Nb	(Bq/g)	-	<1.2e+03
^{106}Ru	(Bq/g)	-	<1.7e+04
^{90}Sr	(Bq/g)	5.17e+06	5.29e+06
^{95}Zr	(Bq/g)	-	<6.6e+03
Alpha emitters			
^{233}U	(Bq/g)	-	2.05e+03
^{235}U	(Bq/g)	-	<1.4e+04
^{239}Pu/^{240}Pu	(Bq/g)	-	3.22e+03
^{238}Pu/^{241}Am	(Bq/g)	-	1.12e+04
^{233}Cm	(Bq/g)	-	<1.3e+04
^{244}Cm	(Bq/g)	-	6.89e+04

[a] Density was not measured on W31-H because the sample had dried to hard lumps and meaningful data could not be obtained.

APPENDIX D

ORGANIC CHEMICAL CHARACTERIZATION

APPENDIX D CONTENTS

D.1 INTRODUCTION

Wastes are segregated as much as possible, and in general the liquid low-level waste system at the Melton Valley Storage Tank (MVST) facility is not used for disposal of organic solvents.[1] However, the waste acceptance criteria are based on the primary hazard. Small quantities of organics may have been associated with the aqueous wastes. Therefore, liquid and sludge samples from three tanks (W-24, W-25, and W-31) at the MVST facility were analyzed for volatile and semivolatile organic compounds on the U.S. Environmental Protection Agency's (EPA's) Target Compound Lists. In addition, liquid samples from MVST tanks W-29 and W-30 were characterized in support of a planned campaign to remove supernatant liquid from these tanks and solidify the waste in a cement matrix.

The methods of analysis are detailed in the EPA solid waste manual, SW-846.[2] The EPA methods were not designed for radioactive hazardous (mixed) waste samples. Modifications for analyzing radioactive samples were developed and tested during studies of the inactive waste tanks at ORNL. The approach taken for the determination of targeted organic compounds in the samples was to prepare decontaminated extracts in a radiation contamination-zoned laboratory at the High Radiation Level Analytical Laboratory (Building 2026). The extracts were then transferred to the conventional organic analysis laboratory (Building 4500S), where the quantitative measurements were performed. The preparation methods followed EPA SW-846 methodology as closely as possible.[2] Some modifications, such as reducing the sample size, were necessary to minimize radiation exposure to both the field sampling crew and the analyst. Deviations from the method required by the radioactive nature or other characteristics of the samples were documented. All quantitative measurements were performed using the EPA Contract Laboratory Program (CLP) methodologies which are equivalent to SW-846 Method 8240 and Method 8270.

The Inorganic and Physical Analysis Group received and logged in the samples, prepared composite sludge samples for each tank, and transferred liquid samples and aliquots of the sludge to the Separations and Synthesis Group for organic analytical preparation. Most quantitative measurements were made by the Organic Analysis Group; however, direct aqueous injection gas chromatography (DAIGC) was done by the Separations and Synthesis Group. All sample transfers were accompanied by chain-of-custody documentation.

Results of the characterization of organic chemicals are summarized in Sect. 4.3. A more-detailed discussion of the results and brief descriptions of the methods are presented in this appendix.

D.2 METHODS AND MATERIALS

D.2.1 Volatile Organic Components of Aqueous Samples

The following is a brief description of the analysis of organic volatiles in radioactive waste samples by a modification of SW-846 Method 5030 and Method 8240. The detailed description of the procedure has been reported previously.[3] All samples were received in Building 2026 and externally monitored for gamma radiation levels prior to processing. The samples were contained in 250-mL wide-mouth jars with approximately 15 to 30 mL of headspace in the jar. The sampling of the liquid contents for analysis of targeted organic volatiles was always performed at the first opening of the jar. Sparging of the samples for volatile organic components was accomplished in a radiation contamination-zoned glove box. Prior to the opening of the sample, the sparging assembly system was tested for free flow of nitrogen gas through the sampling head and trap. The sample bottle was opened, and a 5-mL aliquot was placed in a 40-mL volatile organic analysis (VOA) vial; then 10 μL of the CLP purgeable surrogate standard (Sect. D.2.6) containing 25 μg/mL of each component was added to the sample. The VOA vial was attached to the sampling head, and the sample was sparged for 11 min at 30 mL/min with nitrogen. The nitrogen and sparged volatile organics passed through a capillary Teflon tubing, and the volatile organic compounds were collected in a solid sorbent trap (EPA Method 624) attached externally to the glove box. A second 5-mL aliquot plus purgeable surrogate was sparged for a back-up sample.

After the traps had been removed from the glove box and sealed, they were monitored for radioactivity with standard probe and smear techniques before being transferred to a nonradioactivity-zoned laboratory for quantitation of volatile organics by GC/MS Method 8240.

An integral component of method performance evaluation was the addition of purgeable surrogate standard to all samples and to a water blank with each set of sample preparations. A matrix spike and a matrix spike duplicate were prepared with each sample group.

In the nonradioactivity-zoned laboratory, the traps were thermally desorbed (similar to Method 5040) through 5 mL of distilled water containing CLP purgeable internal standard mix. Both the thermally desorbed organic compounds and the internal standards were collected in the internal trap of a Tekmar liquid sample concentrator. The organic components were desorbed from the trap by heating and were swept by a helium flow onto a gas chromatography column located in a Hewlett-Packard GC/MS. The analytes were detected by the mass spectrometer, which was checked daily against a calibration curve. Reporting limits were 5 to 10 μg/L.

D.2.2 Direct Aqueous Injection Gas Chromatography for Major Organic Volatiles

Several highly polar, water-soluble organic compounds (e.g., methyl and ethyl alcohol) are poorly detected by purge-and-trap methods. Therefore, DAIGC patterned after SW-846 Method 8015 was used to analyze sample aliquots that had been placed in 1.5-mL vials when the samples were first opened in the glove box. Injections of 3 μL were made into a gas chromatograph equipped with a 3.2-mm-OD stainless steel column packed with 1% SP-1000 coated on 60/80 mesh carbopack B, a flame ionization detector, and a reporting integrator. The column packing is the same as that used for the detection of volatiles by GC/MS. The flow rate of the helium carrier gas was 30 mL/min. The initial column temperature of 70°C was held for 2 min, followed by a programmed 16°C/min increase to 220°C and a final isothermal hold of 16 min. The inlet and detector temperatures were 150 and 250°C, respectively.

The chemical components were quantified by comparing peak areas of the sample with peak areas of external standards at four concentrations ranging from 4 to 40 mg/L. Distilled-in-glass water blanks and matrix spikes (Sect. D.2.6) were analyzed with each group of samples.

The GC conditions were slightly modified from Method 8015, and the calibration was performed daily with standards of four concentrations. Method 8015 suggests a weekly calibration using five concentrations of standards and a daily calibration with a single standard. The detection limit under the conditions described was 1 to 2 mg/L.

D.2.3 Semivolatile Organic Components of Aqueous Samples

Semivolatile organic compounds can be extracted from aqueous solutions by the liquid-liquid extractions procedures described in SW-846 Method 3510. However, direct application of this method to the extraction of mixed waste would result in contamination of the GC/MS equipment and exposure of laboratory staff members to unsafe levels of radiation. Modifications of the semivolatile organic compound analysis (SVOA) method for use with mixed waste and the subsequent analysis of an extract of the radioactive wastes have previously been reported.[4] Briefly, the samples were checked for pH using wide-range pH paper. Aliquots of CLP acid and base/neutral surrogate standards (Sect. D.2.6) were added to a 20-mL sample that was extracted three times with 5-mL volumes of methylene chloride. The methylene chloride was removed with a Pasteur pipette after each extraction and put through a Separator X filter unit to remove trace amounts of water; then the organic solvent aliquots were collected and pooled. Each sample was extracted at two pH levels: >10 and <2. The extracts from the acidic and basic pH were pooled and concentrated to approximately 2 to 4 mL by a flow of dry nitrogen gas. The sample extracts were further concentrated to 1 mL in a volumetric flask and then transferred to a crimp-top vial and spiked with CLP internal standard mix. One sample containing the SVOA matrix spike was extracted in duplicate with each daily preparative sample set.

Following extraction and concentration, each sample was screened for gross alpha and beta/gamma radioactivity, and the vials were checked for radioactive contamination by standard probe and smear techniques prior to transfer to a conventional GC/MS laboratory for quantitation of the semivolatile components. In virtually all cases, the samples were depleted of radioactive contamination.

All extracts were screened by GC qualitatively against a multiple-component (50 ppm) GC/MS daily calibration standard to identify those which might need dilution prior to GC/MS analysis. Final identification and quantitation of the semivolatile organics were performed by GC/MS as described in SW-846 Method 8270. The reporting limits for the aqueous sample aliquots are 250 to 1300 μg/L.

D.2.4 Semivolatile Organic Components of Sludge Samples

Due to the high levels of radioactivity and limited volumes of sample, the sludges were extracted for semivolatile organic compounds using a modification of SW-846 Method 3550. Samples with a radioactivity level greater than approximately 500 mR were extracted in a hot cell. All other samples were extracted in a radiochemical hood.

Approximately 3 to 4 g of sludge slurry was weighed into a 250-mL beaker and spiked with CLP base/neutral and acid surrogate standard solutions. The slurry was stirred, and approximately 10 to 20 g of anhydrous sodium sulfate was slowly mixed into the sample. The sludge mixture was extracted three times with 40-mL aliquots of methylene chloride/acetone (1/1, vol/vol) using a 350-W ultrasonicator fitted with a 1.5-cm-OD horn. Each aliquot was extracted at a 50% duty cycle and a power level of 5 for 3 to 5 min. After each extraction, the supernatant liquid was decanted into a 60- or 150-mL medium-porosity, sintered glass funnel, and the extracts were filtered and collected as a single sample. The combined extract was concentrated to 1 mL by nitrogen blowdown, placed in a crimp-top vial, and spiked with internal standard (Sect. D.2.6).

A blank was prepared by extracting reagent-grade sea sand. One sludge containing matrix spike was extracted in duplicate with each preparative set of samples. All samples were qualitatively screened by GC for semivolatile organic components and checked for radioactive contamination prior to being transferred to the conventional GC/MS laboratory. The reporting limits varied from 2500 to 17,000 μg/kg, depending on the exact mass of sludge extracted.

D.2.5 Leach Test of Organic Layer Sampler

A polyvinyl chloride (PVC) organic sampler was tested for leaching of trace organic compounds by filling the collector with 250 mL of hexane for 24 h. After 24 h, a 1-mL aliquot of the hexane was diluted to 10 mL with methylene chloride and subsequently analyzed by GC/MS for targeted organic semivolatile components (Waste Dilution Method 3580 followed by GC/MS Method 8270).

D.2.6 Chemicals, Surrogates, Spikes, and Internal Standards

All organic solvents were of high purity and were obtained from Burdick and Jackson Laboratories, Inc. (Muskegon, MI) or J. T. Baker, Inc. (Phillipsburg, NJ).

The VOA CLP purgeable surrogate standard mix contained toluene-d8, 1,2-dichloroethane-d4, and 4-bromofluorobenzene. The purge-and-trap matrix spike contained 1,1-dichloroethene, trichloroethene, benzene, toluene, and chlorobenzene.

The standards and matrix spike compounds for DAIGC contained methyl alcohol, ethyl alcohol, acetone, isopropyl alcohol, allyl alcohol, 2-butanone, isobutyl alcohol, n-butyl alcohol, and 4-methyl-2-pentanone.

The SVOA surrogate standard contained nitrobenzene-d5, 2-fluorobiphenyl, p-terphenyl-d14, 2-fluorophenol, phenol-d5, and 2,4,6-tribromophenol. The matrix spike solution for SVOA organic analysis contained phenol, 2-chlorophenol, 1,4-dichlorobenzene, N-nitroso-di-n-propylamine, 1,2,4-trichlorobenzene, 4-chloro-3-methylphenol, acenaphthene, 4-nitrophenol, 2,4-dinitrotoluene, pentachlorophenol, and pyrene. The SVOA internal standard contained acenaphthlene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10. All spikes and standards were obtained from Supelco, Inc. (State College, PA).

D.3 RESULTS AND DISCUSSION

The EPA Target Compound Lists of volatile and semivolatile organic compounds are given in Sect. 4.3, Tables 4.3.1 and 4.3.2. The reporting limits, the concentrations above which the response of the GC/MS for a calibrated range of concentrations is linear, are included in the tables for the volumes and/or weight of the MVST samples analyzed.

D.3.1 Volatile Organic Components of Aqueous Samples

The results of the analysis of the MVST liquid waste samples for volatile organics are shown in Table 4.3.3. The table lists only the volatile organic compounds whose possible presence was indicated by the GC/MS analysis. The targeted volatile compounds, methylene chloride, acetone, and toluene, were observed in each of the tank samples. Since these compounds were also observed in the blanks at similar concentrations, they probably cannot be attributed to the aqueous samples. EPA SW-846 requires that up to 20 unidentified compounds be reported as tentatively identified compounds (TICs) if volatile organic compounds other than those on the Target Compound List were detected by GC/MS. These compounds are identified solely by mass spectrum, and quantitation is based on the response factor of the nearest internal standard present in the gas chromatogram. TICs were observed in samples W25-L2, W29-L1, W30-L1, and W30-L4, and no compounds with similar GC retention time or mass spectra were observed in the blank. One compound, trichlorofluoromethane, was identified as a TIC at concentrations up to 36 μg/L in four of the tanks. The water blank contained 10 μg/L of this compound.

The addition of purgeable surrogate standard to the samples in the glove box permitted the evaluation of recoveries through the entire procedure, sampling and spiking within the glove box, purge-and-trap, and thermal desorption purge-and-trap GC/MS. Generally, recoveries of the purgeable surrogate standards in the glove box were comparable with the quality control acceptance limits specified by EPA Method 8240 for groundwater samples. The percent recoveries of the VOA surrogates were as follows: toluene-d8 (84 ± 19); 4-bromofluorobenzene (70 ± 33); and 1,2 dichloroethane (86 ± 11). The QC acceptance limits for these compounds in groundwater are 88 to 110, 86 to 115, and 76 to 114, respectively. In three cases, the recoveries of 4-bromofluorobenzene were significantly below the limits for groundwater. This is probably due to the necessity of work within the glove box and the subsequent transfer of the traps to the GC/MS laboratory for analysis as well as a matrix effect. Since the most volatile compound had the highest recoveries, it is possible that the other compounds were not as completely purged from the off-line trap. The recoveries of the matrix spikes were usually within the ranges specified by the EPA CLP guidelines for groundwater. The percent recoveries were as follows: 1,1-dichloroethene (134 ± 30); trichloroethene (118 ± 24); benzene (120 ± 26); toluene (98 ± 27); and chlorobenzene (82 ± 16). The CLP quality control acceptance limits for the matrix spikes are 61 to 145, 71 to 120, 76 to 127, 76 to 125, and 75 to 130, respectively. A Quality Control Acceptance Limit for matrix spikes is not listed in EPA SW-846.

D.3.2 Direct Aqueous Injection Gas Chromatography for Major Organic Volatiles

No organic volatiles were detected by DAIGC of any of the MVST tank samples. The detection limits for the compounds listed in Sect. D.2.2 were 1 to 2 mg/L. Matrix spike (Sect. D.2.6) recoveries were very good — greater than 85% for each of the compounds in all assays. Although there are no EPA quality control acceptance limits for this procedure, the recoveries are typical of previous performance.

During the course of the analysis of the tank liquids, the project management requested an evaluation of DAIGC for the determination of 0.25 and 0.5 mg/L of methanol and pyridine, respectively. To permit this evaluation, the procedure was modified by changing the volume of sample injected, changing the column temperature program, and increasing the sensitivity. These changes resulted in detection limits for methanol at 0.5 mg/L and pyridine at 1.0 mg/L; however, the sizes and shapes of the peaks and the sample blank level did not permit accurate quantitation. Quantitative determination of these lower concentrations of methanol and pyridine would require some development of the present procedures. One approach that should be considered, if these quantitation limits are needed, is the use of a more efficient wall-coated fused silica "Megabore" GC column rather than the conventional packed column that was used during the MVST and inactive tank sample analyses.

D.3.3 Semivolatile Organic Components of Liquids and Sludges

Table 4.3.4 shows the results of the analyses of the MVST liquids and sludges for semivolatile organics. Only a few organics were identified, for example, benzoic acid, naphthalene, 2-nitrophenol, phenanthrene, diethylbenzene, dimethylbenzene, nitrophenols, and phthalates. These compounds were also observed in studies of the inactive tanks.[3,4] These organics are compounds or degradation products of organic chemicals that are known to have been used in various plant processes over the years. The compounds constituting the greatest organic mass of semivolatiles were the phthalates, which are almost ubiquitous in nature. As further confirmation of their ubiquitous nature, phthalates were also present in relatively high concentrations in the water and sand blanks. The majority of the recovered semivolatiles were TICs: unknown, unknown hydrocarbons, and unknown phthalates. It is interesting that tributyl phosphate (a common extractant) was only detected in the sludge of tank W-31. If it was present in the waste streams added to the other tanks, it could have decomposed due to unique chemical or radiolytic interactions in the highly alkaline conditions.

Recoveries of the surrogate standards were generally within the quality control acceptance limits specified for groundwater samples by EPA SW-846. The percent recoveries for the SVOA surrogate spike were as follows: nitrobenzene-d5 (65 ± 21); 2-fluorobiphenyl (73 ± 16); p-terphenyl-d14 (145 ± 26); phenol-d5 (47 ± 41); 2-fluorophenol (33 ± 30); and 2,4,6-tribromophenol (99 ± 33). The QC acceptance limits for these compounds are 35 to 114, 43 to 116, 33 to 141, 10 to 94, 21 to 100, and 10 to 123, respectively, but their applicability to waste samples is unknown at present. The large variation of the phenols was due, at least in part, to a matrix effect in tank samples W-25 and W-31. No phenol surrogates were recovered in these samples. Matrix spike recoveries, with the exception of the highly variable recovery of the acidic phenols, were within the quality control limits defined by the EPA Contract Laboratory Program. The percent recoveries of the SVOA matrix spikes were as follows: phenol (36 ± 20); 2-chlorophenol (33 ± 9); 1,4-dichlorobenzene (30 ± 7); N-nitroso-di-n-propylamine (68 ± 10); 1,2,4 trichlorobenzene (38 ± 3); 4-chloro-3-methylphenol (47 ± 35); acenaphthene (58 ± 3); 4-nitrophenol (88 ± 16); 2,4-dinitrotoluene (90 ± 10); pentachlorophenol (85 ± 27), and pyrene (89 ± 6). The QC acceptance limits for these compounds are 26 to 90, 25 to 102, 28 to 104, 41 to 126, 38 to 107, 26 to 103, 31 to 137, 11 to 114, 28 to 89, 17 to 109, and 35 to 142, respectively. We do not know the reason for the poor recoveries of the matrix spike acid phenols during these studies and those of the inactive tanks,[3,4] but two possible explanations are proposed: (1) the adjusted pH of the final extract was not sufficient to permit quantitative extraction of the smaller acidic phenols, or (2) the phenols were decomposed by the basic pH of the waste samples. Decomposition of the phenols is the more likely cause of their poor recovery. All of the MVST samples were strongly basic due to the treatment of these wastes with alkali. It has been demonstrated by the Organic Analysis Laboratory that the phenolic organics are best recovered from acid solution or from acidification of basic solutions that were within a relatively narrow pH range of approximately 10 to 11 (the phenolic spikes tended to decompose at higher pH levels). A further complication is the length of time that these compounds are retained under highly basic conditions. The time required for extraction may have been too long due to problems, such as foaming, that have been described previously.[4]

As agreed at the start of the project, polychlorinated biphenyls (PCBs) were not specifically determined in the analyses of the tank liquids and sludges. However, individual PCBs would be detected and estimated as TICs in the semivolatile organic compound analysis. The estimated reporting limits for individual PCBs (not Aroclor mixtures) were 2.5 mg/L for aqueous liquids and 13 to 17 mg/kg for sludges (depending on whether 4 or 3 g of sludge was extracted). The mass spectral fragmentation pattern arising from the chlorine isotopes is easily identified, and PCB cogeners present in the TICs would have been identified. Detection limits of Aroclors (mixtures of PCBs) would be much higher since each component would have the same reporting limit.

D.3.4 Accountability for Total Organic Carbon in Samples

The samples were analyzed for total organic carbon content (TOC) by the Inorganic and Physical Analysis Group (Sect. 4.2). The resulting values were then used to calculate the percent of the TOC contributed by the volatile and semivolatile organic compounds. No correction was made for contributions from the blanks; therefore, the accountability factor is exaggerated. The calculations indicate that volatile (Table 4.3.3) plus semivolatile (Table 4.3.4) organic compounds determined by the modified SW-846 methods comprise only 4 to 14% of the TOC in the aqueous and/or sludge samples from the MVSTs. These results are similar to those obtained in studies of the inactive tanks at ORNL.

The organics that are not accounted for by EPA methods may consist of highly polar, water-soluble, and possibly polymeric compounds arising from radiolysis or chemical degradation, or compounds originally present in the waste. For example, low-molecular-weight organic acids/salts such as oxalate, acetate, and butyrate are not detected by the EPA methods. In a preliminary study of the organic matter in the inactive tank samples for another project,[5] the quantity of the TOC that could be accounted for was significantly increased by treating the samples with silylating or alkylating reagents so that compounds not normally analyzed by GC became more volatile or perhaps more thermally stable and could be detected and/or separated for analysis by GC. The TOC accounting in the aqueous waste liquids was increased from about 2% to 25-100% for three inactive waste tank samples by derivatizing the dried residues and analyzing by GC. Many of the non-regulatory compounds identified by this procedure were chelators, such as oxalates or ethylenediaminetetraacetic acid and its decomposition products, or tributyl phosphate and its degradation products.

We feel that many of the organic compounds that contribute to the TOC in the MVST tanks are of the non-regulatory type. Identification of these compounds would require additional development and application of analytical methods.

D.3.5 Leach Test of Organic Sampler

Analysis of the hexane used for determination of the leaching of semivolatiles from the organic sample collection device showed no semivolatile organic compounds, indicating that the PVC material used for the collector was a satisfactory construction material. The reporting limits for the leach test were 50 to 250 μg/L.

D.4. REFERENCES

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APPENDIX E

SAMPLING PROCEDURES - MELTON VALLEY AND EVAPORATOR STORAGE TANKS FOR WASTE CHARACTERIZATION

APPENDIX E CONTENTS

SAMPLING FOR WASTE CHARACTERIZATION

SAMPLING PROCEDURES

Approved by:

11/15/89

C. B. Scott
Liquid and Gaseous
Waste Operations Group Leader
Date

11/10/89

R. C. Mason, Task Leader
Waste Characterization
Date

CHBrown, Jr.
11/14/89

C. H. Brown, Program Manager
Liquid Low-Level Waste Solidification
Date

11-13-89

M. E. Baldwin, Safety Officer
Environmental and Health Protection Division
Date

Procedure SC-001 General Sampling Procedure for Liquid Low-Level Waste Storage Tanks

Eight low-level waste storage tanks at ORNL are to be sampled and analyzed to determine major chemical constituents, radionuclides, organics, possible constituents listed as hazardous under RCRA, and general waste characteristics. This procedure covers sample collection activities which are common to all of the tanks. The two groups of tanks that will be sampled are the Melton Valley Storage Tanks (MVSTs) and the Evaporator Concentrate Storage Tanks. A Radiation Work Permit (RWP) is required prior to field activities near any of the waste storage tanks (Fig. 1-1). Sampling is to be conducted by trained chemical operators in "full dress out" protective clothing for handling radioactive wastes. Sampling activities shall be continuously monitored by radiation protection personnel. Air sampling is required. Electrical power (110 V) should be provided at the site to operate the radiation protection air sampler. Sampling shall be conducted during dry weather.

Plastic sheeting, absorbent paper, and where appropriate pans shall be placed to confine the radioactive materials and prevent contact with the vault roof and other clean surfaces. Waste rags and materials used to wipe down handles and sampler assemblies should be placed in a plastic bag. Spill containment and clean-up materials shall be maintained and readily available within the work area.

Extremity dosimeters (finger rings) are required for all employees that directly handle the filled sample containers. All exposures of the employees involved in this task should be kept segregated from their overall exposures from day-to-day activities (by use of recording pocket meter readings) so that the overall exposure information can be further utilized in future waste tank projects.

The sampling crew shall have training in handling low level, TRU, and mixed wastes, in the use of respirators, and in the project specific procedures.

Labels should be attached to the sample jar and to the plastic bags and the container which will be used to package the sample before the sample is collected. Preprinted labels will be provided by J. J. Ferrada.

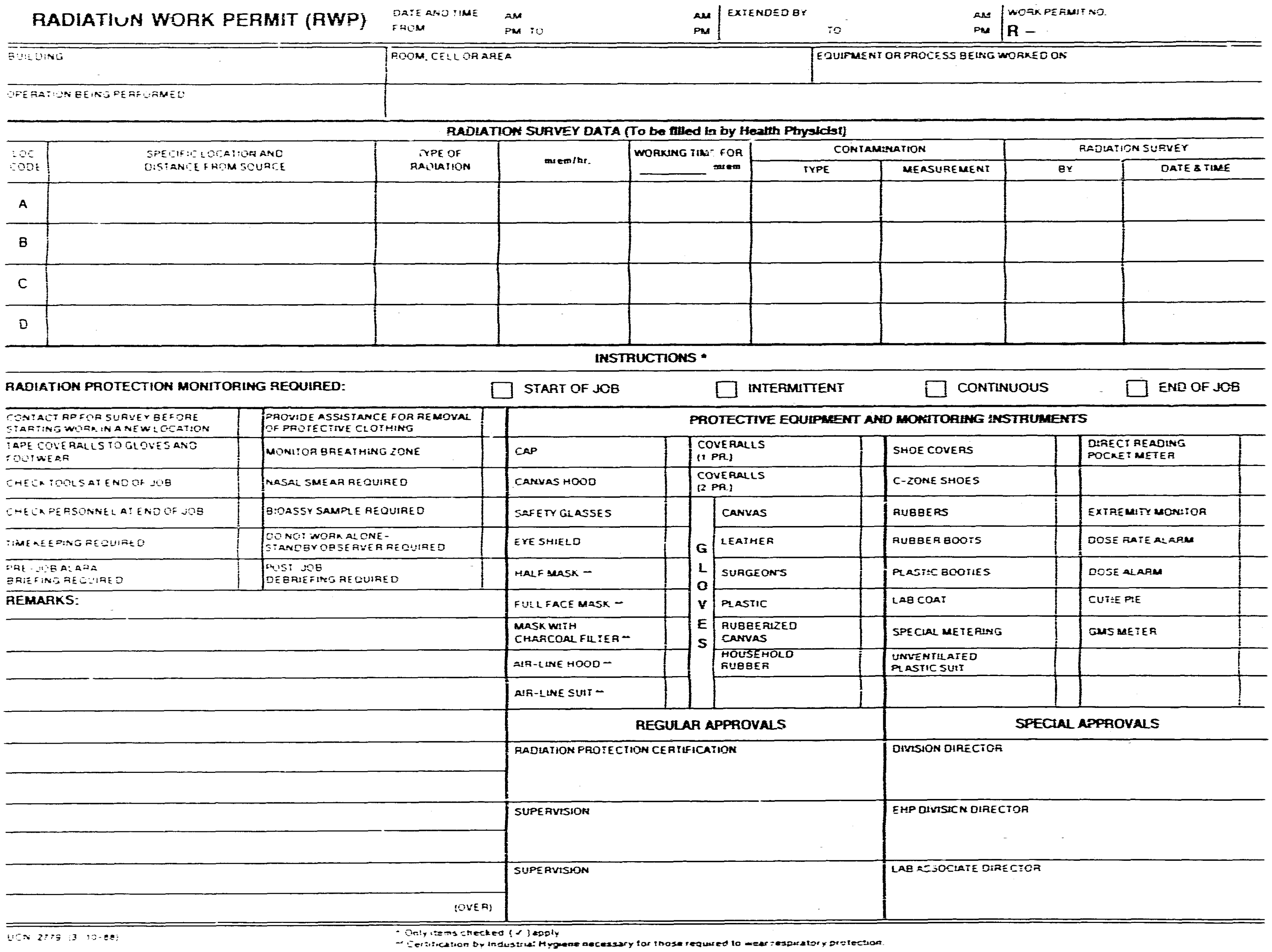
Care should be taken to keep the samples upright during handling and transport.

Presampling

1. If wastes have recently been transferred into the storage tank, the tank contents should be aerated to agitate and mix the liquid wastes before sampling. The air spargers should be left on for at least 24 hours (1 day). Omit this step if wastes are already mixed.

2. After mixing, turn off the air spargers which agitate the tanks and allow the solids to settle for at least 6 days before measuring the interface or collecting samples. Record on the log sheet (Fig. 1-2) under comments the date the air spargers were turned off.

3. Sampling equipment must be cleaned and allowed to dry prior to each use per Procedure SC-005, Decontamination of Sampling Equipment Procedure. Some new equipment must be cleaned prior to the first use. This equipment is spelled out in Procedure SC-005.



RADIATION WORK PERMIT (RWP)

DATE AND TIME FROM AM PM TO AM PM | EXTENDED BY AM PM TO AM PM | WORK PERMIT NO. R –

BUILDING	ROOM, CELL OR AREA	EQUIPMENT OR PROCESS BEING WORKED ON
OPERATION BEING PERFORMED		

RADIATION SURVEY DATA (To be filled in by Health Physicist)

LOC CODE	SPECIFIC LOCATION AND DISTANCE FROM SOURCE	TYPE OF RADIATION	mrem/hr.	WORKING TIME FOR ____ mrem	CONTAMINATION		RADIATION SURVEY	
					TYPE	MEASUREMENT	BY	DATE & TIME
A								
B								
C								
D								

INSTRUCTIONS *

RADIATION PROTECTION MONITORING REQUIRED: ☐ START OF JOB ☐ INTERMITTENT ☐ CONTINUOUS ☐ END OF JOB

CONTACT RP FOR SURVEY BEFORE STARTING WORK IN A NEW LOCATION		PROVIDE ASSISTANCE FOR REMOVAL OF PROTECTIVE CLOTHING	
TAPE COVERALLS TO GLOVES AND FOOTWEAR		MONITOR BREATHING ZONE	
CHECK TOOLS AT END OF JOB		NASAL SMEAR REQUIRED	
CHECK PERSONNEL AT END OF JOB		BIOASSY SAMPLE REQUIRED	
TIMEKEEPING REQUIRED		DO NOT WORK ALONE - STANDBY OBSERVER REQUIRED	
PRE-JOB ALARA BRIEFING REQUIRED		POST JOB DEBRIEFING REQUIRED	

REMARKS:

PROTECTIVE EQUIPMENT AND MONITORING INSTRUMENTS

CAP		COVERALLS (1 PR.)		SHOE COVERS		DIRECT READING POCKET METER	
CANVAS HOOD		COVERALLS (2 PR.)		C-ZONE SHOES			
SAFETY GLASSES		GLOVES CANVAS		RUBBERS		EXTREMITY MONITOR	
EYE SHIELD		LEATHER		RUBBER BOOTS		DOSE RATE ALARM	
HALF MASK **		SURGEON'S		PLASTIC BOOTIES		DOSE ALARM	
FULL FACE MASK **		PLASTIC		LAB COAT		CUTIE PIE	
MASK WITH CHARCOAL FILTER **		RUBBERIZED CANVAS		SPECIAL METERING		GMS METER	
AIR-LINE HOOD **		HOUSEHOLD RUBBER		UNVENTILATED PLASTIC SUIT			
AIR-LINE SUIT **							

REGULAR APPROVALS	SPECIAL APPROVALS
RADIATION PROTECTION CERTIFICATION	DIVISION DIRECTOR
SUPERVISION	EHP DIVISION DIRECTOR
SUPERVISION	LAB ASSOCIATE DIRECTOR

(OVER)

UCN 2779 (3 10-88)

* Only items checked (✓) apply

** Certification by Industrial Hygiene necessary for those required to wear respiratory protection.

Figure 1-1. Radiation Work Permit, page 1.

1. Notify Radiation Protection of any deviations from instructions and changes in working conditions.
2. Personnel survey is required when leaving contamination zones.
3. Return work permit to Health Physicist upon completion of job or expiration of permit.

Timekeeping By

Department

PERSONNEL AND EXTERNAL EXPOSURE CONTROLS							Planned Exposure (mrem)	TIME RECORD							Estimated Exposure (mrem)
Name	Job* Class.	Dept.	P.R. No.	Location Code	Dose Rate Used	Working Time		Begin	End	Begin	End	Begin	End	Total Time	

* Job Classification such as Welder, Electrician, Chemical Operator, Health Physicist, Etc., should be recorded in this column.

1. **Radiation Work Permit is required when:**
   - (a) expected dose is > 20 mrem to the body or 200 mrem to extremities or skin for an individual during a single shift;
   - (b) exposure of an individual to a dose rate > 1 rem/hr (total body); > 10 rem/hr (extremities)
   - (c) airborne radioactivity in work environment is > DAC for a 40-hour week;
   - (d) specified by divisional operating rules and procedures or by posted regulations.

2. **Supplementary Time Sheet**

   To be used if extra space is needed for the timing of individuals into and out of an area, etc.

3. **Special Approvals**

   (a) Dose Rate rem/hr (total body)

   > 5 Division Director in charge of work area. — Oral or written; noted and initialed on the permit by the person obtaining the approvals.

   > 20 Above and Environmental & Health Protection Division Director
   > 50 Above and Laboratory Associate Director

   (b) Dose (total body)

   > 60 mrem/day for nonoperating personnel, or > 300 mrem/wk for operating personnel — Division Director in charge of individual

   > 1 rem — Above and Laboratory Associate Director for Support and Services

4. **Copies**

White – The RWP must be posted or available at work site.
Yellow – The Health Physicist maintains a copy for record and reference purposes.
Blue – A copy must be distributed to appropriate line supervision.
Pink – Radiation Protection Section

UCN-2778 Back

* Posted regulations may be used in lieu of an RWP for operating Personnel under specified conditions. (See Regulation 8, Procedure NO. 3.6, ORNL Health Physics Manual.)

Figure 1-1. Radiation Work Permit, page 2.

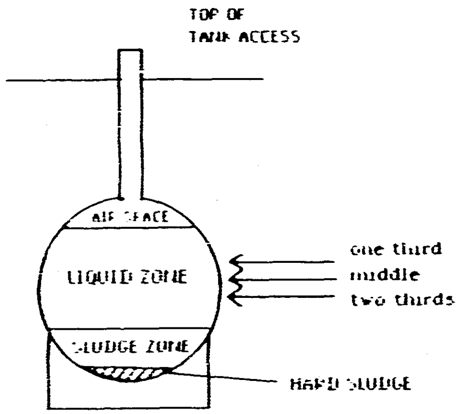
TANK ID __________

LIQUID LOW-LEVEL WASTE
SAMPLING PROJECT
TANK DESCRIPTION INFORMATION
FORM 1 of 2

DATE __________

TIME __________

TANK CONTENTS PROFILE



LIQUID: Depth to
______ One third
______ Midpoint
______ Two thirds

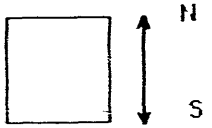
SLUDGE: Depth to
______ Top of soft sludge
______ Top of hard sludge
______ Depth to bottom of tank

CONTAMINATION LEVELS

RADIATION LEVELS:
__________ Ground surface (R/hr)
__________ Tank access (R/hr)

COMMENTS:

POINT OF ACCESS: Mark entry point with X



Names of sampling personnel (print):
____
____
____

Signature of responsible supervisor: ____________________

Health Physics Attendant: ____________________

HP log book cross-reference :

Variations from procedure:

Variation approved by: ____________________

Figure 1-2. Field log book.

4. A presampling survey will be conducted before collecting the samples. At this time (1) the air-liquid and the liquid-sludge interfaces will be located with the Markland sludge level detector, thus establishing the depth of the supernatant liquid, and (2) a rough estimate of the beta-gamma radiation level will be made. The presampling survey should be conducted at least one day in advance of sample collection to allow time for the disturbed solids to settle.

    a. Have the Instrument and Controls (I&C) technician disconnect the liquid level instrumentation. Open the tank access. Radiation levels should be monitored as the access is opened.

    b. Measure the air-liquid and liquid-sludge interfaces. Raise and lower the sludge level detector slowly and carefully to minimize the disturbance of the liquid-sludge interface and any stratified liquid layers. Check also for the presence of immiscible or stratified liquid layers such as an organic layer and measure any interfaces which are observed.

    c. Record in the log sheet (Fig. 1-2) the distance from the top of the tank opening to the liquid surface and the distance from the top of the tank opening to the liquid-sludge interface. If immiscible or stratified layers are observed record the distance from the top of the tank opening to the interface under comments.

    d. Wipe down the detector head and cable with spray cleaner and rags as described in Procedure SC-005.

    e. Close the tank access.

    f. The information will be evaluated and final plans made for collecting samples. This will include a review of the radiation protection measures which will be needed.

    g. Prepare sampling equipment.

<u>Sample Collection</u>

5. Open the tank access. Radiation levels should be monitored continuously as the access is opened. Record the radiation level at the tank access on the data collection form.

    Samples should be collected in the order (1) aqueous liquid samples, (2) organic layer samples (if present), and (3) sludge samples.

6. Take the first liquid sample at the one-third level below the air-liquid surface. Refer to the liquid sampler operating instructions in Procedure SC-002. The bottle should be labeled before collecting the sample. Repeat the sampling at the one-half and then at the two-thirds supernate depth measured from the top of the liquid as described in the Procedure SC-002. After a liquid sample has been taken, prepare the sample as follows:

    a. Seal the bottle.

    b. Wipe off the exterior of the bottle to remove any spilled liquid or possible contamination.

c. Place the bottle in plastic bag(s) and seal the bag with tape. Have the HP measure the radiation level of the sample. Then place it in a lead pig for transport. Label the container with information on the radiation level. The lid of the lead pig should have a wire handle.

d. Record sample data on page 2 of the sample collection form (Fig. 1-3). Complete chain-of-custody form for the sample.

e. Have the HP monitor the radiation level and tag with the "HP" tag (Radiation Hazard Materials Transfer Tag). If the radiation level at the surface of the pig is 100 mrem/h or less, the sample will be transported in the pig.

f. In the event that the radiation level at the outer surface of the pig should exceed 100 mrem/h, place the pig in a paint can with crumpled plastic for padding and then into the stainless steel transport carrier.

7. The instructions for organic layer sampling in steps 7-9 are for the most probable scenarios which are either a relatively thin or no organic layer over the aqueous layer. If a thick organic layer (approximately 10 inches thick) is detected with the Markland detector during the presampling survey omit steps 7 to 9 and follow the alternate directions in step 10.

The bottom opening sampler developed for sampling soft sludge will be used to collect a column of liquid at the air-liquid interface to determine if an organic layer is present and if present the depth of the layer. Refer to Procedure SC-007 for detailed sampling instructions. Operation of the bottom opening sampler is described in Procedure SC-003.

a. Raise the soft sludge sampler to the surface. Inspect the sample visually for the presence of immiscible liquid phases. If an immiscible (i.e. organic) layer is observed on top of the aqueous supernate estimate the thickness of the organic layer in the sample collection tube and record on the data collection form.

b. If an organic layer is present, remove the soft-sludge sampler tube from the handle and follow instructions in step 8.

8. If detectable organics are present, the two-phase sample in the soft sludge sampler tube will be packaged and a larger sample of the organic layer will be taken according to Procedure SC-007.

a. Remove the handle from the soft sludge sampler containing the liquid layers. Cap and wipe the sampler tube.

b. Place the sample tube into the prelabeled plastic bag and tape the bag closed. Place the wrapped sample into a second plastic bag. Close the bag, place it into the prelabeled can, and then place the packaged sample into the shielded transport carrier. This sample will be taken to the High Radiation Level Analytical Laboratory (Building 2026) in order to measure the exact height of the organic layer. The packing should keep the sample tube approximately vertical. Record the requested sample data on page 2 of the data collection form (Fig. 1-3). Complete the chain of custody form for the sample.

LIQUID LOW-LEVEL WASTE
SAMPLING PROJECT
FIELD DATA LOG SHEET
Form 2 of 2

TANK ID ______________ DATE ______________________

SAMPLE ID	SAMPLE TYPE (Liquid, soft sludge, air-liquid interface, organic, hard sludge or duplicate)	SAMPLING POINT, DEPTH (ft)	RAD LEVEL (R/hr)	DEPTH OF SOLIDS OR ORGANIC LAYER IN SAMPLER, FT	REMARKS
1)					
2)					
3)					
4)					
5)					
6)					
7)					
8)					
9)					
10)					
11)					
12)					

Immiscible (i.e. organic) liquid layer present ________(yes) ________(no)

Figure 1-3. Field data collection form.

c. Collect a larger sample of the organic layer following Procedure SC-007. Cap and wipe the organic sampler tube, and place it in the prelabeled plastic bag. Place it into a second plastic bag, and then into a labeled can. Place the packaged sample into the shielded transport carrier. The packing should keep the sample tube upright. Record the requested sample data on page 2 of the data collection form (Figure 1-3). Complete the chain of custody form for the sample.

d. If the height of the organic layer is less than one-third the height of the organic sampler, take a second sample repeating step 8c.

9. If detectable organics are not found, return the liquid sample to the tank, and proceed with the sludge sampling procedure, step 11.

10. This alternate procedure is followed if a thick organic layer (> 10 inches thick) is detected with the Markland detector during the presampling survey. Determine the thickness of the organic layer from the Markland detector. Take one 250 mL sample at the one-half level (i. e. midpoint) of the organic layer with the vacuum pump liquid sampling system. Refer to Procedure SC-002 for sampler operating instructions, and step 6 of this procedure for handling and preparing the sample for transport.

11. Sample sludge in the tank using the soft sludge sampler as described in Procedure SC-003, Soft Sludge Sampling Procedure. The sludge sampler is capable of taking a 15-inch long core sample. If the sludge depth is suspected to be more than 15 inches, or if the sampler has been lowered 15 inches from the top of the sludge without reaching the bottom of the tank, do not attempt to collect more than a 15-inch core with the first sample.

a. Monitor radiation levels continuously as the sampler is removed from the tank, and wipe down the sampler handle and cap the tube.

b. Visually inspect the sample, and estimate the sludge depth in the sample tube.

c. Place the sample tube into the prelabeled plastic bag. Tape the bag closed. Place the wrapped sample into another plastic bag. Close the bag, place it in a labeled can and then into the shielded transport carrier. The packing should keep the sample tube approximately vertical.

d. Record the requested sample data on page 2 of the data collection form. Complete the chain-of-custody form for the sample.

If the sludge depth is greater than 15 inches, or the sampler did not reach the bottom of the tank, take a second sample below the first sample to obtain a full vertical core of the sludge in the tank. Close the sampler until the bottom tip of the sampler is approximately 1 inch above the lowest point previously sampled. Then open the sampler, lower the sampler, and collect the sludge sample. Remove and package the sample as above. Continue collecting samples at successively lower depths until a hard surface is encountered. Record the depth to the level resistance was encountered.

12. If hard sludge is encountered which cannot be collected with the soft-sludge sampler, use the sampler described in Procedure SC-004, Hard Sludge Sampling Procedure.

    After the hard sludge sample as been taken, prepare the sample:

    a. Place the sampler into a labeled PVC container. Seal the PVC container with the cap. Place the PVC container in a plastic bag, place it into a labeled can, and place the can in the shielded transport carrier.

    b. Record the radiation level of the sample.

    c. Complete the chain-of-custody form for the sample. Record the sample data on page 2 of the data collection form.

13. Close the tank access. Have I&C personnel reconnect the liquid level instrumentation. Verify that the liquid level instrumentation is working properly.

14. Decontaminate the sampling equipment per the instructions in Procedure SC-005. Tag with the HP tag.

15. Package the waste, tag it with the HP tag, and dispose of the waste per the Waste Management Plan.

16. Deliver the samples, with the HP tags, the chain-of-custody forms (Procedure SC-006, Sampling Custody) and the Request for Analytical Services form to the sample custodian or designated alternate authorized to receive samples for Inorganic and Physical Analysis, at the High Radiation Level Analytical Laboratory (Bldg.2026). All samples collected should be delivered the same day before 3:00 p.m.

Procedure SC-002 Vacuum Pump Liquid Sampling Procedure

A vacuum pump sampling system will be used to take liquid samples from the waste tanks. A schematic of the system is shown in Fig. 2-1. The samples will be pumped through Teflon tubing directly into the sample bottles. Precleaned glass bottles with Teflon-lined lids will be provided for liquid samples when required for the planned analyses. The pump is arranged with a safety surge bottle as a backup if an overflow should occur, thus minimizing the potential for contamination of the pump. Both bottles should be placed inside a pan for containment in the event that a spill or leak should occur. The sampling bottle system has blotter paper underneath it so that any spills can be contained, collected, and disposed of properly. A small cartridge type HEPA filter will be installed on the vacuum pump air discharge. This is a precautionary measure. No airborne radioactive emissions were detected by the air monitor in previous sampling of these tanks when no filter was used. The waste solutons are viscous and the sample must be lifted by suction a height of 12 ft or more. In the event that the filter causes problems, the filter will not be used.

Presampling Procedure

1. A presampling survey will be conducted (see Procedure SC-001). This should be done at least one day in advance to allow time for the disturbed solids to settle. At this time the air-liquid and the liquid-sludge interfaces will be located, thus establishing the depth of the supernatant liquid..

2. After the liquid depth had been determined, cut Teflon tubing to the lengths specified by 1/3, 1/2, and 2/3 of the supernatant depth plus the distance from the top of the supernatant liquid to the sample bottle. Premark the tubes with tape to indicate when the appropriate level has been reached in the tank. Attach a stainless steel weight to the zero end of the tubing and a cap on the sample bottle end. New tubing will be used at each sample location to avoid cross-contamination of the samples. Label the sample bottle before collecting the sample.

Sample Collection

3. Slowly lower the Teflon tubing into the tank to the specified sampling level. The top end of the tubing is plugged to restrict entry of tank liquid into the tubing while it is lowered to the specified sampling level. The stainless steel weight attached to the lower end of the tubing will keep the tubing vertical during sampling.

4. When the tubing has reached the specified depth, remove the cap from the top of the tubing, attach the sample bottle, and turn on the vacuum pump. When the 250-mL sample bottle is nearly full turn the pump off and release the vacuum remaining in the system. Disconnect and cap the sample bottle. If duplicate samples are requested, replace it with an empty bottle and collect another liquid sample.

5. After the required sample(s) has been taken, allow any remaining liquid in the tubing to drain back into the tank. The tubing and weight assembly is removed from the tank and placed in a plastic bag along with absorbent paper to absorb any residual free liquid. The bag is sealed for disposal per the Waste Management Plan.

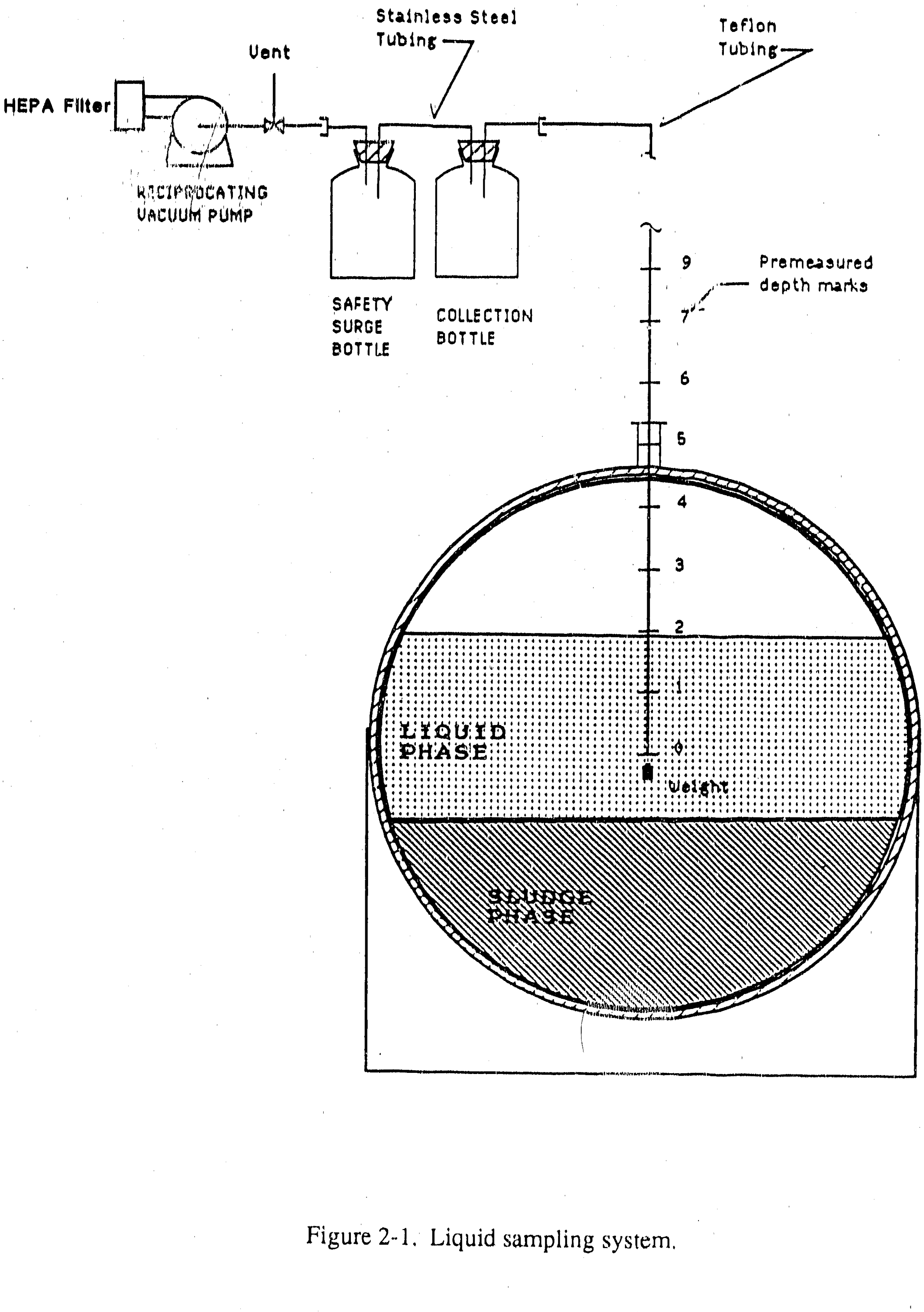


Figure 2-1. Liquid sampling system.

Procedure SC-003 Soft Sludge Sampling Procedure

The soft-sludge sampler developed for the inactive tanks sampling campaign with minor modifications will be used to sample soft tank sludge (see Fig. 3-1). (This bottom opening sampler will also be used to collect a column of liquid to check for immiscible layers or if stratified layers are suspected.). The handle for these samplers can be broken down into 5-foot sections by removing the lock pins. Operation of these samplers is described below. Label the plastic bags and the can which will be used to package the sample in advance of collecting the sample.

1. Assemble the sampler sections and check that the sampler alignment is correct and the sampler operates properly. With the handle in position A (Fig. 3-1), seal the sample collection tube by depressing the handle completely until it contacts the locking hole lug.

   Note: Never move the handle from position A without depressing the handle or damage to the gasket at the bottom of the sample collection tube could occur.

   Turn the handle to position B, and raise the handle until hole A aligns with the locking hole. Check that the small pipe plug is removed from the side of the PVC sample collection tube.

2. Insert the sampler into the tank until the tip of the sample collection tube is approximately 12 inches below the liquid surface as was measured with the Markland Sludge Level Detector. If the depth of the liquid in the tank is less than 12 inches, lower the sampler until the tip of the sample collection tube is just below the liquid surface.

   Note: If evidence exists of an organic layer on top of the liquid layer, do not open the sampler until well below the organic layer.

3. Open the sample collection tube by depressing the handle completely. Then turn the handle back to position A. Raise the handle until hole A aligns with the locking hole.

4. Take the sludge sample by slowly lowering the sampler to the bottom of the tank. If the sludge of the tank is known or suspected to be more than 15 in deep, follow instructions in Procedure SC-001, Step 11 for collecting more than one sample to obtain a full core of sludge.

5. After the sample has been taken, the sample collection tube must be resealed. Depress the handle until it contacts the locking lug. To do this, the sampler assembly must be raised slightly off the tank bottom, approximately 1/4 to 1/8 inch. With the handle completely depressed, turn it to position B. Raise the handle until hole B aligns with the locking hole and reinsert the locking pin.

6. Carefully remove the sampler from the tank, maintaining the sampler in the vertical position. Wipe down the outside of the sampler as it is removed from the tank. Place wipes in a plastic bag.

7. Unscrew the sample collection tube from the handle, and replace the small pipe plug in the side of the sampling tube. Place a 1-in NPT pipe cap which has been prelabeled on the top of the sample collection tube.

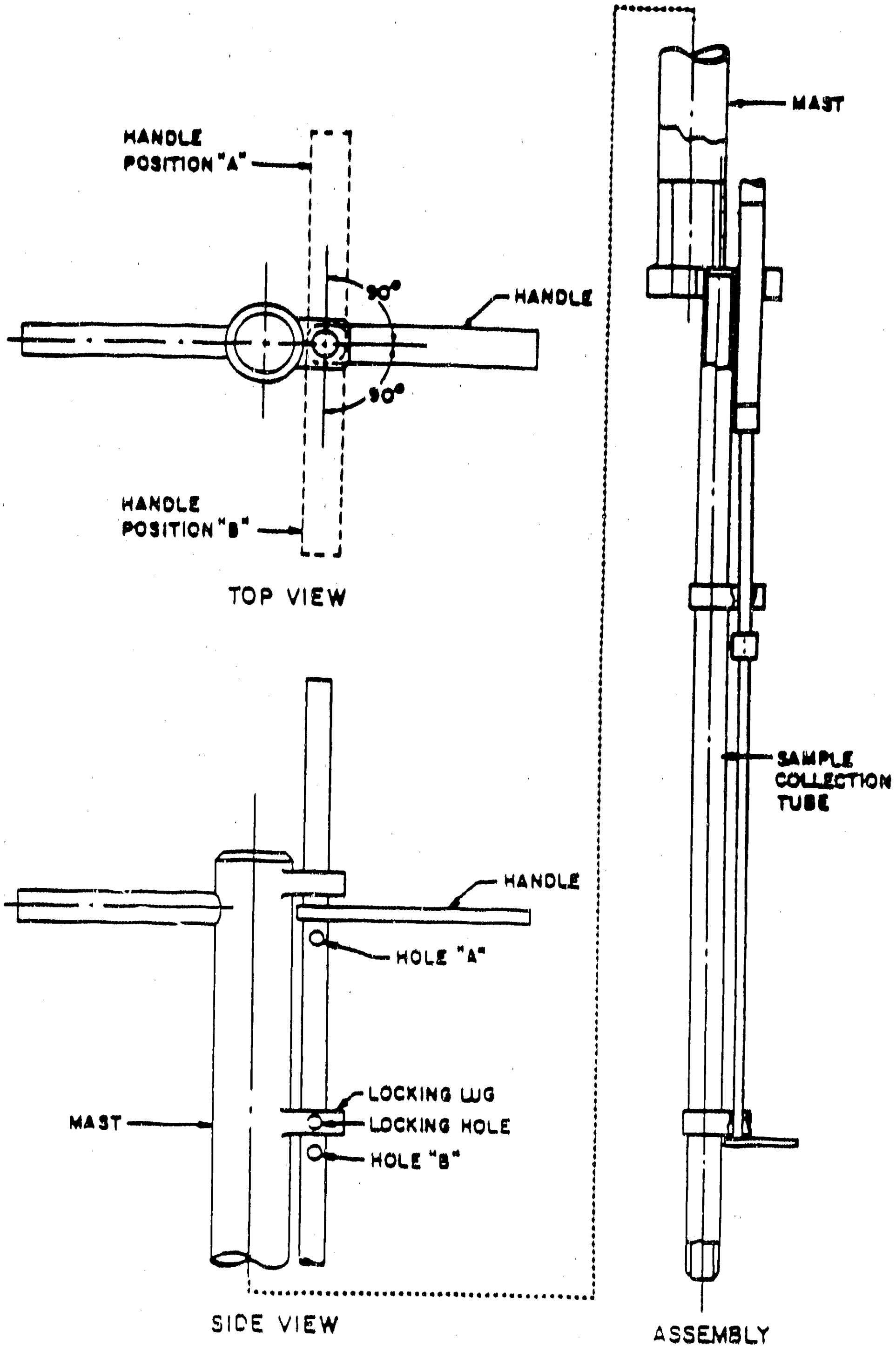


Figure 3-1. Soft sludge equipment.

8. Place the sample collection tube in the prelabeled plastic bag and tape the bag closed. Place the wrapped sample tube in a second bag, close the bag, and then put the wrapped sample in the prelabeled can. Place the packaged sample into the shielded transport carrier.

9. Take a second sample if required:
   a. If the sludge depth is suspected to be more than 15 inches or if the sampler did not reach bottom take a sample from the lower part of the same hole. Close the sampler until the bottom tip of the sampler is approximately 1 inch above the lowest point previously sampled. Then open the sampler, lower the sampler, and collect the sludge sample. Remove and package the sample as above. Continue collecting samples at successively lower depths until a hard surface is encountered. Record the depth to the level resistance was encountered.

   b. If the solids fill less than 2/3 of the sampler used for the bottom of the tank take a second sample from a different hole as much as possible to obtain a larger quantity of solids.

10. After the sample has been taken, the handle must be decontaminated as described in Procedure SC-005, Decontamination of Sampling Equipment.

Procedure SC-004 Hard Sludge Sampling Procedure

Commercial Hard Sludge Sampler

A commercial hard sludge sampler with a sharper tip will be available for use if the consolidated sample cannot be obtained with the soft sludge sampler. This sampler consists of a stainless steel pipe (barrel) with a liner, sharpened blades at the bottom, a gate valve to hold the sample in, a vented cap, and handle sections. A schematic of the apparatus is shown in Fig. 4-1. The sampler can be assembled with either an auger type bit for hard sludges (Fig. 4-1) or a push type cutting end for sticky, "mud" consistency sludges. The bit has been designed to cut the hard sludge with little disturbance of the rest of the material. A cross handle will be used to apply turning pressure on the sampler to cut the sludge.

1. Assemble the sampler sections and handle. Label the PVC container, plastic bag, and and can which will be used to package the sample. Place the PVC container near the sampling port.

2. Lower the sampler into the tank. When the sampler reaches the hard sludge, turn the cross handle to cut the sludge. Use only manual pressure and do not force.

3. After the hard sludge has been cut, remove the sampler from the tank. Wipe down the handle and outside of the sampler as the assembly is removed from the tank. Do not wipe the cutting blades. Remove the handle and place the sampler into the PVC container. Seal the PVC container with the cap. Wrap the PVC container in the plastic bag and place it into the can. Place the packaged sample into the shielded transport carrier. Place the wipes in a plastic bag.

4. After the sample has been taken, the handle must be decontaminated as described in Procedure SC-005, Decontamination of Sampling Equipment.

Alternate Hard Sludge Sampler

The hard sludge sampler developed for the inactive tanks sampling project will be available as a backup to the commercial sampler. This device consists of a stainless steel pipe which has a sharp, machine-bevel cutting edge on one end, and is threaded at the other end so that it can be attached to a handle. This sampler is suitable only for very thick, sticky sludges. The cores are stored in a specially designed stainless steel sample containers.

1. Assemble the mast (handle) sections and attach to the sampler. Label the stainless steel container and a "paint" can.

2. Lower the sampler into the tank. Force the sampler into the sludge by pushing down or twisting the handle. Do not use any impact force or allow more than one person at a time to push on the sampler.

3. Position the sample container near the tank port.

4. Remove the sampler assembly from the tank, wiping down the mast sections and removing all but the last mast section as they clear the tank. Place the wipes in a plastic bag.

ORNL DWG 89-281

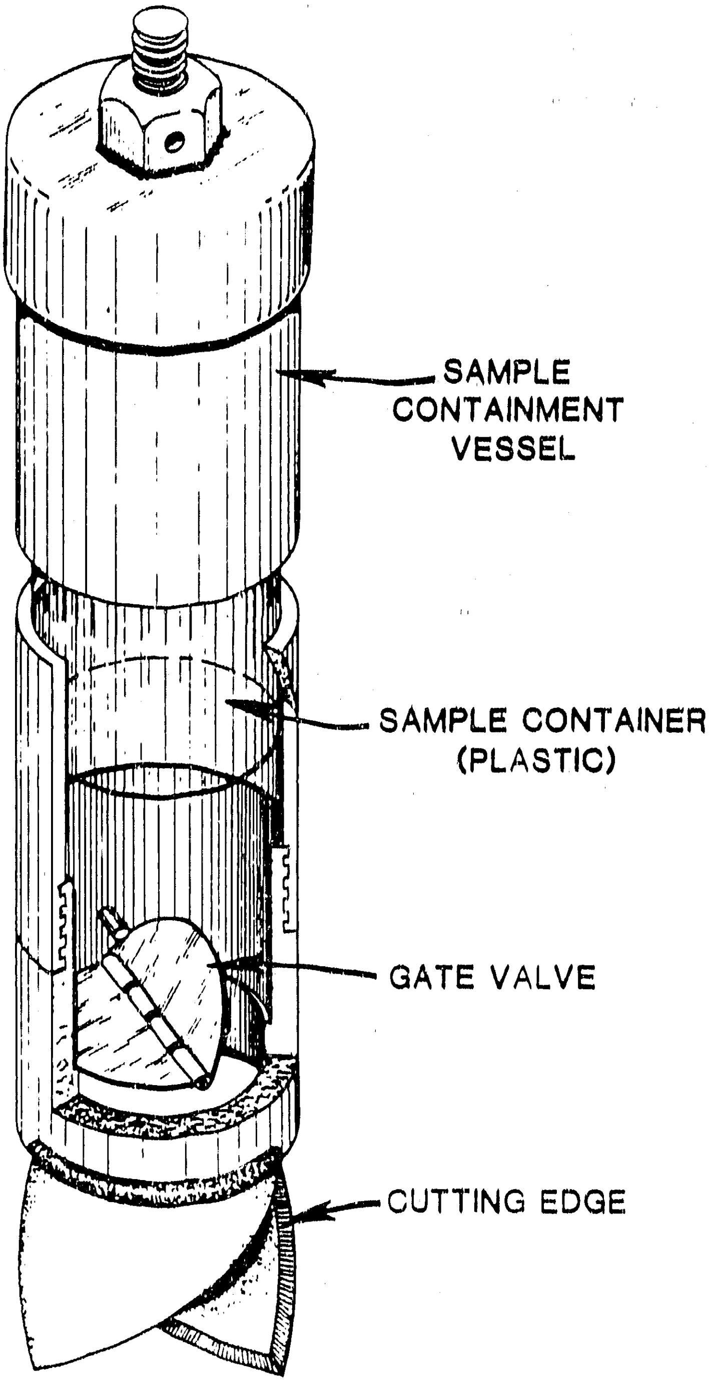


Figure 4-1. Scheme of the hard sludge sampler.

5. Lift the final mast section and hard sludge sampling device from the tank, and insert the sampler into the sample container. Unscrew the mast section from the sampler. Seal the sample container using the cap. Wipe any residues from the outside surface of the container, wrap it in a plastic bag, and place it into a "paint" can. Place the packaged sample in the stainless steel transport carrier.

6. Decontaminate the handle as described in Procedure SC-005, Decontamination of Sampling Equipment.

Procedure SC-005 Decontamination of Sampling Equipment Procedure

This procedure describes methods to decontaminate sampling equipment before and after use to prevent contamination of the samples and to reduce radiation exposure to personnel from contaminated sampling equipment. All sludge sampling equipment must be decontaminated prior to the first use to remove shop oils or soil to avoid contamination of the sample. The I-Chem glass sample bottles have been purchased precleaned and should not be opened until just before the sample is collected. The liquid sampling equipment such as the stainless steel tubing should be rinsed with deionized water and methanol prior to use and allowed to dry. It may not be practical to preclean some equipment, such as the Teflon tubing before use.

Cleaning of the PVC sludge sample collectors, the plastic containers for the sludge samplers and the "Mason" jars used with the pump module sampler prior to use: Wash with tap water and "Micro" detergent (can be obtained from Analytical Chemistry Division), rinse with tap water, and then rinse well with deionized water. Allow to dry in a clean area. After drying place equipment in a plastic bag or wrap in plastic to keep equipment clean until use. Leave the bottom of the sludge sampler open so the probe does not indent the gasket.

Hard sludge samplers (except for the handles) should be cleaned in a similar manner to the PVC sludge sample containers prior to use.

Organic layer samplers should be cleaned in a similar manner to the PVC sludge sample containers prior to use.

Cleaning of sludge sampler handles: Prior to first use clean the outside of the sampler handles with spray cleaner and rags. Between tanks wipe down the outside of the sampler handles with a spray cleaner and rags to remove the residues as the handle is withdrawn from the tank. Place the wipes in a plastic bag. Then wipe down the entire handle exterior with spray cleaner. If sludge has gotten into the handle interior, try to wipe it out. Have the HP check the handle. If the handle cannot be cleaned in the field to levels approved by the HP, wrap the handle in plastic, have it tagged by the HP, and transport it to Building 3074 for decontamination.

Sludge level detector: Wipe down the detector head and cable with spray cleaner and rags after use in each tank. Visible contamination and oils should be removed. Have it checked by the HP.

Any contaminated equipment which is to be transported within the plant area or stored must be tagged by the HP as a radioactively contaminated item.

Procedure SC-006 Sampling Custody

A sample is considered to be under a person's custody if it is (1) in a person's physical possession, (2) in view of the person after taking possession, (3) secured by that person so that no one can tamper with it, or (4) secured by that person in an area that is restricted to authorized personnel.

1. Sample Labels.- Sample labels are necessary to prevent the misidentification of samples. Labels or tags with identification written in waterproof ink is appropriate. The label should include the following information:
   - Sample number
   - Date and time of collection
   - Location of collection point

2. Field Log Sheets and Field Log Book. Field log sheets or log book are necessary to record enough information that someone can reconstruct the sampling without reliance on the collector's memory. The log sheets or log book should contain the following information for completeness of the sampling situation:
   - Project name
   - Purpose of sampling
   - Sample number
   - Location of sampling point
   - Type of sample (sludge, water, etc.)
   - Quantity of sample taken
   - Description of sampling point and sampling methodology
   - Date and time of collection
   - Name(s) of collector(s)
   - Signature(s) of person(s) responsible for sampling or observations written in the log sheets/book.

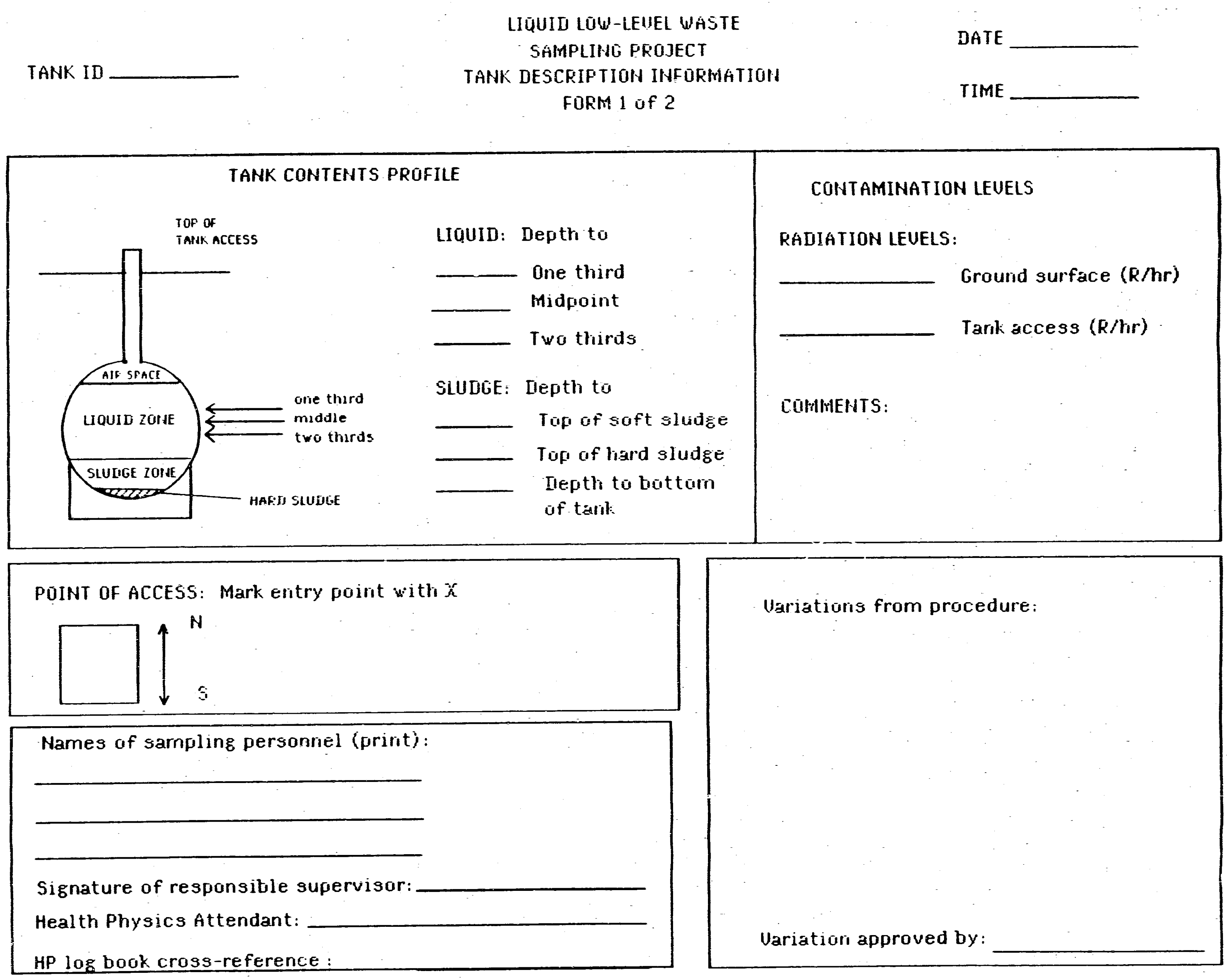
Examples of the field log sheets are provided in Figs. 6-1 and 6-2.

3. Chain-of-Custody. The chain-of-custody form should accompany the sample to the analytical laboratory (See Fig. 6-3).

Custody is then relinquished to the laboratory custodian who signs for acceptance of the sample(s). When the sample is relinquished, that person should sign the chain-of-custody form and indicate the date and time custody was relinquished. The person receiving custody of the sample should provide a signature, date, time, department, building, and phone number on the chain-of -custody form. This procedure should be repeated each time the sample custody changes through the time that the sample is received and signed for by the analytical laboratory.

The chain-of-custody record should include the following:
- Sample number
- Signature(s) of collector(s)
- Date and time of collection
- Place and location of collection
- Sample type
- Signature(s) of person(s) involved in the chain of possession.

4. The samples should be delivered to the analytical laboratory for analysis as soon as practicable after collection. The samples must be accompanied by the chain-of-custody



LIQUID LOW-LEVEL WASTE
SAMPLING PROJECT
TANK DESCRIPTION INFORMATION
FORM 1 of 2

TANK ID ________

DATE ________

TIME ________

TANK CONTENTS PROFILE

LIQUID: Depth to

________ One third

________ Midpoint

________ Two thirds

SLUDGE: Depth to

________ Top of soft sludge

________ Top of hard sludge

________ Depth to bottom of tank

CONTAMINATION LEVELS

RADIATION LEVELS:

________ Ground surface (R/hr)

________ Tank access (R/hr)

COMMENTS:

POINT OF ACCESS: Mark entry point with X

Names of sampling personnel (print):

____

____

____

Signature of responsible supervisor: ________

Health Physics Attendant: ________

HP log book cross-reference :

Variations from procedure:

Variation approved by: ________

Figure 6-1. Example of field log sheets.

LIQUID LOW-LEVEL WASTE
SAMPLING PROJECT
FIELD DATA LOG SHEET
Form 2 of 2

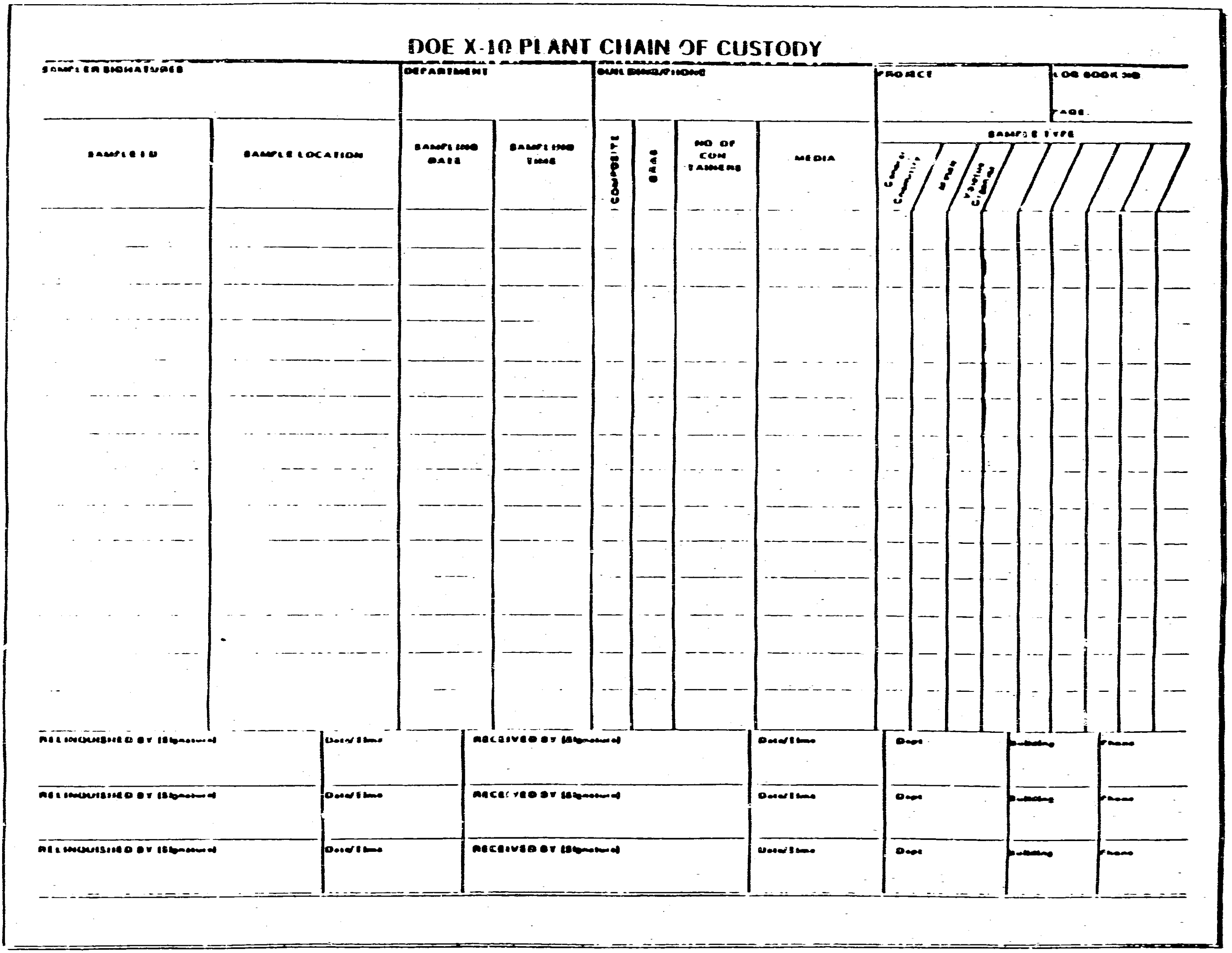
TANK ID ______________

DATE ______________

SAMPLE ID	SAMPLE TYPE (liquid, soft sludge, air-liquid interface, organic, hard sludge or duplicate)	SAMPLING POINT, DEPTH (ft)	RAD LEVEL (R/hr)	DEPTH OF SOLIDS OR ORGANIC LAYER IN SAMPLER, FT	REMARKS
1)					
2)					
3)					
4)					
5)					
6)					
7)					
8)					
9)					
10)					
11)					
12)					

Immiscible (i.e. organic) liquid layer present ________(yes) ________(no)

Figure 6-2. Example of field log sheets.



DOE X-10 PLANT CHAIN OF CUSTODY

SAMPLER SIGNATURES		DEPARTMENT		BUILDING/PHONE				PROJECT	LOG BOOK NO PAGE
SAMPLE I D	SAMPLE LOCATION	SAMPLING DATE	SAMPLING TIME	COMPOSITE	GRAB	NO OF CON TAINERS	MEDIA	SAMPLE TYPE General Chemistry Metals Volatile Organics	

RELINQUISHED BY (Signature)	Date/Time	RECEIVED BY (Signature)	Date/Time	Dept	Building	Phone
RELINQUISHED BY (Signature)	Date/Time	RECEIVED BY (Signature)	Date/Time	Dept	Building	Phone
RELINQUISHED BY (Signature)	Date/Time	RECEIVED BY (Signature)	Date/Time	Dept	Building	Phone

Figure 6-3. The chain-of-custody form.

record. The samples must be delivered to the person in the laboratory authorized to receive the samples. Custody must be relinquished to the custodian who must sign for acceptance of the samples. Once the sample has been accepted at the laboratory, standard laboratory chain-of-custody procedures will be followed. The completed chain-of-custody forms should be returned to the Task Leader with a xerox copy to J.J. Ferrada.

5. Archive samples should be delivered to the storage area. Initially the northeast cell of the east cell bank in Bldg. 3503 will be used to store samples. The long-term archive plan is to use the east pipe tunnel of Bldg. 3019 for storing samples. The samples must be delivered to the person in the Engineering Development Section of the Chemical Technology Division authorized to receive the samples. J. B. Berry (or designated alternate) should be notified in advance that samples are ready to be archived. Custody must be relinquished to the custodian who must sign for acceptance of the samples. Once the sample has been accepted at the archive, the sample custodian for the Engineering Development Section will maintain the chain-of-custody. The completed chain-of-custody forms should be returned to the Task Leader with a xerox copy to J. J. Ferrada.

Procedure SC-007 Organic Layer Sampling Procedure

The organic layer sampling is in two parts: (1) to determine if an organic layer is present and if so the depth of the layer, and (2) if an organic layer is detected a larger sample of the organic phase is collected using a specially designed organic layer sampler. Information about the location of the air-liquid interface will be available from the presampling survey. If an organic layer which is several inches thick is present, information about the organic-aqueous interface may be available from the presampling survey.

1. Take a vertical "core" of liquid at the air-liquid interface using the bottom opening soft sludge sampler to check for the possible presence of an organic layer above the aqueous layer and to estimate the depth of the organic phase. Refer to Procedure SC-003 for details of the mechanical operation of the sampler. Submerge the soft sludge sampler, opened at the bottom, until the bottom is approximately 8 inches below the liquid surface. If an organic layer more than 4 inches thick is suspected, submerge the sampler until the bottom is approximately 5 inches below the organic-aqueous interface and not more than about 15 inches below the air-liquid interface. Seal the bottom of the sampling tube. Raise the soft sludge sampler to the surface. Visually inspect the sample for the presence of immiscible phases. If an immiscible (i.e. organic) layer is observed on top the aqueous phase proceed with step 2 of this procedure. If no immiscible phase is present return the sampler to the tank at the same point where it was pulled, release the liquid, and proceed with sampling the sludge as described in Procedure SC-001, step 11, and Procedure SC-003.

2. If an organic phase is present wipe the outside of the soft sludge sampler tube, put the Allen screw back in position, remove the handle, and cap the top of the sampler tube.

3. Place the sampler tube in the prelabeled plastic bag and tape the bag closed. Insert the wrapped sample tube into the second plastic bag and tape the outer bag closed. Then place it into the prelabeled can, and put it into the shielded transport carrier.

4. Collect a second (larger) sample of the organic phase using the special organic sampler. This is a PVC tube with a sealed bottom and a lateral tube for liquid intake near the top (see Fig. 7-1). The handle of the sampler is the same as is used with the soft sludge sampler. Premeasure and mark the handle with tape the appropriate distance for the lateral tube to reach the liquid organic surface. Remove the cap from the lateral tube and the Allen screw from the side. Label the plastic bags and the can which will be used to package the sample.

5. Lower the sampler until the lateral tube reaches the liquid surface. Hold the sampler in that position for 30 seconds to assure that the sampler has filled with liquid.

6. After the time has elapsed, carefully remove the sampler from the tank, maintaining the sampler in the vertical position. Cap the lateral tube with a 1-inch NPT pipe cap and wipe the sampler down as it is removed from the tank.

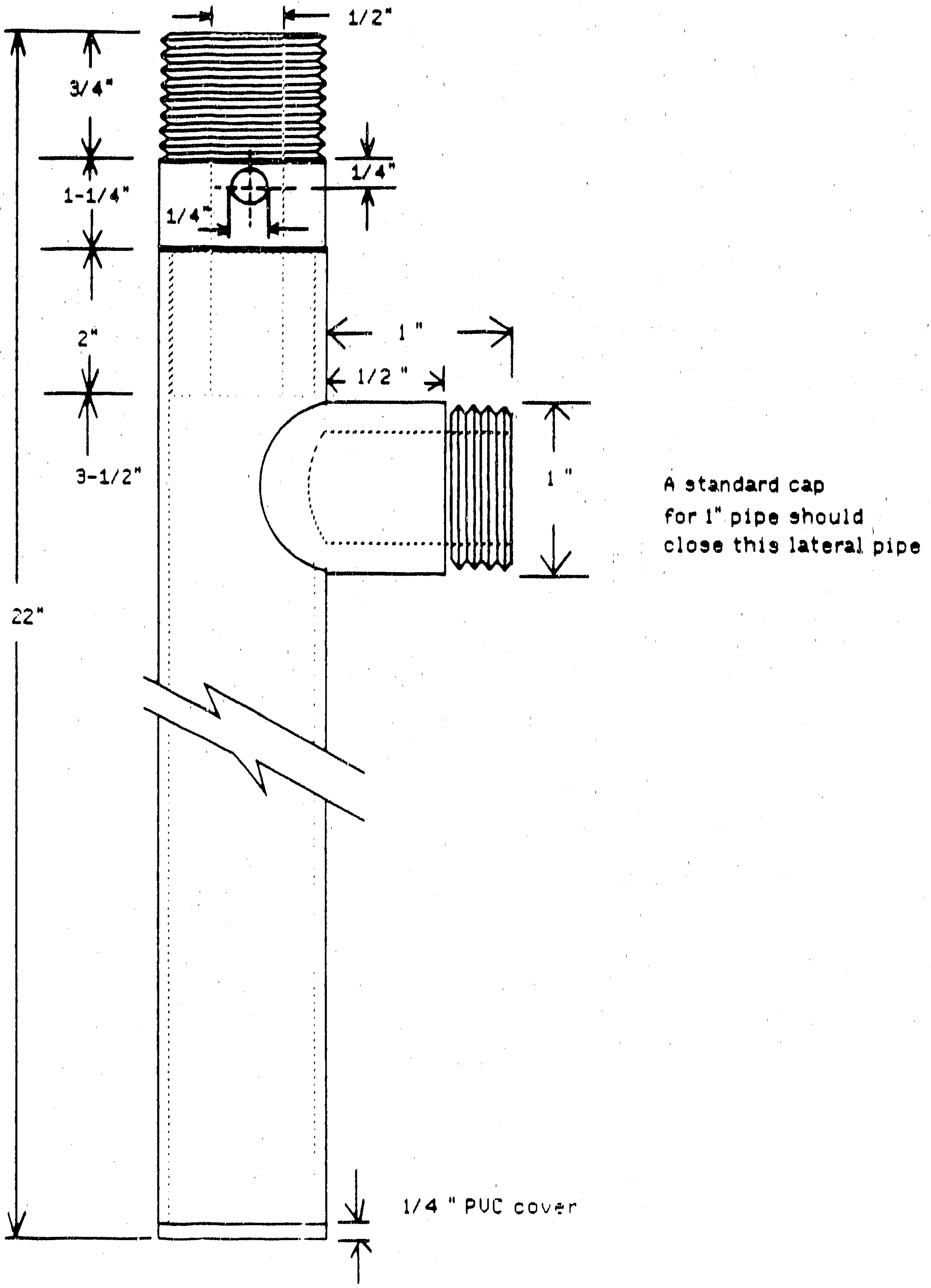


Figure 7-1. Organic layer sampler.

7. Unscrew the sample collection tube from the handle. Place a 1-inch NPT pipe cap on the top of the collection tube, and replace the Allen screw in the side of the collection tube.

8. Place the sample collection tube in the prelabeled plastic bag and tape the bag closed. Insert the wrapped sample tube into the second plastic bag and tape the outer bag closed. Then place it into the labeled can, and put it into the shielded transport carrier.

9. If the height of the organic phase is less than one third of the length of the organic sampler tube, take a second sample.

10. Decontaminate the handle as described in Procedure SC-005, Decontamination of Sampling Equipment.

Procedure SC-008 Archive for Liquid Low-Level Waste Samples

After the planned analyses have been completed, the residual sample may be stored for use later in experiments to develop methods for processing the wastes for disposal. Duplicate samples from the field or portions of samples which have been divided at the analytical laboratory may also be archived so that additional analyses can be performed if needed.

The northeast cell of the east cell bank in Bldg. 3503 will be used to store samples initially. The long-term archive plan is the use the east pipe tunnel of Bldg. 3019 as the storage area. This area is being prepared for use. When the east pipe tunnel of Bldg. 3019 is ready for sample storage, all samples will be transferred from Bldg. 3503, and Bldg. 3503 will no longer be used for sample storage.

The samples will be in glass jars, which are placed in plastic bags and the bags sealed with tape. The jar will be labeled with the sample number, the identification code of the tank sampled, and the date collected. Each sample will then be placed in a lead pig, which should be marked with the sample number and date collected on the outside of the pig. The HP tag should be attached to the lead pig. Each pig should be sealed with a custody seal which must be broken to open the pig. The lid of the lead pig should have a wire handle.

The archive custodian (J. B. Berry or designated alternate) for the Engineering Development Section of the Chemical Technology Division is responsible for the sample archive. The custodian should be notified in advance when samples are ready to be archived.

An inventory of stored samples will be maintained and posted outside the storage area. An inspection of the storage area will be conducted at least once a year. A new chain-of-custody seal should be used with the initials of the inspector and the date of inspection marked on the seal if a lead pig is opened.

Health Physics personnel will monitor the transfer of samples and Health Physics procedures for radiation protection will be followed.

APPENDIX F

PROCEDURE FOR SAMPLING TANKS W-29 AND W-30 USING THE PUMP MODULE (ISOLOCK) SAMPLER

INTRODUCTION

The procedure for sampling tanks W-29 and W-30 using the pump module (Isolock) sampler follows in this appendix as the procedure was written. The sampler operated slower than expected which was probably because of corrosion. It was necessary to change some of the switch settings to increase the speed of the sampler.

SAMPLING FOR WASTE CHARACTERIZATION

PROCEDURE FOR SAMPLING TANKS W-29 AND W-30 USING THE PUMP MODULE (ISOLOCK) SAMPLER

Approved by:

CBScott 11/13/89

C. B. Scott Date
Liquid and Gaseous
Waste Operations Group Leader

RC Mason 11/10/89

R. C. Mason, Task Leader Date
Waste Characterization

CH Brown, Jr. 11/14/89

C. H. Brown, Program Manager Date
Liquid Low-Level Waste Solidification

ME Baldwin 11-13-89

M. E. Baldwin, Safety Officer Date
Environmental and Health Protection Division

Procedure SC-009 Procedure for Sampling Tanks W-29 and W-30 Using the Pump Module (Isolock) Sampler

Tanks W-29 and W-30 were modified during the construction of the Emergency Avoidance Solidification Campaign (EASC) processing equipment. The penetrations used to house the mechanical level instrumentation were used for the pump module suction legs. Along with the suction legs, pneumatic tubing was put into the tank and tied into instrumentation used to give level readouts. Since it is not possible to gain access through these penetrations and sample the tanks as per Procedure SC-001, General Sampling Procedure for Liquid Low-Level Waste Storage Tanks," the "Isolock" sampler housed in the EASC pump module will be used to pull the supernatant samples from W-29 and W-30. Sludge samples will not be pulled from these tanks. The sampling is to be conducted by operators familiar with the EASC processing equipment and certified on same.

1. General Requirements and Presampling

a. A Radiation Work Permit (RWP) is required for sampling any of the waste storage tanks. Sampling is to be conducted by trained chemical operators in protective clothing as specified on the radiation work permit. Sampling activities shall be continuously monitored by radiation protection personnel. Air sampling is required. Electrical power (110 V) should be provided at the site to operate the radiation protection air sampler. There shall be no sampling operations if the temperature is below 35°F inside the building which houses the pump module.

Extremity dosimeters (finger rings) are required for all employees that directly handle the filled sample containers. All exposures of the employees involved in this task should be kept segregated from their overall exposures from day-to-day activities (by use of recording pocket meter readings) so that the overall exposure information can be further utilized in future waste tank projects.

The sampling crew shall have training in handling low level, TRU, and mixed wastes, in the use of respirators, and in the project specific procedures.

b. Absorbent material shall be placed beneath the sampler in the sampler box to contain any drips or small spills. Try to avoid contaminating the drain in the sampler box. Do not install anything which might block or plug the drain. The drain must be open since it serves as both the ventilation vent for the sampler compartment and an emergency drain in case of a spill. Absorbent paper and plastic sheeting as appropriate shall be placed in the work area adjacent to the sampler compartment to confine the radioactive materials and prevent contact with the floor and other clean surfaces. Waste rags and materials used to wipe down equipment should be placed in a plastic bag. Spill containment and clean-up materials shall be maintained and readily available within the work area.

c. The glass "Mason" jars used with the pump module sampler must be cleaned and allowed to dry prior to use per Procedure SC-005, "Decontamination of Sampling Equipment Procedure." The jars for the pump module sampler are too large to put into a standard lead pig and do not have EPA approved caps. Therefore, immediately after the sample is collected it will be transferred to a 250-mL, wide-mouth I-Chem jar. This transfer is made inside the sampler compartment which is at a small negative pressure with respect to the atmosphere and has an emergency drain. Precleaned I-Chem jars with Teflon-lined lids will be provided.

d. Labels should be attached to the I-Chem sample jar and the lead pig before the sample is collected. Preprinted labels will be provided by J. J. Ferrada.

e. Care should be taken to keep the samples upright during handling and transport.

2. Preoperational Facilities Preparation

Note: Before the pump module is used, pertinent sections of Section 4, "Procedures for Preoperational Facilities Preparation," of WM-HRWO-601R1, Operating Procedures for the Emergency Avoidance Solidification Campaign, should be accomplished. These sections are as follows:

4.1 Start-up and Balancing of Solidification Building HVAC
4.2 Balancing of Pump Module Ventilation
4.3 Pressurization of Transfer Piping Annulus
4.4 Calibration of Tanks W-29 and W-30 Level Indicators
4.9 Preoperational Checkout of Safety Systems

Also, it should be assured that a positive blockage (i.e., blind flange, pancake, etc.) exits in the system after HCV 1002 to assure no contaminated liquid exits P-1003 -1"-146 into the solidification building.

After the pertinent parts of checksheet EASC-4.0 are filled out, the procedures below should be followed.

3. Set Up Sampler as Follows

In sampler control box, set up switch 1TR (cycle extend) switches so that 1 and 2 are "on." The rest of the switches (4, 8, 16, 32, 64, 128, 256, 512) should be in the "off" mode. This will give a cycle extend stroke time of 3 seconds. In the same box, set up switch 2TR (cycle retract) switches so that 1, 4, and 8 are "on" and the rest of the switches are "off." This setup will give a 25 mL sample every 15 seconds, or 100 mL per minute.

4. Performing Necessary Valving at the Pump Module

Note: It should be ascertained, from previous operational records, that all valves at the pump module are closed before these procedures are started. Source of prime water will also be tied into the quick disconnect connection at HV-38.

a. Open valve HV-29 (W-29) or HV-30 (W-30), depending upon which tank is to be sampled. These are the suction valves for transfer pump J-01.

b. Open HV-28, air supply to transfer pump.

c. Open HV-31 (W-30) or HV-32 (W-29), return line to the tank not being sampled.

5. <u>In Building 7877</u>

   a. Assure Programmable Logic Controller (PLC) is working properly

   b. Assure all alarms are cleared

   c. Push MMES "transfer ready" button

   d. Short wires together to give vendor "transfer ready" indication

   e. Switch pump controller to "local"

6. <u>At Pump Module</u>

   a. Open the door of the sampler compartment. Have the HP check with a smoke tube that there is an inflow of air to the sampler compartment.

   b. Attach a precleaned, 1-pint sample collection jar to sampler.

   c. Start pump. Read the background on the piping to/from W-29 and W-30 to ascertain fluid transfer. If the pump has not picked up, prime it by opening valves HV-38 and HV-36. After priming close valves HV-36 and HV-38.

   d. After it is ascertained that fluid is being circulated, wait 2 minutes and switch the sampler control switch to "auto." Wait until the proper amount of sample is collected (100 mL/minute). Turn the sampler to "off" position, and shut down pump J-01. Open the sampler door. Carefully unscrew the sample collection jar from the sampler, and pour the sample into a prelabeled, 250-mL, wide-mouth I-Chem jar. Seal the I-Chem jar. Make this transfer inside the sampler compartment. Place wipes in a plastic bag. Use only lint-free wipes to wipe the nozzle of the sampler.

   e. After a liquid sample has been taken, prepare the sample as follows:

      Wipe off the exterior of the sample jar to remove any spilled liquid or possible contamination.

      Place the jar in plastic bag(s) and close the bag with tape. Have the HP measure the radiation level of the unshielded sample. Place the wrapped sample in a lead pig. Label the container with information on the radiation level. The lid of the lead pig should have a wire handle.

      Record sample data on page 2 of the field data collection form (see Attachment).

   f. Collect three more samples by repeating the above process. Use a clean collection jar for each sample.

g. After sampling the tank is complete, flush the module piping with water by doing the following:

Open HV-38
Open HV-36
Flush for 30 seconds
Close HV-36
Open HV-34
Flush for 30 seconds
Close HV-34
Close HV-38
Close HV-29 (HV-30)
Close HV-31 (HV-32)

h. Perform the necessary valving per step 4 to sample the other tank.

i. Before sampling the next tank, let the pump circulate waste for 1 hour 20 minutes before activating the sampler.

j. Collect four samples from the second tank.

k. After the sampling of the second tank is complete, flush the module piping per step 6g.

When the module flush is completed after the second flush, open following valves on the module to drain it completely:

HV-29
HV-30
HV-31
HV-32
HV-33
HV-34
HV-36

Let drain for 5 minutes.

l. Close all valves.

m. Disconnect the prime water source.

7. Waste Management

Package the waste, tag it with the HP tag, and dispose of the waste per the Waste Management Plan.

8. Sample Handling

a. Fill out documentation. See Attachment for the field log forms. Record on the field log sheet under comments that the pump module sampler was used. Complete the chain-of-custody form (Procedure SC-006, "Sampling Custody").

b. Seal the lead pigs with tape for transport.

c. Have the HP monitor the radiation level and tag with the "HP" tag (Radiation Hazard Materials Transfer Tag). If the radiation level at the surface of the pig is 100 mrem/h or less, the sample will be transported in the pig.

In the event that the radiation level at the outer surface of the pig should exceed 100 mrem/h, place the pig in a paint can with crumpled plastic for padding and then into the stainless steel transport carrier.

d. Three samples from each tank -- the first, second, and fourth samples collected -- are to be analyzed. Deliver these samples, with the HP tags, the chain-of-custody forms (Procedure SC-006, "Sampling Custody") and the Request for Analytical Services form to the sample custodian or designated alternate authorized to receive samples for Inorganic and Physical Analysis, at the High Radiation Level Analytical Laboratory (Bldg. 2026). All samples collected should be delivered the same day before 3:00 p.m.

e. One sample from each tank -- the third sample collected -- is to be archived. Attach a chain-of-custody seal over/across the tape which seals the pig. Either a preprinted label initialed and dated by the sample collector or a signed custody seal may be used. Deliver the archive samples, with the HP tags and the chain-of-custody form to J. B. Berry, or designated alternate, at Bldg. 3503. Contact J. B. Berry or designated alternate in advance so that arrangements can be made.

9. Post-operational Steps

a. Remove the jumpered condition applied in Step 5d.

b. Verify equipment is returned to shutdown status.

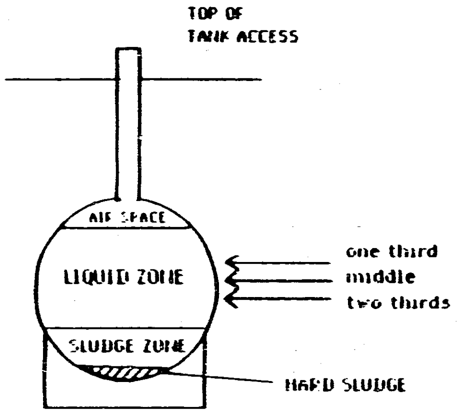
TANK ID ____________

LIQUID LOW-LEVEL WASTE
SAMPLING PROJECT
TANK DESCRIPTION INFORMATION
FORM 1 of 2

DATE ____________

TIME ____________

TANK CONTENTS PROFILE



LIQUID: Depth to

_______ One third

_______ Midpoint

_______ Two thirds

SLUDGE: Depth to

_______ Top of soft sludge

_______ Top of hard sludge

_______ Depth to bottom of tank

CONTAMINATION LEVELS

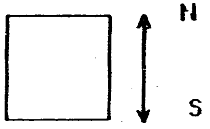
RADIATION LEVELS:

_____________ Ground surface (R/hr)

_____________ Tank access (R/hr)

COMMENTS:

POINT OF ACCESS: Mark entry point with X



Names of sampling personnel (print):

____

____

____

Signature of responsible supervisor: ____________________

Health Physics Attendant: ____________________

HP log book cross-reference :

Variations from procedure:

Variation approved by: ______________

LIQUID LOW-LEVEL WASTE
SAMPLING PROJECT
FIELD DATA LOG SHEET
Form 2 of 2

TANK ID ________

DATE ________

SAMPLE ID	SAMPLE TYPE (liquid, soft sludge, air-liquid interface, organic, hard sludge or duplicate)	SAMPLING POINT, DEPTH (ft)	RAD LEVEL (R/hr)	DEPTH OF SOLIDS OR ORGANIC LAYER IN SAMPLER, FT	REMARKS
1)					
2)					
3)					
4)					
5)					
6)					
7)					
8)					
9)					
10)					
11)					
12)					

Immiscible (i.e. organic) liquid layer present ________(yes) ________(no)

END

DATE FILMED

11 / 14 / 90