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Accession #: D196007941

Document #: SD-WM-TI-723

Title/Desc:

SAMPLE EXCHANGE & EVALUATION [SEE] REPORT PHASE
III

Pages: 113

JAN 19 1996

ENGINEERING DATA TRANSMITTAL

Page 1 of 1
1. EDT **No 614772**

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Inorganic Chemistry,	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: SEE/Waste Management/Inorganic Chemistry/Analytical Services	6. Cog. Engr.: William (Bill) Winters	7. Purchase Order No.: N/A
8. Originator Remarks: This document is being released into the supporting document system for retrievability purposes.		9. Equip./Component No.: N/A
11. Receiver Remarks: For release		10. System/Bldg./Facility: N/A
		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: 01-18-96

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	WHC-SD-WM-TI-723	N/A	0	Sample Exchange/Evaluation (SEE) Report - Phase III	N/A	2	1	1

16. KEY									
Approval Designator (F)		Reason for Transmittal (G)				Disposition (H) & (I)			
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)		1. Approval 2. Release 3. Information		4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)		1. Approved 2. Approved w/comment 3. Disapproved w/comment		4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged	
(G)	(H)	17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)						(G)	(H)
Reason	Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN
2	1	Cog.Eng.William (Bill) Winters	<i>[Signature]</i>	1/18/96					
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		QA							
		Safety							
18.		Env.	19.		20.		21. DOE APPROVAL (if required) Ctrl. No.		
Lola B. Webb <i>[Signature]</i> Signature of EDT Originator		N/A Authorized Representative Date for Receiving Organization		Thomas H. Bushaw <i>[Signature]</i> Cognizant Manager Date		☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments			

SAMPLE EXCHANGE/EVALUATION (SEE) REPORT - PHASE III.

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U.S. Department of Energy Contract DE-AC06-87RL10930

EDT/ECN: EDT-614772 UC: 2070
Org Code: 75763 Charge Code: N4K1B
B&R Code: EW 3120074 Total Pages: 109110 1/18/96 KMA

Key Words: SEE Program Phase III, Sample Exchange/Evaluation

Abstract: N/A

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WHC-SD-WM-TI-723 Rev. 0

SAMPLE EXCHANGE/ EVALUATION (SEE) REPORT - PHASE III

October 13, 1995

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EXECUTIVE SUMMARY

This report describes the results from Phase III of the Sample Exchange Evaluation (SEE) program. The SEE program is a joint effort of Westinghouse Hanford Company, Analytical Services (AS), and Pacific Northwest National Laboratory's Analytical Chemistry Laboratory (ACL), to compare analytical laboratory performance on samples from the Hanford Site's high level waste tanks. Phase I of the SEE program compared radiochemical results on prepared extracts from two waste tanks, B-111, and T-107. In Phase II, the program was expanded to include inorganic constituents in addition to radionuclides on prepared extracts of waste from tanks C-112 and B-201. Phase III of the SEE program was designed to compare laboratory performance for inorganic and radiochemical measurements including sample preparations such as, acid digestion, water leaching, and fusions. Results from Phase III that exceeded a 20% relative percent difference (RPD) criteria are identified in Table ES-1.

A composite of three archived segments from core 4 of tank B-110 was prepared by the ACL. The ACL homogenized the composited material until the reproducibility for most of the metals determined by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) were less than 10%. The composite was then split and a portion sent to ACL and the 222-S Laboratory. The laboratories performed four replicates for each type of sample preparation (acid digestion, water leach and fusion) and analyzed these solutions for the appropriate metals, anions and radionuclides. The laboratories also carried out several tests in quadruplicate on direct solid aliquots of the composited material as illustrated in

Table ES-2. Control standards, provided by the 222-S Standards Laboratory, were analyzed in duplicate along with the samples. Data from the analyses were submitted to the Analytical Services statistics group for evaluation.

Phase III of the SEE program identified three major areas of concern:

- 1) Differences in the ion chromatography anion results indicate that differences in the water leach procedure may exist.

Corrective Action: Continue to monitor the water leach procedure in the SEE program. Evaluate and document the technical basis for the water leach procedure.

- 2) Differences continue to be observed for total inorganic carbon and total organic carbon results.

Corrective Action: Continue to monitor the TIC/TOC hot persulfate oxidation procedure. Reexamine both laboratory procedures for areas that may lead to the observed differences.

- 3) Differences continue to be observed in total alpha results. 222-S Laboratory total alpha procedure potentially produces low results and should be modified to control the amount of self absorption from solids and permit measurement of total alpha at 100 nCi/g levels.

Corrective Action: 222-S Laboratory should establish the solids limits

from fusions for their mounting method and/or implement new mounting and counting procedures.

Other differences that were observed in the data, but are not considered as significant are:

- 1) Trace metal results from the ICP/AES analysis of acid digestions exceed the 20% RPD criteria but in most cases the metals are near the detection limit for at least one laboratory. Silicon results for the acid digestion are significantly different but silicon is normally measured on the fused sample where it is more reproducible. Differences in the ICP/AES fusion sodium results were near the 20% RPD criteria and greater than observed in Phase II.
- 2) Cyanide results were significantly different. However, the cyanide concentration was very low and the laboratories used different preparation methods.
- 3) A difference was observed in differential scanning calorimetry (DSC) results for the major endotherm on the sample. Results for the DSC standard material indicated that the laboratories produced comparable results. Continued monitoring in the SEE program is recommended.
- 4) The difference in total beta results were slightly greater than 20% RPD. The 222-S Laboratory has changed the efficiency basis for its total beta determination

to Cs-137 which should make the results more comparable to the SrY-90 efficiency used by ACL. Differences may be associated with solid absorption effects on 222-S Laboratory beta mounts. Continued monitoring of the total beta procedures in the SEE program is recommended.

- 5) The results for Sr-90 determination exceeded the 20% RPD SEE criteria. The relative standard deviation (RSD) for the replicate results for each laboratory were reasonably large indicating potential sample heterogeneity effects. Even though the RPD criteria was exceeded the difference in the mean results between laboratories was not statistically significant.
- 6) Standard recovery results for Tc-99 were poor and significantly different for both laboratories. This large of difference for Tc-99 standards was not observed in Phases I and II. The reason for the difference has not been identified. Continued monitoring of Tc-99 in the SEE program is recommended.
- 7) The RPD for the Am-241 results exceeded the 20% criteria but the Am-241 was low and the counting uncertainties were large. This is reasonable agreement considering the Am-241 concentration and that ACL used GEA and 222-S Laboratory used alpha counting for the determination.

Several areas identified in Phase I and II of the SEE program have been addressed in Phase III. Problems with the 222-S Laboratory alpha counting instrumentation that resulted in high

total alpha results has been corrected. However, this could not be confirmed in Phase III because of the new problem from solids on the mount causing low alpha results. The 222-S Laboratory changed the efficiency basis for total beta in January 1995 to ^{137}Cs making the total beta results more comparable in Phase III. The 222-S Laboratory has implemented a new total uranium method that showed reproducibility comparable to that observed for ACL. Concerns raised in Phase II about the ion chromatography fluoride results were evaluated in Phase III by analyzing the sample at ACL with an independent method, ion selective electrode (ISE). Phase III fluoride data from ACL showed that for the B-110 matrix that the ISE and IC produced comparable fluoride results. Further evaluation of the ISE fluoride method on other waste matrices should be considered in the SEE program.

Conclusion:

Except for the water leach preparation, the Phase III data indicate that the sample preparation methods used by the laboratories are comparable. Unexplained differences are still being observed on the TIC/TOC results even when the laboratories use methods based on the same principles. The 222-S Laboratory continues to have problems producing accurate total alpha results for samples containing low levels of alpha activity in high levels of salts and beta/gamma activity. Except for the ^{99}Tc results in Phase III, which may be an anomaly, standards data from all Phases of SEE indicate that the analytical measurement procedures used after sample preparation are comparable. Definitive explanations for some of the observed differences are not possible with the limited amount of data available. Continued monitoring of laboratory performance through the SEE program will provide a better data base for accurately identifying problems and solutions. It is recommended that Phase IV of the SEE program initiate transitioning of the program to a regular referee program. In the

referee program the Tank Waste Remediation System (TWRS) Characterization organization should identify waste samples and analytes that will be monitored by analysis from a second laboratory. The TWRS Characterization Program should work with the Office of Quality Assessment in the selection of waste types and analytes to ensure that the referee program collects sufficient data for all the applicable measurements. The goal of the referee program would be to collect more data for comparison on key analytes from a wider variety of waste types.

Table ES-1. Summary of Analytes with RPD Greater than 20%.

Analyte	RPD	Explanation
Ag (Acid)	22.8%	Concentration only 2 times the detection limit (IDL).
B (Acid)	54.2%	Concentration only 3 times the detection limit (IDL).
Cu (Acid)	20.2%	Concentration only 2 times the detection limit (IDL)
Ni (Acid)	20.4%	Concentration is at detection limit (IDL).
Si (Acid)	146.1%	Possible digestion difference or contamination. Silicon normally determined on fused sample.
Zn (Acid)	41.2%	Possible contamination or ICP/AES interelement correction differences.
Fluoride (Water)	36.9%	Possible water leaching method difference
Phosphate (Water)	45.0%	Possible water leaching method difference
Sulfate (Water)	27.3%	Possible water leaching method difference
Cyanide (Direct)	Not calculable	Possible sample preparation procedure difference
TIC (Direct)	82.5%	Unexplained difference
TOC (Direct)	109.7%	Unexplained difference
TC (Direct)	75%	Unexplained difference
DSC (Direct) Endothermic	55.3%	Possible difference in baseline selection and integration of water endothermic region
Total Alpha (Fusion)	90.2%	Solids absorption effects for 222-S Laboratory mounting procedure
Total Beta (Fusion)	21.2%	Possible solids absorption effect for 222-S Lab
Strontium -90 (Fusion)	34.7%	Possible sample heterogeneity effect. Relatively large RSDs for replicates at each lab.
⁹⁹ Tc (Standard)	194%	Unexplained difference
²⁴¹ Am (Fusion)	26.6%	Low concentration with relatively large counting uncertainty (19%).

Note: The 20% SEE criteria is not applicable to analytes with concentrations less than 5 times the method detection limit or with counting errors greater than 15%.

Table ES-2. Phase III Sample Analysis Design.

Sample Preparation Method Comparison			
Direct	Water Leach	Acid Digestion	Fusion
CVAA (Hg)	IC-Anions	ICP Metals	GEA
TOC/TIC/TC	Fluoride by ISE		Total Alpha
Cyanide			Total Beta
DSC/TGA			^{239/240} Pu
			⁹⁰ Sr
			⁹⁹ Tc
			Total Uranium
			ICP Metals

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LIST OF TERMS

222-S	222-S Laboratory, (WHC)
ACL	Analytical Chemistry Laboratory, (Pacific Northwest National Laboratory)
AS	Analytical Services, (WHC)
CLP	Contract Laboratory Program (EPA)
CVAA	cold vapor atomic absorption
DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
GEA	gamma energy analysis
HEDTA	hydroxylethylethylenediaminetriacetic acid
IC	ion chromatography
ICP/AES	inductively coupled plasma atomic emission spectroscopy
ISE	ion selective electrode
KPA	kinetic phosphorescent analyzer
RPD	relative percent difference
RSD	relative standard deviation
SEE	Sample Exchange/Evaluation
SD	standard deviation
TC	total carbon
TGA	thermal gravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
WHC	Westinghouse Hanford Company

SAMPLE EXCHANGE/EVALUATION (SEE) REPORT - PHASE III

1.0 INTRODUCTION

The sample exchange/evaluation (SEE) program is a joint effort of Westinghouse Hanford Company (WHC), Analytical Services (AS) and the Pacific Northwest National Laboratory, Analytical Chemistry Laboratory (ACL), to compare analytical laboratory performance on sample materials unique to the Hanford Site. The program is currently managed by the WHC Office of Quality Assessment. The laboratories that participated in Phase III of the SEE program were the Northwest Laboratory's ACL and the WHC 222-S Laboratory.

The SEE program is designed to evaluate all the major measurement systems that are common to the participating laboratories. The objective of the SEE program is to understand the variances associated with analytical processes used to provide data in support of Hanford Site initiatives. This is best accomplished by the regular exchange of Hanford sample materials. The program is being implemented in phases in which each new phase includes:

- Tests to evaluate lessons learned in previous phases
- Additional analytical systems
- Increased complexity (evaluation of subsampling and sample preparation in addition to measurements) in the analytical system being evaluated
- Evaluation of different types of waste materials.

The SEE program is currently focused on evaluating laboratory performance and comparability in the analysis of high level waste tank samples at the Hanford Site.

Phase I of the program, whose results were reported in PNL-9385 (PNL 1993), focused on the comparison of radiochemical measurements on homogenous liquid samples prepared by fusion dissolution of waste samples from two waste tanks (Tank B-111 and Tank T-107). Phase II of the program was expanded to include the following for two additional tanks, Tank C-112 and Tank B-201. Phase II results are reported in WHC-SD-WM-TI-666 (WHC 1994).

- Analysis of metals in homogenous liquids prepared by both potassium hydroxide (KOH) fusion and acid digestion.
- Analysis of anions, tritium and total organic carbon (TOC) and inorganic carbon (TIC) by water leaching.
- Analysis of radionuclides prepared by fusion as in Phase I

This report documents the results from Phase III of the SEE program. Phase III of the program was further expanded to evaluate and compare the sample preparation procedures for the two laboratories. This is the first time that a solid waste sample was split and analyzed by both laboratories. A single waste tank sample was analyzed for the majority of those analytes tested in Phase II. In addition, measurements that are normally applied directly to solid samples such as mercury (Hg), total organic carbon/total inorganic carbon (TOC/TIC), cyanide, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA) were also evaluated.

2.0 SUMMARY OF PHASE III PLAN

The Phase III tank waste test material was prepared from archive samples from core 4 of tank B-110 that was sampled in September 1989. The waste from this tank had been previously analyzed in 1990. This material was chosen because there was insufficient quantities of recently sampled waste. The ACL prepared the test material by compositing 63.5 g of Archive 1 (segment 2), 29.2 g of Archive 2 (segment 3), and 84.1 g of Archive 3 (segment 4). Quantities taken were designed to maximize the amount of tank material available for testing. No attempt was made to quantitatively ratio the materials selected.

The composited sample was homogenized following technical procedure PNL-ALO-135 in a stainless steel container for 15 minutes using an OMNI¹ mixer equipped with a four blade rotor. Duplicate 3 g samples were taken from both the top and bottom of the composited sample to evaluate the homogenization process. These samples were analyzed for inductively coupled plasma atomic emission spectroscopy (ICP/AES) metals to determine if their concentrations were different at the two locations sampled. These data indicated that the sample was not adequately homogenized. The sample was homogenized again in its glass jar container using the rotor-stator attachment of the OMNI mixer. Resampling and analysis indicated that 18 of the 22 ICP analyte concentrations from two locations differed by less than 10%. The sample was labeled as 95-04043 and split into two portions: one for ACL and one for the 222-S Laboratory.

One of the major concerns in implementing Phase III was ensuring and maintaining the homogeneity of the test sample. If the sample is not homogenous, with respect to the analytes being tested, then it will not be possible to accurately compare the sample preparation and analytical methods. Drying of the sample during preparation and analysis was another factor that could affect the comparison of results. Duplicate samples of the composited sample were analyzed for weight percent solids according to gravimetric procedure PNL-ALO-504. The results of this analysis was 50.5 wt% solids or 49.5 wt% water assuming all of the weight loss was from water.

In addition to the test sample, the following standards were provided for the analytes of interest.

¹OMNI is a registered trademark of OMNI International Incorporated, Gainesville, VA.

- Wt% Water Standard - Book #42N8-A
- DTA Standard - Book #60N16-E
- Metal Standard - Book #19N14-A
- Anions -I (TIC/TOC) Standard - Book # 20N14-A
- Anions -II Standard - Book # 23N14-A
- Cyanide Standard - Book # 21N14-A
- SEE Mixed Isotope Standard - Book# 108B52

These aqueous standards were prepared and distributed by the 222-S Standards Laboratory. The standards provide a verification that the laboratory methods and calibrations are comparable and aid in identifying systematic errors in the procedures and laboratories.

The Phase III sample analysis plan is outlined in Figure 1. After ACL prepared homogenized sample material, the laboratories were requested to verify that the sample had not dried out by performing a wt% water measurement before subsampling for analysis. The gravimetric weight percent water results (46.3%) at the 222-S Laboratory indicated that the material may have lost 6 to 7% of the water from when it was initially prepared for shipment. There was insufficient sample to prepare an archive split for later verification of differences. Each lab was to perform each sample preparation (direct analysis, water leach, acid digest, and fusion) in quadruplicate. In addition to determining fluoride by ion chromatography (IC), the Northwest Laboratory was to perform the measurement by ion selective electrode (ISE) to verify the IC results. Each of the aqueous standards were to be analyzed in duplicate. Data were collected from each laboratory and submitted to the WHC statistics group for evaluation. When sufficient sample and time was available, reruns or additional testing was performed to verify and understand the reasons for differences.

The number of replicate preparations for sample analyses was four; the same as in Phase II. This permits a better statistical evaluation of the results. The replicates for the aqueous standards was reduced to two for Phase III. Based on Phase II this was adequate to evaluate differences between lab calibrations.

Even though the tank waste material was analyzed previously, the composited sample was unique and was distributed as a single blind sample (laboratories knew they were control tank waste samples, but did not know the concentrations or the specific tank).

3.0 DATA EVALUATION

The data from the laboratories were sent to the WHC statistical group for compilation and evaluation. The statistical report is provided in Appendix A. The relative percent difference

of the means is based on the following formula:

$$RPD = \frac{(222S - ACL)}{(222S + ACL)} \times 100 \quad (100)$$

Positive (+) RPD indicates 222-S Laboratory has the higher value.
Negative (-) RPD indicates ACL has the higher value.

Normally RPD is reported as an absolute number; however, in this report the sign may be retained to indicate the direction of the difference between the laboratories. No bias relative to a known or true value is implied.

Several criteria may be used to evaluate the data. The SEE program has established a fixed RPD value of 20%, that when exceeded requires further investigation. However, this 20% criteria is not applicable when the results are less than five times the detection limit or the counting error is greater than 15%. The statistical evaluation identifies results that have (1) statistically different means and/or (2) statistically different variances. When the data is found to be statistically different or exceed a fixed criteria, it must be examined further to determine the cause of the difference and to determine what action is required. Table 1 summarizes the data that exceeded either fixed and/or statistical criteria. The table also includes a category for data with RPD between 15 and 20% to ensure that tests with the potential of exceeding the criteria are also evaluated. Explanations for the differences are described in the following sections of this report.

More detailed comparison of the data are provided in the tables found in Appendix B for ICP/AES and cold vapor atomic absorption (CVAA) metals, wet chemical analyses, DSC/TGA, and radiochemical analyses. The mean, standard deviation (Std Dev) and relative standard deviation (RSD) from the analysis of the four samples are provided for both laboratories in these tables. This is followed by the relative percent difference (RPD) of the mean for the labs and an assessment of the results using:

- SEE criteria of RPD < 20% (Pass/Fail)
- Variance statistically significant (Var Sig)
- Mean statistically significant (Mean Sig).

Appendix C contains estimates of the detection limits and also the radiochemical counting uncertainties. The radiochemical counting uncertainties for the ACL contain both the counting error and the systematic error; whereas, the 222-S Laboratory values are based only on counting statistics. The radiochemical table (C-3) in Appendix C also contains ratios for (1) the total alpha to the sum of the Pu and Am result and (2) the total beta to the sum of the ^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$ results. The beta ratio has been adjusted for the ^{90}Y equilibrium but not for differences in the counting efficiencies used for total beta measurements. The beta efficiencies for $^{90}\text{Sr}/^{90}\text{Y}$ used at ACL and the ^{137}Cs used at 222-S Laboratory are close enough that adequate comparisons of the data without efficiency corrections should be possible.

The detection limits are based on method performance on optimum matrices and normal sample sizes. The ICP metal limits are estimates of the instrument detection limit. The detection limits in Appendix C will increase for more complex matrices. The limits provided are intended for evaluation purposes to permit better understanding of the data. In order to compare the results in Appendix B with the detection limits, the detection limits must be multiplied by the appropriate dilution factor for the method. Preparation blank results may be used to estimate the detection limits attainable in the sample. Individual results for each of the four replicate samples may be obtained in the statistical report in Appendix A.

Figure 1. SEE Phase III Flow Diagram.

Table 1. Areas of Significant Differences in Phase III SEE Data. (Sheet 1 of 2)

Analyte	Exceeds 20% RPD Criteria	Near 15-20% RPD Criteria	Statistical Mean Difference	Statistical Var.
Ag	Acid (22.8%)		Standard	
Al			Standard	
B	Acid (54.2%)		Acid	
Bi				Acid
Ca			Standard	
Cu	Acid (20.2%)			
Fe				Acid
Na		Fusion (17.9%)		Acid
Ni	Acid (20.4%)			Acid
Si	Acid (146.1%)		Acid	
Zn	Acid (41.2%)		Acid	Acid
Hg				Direct
Fluoride	Water (36.9%)		Water Standard	
Nitrite		Water (18.7%)	Water	
Nitrate		Water (17.9%)	Water, Std	
Phosphate	Water (45%)		Water	
Sulfate	Water (27.3%)		Water, Std	
Cyanide	Direct (NC)		Standard	Standard
TIC	Direct (82.5%)		Direct, Std	
TOC	Direct		Direct, Std	Direct
TC	Direct (75%)		Direct, Std	Direct
TGA				Direct
DSC (Endo - 1)	Direct (55.3%)		Direct	Direct
DSC (Endo - 2)				Direct
Total Alpha	Fusion (90.2%)		Fusion, Standard	
Total Beta	Fusion (21.2%)		Fusion	
^{239/240} Pu			Standard	

Table 1. Areas of Significant Differences in Phase III SEE Data. (Sheet 2 of 2)

²⁴¹ Am	Fusion (26.6%)		Fusion	
⁹⁰ Sr	Fusion (34.7%)			
Uranium		Std (16.5%)		
⁹⁹ Tc		Standard	Standard	

4.0 SAMPLE PREPARATION PROCEDURES

This section describes the sample preparation procedures used for the solid samples before the analyses were performed. Sample preparation for analytes analyzed directly (cyanide, TOC/TIC, Hg and DSC/TGA) will be discussed as a part of the analytical method and are not included in this section. Three sample preparation procedures are routinely used in the analysis of high level tank waste at the Hanford Site: acid digestion, water leach, and potassium hydroxide (KOH) fusion. The acid digestion is primarily used for metal analyses. The water leach is used to analyze water soluble anions such as nitrates and nitrites. It may also be used to analyze some radionuclides such as tritium. The fusion is primarily used to analyze insoluble radionuclides, but may also be used to analyze acid insoluble metals such as silicon. Because of the large amounts of KOH in the fusion, large dilutions are necessary and the analysis for trace metals in the KOH fusion is not as good as for the acid digestion. ACL performs the sample preparations in a hot cell; whereas, the 222-S Laboratory performs the preparations in open face hoods.

4.1 COMPARISON OF ACID DIGESTION PROCEDURES

The acid procedures used by both laboratories are based on Environmental Protection Agency (EPA) methods. The acid digestion procedure number used by ACL was PNL-ALO-101. The 222-S Laboratory acid digest procedure number is LA-505-159. Both these procedures use an initial digestion in 1:1 HNO₃ followed by treatment with 30% H₂O₂ and digestion with HCl. The 222-S Laboratory acid digest procedure follows the SW-846 (EPA 1986) direction and evaporates the HNO₃ digestion down to nearly 5 mL before performing the H₂O₂ treatment. The ACL procedure follows the CLP (EPA 1990) version of the acid digestion procedure, which does not require reduction of the volume before the H₂O₂ addition is made. The 222-S Laboratory procedure uses 5 mL of concentrated HCl; whereas, the ACL procedure uses 5 mL of 1:1 HCl. The ACL procedure results in a final volume of 250 mL; whereas, the 222-S Laboratory procedure results in a final volume of 100 mL. The weight of sample used and the final volumes may change depending on the amount of sample available and radiological considerations.

4.2 COMPARISON OF WATER LEACH PROCEDURES

The water leach procedures used by ACL and the 222-S Laboratory were PNL-ALO-103 and LA-504-101 respectively. Both of these methods are based on leaching a 1 g sample in 100 mL of water at room temperature using an ultrasonic bath. The major differences in the procedures are the vessels used for leaching and storing and the filtration technique. The 222-S Laboratory uses 125 mL jars for leaching and storing; whereas, ACL uses 125 mL Erlenmeyer flasks for leaching and plastic bottles for storage. Both labs filter the leach solutions through 0.45 micron filters. The 222-S Laboratory uses syringe filters and ACL uses vacuum filtration through disposable plastic filters. The size and models of the ultrasonic baths are also not the same. The final weights and volumes may change depending on the available sample and radiological considerations.

4.3 COMPARISON OF FUSION PROCEDURES

The fusion procedures used by ACL and the 222-S Laboratory were PNL-ALO-102 and LA-549-141 respectively. Both of these methods are based on fusion of the sample in nickel crucibles with a KOH-KNO₃ mixture. However, there are several differences in the techniques used to perform these fusions. ACL disperses the sample with water in the crucible and dries the sample before determining the amount of KOH needed in the fusion based on the dry weight of the sample. The 222-S Laboratory does not necessarily predry the sample and uses a constant (4.5 to 5.0 g) amount of KOH for each fusion. ACL uses a larger quantity (0.5 g) of KNO₃ than the 222-S Laboratory (0.1 to 0.2 g). The 222-S Laboratory melts the KOH on a hot plate before fusing the sample for 15 minutes in a furnace at a temperature between 425 and 475 degrees centigrade. ACL fuses the sample for 30 minutes in a furnace at temperatures between 450 and 550 degrees centigrade. Both laboratories leach the fused sample from the crucible with water. ACL uses a larger quantity (50 mL) and higher HCl concentration (6M) than the 222-S Laboratory. The 222-S Laboratory uses only 5 to 10 mL of 4M HCl to leach the nickel crucible. If the solids do not dissolve in this amount of acid, the 222-S Laboratory will add 5 to 10 mL of concentrated HNO₃. Both laboratories may use heat to complete the dissolution and bring the fusion to a 250 mL final volume. The weight of sample used and the final volumes may change depending on the amount of sample available and radiological considerations.

The following table is a summary of the weights and volumes used for the different sample treatments in Phase III of the SEE program. A list of the analytical procedures used in Phase III is provided in Appendix D.

Table 2. Summary of Sample Preparation Weights and Volumes.

Laboratory Replicate	Acid Digestion		Water Leach		Fusion	
	Weight (g)	Vol. (mL)	Weight (g)	Vol. (mL)	Weight (g)	Vol. (mL)
222-S - 1	0.2738	50	0.5234	100	0.1546	250
222-S - 2	0.2745	50	0.5854	100	0.1323	250
222-S - 3	0.2779	50	0.5905	100	0.1181	250
222-S - 4	0.2745	50	0.5423	100	0.1109	250
ACL - 1	0.5016	50	0.5028	50	0.3496	100
ACL - 2	0.5022	50	0.5013	50	0.3132	100
ACL - 3	0.5008	50	0.5032	50	0.2825	100
ACL - 4	0.5032	50	0.5001	50	0.2770	100

5.0 METALS DATA EVALUATION

5.1 COMPARISON OF ANALYTICAL METHODS

Both laboratories use inductively coupled plasma atomic emission spectroscopy (ICP/AES) to determine the metal concentration in the acid digested and fused waste samples. The Phase II report (WHC 1994) discussed some of the differences in the ICP/AES systems used by the laboratories. In Phase III, the 222-S Laboratory used a new Thermo Jarrel Ash² Model 61E ICP instead of the ARL 3580 ICP used in Phase II. The ACL used a Jarrel Ash Model 800A ICP, which was the same as the system used in Phase II.

The 222-S Laboratory diluted the acid digest by a factor of 5 before analyzing on the ICP. The ACL ran the ICP analysis both directly and on a five fold dilution. The 222-S Laboratory overall dilution factor was about 9 times greater than ACL for the ICP acid digest analysis. This reduced the 222-S sensitivity and probably increased its uncertainty for trace analytes. Therefore, the comparison of trace analytes in the waste was limited in Phase III. However, comparisons were also limited because this waste type was not rich in trace analytes. The 222-S Laboratory also diluted the fusion preparation greater for ICP analysis than ACL; however, because the fusion ICP results were only used to evaluate the major analytes, the difference is not as significant as for the acid digestions.

²Thermo Jarrel Ash is a trademark of Thermo Jarrel Ash Corporation, Franklin, MA.

Mercury was determined by cold vapor atomic absorption (CVAA) methods at both laboratories. The 222-S Laboratory used a Perkin Elmer³ Model 2380 atomic absorption spectrophotometer with a Perkin Elmer MHS-20 mercury/hydride system. The ACL used a Perkin Elmer Model 5000 atomic absorption spectrophotometer with a cold vapor attachment. Even though the sample sizes and reagent volumes may differ, both laboratory procedures are based on EPA cold vapor mercury methods. Both laboratories digest the samples in a mixture of concentrated sulfuric and nitric acid. This is followed by oxidation treatments with potassium permanganate and persulfate. The excess permanganate is destroyed by hydroxylamine before reducing the sample with stannous chloride and purging the mercury through the CVAA system. The 222-S Laboratory procedure uses a 0.04 g sample size compared to 0.2 g for ACL.

5.2 DISCUSSION OF METAL RESULTS

The metal analysis results for the ICP/AES and mercury by CVAA are summarized in Table B-1 in Appendix B. In general, the ICP/AES data for the two laboratories were in agreement. The 222-S Laboratory acid ICP data showed significantly larger variations than the ACL data. This variance was not observed for the ICP fusion data. Even with this large variation, the means of the ICP acid results from the two laboratories were in agreement. The individual 222-S Laboratory acid ICP data in Appendix A indicated that the quadruplicate data was split into two pairs; numbers 1 and 2 are high and numbers 3 and 4 are low. The ratio of the averages of the high pair to the low pair for all the major analytes was 1.50. Because of the reproducibility of this ratio for each analyte, the cause of the variability was expected to be a laboratory systematic error (such as dilution) rather than a sample homogeneity effect. A rerun of the ICP analyses on new dilutions of the acid digestions resulted in the same pairing of results. During this rerun, it was observed that the color of the higher concentration pair was darker than the other pair, indicating that there may be differences in the digested samples. Because this variability was not observed for other sample preparations or methods, it can only be concluded that the variability was probably caused in the acid digestion procedure. There was insufficient sample remaining to repeat the digestions to confirm the source of the variability.

Only trace metals results from the acid digestion exceeded the SEE RPD criteria of 20%. These differences were the result of the concentrations being near the detection limit or they could have been partly caused by sample contamination during analysis. In the individual element evaluations listed in Sections 5.2.1 through 5.2.18, trace concentrations are considered to be less than 0.1 wt%, minor concentrations are considered to be between 0.1 wt% and 1 wt% and major components are considered to be greater than 1 wt%. Statistical mean differences for the metals were not practically significant and were probably observed because of the excellent reproducibility for the replicates. Other than the large variability in the 222-S Laboratory acid digest data, no significant problem areas were identified. Data from both Phase II and Phase III indicate that the analysis of metals by ICP at the two laboratories are comparable. Continued monitoring of the laboratory ICP results for the acid

³Perkin Elmer is a trademark of Perkin Elmer Corporation.

digestion and for important trace and major metals is needed to provide a better database for a wider range of waste types.

5.2.1 Silver (Ag)

The RPD (22.8%) for the acid ICP silver results exceeded the SEE 20% criteria. The Ag is present in trace concentrations and was only about a factor of 2 above the 222-S Laboratory detection limit. The higher RSD for Ag at the 222-S Laboratory may be the result of the data pairing discussed earlier and the nearness of the result to the detection limit. ACL's analyses of undiluted acid digest solutions are significantly above the detection limit. The mean and variance of the data for Ag from the two laboratories were not statistically different. The means of the Ag standards data were statistically different, however, both results were between 90 and 110% recovery. The good reproducibility (small RSD) for the duplicate standard results allow the statistical process to detect small differences in the means. Even though the means may be statistically different, they are practically the same. These differences are not considered significant considering that the Ag is a trace element and near the detection limit for one of the laboratories.

5.2.2 Aluminum (Al)

Aluminum was present at a relatively low concentration in the waste sample, but was still 10 times above the 222-S Laboratory detection limit. The RPD for the means of the two labs was 14.8% and no aluminum data exceeded the SEE 20% criteria. The means for the Al standard data were found to be statistically different, but like silver were not practically different. In Phase II there appeared to be some differences in the Al results. In both Phase II and III the aluminum concentrations were relatively low and the largest RPDs were comparable (15% to 17%). No Al standard was run in Phase II.

5.2.3 Boron (B)

Boron was found in relatively low concentrations in the tank waste sample by both laboratories. The RPD (54.2%) for the data exceeded the SEE criteria and the means were statistically different. The average boron concentration was about 3 times the 222-S Laboratory detection limit. Boron is a common contaminate in the acid digestion because of the borosilicate glass vessels used in the preparation and storage of the sample. However, preparation blanks indicated that the boron contamination was 3 to 4 times below the levels found in the sample. No standard data were available for evaluating systematic calibration differences in the data. Because the boron was present at low concentrations and boron is not normally a high priority analyte, no further investigations are recommended other than continued monitoring.

5.2.4 Bismuth (Bi)

Bismuth is a major metal component in this waste sample and was analyzed in both the acid and fusion digestions. Only the variance for the acid digestion data was found to be significantly different between the two laboratories. This may be the result of the pairing observed for the 222-S Laboratory data as discussed earlier. The variance for the Bi fusion data from each lab are more comparable. In Phase II, the Bi results exceeded the 20% RPD criteria, but it was present in trace quantities. Phase III data indicates that when Bi is present in significant quantities, the laboratory results are comparable.

5.2.5 Calcium (Ca)

Calcium is a minor component in this waste sample. In Phase II, Ca exceeded the 20% RPD criteria because of expected sample contamination by the 222-S Laboratory. In Phase III the means for the Ca sample data were in agreement. Only the Ca standard results showed a statistically different mean between the labs. The reproducibility of the standards data was very good for both labs. The percent recovery for Ca was high for both labs (135.5% for 222-S and 119.7% for ACL). These high recoveries could be the result of either contamination of the standard during preparation or variable Ca contamination in the labs during analysis. Even though calcium contamination problems were not as significant in Phase III as in Phase II, further monitoring of Ca ICP data is recommended to better understand the limitations of the analysis. It could be worthwhile to investigate further the potential of contamination during the preparation of the standard materials.

5.2.6 Chromium (Cr)

Chromium was a minor component in the waste sample. No significant differences were observed in the acid, fusion, or standard ICP data.

5.2.7 Copper (Cu)

Copper is present in the waste as a trace analyte. The RPD for Cu barely (20.2%) exceeded the SEE criteria. The Cu concentration was only about 2 times above the 222-S Laboratory detection limit. At this concentration level, these results are considered satisfactory.

5.2.8 Iron (Fe)

Iron is a major metal component in the waste. The variances between labs for the acid digestion were found to be statistically significant. As discussed earlier this may be caused by a larger than normal variance in the 222-S Laboratory from data pairing. Iron standard percent recovery results for both labs are slightly high, but still between 90% and 110%.

5.2.9 Magnesium (Mg)

Magnesium is present in the waste sample in trace quantities. No significant differences in the data was observed.

5.2.10 Manganese (Mn)

Manganese is present in the waste sample in trace quantities. No significant differences in the data was observed.

5.2.11 Sodium (Na)

Sodium is a major component in the waste sample. The variance between labs for the acid ICP data was statistically different, which may be the result of the pairing in 222-S Laboratory data. The RPD for the sodium fusion results (17.9%) is near the SEE criteria and significantly larger than observed in Phase II. Sodium contamination is possible from the large quantities of KOH used or from the glassware used in the preparation, storage, and analysis of the sample. The preparation blanks for the fusion data indicate that the sodium contamination is not a factor. The Na standard recoveries are high for both laboratories (144.0% for 222-S and 131.5% for ACL). Phase II sodium standard results were excellent. The high standard recoveries could be the result of contamination during the preparation of the standard by the standards lab or from the preparation and analysis of the standard in the laboratories. The agreement in contamination levels is unusual. These high sodium results for the standard are considered significant. The 13% difference in standards results could explain part of the large RPD observed for the sample. Rerunning the standard by both laboratories could help identify, if the problem is in the ICP results or in the standard preparation. Continued comparisons of the ICP sodium results is recommended to more accurately assess the frequency and magnitude of differences for the analysis of Na.

5.2.12 Nickel (Ni)

Nickel is present in the tank waste sample in trace concentrations. The RPD for the means for Ni (20.4%) barely exceeded the SEE criteria. This concentration is just above the 222-S Laboratory detection limits. The variance between labs was also statistically different. Considering the pairing in the 222-S data and the nearness of the Ni concentration to the detection limit, which increases the uncertainty, this data looks reasonable and acceptable.

5.2.13 Phosphorus (P)

Phosphorus is a major component in the waste sample. No significant differences in the data were observed. Standard results, which were not evaluated in Phase II, were between 90% and 110% recovery.

5.2.14 Lead (Pb)

Lead is present in trace quantities in the waste sample. No significant differences in the data were observed.

5.2.15 Silicon (Si)

Silicon is a major component in the waste sample. Because of acid insolubility of many silicon compounds, the fusion data are considered to be the more reliable. There is a very large difference in the acid silicon results for the two labs that exceeds the SEE criteria and is statistically significant. The standard recovery results for Si are over 200% for both labs (251% for 222-S and 224% for ACL). Because both lab standard results agree, the large recoveries that are twice the expected recovery are believed to be an error in the standard makeup. It is possible that the Si aliquot was added twice during the preparation of the standard. If this occurred the recoveries would be a more reasonable 125.5% for 222-S and 112% for ACL. These standard data do not explain the factor of six difference in the acid Si results. It is possible that Si contamination could cause such large errors; however, this is not reflected in the preparation blank results. Based on the 1990 ACL results for this waste provided in Appendix E, the 222-S results look like they are exceptionally high. They also seem high considering the solubility of silicon compounds in acid solutions. It is also possible that this is the result of differences in the digestion procedures. The 222-S Laboratory acid digestion is probably more rigorous than the ACL procedure because it evaporates the acids down to lower volumes, which takes a longer time and may result in the sample being exposed to higher acid concentrations. This may solubilize more silica in the sample or increase the potential for contamination from the glass ware. Other analytes that may form insoluble silicates do not show this large difference. Silicon concentrations in Phase II were much lower and did not show this large variability. Continued monitoring of silicon acid ICP results for different waste types is recommended. There were no significant differences in silicon results for the fused samples.

5.2.16 Strontium (Sr)

Strontium is present in the waste in trace concentrations. No significant differences were observed in the strontium data.

5.2.17 Zinc (Zn)

Zinc is present in trace quantities in the waste sample. The RPD (41.2%) for the Zn data exceeded the SEE criteria and the mean and variances between the laboratories were statistically significant. A similar problem was observed in the Phase II data. In Phase II, ACL reported the higher concentration and in Phase III, 222-S Laboratory had the higher value. Zn is a common contaminate, but the preparation blanks do not indicate that

contamination is a significant problem. These differences could also be the result of differences in the ICP interelement corrections. The Zn standard results do not indicate any significant systematic differences in the calibrations. At these low concentrations and complex matrices, this difference in RPD is not considered significant. Further monitoring for Zn and other trace metals is recommended to obtain a more accurate assessment of the laboratories performance for these low level determinations.

5.2.18 Mercury (Hg)

Mercury is present in the waste in very low concentrations (1 $\mu\text{g/g}$). No significant differences in the mean results were observed, but there was a significant difference in the variances between laboratories. The larger variance in the 222-S Laboratory may be the result of the smaller sample size (0.04 g) used compared to the ACL sample size (0.2 g). The smaller sample sizes may lead to greater variability because they are more sensitive to sample heterogeneity. Both laboratory standard recoveries were 12 to 14% low. These differences for Hg are not significant at these concentration levels and the mercury methods for the labs are considered comparable. Mercury is not expected to be found in large quantities in the waste and presently is not a high priority. Further comparisons of the data may not be needed until mercury is identified as a requirement for the programs.

6.0 WET CHEMICAL ANALYSIS SUMMARY

6.1 COMPARISON OF ANALYTICAL METHODS

Both labs determine most of the anions by ion chromatography. The ion chromatography methods were compared in the Phase II SEE report (WHC 1994). This review indicated that both the methods were based on the EPA method 300.0 and used similar instrumental conditions. Properly calibrated and operated, the IC procedures should have comparable performance even with minor differences in instrument configuration. The procedures used for IC measurements were LA-533-105 and PNL-ALO-212 for the 222-S Laboratory and ACL respectively.

The ACL also determined fluoride by an ion selective electrode method (PNL-ALO-243). This analysis was performed because of potential problems associated with determining fluoride by IC. Fluoride determinations by IC are subject to interferences from other co-eluting species, baseline flatness, and metal complexes. The ACL ISE method measures fluoride in a buffer solution to control pH. A complexing agent is added to the buffer to break up metal complexes. The electrode is calibrated just before measuring the samples by plotting the mV readings of several standards against the standard values on semi-log graph paper.

Because cyanide may exist in Hanford Site wastes as insoluble sodium nickelferrocyanide

compounds, cyanide analyses on solid samples require a special digestion in a solution of ethylenediaminetetraacetic acid (EDTA) and ethylenediamine to ensure that the cyanide is solubilized and can be distilled. Cyanide was distilled from concentrated sulfuric acid using a microdistillation system at both laboratories. The distilled hydrogen cyanide is trapped in sodium hydroxide and measured using either a spectrophotometric method based on pyridine-barbituric acid or titrametric method. Even though there may be some procedural differences, the methods are based on the same technology.

In order to overcome differences caused by using different TOC/TIC procedures in Phase II, the Phase III plan specified that the TOC/TIC should be determined on the direct solid sample using a hot persulfate oxidation procedure. The TOC/TIC procedure used at the 222-S Laboratory was patterned after the ACL procedure. Both methods determine the TIC first by the addition of acid to release carbon dioxide from the carbonate salts. The carbon dioxide is measured by coulometric titration. The TOC is then oxidized to carbon dioxide by adding persulfate to the carbonate free sample and digesting at about 90 degrees centigrade. The carbon dioxide from this oxidation is then measured by coulometric titration. Even though there are some differences in equipment configuration, the procedures use the same basic technology and should provide comparable results.

6.2 DISCUSSION OF WET CHEMICAL ANALYSIS RESULTS

There were significant differences between laboratories for essentially all the IC results. Depending on the anion, the ACL results were 20% to 50% higher than the 222-S Laboratory. Each laboratory's IC results showed reasonable RSDs, indicating that subsampling was not a problem. RSDs for the 222-S Laboratory were about 2 times greater than ACL for most anions but were not statistically different. Except for fluoride, there were no significant differences in the standard recoveries for the IC results. Differences in the IC standard results are biased in the opposite direction of the sample results. Phase II results indicated that the IC procedures for common water digested samples were comparable and the RPDs were much lower than observed in Phase III. Because of these facts, the differences observed in Phase III are believed to be caused by differences in the water digestion procedure. Fundamentally the water digestion procedures look the same. The procedures rely on the ultrasonic action of the water bath for agitation. The efficiency and heat produced from these ultrasonic baths could vary enough to cause differences in the solubility of the waste sample. There is little information supporting the technical basis for the water leach procedure. It is recommended that the efficiency, kinetics, and variables of the water leach procedure be evaluated and compared with other agitation techniques to establish that equilibrium is being achieved with actual waste samples. The water leach and IC procedures should continue to be monitored to permit a better assessment of their performance.

The table in Appendix E was prepared to compare the 1990 results for Core 4 from tank B-110 with the Phase III composite sample to assist in evaluating the differences in data. Data from the 1990 report for segments 2, 3, and 4 were weighted according to the composite procedure used in Phase III to arrive at an estimate of the composite composition.

These results were then corrected for sample drying based on the wt% solids results from 1990 and Phase III. The ratio of the 1990 (historical) estimate to the Phase III result for each lab was calculated. For analytes (ICP fusion), in which there was good agreement between labs in Phase III, this ratio appears to be about 0.7 to 0.9. Based on this ratio, it appears that the ACL IC results agree closer with the earlier 1990 data.

Significant differences were also observed for the TOC, TIC and cyanide determinations made on direct sample. The results for wet chemical analyses are summarized in Table B-2 in Appendix B.

6.2.1 Fluoride

Fluoride was present in the waste as a minor component. The RPD for fluoride in the waste sample (-36.9%) and the standard (+33.2%) exceeded the SEE criteria. The means for both of these analyses were also statistically different. The 222-S Laboratory had higher standard results and ACL had higher sample results; therefore, the differences in the standards do not help explain the sample results. The ACL standard results were about 20% low and the 222-S standard results were 13% high. The RSDs for all the analyses were less than 10%. The ACL ISE fluoride results for the sample and standard were in agreement with their IC results. Therefore, for this waste matrix with relatively high fluoride, the ISE and IC procedures appear to be comparable.

6.2.2 Chloride

The chloride was present in the waste as a minor component. The chloride IC results are the only IC analyses in which the data for the two labs were not significantly different. The ACL chloride sample results were only about 10% higher than the 222-S Laboratory result.

6.2.3 Nitrite

Nitrite was a major anion in the waste. Even though the nitrite RPD results did not exceed the SEE criteria, they were determined to be statistically different. The RPD for nitrite (18.7%) was very near the SEE limits. The nitrite standard results were not significantly different.

6.2.4 Nitrate

Nitrate is a major component of the waste. Like nitrite, the RPD (17.9%) for nitrite did not exceed the SEE criteria, but was very close. The mean results for the nitrate in the sample and standard were determined to be significantly different. The ACL standard recovery results were 92.9% compared to 99.2% for the 222-S Laboratory. The precision for nitrate results for both labs was very good. Even though the standard recovery results are

statistically significant, the results are acceptable for practical purposes.

6.2.5 Phosphate

Phosphate is a major waste component. IC phosphate sample results for the two laboratories had the largest RPD (45.0%). The difference in the means for the sample were statistically significant. There were no significant differences in the phosphate standard results. Both laboratories had acceptable RSDs for their replicate analyses. ICP analysis for phosphorus in the 222-S Laboratory water leach gave phosphate estimates between the two laboratories. The ACL average ICP results for phosphorus on the water leach was 47,000 $\mu\text{g/g}$ or about 18% higher than the ACL/IC result. Compared to the 1990 analytical results summarized in Appendix E, the 222-S Laboratory ratio is higher than expected, indicating that the results are low. The sample is from a bismuth phosphate waste type. Differences in the ability of the ultrasonic baths to solubilize the phosphate may explain the large differences in the data.

6.2.6 Sulfate

Sulfate is a major waste component. The RPD (27.3%) for the sample results exceeds the SEE criteria. The difference in the sample means are also statistically significant. The precision for sulfate results for both labs was very good. Even though the sulfate standard results are statistically different, the results are acceptable for practical purposes. Standard recoveries for ACL are lower (92.1%) than the 222-S Laboratory (98.4%).

6.2.7 Cyanide

Cyanide concentration in the waste sample was very low. ACL reported less than 0.36 $\mu\text{g/g}$ of cyanide; whereas the 222-S Laboratory reported 7.8 $\mu\text{g/g}$. Because of the ACL less than values, a statistical evaluation is not possible, but the difference does exceed the SEE criteria because the value is less than the value found by the 222-S Laboratory. ACL performed the distillation directly on the solids without the EDTA/ ethylenediamine sample preparation. The 222-S Laboratory performed the EDTA/ ethylenediamine leach on a single solid aliquot and analyzed the leachate four times rather than performing four individual leaches. Therefore, the variability of the 222-S Laboratory data does not reflect the effect of sample preparation. There were no significant differences in the laboratories standard results for cyanide. The 222-S Laboratory spike recovery results were low (44%). The 222-S Laboratory used an unusually large sample size (1.4 g compared to a normal 0.5 g) in the leach, but only used 0.75 mL for the distillation and analysis. The absorbance readings were well above the detection limits. The positive cyanide results from 222-S Laboratory do not appear to be an artifact of multiplying something near the detection limit by a large dilution factor. The preparation blank for the 222-S Laboratory cyanide results do not indicate a contamination problem. Another possible explanation for the difference is that the ACL direct distillation of the sample did not effectively form hydrogen cyanide because of insoluble or complex cyanide species. At this low cyanide concentration, these differences

probably are not significant. However, cyanide results should continue to be compared, particularly for ferrocyanide waste where larger quantities of cyanide are expected.

6.2.8 Total Inorganic Carbon (TIC)

Carbonates or TIC is a trace component in the waste. The RPD (82.5%) for the TIC data exceeded the SEE criteria and the means were statistically different. The 222-S Laboratory result is about 2 times greater than ACL's result. The RSDs for both laboratories data are very good. Even though the mean recoveries for the TIC standards data were statistically different, they were both between 90% and 110% and acceptable. The 222-S Laboratory TIC spike results were good. Based on comparisons of the data with the 1990 results in Appendix E, both laboratory results are significantly lower in TIC than expected. This could be due to an aging process of the waste or because different procedures were in use. The 1990 TIC data were generated on the water leach of the waste. No reasonable explanation for the TIC differences has been identified. At these low concentrations the differences may not be practically significant; however, continued monitoring of the TIC results is recommended.

6.2.9 Total Organic Carbon

TOC is a minor component in the waste sample. The RPD (109.7%) for the TOC sample determinations exceeds the SEE criteria and the difference is statistically significant. The variances between laboratories are also statistically significant, but the RSDs for both labs are less than 10%. The mean recoveries of the standards are statistically different, but both lab recoveries are between 90 and 110%. TOC spike recovery for the 222-S Laboratory was good. Data within the laboratories are consistent, but the ACL results are about 3 times greater than the 222-S Laboratory. No reasonable explanation for the TOC differences has been identified. Further review of the procedures and continued monitoring of the TOC results is recommended.

The total carbon result is the sum of the TIC and TOC and therefore reflects the same differences and problems that are discussed for these measurements.

7.0 THERMAL ANALYSIS SUMMARY

7.1 COMPARISON OF ANALYTICAL METHODS

Both laboratories perform thermal analysis using differential scanning calorimetry (DSC) systems with thermal gravimetric (TGA) analysis attachments. The 222-S Laboratory uses

Mettler and Perkin Elmer DSC/TGA systems. The ACL used a Seiko⁴ DSC/TGA system. Even though the instruments are based on the same principles, the electronic manner in which they measure enthalpy is different. Studies (Valenzuela 1995) at the 222-S Laboratory showed, that even though there are operational differences in the Mettler and Perkin Elmer equipment, they produce comparable results. In performing DSC/TGA analyses, there are several parameters that may be varied. The SEE Phase III plan only specified that the DSC/TGA measurements be performed under a nitrogen atmosphere.

The TGAs for the samples at 222-S Laboratory were measured on the Perkin Elmer system and the standards on the Mettler. A 20 mg sample was loaded into a stainless steel pan and heated at a scan rate of 10 °C per minute. ACL initially used aluminum pans, but were unable to analyze the caustic liquid DSC standard material provided because of reactions with the pan. They reran the analyses using platinum (Pt) pans and heating at a rate of 5 °C per minute. ACL used about 15 mg of sample for most of the TGA analyses. Typical TGA scans for both labs are provided in Appendix F. The TGA scans show several inflections indicating different types of weight loss. The most likely cause of the inflections are from different types of water of hydration. These multiple loss of weight events are also apparent in the endothermic region of the DSC scans. The 222-S Laboratory TGA weight loss ends at a temperature of about 200 °C. ACL TGAs weight loss end near 150 °C. This could be the result of different scan rates.

The DSCs samples for the 222-S Laboratory were also measured with the Perkin Elmer system and the control standard measured on the Mettler. The 222-S Laboratory sample size and scan rates for DSC were the same as those for TGA, 20 mg and 10 °C/minute. The ACL DSC sample sizes were on the average about 9 mg and the scan rate was 5 °C/minute. The type of pans used were the same as for the TGA. Typical DSC scans for both laboratories are provided in Appendix F. The 222-S Perkin Elmer system shows the endothermic peaks pointing up; whereas, the ACL and 222-S Laboratory Mettler systems show endothermic peaks pointing down. Both laboratories DSC scans show multiple endothermic peaks before 200 °C and a small endothermic peak near 300 °C.

The waste sample tested did not show an exothermic reaction. Measurement of the enthalpy for exothermic reactions is important for safety programs. The DSC control standard contains organic complexant, hydroxylethylethylenediaminetriacetic acid (HEDTA), in a caustic solution containing sodium nitrate. This control standard produces a small exothermic reaction, which can be used for comparing the laboratories performance for this type of material. Examples of DSC scans for this standard are also provided in Appendix F. The results for thermal analysis measurements are summarized in Table B-3 in Appendix B.

7.2 THERMAL GRAVIMETRIC ANALYSIS RESULTS

Even though there are differences in the operating parameters for the laboratory TGA systems, the TGA results showed no differences in the means for the data. The RPD for the

⁴Seiko is a trademark of Seiko Instruments USA Inc., Torrance, CA.

TGA data was 1.1%. Both laboratories had RSDs of less than 5% for the replicate analyses. The variances between laboratories were determined to be statistically different. There were no significant differences in the TGA standard results. This data indicates that the TGA methods are comparable. Because the thermal behavior is different for different types of waste, it is recommended that TGA method continue to be monitored to establish a better understanding of their performance.

7.3 DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS RESULTS

The waste sample exhibited two endothermic regions, identified as Endo-1 and 2 in Table B-3, and no exotherms. The temperature range over which these endotherms were observed varied 10 to 20 °C between the laboratories, but generally appeared the same. The RPD for the first endotherm exceeded the SEE criteria and the means and variances for the data were statistically different. It is possible that this difference is the result of how the baselines for the endothermic regions were established or how the enthalpy at lower temperatures were integrated. The scan rate could also have an effect. This difference was not observed for the DSC control standard. The enthalpy results for the small endotherms in region 2 were not significantly different. However, the variances for the results in this region were statistically different. The RSDs for the DSC sample analyses for the 222-S Laboratory are considerably smaller than ACLs. The RSDs for the standard DSC results are more comparable. Further consultation between cognizant scientist and continued monitoring of DSC on different waste materials is recommended.

The DSCs on the control standards showed a single endotherm and two small exotherms. No significant differences were observed in the enthalpy measurements on this standard material.

8.0 RADIOCHEMICAL ANALYSIS SUMMARY

8.1 COMPARISON OF RADIOCHEMICAL METHODS

A comparison of the radiochemical measurements was included in the Phase I SEE report (PNL 1993). Since that report, the 222-S Laboratory has changed several of its methods. The plutonium method has been changed from a nitrate anion exchange separation to a chloride anion exchange separation. The Pu is oxidized to Pu(IV) in concentrated HCl and loaded on the anion exchange resin. Uranium and iron are removed by nitric acid column rinses. The Pu is then eluted with 2M HCl. The eluted Pu is electroplated for alpha energy analysis as done previously.

The 222-S Laboratory procedure for ²⁴¹Am now uses TRU-SPEC⁵ resins for the separation. ²⁴¹Am is loaded onto the resin in 2M HNO₃. The Pu on the resin is converted to Pu(IV) with

⁵TRU-SPEC is a trademark of EIChroM Industries Inc., Darien, Ill.

nitrite to prevent it from eluting with the Am. After multiple rinses with HNO₃ and HCl, the Am is eluted with 4M HCl and electroplated for alpha energy analysis.

The new 222-S Laboratory total uranium procedure uses a kinetic phosphorescence analyzer (KPA). Samples are evaporated down in HNO₃ to remove chloride. The KPA is calibrated with a series of standards for calibration rather than the method of standard additions that was used with the earlier procedure. The KPA uses electronic circuitry to minimize quenching and fluorescence effects from the matrix.

8.2 DISCUSSION OF RADIOCHEMICAL RESULTS

All the radiochemical analyses were performed on a fused aliquot of the sample. Several radionuclide measurements (total alpha, total beta, ²⁴¹Am and strontium-90) on the tank waste sample exceeded the SEE RPD criteria. Technetium-99 standard results from both labs did not agree with the standard value or with each other. The radionuclide results are summarized in Table B-4 in Appendix-B.

8.2.1 Total Alpha

The RPD between laboratories for the total alpha results was 90.2%, which exceeds the SEE criteria and is statistically significant. The RSDs for each labs data are reasonable and the counting errors shown in Appendix C for both labs are less than 10%. When the sum of the ^{239/240}Pu and ²⁴¹Am results are compared to the total alpha by the ratios calculated in Appendix-C, the 222-S total alpha results appear to be about 50% low. The means for the standard recoveries for total alpha are statistically different but still between 90% and 110%. The standard differences are in the opposite direction as the sample results with the 222-S Laboratory being higher. The ACL results agree closer with the results that were obtained in 1990 (Appendix E) for this waste material.

The large RPD is believed to be caused by differences in the total alpha mounting procedures. The 222-S Laboratory fusion matrix is essentially 20 g/L KCl after the fusion and acidification. The low results at the 222-S Laboratory are caused by excessive solids on the alpha mount. The mount may also be affected by corrosion from the HCl in the fused sample, if the sample is not converted to a nitrate matrix. The 222-S uses a 2 inch planchet for mounting the sample so that it can be counted on automated alpha/beta counters. After the sample is mounted, it is dried and counted. The ACL uses a 1 inch disc for mounting the sample. After this disc is dried, it is heated in an open flame to reduce the salt deposits. This process helps to remove solids from the disc. The 1 mL sample size used by the 222-S Laboratory results in about 20,000 µg of KCl being deposited on the planchet. These solids prevent the alpha particles from getting to the alpha detector and therefore produce low results. The 222-S Laboratory does not use corrected detector efficiencies for varying solid quantities on the mount. It is recommended that the 222-S Laboratory:

- Establish the limit for solids on the 2" planchets or

- Establish a solids efficiency correction or
- Implement a different mounting/ counting procedure that can provide total alpha measurements below the TRU limits of 100 nCi/g.

8.2.2 Total Beta

The RPD (21.2%) for the two laboratories total beta results barely exceeded the SEE criteria. The difference in the means is statistically significant. No significant differences were observed in the total beta standard results. Both laboratories had comparable RSDs for the replicate analyses. The difference cannot be explained by the counting errors. Some of the difference may be caused by differences in the efficiencies used for total beta determinations. In January 1995, the 222-S Laboratory changed the efficiency basis for its total beta measurement from ^{60}Co to ^{137}Cs . This was expected to make the total beta measurements more comparable because the efficiencies of the ^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$ betas are closer than $^{90}\text{Sr}/^{90}\text{Y}$ and ^{60}Co . Some of the difference in the total beta results may also be from solid absorption of beta particles similar to the alpha problem. The ratios of the total beta to the sum of the ^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$ results (Appendix C) are about 15% low for the 222-S Laboratory and 12% high for the ACL. Solids effects on total beta should be evaluated at the 222 -S Laboratory and the total beta results should continue to be monitored.

8.2.3 Plutonium - 239/240

Plutonium activity in the waste is about 2 times the TRU limit. The means for the standard recovery results were statistically different, but the recovery for both labs were between 90% and 110%. The RPD for Pu data did not exceed the SEE criteria and the differences are not considered significant.

8.2.4 Americium - 241

The ^{241}Am activity in the sample is very low; 5 times below the TRU limit. The RPD between the laboratory mean results was 26.6%. The difference of the means were also statistically significant at the 95% confidence level. The ACL laboratory determined Am by gamma energy analysis; whereas, the 222-S Laboratory used a chemical separation and alpha counting. The counting uncertainty for the ACL was 19%, which is near the RPD level. At this low concentration and with this level of counting uncertainty, this RPD is not considered significant.

8.2.5 Strontium - 90

The RPD (34.7%) for the means of the ^{90}Sr data exceeded the SEE criteria, but were not determined to be statistically different. No differences were observed in the Phase II SEE ^{90}Sr results; but, the ^{90}Sr activity was considerably higher. Counting errors do not indicate

that this large of difference should be expected. However, the RSD for the ^{90}Sr replicates from each laboratory is relatively large (18% for 222-S and 26% for ACL). There are no significant differences in the ^{90}Sr standard results. Both of the laboratories Sr-90 and total beta results are much lower than the estimated 1990 values. The 1990 results are based on a single composite that contained waste from an additional segment. No immediate corrective action can be identified for the ^{90}Sr measurement; however, the ^{90}Sr performance should continue to be monitored.

8.2.6 Gamma Energy Analysis (^{137}Cs)

No significant differences were observed between the laboratories for the GEA measurement of ^{137}Cs . No other gamma emitting isotopes were present at high enough concentrations to be comparable. The RPD between labs was only 1.4% and the RSDs for both labs were about 5%. GEA from all three Phases of the SEE program have been comparable. Continued monitoring is recommended because ^{137}Cs is a major isotope in the waste and the excellent comparability of the method can be used as a gage in the evaluation of homogeneity and comparability of other analytes.

8.2.7 Technetium-99

Technetium-99 concentrations in the waste were low. The 222-S Laboratory reported a less than value of $<0.035 \mu\text{Ci/g}$ and ACL reported a positive value of $0.028 \mu\text{Ci/g}$. Because of the 222-S Laboratory less than value, it is not possible to make a quantitative comparison. In the previous phases the 222-S Laboratory ^{99}Tc sample and standard results have been higher than ACL with RPDs between 15 and 30%. Both laboratories ^{99}Tc standard results did not agree with the standard value. The ACL ^{99}Tc standard results were a factor of 10 high and the 222-S Laboratory results were a factor of 5 low. Reruns of the ^{99}Tc standard at the 222-S Laboratory agreed better with the ACL data but were 19% higher. The rerun was done in duplicate and the data had a RPD of about 33%. Based on the 222-S Laboratory ^{99}Tc rerun data, both laboratories appear to be a factor of 10 high. This would indicate that there is a problem in the standard value. Problems with ^{99}Tc standard analyses have not been observed in earlier phases of the program. Further monitoring of the Tc-99 measurement systems is recommended.

8.2.8 Total Uranium

No significant differences between laboratories for the total uranium measurement were observed. The RPD for the uranium standard result (16.5%) was near the SEE limit. The RPD for the sample analyses was 3.7%. The RSDs for the replicate U determinations were less than 10% for both labs. Continued monitoring is recommended to evaluate how the new 222-S Laboratory uranium method compares to the ACL method.

9.0 REFERENCES

EPA, 1986, Test methods for Evaluating Solid Waste, SW-846, Rev. 0, U. S. Environmental Protection Agency, Washington D.C.

EPA, 1989, Test Method: The Determination of Inorganic Anions in Water by Ion Chromatograph - Method 300.0, John D. Pfaff, Carol A. Brockhoff, and James W. O'Dell, Environmental Monitoring and Systems Laboratory, Cincinnati, OH.

EPA, 1990, Contract Laboratory Program Statement of Work for Inorganic Analysis Multi-Media Multiconcentration, EPA SOW 787, U.S. Environmental Protection Agency, Washington D.C.

Northwest Laboratory, Sample Exchange and Evaluation (SEE) Phase I Report, PNL-9385, Rev 1, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, Acid Digestion for Metals Analysis, PNL-ALO-101, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, Fusion of Hanford Tank Waste Solids, PNL-ALO-102, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, Water Leach of Sludges, Soils, and Other Solid Samples, PNL-ALO-103, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, 1989, Laboratory Procedure for Homogenization of Solutions, Slurries, and Sludges, PNL-ALO-135, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, Determination of Inorganic Anions by Ion Chromatography, PNL-ALO-212, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, Water Leachable Chloride and Fluoride in Cloth and Other Materials, PNL-ALO-243, Pacific Northwest National Laboratory, Richland, Washington.

Northwest Laboratory, 1992, Percent Solids Determination of Soils/Sludges/Solids, PNL-ALO-504, Pacific Northwest National Laboratory, Richland, Washington.

Valenzuela B.D., 1995, Letter to T.H. Bushaw, Comparison of Perkin Elmer/Mettler TGA/DSC, 8E450-95-016, dated February 6, 1995, Westinghouse Hanford Company.

WHC, 1994, Sample Exchange Evaluation (SEE) Report - Phase II, WHC-SD-WM-TI-666, Rev. 0, Westinghouse Hanford Company, Richland Washington

APPENDIX A

SEE PHASE III STATISTICAL DATA EVALUATION

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APPENDIX A

From: Process Chemistry and Statistics 75764-PCS95-101
 Phone: 373-2475 T6-07
 Date: November 10, 1995
 Subject: STATISTICAL ANALYSIS OF THE PHASE III SEE DATA

To: P. M. Morant S3-30
 cc: L. Jensen T6-07
 J. R. Jewett T6-09
 K. J. Kuhl-Klinger (PNL) P7-27
 W. I. Winters T6-50
 TLW File/LB

Reference: Book, G. W. Snedecor and W. G. Cochran, Statistical Methods, Sixth Edition, Iowa State University Press, Ames, Iowa, dated 1967.

Introduction

The Statistics Team received data generated from Phase III of the Sample Exchange Evaluation (SEE) program. The purpose of the statistical analysis was to compare the data generated by the 222-S Laboratory (222S) to the data generated by the 325 Laboratory (325). The between-laboratory comparison is based on the mean concentration for each analyte measured.

A portion of a homogenized core sample was provided to each laboratory. Sets of four aliquots were prepared for analysis by fusion, acid digestion, and water digestion. Four additional aliquots were prepared for direct analyses. Thus, each analyte of interest was analyzed four times by each laboratory. A single blind quality control (QC) standard was also provided to each laboratory and analyzed in duplicate.

The data used in the statistical analysis are listed in Attachment 1. The statistical analysis was performed for only those analytes which were reported with "actual" values by both laboratories; i.e., analytes with "less than" values were not included in the comparison.

Summary

For the acid digestion sample preparation, there were seventeen analytes with comparison

data (Table 1, Attachment 2). For 5 of the 17 comparisons (29.4%), the test for equality of variances (0.05 level of significance) was rejected; i.e., the variability of one laboratory was significantly different from the variability of the other laboratory. For 12 of the 17 comparisons (70.6%), the test for equality of variances (0.05 level of significance) was not rejected. For B, Si, and Zn (3 of the 17 comparisons [17.6%]), the test for equality of means was rejected using the random analytical variability only (0.05 level of significance). For 14 of the 17 comparisons (82.4%), the test for equality of means was not rejected using the random analytical variability only (0.05 level of significance). If the hypothesis of equality of means is evaluated at the 0.01 level of significance, then only the hypothesis test for Si is rejected.

For the fusion sample preparation (Tables 2 and 6, Attachment 2), there were six inductively coupled plasma (ICP) metal analytes and seven radionuclides with comparison data. For all 13 comparisons (100%), the test for equality of variances (0.05 level of significance) was not rejected; i.e., the variability of one laboratory was not significantly different from the variability of the other laboratory. For Na, Alpha Total, Total Beta, and ^{241}Am by alpha energy analysis (AEA) (4 of the 13 comparisons [30.8%]), the test for equality of means was rejected using the random analytical variability only (0.05 level of significance). For 9 of the 13 comparisons (69.2%), the test for equality of means was not rejected using the random analytical variability only (0.05 level of significance). If the hypothesis of equality of means is evaluated at the 0.01 level of significance, then the hypothesis tests for Na and Alpha Total are rejected.

For the water digestion sample preparation (Table 4, Attachment 2), there were six analytes with comparison data. For all 6 comparisons (100%), the test for equality of variances (0.05 level of significance) was not rejected; i.e., the variability of one laboratory was not significantly different from the variability of the other laboratory. For F^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} (5 of the 6 comparisons [83.3%]), the test for equality of means was rejected using the random analytical variability only (0.05 level of significance). For 1 of the 6 comparisons (16.7%), the test for equality of means was not rejected using the random analytical variability only (0.05 level of significance). If the hypothesis of equality of means is evaluated at the 0.01 level of significance, then the hypothesis tests for F^- , PO_4^{3-} , and SO_4^{2-} are rejected.

For the direct analyses, there were seven analytes with comparison data (Table 4, Attachment 2). For 6 of the 7 comparisons (85.7%), the test for equality of variances (0.05 level of significance) was rejected; i.e., the variability of one laboratory was significantly different from the variability of the other laboratory. For 1 of the 7 comparisons (14.3%), the test for equality of variances (0.05 level of significance) was not rejected. For total inorganic carbon (TIC), total organic carbon (TOC), total carbon (TC), and differential scanning calorimetry (DSC1) (4 of the 7 comparisons [57.1%]), the test for equality of means was rejected using the random analytical variability only (0.05 level of significance). For 3 of the 7 comparisons (42.9%), the test for equality of means was not rejected using the random analytical variability only (0.05 level of significance). If the hypothesis of equality of means is evaluated at the 0.01 level of significance, then the hypothesis tests for TIC, TOC, and TC

are rejected.

For the QC standards, there were 40 analytes with comparison data (Tables 3, 5, and 7, Attachment 2). For 3 of the 40 comparisons (7.5%), the test for equality of variances (0.05 level of significance) was rejected; i.e., the variability of one laboratory was significantly different from the variability of the other laboratory. For 37 of the 40 comparisons (92.5%), the test for equality of variances (0.05 level of significance) was not rejected. For Al, Bi, Ca, La, Ag, F, NO_3^- , SO_4^{2-} , TIC, TOC, TC, Alpha Total, $^{239/240}\text{Pu}$, and ^{99}Tc (14 of the 40 comparisons [35%]), the test for equality of means was rejected using the random analytical variability only (0.05 level of significance). For 26 of the 40 comparisons (65%), the test for equality of means was not rejected using the random analytical variability only (0.05 level of significance). If the hypothesis of equality of means is evaluated at the 0.01 level of significance, then the hypothesis tests for Bi, Ca, F, SO_4^{2-} , TOC, and TC are rejected.

Statistical Methods

The two laboratory means were compared using either (1) analysis of variance (ANOVA) techniques or (2) Students' t-test for equality of means. Both statistical techniques use the estimate of the random analytical uncertainty in the calculations.

For each analyte a comparison using the ANOVA is appropriate if the variances for each laboratory are equal. An F test was used to test this hypothesis. Let $S_{222\text{s}}^2$ denote the variance of the 222S data and S_{325}^2 denote the variance of the 325 data. The test criterion is

$$F = S_1^2 / S_2^2,$$

where S_1^2 is the greater of $S_{222\text{s}}^2$ and S_{325}^2 , and S_2^2 is the lesser of $S_{222\text{s}}^2$ and S_{325}^2 (see pages 116-117 of the reference for details). If this F value was larger than the tabular value of F with the appropriate degrees of freedom at the 0.05 level of significance, then the assumption of equal variances is rejected.

If the assumption of equal variances was rejected, then the approximate Students' t-test (see pages 114-116 of the reference for details) was used to compare the two means.

The number of observations in the sample analysis, the mean, and the standard deviation for each analyte by each laboratory are provided in Attachment 2. Attachment 2 also states (1) whether or not the assumption of equal variances was rejected, (2) the difference between the two means, and (3) whether or not the difference between the two means is statistically significant at both the 0.05 and the 0.01 level.

An additional comparison between the two means for the sample data was performed using both the random analytical uncertainty (estimated from the replicate analyses) and the systematic uncertainty (estimated from the analysis of the standards). The degrees of freedom associated the random error uncertainty were used as the degrees of freedom for this comparison. This comparison was evaluated at the 0.01 level of significance. The

systematic uncertainty for each analyte is also provided in Attachment 2. Altogether there were nine analytes such that the sample data indicated that the hypothesis of equality of means was rejected (using only the random analytical variability) at the 0.01 level of significance. When both sources of variability (random analytical and systematic analytical) are included in the comparison, only five analytes (PO_4^{3-} , TIC, TOC, TC, Alpha Total) indicate that the hypothesis of equality of means is rejected.

A 95% confidence interval for the sample's mean laboratory concentration (using both the degrees of freedom and the random analytical uncertainty from the ANOVA) for each analyte by laboratory is illustrated in Attachment 3.

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tlw

Attachments 3

Table 1. ICP Data - Acid Digest.

	Ag ($\mu\text{g/g}$)	Al ($\mu\text{g/g}$)	B ($\mu\text{g/g}$)	Bi ($\mu\text{g/g}$)	Ca ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)
PNL (325)	1.74E+01	5.07E+02	8.76E+01	2.83E+04	1.04E+03	1.16E+03
PNL (325)	1.51E+01	4.56E+02	6.95E+01	2.65E+04	9.88E+02	1.08E+03
PNL (325)	1.88E+01	5.55E+02	5.49E+01	3.03E+04	1.13E+03	1.28E+03
PNL (325)	2.05E+01	5.49E+02	7.89E+01	2.95E+04	1.14E+03	1.28E+03
222S	2.49E+01	6.49E+02	1.38E+02	3.12E+04	1.05E+03	1.47E+03
222S	3.17E+01	7.86E+02	1.64E+02	3.77E+04	1.26E+03	1.78E+03
222S	1.69E+01	4.86E+02	1.01E+02	2.32E+04	7.83E+02	1.09E+03
222S	1.67E+01	4.77E+02	1.01E+02	2.27E+04	7.57E+02	1.06E+03
	Cu ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Mg ($\mu\text{g/g}$)	Mn ($\mu\text{g/g}$)	Na ($\mu\text{g/g}$)	Ni ($\mu\text{g/g}$)
PNL (325)	2.21E+01	2.63E+04	2.39E+02	7.22E+01	1.33E+05	1.94E+01
PNL (325)	1.78E+01	2.47E+04	2.27E+02	6.64E+01	1.41E+05	1.83E+01
PNL (325)	2.03E+01	2.83E+04	2.61E+02	7.88E+01	1.47E+05	2.10E+01
PNL (325)	1.83E+01	2.75E+04	2.65E+02	7.89E+01	1.49E+05	2.04E+01
222S	1.73E+01	2.85E+04	2.49E+02	8.80E+01	1.43E+05	2.33E+01
222S	2.09E+01	3.45E+04	3.06E+02	1.06E+02	1.75E+05	3.20E+01
222S	1.31E+01	2.11E+04	1.92E+02	6.47E+01	1.09E+05	2.09E+01
222S	1.29E+01	2.06E+04	1.90E+02	6.32E+01	1.05E+05	2.11E+01
	P ($\mu\text{g/g}$)	Pb ($\mu\text{g/g}$)	Si ($\mu\text{g/g}$)	Sr ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	
PNL (325)	2.47E+04	1.88E+02	8.74E+02	2.35E+02	6.16E+01	
PNL (325)	1.97E+04	1.81E+02	1.20E+03	2.15E+02	5.49E+01	
PNL (325)	2.66E+04	2.00E+02	1.41E+03	2.57E+02	6.44E+01	
PNL (325)	2.59E+04	2.14E+02	1.27E+03	2.57E+02	6.30E+01	
222S	2.69E+04	2.25E+02	7.64E+03	2.89E+02	9.57E+01	
222S	3.29E+04	2.61E+02	8.38E+03	3.53E+02	1.11E+02	
222S	2.05E+04	1.61E+02	7.35E+03	2.17E+02	9.30E+01	
222S	1.94E+04	1.52E+02	7.09E+03	2.10E+02	7.09E+01	

Table 2. ICP Data - Fusion Digest.

	Bi	Cr	Fe	Na	P	Si
PNL (325)	3.00E+04	1.42E+03	2.73E+04	1.54E+05	2.86E+04	1.58E+04
PNL (325)	2.87E+04	1.36E+03	2.62E+04	1.39E+05	2.73E+04	1.50E+04
PNL (325)	3.02E+04	1.43E+03	2.76E+04	1.37E+05	2.85E+04	1.62E+04
PNL (325)	2.70E+04	1.28E+03	2.48E+04	1.46E+05	2.59E+04	1.43E+04
222S	2.95E+04	1.38E+03	2.78E+04	1.66E+05	3.14E+04	1.67E+04
222S	2.45E+04	1.26E+03	2.45E+04	1.73E+05	2.69E+04	1.52E+04
222S	2.39E+04	1.28E+03	2.44E+04	1.72E+05	3.13E+04	1.47E+04
222S	2.65E+04	1.34E+03	2.46E+04	1.78E+05	2.81E+04	1.46E+04

Table 3. ICP Standards Data - Percent Recovery.

	Al	Ba	Bi	Ca	Cr	Fe
PNL (325)	98.80	97.66	95.96	120.42	100.36	103.83
PNL (325)	97.66	96.37	94.99	118.97	98.99	102.40
222S	104.40	102.94	102.24	135.00	102.22	106.38
222S	102.40	99.18	101.60	135.90	106.06	109.98
	La	Pb	Mg	Mn	Ni	P
PNL (325)	94.53	107.02	NA	98.95	100.43	96.62
PNL (325)	93.38	105.60	NA	97.64	99.12	94.86
222S	99.76	102.14	NA	99.36	100.26	101.10
222S	101.90	105.08	NA	103.02	104.78	104.10
	K	Si	Ag	Na	St	Zn
PNL (325)	97.47	225.84	95.57	132.22	97.09	99.62
PNL (325)	97.55	222.71	94.31	130.79	96.18	98.32
222S	100.20	274.20	103.46	148.40	102.24	102.56
222S	103.30	228.80	100.84	139.60	99.06	105.62

NA = Not Available, analyte not in the standard.

Table 4. Water Digestion and Direct Analyses Data.

	F ⁻ (IC) (μg/g)	Cl ⁻ (μg/g)	NO ₂ ⁻ (μg/g)	NO ₃ ⁻ (μg/g)	PO ₄ ³⁻ (μg/g)	SO ₄ ²⁻ (μg/g)
PNL (325)	2.60E+03	1.80E+03	1.65E+04	2.41E+05	3.70E+04	1.65E+04
PNL (325)	2.90E+03	1.90E+03	1.71E+04	2.39E+05	4.00E+04	1.83E+04
PNL (325)	2.70E+03	1.70E+03	1.54E+04	2.41E+05	4.10E+04	1.70E+04
PNL (325)	3.00E+03	1.80E+03	1.65E+04	2.59E+05	4.20E+04	1.74E+04
222S	1.76E+03	1.51E+03	1.26E+04	1.91E+05	2.33E+04	1.30E+04
222S	1.86E+03	1.62E+03	1.27E+04	1.90E+05	2.34E+04	1.48E+04
222S	2.18E+03	1.84E+03	1.55E+04	2.34E+05	2.94E+04	1.25E+04
222S	1.91E+03	1.59E+03	1.35E+04	2.04E+05	2.51E+04	1.23E+04
	Hg (μg/g)	TIC (μg/g)	TOC (μg/g)	TC (μg/g)	TGA (%)	DSC1 (J/g)
PNL (325)	1.09E+00	2.67E+02	2.57E+03	2.84E+03	4.56E+01	5.35E+02
PNL (325)	1.06E+00	2.41E+02	3.10E+03	3.34E+03	4.42E+01	4.82E+02
PNL (325)	1.12E+00	2.28E+02	3.16E+03	3.39E+03	4.76E+01	8.17E+02
PNL (325)	1.08E+00	2.32E+02	2.78E+03	3.01E+03	4.36E+01	4.84E+02
222S	8.45E-01	5.93E+02	8.36E+02	1.43E+03	4.46E+01	1.03E+03
222S	1.24E+00	5.98E+02	8.51E+02	1.45E+03	4.46E+01	9.91E+02
222S	9.37E-01	5.55E+02	8.51E+02	1.41E+03	4.49E+01	9.94E+02
222S	1.00E+00	NA	NA	NA	4.50E+01	1.07E+03
	DSC2 (J/g)					
PNL (325)	5.20E+01					
PNL (325)	6.60E+01					
PNL (325)	3.90E+01					
PNL (325)	4.70E+01					
222S	4.46E+01					
222S	4.26E+01					
222S	4.20E+01					
222S	4.62E+01					

Table 5. Water Digestion and Direct Analyses Standards Data - Percent Recovery.

	F ⁻ (IC) (%)	Cl ⁻ (%)	NO ₂ ⁻ (%)	NO ₃ ⁻ (%)	PO ₄ ³⁻ (%)	SO ₄ ²⁻ (%)
PNL (325)	80.20	94.18	92.90	91.10	93.29	91.60
PNL (325)	81.40	87.46	95.86	94.00	92.42	92.54
222S	114.40	105.97	102.17	99.42	94.59	98.69
222S	111.60	102.69	99.61	99.03	94.37	98.13
	Hg (%)	TIC (%)	TOC (%)	TC (%)	CN (%)	
PNL (325)	86.80	104.63	102.90	103.77	93.57	
PNL (325)	88.60	104.20	104.60	104.40	88.69	
222S	84.20	98.67	93.36	96.02	98.44	
222S	87.20	100.33	93.03	96.68	93.96	
	DSC1 (J/g)	DSC2 (J/g)	DSC3 (J/g)			
PNL (325)	1.56E+03	-3.70E+01	-4.50E+01			
PNL (325)	1.23E+03	-4.50E+01	-4.70E+01			
PNL (325)	1.32E+03	-4.50E+01	-4.10E+01			
PNL (325)	1.36E+03	-4.50E+01	-3.50E+01			
222S	1.53E+03	-4.78E+01	-4.31E+01			
222S	1.22E+03	-4.85E+01	-4.63E+01			

Table 6. Radionuclide Data.

	Alpha Total ($\mu\text{Ci/g}$)	$^{239/240}\text{Pu}$ ($\mu\text{Ci/g}$)	Uranium ($\mu\text{g/g}$)	Total Beta ($\mu\text{Ci/g}$)	^{90}Sr ($\mu\text{Ci/g}$)
PNL (325)	2.23E-01	2.08E-01	3.50E+02	3.07E+01	4.81E+00
PNL (325)	2.13E-01	1.43E-01	3.40E+02	3.23E+01	6.54E+00
PNL (325)	2.21E-01	1.87E-01	3.58E+02	2.95E+01	4.11E+00
PNL (325)	2.02E-01	1.94E-01	3.27E+02	2.65E+01	3.75E+00
222S	8.23E-02	1.71E-01	3.93E+02	2.54E+01	4.28E+00
222S	7.00E-02	1.42E-01	3.44E+02	2.09E+01	3.01E+00
222S	8.52E-02	1.49E-01	3.30E+02	2.43E+01	3.13E+00
222S	8.61E-02	1.72E-01	3.61E+02	2.56E+01	3.11E+00
	^{137}Cs ($\mu\text{Ci/g}$)	^{241}Am (AEA) ($\mu\text{Ci/g}$)			
PNL (325)	2.30E+01	2.46E-02			
PNL (325)	2.16E+01	2.69E-02			
PNL (325)	2.25E+01	2.61E-02			
PNL (325)	2.06E+01	2.00E-02			
222S	2.27E+01	2.03E-02			
222S	2.10E+01	1.80E-02			
222S	2.03E+01	1.78E-02			
222S	2.23E+01	1.86E-02			

Table 7. Radionuclide Standards Data - Percent Recovery.

	Alpha Total (%)	^{239/240} Pu (%)	Uranium (%)	Total Beta (%)
PNL (325)	93.71	103.66	95.78	104.33
PNL (325)	94.56	105.77	105.88	109.32
222S	104.24	94.48	86.00	116.68
222S	107.93	97.33	84.80	114.84
	⁹⁹ Tc (%)	⁹⁰ Sr (%)	¹³⁷ Cs (%)	²⁴¹ Am (AEA) (%)
PNL (325)	1290.59	90.51	99.88	95.41
PNL (325)	1394.94	103.03	99.28	94.70
222S	19.17	92.11	100.61	97.14
222S	19.01	93.39	99.80	98.39

Analyte	Units	N	222S Mean	222S RSD (%)	N	PNL (325) Mean	PNL (325) RSD (%)	Percent Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)	Diff ⁴ Sign? (0.01)
Ag	µg/g	4	2.26E+	32.0	4	1.79E+01	12.7	23.0	No	No	No	No
Al	µg/g	4	6.00E+	24.6	4	5.17E+02	8.8	14.8	No	No	No	No
B	µg/g	4	1.26E+	24.6	4	7.27E+01	19.2	53.6	No	Yes	No	No
Bi	µg/g	4	2.87E+	24.9	4	2.87E+04	5.7	0.1	Yes	No	No	No
Ca	µg/g	4	9.62E+	24.8	4	1.07E+03	6.9	-11.0	No	No	No	No
Cr	µg/g	4	1.35E+	25.3	4	1.20E+03	8.2	11.7	No	No	No	No
Cu	µg/g	4	1.61E+	24.0	4	1.96E+01	9.9	-20.0	No	No	No	No
Fe	µg/g	4	2.62E+	25.3	4	2.67E+04	5.8	-2.0	Yes	No	No	No
Mg	µg/g	4	2.34E+	23.5	4	2.48E+02	7.2	-5.8	No	No	No	No
Mn	µg/g	4	8.04E+	25.3	4	7.41E+01	8.1	8.2	No	No	No	No
Na	µg/g	4	1.33E+	24.6	4	1.42E+05	5.1	-6.8	Yes	No	No	No
Ni	µg/g	4	2.43E+	21.5	4	1.98E+01	6.0	20.7	Yes	No	No	No
P	µg/g	4	2.49E+	25.1	4	2.42E+04	12.9	2.9	No	No	No	No
Pb	µg/g	4	2.00E+	26.1	4	1.96E+02	7.3	2.0	No	No	No	No
Si	µg/g	4	7.62E+	7.3	4	1.19E+03	19.1	146.0	No	Yes	Yes	No
Sr	µg/g	4	2.67E+	25.3	4	2.41E+02	8.4	10.4	No	No	No	No
Zn	µg/g	4	9.27E+	18.0	4	6.10E+01	6.9	41.3	Yes	Yes	No	No

- 1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.
2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).
3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).
4: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used both random and systematic variability).

N: Number of observations.

RSD: Relative standard deviation.

VAR: Variance.

Diff: Difference.

Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

Table 1. Statistical Tests - ICP Acid Digest Data.

Table 2. Statistical Tests - ICP Fusion Digest Data.

Analyte	Units	N	222S Mean	222S RSD (%)	N	PNL (325) Mean	PNL (325) RSD (%)	Percent Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)	Diff ⁴ Sign? (0.01)
Bi	µg/g	4	2.61E+0 4	9.7	4	2.90E+04	5.1	-10.5	No	No	No	No
Cr	µg/g	4	1.32E+0 3	4.3	4	1.37E+03	4.9	-4.3	No	No	No	No
Fe	µg/g	4	2.53E+0 4	6.6	4	2.65E+04	4.9	-4.4	No	No	No	No
Na	µg/g	4	1.72E+0 5	2.9	4	1.44E+05	5.3	17.9	No	Yes	Yes	No
P	µg/g	4	2.94E+0 4	7.7	4	2.76E+04	4.5	6.5	No	No	No	No
Si	µg/g	4	1.53E+0 4	6.3	4	1.53E+04	5.6	0.0	No	No	No	No

1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.

2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).

3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).

4: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used both random and systematic variability).

N: Number of observations.

RSD: Relative standard deviation.

VAR: Variance.

Diff: Difference.

Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

Table 3. Statistical Tests - ICP Standards Data.

Analyte	Units	N	222S Mean	222S Standard Deviation	N	PNL (325) Mean	PNL (325) Standard Deviation	Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)
Al	%	2	103.40	1.414	2	98.23	0.804	5.17	No	Yes	No
Ba	%	2	101.06	2.659	2	97.01	0.916	4.05	No	No	No
Bi	%	2	101.92	0.453	2	95.47	0.686	6.45	No	Yes	Yes
Ca	%	2	135.45	0.636	2	119.70	1.027	15.75	No	Yes	Yes
Cr	%	2	104.14	2.715	2	99.68	0.969	4.47	No	No	No
Fe	%	2	108.18	2.546	2	103.12	1.008	5.07	No	No	No
La	%	2	100.83	1.513	2	93.95	0.816	6.88	No	Yes	No
Pb	%	2	103.61	2.079	2	106.31	1.003	2.70	No	No	No
Mn	%	2	101.19	2.588	2	98.29	0.931	2.90	No	No	No
Ni	%	2	102.52	3.196	2	99.77	0.926	2.75	No	No	No
P	%	2	102.60	2.121	2	95.74	1.249	6.86	No	No	No
K	%	2	101.75	2.192	2	97.51	0.052	4.24	Yes	No	No
Si	%	2	251.50	32.103	2	224.28	2.209	27.22	No	No	No
Ag	%	2	102.15	1.853	2	94.94	0.891	7.21	No	Yes	No
Na	%	2	144.00	6.223	2	131.51	1.008	12.50	No	No	No
Sr	%	2	100.65	2.249	2	96.63	0.642	4.02	No	No	No
Zn	%	2	104.09	2.164	2	98.97	0.919	5.12	No	No	No

1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.

2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).

3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).

N: Number of observations.

RSD: Relative standard deviation.

VAR: Variance.

Diff: Difference.

Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

Table 4. Statistical Tests - Water Digestion and Direct Analyses Data.

Analyte	Units	N	222S Mean	222S RSD (%)	N	PNL (325) Mean	PNL (325) RSD (%)	Percent Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)	Diff ⁴ Sign? (0.01)
F ⁻ (IC)	µg/g	4	1.93E+03	9.3	4	2.80E+03	6.5	-36.9	No	Yes	Yes	No
Cl ⁻	µg/g	4	1.64E+03	8.6	4	1.80E+03	4.5	-9.3	No	No	No	No
NO ₂ ⁻	µg/g	4	1.36E+04	9.9	4	1.64E+04	4.3	-18.7	No	Yes	No	No
NO ₃ ⁻	µg/g	4	2.05E+05	10.0	4	2.45E+05	3.8	-17.9	No	Yes	No	No
PO ₄ ³⁻	µg/g	4	2.53E+04	11.3	4	4.00E+04	5.4	-45.0	No	Yes	Yes	Yes
SO ₄ ²⁻	µg/g	4	1.32E+04	8.7	4	1.73E+04	4.4	-27.3	No	Yes	Yes	No
Hg	µg/g	4	1.01E+00	16.8	4	1.09E+00	2.3	-7.8	Yes	No	No	No
TIC	µg/g	3	5.82E+02	4.0	4	2.42E+02	7.2	82.5	No	Yes	Yes	Yes
TOC	µg/g	3	8.46E+02	1.0	4	2.90E+03	9.6	-109.7	Yes	Yes	Yes	Yes
TC	µg/g	3	1.43E+03	1.5	4	3.14E+03	8.4	-75.0	Yes	Yes	Yes	Yes
TGA	%	4	4.48E+01	0.4	4	4.53E+01	3.9	-1.1	Yes	No	No	No
DSC1	J/g	4	1.02E+03	3.5	4	5.80E+02	27.6	55.2	Yes	Yes	No	No
DSC2	J/g	4	4.39E+01	4.4	4	5.10E+01	22.2	-15.0	Yes	No	No	No

- 1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.
- 2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).
- 3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).
- 4: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used both random and systematic variability).

N: Number of observations.

RSD: Relative standard deviation.

VAR: Variance.

Diff: Difference.

Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

Table 5. Statistical Tests - Water Digestion and Direct Analyses Standards Data.

Analyte	Units	N	222S Mean	222S Standard Deviation	N	PNL (325) Mean	PNL (325) Standard Deviation	Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)
F ⁻ (IC)	%	2	113.00	1.980	2	80.80	0.849	32.20	No	Yes	Yes
Cl ⁻	%	2	104.33	2.322	2	90.82	4.749	13.51	No	No	No
NO ₂ ⁻	%	2	100.89	1.813	2	94.38	2.092	6.51	No	No	No
NO ₃ ⁻	%	2	99.23	0.274	2	92.55	2.052	6.67	No	Yes	No
PO ₄ ³⁻	%	2	94.48	0.153	2	92.86	0.612	1.62	No	No	No
SO ₄ ²⁻	%	2	98.41	0.396	2	92.07	0.660	6.34	No	Yes	Yes
Hg	%	2	85.70	2.121	2	87.70	1.273	-2.00	No	No	No
TIC	%	2	99.50	1.179	2	104.42	0.306	-4.92	No	Yes	No
TOC	%	2	93.20	0.236	2	103.75	1.202	-10.55	No	Yes	Yes
TC	%	2	96.35	0.471	2	104.08	0.448	-7.73	No	Yes	Yes
CN	%	2	96.20	3.170	2	91.13	3.446	5.07	No	No	No
TGA	%	2	99.46	0.048	2	98.16	1.672	1.30	Yes	No	No
DSC1	J/g	2	1.37E+03	15.6*	4	1.37E+03	10.3*	0.5\$	No	No	No
DSC2	J/g	2	-4.82E+01	1.0*	4	-4.30E+01	9.3*	11.3\$	No	No	No
DSC3	J/g	2	-4.47E+01	5.1*	4	-4.20E+01	12.6*	6.2\$	No	No	No

1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.

2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).

3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).

N: Number of observations.

RSD: Relative standard deviation.

VAR: Variance.

Diff: Difference.

Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

*: Relative standard deviation.

\$: Percent difference.

Table 5 Statistical Tests - Water Digestion and Direct Analyses Standards Data.

Analyte	Units	N	222S Mean	222S RSD (%)	N	PNL (325) Mean	PNL (325) RSD (%)	Percent Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)	Diff ⁴ Sign? (0.01)
Alpha Total	μCi/	4	8.09E-02	9.2	4	2.15E-01	4.4	-90.5	No	Yes	Yes	Yes
^{239/240} Pu	μCi/	4	1.59E-01	9.6	4	1.83E-01	15.3	-14.3	No	No	No	No
Uranium	μg/g	4	3.57E+02	7.6	4	3.44E+02	3.9	3.8	No	No	No	No
Total Beta	μCi/	4	2.41E+01	9.0	4	2.98E+01	8.2	-21.2	No	Yes	No	No
⁹⁰ Sr	μCi/	4	3.38E+00	17.8	4	4.80E+00	25.8	-34.7	No	No	No	No
¹³⁷ Cs	μCi/	4	2.16E+01	5.2	4	2.19E+01	4.8	-1.6	No	No	No	No
²⁴¹ Am	μCi/	4	1.87E-02	6.1	4	2.44E-02	12.6	-26.6	No	Yes	No	No

- 1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.
 - 2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).
 - 3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).
 - 4: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used both random and systematic variability).
- N: Number of observations.
RSD: Relative standard deviation.
VAR: Variance.
Diff: Difference.
Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

Table 7. Statistical Tests - Radionuclide Standards Data.

Analyte	Units	N	222S Mean	222S Standard Deviation	N	PNL (325) Mean	PNL (325) Standard Deviation	Difference (222S-325)	Var ¹ Sign? (0.05)	Diff ² Sign? (0.05)	Diff ³ Sign? (0.01)
Alpha Total	%	2	106.09	2.609	2	94.14	0.599	11.95	No	Yes	No
^{239/240} Pu	%	2	95.90	2.020	2	104.71	1.495	-8.81	No	Yes	No
Uranium	%	2	85.40	0.849	2	100.83	7.140	-15.43	No	No	No
Total Beta	%	2	115.76	1.295	2	106.83	3.530	8.93	No	No	No
⁹⁹ Tc	%	2	19.09	0.112	2	1342.77	73.785	-1323.68	Yes	Yes	No
⁹⁰ Sr	%	2	92.75	0.905	2	96.77	8.852	-4.02	No	No	No
¹³⁷ Cs	%	2	100.20	0.573	2	99.58	0.423	0.62	No	No	No
²⁴¹ Am	%	2	97.76	0.885	2	95.05	0.498	2.71	No	No	No

1: The hypothesis, equality of variances (versus not equal), was tested at the 0.05 level of significance.

2: The hypothesis, equality of means (versus not equal), was tested at the 0.05 level of significance (used the random analytical variability).

3: The hypothesis, equality of means (versus not equal), was tested at the 0.01 level of significance (used the random analytical variability).

N: Number of observations.

RSD: Relative standard deviation.

VAR: Variance.

Diff: Difference.

Sign?: Is the test statistically significant at the stated significance level (was the hypothesis rejected)?

SEE Data - Phase 3
Silver - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Aluminum - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Boron - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Bismuth - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Magnesium - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Manganese - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Sodium - acid digest

Laboratory (1=325, 2=222S)

SEE Data - Phase 3
Nickel - acid digest

Laboratory (1=325, 2=222S)

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APPENDIX B

SUMMARY OF SEE PHASE III DATA

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Table B-1. Metals Analysis Summary. (Sheet 1 of 4)

Analyte	Prep.	222-S	222-S	222-S	ACL	ACL	ACL	(222-S - ACL)	SSE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	%	Criteria	Criteria	Criteria
		µg/g	µg/g	%	µg/g	µg/g	%	%	Pass/Fail	Yes/No	Yes/No
Ag	Acid	22.5	7.2	32.0	17.9	2.3	12.7	22.8	Fail	No	No
Ag (Std)	% Rec.	102.2	1.9	NA	94.9	0.9	NA	7.4	Pass	No	Yes
Al	Acid	599.6	147.4	24.6	516.9	45.5	8.8	14.8	Pass	No	No
Al (Std)	% Rec.	103.4	1.4	NA	98.2	0.8	NA	5.2	Pass	No	Yes
B	Acid	125.9	31.0	24.6	72.7	14.0	19.2	53.6	Fail	No	Yes
Bi	Acid	28700	7153	24.9	28622	1640	5.7	0.3	Pass	Yes	No
Bi	Fusion	26092	2533	9.7	28973	1478	5.1	-10.5	Pass	No	No
Bi (Std)	% Rec.	101.9	0.5	NA	95.4	0.7	NA	6.6	Pass	No	No
Ca	Acid	962.4	238	24.8	1074	74	6.9	-11.0	Pass	No	No
Ca (Std)	% Rec.	135.5	0.6	NA	119.7	1.0	NA	12.4	Pass	No	Yes
Cr	Acid	1350	342	25.3	1200	98.5	8.2	11.8	Pass	No	No
Cr	Fusion	1317	57.0	4.3	1374	67.8	4.9	-4.2	Pass	No	No

Table B-1. Metals Analysis Summary. (Sheet 2 of 4)

Analyte	Prep.		Mean	Std Dev	RSD	Mean	Std Dev	RSD	ACL	ACL	(222-S - ACL)	SEB	Criteria	Pass/Fail	Yes/No	Yes/No	Sig	Criteria	Yes/No
Cr (Std)	% Rec.	104.1	2.7	NA	99.7	1.0	NA	4.3	Pass	No	No	Pass	Pass/Fail	Yes/No	Yes/No	No	No	Criteria	Yes/No
Cu	Acid	16.0	3.8	24.0	19.6	1.9	9.9	-20.2	Fail	No	No	Pass	Pass	Yes	No	No	No	Criteria	Yes/No
Fe	Acid	26175	6622	25.3	26715	1546	5.8	-2.0	Pass	Yes	No	Pass	Pass	Yes	No	No	No	Criteria	Yes/No
Fe	Fusion	25334	167	6.6	26478	1289	4.9	-4.4	Pass	No	No	Pass	Pass	No	No	No	No	Criteria	Yes/No
Fe (Std)	% Rec.	108.2	2.5	NA	103.1	1.0	NA	4.8	Pass	No	No	Pass	Pass	No	No	No	No	Criteria	Yes/No
Mg	Acid	234	54.9	23.5	248	18.0	7.2	-5.8	Pass	No	No	Pass	Pass	No	No	No	No	Criteria	Yes/No
Mn	Acid	80.4	20.3	25.3	74.1	6.0	8.1	8.2	Pass	No	No	Pass	Pass	No	No	No	No	Criteria	Yes/No
Mn (Std)	% Rec	101.2	2.6	NA	98.3	0.9	NA	2.9	Pass	No	No	Pass	Pass	No	No	No	No	Criteria	Yes/No
Na	Acid	133000	32782	24.65	142345	7269	5.1	-6.8	Pass	Yes	No	Pass	Pass	Yes	No	No	No	Criteria	Yes/No
Na	Fusion	172228	5041	2.9	143922	7561	5.3	17.9	Pass	No	Yes	Pass	Pass	No	Yes	Yes	Yes	Criteria	Yes/No
Na (Std)	% Rec.	144.0	6.2	NA	131.5	1.0	NA	9.1	Pass	No	No	Pass	Pass	No	No	No	No	Criteria	Yes/No
Ni	Acid	24.3	5.2	21.5	19.8	1.2	6.0	20.4	Fail	Yes	No	Fail	Fail	Yes	No	No	No	Criteria	Yes/No

Table B-1. Metals Analysis Summary (Sheet 3 of 4)

Analyte	Prep.	222-S	222-S	222-S	ACL	ACL	ACL	(222-S-ACL)	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	%	Criteria	Criteria	Criteria
		ug/g	ug/g	%	ug/g	ug/g	%	%	Pass/Fail	Yes/No	Yes/No
Ni (Std)	% Rec.	102.5	3.2	NA	99.8	0.9	NA	2.7	Pass	No	No
P	Acid	24925	6261	25.1	24201	3111	12.9	3.0	Pass	No	No
P	Fusion	29430	2278	7.7	27574	1254	4.6	6.5	Pass	No	No
P (Std)	% Rec.	102.6	2.1	NA	95.7	1.2	NA	7.0	Pass	No	No
Pb	Acid	200	52.1	26.1	196	14.3	7.3	2.0	Pass	No	No
Pb (Std)	% Rec.	103.6	2.1	NA	106.3	1.0	NA	-2.6	Pass	No	No
Si	Acid	7615	557	7.3	1188	227	19.1	146.0	Fail	No	Yes
Si	Fusion	15299	964	6.3	15305	855	5.6	-0.0	Pass	No	No
Si (Std)	% Rec	251	32.1	NA	224	2.2	NA	11.4	Pass	No	No
Sr	Acid	267	67.5	25.3	241	20.2	8.4	10.2	Pass	No	No
Sr (Std)	% Rec.	100.7	2.2	NA	96.6	0.6	NA	4.2	Pass	No	No
Zn	Acid	92.7	16.7	18.0	61.0	4.2	6.9	41.2	Fail	Yes	Yes

Table B-1. Metals Analysis Summary (Sheet 4 of 4)

Analyte	Prep.	222-S	222-S	222-S	ACL	ACL	ACL	ACL	222-S -ACL	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	RPD	Criteria	Criteria	Criteria	Criteria
		ug/g	ug/g	%	ug/g	ug/g	%	%	Pass/Fail	Yes/No	Yes/No	Yes/No
Zn(Std)	% Rec.	104.9	2.2	NA	99.0	0.9	NA	5.8	Pass	No	No	No
Hg(AA)	Direct	1.01	0.17	16.8	1.09	0.03	2.3	-7.6	Pass	Yes	No	No
Hg(Std)	% Rec.	85.7	2.12	NA	87.7	1.3	NA	-2.3	Pass	No	No	No

Table B-2. Wet Chemistry Analysis Summary. (Sheet 1 of 3)

Analyte	Prep.	222-S	222-S	222-S	ACL	ACL	ACL	222-S	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	RPD	Criteria	Criteria	Criteria
		ug/g	ug/g	%	ug/g	ug/g	%	%	Pass/Fail	Yes/No	Yes/No
F (IC)	Water	1928	180	9.3	2800	183	6.5	-36.9	Fail	No	Yes
F (ISE)	Water	NA (a)	NA	NA	2849	106	3.7	NA	NA	NA	NA
F (Std)	% Rec.	113.0	2.0	NA	80.8	0.8	NA	33.2	Fail	No	Yes
F (ISE-Std)	% Rec	NA	NA	NA	80.3	1.3	NA	NA	NA	NA	NA
Cl (IC)	Water	1640	141	8.6	1800	82	4.5	-9.3	Pass	No	No
Cl (Std)	% Rec.	104.3	2.3	NA	90.8	4.7	NA	13.8	Pass	No	No

Table B-2. West Chemistry Analysis Summary. (Sheet 2 of 3)

Analyte	Prep.	222-S	222-S	222-S	222-S	ACL	ACL	ACL	222-S - ACL	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	RPD	Criteria	Pass/Fail	Criteria	Criteria
		$\mu\text{g/g}$	$\mu\text{g/g}$	%	$\mu\text{g/g}$	$\mu\text{g/g}$	%	%			Yes/No	Yes/No
NO ₂ (IC)	Water	13575	1345	9.9	16375	709	4.3	-18.7	Pass	Pass	No	Yes
NO ₂ (Std)	% Rec.	100.9	1.8	NA	94.4	2.1	NA	6.7	Pass	Pass	No	No
NO ₃ (IC)	Water	20750	20516	10.0	245000	9381	3.8	-17.9	Pass	Pass	No	Yes
NO ₃ (Std)	Water	99.2- S99.	0.3	NA	92.6	2.1	NA	6.9	Pass	Pass	No Sig	Yes
PO ₄ (IC)	Water	25300	2855	11.3	40000	2160	5.4	-45.0	Fail	Fail	No	Yes
PO ₄ (Std)	% Rec.	94.5	0.2	NA	92.9	0.6	NA	1.7	Pass	Pass	No	No
SO ₄ (IC)	Water	13150	1139	8.7	17300	762	4.4	-27.3	Fail	Fail	No	Yes
SO ₄ (Std)	% Rec.	98.4	0.4	NA	92.1	0.7	NA	6.6	Pass	Pass	No	Yes

Table B-2. Wet Chemistry Analysis Summary. (Sheet 3 of 3)

Analyte	Prep.	222-S	222-S	222-S	222-S	ACL	ACL	ACL	222-S - ACL	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	RPD	Criteria	Pass/Fail	Criteria	Criteria
		$\mu\text{g/g}$	$\mu\text{g/g}$	%	$\mu\text{g/g}$	$\mu\text{g/g}$	%	%	%		Yes/No	Yes/No
Cyanide	Direct	7.8	1.3	17.2	<0.36	NA	NA	NA	NA	Fail	NA	NA
CN (Std)	% Rec	96.2	3.2	NA	91.1	3.4	NA	5.3		Pass	Yes	Yes
TIC	Direct	582	23.5	4.0	242	17.5	7.2	82.5		Fail	No	Yes
TIC	% Rec.	99.5	1.2	NA	104.4	0.3	NA	-4.8		Pass	No	Yes
TOC	Direct	846	8.7	1.0	2901	278	9.6	-109.7		Fail	Yes	Yes
TOC (Std)	% Rec	93.2	0.2	NA	103.8	1.2	NA	-10.8		Pass	No	Yes
TC	Direct	1428	21.5	1.5	3142	265	8.4	-75.0		Fail	Yes	Yes
TC (Std)	% Rec.	96.3	0.5	NA	104.1	0.4	NA	-7.8		Pass	No	Yes

NA - Not Applicable

(a) ISE performed only by PNL

Table B-3. Thermal Analysis Summary.

Analyte	Prep.	222-S	222-S	222-S	ACL	ACL	ACL	ACL	(222-S -ACL)	SHE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD		RPD	Criteria	Criteria	Criteria
		Wt %	Wt %	%	Wt %	Wt%	%		%	Pass/Fail	Yes/No	Yes/No
TGA	Direct	44.8	0.2	0.4	45.3	1.8	3.9		-1.1	Pass	Yes	No
TGA (Std)	% Rec.	99.1	0.05	NA	98.2	1.7	NA		0.9	Pass	No	No
		I/g	I/g	%	I/g	I/g	%		%	Pass/Fail	Yes/No	Yes/No
DSC	Endo- 1 40-180 C	1021	35.4	3.5	580	160	28		55.1	Fail	Yes	Yes
DSC	Endo- 2 250-300C	43.9	1.9	4.4	51	11.3	22.2		-15.0	Pass	Yes	No
DSC (Std)	Endo- 1 20-140 C	1374	214	15.6	1367	141	10.3		0.5	Pass	No	No
DSC (Std)	Exo -1 190-250C	-48.2	0.5	1.03	-43	4.0	9.3		11.4	Pass	No	No
DSC (Std)	Exo -1 260-340C	-44.7	2.3	5.1	-42	5.3	12.6		6.2	Pass	No	No

Table B-4. Radiochemical Analysis Summary. (Sheet 1 of 2)

Analyte	Prep.	222-S	222-S	222-S	ACL	ACL	ACL	(222-S-ACL)	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	RPD	Criteria	Criteria	Criteria
		uCi/g	uCi/g	%	uCi/g	uCi/g	%	%	Pass/Fail	Yes/No	Yes/No
Total Alpha	Fusion	0.081	0.0074	9.2	0.215	0.0095	4.4	-90.5	Fail	No	Yes
Total Alpha (Std)	% Rec.	106.1	2.6	NA	94.1	0.6	NA	12.0	Pass	No	Yes
Total Beta	Fusion	24.1	2.2	9.1	29.8	2.5	8.2	-21.2	Fail	No	Yes
Total Beta (Std)	% Rec.	115.8	1.3	NA	106.8	3.5	NA	8.1	Pass	No	No
Pu-239	Fusion	0.16	0.015	9.6	0.183	0.028	15.3	-13.4	Pass	No	No
Pu (Std)	% Rec	95.9	2.0	NA	104.7	1.5	NA	-8.8	Pass	No	Yes
Am-241	Fusion	0.019	0.0011	6.1	0.024	0.003	12.6	26.6	Fail	No	Yes
Am(Std)	% Rec	97.8	0.9	NA	95.1	0.5	NA	2.8	Pass	No	No
Sr-90	Fusion	3.38	0.60	17.8	4.80	1.24	25.8	-34.7	Fail	No	No
Sr(Std)	%Rec.	92.8	0.9	NA	96.8	8.9	NA	-4.2	Pass	No	No

Table B-4. Radiochemical Analysis Summary. (Sheet 2 of 2)

Analyte	Prep.	222-S	222-S	222-S	222-S	ACL	ACL	ACL	ACL	(222-S -ACL)	SEE	Var. Sig	Mean Sig
		Mean	Std Dev	RSD	Mean	Std Dev	RSD	RPD	Criteria	Yes/No	Criteria	Yes/No	Criteria
		uCi/g	uCi/g	%	uCi/g	uCi/g	%	%	Pass/Fail	Yes/No	Pass/Fail	Yes/No	Yes/No
Cs-137	Fusion	21.6	1.1	5.2	21.9	1.1	4.8	-1.4	Pass	No	Pass	No	No
Cs (Std)	% Rec.	100.2	0.6	NA	99.6	0.4	NA	0.6	Pass	No	Pass	No	No
Tc-99	Fusion	<0.035	NA	NA	0.028	0.0018	6.3	NA	NA	NA	NA	NA	NA
Tc (Std)	% Rec.	19.1	0.1	NA	1343	74	NA	194.0	Fail	Yes	Fail	Yes	Yes
		ug/g	ug/g	%	ug/g	ug/g	%	%	Pass/Fail	Yes/No	Pass/Fail	Yes/No	Yes/No
Total U	Fusion	357	27.1	7.6	344	13.4	3.9	3.7	Pass	No	Pass	No	No
Total U (std)	% Rec.	85.4	0.8	NA	100.8	7.1	NA	-16.5	Pass	No	Pass	No	No

NA - Not Applicable

APPENDIX C

DETECTION LIMITS AND COUNTING ERRORS FOR PHASE III DATA

Table C-1. Metal Detection Limits.

Analyte	222-S Laboratory	ACL
	$\mu\text{g/mL}$	$\mu\text{g/mL}$
Ag	0.01	0.015
Al	0.05	0.06
B	0.05	0.02
Bi	0.1	0.1
Ca	0.1	0.05
Cr	0.01	0.02
Cu	0.01	0.01
Fe	0.05	0.02
Mg	0.1	0.1
Mn	0.01	0.005
Na	0.1	0.08
Ni	0.02	0.03
P	0.2	0.1
Pb	0.1	0.06
Si	0.05	0.08
Sr	0.01	0.005
Zn	0.001	0.02
Hg	0.005	0.002

Table C-2. Wet Chemical Detection Limits.

Analyte	222-S Laboratory	ACL
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Fluoride by ISE	NA	0.2
Fluoride by IC	0.1	0.2
Chloride	0.2	0.2
Nitrite	1	0.4
Nitrate	1	0.4
Phosphate	1	0.4
Sulfate	1	0.4
TIC	5	0.5
TOC	5	0.5
Cyanide	0.03	0.01

Table C-3. Radiochemical Estimated Counting Errors and Uncertainty.

Analyte	222-S	ACL	222-S	ACL
	Counting Error	Uncertainty	Ratio (a)	Ratio (a)
	%	%		
Total Alpha	8	6	0.5	1.05
Total Beta	0.3	5	0.85	1.12
GEA	1.5	4		
$^{239/240}\text{Pu}$	3	10		
^{241}Am	2.7	19		
^{90}Sr	1.6	8		
^{99}Tc	5.6	6		

(a) Ratio for total alpha = total alpha/(Pu + Am)

Ratio for total beta = total beta/($^{90}\text{Sr}/^{90}\text{Y}$ + ^{137}Cs)

APPENDIX D

LABORATORY PROCEDURES FOR SEE PHASE III

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Table D-1. Laboratory Procedures for Phase III of the SEE Program.

Analyte	222-S Procedure	ACL Procedure
Acid Digestion	LA-505-159 (B-2)	PNL-ALO-101
Water Leach	LA-504-101 (C-0)	PNL-ALO-103
Fusion	LA-549-141 (D-0)	PNL-ALO-102
Metals by ICP/AES	LA-505-161 (A-10)	PNL-ALO-211
Mercury by CAVA	LA-325-104 (B-1)	PNL-ALO-213
Anions by IC	LA-533-105 (C-2)	PNL-ALO-212
Fluoride by ISE	NA	PNL-ALO-243
Cyanide	LA-695-102 (C-0)	PNL-ALO-287/289
TOC/TIC	LA-342-100 (A-1)	PNL-ALO-381
DSC	LA-560-112 (A-2) LA-514-113 (B-1)	PNL-ALO-508
TGA	LA-560-112/114 (A-2/B-0)	PNL-ALO-508
Total Alpha	LA-508-101 (D-2) LA-548-101	PNL-ALO-420/421
Total Beta	LA-508-101 (D-2) LA-548-101	PNL-ALO-430/431
GEA	LA-548-121 (D-1)	PNL-ALO-450
^{239/240} Pu	LA-943-127 (A-1)	PNL-ALO-422/423
²⁴¹ Am	LA-953-103 (A-4)	PNL-ALO-450
⁹⁰ Sr	LA-220-101 (D-1)	PNL-ALO-431/433
⁹⁹ Tc	LA-438-101 (D-2)	PNL-ALO-431/432
Total Uranium	LA-925-009 (A-1)	PNL-ALO-445

NA - Not Applicable

APPENDIX D REFERENCES

The following procedures originated at the Westinghouse Hanford Company, Richland, Washington.

LA-505-159, B-2, Acid Digestion of Sediments, Sludges, and Soils for ICP and AA Analysis

LA-504-101, C-0, Water Leach of Solids With Residual Solids Collection

LA-549-141, D-0, Fusion With Alkali Metal Hydroxide

LA-505-161, A-10, Inductively Coupled Plasma (ICP) Emission Spectrometric Method for the Thermo Jarrel Ash (TJA) Type 16E

LA-325-104, B-1, Mercury Analysis by Atomic Absorption - Cold Vapor Technique

LA-533-105, C-2, Anion Analysis on Dionex Model 4000i and 4500i

LA-695-102, C-0, Microdistillation and Spectrophotometric Determination of Cyanide

LA-342-100, A-1, Determination of Carbon by Hot Persulfate Oxidation and Detection

LA-560-112/114, A-2/B-0, Determination of Weight Loss as Percent Water by Thermogravimetric Analysis (TGA) Mettler TC II Analyzer

LA-514-113, B-1, Differential Scanning Calorimetry (DSC)

LA-508-101, D-2, Alpha and Beta in Liquid Samples

LA-548-101, Preparation of Aqueous Mounts for Total Alpha and/or Alpha Energy

LA-548-121, D-1, Preparation of Sample Mounts for Gamma Energy Analysis

LA-943-127, A-1, Determination of PU by Ion Exchange

LA-953-103, A-4, Determination of Americium by Extraction with TRU Spec Resin

LA-220-101, D-1, High Level Strontium 89, 90 in Aqueous Samples

LA-438-101, D-2, Determination of TC-99 by Solvent Extraction and Liquid Scintillation Counting

LA-925-009, A-1, Determination of Uranium by Kinetic Phosphorescence

The following procedures originated at the Pacific Northwest National Laboratory, Richland, Washington.

PNL-ALO-101, Acid Digestion for Metals Analysis

PNL-ALO-103, Waterleach of Sludges, Soils, and Other Solid Samples

PNL-ALO-102, Fusion of Hanford Tank Waste Solids

PNL-ALO-211, Determination of Elements by Inductively Coupled Argon Plasma Atomic Emissions Spectrometry

PNL-ALO-213, Mercury in Water, Solids and Sludges by Manual Cold Vapor Technique

PNL-ALO-212, Determination of Inorganic Anions by Ion Chromatography

PNL-ALO-243, Water Leachable Chloride and Fluoride in Cloth and Other Materials

PNL-ALO-287, Midi and Micro Distillation of Cyanide in Liquid and Solid Samples

PNL-ALO-289, Determination With Spectrophotometry (Manual or Automated) or Argentometric Titration

PNL-ALO-381, Determination of TC, TOC, and TIC in Radioactive Liquids, Soils and Sludges by Hot Persulfate Method

PNL-ALO-508, Laboratory Procedure for Operation of the Differential Scanning Calorimeter (DSC), Thermogravimetric Analyzer (TG), and High Temperature Differential Thermal Analyzer (DTA) and DSC

PNL-ALO-420, Solution Analysis: Preparation of Alpha Sources by Direct Evaporation

PNL-ALO-421, Solutions Analysis: Alpha Counting

PNL-ALO-430, Preparation of Beta Sources by Direct Evaporation

PNL-ALO-431, Total Beta Counting and Analysis

PNL-ALO-450, Gamma Energy Analysis - TRACK Detector

PNL-ALO-422, Solutions Analysis: Alpha Spectrometry

PNL-ALO-423, Separation of Plutonium by Solvent Extraction Prior to Measurement by Alpha Counting

PNL-ALO-433, Separation of Sr-90 by Cation Exchange Prior to Measurement by Beta Counting

PNL-ALO-445, Solution Analysis: Uranium by Laser Excited Fluorescence

APPENDIX E

COMPARISON OF PHASE III DATA WITH 1990 HISTORICAL WASTE ANALYSIS

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Table E-1. Comparison of SEE Results with Historical Data for Tank B-110. (Sheet 1 of 2)

Analyte	Historical	ACL	Ratio	222-S	Ratio
	μg or $\mu\text{Ci/g}$	μg or $\mu\text{Ci/g}$	Historical/ACL	μg or $\mu\text{Ci/g}$	Hist./222-S
Wt% Water	61.05 %	45.3 %	1.35	44.8 %	1.36
Bi (Fusion)	22137	28973	0.76	26092	0.85
Fe (Fusion)	20590	26477	0.78	25333	0.81
Na (Fusion)	127615	143922	0.89	172228	0.74
P (Fusion)	19561	27573	0.71	29429	0.66
Si (Fusion)	10478	15304	0.68	15299	0.68
Bi (Acid)	16171	28622	0.57	28700	0.56
Fe (Acid)	20685	26714	0.77	26175	0.79
Na (Acid)	127134	142344	0.89	133000	0.96
P (Acid)	19814	24200	0.82	24925	0.79
Al (Acid)	544	516.9	1.05	599.6	0.91
Cr (Acid)	1063	1200	0.89	1350	0.79
Fluoride	1826	2800	0.65	1928	0.95
Chloride	1522	1800	0.85	1640	0.93
Nitrite	13899	16375	0.85	13575	1.02
Nitrate	230479	245000	0.94	204750	1.13
Phosphate	29057	40000	0.73	25300	1.15
Sulphate	14978	17300	0.87	13150	1.14
TIC (a)	1266	242	5.23	582	2.18
TOC (a)	669	2900	0.23	846	0.79
TC (a)	1936	3142	0.62	1428	1.36
Cyanide	6.2	<0.36	NA	7.8	0.79

Table E-1. Comparison of SEE Results with Historical Data for Tank B-110. (Sheet 2 of 2)

Analyte	Historical	ACL	Ratio	222-S	Ratio
	μg or $\mu\text{Ci/g}$	μg or $\mu\text{Ci/g}$	Historical/ ACL	μg or $\mu\text{Ci/g}$	Hist./222-S
Hg	1.6	1.09	1.47	1.01	1.58
^{137}Cs	20.3	21.9	0.93	21.6	0.94
T Alpha (b)	0.24	0.214	1.12	0.081	2.96
T Beta (b)	354	29.8	11.88	24.1	14.69
^{90}Sr (b)	199	4.8	41.46	3.38	58.88
^{99}Tc (b)	0.028	0.028	1.00	<0.03	NA
U (b)	304	344	0.88	357	0.85

- (a) Historical analyses performed on water leach rather than direct sample as in SEE Phase III.
- (b) Results based on historical composite sample rather than individual segments

APPENDIX F

EXAMPLES OF DSC/TGA SCANS FOR PHASE III SAMPLE AND STANDARDS

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Figure F-1. 222-S Laboratory DSC Sample Scan.

Figure F-2. 222-S Laboratory DSC Standard Scan.

Figure F-3. ACL DSC Sample Scan.

Figure F-4. ACL DSC Standard Scan.

Figure F-5. 222-S Laboratory TGA Sample Scan.

Figure F-6. 222-S Laboratory TGA Standard Scan.

Figure F-7. ACL TGA Sample Scan.

Figure F-8. ACL TGA Standard Scan.

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