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Sample Exchange Evaluation (SEE) Report - Phase II

September 28, 1994

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EXECUTIVE SUMMARY

This report describes the results from Phase II of the Sample Exchange Evaluation (SEE) program. The SEE program is a joint effort of Westinghouse Hanford Company, Analytical Services (AS), and Pacific Northwest Laboratory, 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 samples from two waste tanks, B-111 and T-107. In Phase II, the program has been expanded to include inorganic constituents in addition to radionuclides. Results from Phase II that exceeded a 20% relative percent difference (RPD) criteria are identified in the table at the end of this summary.

Evaluation of data from Phase II of the SEE program did not identify any areas that required immediate corrective action. Several areas were identified that should continue to be monitored or evaluated further. They are as follows:

- Trace metal analyses by Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES)
 - Examples: Al, Si, Zn, Ca, Ti
- Fluoride analyses by ion chromatography (IC)
 - Comparison of IC with ion selective electrode (ISE)
- Total organic carbon (TOC) analyses
 - Compare hot persulfate oxidation methods on solid samples
 - Complete method comparisons for different organics
- Total inorganic carbon (TIC) analyses
- Cyanide (CN) analyses
 - Compare cyanide methods on solid ferrocyanide wastes
- Total alpha analyses
 - Confirm that recent 222-S Laboratory instrumentation modifications will produce comparable results
- Total beta analyses
 - Monitor after 222-S Laboratory changes total beta calibration efficiency to ^{137}Cs in 1995
- Continue to monitor $^{239/240}\text{Pu}$, ^{99}Tc and uranium analyses.

Phase I and II sample exchange results have shown that the analytical methods tested from ACL and the 222-S Laboratory produce comparable results on homogeneous waste solutions. Total alpha measurement problems, identified in Phase I, at 222-S Laboratory were not completely corrected in Phase II. Additional corrections have been made to the alpha systems since Phase II was completed and will be evaluated in Phase III. Phase I recommended further evaluation of uranium data in Phase II. Phase II uranium data showed that the 222-S Laboratory precision for uranium was significantly larger than ACL. It is recommended that the 222-S Laboratory investigate ways to improve the

uranium method's reproducibility. As identified in Phase I, it is imperative that the beta energy (isotope) used for calibration of total beta measurements be reported with total beta data so that reported values can be converted to the same base for comparison.

Results from Phase I and II provide sufficient information to permit the SEE program to initiate testing of procedures on solid waste samples. Phase III will include testing of laboratory digestion procedures and analytical methods that are normally applied directly to solid waste samples. Continued monitoring of some methods and comparison with alternative technologies such as inductively coupled plasma mass spectrometry and ion selective electrode (ICP/MS, ISE) will improve the confidence in the method evaluations.

Discussion:

The SEE program is being performed in phases to permit a systematic evaluation of observed differences between laboratories. Phases I and II have focused on the comparison of analytical methods by performing the analyses on homogenous solutions of commonly prepared samples. Later phases of the program will include comparison of sample preparation and solid handling procedures.

For Phase II, ACL performed three different types of sample preparations (fusion, acid digestion, and water leach) on waste samples from tanks C-112 and B-201. These tanks represent wastes from the ferrocyanide and bismuth phosphate processes respectively. Four replicate aliquots from each preparation were submitted to ACL and 222-S Laboratory for analysis. In addition, four replicate aliquots of standard materials were also submitted to each laboratory. The number of replicates were increased in Phase II to permit the statistical evaluation of the data. These aliquots were submitted to the laboratories as single blind samples; laboratory personnel knew they were part of the SEE program but did not know the concentration values for the samples or the standards.

The fusion and acid digestions were analyzed by both laboratories for 15 metals using inductively coupled plasma atomic emission spectroscopy (ICP/AES). In addition, PNL performed inductively coupled plasma mass spectrometry (ICP/MS) analyses on these same solutions. Water leaches were analyzed for 6 anions by ion chromatography, cyanide, total organic carbon and inorganic carbon, and tritium. Radiochemical measurements for total alpha, total beta, gamma energy analysis (GEA), $^{239/240}\text{Pu}$, ^{241}Am , ^{90}Sr , ^{99}Tc and uranium were performed on the fused sample aliquots. The analytical measurement scheme for Phase II is summarized in Figure 1.

The results from the laboratories were initially evaluated against a SEE criteria of 20% relative percent difference (RPD) between laboratory means whose results were greater than five times the method detection limit or had counting errors of less than 15%. The analytes that exceeded this RPD criteria were identified in a preliminary letter report as shown in Appendix A. The data was also submitted for statistical evaluation of the differences. Letter reports of this study were issued as shown in Appendix B. This final report on the Phase II data summarizes these evaluations and provides additional explanation for the observed differences.

Metals - The ICP/AES results for all the major analytes and most of the minor analytes from the laboratories were in agreement. Large percent differences in the results for trace amounts of Zn and Ti in the samples could not be fully explained. Trace element results may be subject to many interferences in these complex waste matrices.

Initially the 222-S Laboratory ran the ICP/AES analyses on diluted (1:10) samples. Differences of 10% to 20% were observed for some major components (e.g., Bi, Na, and P) when comparing samples analyzed directly with those determined on larger dilutions. The diluted samples normally gave higher results. ICP/AES analyses were later rerun on direct (undiluted) samples to provide a more comparable data set.

The precision on the replicates was very good for both laboratories. Because of this very small variance within the laboratories, the statistical data evaluation indicated significant differences between laboratories in the means and variances for many of the ICP/AES analyses. Even though there may be statistically significant differences between the laboratories, these differences are not considered practically significant because they represent relatively small errors for normal ICP/AES operation. Future phases of SEE should include additional ICP/AES comparisons to confirm these observations and to provide a better understanding of the ICP/AES differences for trace analytes.

Anions/Wet Chemical Analyses - The anion results by ion chromatography were all within the SEE 20% RPD criteria except for the C-112 tank fluoride result and the B-201 tank phosphate result. In both these cases the ions were present in low concentrations. The chromatograms in the C-112 tank sample indicated the presence of potentially interfering anions or water soluble organic species. Further evaluation of the fluoride measurements will be performed in Phase III by comparing ion chromatography fluoride results with ion selective electrode (ISE) measurements. Phosphate results for the C-112 tank wastes, where the concentration of phosphate was higher, were acceptable. Evaluation of the ion chromatography performance for phosphate and other anions near the detection limit will be included in future SEE testing.

The cyanide concentrations in the B-201 tank waste were too low for accurate comparison. Even though the cyanide results for the C-112 tank samples did not fail the 20% RPD criteria, the differences were larger than desired for this analyte. The relative standard deviation (RSD) for the C-112 replicates for the 222-S Laboratory were larger than normal. Additional testing on ferrocyanide wastes should be performed on solid samples using the new ethylenediaminetetraacetic acid (EDTA)/ethylenediamine (EN) dissolution procedure for these materials.

Poor agreement between laboratories was obtained for all TOC measurements. The level of TOC in the B-201 tank waste sample was near the method quantitation limits which caused large variations in the results and made accurate comparisons impossible. The levels of TOC in the C-112 tank were about three times higher than the B-201 tank and the precision for the analyses were much better. The large RPD (+55%) observed for the C-112 tank data could be the result of differences in the laboratory methods. The ultra violet(UV)/persulfate oxidation method used by the ACL may not have oxidized the relatively large quantities of cyanide in the C-112 tank sample. This

would produce lower results than the furnace oxidation method used by the 222-S Laboratory, which is expected to oxidize the cyanide in the sample. Even though there is some evidence that this is the reason for the differences, further evaluation and comparison of the TOC methods is needed to confirm the explanation. The 222-S Laboratory TOC standard results are biased about 20% low, when they should have been biased 15% high, if the cyanide was being oxidized in the TOC procedure. The cause of the low standard results for the 222-S Laboratory cannot be explained. Further comparison of TOC results on liquid and solid samples is recommended. Comparison of the hot persulfate TOC methods used by both laboratories should be evaluated for solid waste samples.

Total inorganic carbon RPD results for the B-201 tank and the standard exceeded the 20% limit. The ACL standard results were biased 25% high and had a relatively large standard deviation (16%). This could explain the RPD differences for the B-201 tank result. The C-112 tank TIC results for both laboratories agreed very well and had good precision. The cause of high standard recoveries for the ACL could not be identified. Because of the inconsistency in the data, additional evaluation of the TIC analyses will be required.

Radiochemical Analyses - The total alpha results for the C-112 tank waste sample had an RPD of + 29%. This difference is believed to have been caused by a 222-S Laboratory alpha counting system that counts a small fraction of the beta activity in the alpha measurement. This is primarily a problem for samples containing large quantities of beta emitting isotopes such as $^{90}\text{Sr}/^{90}\text{Y}$ and ^{137}Cs . The problem is not observed for the B-201 tank samples because the beta activity is low. Efforts to correct this problem, after it was identified in Phase I of the SEE program, did not completely resolve the problem. Since Phase II, software controlling the alpha counting system has been improved further and based on recent testing no future problems are expected. Total alpha measurements will continue to be monitored in the next phase of the SEE program.

The plutonium RPD results (-34%) for the B-201 tank exceeded the 20% criteria. Evaluation of the data and discussions with the technical staff indicate that problems with the ^{236}Pu tracer used at 222-S Laboratory may have been the cause of the difference. During the time period of Phase II Pu analyses, the amount (volume) of tracer available was limited because of difficulties in purchasing the isotope. The remaining small tracer volumes were more sensitive to evaporation and may have become more concentrated. Reanalysis of the samples with a new batch of tracer produced comparable results (RPD = 3.8%).

All other radiochemical results were within the SEE 20% limit. ^{99}Tc RPD results for the C-112 tank were relatively large (+16%). This may be explained by the ^{99}Tc standard results for the ACL which were biased low by about the same amount (+17%). Even though there were no significant differences in the means for the uranium fluorometric results, the 222-S Laboratory method appears to have a significantly larger variance than the ACL. The cause of this larger variation will require further evaluation. No immediate action other than to continue to monitor the performance of these methods is planned at this time. See Table ES-1 for additional information.

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

Analyte	Tank	RPD	Explanation
Bi	B-201 (Acid)	22%	Comparison of different dilutions
Ca	Standard	33%	Possible contamination in 222-S result
Zn	B-201 (Fusion)	119%	Near quantitation limit (1)
	C-112 (Fusion)	87%	Near quantitation limit (1)
	B-201 (Acid)	22%	Possible matrix effect
Ti	C-112 (Acid)	124%	Near quantitation limit (1) Possible matrix effect
Total alpha	C-112	29%	Alpha instrument problem (222-S)
Pu	B-201	34%	Possible Pu-236 tracer problem (222-S)
Cyanide	B-201	59%	Near detection limit (2)
TOC	B-201 C-112 Standard	75% 55% 22%	Near detection limit (2) Possible method difference Unexplained (222-S)
TIC	B-201	25%	Near detection limit (2)
	Standard	23%	Unexplained (ACL)
Fluoride	C-112	57%	Interfering ions Near quantitation limit (1)
Phosphate	B-201	54%	Near detection limit (2)

(1) Analytes with concentrations near the quantitation limit - 10 times the method detection limit.

(2) The 20% RPD criteria is not applicable to analytes with concentrations less than 5 times the method detection limit or with counting errors greater than 15%.

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LIST OF TERMS

ACL	Analytical Chemistry Laboratory
ALO	Analytical Laboratory Operation
AS	Analytical Services
CN	cyanide
EDTA	ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
GEA	gamma energy analysis
IC	ion chromatography
ICP/AES	inductively coupled plasma atomic emission spectroscopy
ICP/MS	inductively coupled plasma mass spectrometry
ISE	ion selective electrode
MEAN SIG	mean statistically significant
PNL	Pacific Northwest Laboratory
QA/QC	quality assurance/quality control
RPD	relative percent difference
RSD	relative standard deviation
SD	standard deviation
SEE	Sample Exchange Evaluation
TC	total carbon
TIC	total inorganic carbon
TIC/TOC/CN	total inorganic carbon/total organic carbon/cyanide
TIC/TOC	total inorganic carbon/total organic carbon
TOC	total organic carbon
UV	ultra violet
VAR SIG	variance significant difference
WHC	Westinghouse Hanford Company

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1.0 INTRODUCTION

The sample exchange evaluation (SEE) program is a joint effort of Westinghouse Hanford Company (WHC), Analytical Services (AS) and Pacific Northwest Laboratory (PNL), Analytical Chemistry Laboratory (ACL) to compare analytical laboratory performance on sample materials unique to the Hanford Site Nuclear Reservation. The program is administered by the quality assurance/quality control (QA/QC) Triad consisting of representatives from the two participating laboratories, 222-S Laboratory (WHC) - Analytical Laboratory Operation (ALO) and the Analytical Chemistry Laboratory (PNL), and the Office of Quality Assessment group from the WHC Analytical Services organization. This Triad is responsible for developing the sample exchange plan, setting the schedules, coordinating data evaluation, and reporting the findings to management.

The SEE program is designed to evaluate all the major measurement systems that are common between the participating laboratories. The objective of the SEE program is to understand the analytical variances associated with each step in the analytical process (analytical measurement, sample preparation, subsampling), with the final goal of implementing a routine exchange of samples. 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's primary focus is on evaluating laboratory performance and comparability in the analysis of high level waste tank samples at the Hanford Site.

This report documents the results from Phase II of the SEE program. 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) located on the Hanford Site. Phase II of the program has been expanded to include the following:

- Analysis for metals in homogeneous liquids prepared by both KOH fusion and acid digestion
- Analysis of anions, tritium and total organic and inorganic carbon prepared by water leaching
- Analysis of radionuclides prepared by fusion as in Phase I.

2.0 SUMMARY OF PHASE II PLAN

Exchange samples were prepared by the ACL from the C-112 and B-201 tanks core material. These tanks represent waste from two different Hanford Site processes. Tank C-112 contains waste from the ferrocyanide cesium removal process and tank B-201 contains waste from the bismuth phosphate process. ACL performed three different types of sample preparations (fusion, acid digestion, and water leach) on aliquots of each waste tank sample. The preparations resulted in a sufficient volume of homogenous solution to supply each lab with four replicate aliquots for analysis. The Phase II sample analysis scheme is outlined in Figure 1.

In addition to the multiple samples of wastes, four aliquots of five blind QC standards were submitted to each laboratory for analysis. The different standards were:

- One mixed radionuclide standard
- Two mixed metal standards
- One TOC/TIC/CN mixed standard
- A mixed anion standard.

The radiochemical standards were prepared by the ACL standards laboratory and the inorganic standards were prepared by the AS standards laboratory.

The limited number of replicates in Phase I made it difficult to assess the variability of the results within a given laboratory and significant differences between the laboratories. The number of replicates were increased from two to four in Phase II to improve variability estimates and to permit a statistical evaluation of the data.

Even though the waste material had been analyzed previously, the samples were distributed as single blind samples (laboratories knew they were control samples but did not know the concentrations). Data on the weight and volumes used to prepare the samples were not distributed to the laboratories.

3.0 DATA EVALUATION

Each laboratory compiled their results and submitted the data to the QA/QC Triad for review. The Triad performed an initial review of the data by evaluating the relative percent difference (RPD) between means of the four sample results for each analyte. This initial evaluation was summarized in a letter report issued on March 31, 1994 and is provided in Appendix A.

In addition, the Triad submitted the data for statistical analysis by the AS statistics group. The statistical analysis is provided in two letter reports in Appendix B. The first statistical report (April 1, 1994) used ICP/AES data from the 222-S Laboratory that was based on diluted (1:10) sample preparations. Because of the dilution, several of the analytes were near or below detection limits and could not be properly compared to the ACL

Figure 1. SEE Phase II Analysis Scheme.

data, which were based on direct analysis of the samples. After the initial data evaluation, the 222-S Laboratory was asked to reanalyze the samples without dilution to provide a more comparable data set. The statistical evaluation of this undiluted sample ICP/AES data is described in the second letter (July 21, 1994) in Appendix B.

The relative percent difference of the means is based on the following formula:

$$RPD = \frac{(ALO - ACL) * 100}{\frac{(ALO + ACL)}{2}}$$

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

Normally RPD is reported as an absolute number. However, in this report a positive or negative RPD sign may be used to indicate that the 222-S Laboratory reported a higher or lower value than the ACL.

Several criteria may be used to evaluate the data. The QA/QC Triad has established a fixed RPD value of 20%, that when exceeded requires further investigation. However, this 20% RPD 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 1) have 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 near (RPD = 15% to 20%) the fixed criteria 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 Appendices C through H. The mean, standard deviation (SD) 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).

Results near the SEE limit have been flagged in the tables using parentheses as follows: (Pass). Appendix G contains estimates of the method detection limits and also the radiochemical counting uncertainties. The radiochemical 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 also contains ratios for 1) the total alpha to the sum of the Pu and Am result and 2) total beta to the sum of the

Table 1. Areas of Significant Differences In Phase II SEE Data. (2 sheets)

Analyte	Exceeds 20% Criteria	Near 15-20% Criteria	Statistical Mean Difference	Statistical Variance Difference
Al		C (A)	C(F), B(A), C(A)	B(A), C(A)
Bi	B(A)		B(A), C(A) ^a , Std	B(F), B(A), Std
Ca	Std			C(F), C(A), Std
Cr			B(F) ^a , B(A) ^a , C(A) ^a	Std
Fe			B(F) ^a , C(F) ^a , B(A) ^a , Std	C(F), C(A), Std
La			C(A) ^a , Std	B(F), B(A), Std
Mn			B(F) ^a , Std	B(F), C(A), Std
Na				C(A)
P			C(F), B(A), C(A)	C(A)
Si			B(F), C(F), C(A)	B(A)
Sr			C(A) ^a , Std	B(F), C(F)
Zn	B(F), C(F), B(A)		B(F), C(F), B(A), C(A) ^a	C(A)
Pb			B(A) ^a	C(A), Std
Ti	C(A)		C(A)	
U (ICP)				
T. Beta		B	B, C, Std	C, Std
T. Alpha	C	B	B, C	Std
Cs-137			B	B, Std
U (Fluor)				B, C, Std
Pu	B	C	B	C
Am			Std	
Tc-99		C, Std	C, Std	C, Std
Sr-90			Std	B
H-3			B	Std
CN	B	C	Std	C
TOC	B, C, Std		C	Std

Table 1. Areas of Significant Differences In Phase II SEE Data. (2 sheets)

Analyte	Exceeds 20% Criteria	Near 15-20% Criteria	Statistical Mean Difference	Statistical Variance Difference
TIC	B, Std			Std
F	C		B, C, Std	
C1			Std	B, C, Std
N02				
N03			Std	
P04	B		B, Std	B, C
S04			Std	C

a) Not significant at 0.01 significance level when both random and systematic errors are used.
 B = Tank B-201, C = Tank C-112, A = Acid Digestion, F = Fusion, Std = Standard

^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$ results. The beta ratio has been adjusted for the ^{90}Y equilibrium and differences between laboratories in the counting efficiency used for total beta measurements.

The detection limits are based on method performance on simple matrices and normal sample sizes. The ICP/AES limits are estimates of the instrument detection limit. These detection limits will increase for more complex matrices. The limits provided are intended for evaluation purposes to permit better understanding of the data. Some analyses, such as ion chromatography, require dilution before measurement. In these cases, the results must be divided by the dilution factor before comparing to the detection limits. Appendix H contains additional summary tables and graphical representations of the results. Individual results for each of the four replicate samples may be obtained in the statistical report in Appendix B.

4.0 METALS ANALYSIS

4.1 COMPARISON OF ANALYTICAL METHODS

Metal concentrations were determined by both laboratories in the fused and acid digested samples using ICP/AES. The 222-S Laboratory performed the analysis using an ARL 3580 direct reading ICP/AES as described in procedure LA-505-151 (Wels 1994). The ACL performed the metals analysis using a Thermo Jarrel Ash Model 61 direct reading ICP/AES as described in PNL-ALO-211. PNL also analyzed the metals by inductively coupled plasma mass spectrometry (ICP/MS) according to procedure PNL-ALO-280 and PNL-ALO-281 using a VG PlasmaQuad spectrometer.

The technical basis of the ICP/AES systems for both laboratories are essentially the same. Some differences in instrument configuration, such as wavelengths used for measurement and types of nebulizers, may exist. A comparison of the wavelengths and instrument parameters used by both laboratories is summarized in Table 2. Other differences may exist in the techniques used to make interelement and background corrections depending on the software available on the ICP instrument.

Initially the 222-S Laboratory analyzed the samples using a 1:10 dilution. This dilution can affect the comparability of both trace and major analytes. Because of the dilution, the sensitivity of the ICP/AES analysis is reduced for some analytes and the relative error for trace metals increased. Dilution can also affect the rate of nebulization and emission suppression effects that can cause differences in the major analytes. The 222-S Laboratory ICP/AES analyses were rerun without dilution to obtain a more comparable data set to ACL results. Both the diluted and undiluted data sets have been statistically evaluated in Appendix B.

Because the ICP/MS uses a different measurement basis than ICP/AES for the measurement of metals, it represents an independent check for metal results. The ICP/MS technique is more sensitive for most metals than ICP/AES and is subject to different types of interferences. In general, the mass spectra are more simple than atomic emission spectra but the mass spectra must be evaluated for isobaric interferences. Even though the ICP/MS is not as mature as the ICP/AES technology, the method provides excellent complementary results for some analytes. A summary of the ICP/MS results is provided in Appendix D.

The fusion preparation of samples requires the addition of large quantities of KOH and results in nickel contamination of the sample from the nickel crucible. The fusion normally results in a 1:400 dilution of the waste after about 0.2 g to 0.5 g of waste is fused in several grams of KOH and dissolved and brought to a 200 mL volume with water and HCl. Additional dilution of the fused sample is required before analyzing by ICP/AES to reduce the high salt concentration from the KOH. Because of the large dilution and introduction of contaminants, the fusion is normally used for the analysis of major metals and acid insoluble components such as silicon rather than trace analytes. However, if the ICP/AES has adequate sensitivity for the trace analyte, reasonable results may be obtained for those analytes on the fused material. Some of the trace analytes, such as Pb, U, and Ti, are not reported for the fused samples because of inadequate sensitivity.

The acid digestion procedure is based on the SW-846 method 3050 (EPA 1990). Approximately 1 g of waste is digested in concentrated HNO_3 followed by treatment with H_2O_2 and a final digestion in HCl. The sample is brought to a final volume of 100 mL, which results in an approximate dilution factor of 100. The acid digestion method is not considered a total dissolution technique since silica and other highly insoluble compounds may not dissolve completely. The final digestion solution is normally filtered to remove suspended solids before analysis by ICP/AES. Because the acid digestion provides a less complex, more concentrated solution of the waste, it is normally the preferred method for determining trace analytes.

Table 2. Comparison of ICP/AES Instrumentation.

Parameter	222-S Laboratory	ACL
ICP/AES Wavelengths	ARL 3580	TJA 61
Al	308.22	308.22
Bi	223.06	223.06
Ca*	393.37	317.90
Cr*	267.72	205.50
Fe*	259.94	381.90
La*	379.48	398.85
Mn	257.61	257.60
Na*	589.59	588.90
P*	178.29	214.90
Pb	220.35	220.30
Si	288.16	288.10
Sr	421.55	421.50
Ti*	337.28	334.90
U*	409.01	378.28
Zn	213.86	213.80
Nebulizer	Hildebrand platinum grid - high solids	Fixed position -cross flow
Interelement Correction	YES- On Line	YES - On Line
Background	YES - Off Peak	NO

* Laboratories used different wavelength

The actual weights and volumes used in the preparation of the fusion, acid and water preparations are summarized in Table 3. The fused samples were diluted 20 mL to 200 mL before submitting to the laboratory for analysis. The acid digestions were diluted to 200 mL volume to provide adequate volume for eight 25 mL aliquots. The normal water leach conditions were doubled from 1 g to 100 mL to 2 g to 200 mL to provide the additional volumes of sample needed for replicates. Several different water leaches were prepared for the analytes of interest.

Table 3. Sample Preparation Summary.

Tank	Digestion	Weight (g)	Volume (mL)
B-201	Fusion (a)	0.1628	200
	Acid	1.0631	200
	Water	2.0731	200
	(TIC/TOC/CN)		
C-112	Fusion (a)	0.2365	200
	Acid	1.0133	200
	Water	2.0491	200
	(TIC/TOC/CN)		
B-201	Water (H-3)	2.15054	200
	Water (CN)	2.0451	200
C-112	Water (H-3)	2.0726	200
	Water (CN)	2.0473	200
(a) Fused samples were diluted 20 mL to 200 ml before submitting to the laboratories for analysis.			

4.2 DISCUSSION OF METALS RESULTS

The metal analysis results for the ICP/AES and ICP/MS are summarized in Appendix C and D respectively. The table is organized by analyte providing information for the fusion, acid, and standards. Because the purpose of this study was not to compare ICP/AES to ICP/MS, the ICP/MS data was primarily used to help explain areas where the laboratory ICP/AES data are in disagreement. The percent difference between each laboratory's ICP/AES result and the ICP/MS values is provided in Appendix D.

In general, the ICP/AES data from the two laboratories agreed very well with only a few analytes exceeding the SEE RPD criteria. Data from both laboratories showed very good precision for the four samples analyzed. The ACL results normally showed smaller standard deviations for most analytes than the 222-S Laboratory. Because of these small standard deviations for both laboratories, several of the analytical results showed statistically significant variance and mean differences. The small standard deviations are partly the result of analyzing the samples in the same batch. When the data is analyzed with systematic error, as described in the second letter in Appendix B, many of the differences between means are no longer significant. Even if the mean data is statistically different, they may not be practically significant if the RPDs are small (e.g., <10%). Likewise, the data may show significant variance differences even when the RSDs are relatively small (e.g., < 5%).

4.2.1 Aluminum

Aluminum was a minor component (< 0.1%) in both tank samples. For fusion samples, the Al concentration was slightly above quantitation limits (i.e., 10

times instrument detection limits). The relative standard deviations for the measurements from both labs were less than 2.5%; therefore, statistical variance differences are probably not important. The aluminum RPD result (+16.8%) for the acid digested in tank C-112 samples is the only result that is near the SEE RPD limit. Both the acid and fusion Al results for C-112 show the 222-S Laboratory high compared to the ACL. These means were also statistically significant. The C-112 tank waste contains a significant quantity of uranium that has a complex spectra that could potentially cause high results. Both laboratories used the same Al wavelength for analysis and performed interelement corrections. The ICP/MS aluminum results agree closer with the 222-S Laboratory ICP/AES results. No aluminum was included in the standards analyzed; therefore, systematic error effects on the mean differences cannot be evaluated. There appears to be a potential difference in the Al results; however, its practical significance at these low concentrations is questionable. Further evaluation will be needed to determine if the difference is significant and consistent.

Aluminum was identified in the preliminary report (Appendix A) as exceeding the SEE RPD limit for the fusion analysis on both tank materials. The reanalysis of the undiluted samples by 222-S Laboratory reduced this difference to acceptable levels. The diluted fusion samples were very near the instrument detection limits.

4.2.2 Bismuth

Bismuth is a major component in the B-201 tank sample and a minor component in the C-112 tank material. All of the RSDs are less than 2%; therefore, the statistically significant variances are not critical in the evaluation. The bismuth RPD result (+22.2%) for the acid digestion of the B-201 tank material exceeded the SEE RPD criteria. This is the result of comparing diluted (222-S) versus undiluted (ALO) data. When the 222-S Laboratory reanalyzed the undiluted B-201 tank acid sample, the Bi concentration exceeded their calibration range and the data was not reported. Therefore, the data summary in Appendix C used the earlier diluted result (noted by an *) for comparison. Examination of the raw data shows that the Bi result on the direct sample analysis (541 ug/mL), that was not reported by 222-S Laboratory, has an RPD of about 2% compared to the ACL. This difference is not considered significant. However, it does indicate that fairly large differences (10-20%) in data can be observed from different dilutions of major components. ICP/MS results fall between the two laboratory values. The standard results do not indicate any significant systematic errors. However, the means of the standards are statistically significant even though the RPD is only 2.4%.

Bismuth was reported in the preliminary report to exceed the SEE limit for the acid and fused B-201 tank samples. The difference in the acid results is explained above. The difference in the fusion results was eliminated when undiluted sample data was used in the comparison.

4.2.3 Calcium

The calcium concentration in both waste tank samples was above the trace level (0.1%) but not over 1%. Except for the standards data, the RSDs for the data were less than 5%. The ACL calcium data appears to be more precise than the 222-S data. This may be the result of calcium contamination problems at the 222-S Laboratory. The standards data are the only results that exceeded the SEE limit. Contamination of the sample during analysis is the expected cause for the difference. Three of the four standards were bias high and the variability of the data was large ranging from 9.8 ug/mL to 19.8 ug/mL. Calcium contamination is an occasional problem at the 222-S Laboratory. This is primarily caused by the powdered talc used on the latex gloves worn during analysis. This problem reoccurs even though efforts are made to wash the talc from the gloves before use. Other 222-S Laboratory calcium analyses do not appear to be bias high because of contamination. There were no statistical differences in the means of the tank sample data.

4.2.4 Chromium

Chromium concentration in the C-112 tank waste was about twenty times lower than the Cr levels in the B-201 tank, which were near 0.2%. The RSDs for the data were less than 2.5%; therefore, the variance differences are probably not significant. Even though the difference in the means from three of the samples were statistically significant based on the random error, they were not significant when both random and systematic errors were used in the evaluation. The ACL sample results appear to be a few percent higher than the 222-S Laboratory data but the RPDs are all less than 5%. The standards data show good recoveries for both labs with no significant difference in the mean.

4.2.5 Iron

Iron was a major component in both tank wastes. The RSDs for all the Fe results were less than 2% except for the 222-S Laboratory acid digest C-112 tank result, which was 4.6%. Differences in variances between labs are probably not important. Three of the sample analyses and the standard had statistically significant means; however, the sample mean differences were not significant when the systematic error was included in the evaluation. All of the RPDs were less than 10%.

4.2.6 Lanthanum

Lanthanum was a major component in the B-201 tank waste and a minor constituent in the C-112 tank material. The RSDs were all 3% or less; therefore, the differences noted for variance are probably not important. The C-112 tank acid results had a relatively large RPD (-11.9%). The C-112 tank La concentration was near the quantitation limits where larger errors may be expected. The ICP/MS result for the La in the acid C-112 tank sample was considerably higher than both laboratory ICP/AES results. The only statistically significant mean difference was for the standard material whose RPD was 6.5%. The 222-S Laboratory standard results are bias 2% high and the

ACL results are bias 4% low. This is still reasonable performance for the ICP/AES method.

In the preliminary report (Appendix A) the La results for the acid C-112 tank samples were reported to be outside the SEE limit. However, the RPD was brought within the limits when the sample was reanalyzed without dilution because of improved analysis sensitivity. As noted above, the C-112 tank La concentration is low; therefore, the initial 1:10 dilutions were near the instrument detection limit.

4.2.7 Manganese

Manganese is a major metal in the B-201 tank waste and a minor constituent in C-112 tank material. The RSDs are all less than 5%; therefore, statistically significant differences in variance are probably not important. The RPDs for the mean were all less than 10% and only the standard showed a statistically significant mean after the systematic error was considered in the evaluation. The standard result RPD was -4.8%, with one lab bias slightly low and the other bias slightly high. This is reasonable performance for the ICP/AES and is not considered important.

4.2.8 Sodium

Sodium is a major metal in both tank wastes. The RSDs for the Na analysis are all less than 5% indicating that the significant variance differences are probably not important. The RPDs for the mean are all less than 6% and no statistically significant means were identified.

4.2.9 Phosphorus

Phosphorus is a major component in the C-112 tank waste and at a relatively high concentration (0.3%) in the B-201 tank material. All the RSDs for the P data were less than 3%, except for the C-112 tank acid data for 222-S Laboratory which was 5.1%. Even though the C-112 tank variance was higher than the other data and was statistically significant, it is still considered reasonable performance for the laboratory and was not evaluated further. The RPDs were all less than 6% except for the C-112 tank acid digestion result, which was +9.6%. This larger positive RPD may be caused by the comparison of diluted sample data from 222-S Laboratory to undiluted sample data from the ACL. No standards data were obtained for phosphorus; therefore, the mean significance could not be evaluated with systematic error considerations. The differences in the mean results are considered reasonable for P analysis.

The preliminary report indicated that phosphorus exceeded the SEE limit for the fusion sample of tank B-201 wastes. This difference was eliminated when the undiluted sample data from the 222-S Laboratory was used in place of the original diluted data for comparison. Diluted data for major components such as Bi, Na, and P appear to be biased higher than the direct analysis results.

4.2.10 Silicon

Silicon is a minor constituent in both tanks but is present at a higher concentration (near 0.1%) in the B-201 tank material. The RSDs for all the analyses are less than 5%; therefore, variance differences are not considered important. The RPDs are all less than 11%. The 222-S Laboratory fusion data appears to be about 10% lower than the ACL. The statistical evaluation of this fusion data indicates that the means are different. Systematic error sources cannot be evaluated since no standards data for Si were obtained. The wavelengths used for Si analysis by both laboratories are the same. There was no ICP/MS data for silicon for comparison. Even though the differences in Si results are not large, further comparison of silicon analysis on fused samples may be worthwhile to determine if significant systematic errors exist.

4.2.11 Strontium

Strontium is present in both tanks in trace quantities. The RSDs for all the analyses are less than 3%; therefore, significant variance differences are not considered important. After systematic errors are considered, only the standard results show a statistically significant difference. The RPD for the standard results is -4.8% with one lab biased slightly high and the other slightly low. This difference is considered reasonable for laboratory ICP/AES performance.

4.2.12 Zinc

Zinc is present in both wastes as a trace element. The RSDs for all the analyses are less than 6 %; therefore, significant variance differences are not considered important. Three of the five Zn analyses exceeded the SEE RPD limit. The 222-S Laboratory results were low compared to the ACL results in all cases. The fusion results had the largest RPDs (-119% and -87%). The large differences for the fusion results may be partially explained by the proximity of the Zn concentration in the fused samples to the quantitation limits for the instrument. This condition coupled with the complex fusion and waste matrix could cause significant differences in results of this minor component. The relatively small RSDs do not indicate that being near the quantitation limit is impacting the reproducibility of the measurement. The standard results agree well indicating that there are probably no systematic errors in the calibrations causing the differences. There is no evidence of problems with the preparation blanks that would explain the higher values for the ACL. The differences are probably the result of matrix effects on the measurement of a quantity of Zn near the measurement limit. Both laboratories used the same ICP/AES wavelength. Interelement corrections were made for the Zn analysis by both laboratories. Even though the Zn analyses by ICP/MS showed relatively large variability, the ICP/MS results agree closer (%Dif = 1.4% for the B-201 tank and %Dif = 11.4% for the C-112 tank) with the higher ACL results. Even though the acid B-201 Zn RPD result exceeds (-22%) the SEE limit, the results for the acid digestion for the C-112 tank samples (-5.7%) are more comparable. The ICP/MS result for the acid in the B-201 tank sample agrees better with the high ACL result (%Dif = 2.7%) than with the 222-S Laboratory result (%Dif = 21.8%). ICP/MS data would indicate that the 222-S Laboratory data is questionable. Even

though the acid B-201 Zn results exceed the SEE limit, this difference may be reasonable performance for a trace element in this complex matrix. Normally the acid digestion results would be used for the determination of trace Zn in the wastes rather than the fusion. Therefore, the comparison of the Zn results for fusions is not important.

These same Zn differences were identified in the preliminary report (Appendix A). Reanalysis with undiluted samples did not change the status of these results. This data indicates that the 222-S results for Zn may be low compared to ACL ICP/AES and ICP/MS results. An exact explanation for this is not possible from the examination of this data. Further testing and evaluation will be required to determine the cause of the differences in Zn data.

4.2.13 Lead

Lead is a trace element in both tank wastes. Because of the relatively high detection limits for Pb by ICP/AES, only the data from the acid digestion was evaluated. The RSDs for the analyses were less than 4%; therefore, the variance differences are not considered important. The RPDs for the means were less than 4% and no means were statistically different when the systematic error was considered in the evaluation. The ICP/AES lead results agree well with the ICP/MS results.

4.2.14 Titanium

Titanium is a trace element in both tank wastes; because of the low concentration, only the data from the acid digestion was evaluated. The RSDs for the measurements were less than 6% and there were no statistically significant differences in the variances. The C-112 mean RPD (-123.6%) exceeded the SEE limit and the difference was identified as statistically significant. Initially, when diluted 222-S data was compared to direct ACL results, the RPD was -3.5% and there was no statistical difference in the means. The C-112 tank titanium concentration level in the sample is near the instrument quantitation limits. There are no standards data results to indicate if either laboratory has a systematic error. The ICP/MS results agree better with the ACL higher value (% Dif= +192%) than the 222-S Laboratory result (% Dif= +1138%). Assuming that there are no significant systematic errors (difference in standards), the differences are probably caused by the complex matrix effects on the determination of titanium near its quantitation limit. Laboratory ICPs used different Ti wavelengths for analysis. Interelement corrections were applied to the Ti result by both laboratories. Understanding and making accurate corrections for these interferences, such as U, on trace quantities of other metals can be difficult in complex matrices and lead to larger errors.

4.2.15 Uranium

Uranium is a major analyte in the C-112 tank wastes but its concentration was too low in the B-201 tank waste to be measured by ICP/AES. Fusion sample results were not reported for uranium by ICP/AES because of the technique's

poor sensitivity. The RSDs for U on the C-112 tank wastes were < 2%. The U results from both laboratories agreed very well (RPD = +1.2%). There were no standard results to estimate systematic errors. The ICP/MS uranium results for the acid C-112 tank waste were about 13.5% higher than the ICP/AES results.

5.0 WET CHEMICAL ANALYSIS

Wet chemical analyses were performed on water leached samples of each waste. In this procedure, a gram of waste is leached with 100 mL of deionized water for several hours in an ultrasonic bath. The filtered solution is then analyzed for anions by ion chromatography, cyanide, total organic carbon and inorganic carbon (TOC/TIC) and the radionuclide, tritium. About 2 g of waste was leached in 200 mL of water for Phase II samples.

5.1 CYANIDE

Each laboratory's procedure is based on the same principles; however, they differ in the hydrogen cyanide distillation systems used. The 222-S Laboratory procedure LA-695-102 (Hert 1994) used a microdistillation system to distill the HCN from the wastes before determining the cyanide in the caustic trap solution by a spectrophotometric method based on pyridine-barbituric acid. The ACL procedure PNL-ALO-270 (Urie 1990) used a midi-glass distillation system followed by the same spectrophotometric measurement. The microdistillation system has a limited sample size (5 mL) that can be used. Whereas, the midi-glass distillation system can use much larger samples. The microdistillation system is less subject to contamination problems because they are disposed of after use. Experience has shown that the systems are comparable in performance.

Cyanide was not expected to be present in the B-201 tank wastes. On the other hand, it is a major constituent in the C-112 tank material. The RPD results (-59.4%) for the B-201 tank exceeded the 20% SEE limit. However, the concentration of cyanide in the B-201 tank material was very near the method detection limits. This is reflected in the large (40%) RSDs in the results. The concentration of cyanide in the B-201 tank is too low for accurate comparison; therefore, the SEE RPD limit is not applicable.

The C-112 tank RPD (-18.8%) result did not fail the SEE requirement but was very near the limit. This difference was also identified as being statistically significant. For an unexplainable reason, the 222-S Laboratory C-112 tank results had a relatively large RSD (23.3%). The standard recovery results agree well and have comparable standard deviations. The standard results do not support the observed negative RPD since the standard result difference is positive. Even though the methods and laboratories appear to be comparable, additional cyanide testing on ferrocyanide waste types is recommended. Future testing should include the analysis of ferrocyanide solid wastes using the new ethylenediaminetetraacetic acid (EDTA)/ethylenediamine (EN) dissolution procedure.

The cyanide results for the B-201 tank were identified as being outside the SEE RPD limits in the preliminary report (Appendix A). This is no longer considered significant because of the proximity of the results to the detection limits for the method.

5.2 TOTAL ORGANIC CARBON

The two laboratories used two different types of TOC equipment and procedures to determine TOC in the wastes. The 222-S Laboratory TOC method used in procedure LA-344-105 (Schroeder 1992) is based on the furnace oxidation of the carbon in the sample to produce carbon dioxide which is measured by a coulometric titration after being trapped. The ACL TOC procedure PNL-ALO-382 (Stromatt 1988), used acid persulfate oxidation catalyzed by ultraviolet light to convert the carbon in the sample to carbon dioxide, which was then determined in a flow-through cell by nondispersive infrared absorption. The ACL determined the TOC by measuring the difference between the total carbon (TC) and the total inorganic carbon (TIC). Each TOC system has its advantages and disadvantages. The furnace oxidation is the more rigorous oxidation system, but it has a greater potential of introducing more interferences from nitrogen and sulfur oxides that are produced. The UV/persulfate oxidation may not oxidize some organic compounds, but is less subject to interferences. The efficiency of different TOC systems for oxidizing various organics has recently been evaluated and reported in PNL-SA-23718 (Baldwin, Stromatt, Winters 1994). Some volatile organics will be lost during purging to remove carbonates in TOC procedures.

All of the TOC results failed to meet the SEE 20% limit for RPDs. The TOC concentration in the B-201 tank sample was near the 222-S Laboratory detection limit capability. Both laboratories show relatively large RSDs (about 20%) for the B-201 tank measurements. The 222-S Laboratory result is higher (RPD = +75%) than the ACL data. This difference may be the result of the oxidation methods. At this concentration level for TOC, it is not possible to do an accurate comparison of the methods and the SEE 20% limit is not applicable.

The TOC in the C-112 tank wastes is about three times higher than in B-201 wastes. This waste contains a significant quantity of cyanide. The large positive RPD (+54.8%) for this waste analysis is believed to be caused by the difference in methods. The 222-S Laboratory furnace method should convert the cyanide in the C-112 waste to carbon dioxide and measure it as TOC. The ACL method probably will not oxidize cyanide; therefore, producing a lower TOC value. This difference was statistically significant. If the cyanide concentration in the C-112 tank (28.5 ug/mL CN) is converted to a TOC value (13.2 ug/mL C) and added to the ACL TOC result, the total (32 ug/mL) agrees very well with the 222-S Laboratory TOC result (33 ug/mL). The 222-S Laboratory low results on the mixed TOC/TIC/CN standard do not confirm this explanation. The 222-S TOC standard results should have been about 15% high if the cyanide in the standard was converted to TOC. Further evaluation of TOC methods is needed to confirm this potential difference.

The large RPD (-22.3 %) for the standard results appears to be a problem with the analysis by 222-S Laboratory rather than a difference in procedure.

The original standard analysis by the 222-S Laboratory had a RPD of about 3%. The data reported was based on a rerun which appears to be bias low. The ACL precision for the standard material was relatively large (16.6%) and statistically different.

Even though both samples were identified in the preliminary report (Appendix A) as being outside the SEE limits, only the C-112 tank results are considered significant and represent a potential difference in laboratory methods.

5.3 TOTAL INORGANIC CARBON

The total inorganic carbon methods use the same technology as the TOC methods described above. The 222-S Laboratory procedure LA-622-102 (Bisenius 1992) measures the carbon dioxide generated from the sample on acidification by coulometric titration. The ACL procedure, PNL-ALO-382 (Stromatt 1988), can determine the TIC by either measuring the difference between the total carbon TC and the TOC or by direct measurement of the TIC after acidification. The direct measurement approach was used for Phase II TIC analyses.

The carbonate or TIC concentration in both wastes is relatively low (0.1% -0.3%). The carbon measured in the samples by the 222-S Laboratory was only 2 to 3 times the carbon level in the blank. The RPD results for the B-201 tank wastes (-25.4%) and the standard (-23.3%) exceeded the SEE 20% RPD limit. The TIC difference for the B-201 tank may be partially explained by the low TIC levels in the sample; however, the RSDs are reasonably good and the RPD results for the C-112 tank, which has TIC levels only slightly higher, are excellent. For some unexplainable reason the ACL standard data results are high (125% recovery) and have a large RSD compared to the sample data. These results indicate that potential differences exists but inconsistencies in the data make it difficult to confirm. Additional comparisons of the TIC data from the laboratories are recommended to evaluate TIC procedures and laboratory performance.

The B-201 tank TIC results were identified as exceeding the SEE limits in the preliminary report (Appendix A). This difference cannot be fully explained without further testing.

5.4 ION CHROMATOGRAPHY

The major anions in the wastes were determined by ion chromatography at both laboratories. A summary of the instrument conditions are provided in Table 4.

Table 4. Summary of Ion Chromatography Conditions.

Condition	222-S	ACL
Instrument	Dionex 4000i	Dionex 2000i
Separator Column	Dionex AS4A	Dionex AS4A
Guard Column	Dionex AG4A	Dionex AG4A
Suppressor Column	Dionex SRS	Dionex AMMS
Eluent NaHCO ₃ Na ₂ CO ₃	0.0016M 0.0016M	0.00175M 0.00185M

Both laboratory methods are guided by the Environmental Protection Agency (EPA) method 300.0. IC analyses were performed by the 222-S Laboratory using procedure LA-533-105 (Frye 1994) and by ACL using PNL-ALO-212 (Urie 1990). Properly calibrated and operated the procedures should have comparable performance even with minor differences in instrument configuration. Differences in columns and operating conditions may be more observable in the determination of fluoride and chloride where interferences from organic acids (formates, acetates) are possible.

5.4.1 Fluoride

Fluoride is present in relatively high concentrations (0.7%) in the B-201 tank wastes and low concentrations (<0.1%) in the C-112 tank wastes. The RPD for the C-112 tank fluoride results exceeded the SEE limit (-56.7%). The C-112 tank chromatograms from both laboratories indicated other peaks were present in the region of fluoride and chloride. The laboratories analyzed a 1:10 dilution of the water leach, which resulted in fluoride concentrations 6 to 7 times the detection limit for the method. Both laboratories had good RSDs for the C-112 tank fluoride measurement. The ACL standard results were about 12% high but this does not explain the larger RPD differences for the C-112 tank fluoride values. In addition, the 222-S Laboratory result was higher for the B-201 tank analysis. The means for all three results were statistically different. Accurate fluoride analyses by ion chromatograph are considered difficult because of the potential for interferences and the presence of a water dip that frequently precedes the fluoride peak that impacts the ability of the system to determine accurate baselines. Additional data will be needed to evaluate the fluoride procedures and performances for the laboratories. The next phase of the SEE program will compare fluoride determined by IC to that determined by a ion selective electrode (ISE) method.

The fluoride results for the C-112 tank wastes were identified as exceeding the SEE limits in the preliminary report (Appendix A). Resolution of the fluoride differences will require further evaluation.

5.4.2 Chloride

The chloride levels were comparable (0.1% to 0.2%) in both tank wastes. The RSDs for all analyses were less than 7% and in many cases much better. The statistical differences in variance are not considered important. The mean for the standards was identified as being statistically significant; however, one lab was slightly low and the other high with a RPD of only about 7%. This difference is reasonable for ion chromatography performance.

5.4.3 Nitrite

The nitrite concentration in the B-201 tank was below the detection limit for the 222-S Laboratory after a 1:10 dilution; therefore, no comparison of the data is possible. The nitrite concentration is considerably higher in the C-112 tank wastes and excellent agreement between labs was obtained. The RSDs for the labs were less than 7% and both labs had good standard recoveries.

5.4.4 Nitrate

Nitrate is a major anion in both waste materials. The RSDs for both laboratories were less than 7%. The means for the standard were statistically different. The 222-S Laboratory was biased high about 6% and the ACL was biased low by about 6%. A RPD for the means of the standards of 12.3% is considered a reasonable performance for ion chromatography.

5.4.5 Phosphate

The phosphate concentration in the B-201 tank water digest (0.1 to 0.2%) is about 20 times lower than the C-112 tank wastes. The RSDs for all the data are less than 10% which is acceptable IC performance for this type of wastes. The RPD (+54.0%) for the B-201 tank mean results exceeds the SEE limit. The phosphate concentration in the 1:10 diluted B-201 sample analyzed by the 222-S Laboratory is very near the instrument detection limit. Even though the 222-S Laboratory standard recovery results are high (113%), this is not enough to explain the observed difference in the B-201 tank waste results. The RSDs do not indicate that imprecision caused by being near the detection limit is causing the difference; however, small matrix and operational differences could be impacting the accuracy of the measurement.

The preliminary report identified the phosphate result for the B-201 tank as exceeding the SEE RPD limit of 20%. This difference is probably caused by the low phosphate concentrations in the B-201 tank waste being close to the instrument detection limits after it is prepared for analysis.

5.4.6 Sulfate

The sulfate concentration in the B-201 tank waste was below detectable levels for both laboratories and data could not be compared. The RSDs for the C-112 tank sample and standard results from both laboratories was less than 5%. The variance differences are not considered significant. The differences

in means for the standard were statistically different, but each lab was slightly biased in opposite directions. The RPD for the standard mean results was 10.1%, which is considered satisfactory performance.

6.0 RADIOCHEMICAL ANALYSIS

Radiochemical analyses were performed on a fusion preparation of the waste material. Tritium analysis was performed on a water leach preparation. With the exception of tritium, which was not analyzed in Phase I, all the analyses techniques are the same as those described in the Phase I report.

6.1 TOTAL ALPHA

The total alpha analysis produced an RPD of +29% for the C-112 tank sample and -19% for the B-201 tank. The C-112 tank waste has a beta to alpha ratio of around 10,000 while the B-201 tank is much lower at 4. The crosstalk problem (beta counts appearing in the alpha channel) with the 222-S Laboratory alpha counting system may have led to the high RPD. This problem was identified during Phase I and corrective actions were implemented. The Phase II RPDs are improved over Phase I; however, changes in the 222-S Laboratory alpha counting equipment were not completely resolved. Based on test standards, recent instrumentation improvements have corrected this problem. This analysis will continue to be evaluated. Both laboratories have good standard recoveries for total alpha measurements.

6.2 TOTAL BETA

The total beta results from 222-S Laboratory were reported based on a ^{60}Co calibration efficiency. If the results are converted to simulate a $^{90}\text{Sr}/^{90}\text{Y}$ calibration efficiency to be comparable to the ACL results, the RPDs are -18.2% and -9.5% respectively. The total beta analysis is producing consistent results as long as equivalent calibration efficiencies are utilized. This analysis should need no further evaluation until the total beta efficiency criteria are changed. The 222-S Laboratory is planning to change the total beta calibration efficiency from ^{60}Co to ^{137}Cs in 1995. Because the ^{137}Cs and $^{90}\text{Sr}/^{90}\text{Y}$ beta energies are nearly equal, the total beta data should be comparable without conversions.

6.3 GAMMA ENERGY ANALYSIS (GEA)

The ^{137}Cs results by GEA have acceptable RPDs for both tanks and the standard. The Phase I data also shows that the two laboratories produce consistent, comparable results for the analysis of this radioisotope. No significant amounts of other gamma isotopes were found in the samples.

6.4 TOTAL URANIUM

Total uranium RPDs are all acceptable. A statistical variance difference is noted for both tanks and the standard. The 222-S Laboratory data has noticeably higher RSDs for all samples. This analysis appears to be producing consistent agreement.

6.5 PLUTONIUM 239/240

The ^{236}Pu tracer at the 222-S Laboratory is believed to be the cause of the B-201 tank RPD of -34.1%. The tracer was nearly depleted at the time of the SEE Phase II analyses and could have been experiencing some concentration. Rerun data with a different tracer preparation shows an average result for the B-201 tank of $3.11\text{E}-03$ uCi/mL for an RPD of 3.8%. The 222-S Laboratory C-112 results had a large RSD (27.1%) even though the counting errors were relatively small (2.3%). This large RSD may partially explain the reason for the RPD of +18.3%. The ACL ratio of total alpha to the sum of Pu and Am for the C-112 tank was greater than 1 (1.24). Because the Am results between labs agreed well, this may indicate that the ACL Pu results were low, which would also contribute to the +18.3% RPD for this data. This isotope will continue to be monitored since instances of RPD failure have been observed in both Phase I and Phase II.

6.6 AMERICIUM 241

The B-201 tank shows no detectable ^{241}Am activity. The RPDs for the C-112 tank and the standard are acceptable. A statistical mean difference is noted for the standard which may be due to a poor tracer recovery indicated in the 222-S Laboratory data. The RPD for the standard results was only -8.4%.

6.7 TECHNECIUM 99

The RPDs for the C-112 tank and standard are acceptable but high. It appears that the ACL data is low based on the standard recovery (85%). The ACL result for the C-112 tank is also 15% lower than the 222-S Laboratory results. These low results are most likely the cause of the statistical mean and variance differences noted. The B-201 tank did not have detectable ^{99}Tc activity. The ICP/MS data for ^{99}Tc in the C-112 tank indicated that the Tc activity was much lower than that detected by radioactive counting methods.

6.8 STRONTIUM 90

All RPDs for the ^{90}Sr analysis are less than 6%. Standard recoveries for the 222-S Laboratory are 10% higher than the ACL. The standard data shows a statistical mean difference due to this bias. The B-201 tank data have a statistical variance difference due to the low activity and the 7% RSD of the ACL data compared to the 2% RSD for the 222-S Laboratory.

6.9 TRITIUM

The 222-S Laboratory tritium procedure LA-218-114 (Kawabata 1994) uses disposable plastic microdistillation equipment and hold back carriers to separate the tritium from other isotopes. The separated tritium is diluted into scintillation cocktail and counted on a liquid scintillation counting system. The ACL procedure PNL-ALO-441 (Gillespie 1990) is basically the same but uses standard size glass distillation equipment and similar hold-back carriers. The glass distillation equipment is capable of handling larger sample sizes. The liquid scintillation sample preparation and equipment for the laboratories also differ. If properly calibrated and controlled these counting methods should provide comparable results.

The tritium analysis has acceptable RPDs for both tanks and the standard. A statistical mean difference is noted on tank B-201 data, which may be due to a slight low bias on the 222-S Laboratory standard results. The statistical variance difference on the standard appears to be due to a lower precision in the 222-S Laboratory data ($\pm 5.6\%$) compared to the ACL ($\pm 0.8\%$).

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Appendix A
Phase II Preliminary Report

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9452276

Subject: DEFENSE NUCLEAR FACILITIES SAFETY BOARD MILESTONES COMMITMENT 5.5 OF
THE REFERENCE, "ISSUE A REPORT ON RESULTS OF THE SAMPLE EXCHANGE
PHASE II

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March 31, 1994

9452276

Mr. J. M. Clark, Acting Manager
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Office of Tank Waste Remediation
U.S. Department of Energy
Richland Operations Office
Richland, Washington 99352

Dear Mr. Clark:

DEFENSE NUCLEAR FACILITIES SAFETY BOARD MILESTONES COMMITMENT 5.5 OF THE
REFERENCE, "ISSUE A REPORT ON RESULTS OF THE SAMPLE EXCHANGE PHASE II."

Reference: "Recommendation 93-05 Implementation Plan," U.S. Department of
Energy, Richland Operations Office, DOE/RL 94-0001,
January 1994.

The attached letter report "Sample Exchange/Evaluation (SEE) Program Phase II
Letter Report, Revision 0, March 31, 1994," responds to Commitment 5.5 of the
Reference, "Recommendation 93-05 Implementation Plan." The report has been
written by members of the Quality Assurance/Quality Control Triad, the group
representing Pacific Northwest Laboratory and Westinghouse Hanford Company
laboratories and laboratory quality functions, that oversees and directs the
SEE program. The SEE program is an ongoing effort that provides for
continuous improvement in the analytical laboratories supporting tank waste
analysis.

If you have any questions or require additional information on the SEE
program, please call Mr. L. H. Taylor on 373-1030 or Ms. Kris Kuhl-Klinger on
372-0398.

Very truly yours,

C. DeFigh-Price, Manager
Characterization Program
Tank Waste Remediation System Program Office

dac

Attachment

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Attachment to 9452276

Sample Exchange/Evaluation (SEE) Program
Phase II Letter Report, Revision 0
March, 1994

Page 1 - 5

1.0 INTRODUCTION

The Sample Exchange/Evaluation (SEE) program was developed as a joint effort by the Westinghouse Hanford Company, Analytical Services (WHC/AS) and the Pacific Northwest Laboratory,¹ Analytical Chemistry Laboratory (PNL/ACL) to compare analytical laboratory performance on sample materials unique to the Hanford Nuclear Reservation.

The Quality Assurance/Quality Control (QA/QC) Triad, consisting of technical representatives from both laboratories and the WHC/AS/TQO group, was formed to develop, schedule, coordinate, and implement the SEE program. This report is a preliminary summary of the SEE Phase II data.

2.0 PHASE II TEST PLAN

Under Phase II, of the SEE Program, QC standards and three types of sample preparations (water leach, fusion, and acid digestion) from two archived tank cores (with blanks) were analyzed to compare radiochemical and inorganic methods between the WHC/AS (222-S laboratory) and PNL/ACL (325 laboratory). Table 2.1 lists the analyses performed on each sample preparation.

Table 2.1 Analysis Matrix

Water Leach	Fusion	Acid Digestion
H-3 IC (F, Cl, NO ₂ , NO ₃ , PO ₄ , SO ₄) CN- TOC/TIC	ICP (Al, Bi, Ca, Cr, Fe, La, Mn, Na, P, Si, Sr, Zn) ICP-MS (Metals/U/Tc-99) GEA (All detected isotopes) Sr-90 Pu-238, 239/40 Am-241 TA/TB U-Total Tc-99	ICP (Al, Ca, Fe, Mn, Na, P, Si, Sr, Zn, Bi, Cr, Pb, Ti, U, La)

Sample extracts were prepared using archived tank core sample material from two waste tanks C-112 and B-201. Each sample preparation, (fusion, acid digestion, and water leach) was prepared and submitted in quadruplicate to each participating laboratory. Preparations of tank C-112 are identified as "sample C" and tank B-201 identified as "sample B" throughout this report. The radiochemical QC standards used in this study were prepared by the PNL standards laboratory. The inorganic and total organic carbon QC standards were prepared by the AS standards laboratory. The standards were submitted to the laboratories in quadruplicate.

¹ Pacific Northwest Laboratory is operated for the United States Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830

3.0 DATA EVALUATION

The QA/QC Triad reviewed the data. The review of the data started by compiling the mean of the replicate results and calculating the Relative Percent Difference (RPD) between the means for comparison of the analytical methods listed in Table 2.1. Those analyses that exceeded a RPD value of $\pm 20\%$ received additional review which included checking all documentation for clerical errors, nearness to method detection limits, and technical basis of the method.

To provide a basis for comparison the 325 values are compared to the 222-S values by calculating the RPD according to the following formula:

$$RPD = \frac{(AS - ACL)}{\left(\frac{AS + ACL}{2}\right)} * 100 \quad (1) \text{ RPD Formula}$$

Normally RPD is reported as an absolute value. However using the above formula provides additional information; a positive value indicates 222-S reported a higher result, and a negative value indicates 325 was higher.

A summary of the comparative analysis is listed in Table 3.1. The term analyte is used in Table 3.1 and throughout this report to indicate a specific element, isotope or species (e.g., Al, Pu239/40, TOC, etc.). Reference to "set" or data set" indicates one sample material preparation (e.g., sample C fusion Al in quadruplicate is one data set).

Table 3.1 Analyte sets that exceeded 20 RPD

Fusion Prep Sample C	Fusion Prep Sample B	Acid Prep Sample C	Acid Prep Sample B	Water Leach Sample C	Water Leach Sample B
+Total Beta	-Pu 239/40	+La	+Bi	+TOC	-CN
+Total Alpha	+Al	+Zn		-F	+PO4
+Al	+Bi				+TOC
+Mn	+P				-TIC
+Zn	+Zn				
Number of data sets that exceed 20 RPD					
5 of 17 Analyte sets	5 of 18 Analyte sets	2 of 15 Analyte sets	1 of 14 Analyte sets	2 of 10 Analyte sets	4 of 8 Analyte sets

As can be seen from Table 3.1, only 19 analytes out of 82 tested exceeded the 20 RPD criteria in the samples tested. This indicates a 76% success rate which is reasonable considering the complexity of the material

tested. QC standard performance was very good based on percent recovery. Only three analyte sets out of twenty-nine exceeded the $100 \pm 20\%$ criteria, this corresponds to a 90% success rate in terms of accuracy of the QC standards. A summary of the anomalous results is detailed below:

3.1 Fusion Preparations:

In the fusion preparations only ten of thirty-five data sets exceeded the ± 20 RPD criteria.

Total Beta (1 data set)

As in the Phase I study, the Total Beta RPD was positive (high value reported by 222-S) and exceeded ± 20 RPD for one data set. The cause of this discrepancy was identified in the SEE phase I report. The two participating laboratories (325 and 222-S) use different energies to set their counting efficiencies. 222-S calibrates their Total Beta instrumentation to Co-60; 325 calibrates their Total Beta instrumentation to SrY-90. Because the primary contributor for Total Beta activity at Hanford tanks is SrY-90, it is recommended that Total Beta be reported as SrY-90.

Total Alpha (1 data set)

For sample C, a positive RPD was reported on the Total Alpha. In the SEE Phase I report, 222-S reported numbers with a high bias apparently due to an electronics problem with their Alpha/Beta instrumentation. An electronic gate does not close in time, allowing Beta activity to be counted as part of the Total Alpha activity. Phase II reconfirms this anomaly for high beta activity samples. Since sample C beta activity is considerably higher than the beta activity in sample B this effect is only noted in sample C. Corrective actions have been identified and initiated. Implementation is expected by May 1994.

Pu-239/40 (1 data set)

The Pu-239/40 results for sample C were within the predetermined evaluation window; however, the sample B results had an RPD of -33.98. Preliminary investigation into this discrepancy has not identified a cause. Current "probable cause" investigation includes review of recovery yield calculations employed at both laboratories. 222-S uses a Pu-236 tracer with each sample; 325 uses a historical spike recovery basis for yield corrections. Because a higher precision was reported by 325, a secondary investigation into possible contamination or "hot spot" analysis by 222-S is also being investigated.

Metals Analysis (7 data sets)

Five analytes out of 12 were found to exceed the pre-determined evaluation window. P and Bi (sample B), Mn (sample C), and Al and Zn (sample B and C), all had positive RPDs. The Mn, Bi and P exceeded the 20 RPD criteria but were less than 35%. The Al and Zn RPDs were greater than 43%. An investigation is underway to determine a cause of the bias.

3.2 Acid Digestion:

In the acid digestion preparation, only three out of twenty-nine data sets exceeded the RPD criteria: Bi (sample B), La (sample C), and Zn (sample C) all had positive RPDs. Preliminary investigation indicates the La anomaly can be discounted since the results reported are at or near the detection limit. An investigation is underway to determine the cause of the bias for the remaining metals.

3.3 Water Leach:

Six data sets out of 18 exceeded the RPD Criteria: CN, PO₄ and TIC (sample B), F (sample C) and TOC (samples B and C).

Each of these anomalies are being investigated. A preliminary investigation into the fluoride has determined that the high value reported by the 325 may be due to interferences from co-eluting organic anions.

3.4 QC Samples:

The QC samples were evaluated based on percent recovery. Only three measurement sets out of twenty-nine were outside the $100 \pm 20\%$ recovery criteria for the QC samples.

The 325 recovery for TIC was 125%. A preliminary hypothesis is that the 325 TIC method detected both CO₂ and CN as carbon in the QC standards.

The 222-S recovery for Ca was 145%. It is believed to be a result of sample contamination from glove powder. The high bias was not evident for other ICP analytes, which indicates a problem unique to Ca.

The 222-S Total Beta recovery was 145%, again indicating the different calibration and reporting basis used by 222-S (Co-60 vs. SrY-90). When reported as SrY-90 the recovery is 102%.

4.0 PRELIMINARY CONCLUSIONS *

The majority of results reported under phase II of the SEE program were comparable between the two participating laboratories. For the most part, discrepancies found were minor and should have little or no effect on data reported under any TWRS related characterization program. The program confirmed two analyte differences, Total Alpha and Total Beta. Corrective actions have been initiated.

4.1 Three measurements systems from SEE Phase I were reevaluated. Based upon the reevaluation the following preliminary conclusions were derived:

- The energy base for Total Beta analysis should be reported. A resolution of this issue is expected before the issuance of the final Phase II report.
- The Total Alpha measurement system at 222-S is apparently sensitive to beta cross talk for high beta samples. It is recommended that

222-S proceed with planned instrument system changes to eliminate this problem.

- The uranium measurement in this phase, showed good comparability (within 8%). However, continued testing and comparison is necessary to confirm the comparability.

4.2 The following measurement systems need further investigation based on Phase II data and will be reported when review is complete:

- TOC/TIC and CN will be reviewed for analyte interactions.
- For Pu239/40 possible corrective action measures may include but are not limited to: common yield recovery method, employ improved separations/plating techniques at both laboratories.
- The metals; Al, Bi, Mn, P, and Zn, are being re-analyzed to provide more information for evaluation.
- The PO₄ and F analysis data and methods will be reviewed to determine differences.

Appendix B
Phase II Statistical Reports

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Westinghouse
Hanford CompanyInternal
Memo

From: Process Laboratories and Technology
Phone: 373-2475 T6-07
Date: April 1, 1994
Subject: STATISTICAL ANALYSIS OF THE PHASE II SEE DATA

12100-PLT94-023

To: L. H. Taylor H4-23

cc: L. Jensen T6-07
J. P. Sloughter T6-07
TLW File/LB

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

The Statistics Team received data generated from Phase II 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. Two samples and several standards were analyzed four times each by both laboratories for most of the requested analytes. 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" or negative values were not included in the comparison.

There were a total of 111 comparisons between the two laboratories for Phase II of the SEE program. For 40 of the 111 comparisons (36%), the test for equality of means was rejected using the random analytical variability only (0.01 level of significance). For 71 of the 111 comparisons (64%), the test for equality of means was not rejected using the random analytical variability only (0.01 level of significance). For 65 of the 111 comparisons (58.6%), the test for equality of variances (0.05 level of significance) was rejected; i.e., the variability of one laboratory was significantly larger than the variability of the other laboratory. For 46 of the 111 comparisons, the test for equality of variances (0.05 level of significance) was not rejected.

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.

L. H. Taylor
Page 2
April 1, 1994

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_{2225}^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 maximum value of S_{2225}^2 and S_{325}^2 , and S_2^2 is the minimum value of S_{2225}^2 and S_{325}^2 (see pages 116-117 of the reference for details). If this F value was larger than the tabled 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 those analytes measured for the two samples 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.

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

T. L. Welsh

T. L. Welsh, Senior Statistician
Process Laboratories and Technology

llu

Attachments 3

Table 1. SEE Data - Fusion Digest.

Sample	Lab	TB * μCi/mL	AT μCi/mL	¹³⁷ Cs μCi/mL	U-laser μg/mL	239/240Pu μCi/mL
B	222S	7.96E-03	2.63E-03	1.18E-03	9.81E-01	2.26E-03
		8.03E-03	2.71E-03	1.04E-03	8.93E-01	2.08E-03
		7.96E-03	2.52E-03	1.09E-03	8.42E-01	2.32E-03
		7.88E-03	2.60E-03	1.19E-03	7.38E-01	2.51E-03
B	325	9.50E-03	3.05E-03	1.26E-03	7.89E-01	3.31E-03
		9.50E-03	3.28E-03	1.30E-03	7.89E-01	3.20E-03
		9.60E-03	3.25E-03	1.30E-03	8.09E-01	3.23E-03
		9.80E-03	3.09E-03	1.29E-03	8.17E-01	3.17E-03
Sample	Lab	⁹⁰ Sr μCi/mL	Al μg/mL	Ca μg/mL	Fe μg/mL	Mn μg/mL
B	222S	3.70E-03	6.56E-01	1.47E+00	2.76E+00	5.36E+00
		3.83E-03	5.95E-01	1.41E+00	2.80E+00	5.38E+00
		3.77E-03	6.34E-01	1.36E+00	2.82E+00	5.39E+00
		3.65E-03	5.19E-01	1.34E+00	2.63E+00	5.40E+00
B	325	3.26E-03	2.94E-01	1.37E+00	2.55E+00	5.17E+00
		3.86E-03	2.94E-01	1.40E+00	2.58E+00	5.21E+00
		3.67E-03	2.86E-01	1.37E+00	2.57E+00	5.19E+00
		3.55E-03	2.80E-01	1.38E+00	2.58E+00	5.23E+00
Sample	Lab	Na μg/mL	P μg/mL	Si μg/mL	Sr μg/mL	Zn μg/mL
B	222S	8.60E+00	1.20E+00	2.11E+00	2.05E-01	3.46E-01
		8.51E+00	1.45E+00	2.01E+00	2.01E-01	1.75E-01
		8.56E+00	1.91E+00	2.33E+00	2.02E-01	2.67E-01
		8.42E+00	1.67E+00	1.98E+00	2.05E-01	8.20E-02
B	325	8.32E+00	1.08E+00	2.18E+00	1.92E-01	7.44E-02
		8.46E+00	1.11E+00	2.23E+00	1.93E-01	7.12E-02
		8.08E+00	1.13E+00	2.11E+00	1.92E-01	6.77E-02
		8.17E+00	1.14E+00	2.13E+00	1.94E-01	6.94E-02
Sample	Lab	Bi μg/mL	Cr μg/mL	La μg/mL		
B	222S	2.64E+01	8.21E-01	3.52E+00		
		2.69E+01	7.88E-01	3.40E+00		
		2.62E+01	8.60E-01	3.44E+00		
		2.72E+01	9.06E-01	3.54E+00		
B	325	2.07E+01	7.54E-01	3.16E+00		
		2.09E+01	7.62E-01	3.19E+00		
		2.08E+01	7.67E-01	3.18E+00		
		2.09E+01	7.74E-01	3.20E+00		

*: The total beta data from 222-S Laboratory were multiplied by 0.704.

Table 2. SEE Data - Fusion Digest.

Sample	Lab	TB * μCi/mL	AT μCi/mL	¹³⁷ Cs μCi/mL	U-laser μg/mL	^{239/240} Pu μCi/mL
C	222S	2.14E+00	3.30E-04	7.61E-01	1.22E+02	8.80E-05
		2.11E+00	3.33E-04	7.74E-01	1.67E+02	9.10E-05
		1.87E+00	3.24E-04	7.73E-01	1.37E+02	1.32E-04
		2.09E+00	3.41E-04	7.99E-01	1.37E+02	1.52E-04
C	325	2.32E+00	2.70E-04	7.98E-01	1.21E+02	9.18E-05
		2.34E+00	2.47E-04	7.71E-01	1.28E+02	9.67E-05
		2.35E+00	2.32E-04	8.03E-01	1.20E+02	9.82E-05
		2.26E+00	2.43E-04	7.99E-01	1.31E+02	9.90E-05
Sample	Lab	²⁴¹ Am μCi/mL	⁹⁹ Tc μCi/mL	⁹⁰ Sr μCi/mL	Al μg/mL	Ca μg/mL
C	222S	1.10E-04	2.03E-04	8.36E-01	1.41E+00	2.93E+00
		1.06E-04	1.73E-04	8.46E-01	1.43E+00	3.05E+00
		1.05E-04	1.86E-04	8.71E-01	1.40E+00	2.93E+00
			1.82E-04	8.74E-01	1.10E+00	2.86E+00
C	325	1.11E-04	1.60E-04	7.81E-01	8.57E-01	2.82E+00
		1.03E-04	1.53E-04	8.59E-01	8.56E-01	2.84E+00
		1.00E-04	1.60E-04	8.34E-01	8.69E-01	2.84E+00
		1.03E-04	1.58E-04	8.43E-01	8.46E-01	2.82E+00
Sample	Lab	Fe μg/mL	Mn μg/mL	Na μg/mL	P μg/mL	Si μg/mL
C	222S	5.81E+00	5.24E-02	2.00E+01	6.60E+00	7.19E-01
		5.49E+00	4.51E-02	2.04E+01	6.94E+00	6.27E-01
		5.34E+00	5.06E-02	2.01E+01	6.53E+00	7.41E-01
		5.58E+00	4.88E-02	1.98E+01	6.36E+00	6.49E-01
C	325	5.30E+00	4.43E-02	1.90E+01	5.73E+00	7.84E-01
		5.35E+00	4.48E-02	1.92E+01	5.78E+00	7.91E-01
		5.33E+00	4.43E-02	1.89E+01	5.78E+00	7.38E-01
		5.33E+00	4.44E-02	1.88E+01	5.76E+00	7.31E-01
Sample	Lab	Sr μg/mL	Zn μg/mL			
C	222S	8.00E-02	1.02E-01			
		7.74E-02	1.85E-01			
		7.78E-02	1.42E-01			
		7.26E-02	2.02E-01			
C	325	6.97E-02	7.00E-02			
		7.04E-02	6.70E-02			
		7.02E-02	6.35E-02			
		7.00E-02	6.14E-02			

*: The total beta data from 222-S Laboratory were multiplied by 0.704.

Table 3. SEE Data - Acid Digest.

Sample	Lab	Al μg/mL	Ca μg/mL	Fe μg/mL	Mn μg/mL	Na μg/mL
B	222S	5.42	29.5	60.9	127	197
		5.57	30.6	64.3	133	198
		5.62	30.8	64.0	133	196
		5.73	30.6	64.6	134	198
B	325	5.29	30.4	63.4	131	194
		5.32	30.7	64.0	132	196
		5.29	30.2	63.1	129	193
		5.29	30.3	63.1	130	193
Sample	Lab	P μg/mL	Si μg/mL	Sr μg/mL	Zn μg/mL	Bi μg/mL
B	222S	31.5	5.60	4.87	1.73	644
		31.6	5.91	5.05	1.64	664
		29.9	5.72	5.05	1.58	662
		30.1	5.71	5.10	1.63	668
B	325	27.8	5.85	5.06	1.48	527
		28.0	5.79	5.13	1.50	532
		27.7	5.83	5.09	1.49	525
		27.7	5.85	5.07	1.48	526
Sample	Lab	Cr μg/mL	La μg/mL	Pb μg/mL	Ti μg/mL	
B	222S	19.1	81.9	9.19	0.411	
		20.2	85.4	9.88	0.432	
		20.1	85.0	9.58	0.425	
		20.3	85.6	9.68	0.437	
B	325	19.6	83.3	9.33	0.443	
		19.7	84.1	9.43	0.448	
		19.5	83.2	9.32	0.442	
		19.6	83.2	9.34	0.442	

Table 4. SEE Data - Acid Digest.

Sample	Lab	Al μg/mL	Ca μg/mL	Fe μg/mL	Mn μg/mL	Na μg/mL
C	222S	2.74E+01	7.46E+01	1.57E+02	9.83E-01	5.93E+02
		2.47E+01	6.81E+01	1.43E+02	8.76E-01	5.38E+02
		2.72E+01	7.48E+01	1.57E+02	9.82E-01	5.90E+02
		2.68E+01	7.39E+01	1.53E+02	9.76E-01	5.87E+02
C	325	2.20E+01	6.83E+01	1.41E+02	8.85E-01	5.42E+02
		2.20E+01	6.84E+01	1.41E+02	8.86E-01	5.42E+02
		2.24E+01	6.96E+01	1.43E+02	9.03E-01	5.50E+02
		2.26E+01	7.00E+01	1.44E+02	9.10E-01	5.52E+02
Sample	Lab	P μg/mL	Si μg/mL	Sr μg/mL	Zn μg/mL	Bi μg/mL
C	222S	2.07E+02	4.13E+00	2.15E+00	1.41E+00	3.58E+00
		1.85E+02	4.02E+00	1.95E+00	1.35E+00	3.19E+00
		2.02E+02	4.20E+00	2.15E+00	1.44E+00	3.06E+00
		1.91E+02	4.32E+00	2.11E+00	1.47E+00	3.29E+00
C	325	1.76E+02	3.82E+00	1.94E+00	1.07E+00	2.71E+00
		1.76E+02	3.84E+00	1.94E+00	1.06E+00	2.72E+00
		1.79E+02	3.83E+00	1.98E+00	1.09E+00	2.75E+00
		1.79E+02	3.93E+00	2.00E+00	1.10E+00	2.76E+00
Sample	Lab	Cr μg/mL	Pb μg/mL	Ti μg/mL	U μg/mL	La μg/mL
C	222S	1.24E+00	7.18E+00	1.28E-01	3.56E+02	2.67E-01
		1.03E+00	6.61E+00	1.31E-01	3.26E+02	2.77E-01
		1.18E+00	7.59E+00	1.54E-01	3.58E+02	
		1.04E+00	7.11E+00	1.44E-01	3.51E+02	
C	325	1.00E+00	6.54E+00	1.41E-01	3.19E+02	1.82E-01
		1.01E+00	6.58E+00	1.42E-01	3.19E+02	1.85E-01
		1.03E+00	6.69E+00	1.45E-01	3.24E+02	1.88E-01
		1.03E+00	7.07E+00	1.49E-01	3.26E+02	1.92E-01

Table 5. SEE Data - Water Leach.

Sample	Lab	^3H $\mu\text{Ci/mL}$	TOC $\mu\text{g/mL}$	TIC $\mu\text{g/mL}$	F^- $\mu\text{g/mL}$	Cl^- $\mu\text{g/mL}$
C	222S	3.64E-05	3.20E+01	3.20E+01	6.96E+00	9.16E+00
		3.95E-05	3.40E+01	3.00E+01	6.63E+00	8.60E+00
		3.39E-05	3.40E+01	3.10E+01	6.60E+00	8.10E+00
		3.61E-05	3.20E+01	3.20E+01	6.62E+00	8.18E+00
C	325	4.13E-05	1.80E+01	3.30E+01	1.20E+01	9.00E+00
		3.97E-05	1.80E+01	3.30E+01	1.20E+01	9.00E+00
		3.85E-05	2.00E+01	3.10E+01	1.30E+01	9.00E+00
		3.80E-05	1.90E+01	3.10E+01	1.20E+01	9.00E+00
Sample	Lab	NO_3^- $\mu\text{g/mL}$	NO_2^- $\mu\text{g/mL}$	PO_4^{3-} $\mu\text{g/mL}$	SO_4^{2-} $\mu\text{g/mL}$	CN^- $\mu\text{g/mL}$
C	222S	3.43E+02	4.52E+02	4.33E+02	1.06E+02	1.79E+01
		3.70E+02	4.90E+02	4.34E+02	1.05E+02	2.49E+01
		4.04E+02	5.30E+02	4.30E+02	1.05E+02	2.09E+01
		3.72E+02	5.05E+02	4.40E+02	1.07E+02	3.05E+01
C	325	3.70E+02	5.00E+02	3.80E+02	1.00E+02	2.99E+01
		3.80E+02	5.20E+02	3.90E+02	1.00E+02	2.74E+01
		3.90E+02	5.30E+02	4.40E+02	1.11E+02	2.84E+01
		3.90E+02	5.20E+02	4.30E+02	1.01E+02	2.84E+01

Table 6. SEE Data - Water Leach.

Sample	Lab	^3H $\mu\text{Ci/mL}$	TOC $\mu\text{g/mL}$	TIC $\mu\text{g/mL}$	F^- $\mu\text{g/mL}$
B	222S	7.93E-05	1.30E+01	1.70E+01	7.15E+01
		8.07E-05	1.50E+01	1.70E+01	7.19E+01
		8.09E-05	1.10E+01	1.60E+01	7.47E+01
		8.30E-05	9.30E+00	1.60E+01	7.22E+01
B	325	9.31E-05	6.00E+00	2.10E+01	6.70E+01
		8.76E-05	4.00E+00	2.30E+01	6.70E+01
		9.26E-05	7.00E+00	1.90E+01	6.70E+01
		8.75E-05	5.00E+00	2.20E+01	6.20E+01
Sample	Lab	Cl^- $\mu\text{g/mL}$	NO_3^- $\mu\text{g/mL}$	PO_4^{3-} $\mu\text{g/mL}$	CN^- $\mu\text{g/mL}$
B	222S	2.12E+01	5.33E+02	2.45E+01	4.94E-02
		2.13E+01	5.26E+02	2.38E+01	2.56E-02
		2.09E+01	5.38E+02	2.36E+01	2.56E-02
		2.09E+01	5.26E+02	2.39E+01	
B	325	2.20E+01	5.50E+02	1.50E+01	3.00E-02
		2.10E+01	5.20E+02	1.40E+01	6.30E-02
		2.00E+01	5.40E+02	1.40E+01	6.00E-02
		1.90E+01	5.40E+02	1.20E+01	9.40E-02

Table 7. SEE Data - Standard Results. (sheet 1 of 2)

Lab	TB * μCi/mL	AT μCi/mL	¹³⁷ Cs μCi/mL	U-laser μg/mL	^{239/240} Pu μCi/mL
222S	4.66E-01	1.20E-03	4.17E-01	5.85E+01	5.14E-04
	4.64E-01	1.13E-03	4.15E-01	2.97E+01	4.98E-04
	4.63E-01	1.14E-03	4.13E-01	4.63E+01	5.56E-04
	4.65E-01	1.17E-03	4.11E-01	4.63E+01	5.28E-04
325	4.85E-01	1.19E-03	4.36E-01	4.18E+01	4.95E-04
	4.93E-01	1.19E-03	4.19E-01	4.33E+01	5.07E-04
	5.04E-01	1.19E-03	4.16E-01	4.33E+01	5.12E-04
	4.87E-01	1.17E-03	4.13E-01	4.49E+01	5.43E-04
Lab	²⁴¹ Am μCi/mL	⁹⁹ Tc μCi/mL	⁹⁰ Sr μCi/mL	Ca μg/mL	Fe μg/mL
222S	5.14E-04	7.97E-03	3.28E-02	1.62E+01	4.95E+00
	5.55E-04	7.33E-03	3.39E-02	9.77E+00	4.93E+00
	5.24E-04	7.35E-03	3.28E-02	1.98E+01	4.80E+00
	5.52E-04	7.22E-03	3.18E-02	1.32E+01	4.68E+00
325	5.76E-04	6.32E-03	3.03E-02	1.01E+01	5.03E+00
	5.93E-04	6.36E-03	3.09E-02	1.01E+01	5.08E+00
	5.80E-04	6.25E-03	3.06E-02	1.19E+01	5.10E+00
	5.83E-04	6.12E-03	3.22E-02	1.01E+01	5.06E+00
Lab	Mn μg/mL	Na μg/mL	Sr μg/mL	Zn μg/mL	Bi μg/mL
222S	4.95E+00	1.00E+01	9.87E+00	1.03E+01	4.82E+00
	4.96E+00	1.01E+01	9.97E+00	1.01E+01	4.93E+00
	4.87E+00	9.83E+00	9.61E+00	1.05E+01	4.91E+00
	4.74E+00	1.00E+01	9.64E+00	9.97E+00	4.93E+00
325	5.09E+00	9.80E+00	1.01E+01	1.00E+01	4.78E+00
	5.14E+00	9.92E+00	1.03E+01	1.01E+01	4.80E+00
	5.14E+00	9.95E+00	1.03E+01	1.02E+01	4.80E+00
	5.11E+00	9.85E+00	1.03E+01	1.01E+01	4.75E+00
Lab	Cr μg/mL	La μg/mL	Pb μg/mL	Ba μg/mL	CN ⁻ μg/mL
222S	4.95E+00	5.00E+00	4.73E+00	9.83E+00	1.02E+03
	4.99E+00	5.13E+00	4.86E+00	9.94E+00	9.96E+02
	4.89E+00	5.14E+00	4.90E+00	9.57E+00	
	4.76E+00	5.19E+00	4.88E+00	9.63E+00	
325	5.03E+00	4.79E+00	4.94E+00	9.78E+00	9.49E+02
	5.06E+00	4.80E+00	4.96E+00	9.92E+00	9.30E+02
	5.06E+00	4.81E+00	4.92E+00	9.93E+00	9.23E+02
	5.05E+00	4.77E+00	4.95E+00	9.89E+00	9.34E+02

Table 7. SEE Data - Standard Results. (sheet 2 of 2)

Lab	TOC $\mu\text{g/mL}$	TIC $\mu\text{g/mL}$	^3H $\mu\text{Ci/mL}$	F^- $\mu\text{g/mL}$	Cl^- $\mu\text{g/mL}$
222S	2.43E+03	2.36E+03	4.88E-04	6.13E+01	7.64E+01
	2.45E+03	2.39E+03	4.29E-04	6.20E+01	7.82E+01
			4.61E-04	6.27E+01	7.74E+01
			4.79E-04	6.42E+01	7.76E+01
325	2.90E+03	3.10E+03	4.92E-04	7.10E+01	7.20E+01
	3.50E+03	2.70E+03	4.96E-04	6.60E+01	7.20E+01
	3.40E+03	2.60E+03	4.93E-04	7.20E+01	7.20E+01
	2.40E+03	3.60E+03	4.86E-04	7.20E+01	7.20E+01
Lab	NO_2^- $\mu\text{g/mL}$	NO_3^- $\mu\text{g/mL}$	PO_4^{3-} $\mu\text{g/mL}$	SO_4^{2-} $\mu\text{g/mL}$	
222S	4.85E+02	5.29E+02	5.59E+02	5.32E+02	
	4.94E+02	5.27E+02	5.73E+02	5.37E+02	
	4.96E+02	5.33E+02	5.74E+02	5.38E+02	
	4.97E+02	5.26E+02	5.66E+02	5.28E+02	
325	4.80E+02	4.60E+02	5.00E+02	4.70E+02	
	5.00E+02	4.70E+02	5.40E+02	4.90E+02	
	5.00E+02	4.70E+02	5.30E+02	4.90E+02	
	4.90E+02	4.70E+02	5.20E+02	4.80E+02	

∗∗: The total beta data from 222-S Laboratory were multiplied by 0.704.

Table 1. SEE Data - Fusion Digest (Sample B).

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
TB	μCi/mL	4	1.13E-02	8.16E-05	4	9.60E-03	1.41E-04	No	1.70E-03	Yes	Yes	No
AT	μCi/mL	4	2.62E-03	7.85E-05	4	3.17E-03	1.14E-04	No	-5.53E-04	Yes	Yes	Yes
¹³⁷ Cs	μCi/mL	4	1.13E-03	7.23E-05	4	1.29E-03	1.89E-05	Yes	-1.63E-04	Yes	No	No
U-laser	μg/mL	4	8.64E-01	1.01E-01	4	8.01E-01	1.42E-02	Yes	6.25E-02	No	No	No
^{239/240} Pu	μCi/mL	4	2.29E-03	1.77E-04	4	3.23E-03	6.02E-05	No	-9.35E-04	Yes	Yes	Yes
⁹⁰ Sr	μCi/mL	4	3.74E-03	7.89E-05	4	3.59E-03	2.51E-04	Yes	1.53E-04	No	No	No
Al	μg/mL	4	6.01E-01	6.02E-02	4	2.89E-01	6.81E-03	Yes	3.13E-01	Yes	Yes	NA
Ca	μg/mL	4	1.40E+00	5.80E-02	4	1.38E+00	1.41E-02	Yes	1.50E-02	No	No	No
Fe	μg/mL	4	2.75E+00	8.54E-02	4	2.57E+00	1.41E-02	Yes	1.83E-01	Yes	No	No
Mn	μg/mL	4	5.38E+00	1.71E-02	4	5.20E+00	2.58E-02	No	1.83E-01	Yes	Yes	No
Na	μg/mL	4	8.52E+00	7.76E-02	4	8.26E+00	1.67E-01	No	2.65E-01	Yes	No	No
P	μg/mL	4	1.56E+00	3.03E-01	4	1.12E+00	2.65E-02	Yes	4.43E-01	No	No	NA
Si	μg/mL	4	2.11E+00	1.58E-01	4	2.16E+00	5.38E-02	No	-5.50E-02	No	No	NA
Sr	μg/mL	4	2.03E-01	2.06E-03	4	1.93E-01	9.57E-04	No	1.05E-02	Yes	Yes	No
Zn	μg/mL	4	2.18E-01	1.14E-01	4	7.07E-02	2.87E-03	Yes	1.47E-01	No	No	No
Bi	μg/mL	4	2.67E+01	4.57E-01	4	2.08E+01	9.57E-02	Yes	5.85E+00	Yes	Yes	No
Cr	μg/mL	4	8.44E-01	5.09E-02	4	7.64E-01	8.42E-03	Yes	7.95E-02	No	No	No
La	μg/mL	4	3.48E+00	6.61E-02	4	3.18E+00	1.71E-02	Yes	2.93E-01	Yes	Yes	No

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?

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Table 2. SEE Data - Fusion Digest (Sample C).

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
TB	μCi/mL	4	2.05E+00	1.23E-01	4	2.32E+00	4.03E-02	Yes	-2.65E-01	Yes	No	No
AT	μCi/mL	4	3.32E-04	7.07E-06	4	2.48E-04	1.60E-05	No	8.40E-05	Yes	Yes	Yes
¹³⁷ Cs	μCi/mL	4	7.77E-01	1.60E-02	4	7.93E-01	1.47E-02	No	-1.60E-02	No	No	No
U-laser	μg/mL	4	1.41E+02	1.89E+01	4	1.25E+02	5.35E+00	Yes	1.58E+01	No	No	No
^{239/240} Pu	μCi/mL	4	1.16E-04	3.14E-05	4	9.64E-05	3.23E-06	Yes	1.93E-05	No	No	No
²⁴¹ Am	μCi/mL	3	1.07E-04	2.65E-06	4	1.04E-04	4.72E-06	No	2.75E-06	No	No	No
⁹⁹ Tc	μCi/mL	4	1.86E-04	1.26E-05	4	1.58E-04	3.30E-06	Yes	2.83E-05	Yes	No	No
⁹⁰ Sr	μCi/mL	4	8.57E-01	1.87E-02	4	8.29E-01	3.38E-02	No	2.75E-02	No	No	No
Al	μg/mL	4	1.34E+00	1.57E-01	4	8.57E-01	9.42E-03	Yes	4.78E-01	Yes	Yes	NA
Ca	μg/mL	4	2.94E+00	7.89E-02	4	2.83E+00	1.15E-02	Yes	1.13E-01	No	No	No
Fe	μg/mL	4	5.56E+00	1.97E-01	4	5.33E+00	2.06E-02	Yes	2.28E-01	No	No	No
Mn	μg/mL	4	4.92E-02	3.12E-03	4	4.45E-02	2.38E-04	Yes	4.78E-03	No	No	No
Na	μg/mL	4	2.01E+01	2.50E-01	4	1.90E+01	1.71E-01	No	1.10E+00	Yes	Yes	Yes
P	μg/mL	4	6.61E+00	2.43E-01	4	5.76E+00	2.36E-02	Yes	8.45E-01	Yes	Yes	NA
Si	μg/mL	4	6.84E-01	5.46E-02	4	7.61E-01	3.09E-02	No	-7.70E-02	Yes	No	NA
Sr	μg/mL	4	7.70E-02	3.12E-03	4	7.01E-02	2.99E-04	Yes	6.88E-03	Yes	No	No
Zn	μg/mL	4	1.58E-01	4.49E-02	4	6.55E-02	3.80E-03	Yes	9.23E-02	Yes	No	No

- 1: F-test for equality of variances at the 0.05 level of significance.
 2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
 3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
 4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
 NA: Standards data not available from both laboratories.
 Var: Variance.
 Diff: Difference.
 Std Dev: Standard Deviation.
 Sign?: Is the test statistically significant?

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Table 3. SEE Data - Acid Digest (Sample B).

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
Al	µg/mL	4	5.59E+00	1.29E-01	4	5.30E+00	1.50E-02	Yes	2.88E-01	Yes	No	NA
Ca	µg/mL	4	3.04E+01	5.91E-01	4	3.04E+01	2.16E-01	No	-2.50E-02	No	No	No
Fe	µg/mL	4	6.35E+01	1.72E+00	4	6.34E+01	4.24E-01	Yes	5.00E-02	No	No	No
Mn	µg/mL	4	1.32E+02	3.20E+00	4	1.31E+02	1.29E+00	No	1.25E+00	No	No	No
Na	µg/mL	4	1.97E+02	9.57E-01	4	1.94E+02	1.41E+00	No	3.25E+00	Yes	Yes	No
P	µg/mL	4	3.08E+01	9.00E-01	4	2.78E+01	1.41E-01	Yes	2.98E+00	Yes	Yes	NA
Si	µg/mL	4	5.74E+00	1.29E-01	4	5.83E+00	2.83E-02	No	-9.50E-02	No	No	NA
Sr	µg/mL	4	5.02E+00	1.01E-01	4	5.09E+00	3.10E-02	Yes	-7.00E-02	No	No	No
Zn	µg/mL	4	1.65E+00	6.24E-02	4	1.49E+00	9.57E-03	Yes	1.58E-01	Yes	No	No
Bi	µg/mL	4	6.60E+02	1.06E+01	4	5.28E+02	3.11E+00	Yes	1.32E+02	Yes	Yes	No
Cr	µg/mL	4	1.99E+01	5.56E-01	4	1.96E+01	8.16E-02	Yes	3.25E-01	No	No	No
La	µg/mL	4	8.45E+01	1.73E+00	4	8.35E+01	4.36E-01	Yes	1.03E+00	No	No	No
Pb	µg/mL	4	9.58E+00	2.90E-01	4	9.36E+00	5.07E-02	Yes	2.28E-01	No	No	No
Ti	µg/mL	4	4.26E-01	1.13E-02	4	4.44E-01	2.87E-03	Yes	-1.75E-02	No	No	NA

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?

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Table 4. SEE Data - Acid Digest (Sample C).

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
Al	µg/mL	4	2.65E+01	1.24E+00	4	2.23E+01	3.00E-01	Yes	4.28E+00	Yes	Yes	NA
Ca	µg/mL	4	7.29E+01	3.19E+00	4	6.91E+01	8.54E-01	Yes	3.78E+00	No	No	No
Fe	µg/mL	4	1.53E+02	6.61E+00	4	1.42E+02	1.50E+00	Yes	1.03E+01	No	No	No
Mn	µg/mL	4	9.54E-01	5.23E-02	4	8.96E-01	1.25E-02	Yes	5.83E-02	No	No	No
Na	µg/mL	4	5.77E+02	2.61E+01	4	5.47E+02	5.26E+00	Yes	3.05E+01	No	No	No
P	µg/mL	4	1.96E+02	1.00E+01	4	1.78E+02	1.73E+00	Yes	1.88E+01	Yes	No	NA
Si	µg/mL	4	4.17E+00	1.26E-01	4	3.86E+00	5.07E-02	No	3.13E-01	Yes	Yes	NA
Sr	µg/mL	4	2.09E+00	9.52E-02	4	1.97E+00	3.00E-02	Yes	1.25E-01	No	No	No
Zn	µg/mL	4	1.42E+00	5.12E-02	4	1.08E+00	1.83E-02	No	3.38E-01	Yes	Yes	Yes
Bi	µg/mL	4	3.28E+00	2.21E-01	4	2.74E+00	2.38E-02	Yes	5.45E-01	Yes	No	No
Cr	µg/mL	4	1.12E+00	1.04E-01	4	1.02E+00	1.50E-02	Yes	1.05E-01	No	No	No
Pb	µg/mL	4	7.12E+00	4.02E-01	4	6.72E+00	2.42E-01	No	4.03E-01	No	No	No
Ti	µg/mL	4	1.39E-01	1.20E-02	4	1.44E-01	3.59E-03	Yes	-5.00E-03	No	No	NA
U	µg/mL	4	3.48E+02	1.48E+01	4	3.22E+02	3.56E+00	Yes	2.58E+01	Yes	No	NA
La	µg/mL	2	2.72E-01	7.07E-03	4	1.87E-01	4.27E-03	No	8.53E-02	Yes	Yes	Yes

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?

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Table 5. SEE Data - Water Leach (Sample C).

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
³ H	μCi/mL	4	3.65E-05	2.30E-06	4	3.94E-05	1.47E-06	No	-2.90E-06	No	No	No
TOC	μg/mL	4	3.30E+01	1.15E+00	4	1.88E+01	9.57E-01	No	1.43E+01	Yes	Yes	Yes
TIC	μg/mL	4	3.13E+01	9.57E-01	4	3.20E+01	1.15E+00	No	-7.50E-01	No	No	No
F ⁻	μg/mL	4	6.70E+00	1.72E-01	4	1.23E+01	5.00E-01	No	-5.55E+00	Yes	Yes	Yes
Cl ⁻	μg/mL	4	8.51E+00	4.86E-01	4	9.00E+00	0.00	Yes	-4.90E-01	No	No	No
NO ₂ ⁻	μg/mL	4	3.72E+02	2.50E+01	4	3.83E+02	9.57E+00	No	-1.03E+01	No	No	No
NO ₃ ⁻	μg/mL	4	4.94E+02	3.26E+01	4	5.18E+02	1.26E+01	No	-2.33E+01	No	No	No
PO ₄ ³⁻	μg/mL	4	4.34E+02	4.19E+00	4	4.10E+02	2.94E+01	Yes	2.43E+01	No	No	No
SO ₄ ²⁻	μg/mL	4	1.06E+02	9.57E-01	4	1.03E+02	5.35E+00	Yes	2.75E+00	No	No	No
CN ⁻	μg/mL	4	2.36E+01	5.45E+00	4	2.85E+01	1.03E+00	Yes	-4.98E+00	No	No	No

- 1: F-test for equality of variances at the 0.05 level of significance.
 2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
 3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
 4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
 NA: Standards data not available from both laboratories.
 Var: Variance.
 Diff: Difference.
 Std Dev: Standard Deviation.
 Sign?: Is the test statistically significant?

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Table 6. SEE Data - Water Leach (Sample B).

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
³ H	μCi/mL	4	8.10E-05	1.53E-06	4	9.02E-05	3.07E-06	No	-9.23E-06	Yes	Yes	No
TOC	μg/mL	4	1.21E+01	2.47E+00	4	5.50E+00	1.29E+00	No	6.58E+00	Yes	Yes	
TIC	μg/mL	4	1.65E+01	5.77E-01	4	2.13E+01	1.71E+00	No	-4.75E+00	Yes	Yes	
F ⁻	μg/mL	4	7.26E+01	1.45E+00	4	6.58E+01	2.50E+00	No	6.83E+00	Yes	Yes	No
Cl ⁻	μg/mL	4	2.11E+01	2.06E-01	4	2.05E+01	1.29E+00	Yes	5.75E-01	No	No	No
NO ₃ ⁻	μg/mL	4	5.31E+02	5.85E+00	4	5.38E+02	1.26E+01	No	-6.75E+00	No	No	No
PO ₄ ³⁻	μg/mL	4	2.40E+01	3.87E-01	4	1.38E+01	1.26E+00	Yes	1.02E+01	Yes	Yes	No
CN ⁻	μg/mL	3	3.35E-02	1.37E-02	4	6.18E-02	2.62E-02	No	-2.82E-02	No	No	No

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?

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Table 7. SEE Data Standards Results. (sheet 1 of 2)

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?
TB	µCi/mL	4	4.65E-01	1.29E-03	4	4.92E-01	8.54E-03	Yes	-2.78E-02	Yes	Yes
AT	µCi/mL	4	1.16E-03	3.16E-05	4	1.19E-03	1.00E-05	Yes	-2.50E-05	No	No
¹³⁷ Cs	µCi/mL	4	4.14E-01	2.58E-03	4	4.21E-01	1.03E-02	Yes	-7.00E-03	No	No
U-laser	µg/mL	4	4.52E+01	1.18E+01	4	4.33E+01	1.27E+00	Yes	1.88E+00	No	No
^{239/240} Pu	µCi/mL	4	5.24E-04	2.46E-05	4	5.14E-04	2.05E-05	No	9.75E-06	No	No
²⁴¹ Am	µCi/mL	4	5.36E-04	2.04E-05	4	5.83E-04	7.26E-06	No	-4.68E-05	Yes	Yes
⁹⁹ Tc	µCi/mL	4	7.47E-03	3.40E-04	4	6.26E-03	1.05E-04	Yes	1.21E-03	Yes	Yes
⁹⁰ Sr	µCi/mL	4	3.28E-02	8.58E-04	4	3.10E-02	8.37E-04	No	1.83E-03	Yes	No
Ca	µg/mL	4	1.47E+01	4.27E+00	4	1.06E+01	9.00E-01	Yes	4.19E+00	No	No
Fe	µg/mL	4	4.84E+00	1.26E-01	4	5.07E+00	2.99E-02	Yes	-2.28E-01	Yes	Yes
Mn	µg/mL	4	4.88E+00	1.02E-01	4	5.12E+00	2.45E-02	Yes	-2.40E-01	Yes	Yes
Na	µg/mL	4	9.98E+00	1.12E-01	4	9.88E+00	6.78E-02	No	1.03E-01	No	No
Sr	µg/mL	4	9.77E+00	1.76E-01	4	1.03E+01	1.00E-01	No	-4.78E-01	Yes	Yes
Zn	µg/mL	4	1.02E+01	2.32E-01	4	1.01E+01	8.16E-02	No	1.18E-01	No	No
Bi	µg/mL	4	4.90E+00	5.25E-02	4	4.78E+00	2.36E-02	Yes	1.15E-01	Yes	Yes
Cr	µg/mL	4	4.90E+00	1.00E-01	4	5.05E+00	1.41E-02	Yes	-1.53E-01	No	No
La	µg/mL	4	5.12E+00	8.10E-02	4	4.79E+00	1.71E-02	Yes	3.23E-01	Yes	Yes
Pb	µg/mL	4	4.84E+00	7.68E-02	4	4.94E+00	1.71E-02	Yes	-1.00E-01	No	No
Ba	µg/mL	4	9.74E+00	1.72E-01	4	9.88E+00	6.88E-02	No	-1.38E-01	No	No
CN ⁻	µg/mL	2	1.01E+03	1.70E+01	4	9.34E+02	1.10E+01	No	7.40E+01	Yes	Yes

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Table 7. See Data Standard Results. (sheet 2 of 2)

Analyte	Units	N	222S Mean	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?
TOC	µg/mL	2	2.44E+03	1.41E+01	4	3.05E+03	5.07E+02	Yes	-6.10E+02	No	No
TIC	µg/mL	2	2.38E+03	2.12E+01	4	3.00E+03	4.55E+02	Yes	-6.25E+02	No	No
³ H	µCi/mL	4	4.64E-04	2.60E-05	4	4.92E-04	4.19E-06	Yes	-2.75E-05	No	No
F ⁻	µg/mL	4	6.26E+01	1.24E+00	4	7.03E+01	2.87E+00	No	-7.70E+00	Yes	Yes
Cl ⁻	µg/mL	4	7.74E+01	7.48E-01	4	7.20E+01	0.00	Yes	5.40E+00	Yes	Yes
NO ₂ ⁻	µg/mL	4	4.93E+02	5.48E+00	4	4.93E+02	9.57E+00	No	5.00E-01	No	No
NO ₃ ⁻	µg/mL	4	5.29E+02	3.10E+00	4	4.68E+02	5.00E+00	No	6.13E+01	Yes	Yes
PO ₄ ³⁻	µg/mL	4	5.68E+02	6.98E+00	4	5.23E+02	1.71E+01	No	4.55E+01	Yes	Yes
SO ₄ ²⁻	µg/mL	4	5.34E+02	4.65E+00	4	4.83E+02	9.57E+00	No	5.13E+01	Yes	Yes

1: F-test for equality of variances at the 0.05 level of significance.

2: Test for equality of means at the 0.05 level of significance (used random analytical variability).

3: Test for equality of means at the 0.01 level of significance (used random analytical variability).

NA: Standards data not available from both laboratories.

Var: Variance.

Diff: Difference.

Std Dev: Standard Deviation.

Sign?: Is the test statistically significant?

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Table 8. SEE Data Standards Results.

Analyte	Units	N 222S	222S Systematic Error (%)	N 325	325 Systematic Error (%)
TB	μCi/mL	4	2.74	4	8.88
AT	μCi/mL	4	1.36	4	1.98
¹³⁷ Cs	μCi/mL	4	0.85	4	2.56
U-laser	μg/mL	4	13.12	4	3.87
^{239/240} Pu	μCi/mL	4	2.99	4	2.01
²⁴¹ Am	μCi/mL	4	9.95	4	2.10
⁹⁹ Tc	μCi/mL	4	2.30	4	15.41
⁹⁰ Sr	μCi/mL	4	9.48	4	3.40
Ca	μg/mL	4	47.43	4	5.50
Fe	μg/mL	4	3.20	4	1.35
Mn	μg/mL	4	2.40	4	2.40
Na	μg/mL	4	0.56	4	1.20
Sr	μg/mL	4	2.28	4	2.50
Zn	μg/mL	4	2.18	4	1.00
Bi	μg/mL	4	2.05	4	4.35
Cr	μg/mL	4	2.05	4	1.00
La	μg/mL	4	2.30	4	4.15
Pb	μg/mL	4	3.15	4	1.15
Ba	μg/mL	4	2.58	4	1.20
CN ⁻	μg/mL	2	2.14	4	9.32
TOC	μg/mL	2	18.67	4	1.67
TIC	μg/mL	2	1.04	4	25.00
³ H	μCi/mL	4	7.44	4	1.96
F ⁻	μg/mL	4	0.99	4	12.58
Cl ⁻	μg/mL	4	3.20	4	4.00
NO ₂ ⁻	μg/mL	4	2.76	4	2.86
NO ₃ ⁻	μg/mL	4	5.54	4	6.69
PO ₄ ³⁻	μg/mL	4	13.60	4	4.50
SO ₄ ²⁻	μg/mL	4	6.75	4	3.50

SEE Data - acid digest
Al - Sample C

SEE Data - acid digest
Bi Sample C

SEE Data - acid digest
Ca - Sample C

SEE Data - acid digest
Cr Sample C

SEE Data - acid digest
Fe - Sample C

SEE Data - acid digest
La Sample C

SEE Data - acid digest
Mn - Sample C

SEE Data - acid digest
Na - Sample C

SEE Data - acid digest
TI Sample C

SEE Data - acid digest
U Sample C

SEE Data - acid digest
Zn Sample C

SEE Data - acid digest
Al - Sample B

SEE Data - acid digest
La - Sample B

SEE Data - acid digest
Mn - Sample B

SEE Data - acid digest
Na - Sample B

SEE Data - acid digest
P - Sample B

SEE Data - acid digest
Pb - Sample B

SEE Data - acid digest
SI - Sample B

SEE Data - acid digest
Sr - Sample B

SEE Data - acid digest
TI - Sample B

SEE Data - acid digest
Zn - Sample B

SEE Data - water leach
H3 Sample C

SEE Data - water leach
TOC Sample C

SEE Data - water leach
TIC Sample C

SEE Data - water leach
F Sample C

SEE Data - water leach
Cl Sample C

SEE Data - water leach
NO2 Sample C

SEE Data - water leach
NO3 Sample C

SEE Data - water leach
PO4 Sample C

SEE Data - water leach
SO4 Sample C

SEE Data - water leach
CN Sample C

SEE Data - water leach
H3 Sample B

SEE Data - water leach
F Sample 8

SEE Data - water leach
Cl Sample 8

SEE Data - water leach
NO3 Sample 8

SEE Data - water leach
PO4 Sample 8

SEE Data - fusion digest
Na - Sample C

SEE Data - fusion digest
P - Sample C

SEE Data - fusion digest
Si - Sample C

SEE Data - fusion digest
Sr - Sample C

SEE Data - fusion digest
Bi - Sample B

SEE Data - fusion digest
Ca - Sample B

SEE Data - fusion digest
Cr - Sample B

SEE Data - fusion digest
Fe - Sample B

SEE Data - fusion digest
Si - Sample B

SEE Data - fusion digest
Sr - Sample B

SEE Data - fusion digest
Zn - Sample B

SEE Data
H3 Standard

**Westinghouse
Hanford Company**

WHC-SD-WM-TI-666 Rev. 0

**Internal
Memo**

From: Process Laboratories and Technology
Phone: 373-2475 T6-07
Date: July 21, 1994
Subject: STATISTICAL ANALYSIS OF THE PHASE II SEE RERUN DATA

8E100-PLT94-049

To: L. H. Taylor H4-23

cc: L. Jensen T6-07
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TLW File/LB

- References:
- (1) Internal Memo, T. L. Welsh to L. H. Taylor, "Statistical Analysis of the Phase II SEE Data," dated April 1, 1994.
 - (2) Book, G. W. Snedecor and W. G. Cochran, Statistical Methods, Sixth Edition, Iowa State University Press, Ames, Iowa, dated 1967.

The Statistics Team received and analyzed data generated from Phase II of the Sample Exchange Evaluation (SEE) program (see Reference 1). 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). After reviewing the differences reported in Reference 1, it was discovered that the inductively coupled plasma (ICP) results were not based on the analysis of the same sample (some of the 222S results were from diluted samples). Therefore, 222S reanalyzed the ICP samples using a direct analysis. The ICP rerun data, along with the original data used in the statistical analysis, are listed in Attachment 1.

There were a total of 42 comparisons between the two laboratories for the ICP rerun results. For 20 of the 42 comparisons (48%), the test for equality of means was rejected using the random analytical variability only (0.01 level of significance). For 22 of the 42 comparisons (52%), the test for equality of means was not rejected using the random analytical variability only (0.01 level of significance). For 13 of the 42 comparisons (30.95%), the test for equality of variances (0.05 level of significance) was rejected; i.e., the variability of one laboratory was significantly larger than the variability of the other laboratory. For 29 of the 42 comparisons, the test for equality of variances (0.05 level of significance) was not rejected.

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.

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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_{222s}^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 maximum value of S_{222s}^2 and S_{325}^2 , and S_2^2 is the minimum value of S_{222s}^2 and S_{325}^2 (see pages 116-117 of Reference 2 for details). If this F value was larger than the tabled 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 Reference 2 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 those analytes measured for the two samples 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.

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

T. L. Welsh

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Attachments 3

Table 1. SEE Data - Fusion Digest.

Sample	Lab	Al μg/mL	Ca μg/mL	Fe μg/mL	Mn μg/mL	Na μg/mL
B	222S	6.56E-01	1.47E+00	2.76E+00	5.36E+00	8.60E+00
		5.95E-01	1.41E+00	2.80E+00	5.38E+00	8.51E+00
		6.34E-01	1.36E+00	2.82E+00	5.39E+00	8.56E+00
		5.19E-01	1.34E+00	2.63E+00	5.40E+00	8.42E+00
B	222S RR	2.80E-01	1.38E+00	2.51E+00	4.98E+00	8.26E+00
		2.86E-01	1.36E+00	2.45E+00	4.88E+00	8.12E+00
		2.80E-01	1.33E+00	2.42E+00	4.81E+00	7.94E+00
		2.71E-01	1.31E+00	2.42E+00	4.80E+00	7.90E+00
B	325	2.94E-01	1.37E+00	2.55E+00	5.17E+00	8.32E+00
		2.94E-01	1.40E+00	2.58E+00	5.21E+00	8.46E+00
		2.86E-01	1.37E+00	2.57E+00	5.19E+00	8.08E+00
		2.80E-01	1.38E+00	2.58E+00	5.23E+00	8.17E+00
Sample	Lab	P μg/mL	Si μg/mL	Sr μg/mL	Zn μg/mL	Bi μg/mL
B	222S	1.20E+00	2.11E+00	2.05E-01	3.46E-01	2.64E+01
		1.45E+00	2.01E+00	2.01E-01	1.75E-01	2.69E+01
		1.91E+00	2.33E+00	2.02E-01	2.67E-01	2.62E+01
		1.67E+00	1.98E+00	2.05E-01	8.20E-02	2.72E+01
B	222S RR	1.15E+00	2.01E+00	1.98E-01	1.60E-02	2.13E+01
		1.11E+00	1.96E+00	1.92E-01	1.40E-02	2.09E+01
		1.12E+00	1.94E+00	1.88E-01	1.60E-02	2.06E+01
		1.11E+00	1.95E+00	1.86E-01	1.70E-02	2.05E+01
B	325	1.08E+00	2.18E+00	1.92E-01	7.44E-02	2.07E+01
		1.11E+00	2.23E+00	1.93E-01	7.12E-02	2.09E+01
		1.13E+00	2.11E+00	1.92E-01	6.77E-02	2.08E+01
		1.14E+00	2.13E+00	1.94E-01	6.94E-02	2.09E+01
Sample	Lab	Cr μg/mL	La μg/mL			
B	222S RR	8.21E-01	3.52E+00			
		7.88E-01	3.40E+00			
		8.60E-01	3.44E+00			
		9.06E-01	3.54E+00			
B	222S	7.48E-01	3.31E+00			
		7.34E-01	3.25E+00			
		7.22E-01	3.18E+00			
		7.25E-01	3.14E+00			
B	325	7.54E-01	3.16E+00			
		7.62E-01	3.19E+00			
		7.67E-01	3.18E+00			
		7.74E-01	3.20E+00			

RR: Rerun.

Table 2. SEE Data - Fusion Digest.

Sample	Lab	Al μg/mL	Ca μg/mL	Fe μg/mL	Mn μg/mL	Na μg/mL
C	222S	1.41E+00	2.93E+00	5.81E+00	5.24E-02	2.00E+01
		1.43E+00	3.05E+00	5.49E+00	4.51E-02	2.04E+01
		1.40E+00	2.93E+00	5.34E+00	5.06E-02	2.01E+01
		1.10E+00	2.86E+00	5.58E+00	4.88E-02	1.98E+01
C	222S RR	9.87E-01	2.84E+00	5.23E+00	4.50E-02	1.93E+01
		9.64E-01	2.77E+00	5.09E+00	4.50E-02	1.89E+01
		9.47E-01	2.72E+00	5.06E+00	4.40E-02	1.85E+01
		9.52E-01	2.70E+00	5.06E+00	4.40E-02	1.85E+01
C	325	8.57E-01	2.82E+00	5.30E+00	4.43E-02	1.90E+01
		8.56E-01	2.84E+00	5.35E+00	4.48E-02	1.92E+01
		8.69E-01	2.84E+00	5.33E+00	4.43E-02	1.89E+01
		8.46E-01	2.82E+00	5.33E+00	4.44E-02	1.88E+01
Sample	Lab	P μg/mL	Si μg/mL	Sr μg/mL	Zn μg/mL	
C	222S	6.60E+00	7.19E-01	8.00E-02	1.02E-01	
		6.94E+00	6.27E-01	7.74E-02	1.85E-01	
		6.53E+00	7.41E-01	7.78E-02	1.42E-01	
		6.36E+00	6.49E-01	7.26E-02	2.02E-01	
C	222S RR	6.11E+00	7.02E-01	7.20E-02	3.50E-02	
		6.09E+00	6.80E-01	7.10E-02	2.30E-02	
		5.97E+00	6.81E-01	6.90E-02	2.10E-02	
		6.07E+00	6.78E-01	6.80E-02	2.40E-02	
C	325	5.73E+00	7.84E-01	6.97E-02	7.00E-02	
		5.78E+00	7.91E-01	7.04E-02	6.70E-02	
		5.78E+00	7.38E-01	7.02E-02	6.35E-02	
		5.76E+00	7.31E-01	7.00E-02	6.14E-02	

RR: Rerun.

Table 3. SEE Data - Acid Digest.

Sample	Lab	Al μg/mL	Fe μg/mL	Na μg/mL	P μg/mL	Si μg/mL
B	222S	5.42E+00	6.09E+01	1.97E+02	3.15E+01	5.60E+00
		5.57E+00	6.43E+01	1.98E+02	3.16E+01	5.91E+00
		5.62E+00	6.40E+01	1.96E+02	2.99E+01	5.72E+00
		5.73E+00	6.46E+01	1.98E+02	3.01E+01	5.71E+00
B	222S RR	5.66E+00	6.32E+01	1.98E+02	2.98E+01	6.00E+00
		5.65E+00	6.24E+01	1.97E+02	2.94E+01	5.96E+00
		5.59E+00	6.21E+01	1.95E+02	2.93E+01	5.68E+00
		5.56E+00	6.19E+01	1.93E+02	2.93E+01	5.79E+00
B	325	5.29E+00	6.34E+01	1.94E+02	2.78E+01	5.85E+00
		5.32E+00	6.40E+01	1.96E+02	2.80E+01	5.79E+00
		5.29E+00	6.31E+01	1.93E+02	2.77E+01	5.83E+00
		5.29E+00	6.31E+01	1.93E+02	2.77E+01	5.85E+00
Sample	Lab	Sr μg/mL	Zn μg/mL	Cr μg/mL	Pb μg/mL	Ti μg/mL
B	222S	4.87E+00	1.73E+00	1.91E+01	9.19E+00	4.11E-01
		5.05E+00	1.64E+00	2.02E+01	9.88E+00	4.32E-01
		5.05E+00	1.58E+00	2.01E+01	9.58E+00	4.25E-01
		5.10E+00	1.63E+00	2.03E+01	9.68E+00	4.37E-01
B	222S RR	5.08E+00	1.20E+00	1.95E+01	9.11E+00	4.44E-01
		5.04E+00	1.19E+00	1.92E+01	9.00E+00	4.39E-01
		4.97E+00	1.19E+00	1.91E+01	8.96E+00	4.33E-01
		4.91E+00	1.19E+00	1.90E+01	8.98E+00	4.31E-01
B	325	5.06E+00	1.48E+00	1.96E+01	9.33E+00	4.43E-01
		5.13E+00	1.50E+00	1.97E+01	9.43E+00	4.48E-01
		5.09E+00	1.49E+00	1.95E+01	9.32E+00	4.42E-01
		5.07E+00	1.48E+00	1.96E+01	9.34E+00	4.42E-01

RR: Rerun.

Table 4. SEE Data - Acid Digest.

Sample	Lab	Al μg/mL	Mn μg/mL	Si μg/mL	Sr μg/mL	Zn μg/mL
C	222S	2.74E+01	9.83E-01	4.13E+00	2.15E+00	1.41E+00
		2.47E+01	8.76E-01	4.02E+00	1.95E+00	1.35E+00
		2.72E+01	9.82E-01	4.20E+00	2.15E+00	1.44E+00
		2.68E+01	9.76E-01	4.32E+00	2.11E+00	1.47E+00
C	222S RR	2.64E+01	9.15E-01	4.05E+00	2.05E+00	1.02E+00
		2.64E+01	9.10E-01	4.00E+00	2.03E+00	1.02E+00
		2.65E+01	9.10E-01	4.03E+00	2.03E+00	1.03E+00
		2.63E+01	9.09E-01	4.10E+00	2.01E+00	1.03E+00
C	325	2.20E+01	8.85E-01	3.82E+00	1.94E+00	1.07E+00
		2.20E+01	8.86E-01	3.84E+00	1.94E+00	1.06E+00
		2.24E+01	9.03E-01	3.83E+00	1.98E+00	1.09E+00
		2.26E+01	9.10E-01	3.93E+00	2.00E+00	1.10E+00
Sample	Lab	Bi μg/mL	Cr μg/mL	Pb μg/mL	Ti μg/mL	U μg/mL
C	222S	3.58E+00	1.24E+00	7.18E+00	1.28E-01	3.56E+02
		3.19E+00	1.03E+00	6.61E+00	1.31E-01	3.26E+02
		3.06E+00	1.18E+00	7.59E+00	1.54E-01	3.58E+02
		3.29E+00	1.04E+00	7.11E+00	1.44E-01	3.51E+02
C	222S RR	2.53E+00	9.70E-01	6.94E+00	3.40E-02	3.30E+02
		2.53E+00	9.80E-01	6.91E+00	3.10E-02	3.26E+02
		2.54E+00	9.80E-01	6.93E+00	3.50E-02	3.25E+02
		2.52E+00	9.80E-01	6.94E+00	3.40E-02	3.22E+02
C	325	2.71E+00	1.00E+00	6.54E+00	1.41E-01	3.19E+02
		2.72E+00	1.01E+00	6.58E+00	1.42E-01	3.19E+02
		2.75E+00	1.03E+00	6.69E+00	1.45E-01	3.24E+02
		2.76E+00	1.03E+00	7.07E+00	1.49E-01	3.26E+02
Sample	Lab	La μg/mL				
C	222S	2.67E-01				
		2.77E-01				
C	222S RR	1.73E-01				
		1.61E-01				
		1.65E-01				
		1.63E-01				
C	325	1.82E-01				
		1.85E-01				
		1.88E-01				
		1.92E-01				

RR: Rerun.

Table 1. SEE Data - Fusion Digest (Sample B).

Analyte	Units	N	222S Mean RR	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
Al	µg/mL	4	2.79E-01	6.18E-03	4	2.89E-01	6.81E-03	No	-9.25E-03	No	No	NA
Ca	µg/mL	4	1.35E+00	3.11E-02	4	1.38E+00	1.41E-02	No	-3.50E-02	No	No	No
Fe	µg/mL	4	2.45E+00	4.24E-02	4	2.57E+00	1.41E-02	No	-1.20E-01	Yes	Yes	No
Mn	µg/mL	4	4.87E+00	8.30E-02	4	5.20E+00	2.58E-02	Yes	-3.33E-01	Yes	Yes	No
Na	µg/mL	4	8.06E+00	1.67E-01	4	8.26E+00	1.67E-01	No	-2.03E-01	No	No	No
P	µg/mL	4	1.12E+00	1.89E-02	4	1.12E+00	2.65E-02	No	7.50E-03	No	No	NA
Si	µg/mL	4	1.97E+00	3.11E-02	4	2.16E+00	5.38E-02	No	-1.98E-01	Yes	Yes	NA
Sr	µg/mL	4	1.91E-01	5.29E-03	4	1.93E-01	9.57E-04	Yes	-1.75E-03	No	No	No
Zn	µg/mL	4	1.58E-02	1.26E-03	4	7.07E-02	2.87E-03	No	-5.49E-02	Yes	Yes	Yes
Bi	µg/mL	4	2.08E+01	3.59E-01	4	2.08E+01	9.57E-02	Yes	0.00E+00	No	No	No
Cr	µg/mL	4	7.32E-01	1.17E-02	4	7.64E-01	8.42E-03	No	-3.20E-02	Yes	Yes	No
La	µg/mL	4	3.22E+00	7.53E-02	4	3.18E+00	1.71E-02	Yes	3.75E-02	No	No	No

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
RR: Rerun.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?
Shading: Change in statistical results from those reported in Reference 1.

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Table 2. SEE Data - Fusion Digest (Sample C).

Analyte	Units	N	222S Mean RR	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
Al	µg/mL	4	9.63E-01	1.78E-02	4	8.57E-01	9.42E-03	No	1.06E-01	Yes	Yes	NA
Ca	µg/mL	4	2.76E+00	6.24E-02	4	2.83E+00	1.15E-02	Yes	-7.25E-02	No	No	No
Fe	µg/mL	4	5.11E+00	8.12E-02	4	5.33E+00	2.06E-02	Yes	-2.18E-01	Yes	No	No
Mn	µg/mL	4	4.45E-02	5.77E-04	4	4.45E-02	2.38E-04	No	5.00E-05	No	No	No
Na	µg/mL	4	1.88E+01	3.83E-01	4	1.90E+01	1.71E-01	No	-1.75E-01	No	No	No
P	µg/mL	4	6.06E+00	6.22E-02	4	5.76E+00	2.36E-02	No	2.98E-01	Yes	Yes	NA
Si	µg/mL	4	6.85E-01	1.12E-02	4	7.61E-01	3.09E-02	No	-7.58E-02	Yes	Yes	NA
Sr	µg/mL	4	7.00E-02	1.83E-03	4	7.01E-02	2.99E-04	Yes	-7.50E-05	No	No	No
Zn	µg/mL	4	2.58E-02	6.29E-03	4	6.55E-02	3.80E-03	No	-3.97E-02	Yes	Yes	Yes

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
RR: Rerun.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?
Shading: Change in statistical results from those reported in Reference 1.

Table 3. SEE Data - Acid Digest (Sample B).

Analyte	Units	N	222S Mean RR	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
Al	µg/mL	4	5.62E+00	4.80E-02	4	5.30E+00	1.50E-02	Yes	3.18E-01	Yes	Yes	NA
Fe	µg/mL	4	6.24E+01	5.72E-01	4	6.34E+01	4.24E-01	No	-1.00E+00	Yes	No	No
Na	µg/mL	4	1.96E+02	2.22E+00	4	1.94E+02	1.41E+00	No	1.75E+00	No	No	No
P	µg/mL	4	2.95E+01	2.38E-01	4	2.78E+01	1.41E-01	No	1.65E+00	Yes	Yes	NA
Si	µg/mL	4	5.86E+00	1.49E-01	4	5.83E+00	2.83E-02	Yes	2.75E-02	No	No	NA
Sr	µg/mL	4	5.00E+00	7.53E-02	4	5.09E+00	3.10E-02	No	-8.75E-02	No	No	No
Zn	µg/mL	4	1.19E+00	5.00E-03	4	1.49E+00	9.57E-03	No	-2.95E-01	Yes	Yes	Yes
Cr	µg/mL	4	1.92E+01	2.16E-01	4	1.96E+01	8.16E-02	No	-4.00E-01	Yes	No	No
Pb	µg/mL	4	9.01E+00	6.70E-02	4	9.36E+00	5.07E-02	No	-3.43E-01	Yes	Yes	No
Ti	µg/mL	4	4.37E-01	5.91E-03	4	4.44E-01	2.87E-03	No	-7.00E-03	No	No	NA

- 1: F-test for equality of variances at the 0.05 level of significance.
2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
NA: Standards data not available from both laboratories.
RR: Rerun.
Var: Variance.
Diff: Difference.
Std Dev: Standard Deviation.
Sign?: Is the test statistically significant?
Shading: Change in statistical results from those reported in Reference 1.

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Table 4. SEE Data - Acid Digest (Sample C).

Analyte	Units	N	222S Mean RR	222S Std Dev	N	325 Mean	325 Std Dev	Var ¹ Sign?	222S-325 Diff	Diff ² Sign?	Diff ³ Sign?	Diff ⁴ Sign?
Al	µg/mL	4	2.64E+01	8.16E-02	4	2.23E+01	3.00E-01	Yes	4.15E+00	Yes	Yes	NA
Mn	µg/mL	4	9.11E-01	2.71E-03	4	8.96E-01	1.25E-02	Yes	1.50E-02	No	No	No
Si	µg/mL	4	4.05E+00	4.20E-02	4	3.86E+00	5.07E-02	No	1.90E-01	Yes	Yes	NA
Sr	µg/mL	4	2.03E+00	1.63E-02	4	1.97E+00	3.00E-02	No	6.50E-02	Yes	Yes	No
Zn	µg/mL	4	1.03E+00	5.77E-03	4	1.08E+00	1.83E-02	Yes	-5.50E-02	Yes	No	No
Bi	µg/mL	4	2.53E+00	8.16E-03	4	2.74E+00	2.38E-02	No	-2.05E-01	Yes	Yes	No
Cr	µg/mL	4	9.78E-01	5.00E-03	4	1.02E+00	1.50E-02	No	-4.00E-02	Yes	Yes	No
Pb	µg/mL	4	6.93E+00	1.41E-02	4	6.72E+00	2.42E-01	Yes	2.10E-01	No	No	No
Ti	µg/mL	4	3.35E-02	1.73E-03	4	1.44E-01	3.59E-03	No	-1.11E-01	Yes	Yes	NA
U	µg/mL	4	3.26E+02	3.30E+00	4	3.22E+02	3.56E+00	No	3.75E+00	No	No	NA
La	µg/mL	2	1.66E-01	5.26E-03	4	1.87E-01	4.27E-03	No	-2.13E-02	Yes	Yes	No

- 1: F-test for equality of variances at the 0.05 level of significance.
 2: Test for equality of means at the 0.05 level of significance (used random analytical variability).
 3: Test for equality of means at the 0.01 level of significance (used random analytical variability).
 4: Test for equality of means at the 0.01 level of significance (used both random and systematic variability).
 NA: Standards data not available from both laboratories.
 RR: Rerun.
 Var: Variance.
 Diff: Difference.
 Std Dev: Standard Deviation.
 Sign?: Is the test statistically significant?
 Shading: Change in statistical results from those reported in Reference 1.

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MHC-SD-WM-TI-666 Rev. 0

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 ATTACHMENT 2
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SEE Data - acid digest
Pb - RR Sample B

SEE Data - acid digest
Si - RR Sample B

SEE Data - acid digest
Sr - RR Sample B

SEE Data - acid digest
Ti - RR Sample B

SEE Data - acid digest
Zn - RR Sample B

SEE Data - fusion digest
Al - RR Sample C

SEE Data - fusion digest
Ca - RR Sample C

SEE Data - fusion digest
Fe - RR Sample C

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Appendix C
ICP/AES Metals Analysis Summary

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TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR.SIG.	MEAN SIG
				222-S	222-S	222-S	325	325	325	(222S-325)	Pass/Fail	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%	%		(a)	(a)
B-201	Al	E-01	Fusion	2.79	0.06	2.2	2.89	0.07	2.4	-3.5	PASS	NO	NO
C-112	Al	E-01	Fusion	9.63	0.02	0.20	8.57	0.09	1.1	12	PASS	NO	YES
B-201	Al	E+00	Acid	5.62	0.05	0.89	5.3	0.01	0.19	5.9	PASS	YES	YES
C-112	Al	E+01	Acid	2.64	0.01	0.38	2.23	0.03	1.3	17	(PASS)	YES	YES
Standard	Al		% Rec.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
B-201	Bi	E+01	Fusion	2.08	0.036	1.7	2.08	0.01	0.48	0	PASS	YES	NO
C-112	Bi	E+01	Fusion	Less Than	NA	NA	<0.05	NA	NA	NA	NA	NA	NA
B-201	Bi*	E+02	Acid	6.6	0.11	1.7	5.28	0.03	0.57	22	FAIL	YES	YES
C-112	Bi	E+00	Acid	2.53	0.01	0.40	2.74	0.02	0.73	-8.0	PASS	NO	YES(b)
Standard	Bi		% Rec.	98	1.1	NA	95.7	0.1	NA	2.4	PASS	YES	YES
B-201	Ca	E+00	Fusion	1.35	0.03	2.2	1.38	0.01	0.72	-2.2	PASS	NO	NO
C-112	Ca	E+00	Fusion	2.76	0.06	2.2	2.83	0.01	0.35	-2.5	PASS	YES	NO
B-201	Ca*	E+01	Acid	3.04	0.06	2.0	3.04	0.02	0.66	0	PASS	NO	NO
C-112	Ca*	E+01	Acid	7.29	0.32	4.3	6.91	0.09	1.30	5.4	PASS	YES	NO
Standard	Ca		% Rec.	147.4	29.2	NA	105.5	8.5	NA	33	FAIL	YES	NO

TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RSD	SEE	VAR.SIG.	MEAN SIG
				222-S	222-S	222-S	325	325	(222S-325)	Pass/Fail	YES/NO	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%			(a)	(a)
B-201	Cr	E-01	Fusion	7.32	0.12	1.6	7.64	0.08	1.0	-4.3	PASS	NO	YES(b)
C-112	Cr	E-02	Fusion	3.88	0.001	0.026	ND	ND	NA	NA	NA	YES	NA
B-201	Cr	E+01	Acid	1.92	0.02	1.0	1.96	0.01	0.51	-2.0	PASS	NO	YES(b)
C-112	Cr	E+00	Acid	0.98	0.003	0.31	1.02	0.02	2.0	-4	PASS	NO	YES(b)
Standard	Cr		% Rec.	98	2	NA	101	0.3	NA	-3.0	PASS	YES	NO
B-201	Fe	E+00	Fusion	2.45	0.04	1.6	2.57	0.01	0.39	-4.8	PASS	NO	YES(b)
C-112	Fe	E+00	Fusion	5.11	0.08	1.6	5.33	0.02	0.38	-4.2	PASS	YES	YES(b)
B-201	Fe	E+01	Acid	6.24	0.06	0.96	6.34	0.04	0.63	-1.6	PASS	NO	YES(b)
C-112	Fe*	E+02	Acid	1.53	0.07	4.6	1.42	0.02	1.4	7.5	PASS	YES	NO
Standard	Fe		% Rec.	96.8	2.7	NA	101.4	0.6	NA	-4.6	PASS	YES	YES
B-201	La	E+00	Fusion	3.22	0.08	2.5	3.18	0.02	0.63	1.3	PASS	YES	NO
C-112	La	E+00	Fusion	Less Than	NA	NA	<0.05	NA	NA	NA	NA	NA	NA
B-201	La*	E+01	Acid	8.45	0.17	2.0	8.35	0.04	0.48	1.2	PASS	YES	NO
C-112	La	E-01	Acid	1.66	0.05	3.0	1.87	0.04	2.1	-11	PASS	NO	YES(b)
Standard	La		% Rec.	102.3	1.6	NA	95.9	0.4	NA	6.5	PASS	YES	YES

TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR.SIG.	MEAN SIG
				222-S	222-S	222-S	325	325	325	(222S-325)	Pass/Fail	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%	%		(a)	(a)
B-201	Mn	E+00	Fusion	4.87	0.08	1.6	5.2	0.03	0.58	-6.6	PASS	YES	YES(b)
C-112	Mn	E-02	Fusion	4.45	0.06	4.5	4.45	0.02	0.45	0	PASS	NO	NO
B-201	Mn*	E+02	Acid	1.32	0.03	2.3	1.31	0.01	0.76	0.76	PASS	NO	NO
C-112	Mn	E-01	Acid	9.11	0.03	0.33	8.96	0.13	1.5	1.7	PASS	YES	NO
Standard	Mn		% Rec.	97.6	2.1	NA	102.4	0.5	NA	-4.8	PASS	YES	YES
B-201	Na	E+00	Fusion	8.06	0.17	2.1	8.26	0.17	2.1	-2.5	PASS	NO	NO
C-112	Na	E+01	Fusion	1.88	0.38	20	1.9	0.02	1.1	-1.1	PASS	NO	NO
B-201	Na	E+02	Acid	1.96	0.02	1.0	1.94	0.01	0.52	1.0	PASS	NO	NO
C-112	Na*	E+02	Acid	5.77	0.26	4.5	5.47	0.05	0.91	5.3	PASS	YES	NO
Standard	Na		% Rec.	99.8	0.1	NA	98.8	0.07	NA	1.0	PASS	NO	NO
B-201	P	E+00	Fusion	1.12	0.02	1.8	1.12	0.03	2.7	0	PASS	NO	NO
C-112	P	E+00	Fusion	6.06	0.06	0.99	5.76	0.02	0.35	5.1	PASS	NO	YES
B-201	P	E+01	Acid	2.84	0.02	0.70	2.78	0.01	0.36	2.1	PASS	NO	YES
C-112	P*	E+02	Acid	1.96	0.1	5.1	1.78	0.02	1.1	9.6	PASS	YES	YES
Standard	P		% Rec.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

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TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR.SIG.	MEAN SIG
				222-S	222-S	222-S	325	325	325	(222S-325)	Pass/Fail	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%	%		(a)	(a)
B-201	Si	E+00	Fusion	1.96	0.03	1.5	2.16	0.05	2.3	-9.7	PASS	NO	YES
C-112	Si	E-01	Fusion	6.85	0.11	1.6	7.61	0.31	4.1	-11	PASS	NO	YES
B-201	Si	E+00	Acid	5.86	0.15	2.6	5.83	0.03	0.51	0.51	PASS	YES	NO
C-112	Si	E+00	Acid	4.01	0.04	1.0	3.86	0.05	1.3	3.8	PASS	NO	YES
Standard	Si		% Rec.	ND	ND	ND	ND	ND	ND	ND	PASS	ND	ND
B-201	Sr	E-01	Fusion	1.91	0.05	2.6	1.93	0.01	0.52	-1.0	PASS	YES	NO
C-112	Sr	E-02	Fusion	7	0.18	2.6	7.01	0.03	0.43	-0.14	PASS	YES	NO
B-201	Sr	E+00	Acid	5	0.08	1.6	5.09	0.03	0.59	-1.8	PASS	NO	NO
C-112	Sr	E+00	Acid	2.03	0.02	0.99	1.97	0.03	1.5	3	PASS	NO	YES(b)
Standard	Sr		% Rec.	97.7	1.8	NA	102.5	1	NA	-4.8	PASS	NO	YES
B-201	Zn	E-02	Fusion	1.78	0.1	5.6	7.07	0.29	4.1	-120	FAIL	NO	YES
C-112	Zn	E-02	Fusion	2.58	0.06	2.3	6.55	0.38	5.8	-87	FAIL	NO	YES
B-201	Zn	E+00	Acid	1.19	0.01	0.84	1.49	0.01	0.67	-22	FAIL	NO	YES
C-112	Zn	E+00	Acid	1.02	0.01	0.98	1.08	0.02	1.9	-5.7	PASS	YES	YES(b)
Standard	Zn		% Rec.	102.3	2.2	NA	101	0.8	NA	1.3	PASS	NO	NO
B-201	Pb	E+00	Acid	9.01	0.07	0.78	9.36	0.05	0.53	-3.8	PASS	NO	YES(b)
C-112	Pb	E+00	Acid	6.93	0.01	0.14	6.72	0.24	3.6	3.1	PASS	YES	NO
Standard	Pb		% Rec.	96.9	1.7	NA	98.9	0.3	NA	-2.0	PASS	YES	NO

TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR.SIG.	MEAN SIG
				222-S	222-S	222-S	325	325	325	(222S-325)	Pass/Fail	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%	%		(a)	(a)
B-201	Ti	E-01	Acid	4.37	0.06	1.4	4.44	0.03	0.68	-1.6	PASS	NO	NO
C-112	Ti	E-01	Acid	0.34	0.02	5.9	1.44	0.04	2.8	-124	FAIL	NO	YES
Standard	Ti		% Rec.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
B-201	U	E-01	Acid	Less Than	NA	NA	<3	NA	NA	NA	NA	NA	NA
C-112	U	E+02	Acid	3.26	0.03	0.92	3.22	0.01	0.31	1.2	PASS	NO	NO
Standard	U		% Rec.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

* WHC data is from first set of diluted ICP analyses

(PASS) = Meets 20% RPD criteria but is near (15%-20%) the limit.

(a) Test of equivalence at the 0.05 significance level

(b) Not significant at 0.01 significance level when systematic error is included

ND = no data

NA = Not applicable

Appendix D
ICP/MS Metals Analysis Summary

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TANK NO.	ANALYTE	PREP.	MEAN	SD	RSD	% Difference	% Difference
			325	325	325	222-S/ICP	325/ICP
	ug/mL		ug/mL	ug/mL	%	%	%
B-201	Al	Fusion	0.3	0.008	2.6	-7.5	-3.8
C-112	Al	Fusion	1.06	0.02	2	-10	-23.7
B-201	Al	Acid	5.52	0.67	12.1	1.8	-4.1
C-112	Al	Acid	28.45	1.18	4.1	-7.8	-27.6
Standard	Al	% Rec.	ND	ND	ND	ND	ND
B-201	Bi	Fusion	23.9	1.7	7.2	-14.9	-14.9
C-112	Bi	Fusion	0.13	0.02	15.1	<NC	<NC
B-201	Bi	Acid	575	12.2	2.1	12.9	-8.9
C-112	Bi	Acid	3.05	0.16	5.1	-20.6	-11.3
Standard	Bi	% Rec.	107.2	NA	4.8		
B-201	Ca	Fusion	13.8	3.5	25	-922	-900
C-112	Ca	Fusion	20.6	7.1	34.4	-646	-628
B-201	Ca	Acid	86.5	28.9	33.4	-185	-185
C-112	Ca	Acid	114.2	17.5	15.3	-57	-66
Standard	Ca	% Rec.	60.8	NA	45.5		
B-201	Cr	Fusion	0.9	0.01	1.2	-22.9	-17.8
C-112	Cr	Fusion	0.17	0.007	4.2	-338	<NC
B-201	Cr	Acid	19.6	0.7	3.7	-2.1	0
C-112	Cr	Acid	1.21	0.08	6.3	-23.4	-18.6
Standard	Cr	% Rec.	101.2	NA	19.5		
B-201	Fe	Fusion	3.73	0.05	13.9	-52.2	-45.1
C-112	Fe	Fusion	4.82	0.18	3.8	5.6	9.6
B-201	Fe	Acid	37.4	1.18	3.2	40	41
C-112	Fe	Acid	81	1.31	1.6	47.1	42.9
Standard	Fe	% Rec.	94.8	NA	3.7		

TANK NO.	ANALYTE	PREP.	MEAN	SD	RSD	% Difference	% Difference
			325	325	325	222-S/ICP	325/ICP
	ug/mL		ug/mL	ug/mL	%	%	%
B-201	La	Fusion	2.95	0.04	1.2	8.4	7.2
C-112	La	Fusion	0.003	0.00077	25.7	<NC	<NC
B-201	La	Acid	69.1	2.7	3.9	18.2	17.2
C-112	La	Acid	0.26	0.16	61.4	-56.6	-39
Standard	La	% Rec.	119	0.42	7		
B-201	Mn	Fusion	4.95	0.006	2.3	-1.6	4.8
C-112	Mn	Fusion	0.062	4.5	10	-39.3	-39.3
B-201	Mn	Acid	124	0.04	3.7	6.1	5.3
C-112	Mn	Acid	1.01	0.16	3.8	-10.8	-12.7
Standard	Mn	% Rec.	94.8	NA	3.3		
B-201	Na	Fusion	23	6.3	27.4	-185	-175
C-112	Na	Fusion	33.1	4.1	12.2	-76	-74
B-201	Na	Acid	182.8	18.6	10.2	6.6	5.6
C-112	Na	Acid	542	26	4.8	6.1	0.9
Standard	Na	% Rec.	116.3	NA	10.7		
B-201	Sr	Fusion	0.25	0.008	3.2	-30.9	-29.5
C-112	Sr	Fusion	0.094	0.004	4.6	-34.2	-34.2
B-201	Sr	Acid	5.88	0.21	3.5	-17.6	-15.5
C-112	Sr	Acid	2.52	0.09	3.4	-24.1	-27.9
Standard	Sr	% Rec.	108.5	NA	2.7		
B-201	Zn	Fusion	0.072	0.015	21.4	-304	-1.4
C-112	Zn	Fusion	0.073	0.019	26.1	-183	-11.4
B-201	Zn	Acid	1.45	0.07	4.6	-21.8	2.7
C-112	Zn	Acid	1.3	0.05	4	-27.5	-20.4
Standard	Zn	% Rec.	87.4	NA	3.3		

TANK NO.	ANALYTE	PREP.	MEAN	SD	RSD	% Difference	% Difference
			325	325	325	222-S/ICP	325/ICP
	ug/mL		ug/mL	ug/mL	%	%	%
B-201	Pb	Fusion	0.398	0.018	4.6	<NC	<NC
C-112	Pb	Fusion	0.269	0.018	6.7	<NC	<NC
B-201	Pb	Acid	9.69	0.43	4.4	-7.5	-3.5
C-112	Pb	Acid	7.32	0.17	2.4	-5.6	-8.9
Standard	Pb	% Rec.	109.4	NA	3.6		
B-201	Ti	Fusion	0.042	0.004	10.4	<NC	<NC
C-112	Ti	Fusion	0.033	0.005	13.8	<NC	<NC
B-201	Ti	Acid	0.458	0.044	9.7	-4.8	-3.2
C-112	Ti	Acid	0.421	0.081	19.1	-1138	-192
Standard	Ti	% Rec.	ND	ND	ND	ND	ND
B-201	U	Fusion	0.11	0.004	3.5	(a) -87.3	(a) -86.3
C-112	U	Fusion	12.8	0.23	1.8	(a) -90.9	(a) -89.9
B-201	U	Acid	2.01	0.075	3.7	<NC	<NC
C-112	U	Acid	368	6.98	1.9	12.9	14.3
Standard	U	% Rec.	ND	ND	ND	ND	ND
			uCi/mL	uCi/mL			
B-201	Tc	Fusion	< 8E-06	<NC	<NC	<NC	<NC
C-112	Tc	Fusion	< 8E-06	<NC	<NC	<NC	<NC
B-201	Tc	Acid	5.00e-04	2.20e-04	43	<NC	<NC
C-112	Tc	Acid	< 8E-06	<NC	<NC	<NC	<NC

NA = Not applicable

<NC = Less than ICP/AES is not comparable to ICP/MS result

ND = No Data

%dif = [(ICP/AES - ICP/MS)/ICP/AES]*100

(a) = Data is the percent difference between uranium fluorimeter method and ICP/MS result

Appendix E
Wet Chemistry Analysis Summary

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TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR SIG(a)	MEAN SIG(a)
				222-S	222-S	222-S	325	325	325	222S-325	Pass/Fail	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%	%			
B-201	Cyanide	E-02	Water	3.35	1.37	40.9	6.18	2.62	42.4	-59.4	FAIL	NO	NO
C-112	Cyanide	E+01	Water	2.36	0.55	23.3	2.85	0.1	3.51	-18.8	(PASS)	YES	NO
Standard	Cyanide		% Rec.	101	1.7	NA	93.7	1.2	NA	7.50	PASS	NO	YES
B-201	TOC	E+01	Water	1.21	0.25	20.7	0.55	0.13	23.6	75	FAIL	ND	ND
C-112	TOC	E+01	Water	3.3	0.12	3.64	1.88	0.1	5.32	54.8	FAIL	NO	YES
Standard	TOC		% Rec.	81.3	0.6	NA	101.7	16.6	NA	-22.3	FAIL	YES	NO
B-201	TIC	E+01	Water	1.65	0.06	3.64	2.13	0.17	7.98	-25.4	FAIL	ND	ND
C-112	TIC	E+01	Water	3.12	0.1	3.21	3.2	0.12	3.75	-2.53	PASS	NO	NO
Standard	TIC		% Rec.	99	0.8	NA	125	16.6	NA	-23.2	FAIL	YES	NO
B-201	F	E+01	Water	7.26	0.15	2.07	6.58	0.25	3.80	9.83	PASS	NO	YES
C-112	F	E+00	Water	6.7	0.17	2.54	12	0.82	6.83	-56.7	FAIL	NO	YES
Standard	F		% Rec.	100.2	2	NA	112.6	4.1	NA	-11.7	PASS	NO	YES
B-201	Cl	E+01	Water	2.11	0.02	0.948	2.05	0.13	6.34	2.88	PASS	YES	NO
C-112	Cl	E+00	Water	8.51	0.49	5.76	9	0	0	-5.60	PASS	YES	NO
Standard	Cl		% Rec.	103.2	1	NA	96	0	NA	7.23	PASS	YES	YES

TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR SIG(a)	MEAN SIG(a)
				222-S	222-S	222-S	325	325	325	222S-325	Pass/Fail	YES/NO	YES/NO
	ug/mL			ug/mL	ug/mL	%	ug/mL	ug/mL	%	%			
B-201	NO2	E+01	Water	<11	NA	NA	1.25	0.06	4.8	NA	NA	NA	NA
C-112	NO2	E+02	Water	3.72	0.25	6.72	3.83	0.1	2.61	-2.91	PASS	NO	NO
Standard	NO2		% Rec.	97.2	1.2	NA	97.1	1.9	NA	0.103	PASS	NO	NO
B-201	NO3	E+02	Water	5.31	0.06	1.13	5.38	0.13	2.42	-1.31	PASS	NO	NO
C-112	NO3	E+02	Water	4.94	0.33	6.68	5.18	0.13	2.51	-4.74	PASS	NO	NO
Standard	NO3	E+02	% Rec.	105.5	0.6	NA	93.3	1.1	NA	12.3	PASS	NO	YES
B-201	PO4	E+01	Water	2.4	0.04	1.67	1.38	0.13	9.42	54.0	FAIL	YES	YES
C-112	PO4	E+02	Water	4.34	0.04	0.922	4.1	0.29	7.07	5.69	PASS	YES	NO
Standard	PO4		% Rec.	113.6	1.2	NA	104.5	3.3	NA	8.34	PASS	NO	YES
B-201	SO4	E+00	Water	<11	NA	NA	<5	NA	NA	NA	NA	NA	NA
C-112	SO4	E+02	Water	1.06	0.01	0.943	1.03	0.05	4.85	2.87	PASS	YES	NO
Standard	SO4		% Rec.	106.8	0.9	NA	96.5	2.1	NA	10.1	PASS	NO	YES

(PASS) = Meets 20% RPD criteria but is near (15%-20%) the limit.

NA = Not applicable

(a) Test of equivalence at the 0.05 significance level

Appendix F
Radiochemical Analysis Summary

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TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR SIG(a)	MEAN SIG(a)
				222-S	222-S	222-S	325	325	325	222S-325	Pass/Fail	YES/NO	YES/NO
	uCi/mL			uCi/mL	uCi/mL	%	uCi/mL	uCi/mL	%	%			
B-201	Total Beta	E-02	Fusion	0.8	0.01	1.25	0.96	0.01	1.04	-18.2	(PASS)	NO	YES
C-112	Total Beta	E+00	Fusion	2.11	0.13	6.16	2.32	0.04	1.72	-9.48	PASS	YES	YES
Standard	Total Beta		% Rec.	102.7	0.3	NA	108.8	1.8	NA	-5.77	PASS	YES	YES
B-201	Total Alpha	E-03	Fusion	2.62	0.08	3.05	3.17	0.11	3.47	-19.0	(PASS)	NO	YES
C-112	Total Alpha	E-04	Fusion	3.32	0.07	2.11	2.48	0.16	6.45	29.0	FAIL	NO	YES
Standard	Total Alpha		% Rec.	100	2.8	NA	100.9	3.4	NA	-0.896	PASS	YES	NO
B-201	Cs-137	E-03	Fusion	1.13	0.07	6.19	1.29	0.02	1.55	-13.2	PASS	YES	YES
C-112	Cs-137	E-01	Fusion	7.77	0.16	2.06	7.93	0.15	1.89	-2.04	PASS	NO	NO
Standard	Cs-137		% Rec.	100.85	0.6	NA	102.6	0.2	NA	-1.72	PASS	YES	NO
B-201	U	E-01	Fusion	8.64	1.02	11.8	8.01	0.14	1.75	7.57	PASS	YES	NO
C-112	U	E+02	Fusion	1.41	0.19	13.5	1.25	0.05	4	12.0	PASS	YES	NO
Standard	U		% Rec.	100.31	26.1	NA	96.2	3	NA	4.18	PASS	YES	NO
B-201	Pu-239	E-03	Fusion	2.29	0.18	7.86	3.23	0.06	1.86	-34.1	FAIL	NO	YES
C-112	Pu-239	E-05	Fusion	11.58	3.14	27.1	9.64	0.32	3.32	18.3	(PASS)	YES	NO
Standard	Pu-239		% Rec.	103	4.8	NA	101.2	4.1	NA	1.76	PASS	NO	NO

TANK NO.	ANALYTE	EXP	PREP.	MEAN	SD	RSD	MEAN	SD	RSD	RPD	SEE	VAR SIG(a)	MEAN SIG(a)
				222-S	222-S	222-S	325	325	325	222S-325	Pass/Fail	YES/NO	YES/NO
	uCi/mL			uCi/mL	uCi/mL	%	uCi/mL	uCi/mL	%	%			
B-201	Am-241	E-05	Fusion	<12.1	NA	NA	<6.6	NA	NA	NA	NA	NA	NA
C-112	Am-241	E-04	Fusion	1.07	0.03	2.80	1.04	0.05	4.81	2.84	PASS	NO	NO
Standard	Am-241		% Rec.	90.1	3.7	NA	98	1.2	NA	-8.40	PASS	NO	YES
B-201	Tc-99	E-05	Fusion	<0.9	NA	NA	<0.03	NA	NA	NA	NA	NA	NA
C-112	Tc-99	E-04	Fusion	1.86	0.13	6.99	1.58	0.03	1.90	16.3	(PASS)	YES	YES
Standard	Tc-99		% Rec.	100.9	4.6	NA	84.6	1.8	NA	17.6	(PASS)	YES	YES
B-201	Sr-90	E-03	Fusion	3.74	0.08	2.14	3.59	0.25	6.96	4.09	PASS	YES	NO
C-112	Sr-90	E-01	Fusion	8.57	0.19	2.22	8.29	0.34	4.10	3.32	PASS	NO	NO
Standard	Sr-90		% Rec.	109.5	2.7	NA	103.4	2.6	NA	5.73	PASS	NO	YES
B-201	H-3	E-05	Water	8.1	0.15	1.85	9.02	0.31	3.44	-10.7	PASS	NO	YES
C-112	H-3	E-05	Water	3.65	0.23	6.30	3.94	0.15	3.81	-7.64	PASS	NO	NO
Standard	H-3		% Rec.	92.6	5.6	NA	98.1	0.8	NA	-5.77	PASS	YES	NO

(PASS) = Meets 20% RPD criteria but is near (15%-20%) the limit.

NA = Not Applicable

(a) Test of equivalence at the 0.05 significance level

Appendix G

Estimated Detection Limits and Counting Uncertainties

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Detection Limit Estimates for Metals and
Anions

Analyte	222-S Detect. Limit	325 Detect. Limit
Metals/ICP	ug/mL	ug/mL
Al	0.02	0.01
Bi	0.08	0.5
Ca	0.04	0.05
Cr	0.009	0.02
Fe	0.01	0.01
La	0.014	0.05
Mn	0.002	0.005
Na	0.03	0.08
P	0.06	0.1
Si	0.01	0.08
Sr	0.003	0.005
Zn	0.003	0.02
Pb	0.06	0.06
Ti	0.004	0.005
U	0.4	2.0

Detection Limit Estimates for Metals and
Anions

Analyte	222-S Detect Limit	325 Detect.Limit
Anions/Wet	ug/mL	ug/mL
CN	0.03	0.01
TOC	5	0.5
TIC	5	0.5
F	0.1	0.2
Cl	0.2	0.2
NO2	1	0.4
NO3	1	0.4
PO4	1	0.4
SO4	1	0.4

Estimated Counting Errors and Uncertainty

Analyte	Tank	222-S Count Error	325 Uncertainty	222-S Ratio (a)	325 Ratio (a)
Radiochem		%	%		
Total Alpha	B-201 C-112	3.1 8.7	8 5	1.14 1.49	0.98 1.24
Total Beta	B-201 C-112	1.3 1.4	3 3	1.03 1.1	0.88 1.06
GEA (Cs-137)	B-201 C-112	7.4 0.5	7 7		
Pu-239/240	B-201 C-112	3.9 2.3	10.5 7		
Am-241	B-201 C-112	25.7 17.1	8 10		
Sr-90	B-201 C-112	7.4 0.4	8 7		
Tc-99	B-201 C-112	ND 11.3	ND 9		
H-3	B-201 C-112	14.1 25.8	3.2 5.5		

ND = No data

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

(a) Ratio for total beta = total beta/(SrY-90 + Cs-137)

Appendix H

Relative Percent Difference Tables and Graphical Data Presentations

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RELATIVE PERCENT DIFFERENCE VALUES
FOR ICP METALS ANALYSES

TANK B-201

ANALYTE	FUSION	ACID DIGEST	QC STANDARD
Aluminum	-3.5	5.9	NA
Bismuth	0	<u>22.2</u>	2.4
Calcium	-2.2	0	<u>33.1</u>
Chromium	-4.3	-2.1	-3.0
Iron	-4.8	-1.6	-4.6
Lanthanum	1.3	1.2	6.5
Manganese	-6.6	0.8	-4.8
Sodium	-2.5	1.0	1.0
Lead	NA	-3.8	-2.0
Phosphorus	0	2.1	NA
Silicon	-9.7	0.5	NA
Strontium	-1.0	-1.8	-4.8
Titanium	NA	-1.6	NA
Uranium	NA	NA	NA
Zinc	<u>-119.5</u>	<u>-22.4</u>	1.3

The RPD is positive if the 222-S result > 325 result.

The RPD is negative if the 325 result > 222-S result.

Underlined values indicate the RPD is outside the acceptance criteria of $\pm 20\%$.

NA indicates that the analyte was not detected so the RPD was not applicable.

RELATIVE PERCENT DIFFERENCE VALUES
FOR ICP METALS ANALYSES

TANK C-112

ANALYTE	FUSION	ACID DIGEST	QC STANDARD
Aluminum	11.6	16.8	NA
Bismuth	NA	-8.0	2.4
Calcium	-2.5	5.4	<u>33.1</u>
Chromium	NA	-4.0	-3.0
Iron	-4.2	7.5	-4.6
Lanthanum	NA	-11.9	6.5
Manganese	0	1.7	-4.8
Sodium	-1.1	5.3	1.0
Lead	NA	3.1	-2.0
Phosphorus	5.1	9.6	NA
Silicon	-10.5	3.8	NA
Strontium	-0.1	3.0	-4.8
Titanium	NA	<u>123.6</u>	NA
Uranium	NA	1.2	NA
Zinc	<u>-87.0</u>	-5.7	1.3

The RPD is positive if the 222-S result > 325 result.

The RPD is negative if the 325 result > 222-S result.

Underlined values indicate the RPD is outside the acceptance criteria of $\pm 20\%$.

NA indicates that the analyte was not detected so the RPD was not applicable.

RELATIVE PERCENT DIFFERENCE VALUES
FOR WET CHEMICAL ANALYSES

ANALYTE	B-201	C-112	QC STANDARD
Cyanide	<u>-59.4</u>	<u>-18.8</u>	7.6
Total Organic Carbon	<u>75.0</u>	<u>54.8</u>	<u>-22.3</u>
Total Inorganic Carbon	<u>-25.4</u>	-2.5	<u>-23.2</u>
Fluoride	9.8	<u>-56.7</u>	-11.7
Chloride	2.9	-5.6	7.2
Nitrate	NA	-2.9	0.1
Nitrite	-1.3	-4.7	12.3
Phosphate	<u>54.0</u>	5.7	8.3
Sulfate	NA	2.9	10.1

RELATIVE PERCENT DIFFERENCE VALUES
FOR RADIOCHEMICAL ANALYSES

ANALYTE	B-201	C-112	QC STANDARD
Total Beta	-18.2	-9.5	-5.8
Total Alpha	-19.0	<u>29.0</u>	-0.9
Cs-137	-13.2	-2.0	0.3
Total Uranium	7.6	12.0	4.2
Pu-239	<u>-34.1</u>	18.3	1.8
Am-241	NA	2.8	-8.4
Tc-99	NA	16.3	17.6
Sr-90	4.1	3.3	5.7
Tritium	-10.7	-7.6	-5.8

The RPD is positive if the 222-S result > 325 result.

The RPD is negative if the 325 result > 222-S result.

Underlined values indicate the RPD is outside the acceptance criteria of $\pm 20\%$.

NA indicates that the analyte was not detected so the RPD was not applicable.

Figure H-1. B-201 Metals RPDs.

Figure H-2. C-112 Metals RPDs.

Figure H-3. Wet Chemical RPDs.

WHC-SD-WM-TI-666 Rev. 0
Figure H-4. Radiochemical RPDs.