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EVALUATION OF WET CHEMICAL ICP-AES ELEMENTAL ANALYSIS METHODS USING SIMULATED HANFORD WASTE SAMPLES-PHASE I INTERIM REPORT (U)

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Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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EVALUATION OF WET CHEMICAL ICP-AES ELEMENTAL ANALYSIS METHODS USING SIMULATED HANFORD WASTE SAMPLES-PHASE I INTERIM REPORT (U)

Charles J. Coleman, SRNL
Thomas B. Edwards, SRNL

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Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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REVIEWS AND APPROVALS

6/8/2005
C.J. Coleman, Co-Author, Analytical Development Section, SRNL Date

Thomas B Edwards 6/2/05
T.B. Edwards, Co-Author, Statistical Consulting Section, SRNL Date

Will A Spencer 6/2/2005
W.A. Spencer, Technical Reviewer, Analytical Development Section, SRNL Date

Connie C Herman 6/2/05
C.C. Herman, RPP Program Manager,
Immobilization Technology Section, SRNL Date

RE Edwards 6/6/05
R.E. Edwards, Manager, RPP Project,
Waste Treatment Technology Section, SRNL Date

for AKA 6/8/05
Aruna Arakali, C&T, WTP-RPP Date

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1.0 EXECUTIVE SUMMARY

The wet chemistry digestion method development for providing process control elemental analyses of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Melter Feed Preparation Vessel (MFPV) samples is divided into two phases:

Phase I consists of: 1) optimizing digestion methods as a precursor to elemental analyses by ICP-AES techniques; 2) selecting methods with the desired analytical reliability and speed to support the nine-hour or less turnaround time requirement of the WTP; and 3) providing baseline comparison to the laser ablation (LA) sample introduction technique for ICP-AES elemental analyses that is being developed at the Savannah River National Laboratory (SRNL).

Phase II consists of: 1) Time-and-Motion study of the selected methods from Phase I with actual Hanford waste or waste simulants in shielded cell facilities to ensure that the methods can be performed remotely and maintain the desired characteristics; and 2) digestion of glass samples prepared from actual Hanford Waste tank sludge for providing comparative results to the LA Phase II study.

Based on the Phase I testing discussed in this report, a tandem digestion approach consisting of sodium peroxide fusion digestions carried out in nickel crucibles and warm mixed-acid digestions carried out in plastic bottles has been selected for Time-and-Motion study in Phase II. SRNL experience with performing this analytical approach in laboratory hoods indicates that well-trained cell operator teams will be able to perform the tandem digestions in five hours or less. The selected approach will produce two sets of solutions for analysis by ICP-AES techniques. Four hours would then be allocated for performing the ICP-AES analyses and reporting results to meet the nine-hour or less turnaround time requirement.

The tandem digestion approach will need to be performed in two separate shielded analytical cells by two separate cell operator teams in order to achieve the nine-hour or less turnaround time. Because of the simplicity of the warm mixed-acid method, a well-trained cell operator team may in time be able to perform both sets of digestions. However, having separate shielded cells for each of the methods is prudent to avoid overcrowding problems that would impede a minimal turnaround time.

Selection of the tandem digestion approach of using sodium peroxide fusions in nickel crucibles and warm mixed-acid digestions was based on these advantages:

- ICP-AES laboratory dead-time is minimized by obtaining solutions from the warm mixed-acid method within three hours after the samples are transported into the shielded cells. These solutions can be analyzed by ICP-AES as the sodium peroxide fusions are being completed. The two sets of digestions will be naturally staggered as a function of the time required to perform them, resulting in more efficient use of ICP-AES laboratory time than if the two sets of digestions were completed simultaneously (a likely scenario if two different alkali fusion methods were selected).

- The warm mixed-acid method dissolves Ni in the sludge and four of the five glass-former/glass-modifier elements (Na, Li, B, Zn). This method may also prove better for S, U, Ca, K and other minor component determinations because of the relatively clean matrix of the acid digestion.

- The warm mixed-acid method produces a low concentration of dissolved solids in the solution aspirated into the ICP-AES. Therefore, this solution is less likely than alkali fusion methods to affect nebulizer performance (through evaporative deposition of dissolved solids at the nebulizer tip) which could result in degradation of ICP-AES performance over time. Any degradation of nebulizer/ICP-AES performance would require lengthy recalibration procedures prior to analysis of the sodium peroxide fusion digestions.

- The sodium peroxide fusion is the most rigorous of the alkali fusion methods. The highly oxidizing sodium peroxide flux is superior to most digestion methods for dissolving refractory elements (Al, Si, Fe, Mn, Zr, Ti, Cr, noble metals, and others) in Hanford waste. This method is also effective for the refractory glass-former materials, SiO_2 in particular.

- Both the sodium peroxide fusion and warm mixed-acid method have the potential speed, convenience, and reliability advantages for remote cell operations. The methods have been streamlined to be simple to perform remotely and to minimize tedious, time-consuming manipulations that may result in analytical errors.

The nine-hour-or-less turnaround time requirement will demand close coordination of the shielded cell sample preparation team and the ICP-AES laboratory team. The timetables in Table 1-1 and Table 1-2 show schedules that would successfully meet the turnaround time requirement.

Table 1-1. Sample Preparation Timetable

Activity	Time from Samples Entering Cells (hr.)
Remove up to 8 samples from rabbit bottles	0-1
Sub-sample; weigh sub-samples	1-2
Perform warm mixed-acid method; dry sample for Na_2O_2 fusion method	2-3
Perform Na_2O_2 fusion method	3-5

Table 1-2. ICP-AES Laboratory Timetable

Activity	Time from Samples Entering Cells (hr.)
Calibrate ICP-AES; analyze check standards for mixed-acid digestion	0-3
Analyze up to 8 mixed-acid prep solutions + standards + blanks	3-4.5
Check calibration; re-calibrate if necessary	4.5-6
Analyze up to 8 fusion prep solutions + standards + blanks	6-7.5
Compile results from both preps and report	7.5-9

2.0 TESTING SUMMARY

As part of the Phase I program to develop wet chemistry methods to support WTP, tests were performed to help optimize the speed, efficiency, and reliability of digestion methods followed by elemental analysis of solutions by ICP-AES techniques. Digestions and elemental analyses were performed on two High-Level Waste (HLW)-2A simulants, AY-102/C-106 and AZ-101, and on one HLW-2B simulant, a mixture of AY-102/C-106 sludge and glass-forming/glass-modifying chemicals. The Analytical Development Section (ADS) of SRNL performed the tests. ADS issued a Task Technical and Quality Assurance Plan [1] based on specifications given in the Statement of Work that was provided by WTP [2] for this testing program. The Statistical Consulting Section of SRNL performed the statistical data analysis.

2.1 DIGESTION METHODS

The following digestion methods were tested on the respective sample matrices. Because of the nine-hour or less turnaround time requirement for MFPV samples, emphasis was placed on streamlining methods to reduce turnaround time. C.J. Coleman of ADS performed digestions of simulants in chemical fume hoods.

2.1.1 HLW-2A - AY-102/C-106 Simulant

- Sodium peroxide fusions in both Ni and Zr crucibles [3]
- Cesium hydroxide fusions in both Ni and Zr crucibles [3], [4]
- Mixture of cesium hydroxide/cesium carbonate fusions in Pt crucibles
- Potassium hydroxide fusions in Zr crucibles [5]
- Hot hydrochloric acid-nitric acid mixture (aqua regia) in a sealed Teflon container [6]
- Hot hydrochloric acid-hydrofluoric acid in a sealed Teflon container [7]
- Mixture of nitric acid, hydrogen peroxide, and hydrochloric acid in a plastic bottle. This mixture was not externally heated but became warm from the chemical decomposition of hydrogen peroxide in strong acid solution, as well as from digestion of the sample.

2.1.2 HLW-2A - AZ-101 Simulant

- Sodium peroxide fusion in Ni crucibles [3]
- Potassium hydroxide fusion in Zr crucibles [5]
- Mixture of nitric acid, hydrogen peroxide, and hydrochloric acid in a plastic bottle. This mixture was not externally heated but became warm from the chemical decomposition of hydrogen peroxide in strong acid solution, as well as from digestion of the sample.

2.1.3 HLW-2B - AY-102/C-106 simulant + glass formers

- Sodium peroxide fusion in Ni crucibles [3]
- Cesium carbonate fusion in Pt crucibles [8]
- Potassium carbonate fusion in Pt crucibles [8]
- Mixture of nitric acid, hydrogen peroxide, and hydrochloric acid in a plastic bottle. This mixture was not externally heated but became warm from the chemical decomposition of hydrogen peroxide in strong acid solution, as well as decomposition of the sample.

Table 2-1 summarizes the dissolution methods and the test conditions for both the alkali fusions and mixed-acid digestions. This table provides a link from the digestion conditions to the ICP-AES elemental analyses of the digestion solutions.

Table 2-1. Summary Table of Digestion Methods Tested in Phase I

Alkali Fusion Methods [a.]						
Digestion Method	**Sample Matrix**	**Data in Table**	**Reagents Used**	**Digestion Vessel**	**Heating Time**	**Heating Temp.**
Na_2O_2/NaOH Reference 3	AY-102/ C-106 (as dried powder)	3.1.1	Na_2O_2/NaOH-flux reagent HNO_3-uptake acid	Zr crucible	10 minutes	675 °C
Na_2O_2 Reference 3	AY-102/ C-106 (as dried powder)	3.1.2	Na_2O_2-flux reagent HNO_3-uptake acid	Ni crucible	10 minutes	750 °C
Na_2O_2 Reference 3	AZ-101 (as dried powder)	3.1.3	Na_2O_2- flux reagent HNO_3-uptake acid	Ni crucible	10 minutes	750 °C
Na_2O_2 Reference 3	AY-102/ C-106 + glass formers (as dried powder)	3.1.4	Na_2O_2-flux reagent HNO_3-uptake acid	Ni crucible	10 minutes	750 °C
Na_2O_2 Reference 3	AY-102/ C-106 + glass formers (vitrified into glass wafers)	3.1.5	Na_2O_2-flux reagent HNO_3-uptake acid	Ni crucible	10 minutes	750 °C
CsOH Reference 3, 4	AY-102/ C-106 (as dried powder)	3.1.6	CsOH-flux reagent HCl-uptake acid	Zr crucible	10 minutes	675 °C
CsOH Reference 3, 4	AY-102/ C-106 (as dried powder)	3.1.7	CsOH-flux reagent HCl-uptake acid	Ni crucible	10 minutes	675 °C
Cs_2CO_3/CsOH	AY-102/ C-106 (as dried powder)	3.1.8	Cs_2CO_3/CsOH-flux reagent HCl-uptake acid	Pt crucible	10 minutes	1000 °C

Table 2-1. Summary Table of Digestion Methods Tested in Phase I - continued

Alkali Fusion Methods [a.]- continued						
Digestion Method	**Sample Matrix**	**Data in Table**	**Reagents Used**	**Digestion Vessel**	**Heating Time**	**Heating Temp.**
Cs_2CO_3 Reference 8	AY-102/ C-106 + glass formers (as dried powder)	3.1.9	Cs_2CO_3-flux reagent HNO_3-uptake acid	Pt crucible	10 minutes	1100 °C
Cs_2CO_3 Reference 8	AY-102/ C-106 + glass formers (vitrified into glass wafers)	3.1.10	Cs_2CO_3-flux reagent HNO_3-uptake acid	Pt crucible	10 minutes	1100 °C
KOH Reference 5, 15	AY-102/ C-106 (as dried powder)	3.1.11	KOH/KNO_3 flux reagent HCl-uptake acid	Zr crucible	10 minutes	675 °C
KOH Reference 5	AZ-101 (as dried powder)	3.1.12	KOH/KNO_3 flux reagent HCl-uptake acid	Zr crucible	10 minutes	675 °C
K_2CO_3 Reference 7	AY-102/ C-106 + glass formers (vitrified into glass wafers)	3.1.13	K_2CO_3-flux reagent HNO_3-uptake acid	Pt crucible	10 minutes	1100 °C

Table 2-1. Summary Table of Digestion Methods Tested in Phase I - continued

Mixed Acid Methods [a]						
Digestion Method	**Sample Matrix**	**Data in Table**	**Reagents Used**	**Digestion Vessel**	**Heating Time**	**Heating Temp.**
Warm Acidification with $HNO_3/H_2O_2/HCl$	AZ-101 (as slurry)	3.1.15	$HNO_3/H_2O_2/HCl$	Plastic bottle	~ 10 minutes	~ 80 °C
Warm Acidification with $HNO_3/H_2O_2/HCl$	AY-102/ C-106 + glass formers (as slurry)	3.1.16	$HNO_3/H_2O_2/HCl$	Plastic bottle	~ 10 minutes	~ 80 °C
HF-HCl with external heating Reference 7	AY-102/ C-106 (as slurry)	3.1.17	HF-HCl	Pressurized Teflon Vessel	45 minutes	115 °C
Aqua Regia with external heating Reference 6	AY-102/ C-106 (as slurry)	3.1.18	$HCl\text{-}HNO_3$ (3:1 ratio-aqua regia)	Pressurized Teflon Vessel	45 minutes	115 °C

a. Sample weights were typically 1.5-2.0 grams of slurry. For alkali fusions, an approximate 10:1 ratio of alkali flux reagent to dry powder or glass sample was used. Initial dilution volumes were typically 500 mL or 525 mL. A 5-fold serial dilution with deionized water was made prior to ICP-AES analysis of the solutions.

2.1.4 Use of Matrix Spikes

Two different protocols for matrix spikes were used in the experiments. For approximately 50 % of the digestions, a matrix spike solution consisting of a mixture of Ag, Sb, Cd, Th, S, Tl, and U were added *after* the digestions were performed (the spike was performed just prior to the ICP-AES elemental analysis). This protocol was chosen because none of these 7 elements are found in the Analytical Reference Glass-1 (ARG-1) [9] used as the Laboratory Control Standard (see Table 3-23 for elemental composition of ARG-1 glass standard). After the ICP-AES responses to these elements were measured, subsequent matrix spikes consisted of adding a solution of Y to the slurry *before* the digestion step. For both protocols, the ICP-AES analysis was used to measure the spike recovery percentage. However, the percent spike recovery was not used to adjust the reported values for the other analytes since use of soluble spike elements is not a technically defensible method to measure the accuracy of digestions/ICP-AES analysis of solid materials.

2.1.5 Use of Laboratory Control Standard

The ARG-1 glass standard was digested and analyzed in duplicate concurrently with the HLW-2A and HLW-2B matrices. The measured value of each element in this glass was compared with the average value as reported by Corning Engineering Laboratory Services (CELS) [9] (see Table 3-23 for elemental composition of ARG-1 glass standard) and the percent difference and the sign of the difference (either positive or negative) was noted. However, the relative percent differences in the SRNL measured values versus the CELS values were not used to adjust the reported values. One reason for this is that the glass standard is not in the same form as the slurry samples. Even if slurry standards were available, the use of bias corrections based on elemental analysis of the standards is not a common practice unless it can be shown categorically that the bias in the standard analysis also occurs in the sample analysis.

2.1.6 ICP-AES Analysis of Solutions

Solutions in Phase I tests were analyzed with the ADS ICP-AES spectrophotometer contained in a hood for radioactive samples even though the samples were non-radioactive, with the knowledge that this ICP-AES spectrophotometer would be required for the radiological samples generated in the Phase II tests. ADS QA/QC procedures [10] were used in the ICP-AES determinations. L.L. Farrow performed the ICP-AES determinations with technical oversight from J.C. Hart and spectroscopic analysis assistance from F.M. Pennebaker, all of ADS. Analytical line wavelengths used for ICP-AES analysis of the solutions are listed in Table 3-21.

2.1.7 Measurement of Wt. % Oxides

The three simulants (AY-102/C-106, AZ-101, and AY-102/C-106 plus glass-formers/glass-modifiers) were analyzed for wt. % oxide content by first evaporating the free water at 200 °C in a drying oven followed by heating the samples in platinum crucibles in a muffle furnace set at 1100 °C until constant weight was achieved. C.J. Coleman of ADS performed the wt. % oxide measurements using ADS procedures for wt. % total solids measurements [11]. The wt. % oxide data for the three simulants are shown in Table 3-22.

2.1.8 Statistical Analysis

T.B. Edwards of the Statistical Consulting Section of SRNL performed statistical analysis of elemental analysis data as a function of digestion methods. The full statistical analysis package is documented in three reports that address the analyses of the AY-102 simulant [12], the AZ-101 simulant [13], and the melter feed simulant consisting of AY-102/C-106 sludge and glass-formers/glass-modifiers [14].

2.2 OBJECTIVES

Test requirements were provided in the Statement of Work [2]. The basic objectives of the experimental program for the Phase I of this analytical development project are outlined in the Task Technical and QA Plan [1], pages 12-14.

Although the analytical precision and accuracy requirements have not yet been formally stipulated for the WTP, years of operating the Defense Waste Processing Facility at SRS have shown that a goal of 5 % relative standard deviation for the precision of six or more replicate measurements of the major elements (>0.5 wt % on oxide basis) and ± 10 % of the true value is an appropriate goal.

In order to meet the nine-hour or less turnaround time requirement for MFPV samples, no more than three hours can be allocated for performing up to eight digestions (the clock for digestions is considered to start after the sample vials have been removed from the pneumatic transport bottles and the sample vials have been sub-sampled and each sample weighed into the digestion crucible or bottle). We set as a criterion that an *individual* digestion could require no longer than one hour to perform.

Test Objective	Objective Met (Y/N)	Discussion
1. Test candidate digestion methods on both HLW-2A and HLW-2B matrices to help method selection based on analytical quality and the time required for digestions.	Yes	The following methods were tested on the HLW-2A matrix : • Na_2O_2 fusion using Ni crucible • Na_2O_2 fusion using Zr crucible • CsOH fusion using Ni crucible • CsOH fusion using Zr crucible • $CsOH/Cs_2CO_3$ fusions in Pt crucibles • KOH/KNO_3 fusions in Zr crucibles • Hot $HCl-HNO_3$ in sealed container • Hot HF-HCl in sealed container • Warm $HNO_3/H_2O_2/HCl$ in open container The following methods were tested on the HLW-2B matrix: • Na_2O_2 fusion using Ni crucible • Cs_2CO_3 in Pt crucible • K_2CO_3 in Pt crucible • Warm $HNO_3/H_2O_2/HCl$ in open container

Test Objective	Objective Met (Y/N)	Discussion
2. Demonstrate that the individual method can be performed in one hour or less and that up to eight samples can be digested by the method in 3 hours or less.	Yes	In the laboratory, up to eight digestions can be performed in about two hours. The true time required for performing the methods in the shielded cells will be determined in the Time-and-Motion study in Phase II. The nine-hour turnaround time requirement for the entire analytical scheme will be achievable with adequate training of WTP Laboratory staff.
3. Obtain reliable results in terms of accuracy and precision.	Yes	Although accuracy and precision criteria have not been set for WTP analyses, a goal of 5 % relative standard deviation for precision of at least 3 replicate measurements was set for elements that would comprise at least 0.5 wt. % on the sludge matrices converted to an oxide. A goal of ± 10 % of the true value was set for accuracy. For most sets of determinations, these goals were met.
4. Use QA/QC controls including matrix spikes and laboratory control standards.	Yes	Both matrix spikes and laboratory control standards were used. Normal ADS QA/QC procedures and protocols were followed in the ICP-AES analyses of solutions.

2.3 TEST EXCEPTIONS

None

2.4 RESULTS AND PERFORMANCE AGAINST SUCCESS OBJECTIVES

Success Criteria	**Explain How the Tests Did or Did Not Meet the Success Criteria**
1. Analytical method must meet 9-hour or less turnaround time requirement.	The tests did meet the success criteria. The recommended analytical approach has characteristics needed for overall success in meeting the 9-hour or less turnaround time goal. The digestion methods are relatively simple to perform and can be completed rapidly enough to meet WTP design requirements.
2. Analytical quality in terms of precision, accuracy, and sensitivity must be adequate to support the WTP.	The tests did meet the success criteria. Although the analytical precision and accuracy requirements have not yet been formally stipulated for the WTP, years of operating the Defense Waste Processing Facility at SRS has shown that a goal of 5 % relative standard deviation for precision and ± 10 % of the true value for elements at 0.5 wt. % on an oxide basis is an appropriate goal. In general, the data obtained in the course of the experiments met these requirements. The overall data quality was consistent with that typically observed in SRNL when sludge and glass matrices are analyzed by qualified technicians and professional staff.

2.5 QUALITY REQUIREMENTS

This high-level waste development work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRNL as identified in DOE IWO M0SRLE60. SRNL has provided matrices to WTP demonstrating compliance of the SRNL QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRNL QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices.

2.6 C&T TEST CONDITIONS

A Statement of Work [2] was issued that specified the test objectives and conditions.

2.7 SIMULANT USE

As specified in the WTP Statement of Work [2], AY-102/C-106 and AZ-101 WTP waste simulants were chosen to represent HLW-2A initial MFPV samples. In addition, the melter feed simulant that was prepared by adding glass-formers/glass-modifiers to AY-102/C-106 sludge simulant was chosen to represent HLW-2B MFPV samples. Actual radioactive AY-102/C-106 sludge was characterized [15] by ADS. Several of the same digestion methods tested on the AY-102/C-106 simulant also were used on the actual waste. The digestion characteristics of the actual waste and the simulated waste are similar.

However, as a general disclaimer, no simulant is a perfect stand-in for actual high-level waste from waste tanks to evaluate digestion methods. The compounds used in simulants may have different solubility characteristics (potentially, more or less soluble) than those found in real waste. Hanford high-level waste sludge is particularly complex because of the many chemical processes carried out over the history of the Hanford Site. Certain waste streams may require different digestion/ICP-AES methods than discussed in this report because of the high concentrations of Zr, Bi, or other elements. Unquestionably, the digestion methods must be re-tested periodically to ensure their applicability on actual Hanford wastes.

2.8 DISCREPANCIES AND FOLLOW-ON TESTS

Discrepancies: None

Follow-on Tests: The follow-on testing is part the planned method development program and a natural consequence of dividing the tasks into two phases. Phase II tests will involve implementation of the digestion methods discussed in this Phase I interim report as part of a Time-and-Motion study to ensure that the methods can meet the nine-hour or less turnaround time and also achieve acceptable analytical quality. Moreover, additional development work toward a single digestion method applicable to WTP process control will be performed.

3.0 DISCUSSION

3.1 METHOD DEVELOPMENT GOALS - RATIONALE FOR METHODS TESTED

The method development goals for the chemical digestion/ICP-AES approach for WTP samples are discussed in the following section. Additional discussions are included in the Experimental Section.

- **Develop a reliable, simple, and rapid digestion protocol applicable to both the HLW-2A and HLW-2B matrices that will achieve the nine-hour or less turnaround time.**

Result: The proposed scheme of a sodium peroxide fusion digestion used in conjunction with a warm mixed-acid digestion yields two sets of solutions that when analyzed separately provide the required analyses. Since the % relative standard deviation of determinations of major elements was less than 5 %, excellent precision was obtained. Absolute accuracy of the method is more difficult to assess due to lack of slurry standards, but good agreement of several digestion methods along with acceptable recoveries for glass standard analytes indicates accurate analyses. The scheme is relatively simple to perform remotely and, in terms of cell equipment, requires only an analytical balance to weigh the sample, a drying oven to dry the sample, and a muffle furnace to heat the samples to fusion temperature. The scheme is effective on both the HLW-2A and HLW-2B sample matrices.

Discussion: The WTP turnaround time requirement of nine hours or less for the elemental analysis of HLW-2A and HLW-2B samples breaks down to following task-time allocation:

Task	Time Allocation for Success
Sample Receipt-Sample Preparation	5 hours
ICP-AES Elemental Analysis	2-3 hours
Data Review and Report	1-2 hours

The main challenge to meeting the nine-hour turnaround time is the sample preparation step. Sample preparation includes removing the sample bottles from the pneumatic carrier bottle (rabbits), removing and weighing sub-samples from each sample vial, and dissolving the sub-samples. For the purpose of setting method development goals, we allocated a total of two hours for removing the sample vials from the rabbits, sub-sampling, and weighing the samples to be dissolved. Therefore, only three hours could be allocated for the actual digestions and still have a reasonable expectation of achieving the 9-hour or less turnaround time goal.

In order to meet the three-hour turnaround time for as many as eight digestions, plus standards, plus blanks, we set as a criterion that an *individual* digestion could take no longer than one hour. This criterion eliminated some methods from consideration for testing, such as the multi-heating step microwave-assisted mixed-acid digestion method [16] used for glass samples at the SRS Defense Waste Processing Facility. In fact, microwave heating techniques were not considered at length because the pressure vessels tend to be cumbersome to assemble in a shielded cell environment.

FUSION METHODS:

The fact that both the HLW-2A and HLW-2B samples will have significant concentrations of SiO_2 (after the HLW-2B material is transferred from the MFPV to the melter, a tank heel of up to 30 % will remain, ensuring that significant quantities of the glass-formers/glass-modifiers will be present in both HLW-2A and HLW-2B samples) means that digestions based on either alkali fusions or HF are required to dissolve the SiO_2. HF is very effective for dissolving SiO_2, but leads to high corrosion rates in facilities and adds the potential for a serious HF spill due to increased handling of this reagent. Another problem with prolonged use of HF is that attack of the cell windows and other cell equipment can result in costly facility repairs. The SRS Defense Waste Processing Facility Laboratory recently replaced the alpha shields on all the cell windows because HF attack on the shields had impaired clarity.

Alkali fusions eliminate the need for HF to dissolve SiO_2. An important consideration for favoring the alkali fusions for SiO_2 determinations is that the attack of HF on the ICP-AES spray chamber/nebulizer system can lead to high Si biases unless an HF corrosion resistant spray chamber/nebulizer system is used as well as careful checks and corrections for Si blank values. Furthermore, insoluble fluorides can produce low biases of certain elements. This problem can be corrected to some extent by adding a fluoride complexing reagent such as boric acid to the solution. However, since boron determinations are required, either a second digestion or a split solution protocol (analyzing solutions with and without boric acid) would be required.

Properly performed sodium peroxide fusions normally result in complete digestion of high-level waste sludge and glass matrices, even when HNO_3 is used to dissolve the flux residue. The sodium peroxide method offers the possibility that refractory WTP components such as SiO_2 and metal compounds can be dissolved without using either HF or HCl. The sodium peroxide fusion digestions on the HLW-2A matrix (Table 3-1 and Table 3-2 for AY-102/C-106; and Table 3-3 for AZ-101) and the HLW-2B matrix as both a slurry of melter feed (Table 3-4) and as a melter feed converted to glass (Table 3-5) resulted in clear solutions from which ICP-AES analyses of high precision were obtained.

The sodium peroxide method has, as have most of the common alkali fusion methods based on salts of Na, Li, and K, the serious flaw that it contains an alkali metal (Na) that must be measured reliably in WTP matrices. Because alkali fusions are normally carried out in either Zr or Ni crucibles, analyses of these metals are precluded by attack on the crucible. Lithium borate salts are commonly used for digesting silicate-bearing materials and these fusions are carried out in platinum. However, both Li and B must be measured on both HLW-2A and HLW-2B samples for process control. To summarize the problem with alkali fusions, most preclude the determination of at least two of the required elemental analyses for WTP process control.

A possible solution to these problems that would allow measurement of both required alkali elements and the crucible element is the use of cesium salts for the fusion methods. Cesium hydroxide fusions were introduced [4] for glass dissolutions at SRNL a number of years ago to avoid the problem of adding a required alkali metal during the digestion. Since Zr is usually not an important element in SRS matrices, glass could be made in a platinum crucible and then a shard or wafer of glass transferred to a Zr crucible for cesium hydroxide fusions. Zr is an important element in Hanford high-level waste, eliminating this approach as a cure-all for the WTP and necessitating a second digestion method. However, cesium hydroxide fusions were applied to AY-102/C-106 sludge simulant in both Zr (Table 3-6) and Ni crucibles (Table 3-7) as a possible dual digestion scheme and also as a possible complementary method to sodium peroxide fusions. The cesium hydroxide digestion of the HLW-2A matrix did not result in complete digestion, as evidenced by relatively poor ICP-AES results.

To avoid the Zr-Ni crucible problem, platinum crucibles were considered because platinum will not be measured for routine process control. Since hydroxide ion corrosively attacks platinum crucibles whereas alkali carbonates are compatible with platinum, cesium carbonate fusions in platinum crucibles were tested. Cesium carbonate digestions of glass wafers have been tested [8] as a potential single digestion scheme for glass samples in the SRS Defense Waste Processing Facility. Cesium carbonate is commercially available at high purity (99.994 % pure on a metals basis). Although trace levels of alkali elements are found in the commercially available cesium carbonate, accurate measurements of Li, Na, and K can be obtained at concentrations typical of sludge and glass matrices.

The cesium carbonate fusion method on the HLW-2A simulant AY-102/C-106 produced too many insoluble residues for a reliable analysis, particularly with HNO_3 used as the digestion acid. A possible mechanism for the incomplete digestion is that the sludge components become more refractory before the cesium carbonate flux temperature can be reached (at least 900 °C before the flux becomes free-flowing). An improvement in performance was obtained by adding a solution of cesium hydroxide which has a melting point of less than 300 °C to the slurry of HLW-2A matrix before drying the sludge. The mixture of cesium hydroxide and cesium carbonate in a platinum crucible minimized the corrosion of the platinum crucible and resulted in good elemental determinations (Table 3-8) when HCl was used as the digestion acid. The solid that remained after the $Cs_2CO_3/CsOH$ digestion was identified by x-ray diffraction as cesium platinum chloride, Cs_2PtCl_6, showing that corrosion of the platinum crucible from attack of the hydroxide had not been eliminated. Our overall impression was that this method has promise as a possible single digestion method, but that it requires additional testing to confirm applicability on waste samples.

The cesium carbonate method was very successful when applied to the HLW-2B melter feed matrix with glass-forming chemicals. Cesium carbonate fusions carried out in platinum crucibles on both the HLW-2B matrix as a dried powder (Table 3-9) and as glass wafers made by vitrifying the melter feed powder (Table 3-10) produced clear solutions and reliable ICP-AES analyses using HNO_3 as the digestion acid. Apparently, the glass-forming chemicals in the HLW-2B matrix assist with the oxidizing/complexing power of the cesium carbonate melt. Since cesium hydroxide was not required as a co-reagent to digest the melter feed, there was little evidence of cesium carbonate fusions severely attacking Pt crucibles.

The analogous potassium carbonate fusion applied to the glass was also tested (Table 3-13) should the concentration of K in the Hanford waste stream be inconsequential for glass processing and durability. For reasons not apparent after the small number of experiments, the potassium carbonate fusions were not as successful as the cesium carbonate fusions. Insoluble material and slightly lower elemental analyses were observed for the potassium carbonate fusions of glass versus the cesium carbonate fusions.

Although the cesium carbonate fusion could provide a single digestion method for the HLW-2B matrix both as melter feed powder and as glass, we believe that different digestion methods for the HLW-2A and HLW-2B samples should be avoided to simplify cell operations. Based on the fact that the presence of glass-forming SiO_2 in the sample appears to improve the effectiveness of the cesium carbonate flux, additional experiments were done with other glass formers, such as GeO_2 and P_2O_5, added to the HLW-2A matrix. Results obtained so far have been mixed, with some indication that the added glass formers help with the cesium carbonate fusion digestion of the HLW-2A sludge. In addition, experiments were done by adding $CsNO_3$ both as a solution to the slurry sample before drying and as a solid to the Cs_2CO_3 in an attempt to increase the oxidizing power of the flux and thereby improve digestion of the HLW-2A matrix. The addition of nitrate ion to the flux resulted in significant corrosion of the Pt crucible and did not result in a satisfactory digestion method.

The practical benefits of developing a single digestion method applicable to both the HLW-2A and HLW-2B matrices are important enough to continue the investigative work. However, at this time, a robust single method that fulfills all WTP requirements is not available.

KOH/KNO_3 fusion method in Zr crucibles was applied to the HLW-2A matrix as the AY-102/C-106 simulant (Table 3-11) and as the AZ-101 simulant (Table 3-12). The KOH/KNO_3 method in Zr crucibles was studied as a possible complementary method to sodium peroxide fusions in Ni crucibles. This method is one of the routine methods used at the Hanford 222-S Laboratory [5] and at PNNL. SRNL also used this method in characterization of the actual AY-102/C-106 sludge [15]. Some solids were apparent after the digestions, similar to those observed with the cesium hydroxide fusions. As with the cesium hydroxide fusions, the performance of the method improved with use of HCl rather than HNO_3 for the digestion acid to achieve faster digestions. Table 3-11 and Table 3-12 are from ICP-AES analyses of KOH/KNO_3 fusions with HCl as the uptake acid.

MIXED-ACID DIGESTION METHODS:

The warm-acid method was devised and tested after it became apparent that a single digestion scheme would not be available and that the sodium peroxide method would be the backbone of the analytical approach. Focus shifted to find the simplest, quickest method for accurately measuring sodium and nickel precluded by the sodium peroxide fusion method carried out in nickel crucibles. Three separate mixed-acid digestions were performed on the HLW-2A matrix to help select a suitable complementary method to the sodium peroxide fusion method:

1) A mixture of HF-HCl was heated in a Teflon pressurized container. Boric acid was not used to complex free fluoride because the B determinations from a non-fusion digestion were of interest. Considerable white solids remaining after the digestion were removed by filtration before elemental analysis (Table 3-17).

2) A mixture of 3 parts HCl and 1 part HNO_3 (aqua regia) was also heated in a Teflon pressurized container analogous to the HF-HCl method. Boiling aqua regia is used in tandem with sodium peroxide fusion digestions at SRS to characterize SRS waste tank sludge prior to transfer to the Defense Waste Processing Facility. The considerable white solids remaining after the hot aqua regia digestion were removed by filtration before the ICP-AES analysis of the HLW-2A sludge (Table 3-18).

3) The other mixed acid method applied to the HLW-2A matrix for 2 simulants, AY-102/C-106 (Table 3-14), and AZ-101 (Table 3-15), did not use external heating but instead relied on chemical reactions to warm the solution. The rapid chemical decomposition of 5 mL of 30 % H_2O_2 and caustic waste sample in 15 mL concentrated HNO_3 solution created a warm (70-80 °C), frothy mixture that became clearer but did not completely clarify (SiO_2 is almost completely insoluble in this acid matrix) upon addition of 5 mL of concentrated HCl. The concentrated acid solution was diluted to 500 mL, filtered, and diluted five-fold prior to elemental analysis. This method was also used for the HLW-2B matrix as AY-102/C-106 sludge and glass-formers in slurry form (Table 3-16). No attempt was made to apply this method to glass wafers since this acid mixture will not significantly attack glass. For the Time-and-Motion study in Phase II, the dilution will be to approximately 1000 mL to eliminate the time-consuming serial dilution step prior to Na and Ni determinations by ICP-AES. There was no indication of low bias for Na or Ni determinations from this method versus the other acid methods or alkali fusion methods. This method could be the preferred method for Li, B, Na, and Zn introduced as glass-formers/glass-modifiers because the low-dissolved solid matrix is conducive to superior ICP-AES analyses. Boron is prone to slight losses due to volatility in some alkali fusions, so the warm acid method would be preferred for B determinations. The "before and after" analyses of the glass-formers/glass-modifiers will be of particular interest in the WTP to ensure that the prescribed amounts of these materials are in the HLW-2B sample before feeding the glass melter. The SiO_2 must be measured from the sodium peroxide fusion, but the other glass-formers/glass-modifiers are readily soluble in dilute acid. The warm mixed-acid method should be a reliable, fast, and convenient digestion method to measure these elements.

- **Eliminate or minimize the use of halide acids (HF, HCl) for digestions**

  Result: The proposed scheme uses no HF and a small volume of HCl, the necessity of which can be evaluated periodically in the WTP. Some Hanford high-level waste may have high levels of Zr which could benefit from addition of HF. The effectiveness of the proposed digestion methods will have to be re-evaluated prior to these sludges being processed.

- **Test the effectiveness of using matrix spikes and laboratory control standards for QC purposes**

  Result: Matrix spikes and laboratory control standards were used in conjunction with every digestion method tested. Although the matrix spikes were measured with reasonable reliability, and they have their place in the method development phase, we find them of minimal use for ascertaining analytical quality and recommend that WTP not use them for routine process control analyses.

  Laboratory control standards have much more technical merit than matrix spikes, particularly when they are in the same form and composition of the samples. We recommend that a true matrix laboratory control standard be made available for digestion and analysis throughout the life of the WTP. This would involve the use of slurry simulants as laboratory control standards instead of glass, since the most likely *routine* analytical scenario for the WTP does not include converting the melter feed samples into glass. However, glass samples from the WTP will be analyzed to determine product consistency and durability. Glass standards will be important to the analytical QC protocol for these samples.

- **Provide a statistical analysis of the analytical results**

  Result: The statistical analysis of the data by T.B. Edwards of SRNL's Statistical Consulting Section was documented in three separate reports, one for each of the three simulants tested AY-102/C-106 [12], AZ-101, [13], and AY-102/C-106 plus glass-formers/glass-modifiers[14]. The statistical analysis helps to show graphically information within the data tables. One of the most useful statistical tools is the comparison of element-by-element measurements as a function of each of the digestion methods. For example, Ca values are higher from the sodium peroxide fusion than from all other methods. The first reaction to these data might be that the sodium peroxide fusions were simply more effective at dissolving Ca compounds. In fact, the Ca measurements were high in the Na_2O_2 blank, suggesting that the higher values were due to contamination in the sodium peroxide and not the result of better digestions. Statistical analysis clearly documented higher Ca values from the sodium peroxide fusion blanks as the probable source of the higher Ca values from this digestion method.

> Statistical analysis of the data also is important for comparing digestion approaches. Since the tandem digestion approach of sodium peroxide fusions and warm mixed-acid is being considered for Phase II study, a statistical comparison of the data from these two methods and the data from an alternative method was done. The tandem digestion approach was compared with KOH/KNO_3 for AY-102/C-106 [12] and AZ-101 [13] simulants and compared with Cs_2CO_3 results for the AY-102/C-106 sludge + glass formers [14]. The precision of the analyses was excellent and, for some measurements, there were statistical differences that might not be chemically significant enough to affect WTP processing. That being said, the statistical treatment clearly shows that analytical differences can be expected as a function of digestion method.

The ICP-AES elemental analyses of the three simulants tested are shown in Table 3-1 through Table 3-18. The data tables are grouped by digestion type.

Table 3-1. Elemental Analysis of AY-102/C-106 Simulant - WTP Sample Type: HLW-2A - Digestion Method: Sodium Peroxide-Sodium Hydroxide Fusion in Zr crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] 1 (µg/g)	Spike[b.] 2 (µg/g)	Spike[b.] Avg. (µg/g)	Spike[b.] Recovery (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	error (%)
Ag	39	633	601	511	582	11	0.77 mg/L	0.82 mg/L	0.79 mg/L	99 %	160	133	147	NA
Al	<164	18000	18000	17900	18000	1	18100	17900	18000	NA	23200	23500	23350	-7
B	<65	<57	<66	<61	<66	NA	<57	<57	<57	NA	24600	25200	24900	-7
Ba	<14	595	585	577	586	2	596	587	592	NA	813	828	821	+4
Ca	540	2570	2710	2620	2630	3	2870	2870	2870	NA	11900	12000	11950	+17
Cd	<38	86.1	81.1	86.8	84.7	4	0.82 mg/L	0.82 mg/L	0.82 mg/L	102 %	<118	<117	<118	NA
Ce	243	1050	1020	996	1022	3	1090	1070	1080	NA	996	1090	1043	NA
Cr	<67	823	817	792	811	2	798	822	810	NA	527	561	544	-15
Cu	<22	142	140	140	141	1	152	146	149	NA	<68	<67	<68	NA
Fe	<92	63500	63700	62900	63400	1	63500	62800	63150	NA	97900	99700	98800	+1
K	1330	1410	1490	1480	1460	3	1450	1380	1415	NA	27000	28000	27500	+22
La	107	659	631	626	639	3	656	648	652	NA	431	403	417	NA
Li	55	63.4	54.5	48.8	55.6	13	63.9	63.2	63.5	NA	14900	15000	14950	0
Mg	<13	612	610	604	611	1	665	674	670	NA	4900	5020	4960	-5
Mn	<6	14000	14000	13800	13900	1	14000	13800	13900	NA	14400	14600	14500	-1
Mo	<271	247	326	259	277	15	249	282	265	NA	<846	<833	<846	NA
Na	Not Measured-Na introduced in fusion reagents													
Ni	<132	2030	2080	2020	2040	2	2040	2060	2050	NA	8150	8330	8240	0
P	<1360	<1180	<1370	<1260	<1360	NA	<1180	<1180	<1180	NA	<4240	<4170	<4240	NA
Pb	<955	3140	3060	3030	3180	2	3200	3120	3160	NA	<2980	<2940	<2980	NA
S	<401	<348	<406	<373	<401	NA	0.90 mg/L	0.90 mg/L	0.90 mg/L	113 %	<1250	<1230	<1240	NA
Sb	<103	332	302	280	305	9	0.80 mg/L	0.80 mg/L	0.80 mg/L	100 %	751	810	780	NA
Si	<94	18800	18900	18600	18800	1	19000	18700	18850	NA	23200	23600	23400	+4
Sn	<836	767	<847	<779	<847	NA	<726	<726	<726	NA	<2610	<2600	<2600	NA
Sr	134	981	1030	1000	1000	2.4	1050	1060	1055	NA	2610	2660	2635	>+100
Th	<33	<28	<33	<30	<33	NA	0.79 mg/L	0.79 mg/L	0.79 mg/L	99 %	<102	<100	<100	NA
Ti	<13	<11	<13	<12	<13	NA	<11	<11	<11	<11	6930	7040	6985	+1
Tl	<186	163	354	235	<354	NA	0.92 mg/L	0.94 mg/L	0.93 mg/L	116 %	696	780	738	NA
U	101	329	325	376	343	8	3.24 mg/L	2.62 mg/L	2.93 mg/L	73 %	460	699	579	NA
Zn	<18	168	159	163	163	3	181	171	176	NA	238	240	239	+49
Zr	Not reported-Zr crucibles were used for these fusion digestions													

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

**Table 3-2. Elemental Analysis of AY-102/C-106 Simulant -
WTP Sample Type: HLW-2A -
Digestion Method: Sodium Peroxide Fusion in Ni crucibles**

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Trial 4 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] Recovery (From Trial 3) (%)	Spike[b.] Recovery (From Trial 4) (%)	Avg. Spike[b.] Recovery (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<34.4	1190	1180	1190	1190	1190	1	NA	NA	NA	<66.9	<65.2	<66.0	NA
Al	<313	17800	17700	17700	17800	17800	1	NA	NA	NA	22400	22500	22400	-10
B	<124	<145	<152	<120	<135	< 152	NA	NA	NA	NA	23700	22900	23300	-13
Ba	95.8	717	708	649	651	681	5	NA	NA	NA	1090	1020	1060	+33
Ca	349	2980	3120	2860	3140	2780	20	NA	NA	NA	12400	12200	12300	+20
Cd	<72.2	<84.4	<88.9	<70.1	<78.6	<88.9	NA	NA	NA	NA	<140	<137	<140	NA
Ce	<419	1340	1450	1290	1290	1180	15	NA	NA	NA	932	974	953	NA
Cr	420	1310	1350	1040	1010	1180	15	NA	NA	NA	1790	1310	1550	>100
Cu	<41.3	137	128	140	127	133	5	NA	NA	NA	<80.3	<78.3	<80.3	NA
Fe	<175	67700	67600	67500	67000	67400	1	NA	NA	NA	102000	101000	10200	+4
K	1960	2560	2600	<1620	2610	<2610	NA	NA	NA	NA	26900	30900	28900	+28
La	<141	721	695	671	707	698	3	NA	NA	NA	<274	283	<283	NA
Li	<72.2	<84.4	90.3	<70.1	<78.6	<90.3	NA	NA	NA	NA	16500	16600	16600	+10
Mg	<24.1	645	647	660	645	649	1	NA	NA	NA	5190	5210	5200	0
Mn	<10.3	14800	14800	14800	14700	14800	1	NA	NA	NA	14800	14900	14800	+1
Mo	806	938	967	546	565	< blank	NA	NA	NA	NA	1670	1630	1650	NA
Na	Not Measured-Na introduced in fusion reagents													
Ni	Not Measured-Ni crucibles used in fusions													
P	<2580	<3020	<3180	<2510	<2810	<3180	NA	NA	NA	NA	<5020	<4900	<5020	NA
Pb	<1820	3400	3830	3390	3250	3470	7	NA	NA	NA	<3540	<3450	<3540	NA
S	<763	<892	<940	<741	<831	<940	NA	NA	NA	NA	<1490	<1450	<1490	NA
Sb	1670	1920	1970	758	701	< blank	NA	NA	NA	NA	4260	3000	3630	NA
Si	<179	17000	16900	17300	17000	17000	1	NA	NA	NA	231000	233000	2320000	+3
Sn	<1590	<1860	<1960	<1550	<1730	<1960	NA	NA	NA	NA	<3100	<3020	<3020	NA
Sr	80.9	1080	1110	1040	1110	1080	3	NA	NA	NA	2710	2640	2680	>100
Th	67.9	74.6	89.8	<60.1	72.2	<89.8	NA	NA	NA	NA	175	143	159	NA
Ti	<24.1	<28.1	<29.6	<23.4	<26.2	<29.6	NA	NA	NA	NA	7050	7070	7060	+2
Tl	375	559	584	<344	401	<559	NA	NA	NA	NA	1100	788	944	NA
U	259	263	415	278	295	313	22	NA	NA	NA	679	478	578	NA
Y	<344	<402	<423	1.95 mg/L	1.95 mg/L	1.95 mg/L	1	98	98	98	<669	<652	<669	NA
Zn	1130	1270	1230	406	435	Less than blank	NA	NA	NA	NA	2790	1840	1990	>100
Zr	97.2	993	962	735	770	865	15	NA	NA	NA	1110	1180	1140	+19

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

Table 3-3. Elemental Analysis of AZ-101 Simulant - Type of WTP Waste: HLW-2A - Digestion Method: Sodium Peroxide Fusion in Ni Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] Recovery (From Trial 3) (%)	LCS Trial1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<14.5	124	120	135	124	8	NA	<66.9	<65.2	<66.2	NA
Al	<132	23400	23200	24700	23800	3	NA	24700	24800	24800	-1
B	<52.1	<56.4	<47.7	<56.49	<56.4	NA	NA	24400	24300	24400	-10
Ba	57.2	501	499	497	506	1	NA	1000	934	967	+22
Ca	312	2600	2570	2570	2640	2	NA	12700	12500	12600	+26
Cd	<30.4	3010	2990	3000	3050	1	NA	<140	<137	<140	NA
Ce	258	1720	1730	1760	1770	3	NA	1190	1100	1140	NA
Cr	232	694	745	738	726	4	NA	1360	950	1100	+72
Cu	<17.4	150	163	150	154	5	NA	<80.3	<78.3	<80.3	NA
Fe	17.0	56000	55900	56700	56200	1	NA	102000	102000	102000	+4
K	6490	4450	4280	7350	5360 (less than blank)	NA	NA	38700	45800	42250	+87
La	92.4	1660	1640	1670	1660	1	NA	431	441	436	NA
Li	77.2	68.9	57.0	98.9	75.0 (less than blank)	NA		17400	17500	17400	+17
Mg	<10.1	392	378	393	388	2	NA	5240	5220	5230	+1
Mn	<4.34	1500	1490	1570	1520	3	NA	14900	14800	14800	+1
Mo	572	398	467	502	456	12	NA	2160	1780	1970	NA
Na	Not Measured-Na used in fusion reagent										
Ni	Not Measured- Ni crucibles used in fusions										
P	<1090	<1040	<1040	<1180	<1180	NA	NA	<5020	<4900	<5020	NA
Pb	<766	<734	<829	<734	<829	NA	NA	<3540	<3450	<3540	NA
Sb	1320	690	690	762	Less than blank	NA	NA	4490	2990	3740	NA
Si	<75.3	3800	3800	3940	3850	2	NA	236000	236000	236000	+5
Sn	<670	1520	1520	1530	1520	1	NA	<3100	<3020	<3020	NA
Sr	88.7	1300	1300	1320	1310	1	NA	2640	2580	2520	>100
Ti	<2.66	87.5	87.5	90.4	88.5	2	NA	7100	7110	7100	+ 3
Y	<145	<139	<139	3.98 mg/L	NA	NA	99 %	<669	<652	<669	NA
Zn	1030	361	361	416	379	8	NA	3120	2050	2590	>100
Zr	89.0	17400	17400	16600	17100	3	NA	888	1120	1004	+5

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AZ-101 simulant contained 20.23 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 4.0 mg/L.

Table 3-4. Elemental Analysis of AY-102/C-106 Melter Feed as Dried Slurry - WTP Sample Type: HLW-2B - Sample Digestion Method: Sodium Peroxide Fusion in Ni Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Trial 4 (µg/g)	Avg. (µg/g)	RSD (%)	Avg. Spike[b.] Recovery (From Trials 3,4) (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<34.4	288	425	452	466	408	20	NA	<66.9	<65.2	<66.0	NA
Al	<313	10200	10600	10500	10500	10400	2	NA	22400	22500	22400	-10
B	<124	10100	10100	10300	10300	10200	1	NA	23700	22900	23300	-13
Ba	95.8	431	425	445	467	442	4	NA	1090	1020	1060	+33
Ca	349	1690	1830	2030	1920	1870	8	NA	12400	12200	12300	+20
Cd	<72.2	<56.4	<55.5	<52.6	<44.2	<56.4	NA	NA	<140	<137	<140	NA
Ce	<419	772	818	874	727	798	8	NA	932	974	953	NA
Cr	420	798	834	944	1090	916	14	NA	1790	1310	1550	>100
Cu	<41.3	49.8	55.7	62.4	62.9	57.7	11	NA	<80.3	<78.3	<80.3	NA
Fe	<175	37300	37900	37700	37400	37600	1	NA	102000	101000	102000	+4
K	1960	3480	3170	3450	3410	3380	4	NA	26900	30900	28900	+28
La	<141	397	408	404	394	401	2	NA	<274	283	<283	NA
Li	<72.2	4720	4840	4790	4850	4800	1	NA	16500	16600	16600	+10
Mg	<24.1	392	406	408	407	403	2	NA	5190	5210	5200	0
Mn	<10.3	8180	8280	8280	8200	8240	1	NA	14800	14900	14800	+1
Mo	806	764	811	998	1070	911	16	NA	1670	1630	1650	NA
Na	Not Measured-Na used in fusion reagent											
Ni	Not Measured- Ni crucibles used in fusions											
P	<2580	<2020	<1980	<1880	<1580	<2020	NA	NA	<5020	<4900	<5020	NA
Pb	<1820	2070	2340	2230	2420	2260	7	NA	<3540	<3450	<3540	NA
S	<763	<596	<586	<556	<467	<596	NA	NA	<1490	<1450	<1490	NA
Sb	1670	1660	1540	1950	2470	1900	22	NA	4260	3000	3630	NA
Si	<179	85200	87100	86300	85500	86000	1	NA	231000	233000	232000	+3
Sn	<1590	<1240	<1220	<1160	<975	<1240	NA	NA	<3100	<3020	<3020	NA
Sr	80.9	630	656	713	693	673	6	NA	2710	2640	2680	>100
Th	67.9	63.9	55.5	72.2	75.5	66.7	NA	NA	175	143	159	NA
Ti	<24.1	<18.8	<18.5	<17.5	<14.7	<18.8	NA	NA	7050	7070	7060	+2
Tl	375	311	382	366	314	Less than blank	NA	NA	1100	788	944	NA
U	259	<134	284	163	<105	Less than blank	NA	NA	679	478	578	NA
Y	<344	<268	<264	1.93 mg/L or 96 % recovery	1.96 mg/L or 98 % recovery	1.95	1	97 %	<669	<652	<669	NA
Zn	1130	4040	4030	4350	4660	4270	7	NA	2790	1840	1990	>100
Zr	97.2	634	642	664	676	654	3	NA	1110	1180	1140	+19

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 Melter Feed simulant contained 36.92 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

Table 3-5. Elemental Analysis of AY-102/C-106 Melter Feed Vitrified into Glass - WTP Sample Type: HLW-2B - Sample Digestion Method: Sodium Peroxide Fusion in Ni Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Trial 4 (µg/g)	Avg. (µg/g)	RSD (%)	Avg. Spike Recovery (from trials 3,4) (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<34.4	502	477	405	494	470	9	NA	<66.9	<65.2	<66.0	NA
Al	<313	10600	10600	10600	11000	10700	2	NA	22400	22500	22400	-10
B	<124	10100	9980	9930	9760	9940	1	NA	23700	22900	23300	-13
Ba	95.8	407	645	498	525	519	19	NA	1090	1020	1060	+33
Ca	349	1750	1700	1930	2200	1900	12	NA	12400	12200	12300	+20
Cd	<72.2	<54.0	<54.7	<49.8	<63.1	<54.7	NA	NA	<140	<137	<140	NA
Ce	<419	813	892	785	851	829	7	NA	932	974	953	NA
Cr	420	750	1950	1170	1320	1300	38	NA	1790	1310	1550	>100
Cu	<41.3	60.8	89.7	62.6	63.2	69.1	20	NA	<80.3	<78.3	<80.3	NA
Fe	<175	37900	37600	37900	39000	38100	2	NA	102000	101000	102000	+4
K	1960	3540	3500	3690	3890	3650	5	NA	26900	30900	28900	+28
La	<141	401	412	412	434	415	3	NA	<274	283	<283	NA
Li	<72.2	4720	4690	4870	4910	4800	2	NA	16500	16600	16600	+10
Mg	<24.1	413	304	406	410	383	14	NA	5190	5210	5200	0
Mn	<10.3	8310	8270	8310	8520	8350	1	NA	14800	14900	14800	+1
Mo	806	579	2270	1210	1490	1390	50	NA	1670	1630	1650	NA
Na	Not Measured-Na used in fusion reagent											
Ni	Not Measured- Ni crucibles used in fusions											
P	<2580	<1930	<1960	<1780	<2260	<2260	NA	NA	<5020	<4900	<5020	NA
Pb	<1820	2100	3030	2540	2590	2560	NA	NA	<3540	<3450	<3540	NA
S	<763	<570	<578	<526	<667	<667	NA	NA	<1490	<1450	<1490	NA
Sb	1670	1170	5450	2840	3330	3200	55	NA	4260	3000	3630	NA
Si	<179	86400	85200	86000	88300	86500	2	NA	231000	233000	2320000	+3
Sn	<1590	<1190	1370	<1100	<1390	<1390	NA	NA	<3100	<3020	<3020	NA
Sr	80.9	652	682	706	775	704	7	NA	2710	2640	2680	>100
Th	67.9	49.7	186	106	103	111	51	NA	175	143	159	NA
Ti	<24.1	<18.0	<18.2	<16.6	<21.0	<21.0	NA	NA	7050	7070	7060	+2
Tl	375	318	647	439	494	474	29	NA	1100	788	944	NA
U	259	199	207	189	200	199	4	NA	679	478	578	NA
Y	<344	<257	<260	1.93 mg/L or 96 % recovery	1.93 mg/L or 96 % recovery	1.93 mg/L	0	96 %	<669	<652	<669	NA
Zn	1130	3750	6880	4980	5400	5250	25	NA	2790	1840	1990	>100
Zr	97.2	639	782	695	742	714	9	NA	1110	1180	1140	+19

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 Melter Feed simulant contained 36.92 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

Table 3-6. Elemental Analysis of AY-102/C-106 Simulant - WTP Sample Type: HLW-2A - Digestion Method: Cesium Hydroxide in Zr Crucible

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] 1 (µg/g)	Spike[b.] 2 (µg/g)	Spike[b.] Avg. (µg/g)	Spike[b.] recovery (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<18.0	647	682	581	637	8	0.56 mg/L	0.65 mg/L	0.60 mg/L	75 %	267	108	188	NA
Al	<164	17400	17300	17100	17270	1	17400	17300	17350	NA	22900	23000	22950	-8
B	<65.0	<63.1	<61.7	<67.6	<67.6	NA	<63.1	<63.1	<63.1	NA	24800	24500	24650	-8
Ba	<14.4	559	562	555	559	1	559	559	559	NA	830	832	831	+5
Ca	<57.8	2290	2290	2270	2280	1	2260	2300	2280	NA	10300	10500	10400	+2
Cd	<37.9	82.1	77.2	72.1	77.1	6	0.79 mg/L	0.79 mg/L	0.79 mg/L	99 %	<125	<120	<125	NA
Ce	<220	677	700	549	642	13	560	641	600	NA	<727	<697	<727	NA
Cr	<66.8	788	765	752	768	2	744	765	755	NA	516	527	522	-18
Cu	<21.7	130	130	125	128	2	144	137	141	NA	<71.5	<68.5	<71.5	NA
Fe	<92.0	63200	63000	62100	62770	1	63000	63000	63000	NA	96900	96500	96700	0
K	<875	877	862	<911	<911	NA	<850	887	<887	NA	25400	26000	25700	+14
La	<74.0	505	524	486	505	4	446	467	456	NA	<244	263	<263	NA
Li	<37.9	<36.8	<36.0	<39.4	<39.4	NA	<36.8	<36.8	<36.8	NA	14400	14500	14450	-3
Mg	<12.6	598	602	586	595	1	609	607	608	NA	4880	4830	4855	-7
Mn	<5.41	13800	13700	13500	13670	1	13700	13700	13700	NA	14100	14100	14100	-3
Mo	<271	<263	<257	<282	<282	NA	<263	<263	<263	NA	<894	<857	<894	NA
Na	660	16800	16600	16600	16670	1	16600	16500	16550	NA	83700	84500	84100	-1
Ni	<132	2000	2000	1910	1970	3	1980	2000	1990	NA	7960	7800	7880	-5
P	<1,360	<1320	<1290	<1410	<1410	NA	<1320	<1320	<1320	NA	<4480	<4290	<4480	NA
Pb	<955	2780	2770	2750	2770	1	2840	2960	2900	NA	<3150	<3020	<3150	NA
S	<401	<389	<380	<417	<417	NA	0.83 mg/L	0.85 mg/L	0.84 mg/L	105 %	<1320	<1270	<1320	NA
Sb	<103	242	209	281	244	15	0.79 mg/L	0.81 mg/L	0.80 mg/L	100 %	633	513	573	NA
Si	<93.8	18200	18100	17800	18,000	1	18100	18100	18100	NA	226000	224000	225000	0
Sn	<836	<812	<793	<870	<870	NA	<812	<812	<812	NA	<2760	<2640	<2760	NA
Sr	<28.9	911	932	913	919	1	919	927	923	NA	2340	2360	2350	>+100
Th	<32.5	<31.6	<30.8	<33.8	<33.8	NA	0.80	0.80	0.80	100 %	<107	<103	<107	NA
Ti	<12.6	<12.3	<12.0	<13.1	<13.1	NA	<12.3	<12.3	<12.3	<12.3	6940	6930	6935	0
Tl	<186	<181	<176	<193	<193	NA	0.86	0.86	0.86	107 %	<614	<588	<614	NA
U	<90.2	194	225	164	194	16	1.92 mg/L	2.46 mg/L	2.19 mg/L	55 %	<298	<286	<298	NA
Zn	<18.0	144	144	144	144	1	148	146	147	NA	180	200	190	+19
Zr	Not reported-Zr crucibles were used for these fusion digestions													

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

Table 3-7. Elemental Analysis of AY-102/C-106 Simulant - WTP Sample Type: HLW-2A - Digestion Method: CsOH in Nickel Crucible

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] 1 (µg/g)	Spike[b.] 2 (µg/g)	Spike Avg. (µg/g)	Spike Recov. (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<17.2	567	467	373	469	21	0.14 mg/L	0.22 mg/L	0.18 mg/L	23 %	<56.0	<54.0	<54.0	NA
Al	<156	17500	17000	16900	17130	2	17600	17500	17555	NA	23500	22100	22800	-15
B	<61.9	<62.6	<45.7	<49.5	<62.6	NA	<62.6	<62.6	<62.6	NA	26200	24600	25400	-6
Ba	<13.8	585	556	574	572	3	585	596	590	NA	916	855	885	+12
Ca	<55.0	2440	2270	2330	2350	4	2540	2430	2485	NA	10800	10100	10,450	+2
Cd	<36.1	79.5	86.7	82.1	82.8	4	0.79 mg/L	0.79 mg/L	0.79 mg/L	99 %	<118	<113	<118	NA
Ce	<210	580	594	539	571	5	633	686	660	NA	<683	<659	<683	NA
Cr	<63.6	888	894	868	883	2	870	884	877	NA	732	710	721	+13
Cu	<20.6	8010	139	151	2770	164	7920	7880	7900	NA	<67.2	<64.8	<67.2	NA
Fe	<87.7	65500	63300	63000	63900	2	64900	65500	65200	NA	104000	97700	100850	+3
K	<834	897	772	<667	<897	NA	<843	<843	<843	NA	24500	23400	23950	+6
La	<70.5	497	491	490	493	1	500	501	500	NA	<230	<221	<230	NA
Li	<36.1	<36.5	<26.6	<28.9	<36.5	NA	<36.5	<36.5	<36.5	NA	14900	13700	14300	-4
Mg	<12.0	655	624	640	640	2	674	680	677	NA	5340	5050	5195	0
Mn	<5.16	14800	13700	13900	14130	4	14700	14800	14750	NA	15300	14400	14850	+2
Mo	<258	<261	220	222	<261	NA	262	268	263	NA	<840	<810	<810	NA
Na	<373	16600	15800	15900	16100	3	16500	16400	15450	NA	85800	79500	82650	-3
Ni	Not reported: Ni crucible used in digestion													
P	<1290	<1310	999	<1030	<1310	NA	<1310	<1310	<1310	NA	<4210	<4060	<4210	NA
Pb	<909	3140	2800	2890	2940	6	2990	2910	2950	NA	<2960	<2860	<2960	NA
S	<382	<386	570	<305	<570	NA	0.92 mg/L	1.00 mg/L	0.96 mg/L	120 %	<1240	<1200	<1200	NA
Sb	<98.0	275	272	261	269	3	0.77 mg/L	0.82 mg/L	0.79 mg/L	99 %	600	645	622	NA
Si	<89.4	18700	18200	18000	18300	2	18700	18800	18750	NA	239000	229000	234000	+4
Sn	<796	<805	<587	<636	<805	NA	<805	<805	<805	NA	<2590	<2500	<2590	NA
Sr	<27.5	943	887	904	911	3	974	953	963	NA	2340	2190	2265	>100
Th	<30.9	<31.3	<22.8	<24.7	<31.3	NA	0.72 mg/L	0.75 mg/L	0.73 mg/L	91 %	<101	<97.2	<101	NA
Ti	<12.0	<12.2	<8.88	<9.62	<12.2	NA	<12.2	<12.2	<12.2	NA	7150	6710	6930	0
Tl	<177	<179	<131	<142	<179	NA	0.80 mg/L	0.83 mg/L	0.81 mg/L	101 %	<577	<556	<577	NA
U	<85.9	131	121	115	122	7	2.39 mg/L	2.96 mg/L	2.68 mg/L	67 %	<280	<270	<280	NA
Zn	<17.2	204	176	225	202	12	202	208	205	NA	338	297	318	+100
Zr	<24.1	78.6	76.6	60.3	71.8	14	143	144	144	NA	848	821	835	-13

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

Table 3-8. Elemental Analysis of AY-102/C-106 Simulant - WTP Sample Type: HLW-2A - Digestion Method: CsOH/Cs_2CO_3 Fusion in Pt crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] 1 (µg/g)	Spike[b.] 2 (µg/g)	Spike[b.] Avg. (µg/g)	Spike[b.] Recovery (%)	LCS Trial 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<17.2	364	604	899	622	43%	0.48 mg/L	0.40 mg/L	0.44 mg/L	55 %	416	448	432	NA
Al	<156	17100	17300	17300	17,200	1	17000	16900	16950	NA	22700	22600	22650	-9
B	<61.9	<54.7	<57.7	<62.1	<62	NA	<54.7	<54.7	<54.7	NA	25300	25000	25150	-7
Ba	20.8	616	617	626	620	1	610	600	605	NA	914	910	912	+15
Ca	<55.0	2340	2290	2350	2330	1	2400	2380	2390	NA	10500	10300	10400	+2
Cd	<36.1	85.5	69.6	81.8	79.0	10	0.78 mg/L	0.78 mg/L	0.78 mg/L	98 %	<118	<117	<118	NA
Ce	<210	450	543	554	517	11	488	480	484	NA	<685	<680	<685	NA
Cr	<63.6	855	851	874	860	1	854	830	842	NA	640	676	658	+3
Cu	<20.6	127	108	134	123	11	136	134	135	NA	<67.4	<66.9	<67.4	NA
Fe	<87.7	64800	64300	64900	64700	1	64200	63800	64000	NA	99900	99100	99500	+2
K	<834	<737	<778	<836	<836	NA	<737	<737	<737	NA	23000	23600	23300	+3
La	<70.5	496	521	522	513	3	502	495	499	NA	<230	<228	<230	NA
Li	<36.1	<31.9	<33.7	<36.2	<36.2	NA	<31.9	<31.9	<31.9	NA	14200	14000	14100	-5
Mg	<12.0	633	627	651	637	NA	648	643	645	NA	5190	5130	5160	-1
Mn	<5.16	14300	14200	14400	14300	1	14200	14100	14150	NA	14700	14600	14650	0
Mo	<258	<228	<241	<259	<259	NA	<228	<228	<228	NA	<842	<836	<842	NA
Na	<373	16100	16100	16200	16100	1	16200	16100	16100	NA	81600	81100	81350	-5
Ni	<125	1770	1880	1930	1860	4	1720	1750	1735	NA	8230	7640	7935	-4
P	<1290	<1140	1280	<1300	NA	NA	1400	<1140	NA	NA	<4220	<4180	<4220	NA
Pb	<909	2630	2740	2380	2580	7	2810	2520	2665	NA	<2970	<2950	<2970	NA
S	<382	<337	<356	<383	<383	NA	0.92	0.87	0.90	112 %	<1250	<1240	<1240	NA
Sb	<98.0	239	233	249	240	3	0.81 mg/L	0.78 mg/L	0.80 mg/L	100 %	469	502	486	NA
Si	<89.4	17900	17900	18500	18100	2	17800	17600	17700	NA	227000	225000	226000	+1
Sn	<796	<704	<743	<798	<798	NA	<704	<704	<704	NA	<2600	<2580	<2600	NA
Sr	<27.5	945	931	935	937	1	957	956	956	NA	2330	2300	2315	>+100
Th	<30.9	<27.4	<28.9	<31.0	<31.0	NA	0.75 mg/L	0.75 mg/L	0.75 mg/L	93 %	<101	<100	<100	NA
Ti	<12.0	<10.6	<11.2	<12.1	<12.1	NA	<10.6	<10.6	<10.6	NA	7000	6970	6985	+1
Tl	<177	<157	<165	<178	<178	NA	0.85 mg/L	0.84 mg/L	0.84 mg/L	105 %	<578	<574	<574	NA
U	<85.9	132	120	134	129	6	2.79 mg/L	3.16 mg/L	2.98 mg/L	74 %	<281	330	NA	NA
Zn	<17.2	145	134	194	158	20	147	143	145	NA	286	230	258	+61
Zr	<24.1	184	361	433	326	39	297	281	289	NA	1010	1000	1005	+ 5

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. The elemental analysis concentration of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

Table 3-9. Elemental Analysis of AY-102/C-106 Melter Feed as Dried Slurry - WTP Sample Type: HLW-2B - Digestion Method: Cesium Carbonate Fusion in Pt Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Trial 4 (µg/g)	Avg. (µg/g)	RSD (%)	Avg. Spike[b.] Recovery (From Trials 3 and 4) (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<34.4	636	526	732	677	643	14	NA	122	<88.7	<122	NA
Al	<313	10200	10500	10500	10500	10400	1	NA	23600	23600	23600	-6
B	<124	10900	10900	10700	10900	10900	1	NA	23600	23800	23700	-12
Ba	43.6	343	361	346	358	352	3	NA	921	945	933	+18
Ca	<110	1450	1340	1340	1420	1390	4	NA	10200	10100	10200	+4
Cd	<72.2	<53.1	<69.7	<61.9	<61.0	<69.7	NA	NA	<176	<186	<186	NA
Ce	<419	624	736	646	662	667	7	NA	<1020	<1080	<1080	NA
Cr	<66.2	416	382	410	415	406	4	NA	592	673	632	NA
Cu	<41.3	105	111	101	103	105	4	NA	<101	<106	<106	NA
Fe	<14.2	36400	37200	36500	36800	36700	1	NA	99000	99200	99100	+1
K	<1670	2600	2800	2710	2680	2700	3	NA	23300	24800	24000	+6
La	<141	358	397	369	381	376	4	NA	<344	<364	<364	NA
Li	<72.2	4330	4450	4440	4460	4420	1	NA	14700	14700	14700	-1
Mg	<24.1	400	404	389	396	397	2	NA	5100	5170	5140	-1
Mn	<10.3	7920	8110	7950	8030	8000	1	NA	14400	14500	14400	-1
Mo	<306	<293	<228	<263	<259	<293	NA	NA	<748	<791	<791	NA
Na	<746	30300	30800	30400	30600	30500	1	NA	80300	80100	80200	-6
Ni	<99.7	1190	1258	1210	1190	1210	3	NA	8190	8510	8350	-1
P	<2580	<2470	<1920	<2220	<2180	<2470	NA	NA	<6300	<6660	<6660	NA
Pb	<1820	<1700	<1350	1730	<1700	<1700	NA	NA	<4440	<4690	<4690	NA
Sb	<196	191	262	215	250	230	14	NA	534	814	674	NA
Si	<179	78500	84800	83200	84400	82700	4	NA	222000	225000	22400	0
Sn	<1590	<1170	<1530	<1370	<1340	<1530	NA	NA	<3890	<4110	<4110	NA
Sr	<55.0	545	537	519	542	536	2	NA	2100	2140	2120	>100
Ti	<6.32	18.8	15.7	17.5	18.0	17.5	8	NA	6980	7000	6990	+1
Y	<344	<253	<331	1.94 mg/L (97 % spike recovery)	1.94 mg/L (97 % spike recovery)	1.94	0	97 %	<839	<887	<887	NA
Zn	<34.4	2961	3042	2960	2990	2990	1	NA	199	210	204	+28
Zr	<18.3	492	531	515	514	513	3	NA	864	889	876	-9

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 Melter Feed simulant contained 36.92 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

Table 3-10. Elemental Analysis of AY-102/C-106 Melter Feed Vitrified into Glass - WTP Sample Type: HLW-2B - Digestion Method: Cesium Carbonate Fusion in Pt Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Trial 4 (µg/g)	Trial 5 (µg/g)	Avg. of Trials 1-5 (µg/g)	RSD (%)	Avg. Spike[b.] Recovery (From Trials 4 and 5) (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<19.8	528	499	543	600	596	553	8	NA	125	<57.7	<57.7	NA
Al	<180	11200	11300	11300	11100	11100	11200	1	NA	23700	23900	23800	-5
B	<71.3	10700	11100	10600	10800	11100	10900	2	NA	24700	24600	24600	-8
Ba	35.2	369	381	371	364	358	369	2	NA	928	946	937	
Ca	<63.4	1380	1390	1400	1360	1370	1380	1	NA	10500	10500	10500	+3
Cd	<41.6	46.8	49.8	46.1	45.0	44.6	46.5	4	NA	<115	<121	<121	<121
Ce	<242	614	720	648	589	578	630	9	NA	<666	<703	<703	NA
Cr	<38.1	429	430	423	451	433	433	2	NA	679	578	628	-2
Cu	<23.8	91.1	94.3	92.8	90.6	87.8	91.3	3	NA	67.1	<69.2	<69.2	NA
Fe	<8.20	37100	37400	37000	36900	36700	37100	1	NA	99900	100000	100000	+2
K	1020	3250	3580	3010	3270	2660	3150	11	NA	25500	25400	25400	+13
La	<81.2	359	390	372	357	354	366	4	NA	<224	<236	<236	NA
Li	<41.6	4520	4550	4580	4450	4480	4520	1	NA	15100	15200	15200	+2
Mg	<13.9	418	416	429	408	412	417	2	NA	5200	5260	5240	+1
Mn	<5.94	8120	8190	8200	8040	8040	8120	1	NA	14600	14700	14600	0
Mo	<177	<161	<202	<170	<177	<141	<202	NA	NA	<486	<514	<514	NA
Na	524	32400	33100	32400	31900	31700	32300	2	NA	85500	85600	85600	1
Ni	<57.4	1160	1190	1210	1210	1180	1190	2	NA	8330	8400	8360	1
P	<1490	<1360	<1700	<1430	<1490	<1190	<1490	NA	NA	<4100	<4330	<4330	NA
Pb	<1050	<958	<1200	<1010	<1050	<839	<1050	NA	NA	<2890	<3050	<3050	NA
Sb	<113	226	287	249	224	182	234	16	NA	581	709	645	NA
Si	<103	85400	85900	85900	83900	83900	85000	1	NA	230000	232000	231000	+3
Sn	<917	<839	<1050	<881	<918	<734	<1050	NA	NA	<2530	<2670	<2670	NA
Sr	<31.7	532	531	541	531	535	534	1	NA	2130	2150	2140	>100
Ti	<3.64	19.1	20.0	18.4	18.3	18.9	18.9	4	NA	7020	7070	7040	+2
Y	<198	<181	<227	<190	2.50 mg/L or 98 %	2.52 mg/L or 98 %	2.51 mg/L	1	98 %	<546	<577	<577	NA
Zn	<19.8	3090	3130	3090	3030	3030	3070	1	NA	220	211	215	+34
Zr	<10.5	530	530	539	494	501	516	4	NA	904	928	916	-5

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 Melter Feed simulant contained 36.92 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.56 mg/L.

Table 3-11. Elemental Analysis of AY-102/C-106 Simulant - WTP Sample Type: HLW-2A - Digestion Method: KOH Fusion in Zr crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] 1 (µg/g)	Spike[b.] 2 (µg/g)	Spike[b.] Avg. (µg/g)	Spike[b.] Recovery (µg/g)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<18.0	529	742	578	616	18	0.27 mg/L	0.19 mg/L	0.23 mg/L	29 %	214	204	209	NA
Al	<164	16700	16800	17000	16800	1	16700	16700	16700	NA	22400	22500	22450	-10
B	<65.0	<59.7	<69.2	<60.6	<69.2	NA	<59.7	<59.7	<59.7	NA	23800	23700	23750	-13
Ba	<14.4	375	341	338	351	6	445	449	447	NA	808	921	864	+9
Ca	<57.8	2180	2220	2240	2213	1	2260	2220	2240	NA	10100	10100	10100	-1
Cd	<37.9	54.8	65.3	53.3	57.8	11	0.82	0.79	0.81	101 %	<124	<120	<124	NA
Ce	<220	668	674	632	658	3	775	807	791	NA	<723	<695	<723	NA
Cr	<66.8	802	840	829	824	2	804	852	828	NA	657	703	680	+6
Cu	<21.7	140	135	140	138	2	143	144	144	NA	<71.1	<68.4	<71.1	NA
Fe	<92.0	61700	62700	63100	62500	1	61900	62200	62050	NA	97100	97200	97150	-1
K	K not reported-K salt used in fusion digestion													
La	<74.0	244	205	174	208	17	352	353	353	NA	<243	<234	<243	NA
Li	<37.9	<34.8	<40.4	<35.4	<40.4	NA	<34.8	<34.8	<34.8	NA	13500	13700	13600	-9
Mg	<12.6	607	615	622	615	1	625	619	622	NA	4960	4970	4960	-5
Mn	<5.41	13600	13800	13900	13800	1	13600	13700	13600	NA	14300	14300	14300	-2
Mo	<271	<249	<288	<253	<288	NA	<249	<249	<249	NA	<888	<855	<888	NA
Na	465	15400	15700	15900	15670	2	15800	15700	15750	NA	79500	80000	79750	-6
Ni	<132	1960	1970	1970	1970	1	1950	1970	1960	NA	8170	8060	8120	-2
P	<1360	<1250	<1440	<1260	<1440	NA	<1250	<1250	<1250	NA	<4450	<4280	<4450	NA
Pb	<955	2850	2710	2850	2800	1	2770	2770	2770	NA	<3130	<3010	<3130	NA
S	<401	<368	<427	<374	<427	NA	0.92 mg/L	0.86 mg/L	0.89 mg/L	111 %	<1310	<1260	<1310	NA
Sb	<103	248	257	244	250	3	0.77 mg/L	0.78 mg/L	0.78 mg/L	98 %	477	540	508	NA
Si	<93.8	17400	17800	17900	17600	2	17500	17600	17600	NA	219000	221000	220000	-2
Sn	<836	<768	<890	<780	<890	NA	<768	<768	<768	NA	<2740	<2640	<2740	NA
Sr	<28.9	804	799	800	801	1	856	850	853	NA	2300	2260	2280	>+100
Th	<32.5	<29.8	<34.6	<30.3	<34.6	NA	0.73 mg/L	0.75 mg/L	0.74 mg/L	93 %	<107	<103	<107	NA
Ti	<12.6	<11.6	<13.5	<11.8	<13.5	NA	<11.6	<11.6	<11.6	NA	6840	6830	6840	-1
Tl	<186	<171	<198	<173	<198	NA	0.82 mg/L	0.82 mg/L	0.82 mg/L	103 %	<610	<587	<610	NA
U	<90.2	<82.9	124	<84	<124	NA	3.61 mg/L	3.60 mg/L	3.60 mg/L	90 %	<296	<285	<296	NA
Zn	<18	139	144	144	142	3	148	144	146	NA	194	221	208	NA
Zr	Not reported-Zr crucibles were used for these fusion digestions													

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. The elemental analysis concentration of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

Table 3-12. Elemental Analysis of AZ-101 Simulant - Type of WTP Waste: HLW-2A - Digestion Method: KOH Fusion in Zirconium Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Avg. Spike[b] Rec. (From Trials 1- 3) (%)	LCS Trial 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<14.5	48.9	48.2	45.5	47.5	4	NA	282	173	228	NA
Al	<132	23000	23300	24400	23600	3	NA	23900	23800	23800	-5
B	<52.1	<47.7	<47.5	<41.4	<47.5	NA	NA	24200	24000	24100	-12
Ba	<11.6	343	282	316	314	10	NA	810	784	797	+1
Ca	<46.3	1870	1820	1800	1830	2	NA	10400	10500	10400	+2
Cd	<30.4	3000	2910	2960	2960	2	NA	<138	<135	<138	NA
Ce	178	687	662	691	680	2	NA	1410	1120	1260	NA
Cr	<27.9	596	586	604	595	2	NA	519	375	447	-30
Cu	<17.4	142	138	139	140	2	NA	<78.6	<77.3	<78.6	NA
Fe	<6.00	56600	55600	55700	56000	1	NA	102000	101000	102000	+4
K	Not Measured-K used in fusion reagents										
La	64.4	972	828	858	886	9	NA	390	337	363	NA
Li	52.4	51.6	52.5	55.0	NA- blank values	NA	NA	15700	15500	15600	+5
Mg	<10.1	393	380	389	387	2	NA	5170	5110	5140	-1
Mn	<4.34	1500	1470	1480	1480	1	NA	14700	14500	14600	0
Mo	<129	241	212	205	219	9	NA	587	601	594	NA
Na	748	10900	10500	10600	10700	2	NA	86600	82600	84600	-1
Ni	<42.0	2710	2500	2470	2560	5	NA	8680	8000	8340	+1
P	<1090	<996	<992	<864	<996	NA	NA	<4920	<4840	<4920	0
Pb	<766	<701	<699	<609	<701	NA	NA	<3460	<3410	<3460	NA
Sb	<82.5	314	298	309	307	3	NA	781	643	712	NA
Si	<75.3	3650	3550	3630	3620	2	NA	231000	227000	22900	+2
Sn	<670	1000	1010	994	1000	1	NA	<3030	<2980	<3030	NA
Sr	<23.2	907	807	838	851	6	NA	2130	2140	2140	>100
Ti	<2.66	82.7	77.8	79.9	80.1	3	NA	6930	6880	6900	0
Y	<145	1.25 mg/L or 31 % recovery	1.39 mg/L or 35 % recovery	1.18 mg/L or 30 % recovery	1.27 mg/L or 32 % recovery	8	32 %	<655	<644	<655	NA
Zn	<14.5	81.4	76.3	80.8	79.5	3.5	NA	111	104	108	-33
Zr	Not Measured-Zr crucibles used										

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AZ-101 simulant contained 20.23 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 4.0 mg/L.

Table 3-13. Elemental Analysis of AY-102/C-106 Melter Feed Vitrified into Glass - WTP Sample Type: HLW-2B - Sample Digestion Method: Potassium Carbonate Fusion in Pt Crucibles

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. of Trials 1-3 (µg/g)	RSD (%)	Avg. Spike[b.] Recovery (From Trials 1-3) (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<26.8	443	397	472	437	9	NA	<56	<54	<56	NA
Al	<244	11100	11000	11000	11000	1	NA	25200	24500	24900	0
B	<96.5	10800	10800	10800	10800	0	NA	25800	25300	25600	-5
Ba	<21.5	332	332	337	334	1	NA	901	891	896	+13
Ca	<85.8	1320	1280	1310	1300	2	NA	10600	10200	10400	+2
Cd	<56.3	<42.3	<63.0	<48.2	<63.0	NA	NA	<118	<115	<118	NA
Ce	<327	666	783	755	735	8	NA	<684	<667	<684	NA
Cr	<51.6	411	406	380	399	4	NA	641	417	529	-17
Cu	<32.2	86.4	91.0	93.4	90.3	4	NA	<67	<65	<66	NA
Fe	<11.1	36300	35300	36000	35900	1	NA	101100	96900	99000	+2
K	Not Measured-K used in fusion reagent										
La	<110	382	395	399	392	2	NA	<230	<224	<230	NA
Li	78.0	4560	4400	4550	4500	2	NA	15900	15400	15600	+5
Mg	<18.8	402	382	396	393	3	NA	5200	5040	5120	-2
Mn	<8.04	7900	7830	7860	7860	1	NA	15100	14700	14900	+2
Mo	<239	<180	<267	<205	<267	NA	NA	<500	<488	<500	NA
Na	<582	29000	29100	29000	29000	1	NA	82400	79200	80800	-5
Ni	<77.8	1090	565	929	861	31	NA	5750	4830	5290	-36
P	<2010	<1510	<2250	<1720	<2250	NA	NA	<4200	<4110	<4200	NA
Pb	<1420	1520	<1590	1610	<1610	NA	NA	<2970	<2890	<2970	NA
Sb	<153	242	260	297	266	11	NA	<320	1070	<1070	NA
Si	<139	82000	81300	82400	81900	1	NA	230000	228000	229000	+2
Sn	<1240	<933	<1390	<1060	<1390	NA	NA	<2600	<2530	<2600	NA
Sr	<42.9	543	514	533	530	3	NA	2140	2060	2100	>100
Ti	<4.93	18.9	20.1	18.8	19.3	4	NA	7340	7080	7210	+4
Y	<268	1.93 mg/L or 96 % recovery	1.92 mg/L or 95 % recovery	1.93 mg/L or 95 % recovery	1.93	1	95 %	<561	<547	<561	NA
Zn	<26.8	2960	2930	2970	2950	1	NA	<56.1	<54.7	<56.1	NA
Zr	<14.2	494	483	504	494	2	NA	798	807	802	-16

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 Melter Feed simulant contained 36.92 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

Table 3-14. Elemental Analysis of AY-102/C-106 Simulant - Type of WTP Waste: HLW-2A - Digestion Method: Warm Acidification with $HNO_3/H_2O_2/HCl$

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] Recovery (From Trial 3) (%)	LCS[c] Trial 1 (µg/g)	LCS[c] Trial 2 (µg/g)	LCS[c] Avg. (µg/g)	Error[c] (%)
Ag	<34.4	438	451	798	562	36	NA	<66.9	<65.2	<66.9	NA
Al	<313	13000	12500	15400	13600	11	NA	24600	24800	24700	-1
B	<124	<109	<141	<124	<141	NA	NA	24800	25000	24900	-7
Ba	<27.5	568	547	619	578	6	NA	1020	955	988	+25
Ca	<110	2460	2390	2590	2480	4	NA	12800	12700	12800	+25
Cd	<72.2	<63.8	<82.5	<72.1	<82.5	NA	NA	<140	<137	<140	NA
Ce	<419	1030	1100	1340	1160	14	NA	1310	1180	1240	NA
Cr	<66.2	762	745	855	787	8	NA	1400	1000	1200	47
Cu	<41.3	140	127	151	139	9	NA	<80.3	<78.3	<80.3	NA
Fe	<14.2	68200	67200	72500	69300	4	NA	10300	10300	10300	+5
K	<1670	<1470	<1900	<1660	<1900	NA	NA	30500	29300	29900	+3
La	<141	649	648	732	676	7	NA	430	418	424	NA
Li	<72.2	<63.8	<82.5	109	<109	NA	NA	17300	17500	17400	+17
Mg	<24.1	644	608	684	645	6	NA	5280	5310	5300	+2
Mn	<10.3	15000	14800	16000	15300	4	NA	15000	15100	15000	+3
Mo	<306	<271	<350	<306	<350	NA	NA	2080	1490	1780	NA
Na	<746	18100	17500	18000	17900	2	NA	NA	NA	NA	NA
Ni	<99.7	2270	2110	2290	2220	4	NA	Ni	NA	NA	NA
P	<2580	<2280	<2950	<2580	<2980		NA	<5020	<4900	NA	NA
Pb	<1820	3000	3140	3400	3180	6	NA	<3540	<3450	NA	NA
Sb	<196	215	263	403	293	33	NA	4530	3210	3870	NA
Si	<179	7180	6750	8480	7470	12	NA	237000	239000	238000	+6
Sn	<1590	<1410	<1820	<1590	<<1820	NA	NA	<3100	<3020	<3100	NA
Sr	<55.0	961	938	975	958	2	NA	2640	2610	2620	>100
Ti	<6.32	<5.58	<7.22	<6.31	<7.22	NA	NA	7100	7170	7140	+3
Y	<344	<304	<393	2.13 mg/L or 107 % recovery	NA	NA	107 %	<669	<652	<652	NA
Zn	<34.4	97.2	80.5	126	101	23	NA	3220	2120	2670	+29
Zr	<18.3	223	235	473	310	45	NA	1020	1190	1100	+15

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

c. The warm mixed-acid method is ineffective on glass matrices. Solutions from sodium peroxide fusions were analyzed.

Table 3-15. Elemental Analysis of AZ-101 Simulant - Digestion Method: Warm Acidification with $HNO_3/H_2O_2/HCl$

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD %	Spike[b] Recovery (From Trial 3) (%)	LCS[c] Tria1 1 (µg/g)	LCS[c] Trial 2 (µg/g)	LCS[c] Avg. (µg/g)	Error[c] (%)
Ag	<34.4	107	103	143	118	19	NA	<66.9	<65.2	<66.9	NA
Al	<313	<285	<333	<304	<333	NA	NA	24600	24800	24700	-1
B	<124	<113	<132	<120	<132	NA	NA	24800	25000	24900	-7
Ba	<27.5	466	463	465	465	1	NA	1020	955	988	+25
Ca	<110	2240	2230	2250	2240	1	NA	12800	12700	12800	+25
Cd	<72.2	3150	3150	3100	3130	1	NA	<140	<137	<140	NA
Ce	<419	1910	1960	1880	1920	2	NA	1310	1180	1240	NA
Cr	<66.2	630	598	585	604	4	NA	1400	1000	1200	47
Cu	<41.3	144	139	144	142	2	NA	<80.3	<78.3	<80.3	NA
Fe	<14.2	57600	57900	56800	57400	1	NA	10300	10300	10300	+5
K	<1670	1690	1920	1620	1740	9	NA	30500	29300	29900	+32
La	<141	1710	1720	1720	1720	1	NA	430	418	424	NA
Li	<72.2	86.0	91.9	74.8	84.2	10	NA	17300	17500	17400	+17
Mg	<24.1	352	340	338	343	2	NA	5280	5310	5300	+2
Mn	<10.3	1560	1550	1550	1550	1	NA	15000	15100	15000	+3
Mo	<306	<279	<327	<297	<327	NA	NA	2080	1490	1780	NA
Na	<746	10900	11000	11000	11000	1	NA	NA	NA	NA	NA
Ni	<99.7	2940	2860	2940	2910	2	NA	NA	NA	NA	NA
P	<2580	<2350	<2750	<2510	<2750	NA	NA	<5020	<4900	NA	NA
Pb	<1820	<1660	<1940	<1760	<1940	NA	NA	<3540	<3450	NA	NA
Sb	<196	302	325	258	295	12	NA	4530	3210	3870	NA
Si	<179	<163	<190	<173	<190	NA	NA	237000	239000	238000	+6
Sn	<1590	<1450	<1700	<1540	<1700	NA	NA	<3100	<3020	<3100	NA
Sr	<55.0	1230	1230	1230	1230	0	NA	2640	2610	2620	>100
Ti	<6.32	51.9	61.6	58.7	57.4	9	NA	7100	7170	7140	+3
Y	<344	<313	<366	2.16 mg/L or 108% spike recovery	NA	NA	108 %	<669	<652	<652	NA
Zn	<34.4	51.6	46.7	44.2	47.5	8	NA	3220	2120	2670	+29
Zr	<18.3	16700	16800	16900	16800	1	NA	1020	1190	1100	+15

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AZ-101 simulant contained 20.23 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

c. The warm mixed-acid method is ineffective on glass matrices. Solutions from sodium peroxide fusions were analyzed.

Table 3-16. Elemental Analysis of AY-102/C-106 Melter Feed - WTP Sample Type: HLW-2B - Digestion Method: Warm Acidification with $HNO_3/H_2O_2/HCl$

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD %	Spike[b.] Recovery (From Trial 3) (%)	LCS[c.] Trial1 1 (µg/g)	LCS[c.] Trial 2 (µg/g)	LCS[c] Avg. (µg/g)	Error[c.] (%)
Ag	<34.4	256	125	180	187	35	NA	<66.9	<65.2	<66.9	NA
Al	<313	7130	7140	7870	7380	6	NA	24600	24800	24700	-1
B	<124	11600	11800	11700	11700	1	NA	24800	25000	24900	-7
Ba	<27.5	316	328	326	323	2	NA	1020	955	988	+25
Ca	<110	1420	1430	1430	1430	1	NA	12800	12700	12800	+25
Cd	<72.2	<62.1	<42.9	<44.7	<62.1	NA	NA	<140	<137	<140	NA
Ce	<419	879	706	716	767	13	NA	1310	1180	1240	NA
Cr	<66.2	351	377	382	370	4	NA	1400	1000	1200	47
Cu	<41.3	77.0	76.0	76.8	76.6	1	NA	<80.3	<78.3	<80.3	NA
Fe	<14.2	38200	38000	38100	38100	1	NA	10300	10300	10300	+5
K	<1670	2490	2150	2280	2300	7	NA	30500	29300	29900	+3
La	<141	448	404	407	420	6	NA	430	418	424	NA
Li	<72.2	4860	4790	4880	4840	1	NA	17300	17500	17400	+17
Mg	<24.1	365	388	388	380	3	NA	5280	5310	5300	+2
Mn	<10.3	8540	8490	8490	8510	1	NA	15000	15100	15000	+3
Mo	<306	<264	223	<190	<264	NA	NA	2080	1490	1780	NA
Na	<746	32300	32300	32200	32300	1	NA	NA	NA	NA	NA
Ni	<99.7	1260	1220	1260	1250	2	NA	NA	NA	NA	NA
P	<2580	<2220	<1530	<1600	<2220	NA	NA	<5020	<4900	NA	NA
Pb	<1820	1740	1760	1920	1810	5	NA	<3540	<3450	NA	NA
Sb	<196	232	193	212	212	9	NA	4530	3210	3870	NA
Si	<179	4590	4780	6250	5210	2	NA	237000	239000	238000	+6
Sn	<1590	<1370	<945	<986	<1370	NA	NA	<3100	<3020	<3100	NA
Sr	<55.0	545	547	553	548	1	NA	2640	2610	2620	>100
Ti	<6.32	<5.43	<3.75	<3.91	<5.43	<5.43	NA	7100	7170	7140	+3
Y	<344	<296	<204	4130	2.13 mg/L or 106 % recovery	NA	106 %	<669	<652	<652	NA
Zn	<34.4	3330	3300	3300	3310	1	NA	3220	2120	2670	+29
Zr	<18.3	277	304	258	280	8	NA	1020	1190	1100	+15

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 Melter Feed simulant contained 36.92 ± 0.05 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentration of spiked Y reported in mg/L to facilitate comparison with the theoretical concentration. Y was spiked into sample before the digestion so that the theoretical concentration was 2.0 mg/L.

c. The warm mixed-acid method is ineffective on glass matrices. Solutions from sodium peroxide fusions were analyzed.

Table 3-17. Elemental Analysis of AY-102/C-106 Simulant - WTP Sample Type:HLW-2A - Digestion Method: HF-HCl with Heating

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b.] 1 (µg/g)	Spike[b.] 2 (µg/g)	Spike[b.] Avg. (µg/g)	Spike[b.] recov. (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error (%)
Ag	<17.2	217	229	178	208	13	< 1	<1	< 1	< 1 %	<53.1	<55.3	<55.3	NA
Al	231	11800	11800	11700	11800	1	33200	33200	33200	NA	22400	21000	21700	-13
B	588	732	559	632	641	14	75100	75000	75050	NA	26200	26200	26200	-3
Ba	<13.8	296	285	255	279	8	264	278	271	NA	770	691	730	-7
Ca	<55.0	2010	1980	1920	1970	2	2300	2320	2310	NA	10800	8330	9560	-6
Cd	<36.1	94.2	93.4	91.4	93.0	2	0.72 mg/L	0.73 mg/L	0.72 mg/L	90 %	<111	<116	<116	NA
Ce	<210	<215	<214	<192	<215	NA	<215	<215	<215	NA	<648	<675	<675	NA
Cr	<63.6	837	833	792	821	3	829	847	838	NA	581	574	577	-10
Cu	<20.6	152	152	151	152	1	152	150	151	NA	<63.7	<66.3	<66.7	NA
Fe	<87.7	65200	65000	64700	65000	1	64000	63900	64000	NA	97900	96900	97400	-1
K	<834	<856	<851	<763	<856	NA	1410	1270	1340	NA	21100	20200	20650	-9
La	<70.5	<72.4	<71.9	<64.5	<72.4	NA	<72.4	<72.4	<72.4	NA	<218	<227	<227	NA
Li	<36.1	<37.1	<36.8	<33.0	<37.1	NA	<37.1	<37.1	<37.1	NA	14700	14400	14400	-4
Mg	<12.0	675	671	674	673	1	754	755	755	NA	5120	5100	5110	-2
Mn	<5.16	14400	14400	14300	14370	1	14000	14000	14000	NA	14300	14200	14200	-2
Mo	<258	<265	<263	<236	<265	NA	<265	<265	<265	NA	<796	<829	<829	NA
Na	660	17300	17100	17000	17130	1	75300	75500	75400	NA	84000	81700	82850	-3
Ni	<125	2110	2090	2100	2100	1	2110	2120	2115	NA	8320	8270	8300	0
P	<1290	<1330	1350	1460	<1460	NA	<1330	<1330	<1330	NA	<3990	<4150	<4150	NA
Pb	<909	2970	2870	2920	2920	2	2970	2970	2970	NA	<2810	<2920	<2920	NA
S	<382	<392	<389	<349	<392	NA	1270	0.79 mg/L	0.79 mg/L	99 %	<1180	<1230	<1230	NA
Sb	<98.0	222	223	202	216	5	0.81 mg/L	0.77 mg/L	0.79 mg/L	99 %	322	343	333	NA
Si	Not measured- uncomplexed high HF matrix results in high Si background signal													
Sn	<796	<817	<812	<728	<817	NA	3490	3510	3500	NA	<2460	<2560	<2560	NA
Sr	<27.5	767	760	736	754	2	866	881	872	NA	2400	1870	2135	>+100
Th	<30.9	<31.8	<31.6	<28.3	<31.8	NA	0.73	0.74	0.74	93 %	<95.6	<99.5	<99.5	NA
Ti	<12.0	<12.4	<12.3	11.2	<11.2	NA	92.9	92.8	92.9	NA	6860	6780	6820	-1
Tl	<177	<182	<181	<162	<182	NA	0.74	0.72	0.73	91 %	<547	<569	<569	NA
U	<85.9	<88.2	<87.7	<78.7	<88.2	NA	3.81	3.71	3.76	94 %	<265	<276	<276	NA
Zn	<17.2	144	144	144	144	0	146	148	147	NA	257	187	222	+39
Zr	122	866	859	858	861	1	1500	1500	1500	NA	1030	1020	1020	-7

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

Table 3-18. Elemental Analysis of AY-102/C-106 Simulant - Type of WTP Waste: HLW-2A - Digestion Method: Aqua Regia

Element[a]	Blank (µg/g)	Trial 1 (µg/g)	Trial 2 (µg/g)	Trial 3 (µg/g)	Avg. (µg/g)	RSD (%)	Spike[b] 1 (µg/g)	Spike[b] 2 (µg/g)	Spike[b] Avg. (µg/g)	Spike[b] Recov. (%)	LCS Tria1 1 (µg/g)	LCS Trial 2 (µg/g)	LCS Avg. (µg/g)	Error %
Ag	<17.2	177	167	182	175	4	0.64 mg/L	0.67 mg/L	0.66 mg/L	83 %	<55.6	<49.6	<55.6	NA
Al	<156	11800	11800	11700	11800	1	11800	11800	11800	NA	22400	21000	21700	-13
B	<61.9	<68.4	<56.0	<63.8	<68.4	NA	<68.4	<68.4	<68.4	NA	25600	24200	24900	-7
Ba	<13.8	564	566	567	566	1	572	570	571	NA	774	730	752	-5
Ca	<55.0	2330	2320	2300	2320	1	2310	2300	2300	NA	10200	9750	9980	-2
Cd	<36.1	89.2	86.7	85.2	87.0	2	0.79 mg/L	0.78 mg/L	0.78 mg/L	98 %	<117	<104	<117	NA
Ce	<210	934	913	925	924	1	992	954	973	NA	<678	<605	<678	NA
Cr	<63.6	833	827	845	835	1	824	841	832	NA	568	658	613	-4
Cu	<20.6	142	144	142	143	1	151	148	150	NA	<66.7	<59.6	<66.7	NA
Fe	<87.7	65300	65100	65100	65200	1	65200	65200	65200	NA	99800	94900	97400	-1
K	<834	<921	<755	<860	<921	NA	<921	<921	<921	NA	20500	19500	20000	-3
La	<70.5	534	543	533	537	NA	543	529	536	NA	<228	<203	<228	NA
Li	<36.1	<39.9	<32.7	<37.2	<39.9	NA	<39.9	<39.9	<39.9	NA	14400	13700	14100	-6
Mg	<12.0	665	671	668	668	1	666	665	666	NA	5210	4970	5090	-2
Mn	<5.16	14500	14400	14500	14500	1	14500	14500	14500	NA	14700	14000	14400	-1
Mo	<258	<285	<233	<266	<266	NA	<285	<285	<285	NA	<833	<744	<833	NA
Na	<373	16200	16200	16000	16100	1	16100	16000	16000	NA	80900	77000	79000	-7
Ni	<125	2170	2140	2150	2150	1	2110	2180	2140	NA	8520	8150	8340	+1
P	<1290	<1430	<1170	<1330	<1430	NA	<1430	<1430	<1430	NA	<4170	<3730	<4170	NA
Pb	<909	2950	2940	3010	2970	NA	2890	3100	3000	NA	<2940	<2630	<2940	NA
S	<382	<422	<346	<394	<422	NA	0.91 mg/L	0.82 mg/L	0.86 mg/L	108 %	<1230	<1100	<1230	NA
Sb	<98.0	225	222	223	223	1	0.78 mg/L	0.74 mg/L	0.76 mg/L	95 %	407	337	372	NA
Si	<89.4	1310	1170	1100	1200	9	1350	1270	1310	NA	3670	3840	3760	>-100
Sn	<796	<879	<721	<821	<879	NA	<879	<879	<879	NA	<2570	<2300	<2570	NA
Sr	<27.5	954	957	943	951	1	950	950	950	NA	2260	2140	2200	>+100
Th	<30.9	<34.2	<28.0	<31.9	<34.2	NA	0.76 mg/L	0.74 mg/L	0.75 mg/L	94 %	<100	<89.3	<100	NA
Ti	<12.0	<13.3	<10.9	<12.4	<13.3	NA	<13.3	<13.3	<13.3	NA	5330	4930	5130	-26
Tl	<177	<196	<160	<183	<196	NA	0.83 mg/L	0.80 mg/L	0.81 mg/L	101 %	<572	<511	<572	NA
U	<85.9	<95.0	85.3	111	<111	NA	3.78 mg/L	3.67 mg/L	3.72 mg/L	93 %	<278	<248	<278	NA
Zn	<17.2	149	144	143	145	2	150	149	150	NA	171	170	170	+6
Zr	<24.1	<26.6	<21.8	<24.8	<24.8	NA	<26.6	<26.6	<26.6	NA	138	112	125	>-100

a. Elemental analysis concentrations of slurry simulant reported on wet slurry basis; The AY-102/C-106 simulant contained 23.59 ± 0.03 % solids on oxide basis after heating at 1100 °C. Elemental analysis concentrations of the LCS glass reported on dry powdered glass basis.

b. Concentrations of spiked elements reported in mg/L to facilitate comparison with the theoretical concentrations. Ag, Cd, S, Sb, Th, and Tl were spiked at 0.8 mg/L of the solutions after digestion; U was spiked at 4.0 mg/L of the solutions after digestion.

3.2 EXPERIMENTAL

3.2.1 General

Liter bottles of simulants were mixed by placing them in a rotator used for the Toxicity Characteristic Leaching Procedure (TCLP) and rotating them at a rate of 30 revolutions per minute overnight. About 75 mL of the freshly-mixed slurry was then transferred by pouring into a wide-mouth 125 ml plastic bottle. Before taking sub-samples for analytical work, the 125-mL bottles were shaken manually for about 30 seconds, but no mixing was done as the 1.5-mL sub-samples were being taken. The excellent analytical precision on both the elemental analyses (Table 3-1 through Table 3-18) and weight % oxide measurements (Table 3-22) attest to sample homogeneity. The sub-samples were removed with a plastic slurry pipette with about 1.5 inches cut off from the bottom to increase the pipette opening. The slurry was transferred to the pre-weighed digestion vessel and the sample weight recorded. All elemental analysis data in this report are on an “as-received” or slurry basis.

3.2.2 Alkali Fusion Digestion Methods

All digestions were performed manually in a fume hood. The first alkali fusion step was to evaporate the free water in the slurry to prevent it from reacting with alkali salts or splattering when placed in the high temperature muffle furnace. A drying oven set at 200 °C was used to evaporate the water. Because of the small sample size, excellent heat transfer properties of the metal crucible, and the high temperature of the drying oven, the water was evaporated from the samples in 15 minutes without splattering. The two HLW-2A simulants were dissolved in this form. The HLW-2B simulant was dissolved both as a dried powder and as a glass wafer. For digestions of glass samples, the HLW-2A simulant was first dried in a platinum crucible and then vitrified at 1100 °C for 30 minutes to form a thin glass wafer. The Cs_2CO_3 and K_2CO_3 fusions were carried out in the same platinum crucible and at the same temperature in which the glass wafers were made. For the Na_2O_2 fusion of glass wafers, which is incompatible with platinum ware, the glass wafers were transferred to a nickel crucible and the fusion carried out at 750 °C.

The ratio of alkali flux reagent to dry sample was approximately 10:1 for all types of fluxes. The recipes for the typical 5 g of alkali flux used were:

- Na_2O_2 only- 5 g Na_2O_2
- Na_2O_2/NaOH- 3.5 g Na_2O_2/1.5 g NaOH
- CsOH only- 5 g CsOH (commercial CsOH is available as the monohydrate $CsOH\cdot H_2O$)
- Cs_2CO_3/CsOH- Dissolve 0.5 g CsOH in 2 mL water, add to slurry sample and dry; add 5 g Cs_2CO_3 to the dry sample/CsOH residue
- Cs_2CO_3 only-5 g Cs_2CO_3
- KOH/KNO_3-4.8 g KOH/0.2 g KNO_3 -both as powders

A muffle furnace was used to perform all fusion digestions. The furnace was heated to the desired temperature and the heating time was measured from the time that the furnace re-equilibrated to the pre-set temperature. Ten minutes of flux time was used for all fusions.

After removal from the furnace, crucibles were placed on clean Kevlar boards to cool. The crucibles were then dropped into either 500 mL or 1000 mL wide-mouth bottles that had been pre-charged with a known volume of water/ 30 % hydrogen peroxide mixture to dissolve the alkali salts and to liberate the flux residue from the crucible bottom. A solution of 1.6 M HNO_3 was then added to dissolve metal hydroxides. Dropping the entire crucible into a wide-mouth bottle is a simple technique that reduces the possibility of splattering or spilling the sample which can occur when water is added to the crucible followed by transfer of the slurry to a volumetric flask. This technique also has convenience and speed advantages since the water/hydrogen peroxide mixture and acid solutions can be accurately pre-measured outside the shielded cells to yield a final known volume by simply pouring the pre-measured reagents into the large bottle. Since the outside of the crucible comes into contact with the analytical solution, a modicum of care must be taken to keep the surfaces that the crucibles touch clean. We brushed the crucible bottom across a clean cloth to remove any fibers that might be introduced from the muffle furnace floor or Kevlar pad before dropping the crucibles into the wide-mouth bottle. We also had spare ceramic floors to the muffle furnace (the cost of these is about $25 for the model furnace that we used) in case a crucible was spilled inside the muffle furnace. The use of a rack to hold the crucibles during transfer into and out of the muffle furnace minimizes the spill potential and also helps keep the outside of the crucible clean.

A rate-limiting step in the work-up of alkali fusion digestions is the dissolution of the alkali salts/metal hydroxide pellet that forms in the crucible bottom after the flux cools. Although the alkali residue would dissolve faster if acid were used initially to dissolve the residue, in some conditions we have observed SiO_2 precipitate irreversibly from strong acid solutions and yield Si determinations that are biased low. The solution can be rapidly heated to speed dissolution by chemical decomposition of H_2O_2 in the strongly alkaline solution. We normally add 2-3 drops of H_2O_2 as a chemical oxidant, but by adding as much as 5 mL of H_2O_2, the solution will warm rapidly to help dissolve the alkali (which in turn warms the solution as it dissolves). This technique reduces the time needed to dissolve the alkali residue and eliminates the need to vigorously agitate the bottle to promote alkali dissolution.

Completely clear digestions were accomplished only by the sodium peroxide fusion (for both the HLW-2A and HLW-2B matrices) and by the cesium carbonate fusions (on the HLW-2B matrix, as both a dry powder and after vitrifying into glass wafers). HNO_3 was effective for both the sodium peroxide method and the cesium carbonate method. Although nitric acid was initially used for the cesium hydroxide and potassium hydroxide fusions, considerable residual solids were observed and the digestions were repeated using hydrochloric acid. Fewer solids were observed when HCl was used, but completely clear solutions were not immediately obtained by either the cesium hydroxide fusion or the potassium hydroxide fusion on the HLW-2A matrix. The amount of residual solids lessened upon sitting in the acid solution, but since speed was of the essence, we could not afford the luxury of waiting for dissolution of the more refractory sludge particles. A few drops of 30 % H_2O_2 were usually needed after the acid addition to create a clear solution from the sodium peroxide fusions (the H_2O_2 decomposes so rapidly in caustic that it is usually depleted before the acid addition, necessitating, in these cases, addition of 2-4 drops as a chemical oxidant).

The initial dilution volume after the alkali fusion digestions was either 500 mL or 525 mL. The initial dilution was diluted 5-10 fold with de-ionized water to reduce the dissolved solids content and to reduce the concentration of the major elements to near the concentration range of ICP-AES calibration standards.

The detailed procedure for sodium peroxide fusion method in nickel crucibles is shown in Table 3-19. The other alkali fusion methods are outlined in Table 2-1.

3.2.3 Mixed-Acid Digestion Methods

The externally heated mixed-acid methods, the HF-HCl method and the HCl-HNO_3 (aqua regia) method, were carried out in CEM Corporation 120 PFA Teflon Microwave Vessels with Cap Relief Valve, Part Number-CEM 221001. These vessels are designed for use in a microwave oven but can be used in a conventional heating oven if the temperatures are moderate. A CEM Corporation capping station was used to tighten the caps to the prescribed torque after the vessels were charged with sample and acids. After heating and diluting the solutions to 500 mL, considerable white solids were left from both digestions. The solutions were filtered through a 0.45 micron porosity filter and serially diluted 5-10 fold with de-ionized water before ICP-AES analysis.

The warm mixed-acid method was carried out in 500 mL wide-mouth bottles. The slurry sample was weighed in 30 mL wide-mouth Nalgene™ plastic bottles and then the entire bottle was dropped into the 500 mL wide-mouth bottle. This technique was used rather than weighing the slurry directly into the 500 mL bottles because it is anticipated that this technique will be more convenient to perform remotely. Sequential addition of concentrated HNO_3 and H_2O_2 to the slurry resulted in a warm, frothy solution from the chemical decomposition of H_2O_2 in acid solution coupled with heat of dissolution/neutralization of the caustic sample. Addition of HCl to the warm solution helped to dissolve sludge particles, but white solids remained. After diluting the solution to a final volume of 500 mL, the solution was filtered through a 0.45 micron porosity filter to clarify the solution prior to ICP-AES analysis. For these samples, a 5-fold serial dilution was performed. For the Phase II Time-and-Motion study, a single dilution to 1000 mL will performed to save time by obviating the need for a serial dilution to measure Na and Ni. The procedure discussed in Table 3.20 specifies a final dilution to 1000 mL for this reason.

The detailed procedure for the Warm Acid Method is shown in Table 3-20. The other mixed acids methods are outlined in Table 2-1.

Table 3-19. Procedure for Sodium Peroxide Fusion Method

Step #	Description
1	Preheat the cell drying oven to 200 °C and the muffle furnace to 750 °C.
2	Transfer 1-1.5 mL of slurry into pre-weighed 50 mL Ni crucible. Repeat for all 8 samples and carry these samples through the fusion procedure. Comment: A slurry pipette with about 1.5 inches cut off the bottom to increase the opening is used to transfer the sample. It is important that the slurry sample be deposited on the bottom of the crucible. If sample is deposited high on the crucible sides, the molten Na_2O_2 may not come into contact with the sample and incomplete digestion of some compounds may result. If necessary, guides made from plastic funnels with some of the stem cut off can be used to help deposit the sample on the crucible bottom.
3	Record the sample weight in the data sheet or notebook.
4	Place the crucibles in the drying oven, close the door, and heat for 15 minutes. Comment: The water should be evaporated from the sample in this time.
5	Remove the crucibles and add 5 grams of granular Na_2O_2 on top of the dry sludge. Comment: It is unnecessary to intimately mix the dry powder with Na_2O_2 which is very aggressive and attacks chunks of dried powder.
6	Place the crucibles in the furnace. Heat for 10 minutes after the furnace temp re-equilibrates to 750 °C. The Na_2O_2 should melt and create a black molten pool.
7	Remove crucibles from furnace and let cool for 10 minutes on a clean Kevlar board or similar nonflammable material.
8	Drop the entire crucible into the wide-mouth 1000 mL bottle that has been pre-charged with a solution of 245 mL of de-ionized water and 5 mL of 30 % hydrogen peroxide. If the crucible does not situate itself on its side, gently rock the wide-mouth bottle until the crucible is on its side to facilitate contact with the H_2O/H_2O_2 solution. Comment: One of the rate-limiting steps of the sodium peroxide fusions is the dissolution of the alkali flux residue. The rapid decomposition of the H_2O_2 in caustic solution creates a warm, frothy solution that hastens the dissolution of the alkali flux. Mix briefly by swirling and let stand for 5 minutes. The inside of the Ni crucible bottoms should be clean at this point, although it is impossible to confirm this without removing the crucible. Repeated checks with non-radioactive simulants showed in every case that the Ni crucible bottom was clean and that the entire flux material had been released to the caustic solution after 5 minutes.

Table 3-19. Procedure for Sodium Peroxide Fusion Method - continued

Step #	Description
9	Slowly add 250 mL of 1.6 M HNO_3 (25 mL of concentrated HNO_3 diluted to 250 mL in a plastic volumetric flask) to create final volume of 500 mL. Cap the bottle and swirl to mix, then uncap the bottle. Comment: The solution will either be black or green at this point, depending on whether hydrogen peroxide is still present in the solution. Frequently, the hydrogen peroxide decomposes so quickly in caustic solution that it is depleted and the solution is black in color. To generate the green color from Ni ions, 2-4 drops of 30 % hydrogen peroxide added to the acid solution should be sufficient. Take care not to add excessive hydrogen peroxide as gas evolution from decomposition of hydrogen peroxide in acid solution could pressurize a completely sealed bottle. Although this condition usually results in only a slightly distorted bottle, it can be avoided by minimizing the hydrogen peroxide. Sodium peroxide fusions should be ready for serial dilutions within 5 minutes after acid addition.
10	Serially dilute with DI water prior to ICP-AES analysis. Comment: A 5-fold or 10-fold dilution is suitable for subsequent ICP-AES analysis. The 1000 mL wide-mouth bottle can be rinsed with de-ionized water, allowed to dry, and re-used indefinitely to minimize cell waste. The 250 mL portions of de-ionized water and 1.6 M HNO_3 can also be prepared easily in the cells to minimize cell waste and the need for introducing reagents into the cells.

Table 3-20. Warm Mixed-Acid Method

Step #	Description
1	Transfer 1-1.5 mL of slurry into a pre-weighed or tared 30 mL wide-mouth plastic bottle. Repeat for all 8 samples and carry these samples plus standards and blanks through the entire digestion procedure. Comment: A plastic transfer pipette with about 1.5 inches cut off the bottom to increase the opening is used to transfer the sample. The sample is weighed into a smaller bottle for cell operator convenience (easier to move a small bottle to the cell balance pan than the 1000 mL bottle).
2	Record sample weight in data sheet or notebook.
3	Drop the 30 mL plastic bottle into a 1000 mL wide-mouth plastic bottle. Comment: The large bottle virtually eliminates sample loss through splattering. The 1000 mL bottle is used so that a large initial dilution can eliminate the need for serial dilutions, a time-consuming step when performed remotely.
4	Add 15 mL con. HNO_3. Swirl the 1000 mL bottle to get the acid in contact with the sample. Add 5 mL 30 % H_2O_2. The solution rapidly becomes warm and frothy from the acid decomposition of H_2O_2 together with heat of decomposition/neutralization of the highly caustic sample mixed with strong acid. Let the reaction proceed about 2 minutes before adding the concentrated HCl in the next step. Comment: The large amount of H_2O_2 is added not for the usual reason of being a strong oxidizing reagent. Rather, the decomposition of H_2O_2 in strong acid solution in the presence of the sample provides rapid chemical warming of the acid mixture and makes the HCl strike in the next step more effective. An external heating source for higher temperatures and more prolonged heating can be substituted for this technique should subsequent measurements show that the technique does not fully dissolve Na and Ni in actual Hanford waste tank samples. All reagent volumes are accurately pre-measured in the laboratory and then transferred to the cells to minimize cell operations and analytical time.
5	Add 5 mL con. HCl to the warm nitric/hydrogen peroxide solution. Swirl each bottle for 10-15 seconds to promote mixing. Let stand for 5 minutes. Comment: Additional heat evolution will rapidly occur if peroxide is still present in the solution. Most if not all of the iron-containing sludge particles will dissolve with this method. Since SiO_2 is present in all samples, complete digestion of the sample is impossible with this acid mixture and must be removed by filtration to avoid plugging the ICP nebulizer. The addition of HCl may unnecessary to measure Na and Ni, but it does dissolve more of the sample and lessens the chances that analytes are sequestered in solid particles. It is possible that reliable Na and Ni measurements can be obtained with less HCl, or perhaps no HCl at all, to minimize cell corrosion from HCl attack on metal surfaces.
6	Add 975 mL de-ionized water to create a final volume of 1000 mL. Comment: A large dilution at this step encourages dissolution of Na salts and reduces the Na concentration for convenient ICP-AES measurements with typical calibration protocols without a serial dilution step.
7	Cap the 1000 mL bottle and shake for 15 seconds to mix. Let stand 5 minutes before filtration.
8	Filter about 20 mL of the solution to remove remaining solids before ICP-AES analysis. Comment: A convenient filtration system is a 10 mL plastic disposable syringe with the plunger removed and fitted with a 0.45 micron or 0.70 micron porosity filter disk. The solutions can be filtered quickly with a gravity feed, although a vacuum box such as the Speedmate™ system may also be considered for use. Using the syringe plunger to push the solution through the filter is too inconvenient for shielded cell use.

3.2.4 ICP-AES Experimental

All ICP-AES determinations were performed using a JY 170 C ICP-AES spectrometer with a 1-meter focal length monochromator and a 0.5-meter focal length polychromator. A 3-point calibration protocol was used based on analyzing a blank solution, a 5.00 mg/L concentration solution of elements, and a 10.00 mg/L concentration solution for most elements. QC check standards were analyzed after sample analysis. The closing QC check standards can differ by no more than 10 % from the standard value without a QC flag being issued on the data report. The principal variance from the ± 10 % closing QC criterion in the data in this report was from U, which in some cases differed by 14 % from the initial calibration.

The ICP-AES analytical line wavelengths used for the analysis of the WTP simulants are shown in Table 3-21.

Table 3-21. ICP-AES Wavelengths Used for Elemental Determinations

Element	Wavelength (nm)
Ag	328.068
Al	308.215
B	208.959
Ba	230.424
Ca	393.367
Cd	226.502
Ce	399.924
Cr	205.559
Cu	324.754
Fe	259.940
K Mono	766.490
La	408.672
Li	670.784
Mg	279.553
Mn	257.610
Mo	202.032
Ni	216.556
P	178.225
Pb	220.353
S Mono	180.676
Sb	206.833
Si	251.611
Sn	189.926
Sr	407.771
Th	283.232
Ti	334.940
Tl	351.924
U Mono	385.958
Y Mono	371.029
Zn	213.856
Zr	349.621

3.2.5 Measurement of Wt. % Oxide of Simulants

All elemental analysis results in this report are on a wet slurry basis. In the WTP, elemental results will be reported on an oxide basis which means that the wt. % oxides will have to be measured concurrently with the digestions and elemental analysis in order to obtain a slurry-to-oxide conversion factor. The wt. % oxides of each of the three simulants tested were measured by first evaporating the water from approximately 1.5 mL of slurry followed by heating the powder to constant weight at 1100 °C in platinum crucibles. The individual wt. % oxide measurements for the AY-102/C-106, AZ-101, and AY-102/C-106 plus glass formers/glass modifiers are shown in Table 3-22. More measurements of the wt. % oxide of the AY-102/C-106 plus glass-formers/glass-modifiers were made because the slurry was vitrified to create glass samples for testing digestion procedures.

Table 3-22. Wt. % Oxides Measurements for WTP Simulants

AY-102/C-106 HLW-2A Simulant (wt. % oxides)[a]	**AZ-101 HLW-2A Simulant (wt. % oxides)[a]**	**AY-102/C-106 + Glass Formers HLW-2B Simulant (wt. % oxides)[a]**
23.56	20.20	36.84
23.56	20.29	38.88
23.63	20.19	36.90
23.60	20.29	36.91
23.58	20.20	37.01
		36.94
		36.96
		36.95
		36.97
		36.89
		36.92
Avg.= 23.59 wt. %	Avg.= 20.23 wt. %	Avg. = 36.92 wt.%
1 σ = 0.03 wt. %	1 σ = 0.05 wt.%	1 σ = 0.05 wt.%

a. Wt. % oxides measured at 1100 °C in platinum crucibles.

3.2.6 Use of Matrix Spikes

Two different matrix spike protocols were used.

3.2.6.1 Use of Spike Solution with Ag, Cs, S, Sb, Th, Tl, and U Added After Digestions

The first protocol was to add a stock solution consisting of Ag, Cd, S, Sb, Th, Tl, and U made from single-element ICP-AES standards to a solution of the dissolved sample (the first replicate digestion was arbitrarily chosen to be spiked). The concentration of the stock solution was 1.0 mg/L for Ag, Cd, S, Sb, Th, and Tl. The concentration of U in the stock solution was 5.0 mg/L. A higher concentration of U was used because it is anticipated that U will be at higher concentrations in the high-level waste. Twenty mL of this stock solution was used to dilute 5 mL of the original digestion solution to create a 5-fold dilution of the original digestion solution, analogous to the 5-fold dilution with de-ionized water performed prior to ICP-AES analyses. The theoretical concentration of the spiked elements in this solution was 0.80 mg/L for Ag, Cd, S, Sb, Th, and Tl and 4.0 mg/L for U. The spike was performed in duplicate and analyzed in sequence with the non-spiked solutions. If the spiked elements had a measurable concentration in the non-spiked solution, the average of these measured concentrations was subtracted from the spiked concentration to yield a net spike concentration from which the percent spike recovery was calculated.

The elements Ag, Cd, S, Sb, Th, Tl, and U were selected for the spike addition primarily because these elements are currently on the list of required WTP elements, but are not in the Analytical Reference Glass-1 standard (see following section). The spike experiment provided a way to assess the chemical compatibility of the elements with the digestion matrix (that is, to check for precipitation problems that would be manifested as low recoveries). From the ICP-AES perspective, the spike experiments help to check for spectral interferences either from the matrix elements on the spiked elements or vice versa. The concentrations of non-spiked elements are shown both with and without the spiked elements present in the data tables. In particular, it was of interest to determine if the 4.0 g/L U (an element with an especially complex emission spectrum) in the analytical solution would spectroscopically affect the other analytes. Since there were no significant differences in the measurements spiked versus non-spiked, the concentration of U is not high enough to create problems in this analytical matrix for measuring the important process control elements

The seven-element spike protocol was used for the first seven sets of digestion methods tested. Table 3-1, Table 3-6, Table 3-7, Table 3-8, Table 3-11, Table 3-17, and Table 3-18 show the elemental concentrations in units of μg/g except for the spiked elements, which are shown in units of mg/L to facilitate the comparison of the measured concentration versus theoretical. The percent recoveries of the spike elements are also shown in the tables.

The percent recovery was good for Cd, S, Sb, Th, and Tl on all seven digestions matrices. U recoveries were, in general, over 75 % but less than expected considering the high solubility of U salts in acid solution. It is possible that the less than quantitative percent recoveries reflect the nature of the relatively weak U analytical line used in ICP-AES measurements rather than precipitation of U. In fact, the closing QC analysis of check standards after sample analysis showed that the variance from the accepted value was a much as 14 %. The Ag recovery was good for the sodium peroxide fusion matrix with HNO_3 uptake (Table 3-1), and poorer for the methods that used HCl. Precipitation of AgCl in the high-chloride matrix of these digestion methods is a reasonable chemical explanation for the poor recoveries of Ag.

3.2.6.2 Use of Spike Solution with Y Added Before Digestions

The second spike protocol used was addition of 1.0 mL of a 10,000 mg/L stock solution of Y to the slurry samples prior to the digestion. After digestions and dilutions, the Y concentration in the solutions analyzed by ICP-AES was between 2.0 and 4.0 mg/L. This protocol was applied to 11 sets of digestions and the results are shown in Table 3-2, Table 3-3, Table 3-4, Table 3-5, Table 3-9, Table 3-10, Table 3-12, Table 3-13, Table 3-14, Table 3-15, and Table 3-16. The percent recovery of Y was excellent for all sample preparation methods except the KOH fusion in Zr crucibles used on the AZ-101 simulant. The reason for the poor Y recovery in this matrix is not known at this time.

Review of the elemental analysis data revealed that the Zr values were always higher for the Y spiked solutions versus non-spiked solutions. Tests with single-element Y standards demonstrated that Y has an approximate 7 % spectral interference bias on the Zr 349.621 nm analytical line. This bias was mathematically corrected by measuring the Y concentration in the spike solution and subtracting the Zr signal resulting from Y spectral interference.

3.2.6.3 Appraisal of Spikes for Digestions/ICP-AES Elemental Analysis

The use of spikes to measure analytical reliability is effective in many applications. However, in the opinion of the principal investigator, spikes used in digestions/ICP-AES elemental analysis do not have enough technical merit to justify the effort involved with performing them as part of the routine analytical protocol in the WTP. Adding soluble species to high-level waste solids obviously does not measure the effectiveness of digestions of the solid material in the waste. Spike recoveries of soluble elements could be excellent, whereas the analysis of the actual material in the waste tank could be low due to incomplete digestion. In this case, the spike recovery experiment would give a false reading of the data quality. Another factor against using matrix spikes is that it would add a tedious and time-consuming step for shielded cell operators.

The WTP sample compositions will be reasonably stable for months at a time as particular sludge tanks are processed. Given this and the fact that as many as 8 replicate analyses will be made on each sample to measure analytical quality, there seems little to be gained by adding matrix spikes to the analytical protocol.

3.2.7 Use of Laboratory Control Standard (LCS)

The laboratory control standard (LCS) used was the Analytical Reference Glass-1 (ARG-1) [9]. The elemental composition of ARG-1 glass standard, excluding oxygen, is shown in Table 3-23. The ARG-1 glass was characterized both through a commercial laboratory specializing in glass analyses, the Corning Engineering Laboratory Services (CELS), and through an analytical round robin involving seven laboratories. Very slight differences in elemental analyses were observed between the CELS and the composite results from the laboratories participating in the round robin. In general, the CELS values were slightly higher than the composite results. Since the CELS results were considerably more precise than the composite results, and since the CELS results yield a sum of oxides at 100.07 % versus the composite sum of oxides at 99.48 %, SRNL has historically used the CELS values as the standard values.

Table 3-23. Elemental Composition of ARG-1 Reference Glass

Element	% Element in Glass
Al	2.50
B	2.69
Ba	0.08
Ca	1.02
Cr	0.06
Cu	0.003
Fe	9.79
K	2.26
Li	1.49
Mg	0.52
Mn	1.46
Na	8.52
Ni	0.827
P	0.11
Si	22.4
Sr	0.003
Ti	0.69
Zn	0.016
Zr	0.096

The ARG-1 glass was dissolved in duplicate and analyzed concurrently with the WTP simulants. The average of the duplicate analyses was compared with standard value and a percent error assigned from the difference between the measured and standard elemental analysis value, and a sign to the error depending on whether the LCS elemental analysis was less or more than the standard value. The duplicate LCS analyses, the average of the duplicate analyses, and the error percentages are shown in the last four columns of Table 3-1 through Table 3-18.

LCS analyses in these tests were similar to the SRNL historical experiences with dissolving the ARG-1 glass with various techniques and analyzing the solutions with ICP-AES techniques. Al and B values are almost always biased low versus the standard value, even when the digestion is successful and no solids remain after digestion. The mechanism for this bias is not known, but the magnitude of the bias is low enough that it is of little practical consequence for most applications.

Sr determinations in the ARG-1 glass standard were biased significantly higher than the 30 µg/g that would be expected based on the standard value of approximately 0.003 wt. %. Sr determinations averaged about 2400 µg/g, or almost 100 times the expected value. Spectral interference checks showed that Ca produces about 5 % interference on the Sr 407.771 nm analytical line used at SRNL. Since ARG-1 contains about 10,200 ug/g Ca, this level of Ca interference produces a Sr signal of about 500 ug/g, which obviously precludes accurate determinations of Sr in ARG-1 glass standard, but does not explain the source of the additional 5-fold high bias. The Sr concentration in ARG-1 glass is so low that is of little practical use except as an indicator that low levels of Sr could not be measured accurately without spectroscopic experiments to determine a more appropriate analytical line for this matrix.

The Zn values were biased high as well, though not as severely biased as the Sr values. Analyses of single-element ICP-AES standards to determine the source and magnitude of the spectral interference have not yet pinpointed the source of error. As with Sr determinations, the Zn concentration in ARG-1 glass standard is too low to indicate digestion/ICP-AES analytical quality.

Determinations of the remaining LCS elements were either good or predictably poor as a function of the adequacy of the method to dissolve glass. For example, the hot aqua regia digestion method data (Table 3-18) shows the expected poor results for Si since aqua regia will dissolve little Si in glass. Hot aqua regia does with time leach out most of the components in the fine powder form of the glass. Accurate determinations of the soluble elements are possible despite the fact that large amounts of solid SiO_2 remain after the leach.

The glass form of the LCS is completely inappropriate for the warm acidification method (Table 3-16) used to measure the Na and Ni not obtainable from sodium peroxide fusions carried out in Ni crucibles. To provide at least a QC check on the ICP-AES analyses, the solutions from the sodium peroxide fusion in nickel crucibles were analyzed concurrently with the solutions from the warm acidification of the slurry simulant.

3.2.7.1 Appraisal of LCS Use for Quality Checks

Concurrent analysis of a matrix standard is an important element of the QC protocol. Accurate analysis of matrix standards requires that all operations be done properly, including accurate handling and weighing of the standard, complete digestion of those elements to be measured, and reliable ICP-AES instrumental analysis of the solutions.

It is important that the physical form of the LCS match that of the sample to obtain maximum benefits from carrying the LCS through the analytical procedures. This is particularly true when the sample is dissolved since the overall analytical method quality can be no better than the quality of the digestion. The ARG-1 standard was used as the LCS in these tests because it is used as such at the SRS Defense Waste Processing Facility and at both SRNL and PNNL for research samples. Since excellent analyses were obtained on slurry samples without converting them to glass, the time-saving advantages of analyzing the "as-received" slurries have convinced us that this is the best analytical approach. Therefore, the LCS should be in slurry form instead of glass. We recommend that a sufficient volume of slurry simulants be produced, pre-dispensed into sample bottles, and set aside in air-tight conditions until used in the WTP. One concept that should be considered is to charge the slurry simulants into process sample vials and then transfer them to the analytical shielded cells through the pneumatic transfer system. This system could theoretically be used to make the LCS blind standards.

3.2.8 Sample Tracking

Analytical samples from the tests on WTP simulants were tracked through the Analytical Development Section Laboratory Information Management System. A typical analytical test included a digestion blank, 3-5 replicate analyses of the simulant, 1-3 analyses of simulants with matrix spikes added, and 2 duplicate analyses of the LCS. Each sample was assigned a unique number. The analytical data from the ICP-AES was stored permanently in electronic files at SRNL.

3.2.9 Statistical Analysis

Statistical analysis of the ICP-AES data as a function of the digestion methods for the AY-102/C-106 simulant [12], the AZ-101 simulant [13], and the AY-102/C-106 with glass formers simulant [14], was performed by T.B. Edwards of the Statistical Consulting Section of SRNL. These reports should be consulted for statistical methods and software details.

4.0 FUTURE WORK

Future work will consist of testing the recommended analytical scheme with simulants in the SRNL Shielded Cell Facility. The work will involve performing a Time-and-Motion study to measure the time required to perform the recommended analytical scheme with manipulators. Wet chemistry digestions and ICP-AES elemental analyses of glass samples prepared with actual Hanford high-level waste will be used to support LA-ICP-AES development work on radiological glass samples. Additional non-radiological tests will be performed to help develop a single digestion scheme applicable to both HLW-2A and HLW-2B samples.

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