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1	2	QA J. E. Hyatt	<i>J.E. Hyatt</i>	7/10/96					
1	1	Safety J. L. Pearson	<i>J.L. Pearson</i>	7/11/96					
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PREPARATION OF PRIVATIZATION SAMPLES FOR ENVELOPES "A" AND "C"

W. I. Winters

Westinghouse Hanford Company, Richland, WA 99352

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Abstract: As part of the TWRS Privatization process, the DOE has committed to provide each of the two contractors who submitted successful bids with ten 125 mL samples of Hanford tank waste meeting chemical and radionuclide criteria specified as Waste Envelopes A,B, and C. This test plan describes how the samples will be prepared before shipment.

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Part - A. Background

The Department of Energy Richland Operations issued a request for proposals (RFP) for private companies to demonstrate technologies for the pretreatment and immobilization of materials from the Hanford waste tanks. The TWRS Privatization Program prepared a letter of instruction (LOI) (Reference 1) for the collection, preparation and characterization of three liquids and one sludge fraction of waste for shipment to each of the two successful vendors.

Materials are to be prepared to meet specific ratios of elements, compounds and radionuclides to sodium. Values given in the LOI are the maximum desired; however, the prepared samples are to be as representative of the waste in the prescribed tanks as possible as long as they meet the criteria established in the RFP. It is therefore imperative that modifications to the criteria (LOI) be minimized and any modification receive the concurrence of the TWRS Privatization Program Office.

Samples received at the laboratory will be approximately 10 M sodium with primary components including aluminum, nitrate, nitrite and hydroxide ions. The concentration of the analytes exceed the solubility of their salts in the supernate at less than tank temperature, approximately 38 degrees Celsius. In order that the composition of the waste be maintained as it is in the tank, this material must be returned to slightly above tank temperature for aliquoting for characterization and delivery to the vendors. The solids content of the waste must be less than 5 volume percent at the tank temperature.

Part - B Purpose and Objective

This test plan describes the activities necessary to prepare and characterize waste tank materials for shipment to two vendors for demonstration of pretreatment and immobilization technologies. Details for preparing the materials are described in Part E. Reporting requirements are described in Part F. Multiple samples will be taken from a tank and be combined to produce a single waste composite material. Preliminary samples will be taken to evaluate the composition of the composite against the applicable envelope criteria. After concurrence from the Privatization Program that the waste is acceptable, additional samples will be taken for final characterization and the composite will be split into portions for the vendors and archives.

Part - C Quality Assurance

Any modification to the test plan that would affect the criteria established by the Privatization Program requires concurrence from the program before performing. Where alternative operations are identified in the plan, the cognizant scientist is responsible in selecting and

documenting the alternative chosen. Any other changes in the test plan shall be approved by the cognizant scientist and responsible manager or project coordinator. All changes in the test plan shall be documented in the field notebooks and transmitted to the laboratory project coordinator for inclusion in the data file.

Multiple subsamples will be taken from the composite to estimate the uncertainties in determining waste composition due to subsampling in the presence of heterogeneities such as solids. Duplicate or replicate analyses of these subsamples will be performed to estimate analytical uncertainties. Analysis of variance methods will be used to analyze the data.

Data generated in the laboratory will be approved by the chemist and reviewed and approved by the Laboratory Quality Assurance Officer prior to being reported to the program. The final characterization report will be a standard TWRS Characterization Format IV data package. This report will include all information generated as a result of performing this material preparation. This package will include a narrative that describes the observations made during the preparation and subsampling operations including any modifications to the test plan and any incidences that may impact the characterization or use of the material. The package will include a data summary of the measurements performed including the quality control results. The package will also include rerun results and the raw data needed to verify and trace the computation of the final result. A narrative should also accompany the analytical results describing any procedural changes and any problems or anomalies in the data.

The system of requirements identified by the Hanford Analytical Services Quality Assurance Plan (HASQAP) and consistent with the LOI should be followed in the analysis of these samples. If exceptions are required, the problem and probable reason for the exception should be described in the narrative of the data report. The decision to rerun a particular analysis to meet a specific quality control parameter is left to the professional judgements of the laboratory chemist and project coordinator. All laboratory data is to be reported to the TWRS Privatization Program and is acquired in accordance with "222-S Laboratory Quality Assurance Plan," (WHC-SD-QAPP-016)

Part - D Safety

Precautions must be taken to handle the radioactive caustic samples which are the subject of this activity. Because these double shell tank wastes may be newer and have been concentrated, the radiation levels can be expected to be higher than that found in the older single shell tanks. Because the waste is mostly supernate, the Cs-137 levels are expected to be higher than the SrY-90 and therefore shielding is required to reduce exposure for some operations. The waste contains large quantities of nitrites and carbonates which will produce gas and possible foaming when acidified. Acidification of the waste should be done slowly in containers large enough to handle any splattering or with secondary containment placed around the sample.

Bottles and vials may need to be heated to assist transfer during preparation of the waste composite. These bottles need to be covered to minimize evaporation but should not be sealed tightly since gases produced and/or expanding in the bottle could result in pressurization and breakage of the bottle. Even though these operations are planned for the hot cell where personal injury is not possible, the clean up operations could lead to additional exposure.

Part-E Procedure

Part I - Preparation of Composite

- 1.0 Load the 125 mL bottles of sample into the 11A hotcell in accordance with the established test plan.
- 2.0 Photograph or video the contents of each bottle.
- 3.0 Record the following:
 - a) Weight of the bottle and sample.
 - b) Estimated percent fullness of the bottle.
 - c) Estimated percent settled solids.
 - d) Temperature of the hotcell.

Note: Any waste bottles placed in a heating bath should be covered to prevent concentration by evaporation.

Caution: Sample vials or bottles should not be sealed tight while in heating bath to prevent pressurization and potential breakage. Stoppers covered with Teflon film or small watch glasses may be used to cover the vials or bottles.

Note: If the sample does not contain too many solids and the solids can be adequately suspended so that they can be transferred to the composite tank, then Step 4 does **NOT** need to be performed.

- 4.0 Place the sample bottle in a water bath at 40 °C and heat and shake until the solids are dissolved and / or suspended enough to permit a visually complete transfer of the sample to the composite tank.
- 5.0 Heat the composite tank to 40 °C. (Composite Tank Drawing No - H2826884)
- 6.0 Shake the bottle to suspend any solids and transfer the contents to the composite tank.
 - a) Do not rinse the bottle to transfer residual waste.

7.0 Reweigh the empty bottle with cap.

- a) Record the weight of the empty bottle.

8.0 Repeat Steps 1 through 7 until all the bottles have their contents transferred to the composite tank.

- a) Determine the total volume of waste transferred into the tank by summing the volume estimates for each bottle.
- b) Determine the net weight transferred from each bottle and the total weight of the waste transferred.

Part II - Dissolution of Precipitated Salts

9.0 Stir the waste and heat the composite tank until the composited waste reaches a temperature of 40 °C and until no change in solids content is observed.

- a) Check and periodically record the temperature of the composite.
- b) Record the start time and date for heating and stirring.
- c) Record stirring speed or setting.

Note: Video recording of the changes in the grab samples may be performed to record dissolution progress.

Note: If solids are < 5 vol. % in the samples at room (hot cell) temperature, Step 10 does not need to be performed.

Note: Open valve wide enough in Step 10 to allow salts to be drained. If necessary drain the sample into a beaker and then transfer quickly to a 50 mL centrifuge cone with a 2.5 mL mark (5 vol %).

10.0 Drain a grab sample into a graduated centrifuge cone every 1 to 2 hours while stirring and quickly transfer the sample to a water bath at 40 °C to evaluate solids dissolution, volume % solids and settling rate.

- a) Record: 1) time for bulk of solids to settle, 2) vol % solids after 1 hour for each subsample. Keep the samples in a water bath to maintain temperature when not observing.
- b) Transfer the grab samples back to the tank after viewing and measuring volume % solids and settling time.

Note: After the cognizant scientist concludes that all of the soluble salts have dissolved, samples may be taken to remove excessive solids and verify the volume of settled solids is less than 5%.

Part III - Measurement and Removal of Solids Greater than 5 Volume Percent

Note: If the waste contains 5% or more volume solids, then 5 L of waste would contain at least 250 mL of solids. If the first two 50 mL samples of waste drained from the bottom after settling, contain less than 50% solids and the second sample has less solids content, no additional samples should be necessary. This information and the volume percent solid results from the stirred composite in Step 10 should be adequate to show that the volume % solids are less than 5%.

Note: Tap the sides of the vessel or centrifuge cone lightly to loosen solids that may be adhering to the sides.

11.0 Shut off the stirrer on the composite tank and allow the solids to settle while maintaining the temperature.

Note: If appropriate (settling is slow or a sequence of steps cannot be completed in a shift) the waste may be allowed to settle overnight.

a) Base settling time on experience with grab samples in Step 10, or at least 1 hour.

b) Record the settling time

12.0 Drain about 50 mL of the settled waste into a 50 mL centrifuge cone with a 2.5 mL mark (5% vol) and place the cone in a water bath heated to 40 °C to permit solids to settle.

a) Record sampling time.

13.0 Turn on the stirrer and remix the composite for 1 to 2 minutes to loosen any solids from the sides of the vessel and repeat Steps 11 and 12.

Note: If > 50 volume % solids is observed for over 250 mL notify the cognizant chemist.

14.0 Repeat Steps 11 to 13 until the settled solids after 1 hour in the centrifuge tube are less than 5 vol % or until cognizant chemist concludes that adequate solids are removed.

15.0 Perform the mixing, settling and sampling at least twice to confirm the solids are less than 5 vol% and that no solids are adhering to the sides of the tank.

- 16.0 Based on the results from Step 14 and the volume % solids measurements from Step 10, the cognizant scientist will decide if adequate solids have been removed and that the volume percent solids for the composite is less than 5%.
- 17.0 Return the supernate of the grab samples to the composite tank and save the settled solids for possible future analysis.

Note: The composited waste should now contain less than 5 volume % solids. If during any future subsampling, larger quantities of solids appear to be present the cognizant chemist or project coordinator should be notified before proceeding.

Part IV - Preliminary Sampling for Evaluation of Composition Against Envelope

- 18.0 Stir the waste for at least 15 to 30 minutes to mix and resuspend any remaining solids.

Note: Samples may be taken by 1) pipetting aliquots (subsamples) directly from the tank to analysis vials, or by 2) transferring or draining a larger subsample (25 - 100 mL) to a bottle and placing it in a heat bath before pipetting analytical aliquots. The large volume subsample (2) is the preferred approach. The first approach will not be used unless operational considerations (space or equipment failure) prevent implementation of the second approach.

Note: The size of the analytical aliquot may be determined by 1) pipetting a known volume or 2) measuring the density of the waste and transferring a weighed aliquot to a preweighed vial. The weighed aliquot (2) is the preferred approach and is described in Step 19.3.

The first volumetric approach will not be used unless operational considerations prevent implementation of the second approach.

Note: Pipetting of hot solutions will result in volumetric errors. These errors should be estimated by pipetting several aliquots (1 mL and 5 mL) of water at the 40 °C temperature to estimate the size of the pipetting bias for the pipetting system used.

Note: A weighed and/or known volume of water may be added to the subsample aliquot vials prior to or after adding the sample to the vial. This will prevent salts from precipitating and allow smaller aliquots to be used for analysis. However, if smaller aliquots are used for analysis from these diluted samples, the analysis aliquot should be taken while stirring the subsample to allow any insoluble solids to be sampled. All volumes and/or weights of water or acid added to the subsample must be recorded and provided to the project coordinator.

Note: Any waste aliquots that are removed and placed in a heating bath should be covered and sampled as quickly as possible to prevent concentration from evaporation.

Caution: Sample vials or bottles should not be sealed tight while in heating bath to prevent pressurization and potential breakage. Corks covered with Teflon film or small watch glasses may be used to cover the bottles or vials.

19.0 Pull the sample aliquots using one of the alternate methods below:

19.1 Alternate 1: Take the following sample aliquots (subsamples) from the composite tank while the waste is stirring.

19.1.1 While stirring, pipet the following aliquots directly from the tank into preweighed vials for analysis of the envelope analytes in Table 1.

Note: Tc-99 may also be performed on the acid digested sample depending on its concentration.

- a) 1 mL - ICP/U/Sr-90/TRU/Cs-137 Acid Digestion and Analysis
(Also Total alpha, total beta and Np-237 not in envelope)
- b) 1 mL - ICP/U/Sr-90/TRU/Cs-137 Acid Digestion and Analysis (Duplicate)
- c) 1 mL - ICP Acid Digestion and Analysis (Spike)

Note: CZE for chelates (EDTA, HEDTA, glycolate and acetate) is not an envelope test but is needed to complete multiple analysis requirements.

- d) 1 mL - IC/TOC/TIC/CZE Water Digest or Water Dilution and Analysis
- e) 1 mL - IC/TOC/TIC/CZE Water Digest or Water Dilution and Analysis
(Duplicate)
- f) 1 mL - Hg by CVAA Analysis (Direct or Acid Dilution)
- g) 1 mL - Hg by CVAA Analysis (Duplicate)
- h) 1 mL - Hg by CVAA Analysis (Spike)

Note: Make hydroxide dilution in 5 mL of water and analyze in replicate.

- j) 1 mL - Hydroxide Analysis (Plastic Vial) (Direct or Water Dilution)
- k) 1 mL - Hydroxide Analysis (Duplicate)

Note: Tc-99 may be performed on the acid digested sample and/or on a direct aliquot.

- l) 1 mL - Tc-99 Analysis
- m) 1 mL - Tc-99 Analysis (Duplicate)
- n) 1 mL - Tc-99 Analysis (Spike)

Note: If no reagents are added to the sample, the blank vials may be prepared outside the hotcell using the same batch of vials that were used for the samples.

- o) 1 mL - 1 vial as an ICP blank (Plastic Vial)
- p) 1 mL - 1 vial as an IC/TOC blank with water as appropriate
- q) 1 mL - 1 vial as a Hg blank with acid as appropriate

19.1.2 Weigh the cooled sample aliquots and use weights to calculate solution density (if accurate volume are used) and weight dilution factors.

Note: Aliquots will be prepared by the sample preparation group using standard sample preparation procedures. Samples will have to be transferred from the vials to the digestion beakers by dissolving the samples in water (warming as necessary) and then transferring to the beakers with several rinses. For the ICP aliquots, the final rinse of the vial may be done with the first HNO_3 addition used in the sample preparation which is then transferred to the beaker. Titrations for hydroxide may be done on the direct sample aliquot if the hydroxide concentration is low by adding 2 to 5 mL of water and stirring before titrating. If the hydroxide concentration is high the hydroxide aliquot may be diluted by adding the required measured volume of water, mixing and warming to dissolve the sample and removing a smaller aliquot for titration. Mercury digestions may be performed on the direct aliquot, diluted in acid or transferred to beakers for digestion in the same manner as the ICP aliquot. If the subsample was diluted in water when taken, the subsample should be stirred while removing the analytical aliquot. Dilutions in acid or water may be done by either the process chemistry or sample preparation groups.

19.2 Alternate 2 - Taking a large subsample from the composite tank for analysis.

Note: The larger sample aliquot may be removed by either 1) siphoning, vacuuming or pumping from the middle of the tank or 2) draining from the valve at the bottom of the tank. Draining from the bottom may give a disproportionate amount of solids. Siphoning may give a lower amount of solids but may be subject to a higher risk of waste precipitation. Draining is the preferred method because the stirrer should minimize the preferential solid sampling and the operation will be easier to perform.

Note: Leave sufficient head space in the bottle so that a Teflon stir bar can be added and the contents can be mixed at speeds to suspend solids.

19.2.1 While stirring drain about 100 mL of waste from the tank to flush the valve and add it back into the tank.

19.2.2 While stirring, transfer about 100 mL of the composite sample to a clean glass bottle.

Note: Any waste subsamples that are removed and placed in a heating bath should be sampled as quickly as possible to prevent concentration from evaporation.

Caution: Sample vials or bottles should not be sealed tight while in heating bath to prevent pressurization and potential breakage. Stoppers covered with Teflon film or small watch glasses may be used to cover the bottles or vials..

19.2.3 Place the sample in a heating bath at 40 °C to prevent salts from precipitating.

Note: Aliquots should be removed either while stirring or immediately after shaking to suspend solids. Samples should not be allowed to cool to the point that salts precipitate out.

19.2.4 Shake the bottle or place on a stirrer/hot bath to suspend the solids before removing the aliquots identified in Step 19.1.1.

19.2.5 Transfer aliquots into clean preweighed sample vials and handle in the same manner as described in 19.1.1.

19.2.6 Weigh the cooled vial with sample.

a) Record the weight and calculate the density if accurate volumes are transferred

19.2.7 Submit the aliquots for sample preparation and analysis as described in 19.1.1.

19.2.8 Save the rest of the 100 mL subsample for aliquots of the other required analyses (Step 25), reruns and verification if needed.

Note: Aliquots for the other analytes identified in Part VI, Step 25 should be taken from this 100 mL subsample. This may be done at the same time that aliquots are taken for the envelope analyses or after the HOLD POINT for Step 21. If they are taken after the hold point, which may require a couple of weeks to complete, the subsample should be stored at room temperature. After the hold point is released, the subsample would be reheated and mixed and the aliquots for the other analytes taken.

Note: Another version of this approach would be to remove the 25-100 mL aliquot from the hot cell and set it up in a shielded hood where it can be reheated to 40 °C and stirred. Analytical aliquots would then be taken from this location directly into the analytical procedures.

19.3 Subsampling by Weight rather than by Volume

19.3.1 Pipet 3 five mL aliquots while stirring (using Alternate 1 or 2) into 3 preweighed vials for determination of solution density. Weigh the cooled aliquots. Return aliquots to the composite when completed.

Note: Density of the sample may also be determined by transferring sample to the 10 mL mark in a preweighed graduated 15 mL centrifuge cone, capping and reweighing. This procedure is described in Step 6.7 of LA-519-132.

19.3.2 Transfer, while stirring, the approximate volumes for the aliquots in Step 19.1.1 by transfer pipet. Remove sample using either Alternate 1 or 2 technique.

19.3.3 Weigh the cooled aliquots and calculate the volume transferred using the density calculated from 19.3.1.

19.3.4 Submit the aliquots for sample preparation and analysis as described in 19.1.1.

- a) Provide the sample preparation group and the project coordinator a record of the weights and volumes for each aliquot.

Note: Step 20 is performed if sample aliquots are taken directly from the tank (Alternate 1). If Alternate 2 is chosen the remaining subsample is saved for reruns and future testing.

20.0 Transfer 25 to 50 mL of the composited waste while stirring to a clean bottle and hold for reruns and verification analyses if needed.

21.0 Turn off the stirrer and heating to the composite tank after all preliminary sample aliquots have been taken.

Note: Results from the preliminary sampling shall be reviewed by the responsible analytical chemist and the laboratory project coordinator who is responsible for preparation of the report. The report will be reviewed by the QA Officer and Privatization Laboratory Project Manager who is responsible for forwarding the final report to the Privatization Project.

Do not proceed until 1) preliminary analyses have been completed, 2) results have been evaluated by the Privatization Program against the applicable envelope and 3) the Privatization Program has directed the laboratory to continue with this test plan. If the preliminary results fall outside the envelope specifications the Privatization Program will provide directions to modify the composite composition.

Release of Hold Point

Signature for TWRS Privatization Project

Date

Part V - Resumption of Testing

Note: Testing cannot resume until direction is received from the Privatization Program to continue.

22.0 Heat the waste composite back up to the tank temperature, 40 °C and stir to mix.

- a) Return the saved preliminary sample from Step 20.0 to the composite tank.
- b) Make any adjustments to the composite as directed by the Privatization Program.

Note: If adjustments are made to the composition as part of Step 22 (b), Part IV of the test plan will be repeated and a new hold point initiated. If the composition is not modified continue with Step 23.

23.0 Evaluate completion of dissolution by pulling grab samples as described in Part II.

Note: If adjustments to the composition are not made, additional verification tests may be performed to ensure that the composited waste has attained the same condition as it was during preliminary sampling. For example: 1) Confirm that settled solids are less than 5 vol. %, 2) confirm that density has not changed significantly, or 3) confirm that the sodium concentration is the same as the preliminary results. After the cognizant scientist is confident that the waste has returned to its equilibrium condition for that temperature, work can continue.

Part VI Subsampling for Final Characterization Analyses

Note: If possible the composite material should be kept at equilibrium temperature until Parts VI and VII are completed. This will help to ensure that the samples analyzed are the same as the samples pulled for the vendors. It also eliminates the need for repeating Part V. Work should be planned so that it is not stopped over a weekend.

24.0 Repeat Part IV to obtain the 2 additional aliquots for analysis of the envelop analytes identified in Table 1.

- a) These analytes are identified by "***" or the superscript "2" of Table 1 and in Step 19.1.1.
- b) Alternate 1 - Take 2 additional sample aliquots from the tank for preliminary analytes listed in Step 19.1.1

- c) Alternate 2 - Pull 2 new 100 mL subsamples for the final characterization and take duplicate aliquots of these subsamples as described in Step 19.2 for analysis of the envelope analytes in Step 19.1.1.

Note: Step 25 describes taking aliquots as if they are sampled directly from the tank (Alternate 1). These same aliquots may be taken using Alternate 2 by 1) taking duplicate aliquots for analytes identified in Step 25 from the 2 new 100 mL subsamples taken in Step 24 (c). The third subsample for these analytes using Alternate 2 was taken in Step 19.2.8 If the large sample Alternate 2 approach is used the "**triplicate**" subsamples identified in Step 25 are **NOT** necessary. Also if this multiple 100 mL subsample approach is used, the analyses do not need to be performed in replicate since this approach will produce 6 analytical values from duplicate aliquots.

25.0 Follow the techniques described in Part IV to obtain the following aliquots for analysis of the other analytes needed for characterization of privatization samples as identified in Table 1. These are identified with the subscript "3".

Note: Only 1 spike is required for the analytical batch (a spike is not required for each subsample in Alternate 2) generated in the final characterization.

Note: If the entire aliquot is used in the HYAA analysis using Alternate 1 (aliquoting from the tank) only 3 results will be obtained. If the aliquot is diluted in acid for Alternate 1 prior to analysis, replicate aliquots of the dilution should be taken through the sample preparation and analysis.

- a) 1 mL - As HYAA (Direct or Acid Dilution)
- b) 1 mL - As HYAA Duplicate
- c) 1 mL - As HYAA Triplicate (Not required for Alternate 2)
- d) 1 mL - As HYAA Spike
- e) 1 mL - Se HYAA
- f) 1 mL - Se HYAA Duplicate
- g) 1 mL - Se HYAA Triplicate (Not required for Alternate 2)
- h) 1 mL - Se HYAA Spike

Note: Three aliquots will be shipped to PNNL for ICP/MS analysis. For the Alternate 2 approach one 5 mL aliquot will be taken from each large subsample. PNNL will heat the samples to 40 °C and stir and pull the duplicate aliquots from each subsample for their procedures. They will also pull aliquots for spike analysis and other QC as needed. ICP/MS analytes to be determined are: Cs, Np-237, Pu Isotopic, U Total, U Isotopic, Tc-99, Sn-126, Zr-93, I-129, La and Ba.

Alternate 1 Alternate 2

- i) 5 mL - ICP/MS (Subsample 1)
- j) 5 mL - ICP/MS (Duplicate) (Subsample 2)
- k) 5 mL - ICP/MS (Triplicate) (Subsample 3)

Note: Cyanide sample will have to be transferred to the microdistillation tube using the same technique as water digestion unless it is diluted in water first. Because the 1 mL sample will probably generate too much gas, the 1 mL sample aliquots will be diluted in 5 mL of water prior to analysis. Each dilution will be analyzed in replicate.

- l) 1 mL - Cyanide (Direct or Water Dilution)
- m) 1 mL - Cyanide (Duplicate)
- n) 1 mL - Cyanide (Triplicate) (Not required for Alternate 2)
- o) 1 mL -Cyanide (Spike)

Note: Accurate and reproducible NH_3 analyses may not be possible in caustic samples because of the loss of NH_3 gas. Aliquots should be pulled into acid to stabilize the ammonia as NH_4^+ . However, this must be done carefully since large amounts of gas from NO_x and CO_2 will be generated. Tall 40 mL vials should be used and placed inside beakers for containment. Add 5 mL of water to the 1 mL aliquot. The amount of HNO_3 acid (mMoles) added should be greater than the meq of base. Record the volume of water and acid added to vial for calculation of the dilution factor. Report these to the project coordinator.

$$\text{mMoles HNO}_3 = 1 \text{ mL} [4(\underline{\text{M Al}}) + \underline{\text{M OH}} + 2(\underline{\text{M CO}_3}) + \underline{\text{M NO}_2} + \underline{\text{M PO}_4}]$$

- p) 1 mL - Ammonia (40 mL vials with enough acid to bring pH to below 5 or 6)
- q) 1 mL - Ammonia(Duplicate)
- r) 1 mL - Ammonia (Triplicate) (Not required for Alternate 2)
- s) 1 mL -Ammonia (Spike)

Note: Accurate estimates of conductivity and pH on saturated salt solutions at high temperatures are not possible using standard procedures and may not be meaningful. In order to perform the measurements without interference from solids formation the samples for pH and conductivity will be diluted with an equal volume of water. This approach is used in the determination of pH in solids by EPA procedures (SW-846, 9045). Because the entire sample will be used in the measurement only 3 results will be generated for these analyses

- t) 5 mL - Conductivity (Dilute 1:1 with water)
- u) 5 mL - Conductivity (Duplicate)
- v) 5 mL - Conductivity (Triplicate) (Not required for Alternate 2)
- w) 5 mL - pH (Dilute 1:1 with water)
- x) 5 mL - pH (Duplicate)
- y) 5 mL - pH (Triplicate) (Not required for Alternate 2)

Note: Determine density in the hotcell by weighing 5 mL aliquots or by weighing known volumes in 15 mL graduated centrifuged cones as described in Step 6.7 of LA 519-132.

Note: Aliquots for C-14 and tritium will be diluted in 5 mL water to prevent precipitation of solids. Dilution volumes and/or weights must be recorded and reported to the project coordinator. Replicate (2) aliquots from this dilution will be taken through the procedures.

- aa) 1 mL - Carbon - 14 (Dilute with 5 mL water)
- bb) 1 mL - Carbon - 14 (Duplicate)
- cc) 1 mL - Carbon - 14 (Triplicate) (Not required for Alternate 2)
- dd) 1 mL - Carbon - 14 (Spike)
- ee) 1 mL - Tritium (Dilute with 5 mL water)
- ff) 1 mL - Tritium (Duplicate)
- gg) 1 mL - Tritium (Triplicate) (Not required for Alternate 2)
- hh) 1 mL - Tritium (Spike)

Note: Because Se and iodine may be associated with solids, these analytes should probably be measured on direct aliquots of sample. This will result in only 3 analytical measurements for these analytes.

- ii) 1 mL - Se-79
- jj) 1 mL - Se-79 (Duplicate)
- kk) 1 mL - Se-79 (Triplicate) (Not required for Alternate 2)
- ll) 1 mL - Se-79 (Spike)
- mm) 1 mL - I-129
- nn) 1 mL - I-129 (Duplicate)
- oo) 1 mL - I-129 (Triplicate) (Not required for Alternate 2)
- pp) 1 mL - I-129 (Spike?)

Note: Three aliquots will be submitted to 222-S Lab for Semi-Volatile Organic analyses. The organic lab will warm to 40 °C and take the necessary sample and QC samples needed for analysis.

- rr) 10 mL - Semi-Volatile Organic
- ss) 10 mL - Semi - Volatile Organic (Duplicate)
- tt) 10 mL - Semi - Volatile Organic (Triplicate) (Not required for Alternate 2)

Note: Three aliquots **may** be shipped to PNNL for organic chelate analyses to verify CZE results. PNNL will heat to 40 °C and stir and pull the necessary aliquots for their procedures. They will also pull an aliquot for spike analysis.

uu) 5 mL - Organic Chelators (PNNL)

vv) 5 mL - Organic Chelators (Duplicate)

ww) 5 mL - Organic Chelators (Triplicate) (Not required for Alternate 2)

Note: Step 26 is not necessary if Alternate 2 - subsamples are taken. In this case, these larger subsamples are saved for reruns and verification analyses.

26.0 Pull 100 mL of the composite sample to hold for reruns or verification analyses.

Note: Each sample preparation (acid and water digest) should be analyzed in replicate (For example: 2- ICP dilutions and 2 -Pu-239 aliquots per digestion). For samples where the subsample is totally consumed in the analysis (such as pH or Se-79) only 3 results will be generated using the Alternate 1 approach.

27.0 Submit subsamples and dilution information to the analytical laboratory for analysis. Instruct laboratory to analyze each subsample (primary, duplicate, triplicate or subsample 1 , 2 and 3) in replicate or duplicate respectively so that a total of 6 values will be generated.

28.0 Data shall be reported in accordance with TWRS Characterization Level IV reports. It should include a data summary with replicate or duplicate results, raw data for the analytical batches, and a narrative that explains any significant procedural changes, problems in the analyses or anomalies in the data.

Part VII - Preparation of Subsamples for Shipping to Privatization Contractors

Note: Storage of highly caustic samples in glass bottles can result in increase concentrations of Na, B and Si and other potential trace contaminants in the sample and reduce the hydroxide concentration.

29.0 Label bottles with the following information and preweigh 24 - 125 mL glass bottles with plastic lined caps for preparation of vendor samples.

- a) Tank Identification
- b) Laboratory Composite Number
- c) Date of Packaging (filling)
- d) Bottle number in sequence

Note: If it is necessary to turn off the heat to the composite tank prior to taking vendor samples,

Part V of this procedure should be performed to ensure equilibrium conditions are established. The sample should be at temperature/solubility equilibrium and the stirrer should be on long enough to suspend solids before performing Step 30.

- 30.0 Place the first bottle under the drain valve and fill the bottle with sample with the temperature at 40 °C and the sample stirring to suspend solids.
 - a) Record any observable differences in the samples such as solids content.
 - b) Video the subsamples while hot and after cooling
- 31.0 Repeat Step 30.0 until all 24 bottles are filled.
- 32.0 Drain 1 liter of the composite into a glass bottle with a plastic lined cap and save as an archive.
- 33.0 Allow the bottles to cool overnight and reweigh.
- 34.0 Drain the remaining composite material into 1 liter bottles and hold for disposal instructions.
- 35.0 Flush and clean the tanks for storage and future use.
- 36.0 Store the bottles in the hot cell until shipping instructions are provided by the Privatization Program.
- 37.0 Vent the samples before shipping by opening and retightening the caps on the bottle.
- 38.0 Weigh the bottles again before removing from the hot cell for shipment.
- 39.0 The laboratory will package the sample bottles in hedgehog shipping containers and move them to laboratory shipping dock when requested by WHC Transportation and Packaging.
- 40.0 The Privatization Program will direct WHC Transportation and Packaging to pick up the samples from the laboratory dock for shipment to the vendor.

Table 1 Analytes for Characterization of Privatization Samples

Method	Analyte	Sample Preparation	Replicate ^(a)
ICP/AES LA-505-151/161	Al**	Acid Digestion LA-505-158	2 sets of diln/anal for each digested subspl
	Ba**		
	Ca**		
	Cd**		
	Cr**		
	Fe**		
	K**		
	La**		
	Na**		
	Ni**		
	Pb**		
	P ¹		
	S ^{1, 2}		
	U ¹		
	B ^{2,3}		
	Bi ^{2,3}		
	Cu ^{2,3}		
	Li ^{2,3}		
	Mg ^{2,3}		
	Mn ^{2,3}		
	S ^{2,3}		
	Si ^{2,3}		
	Sm ^{2,3}		
Table 1 Analytes for Characterization of Privatization Samples			

Method	Analyte	Sample Preparation	Replicate ^(a)
	Sr ^{2,3}		
	Te ^{2,3}		
	Tl ^{2,3}		
	V ^{2,3}		
	Zn ^{2,3}		
	Zr ^{2,3}		
CVAA LA-325-104 or 105	Hg**	Direct or Acid Dilution	No replicates 2- analyses/diln
HYAA LA-355-131	As ³	Direct or Acid Dilution	No replicates 2- analyses/diln
HYAA LA-365-131	Se ³	Direct or Acid Dilution	No replicates 2- analyses/diln

Table 1 Analytes for Characterization of Privatization Samples			
Method	Analyte	Sample Preparation	Replicate ^(a)
Ion Chromatography LA-533-105	F**	Water Digestion LA-504-101	2 sets of diln/anal for each digested subspl
	Cl**		
	NO ₃ **		
	NO ₂ **		
	SO ₄ **		
	PO ₄ **		
Titration LA-211-102	Hydroxide**	Direct or Dilution	No replicates 2 - titrations per diln
Persulfate/Coulom. LA-342-100	TIC**	Direct or Dilution	No replicates 2 - analyses/ diln
	TOC**		
Furnace/Coulom LA-344-105	TC**	Direct or Dilution	2 - Injections 2 - analyses/ diln
	TOC**		
SIE LA-631-001	Ammonia ³	Acidified Sample	2 sets of diln/anal for each acidified subspl
Conductivity Probe LA-512-104	Conductivity ³	1:1 Dilution	No Replicates
Electrode LA-212-105/106	pH ³	1:1 Dilution	No Replicates
Gravimetric/Volume (Test Plan Step 20.3.1)	Density ³	Direct	No Replicates
Table 1 Analytes for Characterization of Privatization Samples			

Method	Analyte	Sample Preparation	Replicate ^(a)
Separation/AEA LA-943-128	Pu-238**	Acid Digestion	2 sets of diln/anal for each digested subspl
	Pu-239/240**		
Separation/AEA LA-953-103	Am-241**	Acid Digestion	2 sets of diln/anal for each digested subspl
GEA LA-548-121	Cs-137**	Acid Digestion	2 sets of diln/anal for each digested subspl
	Cs-134**		
	Co-60**		
	Am-241**		
	Eu-154**		
	Eu-155**		
Separation/Beta LA-220-101	Sr-90**	Acid Digestion	2 sets of diln/anal for each digested subspl
Separation /Beta/LS LA-438-101	Tc-99**	Acid Digestion or Direct	2 anal / digested spl No Replicates
Fluorimetric LA-925-009	Total U**	Acid Digestion	2 sets of diln/anal for each digested subspl
Alpha Count LA-508-101	Total Alpha ^{2,3}	Acid Digestion	2 sets of diln/anal for each digested subspl
Beta Count LA-508-101	Total Beta ^{2,3}	Acid Digestion	2 sets of diln/anal for each digested subspl
Separation/AEA LA-933-141	Np-237 ^{2,3}	Acid Digestion	2 sets of diln/anal for each digested subspl
Separation/LS LA-348-104	C-14 ³	Direct or Water Dilution	No Replicates 2 - analyses/ diln
Separation/LS LA-218-114	Tritium ³	Direct or Water Dilution	No Replicates 2 - analyses/ diln
Table 1 Analytes for Characterization of Privatization Samples			
Method	Analyte	Sample Preparation	Replicate ^(a)

Separation/LS LA-365-132	Se-79 ³	Direct or Acid Dilution	No Replicates 2 - analyses/ diln
Separation/LEPS LA-378-103	I-129 ³	Direct	No Replicates
ICP/MS PNNL	Total Cs ³	Acid Digestion	2 sets of diln/anal for each digested subspl
	Total U ¹		
	U Isotopic ³ (U-233, U-235, U-238)		
	Tc-99 ¹		
	Zr-93 ³		
	Sn-126 ³		
	Np-237 ¹		
	Pu Isotopic ³		
	Ba ¹		
	La ¹		
	I-129 ¹		
CZE Blue User	Chelating Organics ²	Water Digest	2 sets of diln/anal for each digested subspl
EXT/GC/MA LA-523-131/406	Semi-Volatile	Extraction	2 sets of diln/anal for each extracted subspl

** Envelope Analytes

- (a) Replicates are defined for Alternate 1 aliquots. Alternate 2 will have duplicate analyses on 3 large subsamples.
 - 1) Used to confirm other methods.
 - 2) Not an envelope analyte but needed to complete 3 subsample requirement for final characterization using Alternate 1 approach
 - 3) Analytes in addition to Envelope Analytes needed for Final Characterization

Part F - Reporting

Preliminary Report

A preliminary report will be prepared for the initial verification of the waste envelope criteria as described in Part IV of this test plan. The report shall consist of a summary of the results including duplicates and other applicable quality control information. The report shall include a narrative that describes any significant observations or events during composite preparation and any problems or anomalies in the analytical data. Raw data will not be reported but must be available for assessment from the laboratory if questionable results or problems are encountered.

This report will be prepared by the project coordinator and reviewed and approved by the laboratory quality assurance officer before issuing to the TWRS Privatization Program. The TWRS Privatization Program will be responsible for evaluating the results against the envelope and shipping requirements and for providing any reports documenting these evaluations. The Privatization Program is responsible for providing the laboratory instructions for continuing operations following their evaluation.

Final Characterization Report

This report will be prepared when all analyses from the final characterization samples as described in Part VI are completed. This report will contain a data summary of all the results including applicable QC information from the final characterization samples. A narrative will accompany the results describing the composite preparation, any modifications in the test plan and any significant observations or problems in the preparation or dispensing of the composite. The narrative will also include an analytical section describing any changes in procedures and problems in analysis including QC difficulties. Raw data will not be provided in this report but must be available for assessment from the laboratory if questionable results or problems are encountered. Raw data (comparable to the Format IV TWRS Characterization Reports (Reference 2)) will be added as an addendum to the final report within 150 days of completing the analyses. Any statistical analysis or evaluation of results against the envelope will be issued in a separate report.

Part G - References

- Reference 1 - Letter of Instruction (LOI) for TWRS Privatization Contractor Samples, Rev 0, June 7, 1996, T. E. Jones, PNNL, Richland WA.
- Reference 2 - Letter, R.D. Schreiber, WHC to C.S. Haller, WHC, "Revised Interim Tank Characterization Plan Guidance", 7E720-94-121, dated May 13, 1994.