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SST Sample Characterization Analysis of Archive Samples 102-C, 105-C, and 106-C

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February 1991

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
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EXECUTIVE SUMMARY

A major effort at Hanford over the next few years will be to sample and analyze wastes contained in 149 single-shell tanks (SSTs). In preparation for this effort, selected analyses were performed on four archived samples to compare analytical methods and to determine applicability of these methods to the waste samples. The analyses, performed by the Pacific Northwest Laboratory (PNL)(a), used a variety of analytical methods including both PNL technical procedures and adaptations of U.S. Environmental Protection Agency (EPA) technical procedures.

Although data are reported for analyses of actual waste tank samples, the data do not serve to characterize any waste in Hanford tanks. Since this investigation was intended only as a comparison of analytical methods, and the samples are from an archive repository, the results are preliminary in nature. The numerical values are to be evaluated with appropriate respect for the limited usefulness of small amounts of data generated through an analytical development process using only four samples.

The analysis of the archived SST waste material provides three important types of data for use in planning later phases of sample analysis. The data serve as input for 1) establishing analysis procedures and methods for waste samples, 2) evaluating the impact that using a silicon-based lubricant and normal paraffin hydrocarbon (NPH) in field sampling has on extracting inorganics or radionuclides from the SST sample, and 3) identifying trends in amounts of occupational radiation exposure expected from performing the various analysis procedures.

Inorganic analysis work was undertaken to determine 1) the applicability of various analytical methods to the test samples, 2) if mercury can be determined by cold vapor atomic absorption (CVAA), 3) if the inductively-coupled plasma (ICP) spectrometer has sufficient sensitivity for the analysis of EP Toxicity metal ions (excluding mercury), and 4) which of the 22 EPA pollutant metal ions can be determined by ICP analysis. Poor reproducibility was obtained

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with water leach and EP Toxicity methods, but acid digestion gave good reproducibility. Some of the procedures were changed if, due to interference by other elements, the methods did not provide the levels of sensitivity, accuracy, or precision usually required for EPA work. When appropriate, other methods are suggested for trial as alternatives. Some procedural adjustments were required for mercury analysis by CVAA. Problems areas identified are ICP sensitivities and ICP spectral corrections when analyzing for minor constituents (e.g., Ag, As, Pb, Se, Tl, and V); if elements of this class are critically important, they should be determined by alternative methods.

Organics analysis investigations were conducted to determine if the EPA semivolatile organic method can be employed on SST samples. Silicone-based lubricants and NPH from the sampling process impact the semivolatile analysis; however, with slight modification the procedure of EPA SOW 288 can be used. The results show that the gas chromatograph/mass spectrometer (GC/MS) is vulnerable to fouling and overload and that a combination of dilution and acidification is required to provide acceptable results. Work also included evaluation of 1) screening procedures for gas chromatography (GC) and total organic carbon (TOC), 2) extraction procedures and related problems, and 3) surrogate spiking to test extraction efficiencies and matrix effects.

Development work was performed to gather information relevant to the potential use of radionuclide ratioing and parent-daughter relationships for the estimation of radionuclides within samples. The radionuclides expected in the SST tank waste samples were measured to determine the level of accuracy and precision that can be expected. These data reveal that some level of procedure development is needed for a large number of the radionuclides analyses.

Tests were conducted to determine whether the NPH from the field sampling process extracted significant quantities of the inorganics or radionuclides from the SST samples. No such extraction was observed; however, the NPH does have a significant adverse effect on organic analysis, and alternatives to NPH should be investigated. Effects of silicon-based lubricant were not experimentally evaluated apart from sample analysis.

Trends in expected occupational exposure were obtained by measuring the radiation level of samples and having the analysts record estimates of the contact time with the samples. Data revealed that the analysts received no significant exposure and that, as expected, the potential dose is directly proportional to the sample size and handling times.

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GLOSSARY

AEA - Alpha energy analysis

ARL - Applied Research Laboratory

CLP - Contract Laboratory Program

CRQL - Contract required quantitation limits (specified by EPA)

CVAA - Cold vapor atomic absorption

DIW - Deionized water

EPA - U.S. Environmental Protection Agency

EP Toxicity - An extraction procedure for toxic metals specified by EPA, also called EP Tox

GC - Gas chromatograph (or gas chromatography)

GEA - Gamma energy analysis

GFAA - Graphite furnace atomic absorption

IC - Ion chromatograph (or ion chromatography)

ICP - Inductively coupled plasma spectroscopy

MS - Mass spectroscopy (or mass spectrometer)

NPH - Normal paraffin hydrocarbon

PNL - Pacific Northwest Laboratory

RPD - Relative percent differences

SOW 288 - Version of EPA CLP organic procedures for CERCLA work, issued in February, 1988

SOW 787 - Version of EPA CLP inorganic procedures for CERCLA work, issued in July, 1987

SW 846 - EPA procedures for RCRA work

SST - Single-shell tank in which Hanford's radioactive waste is stored

TIC - Total inorganic carbon

TOC - Total organic carbon

WHC - Westinghouse Hanford Company

1.0 INTRODUCTION

A major effort at Hanford over the next few years will be to sample and analyze wastes contained in 149 single-shell tanks (SSTs). In preparation for this effort, selected analyses were performed on four archived samples to compare analytical methods and to determine applicability of these methods to the waste samples.

The analyses used a variety of analytical methods including both Pacific Northwest Laboratory (PNL) technical procedures and adaptations of U.S. Environmental Protection Agency (EPA) technical procedures. Quality control included use of blanks and spikes, but did not include all EPA requirements such as use of control charts. Since the objective was evaluation and comparison of methods rather than determining precise values, this degree of quality control was considered to be sufficient.

This report describes and presents results of the preliminary trial analyses of archived SST samples by the Chemical Measurements Laboratory section of PNL. The archived samples were wastes from waste tanks 102-C, 105-C, and 106-C, and a composite of supernatant liquid from waste tanks 102-AX and 106-C. As stated in the Test Plan for Analysis of Archive Samples of Single-Shell Tank Samples Provided by Westinghouse Hanford Company (Project 13924), the test scope and objectives are as follows:

- to determine if there are problems with employing the various analytical methods on the test samples
- to determine if the ICP has sufficient sensitivity for the analysis of EP Toxicity metal ions (excluding mercury, which will be analyzed by the cold vapor method)
- to determine which of the 22 EPA pollutant metal ions can be determined by ICP analysis
- to determine if mercury can be determined by the cold vapor method
- to determine whether the EPA semivolatile organic method can be employed on SST samples
- to determine solubility of inorganic and radiochemical ions in NPH
- to gather information on the radiological exposure and time durations required in utilizing the various methods

- to gather information relevant to the potential use of radionuclide ratioing and parent-daughter relationships for the estimation of radionuclides within samples.

The following tasks were performed: 1) organic and inorganic analyses were performed on sample 102-C, 2) radiochemical analyses and ICP inorganic analyses were performed on samples 105-C and 106-C, and 3) the normal paraffin hydrocarbon (NPH) radiochemical and inorganic measurements were performed on a combined sample of 106-C and 102-AX supernatant (not 105-C and 102-AX as specified in the Test Plan). The Test Plan is included as an Appendix.

The analysis of the SST archive samples involved three types of measurements: inorganic analysis, organic analysis, and radiochemical analysis. This report is divided into five sections; the first three separately discuss each of the measurement categories, a fourth section discusses the NPH study, and the final section addresses radiological exposure measurements. The objectives for each measurement category, which are bulleted on page 1 of the Test Plan, are addressed at the end of each section.

The tables and figures for Sections 2.0 through 6.0 are at the end of each section.

2.0 INORGANIC ANALYSIS

The sample preparation and percent solids determinations are included in this section, as well as a discussion of the results from the following test methods: water leach, EP Toxicity, acid digestion, fusion, mercury analysis, and total cyanide. (The water leach and fusion procedures are PNL techniques; other procedures are EPA-based.) Inorganic analyses addressed four Test Plan objectives, as described in Section 2.3.

The Test Plan for the SST samples calls for duplicate and spike analyses by each of the inorganic test methods (except fusions) to obtain information about the reproducibility of results obtained with these methods and to validate the data generated from the water leach and the EP Toxicity procedures.

To evaluate inorganic test method performance, the EPA contract laboratory procedure (CLP) SOW 787 criteria for sensitivity, reproducibility of duplicate analyses, and spike recovery were applied to all test results, although the criteria are only intended for acid-digested soil and water samples. Detection limits were estimated rather than measured precisely. For reference purposes only, the following criteria (which are similar to those used in SOW 787) are used throughout this report:

- Spike sample analysis--the acceptance range for spike recovery is 75% to 125%.
- Duplicate sample analysis--the relative percent differences (RPD) between duplicate sample analyses must be within $\pm 20\%$ if the results of the element analyzed are at least five times the estimated methods detection limit. RPD is defined as $\{(S - D) / [(S + D)/2]\} \times 100$, where S = sample value and D = duplicate value.
- ICP serial dilution--a five-fold dilution must agree with the original analysis to within a percent difference of $\pm 10\%$ if the element analyzed is at least 50 times the estimated method detection limit. Percent difference is defined as $[(I - D) / I] \times 100$, where I = initial solution value and D = diluted solution value.

2.1 TEST METHODS, RESULTS, AND DISCUSSION

2.1.1 Sample Preparation

In accordance with the Test Plan, portions of SST sample 102-C were prepared for analyses for three analyte categories: 1) inorganic cations by ICP (inductively coupled plasma - atomic emission spectroscopy), 2) inorganic anions by ion chromatography (IC), and 3) total organic carbon (TOC) and total inorganic carbon (TIC). Solid samples from SST 102-C and SST 105-C were crushed, sieved, and homogenized as illustrated in Figure 1 of the Test Plan (see Appendix). (Sample 106-C was previously prepared for earlier tests using a similar process). Samples 105-C and 106-C were then fused for measurement of inorganic cations by ICP and for radiochemical analysis.

2.1.2 Percent Solids Determination

The percent solids content of two 1.0- to 1.5-g portions of SST 102-C were determined by comparing the sample weight before and after drying at 103°C to 105°C, as illustrated in Figure 2 of the Test Plan (see Appendix). The result, defined as $[(\text{sample dry weight}/\text{sample wet weight}) \times 100]$, was approximately 94% solids for both samples.

2.1.3 Water Leach

As shown in Figure 3 of the Test Plan (see Appendix), the water leach procedure involved leaching the samples with deionized water (DIW) in an ultrasonic bath for 1 h, filtering the solution through 0.45- μm filters, and analyzing the filtered solutions. The ICP results for 38 elements are given in Table 2.1. The values in the columns labeled "Raw ICP ($\mu\text{g/mL}$)" are the observed elemental concentrations; the values in the columns labeled "Corr. ($\mu\text{g/mL}$)" are the observed elemental concentrations corrected for spectral interferences from U and Al. Elements that are followed by an (e) are not present in sufficient concentration for accurate results due to low sensitivity by ICP analysis and/or significant spectral corrections for U and Al. Table 2.2 shows the effects of spectral interferences from a standard U solution on elements analyzed by the ICP. Note that U significantly interferes with the Se, Sb, and Tl analyses and, to a lesser degree, the Si and P analyses. Similar interferences occur from Al (especially for As), but for most elements this is to a lesser degree than for U. The data in Table 2.1 demonstrate

interferences clearly, since the raw ICP results for Sb, Se, and Tl are positive, whereas the values after correction for U and Al interference are negative, which mandates reporting a "less than" value or analysis by an alternative method. For those elements that have significant spectral interferences by ICP analysis, analysis by graphite furnace atomic absorption (GFAA) may be required. Note that for most elements the RPD is considerably larger than the $\pm 20\%$ that is considered acceptable according to the performance criteria defined in Section 2.0. As discussed in Section 2.2, dissolution of these matrices in water will yield erratic results, which is reflected in these data.

The IC, TOC, and TIC results are presented in Table 2.3. The low spike recovery for Cl and PO₄ cannot be readily explained. The average orthophosphate value of 1030 mg/kg from IC analysis of samples 1 and 2 is 17% lower than the ICP P value of 405 mg/kg, if the latter is assumed to be all orthophosphate (1242 mg/kg). Total P is measured by ICP, whereas IC is specific for orthophosphate ion. If some of the P were present in other ionic forms, this might explain the higher ICP result.

2.1.4 EP Toxicity

A modified EP Toxicity study was performed on duplicate 10-g portions of SST archive sample 102-C according to EPA SW 846, Method 1310, as shown in Figure 4 of the Test Plan (see Appendix). The study consisted of a spike recovery study for eight elements on the EP Toxicity list; analysis of 10-mL aliquots of the filtered solutions after leaching with dilute acetic acid; and analysis of 5X serial dilutions of the aliquots.

The results of the spike recovery study, measured by ICP analysis with the use of duplicate 10-g samples, are given in Table 2.4. Spike recovery values were anomalously high for Cr, Se, and Tl. Poor ICP sensitivity and significant spectral correction due to U interference may have been the cause for the high values for Se and Tl; GFAA analysis may be required for these elements. The reason for the high Cr recovery is unknown.

Complete ICP analyses were performed on samples prepared by the EP Toxicity protocol. Results on both the original solutions and on 5X serial dilutions are presented in Table 2.5. It is clear from the percent difference

results for the undiluted and 5X diluted measurements for the duplicate samples that the reproducibility of the serial dilution values is within acceptable limits for most of the elements. If acetic acid affects the ICP results, greater differences would be expected between the two solutions since the diluted sample contains only one-fifth the acetic acid concentration (0.02 M versus 0.1 M). The fact that the results of the 5X serial dilution are within the acceptance limits indicates that acetic acid concentration does not significantly affect the ICP results.

Table 2.6 also contains the EP Toxicity results for SST sample 102-C. However, the results are given in units of mg/kg (rather than the typically reported mg/l units) so that the results can be compared more directly with those of the samples prepared by acid digestion and by fusion. Note that for many elements the RPD between duplicate sample analyses is larger than the $\pm 20\%$ that is considered acceptable according to the performance criteria defined in Section 2.0. As discussed in Section 2.2, dissolution of these matrices in dilute acetic acid can yield erratic results, which are reflected in these data.

2.1.5 Acid Digestion

The acid digestion and filtration portion of the sample preparation was performed in the hot cell according to SOW 787 using 1.0- to 1.5-g samples of SST 102-C. Since the sample preparation adhered to the CLP method as closely as was reasonably possible in the hot cell, no further discussion of the sample preparation for the acid digestion method is given in this report. This acid digestion method was selected over the SW 846 method since SW 846 required the solutions to be evaporated without boiling to near dryness, which would significantly increase the sample preparation time.

The ICP and GFAA results given in Table 2.7 show that the RPDs between duplicate analyses are within $\pm 20\%$ except for the elements B, Cd, Cu, K, Si, Tl, and V. All of these elements (except Si) are at or near the estimated detection limit of the ICP analysis. During the acid digestion procedure, silicates partially dehydrate to insoluble SiO_2 . Since this dehydration is not reproducible, the Si results may be erratic. However, Si is currently not identified as an EPA priority pollutant.

Also, five of the elements with poor spike recovery that are listed in Table 2.7 (i.e., As, P, Pb, Sb, and Tl) are noted as having poor instrument sensitivity and significant spectral interference from U and Al when analyzed by ICP. Data for these elements can be used for comparison purposes only. Although corrections are a significant percentage of the "raw" intensity, the observed values agree reasonably well with the GFAA results for Pb. A comparison of the ICP and GFAA results shows that Sb, Se, and Tl cannot be analyzed at low concentrations with good accuracy by ICP due to poor ICP sensitivity and large spectral interference from U. These elements are candidates for GFAA analysis. Only As and Pb have potential for analysis by ICP, and only then in the absence of interferences such as Al and U.

Results of serial dilution measurements on selected elements from the acid-digested samples are given in Table 2.8. The percent difference values for the serial dilution results are much less than $\pm 10\%$, and thus chemical or physical interference effects would not be expected from the matrix.

2.1.6 Fusion: ICP Analysis

As shown in Figure 8 of the Test Plan (see Appendix), portions of SST sample 102-C were fused in the hot cell with KOH in a Ni metal crucible; a second fusion was also performed with Na_2O_2 in a Zr metal crucible. After cooling, the fused mixtures were dissolved in DIW. The solutions were transferred into volumetric flasks, acidified with HCl, diluted to volume, and aliquots were removed from the hot cell for ICP analyses. The ICP analyses of the KOH/Ni and the Na_2O_2 /Zr fusions are presented in Table 2.9 for comparison of analytical methods. The RPD in the ICP results for the two fusion methods is within $\pm 20\%$, except for some cations that are near the estimated detection limit of the ICP method or for cases that require significant spectral corrections due to interferences from U and Al.

Also, the precipitates filtered from the acid digestion of samples 1 and 2 from SST sample 102-C were fused, as shown in Figure 8 of the Test Plan (see Appendix), and analyzed. A summation of the results for the acid-soluble and acid-insoluble fused portions are given in Table 2.10. The major acid-insoluble constituents in these samples are Al, Ca, Fe, Mg, and Si, indicating the presence of some type of zeolite or acid-insoluble mineral compound in the waste tank sample.

Since SST samples 105-C and 106-C were fused and dissolved for radio-chemical analysis (see Section 4.0); ICP analyses were also performed. The ICP results for these samples, as well as for SST sample 102-C, are tabulated in Table 2.11. The three tank samples show significant differences in chemical composition of the major constituents, which is expected.

2.1.7 Comparison of Water Leach, EP Toxicity, Acid Digestion, and Total Fusion ICP Analysis Results

Analytical results from the four methods used for sample preparation of archive SST sample 102-C for inorganic constituents are given in Table 2.12; these are reported in units of mg/kg to allow direct comparison. As mentioned in Section 2.1.6, the acid-insoluble portion of the sample was also fused and analyzed. Thus, the sum of "Acid Digestion" and "Acid Insol Fusion" should be equal to the "Fusion" values, provided that none of the acid-insoluble precipitate was lost during the transfer of the filter to the metal crucible used for fusion of the sample.

Note: A 0.45- μ m membrane disposable plastic filtration apparatus was used to filter the acid digestion solution in the hot cell. When the filtration apparatus was taken apart in the hot cell, some of the precipitate could have been lost. Therefore, the acid-insoluble results should be used for indication purposes only.

The AI result for the water leach sample is higher than the AI value for the EP Toxicity solution. The pH of the EP Toxicity leachate prior to acetic acid addition was 11.4. The pH of the water leach was not measured. However, if it is assumed that the pH of the water leach was similar to that measured for the EP Toxicity method, some of the AI should be in the form of a soluble aluminate. Since the final pH for the EP Toxicity method is adjusted to slightly acid or near neutral (pH 5.0 or until a specified amount of acetic acid has been added), all of the AI should be precipitated as hydroxide. Other metal ions may coprecipitate as well during the formation of the flocculent aluminum hydroxide.

It is interesting that P and Zr were lower for the EP Toxicity sample than for the water leach sample. However, it was observed that the water leach samples that were filtered through the 0.45- μ m filter coagulated a flocculent light-reddish precipitate when the solution was left undisturbed over the weekend. One plausible explanation is that the Zr and P may have

existed as a colloidal suspension in the water leach sample. If so, when the pH was adjusted to 5.0 with acetic acid according to the EP Toxicity method, the colloid coprecipitated when the aluminate ion was converted to $\text{Al}(\text{OH})_3$, thus significantly reducing the concentration of the Zr and P in solution.

2.1.8 Mercury Analysis by Cold Vapor Atomic Absorption (CVAA)

The Hg analysis was performed on 1.1005 g and 1.3188 g samples using CLP SOW 787 method 245.5 with some modification, as described in Section 2.2. The Hg was determined on a Perkin-Elmer atomic absorption unit in an open-faced hood. The Hg values for the duplicate analyses were 0.568 mg/kg and 0.572 mg/kg, giving a RPD of 2.4%. A third sample weighing 1.3347 g was spiked with 1.5 μg of Hg; the spiked sample was treated in the same manner as the other two samples. The spike recovery was 97%.

2.1.9 Total Cyanide

The analysis of total cyanide was performed using CLP SOW 787 method 335.2, rather than SW 846 method 9010 as described in the Test Plan. Method 335.2 was modified by substituting MgSO_4 for MgCl_2 as the catalyst for decomposition of the ferrocyanide complex. It was found that if 1 g of NaNO_3 was added to the cyanide distillation apparatus containing MgCl_2 , very poor cyanide recovery was observed. When MgSO_4 was substituted for MgCl_2 , the cyanide recovery improved dramatically. Due to the high nitrate concentrations in SST wastes, MgSO_4 was used routinely in this analysis. Hach kits utilizing the addition of dry chemicals were used for colorimetric analysis. The cyanide values reported for duplicate analyses are 0.92 mg/kg and 1.10 mg/kg, giving a RPD of 17.8%. These values are significantly lower than the EPA reactivity limit of 250 mg/kg. Total cyanide spike recovery was 87%.

2.2 PROBLEM AREAS AND CORRECTIVE ACTIONS

2.2.1 ICP Spectral Corrections

All EPA ICP analysis protocols require that spectral corrections be applied to all elements to obtain background and interelement corrected results. The ICP analyses performed on the SST samples deviated from these requirements. The Applied Research Laboratory (ARL) ICP used to analyze these samples determines 12 of the 38 elements with the sequential spectrometer.

The analysis time for each element on the sequential system is comparable to the analyses time for all 26 elements on the simultaneous system. Since one third of the required elements were determined sequentially, the time required to scan all of the element combinations to determine spectral correction factors would be prohibitive; therefore, no spectral correction factors were entered into any of the calculation programs. For the analysis results in this report, spectral corrections from U and Al were calculated by hand and the corrections applied to each analysis element.

2.2.2 Poor Reproducibility from Water Leach and EP Toxicity Methods

The RPD values calculated from the water leach and EP Toxicity data are outside the control limit of $\pm 20\%$ for most of the elements. This is true even though the concentrations for several of the elements are a factor of 5 greater than the estimated ICP detection limit. If the RPD values for the duplicate sample analyses on the water leach and EP Toxicity measurements are compared with those for the acid digestion and fusion methods, the values for the latter two procedures are significantly better. This is because when samples are leached with water, or with dilute acetic acid as in the EP Toxicity method, the amount of a given element brought into solution can be highly variable due to small variations in acidity, alkalinity, particle size of the sample, and leaching time and temperature. This is not the case for the more robust acid digestion or fusion techniques.

2.2.3 Modification to CVAA Method

When a significant concentration of Hg (i.e., $>10 \mu\text{g}$) was reduced to metal with SnCl_2 and air sparged into a KMnO_4 solution, a significant portion of the elemental Hg was trapped in the fritted cylinder in the trap solution. Once trapped, the Hg could not be quantitatively recovered. The CVAA Hg method was modified in the following manner for the SST sample analyses.

1. After digestion of the sample with KMnO_4 , a portion of the sample was removed from the hot cell.
2. A measured aliquot of the KMnO_4 -treated sample was pipetted into the CVAA apparatus and the Hg was reduced with SnCl_2 and analyzed.
3. The Hg in the sample was calculated using the dilution of the sample aliquot analyzed and the volume of the solution in No. 1.

2.3 CONCLUSIONS RELATED TO TEST PLAN OBJECTIVES

2.3.1 To Determine if There Are Problems with Employing the Various Analytical Methods on the Test Samples

No major difficulties were encountered in the water leach, EP Toxicity, acid digestion, or fusion procedures for inorganic analysis. It should be recognized that the reproducibility of water leach and EP Toxicity procedures will be very poor on samples where the major metal ions in the basic sludge are multivalent metal ions, since several of these ions would be precipitated as basic hydroxides. Poor reproducibilities are expected since most of the multivalent metal ions are not soluble in basic or slightly acidic solution. Since a significant portion of SST sample 102-C is Al, Ca, Fe, Mn, Ni, U, and Si, the reproducibility of duplicate analyses for these elements is expected to be worse for water leach or EP Toxicity samples than for acid-digested samples. This was substantiated by the analyses that were performed.

An interesting observation from the results presented in Table 2.12 is that several of the metal ions that form insoluble hydroxides are higher in the water leach than in the EP Toxicity sample. When the acid waste from the separation process in the 200 Area chemical processing facilities was neutralized with NaOH, the wastes were made basic to prevent corrosion of the steel SSTs. If the water leach of SST sample 102-C has a starting pH >11, some of the Al will dissolve to form aluminate ions. This is indicated by the high Al content of the water leach sample. Aluminum is amphoteric; therefore, when the solution in the EP Toxicity procedure is neutralized with acetic acid to a pH of 5.0, the soluble aluminate will be neutralized to a gelatinous $\text{Al}(\text{OH})_3$ precipitate, which may coprecipitate any colloidal metal oxides or hydroxides dissolved by the initial water leach in the EP Toxicity procedure.

2.3.2 To Determine if the ICP Has Sufficient Sensitivity for Analysis of EP Toxicity Metal Ions (excluding Hg)

Table 2.13 summarizes the conclusions of this part of the investigation. For the EP Toxicity metal ions As, Pb, and Se, ICP has poor sensitivity, and significant corrections are required for U interference. Elements Se and As require such large spectral corrections for Al and U that these results are not considered reliable at the reported concentration levels.

If the U content in SST sample 102-C were lower, ICP sensitivity would be sufficient to measure all of the EP Toxicity metal ions except Se. The U concentrations in the duplicate analyses after extraction by the EP Toxicity procedure were 430 and 356 $\mu\text{g/mL}$ (Table 2.5). Even this U concentration, however, requires spectral correction to As, Cr, Pb, Se, and Ag of between 50 and 90% of the "raw" intensities. GFAA analysis will be required to measure many of these elements by the EP Toxicity procedure when the samples contain high U and/or Al.

2.3.3 To Determine Which of the 22 EPA Pollutant Metal Ions Can Be Determined by ICP Analysis

Table 2.14 summarizes the conclusions of this part of the investigation. As discussed previously, the ICP has low sensitivity and significant corrections are required because U interferes with measurements of As, Pb, and Se; this is also the case for Sb and Tl. For Ag, Be, Cd, and V (for SST archive sample 102-C) spectral corrections in excess of 50% of the uncorrected ICP values were required. However, because these elements are easily detected, they are still considered measurable by ICP.

2.3.4 To Determine if Mercury Can Be Determined by the CVAA Method

The Hg analysis was performed in duplicate using CLP SOW 787 method 245.5, with modifications. As demonstrated by the excellent test results (i.e., a RPD of 2.4% and spike recovery of 97%), Hg can be determined by CVAA.

TABLE 2.1. SST Sample 102-C Water Leach Measurements by ICP Analysis

Element	Sample 1		Sample 2		RPO (b)	Spike Added ($\mu\text{g/mL}$)	Spike Recovered ($\mu\text{g/mL}$)	% Spike Recovery
	Raw ICP ($\mu\text{g/mL}$)	Corr.(a) ($\mu\text{g/mL}$)	Raw ICP ($\mu\text{g/mL}$)	Corr.(a) ($\mu\text{g/mL}$)				
Ag(e)	-0.009	-0.010	0.008	0.009		0.50	0.43	87
Al	10.5	11.8	17.6	18.4	43.7(c)	1.00	-3.5	-350(d)
As(e)	-0.01	-0.12	0.04	-0.20		1.00	0.38	38(d)
B	1.47	1.65	1.41	1.48	10.9			
Ba	0.006	0.0064	0.016	0.017		1.00	1.04	104
Be	0.0004	0.0004	0.0014	0.0015		0.05	0.054	108
Ca	1.70	1.91	2.66	2.79	37.4(c)	1.00	1.41	141(d)
Cd	0.0		0.0			0.50	0.45	90
Ce(e)	-0.31		-0.25					
Co(e)	-0.009		0.0			0.50	0.47	94
Cr	0.463	0.517	0.609	0.64	21.3(c)	5.00	4.68	94
Cu	0.047	0.053	0.095	0.081	41.8(c)	1.00	1.02	102
Oy(e)	-0.016							
Fe	0.79	0.886	1.65	1.65	60.2(c)	1.00	1.05	105
K(e)	0.41	0.45	0.66	0.69	42.1(c)	4.00	7.15	179(d)
La(e)	-0.025		-0.017					
Li(e)	-0.015		-0.013					
Mg	0.343	0.385	0.63	0.66	52.6(c)			
Mn	0.454	0.509	0.961	1.01	66.0(c)	1.00	1.12	112
Mo(e)	0.012	0.014	0.017	0.018				
Na	113.0	149.0	164.0	172.0	14.3			
Nd(e)	-0.11		-0.085					
Ni	0.604	0.678	1.24	1.30	62.9(c)			
P	4.13	4.63	4.37	4.42	4.6	10.00	11.30	113
Pb(e)	0.115	0.102	0.360	0.296	97.5(c)	1.00	0.90	90
Rh(e)	-0.16		-0.12					
Ru(e)	-0.032		-0.004					
Sb(e)	0.31	-0.061	0.681	-0.020		1.00		(f)
Se(e)	0.32	-0.56	0.974	-1.22		2.00		(f)
Si	12.9	14.5	17.8	18.7	25.3(c)			
Sr	0.013	0.015	0.026	0.028	60.5(c)			
Te(e)	-0.06		-0.034					
Ti	0.018	0.020	0.052	0.055	99.3(c)			
Tl(e)	0.122	-0.27	0.68	-0.30		2.00		(f)
U	5.08	5.70	12.7	13.3	80.0(c)			
V	0.019	0.021	0.03	0.018	15.8	1.00	1.02	102
Zn	0.099	0.112	0.125	0.131	7.4	1.00	0.94	94
Zr	0.270	0.303	0.495	0.52	52.7(c)	1.00	1.05	105

(a) Raw ICP observed results corrected for U & Al interference.

(b) RPD not calculated when analysis results are not 5 times greater than estimated detection limits.

(c) RPD exceeds $\pm 20\%$ criterion defined in Section 2.0.(d) Spike recovery exceeds $\pm 25\%$ criterion defined in Section 2.0.

(e) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

(f) Poor sensitivity and interferences render results meaningless.

TABLE 2.2. Uranium Correction Factors for Elements Measured by the ARL ICP

Direct Reader Elements	Wavelength	$\mu\text{g/mL}$ Element Interference from		Potential to Reduce Interference(a)
		100 $\mu\text{g/mL U}$	500 $\mu\text{g/mL U}$	
Al	309.270	1.07	5.08	?
B	249.680	0.113	0.609	Yes
Ba	455.4	0.022	0.114	Yes
Ca	393.370	0.005	0.101	?
Ce	413.76	0.682	3.096	Yes
Cr	267.720	0.329	1.501	?
Dy	353.170	0.0686	0.322	Yes
Fe	259.94	0.135	0.674	Yes
K	766.49			?
La	379.480	0.085	0.394	Yes
Li	670.780	0.007	0.015	Yes
Mg	279.52	0.005	0.033	Yes
Mn	257.610	0.043	0.140	?
Mo	202.030	0.021	0.075	Yes
Na	589.590	0.261	0.089	Yes
Nd	406.110	0.361	1.710	?
Ni	231.600	0.080	0.332	Yes
Rh	343.49	0.655	3.034	Yes
Ru	240.270	0.240	1.022	?
Si	288.160	1.959	5.912	?
Sr	407.770	0.008	0.062	Yes
Te	214.280	0.154	0.588	Yes
Ti	337.280	0.031	0.135	Yes
Zn	213.860	0.002	0.024	Yes
Zr	339.200	0.052	0.240	Yes
Sequential Elements				
Ag	328.068		1.123	?
Cu	324.754	0.145	0.744	?
Be	313.042	0.009	0.044	?
V	292.402	0.108	0.519	?
Tl	276.787	7.777	37.57	?
Co	228.616	0.050	0.240	?
Pb	220.353	0.477	1.982	?
Sb	206.833	6.210	33.56	No
P	214.914	1.264	5.057	No
Se	196.026	17.05	79.13	No
As	193.696	1.911	6.987	?
Cd	226.502	0.026	0.039	Yes

(a) "Yes" (or "No") indicates there is (or is not) a potential to minimize interference effects by the use of off-peak background correction techniques. "?" indicates the potential is unknown.

TABLE 2.3. Anion Analysis of Water Leach from SST Sample 102-C

Anion	Sample 1 (mg/kg)	Sample 2 (mg/kg)	RPD	Spike Added (mg/kg)	Spike Recovered (mg/kg)	% Spike Recovery
F	301	260	14.6	200	190	95
Cl	388	342	12.6	370	185	50(a)
NO ₂	3,400	3,000	12.5	13,400	14,600	110
NO ₃	9,900	9,690	2.1	1,500	1,105	74(a)
PO ₄	1,140	910	22.4(b)	1,150	805	70(a)
SO ₄	835	814	2.6	2,860	2,586	90
TIC(c)	3,900	3,280	17.2			
TOC(c)	262	284	8.1			

(a) Spike recovery exceeds $\pm 25\%$ criterion defined in Section 2.0.

(b) RPD exceeds $\pm 20\%$ criterion defined in Section 2.0.

(c) TIC = Total inorganic carbon; TOC = Total organic carbon.

TABLE 2.4. EP Toxicity Measurements and Spike Recovery Study by ICP Analysis for SST Sample 102-C

EP Toxicity Element	EP Toxicity Measurements			Spike Recovery Measurements		
	Sample 1 ($\mu\text{g/mL}$)	Sample 2 ($\mu\text{g/mL}$)	RPD	Spike Added ($\mu\text{g/mL}$)	Spike Recovered ($\mu\text{g/mL}$)	% Spike Recovery
Ag(d)	0.003	0.17	193(a)	5.0	4.63	93
As(d)	1.63	2.39	37.8(a)	5.0	4.42	88
Ba	0.018	0.02	10.5	5.0	4.96	99
Cd(d)	0.009	0.068	153(a)	1.0	0.99	99
Cr	1.46	1.74	17.5	5.0	7.25	145(b)
Hg(c)	0.0066	0.0063	4.7			
Pb(d)	0.07	0.54	154(a)	5.0	4.10	82
Se(d)	0.5	8.6	178(a)	1.0	3.90	390(b)

(a) RPD exceeds $\pm 20\%$ criterion defined in Section 2.0.

(b) Spike recovery exceeds $\pm 25\%$ criterion defined in Section 2.0.

(c) Hg analyses performed by CVAA.

(d) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.5. Results of 5X Dilution on EP Toxicity Measurements by ICP for SST Sample 102-C

Element	Sample 1 ($\mu\text{g/mL}$)		Percent Difference	Sample 2 ($\mu\text{g/mL}$)		Percent Difference
	Direct	5X Dil		Direct	5X Dil	
Ag(c)	0.003	0.128	(a)	0.17	0.16	0.59
Al	17.4	18.2	4.4	9.29	9.64	3.6
As(c)	1.63	1.03	37.0	2.39	0.21	165.0
B	1.20	7.97	564(b)	1.39	7.81	462(b)
Ba	0.018	0.021	(a)	0.02	0.02	(a)
Be	0.001	0.0	(a)	0.004		(a)
Ca	17.6	18.7	5.8	14.9	15.7	5.1
Cd	0.009	0.0	(a)	0.068	0.01	(a)
Ce(c)	-0.09		(a)	0.41		(a)
Co(c)	0.005		(a)	0.037		(a)
Cr	1.46	1.60	8.8	1.74	1.62	6.9
Cu	0.49	0.50	2.0	0.40	0.36	10.0
Dy(c)	-0.002		(a)	-0.027		(a)
Fe(c)	-0.025		(a)	0.04		(a)
K	10.8	10.7	0.9	9.9	9.43	4.8
La(c)	-0.009		(a)	0.05		(a)
Mg	1.13	1.28	11.7	1.02	1.10	7.3
Mn	0.611	0.628	2.7	0.51	0.46	9.8
Mo(c)	-0.001		(a)	0.02		(a)
Na	1340.	1330.	0.8	1210.	1260.	4.0
Nd(c)	-0.01		(a)	0.18		(a)
Ni	0.206	0.216	4.6	0.23	0.15	35.0
P(c)	3.04	2.16	29.0	4.35	2.42	44.0
Pb(c)	0.07		(a)	0.54		(a)
Rh(c)	-0.04		(a)	0.3		(a)
Ru(c)	-0.04		(a)	0.13		(a)
Sb(c)	-0.2		(a)	0.1		(a)
Se(c)	0.5		(a)	8.6		(a)
Si	112.	108.	3.6	107.	101.	5.6
Sr	0.54	0.57	5.3	0.45	0.47	4.3
Te(c)	0.009		(a)	0.15		(a)
Ti	0.010	0.01	0.0	0.037	0.0	(a)
Tl(c)	0.31		(a)	3.1		(a)
U	430.	392.	8.8	356.	364.	2.2
V	0.116	0.124	6.5	0.14	0.08	43.0
Zn	0.734	0.83	11.6	0.51	0.55	7.3
Zr	0.004		(a)	0.03		(a)

- (a) RPD not calculated since "direct" results are not 50 times estimated detection limits.
- (b) Reason for large percent difference is unknown, possible borosilicate glass contamination.
- (c) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.6. EP Toxicity Results by ICP Analysis in Units of mg/kg
for SST Sample 102-C

Element	Sample 1 (mg/kg)	Sample 2 (mg/kg)	RPD
Ag(d)	0.006	3.4	(a)
Al	347	185	61(b)
As	32	48	40(b)
B	24	28	15
Ba	0.36	0.4	(a)
Be	0.02	0.08	(a)
Ca	350	297	16
Cd	0.18	1.4	(a)
Ce(d)	-1.8	8.2	(a)
Co(d)	0.1	0.8	(a)
Cr(c)	29	35	19
Cu(c)	9.8	8.0	20
Dy(d)	-0.04	-0.6	(a)
Fe(d)	-0.5	0.8	(a)
K	215	197	9
La(d)	-0.18	1.0	(a)
Mg	22	20	9.5
Mn	12.1	10	19
Mo(d)	0.02	0.4	(a)
Na	26,700	24,000	11
Nd(c, d)	-0.2	3.6	
Ni(c)	4.1	4.6	11
P(d)	61	87	35(b)
Pb(d)	1.4	11	(a)
Rh(d)	0.8	6.0	(a)
Ru(d)	-0.8	2.6	(a)
Sb(d)	-4	2	(a)
Se(d)	10	170	
Si	2,230	2,100	6
Sr	11	9.0	20
Te(d)	0.18	3.0	(a)
Ti	0.2	0.74	(a)
Tl(d)	6.0	62	
U	8,580	7,100	19
V(c)	2.3	2.8	20
Zn	14.6	10	37(b)
Zr	0.08	0.6	(a)

- (a) RPD not calculated; analysis results are not 5 times the estimated detection limit.
 (b) RPD exceeds $\pm 20\%$ criterion defined in Section 2.0.
 (c) U interference correction greater than 50% of element's raw intensity.
 (d) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.7. Acid Digestion Measurements and Spike Recovery Study by ICP for SST Sample 102-C (including GFAA Results)

Element	Sample 1 (mg/kg)	Sample 2 (mg/kg)	RPD	Spike Added	Spike Recovered	% Spike Recovery
Ag(a,b)	26.1	27	3	92.6	89.8	97
Al	132,000	158,000	18			
As(a)	39	42	7	370	279	75
B	200	70	96(c)			
Ba(b)	37.2	39.6	6	370	274	74(d)
Be(a,b)	2.33	2.78	18	9.3	9.8	106
Ca	1,810	2,000	10	1,851	2,040	110
Cd(a,b)	8.56	12.7	39(c)	92.6	91.8	99
Co(a,g)	-0.8	-2.1		92.6	95	102
Cr(a)	243	248	2	2,780	2,890	104
Cu(a)	253	197	25(c)	185		(f)
Fe(a)	10,290	10,950	6			
K(a)	330	463	33(c)	185	36	19(d)
Mg(a)	580	632	9	370	395	107
Mn(a)	1,950	2,070	6			
Na(a)	34,050	34,490	1			
Ni(a)	2,452	2,477	1			
P	1,190	1,250	5	1,970		(e)
Pb(a)	637	683	9	556	395	71(d)
Sb(a,g)	-160	-156		93		(d)
Se(a,g)	160	135	17			
Si	1,245	968	25(c)			
Sr	39.5	40.7	3	185	200	108
Ti	936	1,044	11			
Tl(a,g)	51	38	29(c)	370	143	39
U	21,300	21,300	0.5			
V(a,b,g)	20	25	22(c)	93	100	108
Zn(a)	222	186	18	93	56	60
Zr	317	356	12	185		(f)

GRAPHITE FURNACE ATOMIC ABSORPTION RESULTS

As = 95 mg/kg Pb = 780 mg/kg Sb = <30 mg/kg
Se = <30 mg/kg Tl = <1 mg/kg

(Note: No spike recoveries performed by GFAA)

- (a) EPA pollutant metal ions.
(b) U interference correction greater than 50% of element's raw intensity.
(c) RPD exceeds ±20% criterion defined in Section 2.0.
(d) Spike recovery exceeds ±25% criterion defined in Section 2.0
(e) Zr probably precipitated as a zirconium phosphate compound.
(f) Cu and P channel lost during spike analyses.
(g) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.8. ICP Serial Dilution Results of Acid Digestion of
SST Sample 102-C

Element	Sample 1			Sample 2		
	5X Dil ($\mu\text{g/mL}$)	25X Dil ($\mu\text{g/mL}$)	Percent Difference	5X Dil ($\mu\text{g/mL}$)	25X Dil ($\mu\text{g/mL}$)	Percent Difference
Al	678	695	2.5	684	694	1.5
Ca	9.30	9.75	4.8	8.63	8.95	3.7
Fe	52.9	53.9	1.9	47.3	47.9	1.3
Mg	2.98	3.06	2.7	2.73	2.78	1.8
Mn	10.0	10.2	2.0	8.94	9.03	1.0
Na	175	170	2.3	149	150	0.7
Ni	12.6	12.9	2.3	10.7	10.9	1.9
Ti	4.81	4.86	1.0	4.51	4.55	0.9
U	110	109	0.9	92	90	2.2
Zn	1.14	1.14	0.0	0.804	0.780	3.0
Zr	1.63	1.68	3.1	1.54	1.54	0.0

NOTE: Original digestates required a 5X dilution in order to place the element concentrations within a linear range for ICP analysis. The dilution study was performed by diluting this 5X solution another 5 fold.

TABLE 2.9. Comparison of KOH and Na₂O₂ Fusion of ICP Analysis for SST Sample 102-C

Element	KOH Fusion (mg/kg)	Na ₂ O ₂ Fusion (mg/kg)	RPD
Ag(d)	28	81	(a)
Al	220,000	222,000	0.9
As(d)	590	470	22.6(b)
B	9,800	11,300	13.9
Ba	105	108	2.8
Ca	9,140		(c)
Cr	280	340	19.3
Cu	230	270	16.0
Fe	18,700	19,300	3.2
K		3,500	(c)
Mg	3,400	3,700	8.4
Mn	2,250	2,240	0.7
Na	50,300		(c)
Ni		2,770	(c)
P(d)		1,600	(c)
Pb(d)	730	3,200	126
Sb(d)	860	990	14.0
Se(d)	850	760	11.2
Si	75,700	73,400	3.2
Sr	80	125	(a)
Ti	1,620	1,660	2.4
Tl(d)	1,000	1,200	9.1
U	19,400	21,060	8.2
Zn	260	200	(a)
Zr	940		(c)

- (a) RPD not calculated since analysis results are not 5 times the estimated detection limits.
- (b) RPD exceeds ±20% criterion defined in Section 2.0.
- (c) Results for only one analysis due to the flux and crucible used.
- (d) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.10. Sum of Acid Digestion and Fusion of Acid Insoluble Residue for SST Sample 102-C

Element	Acid Digestion [A] (mg/kg)		Acid Insol Fused [B] (mg/kg)		Total: [A]+[B] (mg/kg)	
	Sample 1	Sample 2	Sample 1(a)	Sample 2(b)	Sample 1	Sample 2
Ag(d)	26.1	27				
Al	135,200	158,000	40,800	41,800	175,800	199,800
As(d)	39	42	240		279	42
B	200	70	1,900	2,100	2,100	3,170
Ba	37	40	40	47	77	87
Be	2.3	2.8			2	3
Ca	1,810	2,000	4,000		5,800	2,000
Cd	9	13				
Cr	243	248	20		263	248
Cu	253	197			253	197
Fe	10,290	10,950	4,550	5,300	14,800	16,250
K	330	463			330	463
Mg	580	632	1,540	2,130	2,120	2,760
Mn	1,950	2,070	107	120	2,060	2,190
Na	34,050	34,500			34,050	34,500
Ni	2,450	2,480			(c)	2,480
P	1,190	1,250	590	220	1,780	1,470
Pb(d)	637	683	150	360	787	1,223
Sb(d)	-160	-156	320		160	-156
Se(d)	160	135			160	135
Si	1,245	968	36,800	49,300	38,000	50,300
Sr	40	41	26	38	80	125
Ti	936	1,040	400	450	1,340	1,490
Tl(d)	51	38			51	38
U	21,400	21,300	95		21,500	21,300
V(d)	20	25			20	25
Zn	220	186	20	20	240	206
Zr	317	356			317	(c)

(a) KOH/Ni Fusion

(b) Na₂O₂/Zr Fusion

(c) Fusion crucible contamination; only one fusion result summed.

(d) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.11. Comparison of ICP KOH Fusion Results for SST Samples 102-C, 105-C, and 106-C

Element	Sample 102-C(a) (mg/kg)	Sample 105-C (mg/kg)	Sample 106-C (mg/kg)
Ag(c)	180	170	2,100
Al	225,000	246,000	115,000
As(c)	230	320	390
B	150	300	350
Ba	110	150	350
Ca	9,400	1,600	1,900
Cd	80	80	
Ce(c)	60	270	490
Cr	280	1,400	1,750
Cu	280	160	300
Fe	19,500	15,300	82,400
Mg	3,520	330	420
Mn	2,300	7,120	4,500
Mo	150		
Na	42,600	64,400	156,000
Nd(c)	60	210	560
P	3,100	5,900	7,300
Pb	890	1,130	2,500
Sb(c)		2,500	2,900
Se(c)		1,000	1,400
Si	76,800	10,800	26,000
Sr	80	160	110
Ti	1,750	230	330
Tl(c)	2,300	1,600	1,200
U	23,300	10,500	(b)
V(c)	90	60	
Zn	160		
Zr	1,320	710	600

- (a) Additional Sample 102-C fusion analysis performed for comparison with Samples 105-C and 106-C. Note values correspond well with those reported in Table 2.9, except for B.
- (b) For Sample 106-C the uranium is below the estimated detection limit of the ICP method--uranium by laser method yielded 8,200 mg/kg and 944 mg/kg for Sample 105-C and 106-C, respectively.
- (c) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.12. Direct Comparison of the Test Methods by ICP for SST Sample 102-C (in mg/kg) (a)

Element	Water Leach	EP Toxicity	[A] Acid Digestion	[B] Acid Insol Fusion	[A]+[B]	Fusion
Ag(b)	0.0	1.7	27			
Al	1,300	266	145,000	41,300	186,300	221,000
As(b)		40	40	40	80	530
B	140	26	235	2,000	2,200	10,600
Ba	1.0	0.19	38	43	80	107
Be	0.08	0.05	2.6		3	
Ca	210	324	1,900	4,000	5,900	9,140
Cd	0.0	0.71	11		11	
Co(b)	0.4					
Cr	51	32	246		246	310
Cu	6.4	8.9	225		225	250
Fe	50		10,620	4,900	15,500	19,000
K	50(b)	206	400		400	3,500
Mg	44	21	606	1,800	2,400	3,560
Mn	65	11	2,010	114	2,120	2,240
Mo	1.4	0.2				
Na	13,850	25,350	34,270	4,300	38,600	50,300
Ni	84	4.4	2,464		2,464	2,770
P	400	74(b)	1,220	400	1,600	1,600
Pb	17(b)	6.2(b)	660	250	900	2,000
Se(b)	58	90	150			
Si	1,430	2,160	1,106	43,000	44,100	74,500
Sr	1.8	10	40	32	70	102
Te(b)		1.6				
Ti	3.1	0.5	990	425	1,420	1,640
Tl(b)		34	44		44	
U	820	7,840	21,300		21,300	20,230
V(b)	1.8	2.5	22		22	
Zn	11	12	204	20	224	235
Zr	35	0.3	336		336	940

(a) All reported results are averages of duplicate analyses.

(b) Because of high dilution factors and interferences, the values reported are not reliable and were included only for understanding the analytical method.

TABLE 2.13. Summary of EP Toxicity Metal Ions by ICP

<u>Element</u>	<u>Sufficient Sensitivity?</u>	<u>Element</u>	<u>Sufficient Sensitivity?</u>
Ag	Probable	Cr	Probable
As	No	Pb	No
Ba	Yes	Se	No
Cd	Yes		

TABLE 2.14. Summary of EPA Pollutant Metal Ions by ICP

<u>Element</u>	<u>Sufficient Sensitivity?</u>	<u>Element</u>	<u>Sufficient Sensitivity?</u>	<u>Element</u>	<u>Sufficient Sensitivity?</u>
Al	Yes	Cr	Yes	Na	Yes
Ag	Yes	Co	Yes	Ni	Yes
As	No	Cu	Yes	Pb	Yes
Ba	Yes	Fe	Yes	Sb	No
Be	Yes	K	Yes	Se	No
Ca	Yes	Mn	Yes	Tl	No
Cd	Yes	Mg	Yes	V	Yes
Zn	Yes				

3.0 ORGANIC ANALYSIS

The objective of the organic analysis task as stated in the Test Plan was to determine whether the EPA semivolatile organic method can be employed on SST samples. Semivolatile organic analyses were performed on methylene chloride extracts of SST samples. A description of the experimental work and the preliminary analytical results is followed by a discussion of the problems and some possible solutions. Conclusions related to the Test Plan objectives are presented in the final section on organic analysis.

The primary purpose of this project, "to gain additional experience with the analysis of SST matrices," was accomplished with respect to semivolatile organic analysis. Problems associated with the extraction process were encountered and a possible solution evaluated. Problems, most probably associated with the sampling process, were encountered that affected the gas chromatography/mass spectrometry (GC/MS) analysis. Laboratory development work will be required to solve these problems.

3.1 TEST METHODS, RESULTS, AND DISCUSSION

3.1.1 Experimental

Semivolatile organic analyses of a blank extract and two extracts of SST Sample 102-C were conducted by GC/MS. Extraction by sonication was performed in the hot cells. The low-level sample extraction process was used in the first extraction. Because the 5-g sample was very basic, it was acidified and a second extraction was performed to ensure acid compound extraction. The acidification technique used initially was to add a small quantity of methylene chloride to slurry the sample and slowly adding 4 M H₂SO₄ to a pH of about 2 as measured with pH indicator paper. When this extract was concentrated to 10 mL, three phases formed, so an alternative acidification process was used (see Section 3.2.2). No problems were encountered in concentrating this extraction procedure with 1-g aliquots.

The GC/MS analysis was run unsuccessfully on both the acidified and unacidified sample extracts (see Section 3.2.3). Extractions were repeated using the medium-level extraction procedure with 1-g aliquots. The GC screening procedure of CLP SOW 288 indicated that dilutions for this extraction

should be about 3 to 0.5 (i.e., undiluted) for the unacidified and acidified aliquots. A second screening method, determination of TOC, yielded results that agree reasonably well with the GC results if the comparison is estimated on a molar basis.

The concentrated extracts were analyzed by GC/MS according to SOW 288. Before analysis, the mass spectrometer was tune checked, and the daily calibration was run to verify the initial calibration. The internal standard checks were within SOW 288 limits for the analyses except for Perylene-d12 in two of the acidified sample extracts. The Perylene-d12 peak areas for the other acidified sample extracts were also very low.

3.1.2 Surrogate and Matrix Spike Test

To test for extraction efficiency and matrix effects, all of the sample aliquots were spiked (before the first extraction) with surrogate compounds and two sets of aliquots were spiked with matrix spike compounds. However, because the samples had to be diluted to lower NPH concentration and the surrogate and matrix spike compounds were divided between the two extracts for each aliquot, the concentrations measured fell below the calibration ranges for those compounds. Consequently, the normal surrogate and matrix spike recovery reports are not included in this report.

3.1.3 Target Compounds

Results for three analyses are shown in CLP Form I (IB and IC) in Figures 3.1, 3.2, and 3.3. These results are for the blank and two extracts of the sample -- one acidified (diluted 1 to 3) and one unacidified (diluted 1 to 10). The double extraction is described in Section 3.2.2.

There were no CLP target compounds found in the sample extracts (target compounds are listed in the 1B and 1C forms, "Semivolatile Organics Analysis Data Sheets"). The "U" signifies that the target compound was undetected at the listed concentration values ($\mu\text{g/kg}$ or ppb), which are the contract required quantification limits (CRQL). The high values for the CRQL reflect the sample dilution.

3.1.4 Tentatively Identified Compounds

Nontarget compounds were found in the two sample extracts. These are shown in the CLP Form 1F in Figures 3.4, 3.5, and 3.6. Note that the estimated concentrations are reported in $\mu\text{g/g}$ (ppm) rather than the typical $\mu\text{g/kg}$ (ppb) because of problems in the report generation software. The concentrations are estimated based on a response factors of 1.0 for all of the compounds.

The unacidified sample extract contained mostly alkane and siloxane compounds and the acidified sample extract contained mostly alkanes. Both extracts had what appeared to be oxidized alkanes and perhaps some amines, but their mass spectra did not match well with spectra in the National Institute of Standards and Technology (NIST) mass spectra library. The mass spectra matches became even worse for compounds with long chromatographic retention times.

The presence of high concentration alkanes is probably due to NPH in the core sampling process. The presence of siloxanes is probably due to the use of silicone-based lubricants, although gas chromatographic column degradation products have similar mass spectra.

3.2 PROBLEM AREAS AND CORRECTIVE ACTIONS

3.2.1 Presence of NPH and Silicone-Based Lubricant Products

The high concentration of alkanes mentioned in Section 3.1.4 will be a problem with respect to the dilution required to prevent overloading the chromatography column. A large dilution will result in such high detection limits that many of the other organic constituents will not be detected. The alkanes are likely from the NPH hydrostatic fluid used in the sampling process.

The siloxanes observed are probably from silicone-based lubricants from the sampler, although they could be chromatography column decomposition products resulting from column reactions with sample constituents. In either case, column performance will be degraded because of stationary phase modifications.

Methods to remove NPH and the silicone compounds from the samples or to eliminate them from the sampling process must be developed if good

identification and quantitation of organic constituents at low concentration are to be achieved.

3.2.2 Extraction

The acidification technique first tested involved adding a small quantity of methylene chloride to slurry the sample and slowly adding 4 M H_2SO_4 to a pH of about 2 as measured with pH indicator paper. Because of the lead glass window in the hot cell and probably the effect of methylene chloride on the pH paper dye, the acidification process was uncertain. When this extract was concentrated to 10 mL, three phases had formed. The solution to this phase-formation problem was to add a calculated amount of H_2SO_4 to adjust the sample pH to 5 (based on the EP Toxicity experiment) and then add additional acid to ensure adequate acidity. Only 1/20 of the acid added using the first method was added by this method. No problems were encountered in concentrating this extract. In future work, a separate, weighed sample will be acidified to the desired pH using a known amount of H_2SO_4 so that a good estimate of the amount of acid needed can be made. Also, pH indicator paper will not be used because the paper could contaminate the sample.

The value of performing this pH adjustment before extraction for the very basic samples is seen by the absence of some acidic compounds in the unacidified sample extracts and their presence in the acidified sample extracts. However, the results are inconsistent. That is, some of the acid surrogate and matrix spikes are in the first extract, and other spikes are in the second extract.

In future analyses of very basic samples, the sample pH will be adjusted to 7 to 9 as described previously. The pH-adjusted sample will then be extracted following the normal procedure. In this pH range, the acidic, basic, and neutral compounds should extract satisfactorily. Although several multivalent metal ions form insoluble precipitates, these precipitates should have little, if any, effect on the extraction of the organic acids.

3.2.3 Sample Concentration and Composition

As mentioned, the sample was first extracted following the low-level procedure using a 5-g sample. The GC/MS analysis was run on both the acidified and unacidified sample extracts with very deleterious effects on the GC

column. Not only was the column overloaded, but it was rendered unusable for subsequent runs. No acidic compounds could be measured in calibration standards, and the baseline was noisy and increased significantly at temperatures above 200°C. Attempts to recover the column were unsuccessful. The extractions were then repeated using the medium-level procedure with 1-g aliquots.

By this time, implementation and calibration of the GC screening procedure had been completed, and the low-level, concentrated extraction samples were screened. The results indicated that the unacidified sample extract was about 150 times too concentrated and the acidified sample about 15 times too concentrated based on protocol criteria. Since this screening would normally be done before the final evaporation of the 10 mL extracts, these extracts appeared to be about 15 and 1.5 times too concentrated for reliable analyses. For the medium-level extract with 1-g sample aliquots, rather than the 5-g low-level extract, the screening indicated that dilutions should be about 3 to 0.5 (i.e., undiluted) for the unacidified and acidified aliquots.

A second screening method tested was the determination of TOC. Results for the TOC were 2.10% and 2.05% C for two aliquots of the sample. Criteria from the SOW 288 screening protocol indicate that the medium-level extraction procedure should be used; the results from the TOC screening agree reasonably well with the GC results if the comparison is estimated on a molar basis.

To minimize GC/MS overload and fouling, the medium-level extracts were analyzed at several dilution ratios of the concentrated extracts. The minimum dilutions that could be analyzed without fouling or overload were 1 to 3 for the acidified sample extract and 1 to 10 for the unacidified sample extract. It would appear that these dilutions do not agree with the screening tests. It is likely that constituents in the extracts are causing the problem, rather than column overload.

In future analyses, the GC screening will be performed before the final evaporation step as a guide to the extraction level procedure to be followed. If an extract dilution is necessary, the extraction will be repeated with larger surrogate and matrix spike additions to account for the indicated dilution. The use of both screening methods is recommended until some pattern emerges after a number of analyses, which will hopefully identify the best screening method.

3.3 CONCLUSIONS RELATED TO TEST PLAN OBJECTIVES

3.3.1 To Determine Whether the EPA Semivolatile Organic Method Can Be Employed on SST Samples

Results indicate that the SST samples can be analyzed for semi-volatile organic compounds by the CLP SOW 288 procedures, but slight modifications will be required due to the problems associated with use of NPH and silicone-based materials in the SST sampling process. If silicone-based materials are to be used, a method to remove them from the sample extract must be found and implemented. The high concentration of NPH presents a problem in that the extract dilution may dilute organics that are in the SST sample to the point that they are difficult to both quantify and identify. Initially, tests will be run to determine if gel permeation chromatography (GPC) can be used for sample cleanup. It is highly recommended that alternatives to GPC be sought and evaluated since it is unlikely that this method will solve the siloxane and NPH problems.

3.4 DESCRIPTION OF DATA SHEETS

Since the data sheets for organic analysis are unfamiliar to most readers, this section describes the format of the data sheets. Results for three analyses are shown in the format specified by EPA for CLP analyses. Results for EPA target compounds are shown in Figures 3.1, 3.2, and 3.3 for a blank, an acidified sample, and an unacidified sample respectively. Values in the next to last column are the contract-required quantitation limits (CRQL) established as specified by EPA, and the "U" in the last column signifies that the target compound was undetected at the CRQL.

Compounds not on the EPA target list were found in the blank and the two sample extracts. These are shown in the CLP Form 1F in Figures 3.4, 3.5, and 3.6, respectively. The column headed RT is the retention time; the estimated concentration is in $\mu\text{g/g}$, while the previous figures were in $\mu\text{g/kg}$. Since the compounds are only tentatively identified, no Chemical Abstracts Service (CAS) number is given.

1B
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

89-0073

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: SOLVENT BLA

Sample wt/vol: 1 (g/mL) G

Lab File ID: >WPL05

Level: (low/med) MED

Date Received: 04/13/89

% Moisture: not dec. ----- dec. -----

Date Extracted: 04/15/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/28/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

CAS NO.	COMPOUND	CONCENTRATION UNITS:	
		(ug/L or ug/Kg)	ug/Kg
			Q
108-95-2	Phenol	20000.	U
111-44-4	bis(2-Chloroethyl) Ether	20000.	U
95-57-8	2-Chlorophenol	20000.	U
541-73-1	1,3-Dichlorobenzene	20000.	U
106-46-7	1,4-Dichlorobenzene	20000.	U
100-51-6	Benzyl alcohol	20000.	U
95-50-1	1,2-Dichlorobenzene	20000.	U
95-48-7	2-Methylphenol	20000.	U
39638-32-9	bis(2-chloroisopropyl) ether	20000.	U
106-44-5	4-Methylphenol	20000.	U
621-64-7	N-Nitroso-Di-n-propylamine	20000.	U
67-72-1	Hexachloroethane	20000.	U
98-95-3	Nitrobenzene	20000.	U
78-59-1	Isophorone	20000.	U
88-75-5	2-Nitrophenol	20000.	U
105-67-9	2,4-Dimethylphenol	20000.	U
65-85-0	Benzoic acid	99000.	U
111-91-1	bis(2-Chloroethoxy)methane	20000.	U
120-83-2	2,4-Dichlorophenol	20000.	U
120-82-1	1,2,4-Trichlorobenzene	20000.	U
91-20-3	Naphthalene	20000.	U
106-47-8	4-Chloroaniline	20000.	U
87-68-3	Hexachlorobutadiene	20000.	U
59-50-7	4-Chloro-3-methylphenol	20000.	U
91-57-6	2-Methylnaphthalene	20000.	U
77-47-4	Hexachlorocyclopentadiene	20000.	U
88-06-2	2,4,6-Trichlorophenol	20000.	U
95-95-4	2,4,5-Trichlorophenol	99000.	U
91-58-7	2-Chloronaphthalene	20000.	U
88-74-4	2-Nitroaniline	99000.	U
131-11-3	Dimethylphthalate	20000.	U
208-96-8	Acenaphthylene	20000.	U
606-20-2	2,6-Dinitrotoluene	20000.	U

FORM I SV-1

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FIGURE 3.1. Target Compounds, Blank Sample

1C
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

89-0073

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: SOLVENT BLA

Sample wt/vol: 1 (g/mL) G

Lab File ID: >WPL05

Level: (low/med) MED

Date Received: 04/13/89

% Moisture: not dec. ---- dec. ----

Date Extracted: 04/15/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/28/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

CAS NO. COMPOUND CONCENTRATION UNITS:
(ug/L or ug/Kg) ug/Kg Q

99-09-2-----	3-Nitroaniline	99000.	U
83-32-9-----	Acenaphthene	20000.	U
51-28-5-----	2,4-Dinitrophenol	99000.	U
100-02-7-----	4-Nitrophenol	99000.	U
132-64-9-----	Dibenzofuran	20000.	U
121-14-2-----	2,4-Dinitrotoluene	20000.	U
84-66-2-----	Diethylphthalate	20000.	U
7005-72-3-----	4-Chlorophenyl-phenylether	20000.	U
86-73-7-----	Fluorene	20000.	U
100-01-6-----	4-Nitroaniline	99000.	U
534-52-1-----	4,6-Dinitro-2-methylphenol	99000.	U
86-30-6-----	N-Nitrosodiphenylamine (1)	20000.	U
101-55-3-----	4-Bromophenyl-phenylether	20000.	U
118-74-1-----	Hexachlorobenzene	20000.	U
87-86-5-----	Pentachlorophenol	99000.	U
85-01-8-----	Phenanthrene	20000.	U
120-12-7-----	Anthracene	20000.	U
84-74-2-----	Di-n-butylphthalate	20000.	U
206-44-0-----	Fluoranthene	20000.	U
129-00-0-----	Pyrene	20000.	U
85-68-7-----	Butylbenzylphthalate	20000.	U
91-94-1-----	3,3'-Dichlorobenzidine	40000.	U
56-55-3-----	Benzo(a)anthracene	20000.	U
218-01-9-----	Chrysene	20000.	U
117-81-7-----	bis(2-Ethylhexyl)phthalate	20000.	U
117-84-0-----	Di-n-octylphthalate	20000.	U
205-99-2-----	Benzo(b)fluoranthene	20000.	U
207-08-9-----	Benzo(k)fluoranthene	20000.	U
50-32-8-----	Benzo(a)pyrene	20000.	U
193-39-5-----	Indeno(1,2,3-cd)pyrene	20000.	U
53-70-3-----	Dibenz(a,h)anthracene	20000.	U
191-24-2-----	Benzo(g,h,i)perylene	20000.	U

(1) - Cannot be separated from Diphenylamine

FORM T 517-2

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FIGURE 3.1. (contd)

1B
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

89-0011

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: TK102C AC E

Sample wt/vol: 1.0115 (g/mL) G

Lab File ID: >WPL10

Level: (low/med) MED

Date Received: 01/25/89

% Moisture: not dec. ---- dec. ----

Date Extracted: 03/28/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/30/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg) ug/Kg	Q
108-95-2	Phenol	59000.	U
111-44-4	bis(2-Chloroethyl) Ether	59000.	U
95-57-8	2-Chlorophenol	59000.	U
541-73-1	1,3-Dichlorobenzene	59000.	U
106-46-7	1,4-Dichlorobenzene	59000.	U
100-51-6	Benzyl alcohol	59000.	U
95-50-1	1,2-Dichlorobenzene	59000.	U
95-48-7	2-Methylphenol	59000.	U
39638-32-9	bis(2-chloroisopropyl) ether	59000.	U
106-44-5	4-Methylphenol	59000.	U
621-64-7	N-Nitroso-Di-n-propylamine	59000.	U
67-72-1	Hexachloroethane	59000.	U
98-95-3	Nitrobenzene	59000.	U
78-59-1	Isophorone	59000.	U
88-75-5	2-Nitrophenol	59000.	U
105-67-9	2,4-Dimethylphenol	59000.	U
65-85-0	Benzoic acid	290000.	U
111-91-1	bis(2-Chloroethoxy) methane	59000.	U
120-83-2	2,4-Dichlorophenol	59000.	U
120-82-1	1,2,4-Trichlorobenzene	59000.	U
91-20-3	Naphthalene	59000.	U
106-47-8	4-Chloroaniline	59000.	U
87-68-3	Hexachlorobutadiene	59000.	U
59-50-7	4-Chloro-3-methylphenol	59000.	U
91-57-6	2-Methylnaphthalene	59000.	U
77-47-4	Hexachlorocyclopentadiene	59000.	U
88-06-2	2,4,6-Trichlorophenol	59000.	U
95-95-4	2,4,5-Trichlorophenol	290000.	U
91-58-7	2-Chloronaphthalene	59000.	U
88-74-4	2-Nitroaniline	290000.	U
131-11-3	Dimethylphthalate	59000.	U
208-96-8	Acenaphthylene	59000.	U
606-20-2	2,6-Dinitrotoluene	59000.	U

FORM I SV-1

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FIGURE 3.2. Target Compounds, Acidified Sample

1C
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

89-0011

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: TK102C AC E

Sample wt/vol: 1.0115 (g/mL) G

Lab File ID: >WPL10

Level: (low/med) MED

Date Received: 01/25/89

% Moisture: not dec. ---- dec. ----

Date Extracted: 03/28/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/30/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

		CONCENTRATION UNITS:	
		(ug/L or ug/Kg)	ug/Kg
CAS NO.	COMPOUND		Q
99-09-2-----	3-Nitroaniline	290000.	U
83-32-9-----	Acenaphthene	59000.	U
51-28-5-----	2,4-Dinitrophenol	290000.	U
100-02-7-----	4-Nitrophenol	290000.	U
132-64-9-----	Dibenzofuran	59000.	U
121-14-2-----	2,4-Dinitrotoluene	59000.	U
84-66-2-----	Diethylphthalate	59000.	U
7005-72-3-----	4-Chlorophenyl-phenylether	59000.	U
86-73-7-----	Fluorene	59000.	U
100-01-6-----	4-Nitroaniline	290000.	U
534-52-1-----	4,6-Dinitro-2-methylphenol	290000.	U
86-30-6-----	N-Nitrosodiphenylamine (1)	59000.	U
101-55-3-----	4-Bromophenyl-phenylether	59000.	U
118-74-1-----	Hexachlorobenzene	59000.	U
87-86-5-----	Pentachlorophenol	290000.	U
85-01-8-----	Phenanthrene	59000.	U
120-12-7-----	Anthracene	59000.	U
84-74-2-----	Di-n-butylphthalate	59000.	U
206-44-0-----	Fluoranthene	59000.	U
129-00-0-----	Pyrene	59000.	U
85-68-7-----	Butylbenzylphthalate	59000.	U
91-94-1-----	3,3'-Dichlorobenzidine	120000.	U
56-55-3-----	Benzo(a)anthracene	59000.	U
218-01-9-----	Chrysene	59000.	U
117-81-7-----	bis(2-Ethylhexyl)phthalate	59000.	U
117-84-0-----	Di-n-octylphthalate	59000.	U
205-99-2-----	Benzo(b)fluoranthene	59000.	U
207-08-9-----	Benzo(k)fluoranthene	59000.	U
50-32-8-----	Benzo(a)pyrene	59000.	U
193-39-5-----	Indeno(1,2,3-cd)pyrene	59000.	U
53-70-3-----	Dibenz(a,h)anthracene	59000.	U
191-24-2-----	Benzo(g,h,i)perylene	59000.	U

(1) - Cannot be separated from Diphenylamine

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FIGURE 3.2. (contd)

1B
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

89-0011

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: TK102C BN E

Sample wt/vol: 1.0115 (g/mL) G

Lab File ID: >WPL11

Level: (low/med) MED

Date Received: 01/25/89

% Moisture: not dec. ---- dec. ----

Date Extracted: 03/28/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/30/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

CONCENTRATION UNITS:
(ug/L or ug/Kg) ug/Kg Q

108-95-2-----	Phenol	200000.	U
111-44-4-----	bis(2-Chloroethyl) Ether	200000.	U
95-57-8-----	2-Chlorophenol	200000.	U
541-73-1-----	1,3-Dichlorobenzene	200000.	U
106-46-7-----	1,4-Dichlorobenzene	200000.	U
100-51-6-----	Benzyl alcohol	200000.	U
95-50-1-----	1,2-Dichlorobenzene	200000.	U
95-48-7-----	2-Methylphenol	200000.	U
39638-32-9-----	bis(2-chloroisopropyl) ether	200000.	U
106-44-5-----	4-Methylphenol	200000.	U
621-64-7-----	N-Nitroso-Di-n-propylamine	200000.	U
67-72-1-----	Hexachloroethane	200000.	U
98-95-3-----	Nitrobenzene	200000.	U
78-59-1-----	Isophorone	200000.	U
88-75-5-----	2-Nitrophenol	200000.	U
105-67-9-----	2,4-Dimethylphenol	200000.	U
65-85-0-----	Benzoic acid	980000.	U
111-91-1-----	bis(2-Chloroethoxy) methane	200000.	U
120-83-2-----	2,4-Dichlorophenol	200000.	U
120-82-1-----	1,2,4-Trichlorobenzene	200000.	U
91-20-3-----	Naphthalene	200000.	U
106-47-8-----	4-Chloroaniline	200000.	U
87-68-3-----	Hexachlorobutadiene	200000.	U
59-50-7-----	4-Chloro-3-methylphenol	200000.	U
91-57-6-----	2-Methylnaphthalene	200000.	U
77-47-4-----	Hexachlorocyclopentadiene	200000.	U
88-06-2-----	2,4,6-Trichlorophenol	200000.	U
95-95-4-----	2,4,5-Trichlorophenol	980000.	U
91-58-7-----	2-Chloronaphthalene	200000.	U
88-74-4-----	2-Nitroaniline	980000.	U
131-11-3-----	Dimethylphthalate	200000.	U
208-96-8-----	Acenaphthylene	200000.	U
606-20-2-----	2,6-Dinitrotoluene	200000.	U

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FIGURE 3.3. Target Compounds, Unacidified Sample

1C
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

89-0011

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: TK102C BN E

Sample wt/vol: 1.0115 (g/mL) G

Lab File ID: >WPL11

Level: (low/med) MED

Date Received: 01/25/89

% Moisture: not dec. ---- dec. ----

Date Extracted: 03/28/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/30/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg) ug/Kg	Q
---------	----------	---	---

99-09-2-----	3-Nitroaniline	980000.	U
83-32-9-----	Acenaphthene	200000.	U
51-28-5-----	2,4-Dinitrophenol	980000.	U
100-02-7-----	4-Nitrophenol	980000.	U
132-64-9-----	Dibenzofuran	200000.	U
121-14-2-----	2,4-Dinitrotoluene	200000.	U
84-66-2-----	Diethylphthalate	200000.	U
7005-72-3-----	4-Chlorophenyl-phenylether	200000.	U
86-73-7-----	Fluorene	200000.	U
100-01-6-----	4-Nitroaniline	980000.	U
534-52-1-----	4,6-Dinitro-2-methylphenol	980000.	U
86-30-6-----	N-Nitrosodiphenylamine (1)	200000.	U
101-55-3-----	4-Bromophenyl-phenylether	200000.	U
118-74-1-----	Hexachlorobenzene	200000.	U
87-86-5-----	Pentachlorophenol	980000.	U
85-01-8-----	Phenanthrene	200000.	U
120-12-7-----	Anthracene	200000.	U
84-74-2-----	Di-n-butylphthalate	200000.	U
206-44-0-----	Fluoranthene	200000.	U
129-00-0-----	Pyrene	200000.	U
85-68-7-----	Butylbenzylphthalate	200000.	U
91-94-1-----	3,3'-Dichlorobenzidine	390000.	U
56-55-3-----	Benzo(a)anthracene	200000.	U
218-01-9-----	Chrysene	200000.	U
117-81-7-----	bis(2-Ethylhexyl)phthalate	200000.	U
117-84-0-----	Di-n-octylphthalate	200000.	U
205-99-2-----	Benzo(b)fluoranthene	200000.	U
207-08-9-----	Benzo(k)fluoranthene	200000.	U
50-32-8-----	Benzo(a)pyrene	200000.	U
193-39-5-----	Indeno(1,2,3-cd)pyrene	200000.	U
53-70-3-----	Dibenz(a,h)anthracene	200000.	U
191-24-2-----	Benzo(g,h,i)perylene	200000.	U

(1) - Cannot be separated from Diphenylamine

FIGURE 3.3. (contd)

1F SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.
89-0073

Lab Name: Battelle-PNL Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL Lab Sample ID: SOLVENT BLA

Sample wt/vol: 1 (g/mL) G Lab File ID: >WPL05

Level: (low/med) MED Date Received: 04/13/89

Moisture: not dec. ----- dec. ----- Date Extracted: 04/15/89

Extraction: (S-pl/Cont/Sonc) SONC Date Analyzed: 4/28/89

GPC Cleanup: (Y/N) N pH: ----- Dilution Factor: 1.00000

CONCENTRATION UNITS: ug/gm

Number TICs found: 3

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.	Unknown	7.92	5.	
2.	Alkane	18.33	16.	
3.	Alkane	20.12	10.	
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

FIGURE 3.4. Tentatively Identified Compounds, Blank Sample

1F SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO. 89-0011

Lab Name: Battelle-PNL Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL Lab Sample ID: TK102C AC E

Sample wt/vol: 1.0115 (g/mL) G Lab File ID: >WPL10

Level: (low/med) MED Date Received: 01/25/89

% Moisture: not dec. ---- dec. ---- Date Extracted: 03/28/89

Extraction: (Sapf/Cont/Sonc) SONC Date Analyzed: 4/30/89

GPC Cleanup: (Y/N) N pH: ----- Dilution Factor: 1.00000

Number TICs found: 14 CONCENTRATION UNITS: ug/gm

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.	Siloxane	7.54	33.	
2.	Siloxane	12.11	78.	
3.	Unknown	14.47	14.	
4.	Unknown	15.51	16.	
5.	Unknown	15.61	60.	
6.	Alkane	16.42	160.	
7.	Unknown	16.71	24.	
8.	Alkane	18.38	680.	
9.	Unknown	18.68	16.	
10.	Alkane	20.17	470.	
11.	Alkane	21.79	35.	
12.	Unknown	23.26	35.	
13.	Unknown	24.15	130.	
14.	Unknown	29.58	160.	
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

FIGURE 3.5. Tentatively Identified Compounds, Acidified Sample

1F
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.

89-0011

Lab Name: Battelle-PNL

Contract: -----

Lab Code: ----- Case No.: ----- SAS No.: ----- SDG No.: -----

Matrix: (soil/water) SOIL

Lab Sample ID: TK102C BN E

Sample wt/vol: 1.0115 (g/mL) G

Lab File ID: >WPL11

Level: (low/med) MED

Date Received: 01/25/89

% Moisture: not dec. ----- dec. -----

Date Extracted: 03/28/89

Extraction: (Sepf/Cont/Sonc) SONC

Date Analyzed: 4/30/89

GPC Cleanup: (Y/N) N pH: -----

Dilution Factor: 1.00000

Number TICs found: 21

CONCENTRATION UNITS:
(ug/L or ug/Kg) ug/Kg
Real 6/18/89

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.	Unknown	6.56	73.	
2.	Unknown	7.52	57.	
3.	541059 Cyclotrisiloxane, hexamethyl	7.76	460.	
4.	Unknown	12.03	210.	
5.	556672 Cyclotetrasiloxane, octameth	12.09	160.	
6.	62108218 Decane, 6-ethyl-2-methyl- (9	14.35	52.	
7.	541026 Cyclopentasiloxane, decameth	15.49	200.	
8.	112403 Dodecane (8CI9CI)	16.45	1500.	
9.	62016346 Octane, 2,3,7-trimethyl- (9C	17.83	48.	
10.	Unknown	18.20	38.	
11.	629505 Tridecane (8CI9CI)	18.42	5700.	
12.	Unknown	18.81	260.	
13.	74645980 Dodecane, 2,7,10-trimethyl-	19.72	36.	
14.	Unknown	20.19	3600.	
15.	629992 Pentacosane (8CI9CI)	21.19	30.	
16.	Unknown	21.39	80.	
17.	Unknown	21.80	320.	
18.	Unknown	22.98	49.	
19.	Unknown	23.26	27.	
20.	Unknown	23.38	35.	
21.	Unknown	24.16	860.	
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

FIGURE 3.6. Tentatively Identified Compounds, Unacidified Sample

DATE	DESCRIPTION	AMOUNT	BALANCE
1950	...	...	...
1951	...	...	...
1952	...	...	...
1953	...	...	...
1954	...	...	...
1955	...	...	...
1956	...	...	...
1957	...	...	...
1958	...	...	...
1959	...	...	...
1960	...	...	...
1961	...	...	...
1962	...	...	...
1963	...	...	...
1964	...	...	...
1965	...	...	...
1966	...	...	...
1967	...	...	...
1968	...	...	...
1969	...	...	...
1970	...	...	...
1971	...	...	...
1972	...	...	...
1973	...	...	...
1974	...	...	...
1975	...	...	...
1976	...	...	...
1977	...	...	...
1978	...	...	...
1979	...	...	...
1980	...	...	...
1981	...	...	...
1982	...	...	...
1983	...	...	...
1984	...	...	...
1985	...	...	...
1986	...	...	...
1987	...	...	...
1988	...	...	...
1989	...	...	...
1990	...	...	...
1991	...	...	...
1992	...	...	...
1993	...	...	...
1994	...	...	...
1995	...	...	...
1996	...	...	...
1997	...	...	...
1998	...	...	...
1999	...	...	...
2000	...	...	...

FIGURE 3.10. Investment Return and Compound Interest

4.0 RADIONUCLIDE ANALYSIS

Radionuclide analyses were performed on fused and dissolved samples from SST 105-C and 106-C. In addition to the radiochemical measurements requested in Table 1 of the Test Plan (see Appendix), Westinghouse Hanford Company (WHC) also asked that total alpha, total beta, and gamma energy analysis (GEA) be performed on both samples. The primary objective of the radionuclide measurements was to gather information relevant to the potential use of radionuclide ratioing and parent-daughter relationships for the estimation of radionuclides within samples. The first steps toward this objective were to determine if the analytical methods were adequate for analysis of SST samples and to identify those cases for which modifications or additional procedure development are needed. Satisfactory measurements were obtained for radioisotopes of Am, Cm, Ni, Pb, Po, Pu, Ra, Se, and U. Further procedure development will be needed for radioisotopes of Ac, Cs, Nb, Pa, Sm, Th, and Zr.

4.1 TEST METHODS, RESULTS, AND DISCUSSION

4.1.1 Sample Fusion

Weighed portions of SST archive samples 105-C and 106-C were fused by two different methods: 1) in KOH using a Ni crucible (KOH/Ni), as described in Figure 8 of the Test Plan (see Appendix), and 2) in Na_2O_2 using a Zr crucible ($\text{Na}_2\text{O}_2/\text{Zr}$). Total alpha, total beta, and GEA measurements were made on acidified aliquots of dissolved samples from both fusion methods. Only the solutions resulting from the KOH/Ni fusions were used for further radiochemistry.

4.1.2 Summary of Radiochemical Measurements

The results of total alpha, total beta, and GEA analyses on SST samples 105-C and 106-C are given in Table 4.1. Satisfactory agreement between duplicate analyses, using the KOH/Ni and $\text{Na}_2\text{O}_2/\text{Zr}$ fusion methods, was obtained for the total alpha and total beta results for sample 105-C. The total alpha and total beta results from the $\text{Na}_2\text{O}_2/\text{Zr}$ fusion were somewhat higher than the results from the KOH/Ni fusion. The ^{137}Cs results by GEA

agreed well for the two fusion methods, and this isotope was by far the predominant gamma activity for both samples.

The radiochemistry results for all analyses except the U isotopic analyses are presented in Table 4.2. The radioactivity is reported in units of nCi/g except for the case of total U, which is given in units of mg/kg for comparison with ICP fusion results. Table 4.2 also gives percent yield values for the duplicate analyses for those cases where a radioactive tracer was added. Some of the radiochemical measurements were not completed because of difficulties with the procedures, as will be discussed later.

The U isotopic measurements were performed by isotope dilution mass spectrometry and are presented in Table 4.3. Each of the SST samples was analyzed directly and also analyzed spiked with 20 ng of ^{233}U .

4.2 PROBLEM AREAS AND CORRECTIVE ACTIONS

4.2.1 Crucible Contamination

Sample 105-C was fused by both the KOH/Ni and $\text{Na}_2\text{O}_2/\text{Zr}$ methods. When the total alpha and GEA results were initially compared, the values were considerably different. Since no visible precipitate or undissolved particles were observed after acidification, the difference could not be attributed to incomplete dissolution of the sample. The problem was determined to be due to a contaminated crucible or volumetric flask. Therefore, the 105-C sample fusions were repeated using new crucibles and new glassware; the reproducibility of the total alpha and GEA values was then within acceptable limits, as reported in Table 4.1. This finding demonstrates that new equipment is required for the analysis of each sample.

Although Ni metal crucibles are inexpensive and easily obtained, they cannot be used when ^{59}Ni and ^{63}Ni measurements are required, since Ni dissolves into the fusion melt and absorbs the low-energy radiation emitted by these isotopes. Zr metal crucibles avoid this problem, but they are expensive, difficult to obtain in quantity, and Zr interferes with the radiochemical measurement of ^{93}Zr in a similar manner. If Zr crucibles are re-used, cross-contamination of samples could be a serious problem because large variations in activity level are anticipated among samples.

4.2.2 Cesium-137 Gamma Activity Level

Although samples fused by the two methods yielded GEA results that agreed well for ^{137}Cs , this was not true for other gamma activities in either sample. A method that would allow selective separation of Cs from the fusion melt solution is needed. This might reduce by orders of magnitude the ^{137}Cs gamma activity and thereby improve the detection limit for other gamma emitters in SST samples.

4.2.3 Procedures for Specific Radionuclides

The two SST archive samples that have been analyzed to date may or may not be truly representative of SST waste tank sludge, and the chemical composition may even vary considerably within a given tank. Considerable adaptation of the various radiochemical procedures may be necessary in order to perform the desired measurements.

The current status of the procedures for each of the radionuclides in Table 1 of the Test Plan (see Appendix) will now be discussed.

Radionuclides ^{227}Ac

Rather than measuring the ^{227}Ac directly, the 18.7-day daughter ^{227}Th was measured. This is a valid method for determining ^{227}Ac in SST samples since the parent and daughter will be in secular equilibrium. The two samples were run in duplicate, with ^{228}Th added as a tracer for chemical yield estimation. Adequate separation from other alpha-emitters was achieved to allow calculation of upper limits to the ^{227}Ac activity for both 105-C and 106-C samples. However, for one of the duplicates, Pu was not separated well enough to allow detection of ^{227}Th . Therefore, further refinements to the separation procedure will need to be developed before this method can be considered reliable.

Radionuclides ^{241}Am , ^{242}Am , ^{243}Am , and ^{242}Cm

Due to their similar chemistry, Am and Cm were separated and purified together and measured by alpha energy analysis (AEA). Results for ^{242}Am are not reported since this isotope cannot be easily measured by counting methods. Since measurement of ^{243}Am was requested, and this isotope is also used as the isotopic tracer in the PNL method, the procedure was performed

twice, once with and once without the addition of ^{243}Am . If measurement of ^{242}Am is also required, a mass spectrometric analysis procedure will need to be used.

Radionuclides ^{135}Cs and ^{137}Cs

Measurement of ^{135}Cs was unsuccessful because, with the procedure that was used, insufficient Cs was recovered for mass spectrometric analysis. The method involved selective retention of the Cs on cation exchange resin, and it is likely that the high K content of the solution resulting from the KOH/Ni fusion prevented the Cs from being retained. A procedure was developed that appeared to remove K successfully from a synthetic SST sample. This involved precipitation of K by addition of sodium tetraphenylborate, and was successful on the synthetic sample, but was not attempted on either of the archive samples. The effect of adding additional Na during the ion exchange separation of Cs was not studied. As an alternative, it may be more straightforward to use the existing procedure, but to separate the ^{135}Cs from an aliquot following acid digestion of the SST sample, since the K content would be much lower. Further procedure development is needed.

Radionuclides ^{59}Ni and ^{63}Ni

Analyses for these Ni radioisotopes are not possible if fusion is performed in a Ni metal crucible, as discussed earlier. An alternate method for measurement of ^{59}Ni may be ICP/MS. This might be simpler if the detection limit proved to be adequate, but the method would have poor sensitivity for ^{63}Ni due to its much shorter half-life. At this time PNL does not have the capability for measuring radioactive samples by ICP/MS, but this capability should be in place during the first half of FY 1990.

Radionuclides ^{94}Nb , ^{231}Pa , and ^{93}Zr

No procedure currently exists for the analyses of these nuclides in SST matrices. Some procedure development work was performed based on ion exchange methods with sequential elution of Zr, Nb, and Pa. Tracer studies look promising, but no measurements were attempted on SST samples. Additional procedure development will be necessary.

Radionuclides ^{210}Pb , ^{226}Ra , and ^{228}Ra

Upper limit values of 0.5 nCi/g for ^{210}Pb and 5 nCi/g for ^{226}Ra are reported. However, significant interferences were observed from gamma-emitting species when the samples were counted. Since some of the anticipated SST samples are expected to contain high levels of gamma emitters, it will be necessary to modify these procedures in order to obtain better separation. Due to these interference problems, ^{228}Ra measurements could not be performed.

An alternative for the measurement of ^{210}Pb would be to measure the ingrowth of the daughter, ^{210}Po . This would improve the sensitivity if a delay of approximately 100 days would be acceptable.

Radionuclide ^{210}Po

Less-than values of 0.002 nCi/g were calculated for ^{210}Po .

Radionuclides ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{242}Pu

Results reported in Table 4.2 for ^{238}Pu and for $^{239-240}\text{Pu}$ were determined by AEA. The PNL procedure that was used requires ^{242}Pu as an isotopic tracer, so it was performed with and without the addition of the tracer. Less-than values were calculated for ^{242}Pu from the latter data. A mass spectrometric procedure is also available at PNL for the measurement of Pu isotopes. This method is more expensive, but is capable of greater accuracy and allows measurement of other Pu isotopes, such as ^{241}Pu .

Radionuclide ^{79}Se

Results for ^{79}Se are reported in Table 4.2. However, the existing PNL procedure is lengthy and has not given reliably good carrier recovery for the analysis of fused SST samples. Modifications currently being made to this method give improved radiochemical yield, and these modifications need to be tested on fused SST samples. Additional procedure development may be necessary.

This radionuclide is a good candidate for analysis by ICP/MS when the capability becomes available.

Radionuclide ^{161}Sm

This radionuclide is difficult to measure by radiochemical means because of its low-energy (21.4 keV) gamma emission. Adequate separation of any radionuclides that emit higher-energy gamma radiation is essential due to Compton background interference. Europium radioisotopes are of particular concern because they are difficult to separate from Sm.

With a procedure using ^{161}Sm radioactive tracer, 85% of the Sm was recovered. A tracer study was then conducted using ^{154}Eu and various carriers to determine the degree of separation of Eu from Sm. The best separation achieved to date is 75% removal of Eu from the Sm fraction. Further procedure development will be necessary to verify that adequate separation from Eu is attainable.

Radionuclides ^{229}Th , ^{230}Th , and ^{232}Th

The chemistry adapted for SST sample analysis of Th isotopes was originally developed for the analysis of groundwater, where the only interfering species are due to naturally occurring radioactivity. In SST samples, fission products, including rare earth beta and gamma emitters, Pu, Am, and other actinides will be present. The adaptations that were investigated to cope with these interferences were not adequate to allow detection of Th alpha emission.

A revised radiochemistry scheme is recommended based on removal of Pu by solvent extraction after reduction to the +3 oxidation state. Several such solvent extraction systems exist. An optimum system should be chosen after consideration of the radionuclides expected to be present in SST samples. Additional methods development will be necessary for measurement of Th isotopes.

Radionuclides ^{233}U , ^{234}U , ^{235}U , ^{236}U , and ^{238}U

An isotope dilution, mass spectrometric procedure was used, with addition of a ^{233}U spike. Since analysis for ^{233}U was requested, the procedure was also repeated without addition of the spike. At one stage of the procedure, unleached glassware was used, so there is the possibility of some sample contamination with natural U leached from the glass.

Total U

No problems were encountered in the laser fluorometric method for total U analysis. For SST sample 105-C, the U result by ICP was 10,500 mg/kg versus a result of 8,200 mg/kg by the laser method. No ICP result was obtained for SST sample 106-C.

4.3 CONCLUSIONS RELATED TO TEST PLAN OBJECTIVES

4.3.1 To Gather Information Relevant to the Potential Use of Radionuclide Ratioing and Parent-Daughter Relationships for the Estimation of Radionuclides within Samples

Because of the large amount of procedure development and modification required for radiochemical analyses of SST samples, few conclusions could be drawn related to the primary objective. Additional procedure development will be required for the measurement of ^{94}Nb , ^{231}Pa , ^{227}Ac , ^{79}Se , ^{93}Zr , ^{229}Th , ^{230}Th , ^{232}Th , ^{242}Am , ^{151}Sm , ^{210}Pb , ^{226}Ra , and ^{228}Ra . Modifications to the existing procedure will be necessary for ^{136}Cs . Approved procedures are not in place for determination of most of the radionuclides listed in Table 1 of the Test Plan (see Appendix) for SST matrices.

TABLE 4.1. Total Alpha, Total Beta, and GEA Results for SST Samples 105-C and 106-C

Radionuclide	Sample 105-C (nCi/g)		Sample 106-C (nCi/g)	
	KOH/Ni	$\text{Na}_2\text{O}_2/\text{Zr}$	KOH/Ni	$\text{Na}_2\text{O}_2/\text{Zr}$
Total α	1.17E3 1.15E3	1.40E3 1.30E3	4.13E3	3.99E3
Total β as $^{90}\text{Sr}/^{90}\text{Y}$	3.63E6 3.89E6	3.89E6 4.03E6	8.83E6 8.56E6	8.56E6 8.15E6 8.34E6
GEA ^{137}Cs	3.02E5	3.05E5	4.82E5	5.04E5
^{60}Co	3.73E2	6.17E2	1.16E3	7.88E2
^{154}Eu	2.68E3	3.82E3	5.40E3	7.97E3
^{125}Sb				5.68E3

TABLE 4.2. Radiochemical Measurements and Tracer Yields for SST Samples 105-C and 106-C

Radionuclide	Sample 105-C		Sample 106-C	
	Activity (nCi/g)	Yield (%)	Activity (nCi/g)	Yield (%)
^{227}Ac	<1.4	1-2	<0.9	1-2
^{241}Am	962 $\pm$ 38	22, 27	2824 $\pm$ 98	42, 26
^{243}Am	4.9 $\pm$ 1.3	"	19.2 $\pm$ 2.1	"
^{242}Cm	3.0 $\pm$ 0.3	"	10.5 $\pm$ 0.7	"
^{244}Cm	29.5 $\pm$ 1.4	"	129 $\pm$ 5	"
^{238}Pu	48 $\pm$ 5	62, 72	422 $\pm$ 11	51, 44
^{239}Pu	747 $\pm$ 126	"	2340 $\pm$ 57	"
^{242}Pu	<0.2	"	<0.4	"
^{135}Cs				
^{69}Ni	128 $\pm$ 5	61, 76	68 $\pm$ 14	87, 88
^{63}Ni	12885 $\pm$ 1804	"	7770 $\pm$ 1508	"
^{94}Nb				
^{231}Pa				
^{210}Pb	<0.2		<0.3	
^{210}Po	<.002		<.002	
^{226}Ra	<5?		<5?	
^{228}Ra				
^{79}Se	2.5, 2.5(a)		0.95, 0.53(a)	
^{151}Sm				
Th Isotopes				
Total U (mg/kg)	8200	98.8	944	101.3

(a) Replicate analysis.

TABLE 4.3. Uranium Isotopic Analyses on SST Samples 105-C and 106-C

U Mass	Sample 105-C		Sample 106-C	
	With ^{233}U (a) Atom %	Without ^{233}U Atom %	With ^{233}U (a) Atom %	Without ^{233}U Atom %
233	0.02264	0.00719	0.19040	0.00067
234	0.00510	0.00913	0.00615	0.00558
235	0.65665	0.65070	0.64334	0.65239
236	0.01247	0.02243	0.01942	0.01157
238	99.30313	99.31055	99.14069	99.32980

(a) Addition of 20 ng of ^{233}U .

5.0 NORMAL PARAFFIN HYDROCARBON STUDIES

Normal paraffin hydrocarbon is used as part of the core sampling process. Therefore, it is important to know whether inorganic anions and cations and radionuclides are soluble in this medium. To evaluate solubility, a slurry consisting of SST sample 106-C and SST sample 102-AX supernate was contacted with NPH for a period of 48 h. An aliquot of NPH was removed for radiochemical analysis. The remaining NPH was then back-extracted with water and 1 M nitric acid and the inorganic species determined by ICP.

5.1 TEST METHODS, RESULTS, AND SIGNIFICANCE

5.1.1 Experimental

A slurry consisting of 14.4 g of solid sample from SST 106-C and 26.8 g of SST sample 102-AX supernate was prepared and contacted with NPH in accordance with Figure 10 of the Test Plan (see Appendix). After centrifuging, a 10 mL aliquot of the NPH phase was removed from the hot cell for GEA analysis. The remaining NPH was then contacted with an equal volume of water, and an aliquot of the aqueous phase was analyzed for inorganic species. The NPH was then contacted with an equal volume of 1 M nitric acid, and the inorganic species were measured in the acid phase. NPH blank solutions were generated by contacting virgin NPH with water and with 1 M nitric acid.

5.1.2 ICP Inorganic Constituent Solubility Results

The primary inorganic constituents found in the NPH were P, Na, and NO_3 , as shown in Table 5.1. The NPH blanks were run to determine what was extractable from the NPH itself. Upon evaluation of the data, it is obvious that the P is not all in the form of phosphate ions. It is suspected that it is present as an organo-phosphorus compound that was extracted from the SST sample. The high Na and NO_3 content in the extracts correlates with the high Na and NO_3/NO_2 content of the SST sample.

5.1.3 Radionuclide Solubility Results

Results of the radiochemical measurements on the NPH in units of nCi/mL are given in Table 5.2. No alpha, beta, or GEA analyses of the combined 106-C and 102-AX supernate slurry were performed; therefore, no direct quantitative determination of the extraction of radionuclides into NPH could be calculated. However, these counting measurements were performed for SST sample 106-C and are presented in Table 4.1. By comparison of Tables 4.1 and 5.2, the level of extraction of radionuclides into NPH is considered to be insignificant. The percent of total alpha and total beta activity extracted was 0.004% and 0.0012%, respectively. From the GEA data, the percentages of ^{137}Cs , ^{60}Co , and ^{154}Eu activity extracted were 0.026%, 0.076%, and 0.003%, respectively.

5.2 CONCLUSIONS RELATED TO TEST PLAN OBJECTIVES

5.2.1 To Determine the Solubility of Inorganic and Radiochemical Ions in NPH

As discussed previously, most of the measured ions showed no significant difference between the NPH/SST and the NPH/blank samples. The higher B and Si in the NPH/SST sample is probably due to radiation damage to the borosilicate glass vessel used for extraction. The high Na and K are probably physical carryover from the synthetic sludge. The source of the P is most likely from a degradation product of tri-butylphosphate (TBP). Even though the ICP, IC, and radiochemical results for this archive composite indicate low solubility of the measured ions in NPH, it may be prudent to confirm these results on future core samples.

TABLE 5.1. ICP and IC Measurements for NPH Equilibrated with Composite of SST Samples 106-C and 102-AX

ICP Elements	NPH Blank ($\mu\text{g/g}$)			NPH SST Sample ($\mu\text{g/g}$)		
	H ₂ O	HNO ₃	Total	H ₂ O	HNO ₃	Total
Ag	0.015	0.031	0.046	0.161	0.058	0.219
As	0.16	0.15	0.31	0.18	0.15	0.32(a)
B	0.005	0.026	0.031	0.405	0.080	0.485
Ba		0.013	0.013	0.019	0.007	0.026(a)
Ca	0.425	0.243	0.668	0.449	0.328	0.777(a)
Cd	0.008	0.014	0.022	0.019	0.014	0.033(a)
Ce		0.101	0.101		0.101	0.101(a)
Co	0.013	0.024	0.037	0.031	0.022	0.053
Cr		0.014	0.014	0.020	0.014	0.034(a)
Cu	0.012	0.018	0.030	0.034	0.021	0.055
Fe		0.040	0.040	0.018	0.035	0.053(a)
K		0.177	0.18	0.714	0.309	1.02
Mg				0.036		0.036
Mn				0.037		0.037
Na	3.47	0.812	4.3	162	15.4	177
Ni					0.054	0.054
P	6.42	7.93	14.4	170	11.9	182
Pb		0.080	0.08	0.055	0.077	0.13(a)
Sb	0.221	0.30	0.52	0.365	0.337	0.70(a)
Se	0.271	0.335	0.60	0.301	0.369	0.67(a)
Si	0.033	0.085	0.12	2.14	0.445	2.59
Tl	0.32	0.43	0.75	0.35	0.47	0.82(a)
U	0.69	1.01	1.70	0.75	1.11	1.86(a)
V	0.016	0.022	0.038	0.017	0.020	0.037(a)
Zn	0.013	0.034	0.047	0.012	0.032	0.042(a)
Zr		0.033	0.033	0.012		0.012(a)
IC						
Anions						
F	<0.08			<0.08(a)		
Cl	0.12			0.4(a)		
NO ₂	<0.08			8.1		
NO ₃	2.8			37.9		
PO ₄	<0.4			4.2(a)		
SO ₄	0.43			4.4(a)		

(a) Elements or anions which show no significant difference between the sample and the blank.

TABLE 5.2. Total Alpha, Total Beta, and GEA Results on NPH Equilibrated with Composite of SST Samples 106-C and 102-AX

<u>Gamma Energy Analysis</u>	<u>(nCi/mL)</u>
^{137}Cs	127.0
^{60}Co	0.88
^{154}Eu	0.17
<u>Total Alpha</u>	<u>Total Beta</u> (as ^{90}Sr - ^{90}Y)
0.18	106.0

6.0 RADIOLOGICAL EXPOSURE STUDY

Estimates of radiological exposure were made based on radiation measurement at contact and at a distance of about 3 ft for the sample aliquots removed from the hot cell for the inorganic, organic, and radiochemical analyses. Estimates were also made of the amount of time that the analyst would be in the contact with the sample when performing each of the various procedures. Thus, it is possible to obtain information on the radiation exposure that would be received in performing the various analyses.

6.1 TEST METHODS, RESULTS, AND DISCUSSION

6.1.1 Experimental

The analyst recorded the volume of sample used in each procedure, and estimated the time in contact with the sample. These data were entered into radiation exposure study forms for each procedure. Exposure was held to a minimum by use of ALARA (As Low As Reasonable Achievable) sample handling methods.

6.1.2 Exposure Summary

The SST samples 102-C and 105-C were much lower in activity than SST sample 106-C. No significant exposure to personnel was received in performing any of the measurements. The data from the radiation exposure study forms were used to summarize the radiation exposure received by the analyst and are presented in Tables 6.1 and 6.2.

6.2 CONCLUSIONS RELATED TO TEST PLAN OBJECTIVES

6.2.1 To gather information on the radiological exposure and time durations required in utilizing the various methods.

As discussed previously, for the specific analytical methods used in this study no significant exposure to personnel was received in performing any of the measurements. Use of other methods or larger sample sizes could increase exposures.

TABLE 6.1. Exposure Data Summary for Radiochemical Separations

	Volume Removed from Hot Cell (mL)	Sample Procedure Used		Volume Used for Analysis (mL)	Time in Contact with Sample (est.) (min)
		Exposure Level Contact (mR/hr)	3 feet (mR/hr)		
Sample 105-C Ni fusion, Radiochemical separation for Ac	5	5	<1	2	20
Sample 106-C Ni fusion, Radiochemical separation for Ac	5	25	2.5	1	10
Sample 105-C Zr fusion, Radiochemical separations for Pu, Am, Ni, Po, Pb, Ra	5	7	<1	4.2	65
Sample 106-C Zr fusion, Radiochemical separations for Pu, Am, Ni, Po, Pb, Ra	5	30	3	4.2	65
Sample 105-C Zr fusion, Radiochemical separations for Po, Pb, U, Th	50	7	<1	20	60
Sample 106-C Zr fusion, Radiochemical separations for Po, Pb, U, Th	50	30	3	20	60

TABLE 6.2. Exposure Data Summary for Inorganic Analyses

Sample	Volume Removed from Hot Cell (mL)	Sample Procedure Used		Volume Used for Analysis (mL)	Time in Contact with Sample (est.) (min)
		Exposure Level Contact (mR/hr-bkgd)	3 feet (mR/hr)		
Sample 102-C EP Toxicity, Sample #1, ICP aliquot	100	40-3	<0.5	100	5
Sample 102-C EP Toxicity, Sample #2, ICP aliquot	100	35-2.5	<0.5	100	5
Sample 102-C KOH Fusion	10	4.5-<0.5	<0.5	10	5
Sample 102-C Na ₂ O ₂ Fusion	10	4.0-<0.5	<0.5	10	5
Sample 102-C Fused Solids from Acid Digestion, Sample #1	10	1.0-<0.5	<0.5	10	5
Sample 102-C Fused Solids from Acid Digestion, Sample #2	10	<0.5-<0.5	<0.5	10	5

APPENDIX

TEST PLAN FOR ANALYSIS OF ARCHIVE SAMPLES OF SINGLE-SHELL
TANK SAMPLES PROVIDED BY WESTINGHOUSE HANFORD COMPANY

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SINGLE-SHELL TANK TECHNOLOGY SUPPORT PROGRAM

TEST PLAN FOR ANALYSIS OF ARCHIVE SAMPLES OF
SINGLE-SHELL TANK SAMPLES PROVIDED BY WESTINGHOUSE HANFORD COMPANY

PROJECT 13924
WBS 8930

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TEST PLAN FOR ANALYSIS OF ARCHIVE SST SAMPLES

I. INTRODUCTION

The purpose of this test plan is to describe the work and methods to be used for the analyses of archived Single-Shell Tank (SST) samples within PNL analytical laboratories. This work will be performed as part of PNL's SST Technology Support Program, Project 13924, under the Analytical Chemistry Task (WBS 8930).

II. TEST SCOPE AND OBJECTIVES

Work conducted under this test plan will consist of analyses of archive samples from SSTs 102-C, 105-C, and 106-C. As described in Section III, organic, inorganic, and the EP Tox analyses will be performed on the sample from SST 102-C and the radiochemical analyses on the sample from SST 105-C. The normal paraffin hydrocarbon test will utilize the sample from SST 106-C. The objectives of these tests are:

- To determine if there are problems with employing the various analytical methods on the test samples,
- To determine if the ICP has sufficient sensitivity for the analysis of EP Tox metal ions (excluding mercury, which will be analyzed by the cold vapor method),
- To determine which of the 22 EPA pollutant metal ions can be determined by ICP analysis,
- To determine if mercury can be determined by the cold vapor (CV) method,
- To determine whether the EPA Semivolatile Organic method can be employed on SST samples
- To determine solubility of inorganic and radiochemical ions in NPH
- To gather information on the radiological exposure and time durations required in utilizing the various methods, and
- To gather information relevant to the potential use of radionuclide ratioing and parent-daughter relationships for the estimation of radionuclides within samples.

The last two objectives support the evaluations which are being performed under the Alternative Techniques Task (WBS 8970).

III. TEST METHODS

Sample Preparation

Sample preparation to establish homogeneity of the sample is outlined on Figure 1. The method of grinding and sieving the sample was selected since the previous archive SST sample was essentially a dry solid. A small portion of the previous archive sample showed some caking but these clumps were easily ground with a mortar and pestle and sieved.

Percent Solids

The percent solids determination method is outlined on Figure 2.

Water Leach

The water leach procedure is outlined on Figure 3. The spike containing the anions is added at the beginning of the sample preparation scheme while the spike containing the cations is added after filtering the sample since the cation spike is prepared in an acid matrix. After filtering the sample, a 10 ml aliquot of the three samples and the blank used for IC, TOC, and TIC analyses are removed from the hot cell. The exposure level of the IC samples will be determined at this time. If the exposure level of the IC samples is low enough to safely work with the sample outside of the hot cell, the samples for ICP analyses will also be removed from the hot cell and subsequent sample preparation done in an open faced hood. The concentrations of the various elements in the anion and cation spikes are selected based on the analyses of previous SST samples and the recommended CLP spiking levels in SOW 787 page E-10. If the ICP analysis detects a significant concentration of water soluble chromium (greater than 1 ug/ml), an aliquot of the sample will be analyzed spectrophotometrically for chromium VI.

EP Tox

The modified EP Tox method is outlined on Figure 4. The spiking level for the EP Tox method was selected at the lower limit of the dangerous waste (DW) maximum concentration limits. After filtering the samples, 10 ml aliquot of the two samples and the blank are removed for the cold vapor mercury analyses. The exposure level of the two aliquot will be determined when the samples are removed from the hot cell. If the exposure level of the Hg samples is sufficiently low, the 15 ml aliquot for ICP analysis will be removed from the hot cells and the subsequent sample preparation will be done in an open faced hood.

FIGURE 1

FIGURE 2

SINGLE SHELL TANK

Percent Solid Determination per
CLP Method Part F page D-84

FIGURE 3

SINGLE SHELL TANK

Water Leach
per PNL Test Procedure HWVP-1

- (a) Anion spike to contain 20 ug F⁻, 20 ug Cl⁻, 100 ug NO₃⁻, 1300 ug NO₂⁻, 100 ug PO₄⁻³, and 300 ug SO₄⁻² per 10 ml of sample.
- (b) Cation spike to contain 10 ug Al, 10 ug Ba, 10 ug Bi, 5 ug Cd, 10 ug Ca, 5 ug Co, 10 ug Fe, 10 ug Pb, 10 ug Mn, 10 ug V, 100 ug P, 40 ug K, 10 ug Zr, 10 ug Cu, 10 ug Sb, 10 ug As, 0.5 ug Be, 20 ug Se, 20 ug Tl, 10 ug V and 10 ug Zn per 10 ml of sample. The second solution to contain 50 ug Cr as Cr⁺⁶ and 5 ug Ag per 10 ml of sample.
- (c) If spike recovery of anion sample 3 is not within limits of 75-125% an aliquot of filtered solution from sample 2 will be spiked and analyzed.

FIGURE 4
Modified EP Tox per SOW 846
Method 1310

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- (c) Spike sample with 0.5 ml of spike containing 100 ug/ml As, 100 ug/ml Ba, 20 ug/ml Cd, 100 ug/ml Cr, 100 ug/ml Pb, 20 ug/ml Se, 100 ug/ml Ni and 100 ug/ml Tl. Also add 0.5 ml of 100 ug/ml Ag solution.

Acid Digestion

Figure 5 outlines the acid digestion procedure. The procedure for sample preparation in the hot cell is the method from SOW 787 (CLP). The spike levels are determined from previous SST sample analysis and the recommended spike levels given on page E-10 of SOW 787 (CLP). The serial dilutions of 5 X will be used to determine the accuracy of the major cations such as Al, Fe, Mn, Ni, and Na. Silicon will not be spiked since the results have no significance in an acid digested solution. The filter from the acid digested sample will be saved and the acid insoluble portion of the sample will be fused and analyzed on the ICP.

Mercury Analysis

The method for mercury analysis is outlined on Figure 6. The sample digestion for mercury analysis is done in the hot cell. After the sample digestion, a preliminary separation of mercury is done in the hot cell by reducing the mercury with stannous chloride and the elemental mercury vapor is trapped into a mercury scrub media of 0.1 M KMnO_4 in 5% H_2SO_4 . After trapping the mercury in the scrub media, the solution is removed from the hot cell and the mercury analysis completed using the cold vapor technique using a Perkin-Elmer AA unit. If the duplicate samples agree within $\pm 20\%$, a third sample will be spiked with a suitable aliquot of mercury and analyzed. If the duplicate samples do not agree within $\pm 20\%$, we must ascertain whether the discrepancy in duplicate samples is from sample nonhomogeneity or some unknown matrix interference in the sample.

Total Cyanide

The total cyanide method is outlined on Figure 7. The analyses are performed on duplicate 2 gram samples using the EPA distillation method 9010. Since we know all SST samples will contain both nitrate and nitrite ions, sulfamic acid will be added to the distillation flask prior to the addition of sulfuric acid. If the duplicate samples agree within $\pm 20\%$, a third sample will be analyzed using an appropriate spike concentration. If the duplicate samples do not agree within the specified values (SOW 787 page E-11), one would suspect a matrix problem.

Fusion Procedure/Radionuclides

The KOH fusion outlined on Figure 8 will be used to dissolve the sample for radiochemical analyses. The radiochemical isotopes measured and the methods of analyses are listed on Table 1. The objectives of this test are (1) Determine if the listed nonroutine and/or environmental radiochemical methods can be used to analyze SST samples, and (2) Gather information relevant to the use of radionuclide ratioing and parent-daughter relationships for estimation of radionuclides within samples.

FIGURE 5

SINGLE SHELL TANK

Acid Digestion
per SOW 787 page D-4

Spike to contain 20 ug Ba, 5 ug Cd, 100 ug Ca, 100 ug Cr, 5 ug Co, 50 ug Pb, 20 ug Mg, 100 ug K, 10 ug Sr, 10 ug Zr, 10 ug Cu, 5 ug Sb, 20 ug As, .5 ug Be, 20 ug Tl, 5 ug V, and 5 ug Zn per 10 ml of sample. A second spike to contain 100 ug P and 5 ug Ag per 10 ml of sample

FIGURE 6

SINGLE SHELL TANK

Mercury Analyses by Cold Vapor Technique
per SOW 787 modified method 245.5

FIGURE 7

SINGLE SHELL TANK

Total Cyanide in Sediment per EPA Method 9010
and CLP Method 335.2

FIGURE 8

SINGLE SHELL TANK

Table 1

RADIOCHEMICAL MEASUREMENTS AND METHODS

Item	Isotope	Procedure
1.	^{227}Ac	PNL-Ac-01
2.	^{241}Am ^{242}Am * ^{243}Am	HTA-4-13 HTA-4-5 and HTA-4-6 * May require mass spectrometer analysis
3.	^{242}Cm	Included in Item 2
4.	^{135}Cs ^{137}Cs	HTA-4-9 HTA-4-40 3-30.6
5.	^{59}Ni ^{63}Ni	PNL-Ni-01
6.	^{94}Nb	PNL-Nb-01
7.	^{231}Pa	PNL-Pa-01
8.	^{210}Pb	RSD-51-DIS6 RSD-51-DIS8
9.	^{210}Po	RSD-51-DIS8
10.	^{238}Pu ^{239}Pu ^{240}Pu ^{242}Pu	HTA-4-15 2-30.5 HTA-4-22 HTA-4-5 and/or -6
11.	^{226}Ra ^{228}Ra	RSD-51-DEQ-4
12.	^{79}Se	HTA-4-18 or 7-40.15
13.	^{151}Sm	PNL-Sm-01
14.	^{229}Th ^{230}Th ^{232}Th	RSD-51-OEQ-3

Table 1(continued)

15.	233U	HTA-4-16
	234U	2-30.6
	235U	HTA-4-36
	236U	
	238U	
16.	93Zr	PNL-Zr-01
17.	Total U	Included in item 15
	Total	Included in item 4 and 10

Semivolatile Organic

The analytical method for the analysis of semivolatile organic is outlined on Figure 9. The solvent extraction of the sample with methylene chloride will be performed in the hot cell. The organic phase is then removed from the cell and the drying and concentration steps will be done in an open faced hood. Again, the primary purpose of this test is to gain additional experience with the analysis on SST matrices. A portion of the sample will be saved to evaluate the screening method on the gas chromatograph/flame ionization detector (GC/FID) at a later date.

Normal Paraffin Hydrocarbon

The normal paraffin hydrocarbon (NPH) laboratory test will use the excess SST sample (241-C-106) presently in the 325 Building hot cell. The flowsheet for this experiment is shown on Figure 10. A slurry will be prepared in the hot cell by mixing the SST sample with the supernate from the 102-AX tank. This slurry will be contacted with an equal volume of NPH and the mixture stirred for 48 hours. The phases will be separated.

The NPH phase analyzed for total alpha, total beta, and a GEA. A portion of the NPH will be leached with water for the analysis of anions by IC. Another portion of NPH will be extracted with 1 M HNO_3 and analyzed for cations. If the volume of separated NPH is insufficient for a water and an acid leach, the NPH will be extracted with DIW and the aqueous layer removed. The same NPH phase will then be extracted with 1 M HNO_3 and both the aqueous sample and the 1 M HNO_3 analyzed by ICP.

The objective of this experiment is to determine if the radionuclides, anions, and cations are NPH soluble.

FIGURE 9

SINGLE SHELL TANK

Semivolatile Organic Method
per SOW 787 Section D-2/SV

A portion of the sample will be saved for screening analyses at a later date.

NPH Extractability Studies

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Figure 10

IV. PRODUCTS

The products of this work are the final report and associated data packages and the residual archive samples from WHC and remaining quantities of derivative archive samples. Disposition of the physical archive materials will be as described in the Section VI "Test Program Prerequisites and Requirements". The content of the final report is given next.

The report will be structured in two parts.

Part 1 will be a description of results and their significance covering the following four items and referencing the supporting data from the data packages. The four items are: (1) State results, identify problem areas and describe what actions are needed to solve the problems; (2) Radiological exposure data showing time and exposure for each step of a procedure; (3) Significance of field changes made and the relevant procedures, and (4) Radiochemical and radioisotope values which will be used in the Alternative Techniques Task (WBS 8970) for comparison with TRAC data.

Part 2 will encompass all the backup information and data referenced in the first part. These data include the (1) Data Package for each method and the inputs to Alternative Techniques Task, (2) All data, including duplicate and serial dilutions and spike recoveries; and (3) copies of draft procedures not previously transmitted to WHC.

V. PRINCIPAL INVESTIGATOR

The Principal Investigator is FT Hara.

VI. TEST PROGRAM PREREQUISITES & REQUIREMENTS

Prerequisites

Personnel Qualifications

The analysis methods being used to conduct the work are standard methods; personnel have been trained and qualified to perform these methods. No special additional training is needed.

Safety

The operations to be conducted during the work are standard analytical chemistry methods for which no unusual safety issues have been identified. The handling of radioactive samples will be controlled by the relevant radiation work permits and monitored by RPT.

M&TE

Analysis procedures contain the requirements and practices for performing calibration and for standardization of instruments. Instrumentation will have calibration stickers for items where calibration is required. The requirements for using calibrated instrumentation are described in the analytical procedures. Documentation for standards and calibration verification solutions are outlined in QA Plan, WTC-033, Rev 1.

Material Identification & Pretest Verifications

Sample control and identification is in accordance with QA Plan WTC-033, Rev 1. Verification of condition of instrumentation and measuring systems is described in the analytical procedures. An instruction on Chain of Custody and appropriate format will be developed and implemented.

Requirements

Expected Results/ Acceptance Criteria

The purpose of the analysis work is qualitative and quantitative characterization to establish composition rather than to determine acceptability to some criteria. Results of the analysis work will also demonstrate that the available techniques and associated field changes will provide accurate and reproducible results.

Results will provide two types of information. First, analysis will quantify the EPA targeted inorganic and organic constituents SST samples. Second, radiochemical and radioisotope analyses will be used to better understand the ability of TRAC in predicting the radiochemical inventories of the SSTs.

Criteria for acceptability of the characterization data will be determined by the reproducibility of the duplicate analyses, serial dilutions and spike samples for organic and inorganic analyses. The organic and inorganic analyses will be done as outlined in the EPA (SW 846) and/or CLP (SOW 787) methods.

Data analyses and data reduction practices are outlined in the methods of analyses used.

Documentation & Data Package Preparation

General documentation will be identified in the records index for task 8930. The principal investigator will define the specific data gathering processes to be used for each method and appropriate format. This data gathering feeds into the data package preparation.

Radiological exposure data will be documented for each procedure used on samples. Each step in each procedure will be evaluated and results documented on radiological exposure data sheet. These data sheets will be accumulated for each procedure. Precautions to limit/control background radiation for in-cell measurements will be described.

The radiological exposure data sheets will contain the following information: Origin of aliquot, name of analyst, Date, volume of aliquot, exposure levels at contact and 1 meter, description of operation, time started and time completed.

Data packages will be individually collated and reviewed for content and reproducibility in accordance with PNL-SA-30. Each data package will be signed by the Principal Investigator and Evaluator. PNL-SA-30 does not cover all the points for a data package for this project. An instruction for preparation of data packages will be prepared and implemented by the Principal Investigator to supplement PNL-SA-30.

Data packages will contain the following: Results of work including problem areas and proposed solutions; procedures used will be listed and any field changes described; radiological exposure information showing time and exposure data; copies of draft procedures not previously transmitted to WHC, and all raw data. Raw data includes duplicates, serial dilutions and spike recovery, printouts, etc. Where data bases were developed they will be shown in hardcopy and a working disk provided.

Hazardous materials and waste information generated in the HMM task will be organized and retained for use in follow-on work with SST samples.

Change Control and Test Modifications

Changes to the technical content of test planning will require review and approval equivalent to that of the original; field changes during work will be documented and discussed with the project manager and included in the final data package. Changes in scope, cost or schedule require the approval of the line manager, project manager and customer.

Data Review & Evaluation

Data review and evaluation will use a three stage process. First, the person(s) doing analysis will obtain the verification of their work by the Principal Investigator on a regular basis. Regular means with each set of analyses of each sample; review will be documented by initials and date in the appropriate place.

Second, Principal Investigator will review results in a systematic way to ensure that results are meaningful. This review will be used to determine when additional samples are to be run and/or when progress is deviating from expectations.

Third, the Independent Evaluator, per PAP-1101, will be appointed by the project manager and performs the following: (1) Independent review per PNL-MA-70; (2) Concurs in the data packages, and (3) Concurs in the final report confirming that the results are consistent with the raw data, data reduction techniques were valid and the conclusions are supported by the data.

Instructions and Procedures

Analysis methods to be used are described in the test description. PNL Technical Procedures numbered PNL-SA-21 through -SA-50 are key routine procedures which will be followed during the work. These, in conjunction with the specific methods, provide additional administrative control ensures the quality of the data.

Procedures used, including field changes and test instructions, shall be adequate for a person familiar with the equipment and techniques to reproduce the data.

Hazardous Materials Management

The processes used will be evaluated for both personnel hazards and waste disposal and environmental requirements. The identification of chemicals and materials to be used and/or generated provide the basis for specific decisions. These data are used to identify any unique safety, environmental or waste issues and to chose between the various options for resolving issues. An example of an important issue would be handling excess input or derivative archive materials, waste streams treatment & disposal.

Characteristics and volume(s) of materials used /generated are necessary for the development of a waste disposal plan, environmental compliance evaluation and decisions on need for MSDSs and hazards communication.

The waste disposal plan preparation and content are described below under "Requirements".

The archive samples, provided by Westinghouse Hanford Company, are radioactive mixed waste samples for characterization by PNL. Radioactive mixed waste materials must be controlled. Dilutions of these archive materials will be made to use as starting points for various analyses; these derivative archive samples will be identified as such and included in the discussions with WHC regarding disposition.

Waste Disposal Plan

A waste disposal plan will be prepared for the work and will be reviewed with Waste Management/Environmental Control section of Laboratory Safety. Preparation will be done in conjunction with 325 hot cell facility personnel. No disposal of liquids to the Hot cell radioactive liquid waste sewer will be done prior to review and acceptance of the planning by Laboratory Safety.

Planning will be based on identified waste streams from each process step for each method, the composition and volumes using PNL-MA-8 for guidance and assistance from Laboratory Safety staff. This information is provided to Materials and Chemical Sciences Center Operations Manager for use in developing and updating waste projections.

Hazardous materials and waste information generated in the HMM task will be organized and retained for use in follow-on work with SST samples.

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