PNL-7258
UC-721

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

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April 1990

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

Pacific Northwest Laboratory
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PNL-7258

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EXECUTIVE SUMMARY

A substantial effort is planned to be initiated at the Hanford Site regarding the characterization of 149 single-shell tanks (SSTs) containing the byproducts of reprocessing during the 1950s and 1960s. Sampling and analysis, in distinct phases, are planned to involve laboratory investigations to determine both chemical and radionuclide inventories, so that waste disposal decisions can be developed.

During 1989, trial analyses were performed on four archived samples from SSTs at the Pacific Northwest Laboratory using established U.S. Environmental Protection Agency (EPA) protocols and radiochemical procedures.

The analysis of the archived SST waste material provides three important types of data for use in planning Phase I-A and Phase I-B sample analysis. The types of data served as input to 1) finalizing the waste sample analysis procedures and methods and identify where procedure development may be needed, 2) evaluating the impact of normal paraffin hydrocarbon (NPH) lubricant (used in field sampling) 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.

Overall, the results are qualitative in nature, and the conclusions given are to be used with appropriate respect for the limitations of small amounts of data from four samples used in development processes. The results of the Phase I-A and I-B sample analysis will provide essential data for method performance for use in finalizing Phase I-C planning and methods development scope.

Section 2.0, Inorganic Analysis, encompasses sample preparation, sample analysis, identification of methods performance limitations, and possible alternatives. Performance of the inorganic analytical methods was evaluated and changes were made to some of the procedures. In some cases, inductively coupled plasma-atomic emission spectroscopy (referred to in this report as ICP) did not provide the levels of accuracy and precision usually required for EPA work due to interference by other elements. In these cases, other methods are suggested as appropriate for trial as alternatives. In all

cases, duplicates, spikes, and blanks were used to establish performance of the methods for the specific waste matrix. Results focused on problems in using the methods tested on the samples, the suitability of the ICP method of determining EP Toxicity metal ions and 22 EPA pollutant metal ions, and the suitability of cold vapor atomic absorption (CVAA) for mercury determinations. Problems areas identified are ICP spectral corrections, poor reproducibility from water leach and EP Toxicity methods, and adjustments needed for mercury analysis by CVAA.

Section 3.0, Organics Analysis, details two screening procedures [total organic carbon (TOC) and gas chromatography (GC)], extraction procedures and related problems, surrogate spiking to test extraction efficiencies and matrix effects, and semivolatile organics via GC/mass spectroscopy (MS). The results show that the GC/MS is vulnerable to fouling and overload and that a combination of dilution and perhaps acidification are required to provide acceptable results. NPH and silicone-based lubricants from the sampling process impact the semivolatile analysis; however, with some modification the semivolatile method based on EPA SOW 288 can be used.

Section 4.0, Radionuclide Analysis, evaluates procedures used to measure the radionuclides that might be found in the SST tank waste samples and establishes the level of accuracy and precision that can be expected. These data reveal that additional procedure development is needed in order to measure all of the radionuclides listed in Table 4-14 of the Waste Characterization Plan. In addition, the archive samples analyzed may not be representative of the tank population and considerable adaptation of the radiochemical procedures may be necessary to perform the desired measurements.

NPH 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. Results indicate that no such extraction is anticipated; however, the NPH does have a significant effect on the organic analysis and its use should be investigated.

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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1.0 INTRODUCTION

This report describes the analysis of archived single-shell tank (SST) samples 102-C, 105-C, and 106-C by the Chemical Measurements Laboratory section of Pacific Northwest Laboratory (PNL). As requested in the Test Plan for Analysis of Archive Samples of Single-Shell Tank Samples Provided by Westinghouse Hanford Company (Project 13924), the following tasks were performed: 1) organic and inorganic analyses were performed on sample 102-C, 2) radiochemical 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 supernate. The Test Plan is included as the 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, one for each of the measurement categories, a fourth section discussing the NPH study, and the final section addressing radiological exposure measurements. At the end of each section, the objectives for each measurement category, which are bulleted on page 1 of the Test Plan, are addressed.

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 Test Plan for the SST samples includes duplicate and spike analyses with each of the inorganic test methods to obtain information about reproducibility of these methods and to validate the data generated from the water leach and the EP Toxicity procedures.

To evaluate inorganic test method performance, the USEPA CLP SOW 787 criteria for sensitivity, reproducibility of duplicate analyses, and spike recovery were applied to the test results, although the criteria are only applicable for acid-digested soil and water samples. For reference purposes only, the following SOW 787 criteria 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 procedure detection limit. RPD is defined as $((S - D) / [(S + D)/2]) \times 100$, where S = sample value and D = duplicate value.
- ICP serial dilution--if the element analyzed is at least 50 times the instrument detection limit, a five-fold dilution must agree with the original analysis to within a percent difference of $\pm$10%. 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 SIGNIFICANCE

2.1.1 Sample Preparation

Solid samples from SST 102-C, SST 105-C, and 106-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.) In accordance with the Test Plan, sample 102-C was prepared for analysis of inorganic cations by inductively coupled plasma-atomic emission

spectroscopy (ICP/AES, hereafter referred to simply as ICP), for inorganic anions by ion chromatography (IC), and for total organic carbon (TOC) and total inorganic carbon (TIC); also, SST samples 105-C and 106-C were fused for radiochemical analysis and measurement of inorganic cations by ICP.

2.1.2 Percent Solids Determination

The percent solids content of two 1- 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 [(sample dry weight/sample wet weight) X 100], was approximately 94% solids for both samples.

2.1.3 Water Leach

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 (μg/mL)" are the observed elemental concentrations; the values in the columns labeled "Corr. (μg/mL)" are the observed elemental concentrations corrected for spectral interferences from U and Al. Elements that are followed by an (e) have low sensitivity by ICP analysis and also require significant spectral corrections due to the presence of 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. The data in Table 2.1 demonstrate this 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. 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 ±20% that is considered acceptable according to the Contract Laboratory Program (CLP) protocol. 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 PO_4 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 nine 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. EP Toxicity measurement results performed by ICP methods 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 so that the results can be directly compared 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 ±20% control limit for ICP analysis method 6010 in EPA SW 846. As discussed in Section 2.2, dissolution of these matrices in dilute acetic acid can yield erratic results, which is 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 and required 1- 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 ±20% except for the elements B, Cd, Cu, K, Si, Tl, and V. Note that all of these elements (except Si) are at or near the 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. Although these corrections are a significant percentage of the "raw" intensity, the observed values agree reasonably well with the GFAA results for As and Pb. A comparison of the ICP and GFAA results show that Sb, Se, and Tl cannot be analyzed with good accuracy by ICP due to poor ICP sensitivity and large spectral interference from U. These elements are candidates for GFAA analysis.

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 ±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. The RPD in the ICP results between the two fusion methods is within ±20%, except for cations that are near the 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 radiochemical analysis (see Section 4.0), ICP analyses were also performed. The results for these samples, as well as 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-μm 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 Al result for the water leach sample is higher than the Al 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 Al should be in the form of a soluble aluminate. Since the final pH for the EP Toxicity method is adjusted to 5.0, all of the Al should be precipitated as hydroxide.

It is surprising 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-μm 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 $Al(OH)_3$, 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 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 total cyanide procedure (SOW 797 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. 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

CLP protocol requires 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 ±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 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 the acidity or alkalinity of the sample matrix. 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 μg) 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 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. Since most of the multivalent metal ions are not soluble in basic or slightly acidic solution, good reproducibility would not be expected for these analyses. 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 $Al(OH)_3$ precipitate, which will 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 of EP Toxicity Metal Ions (excluding Hg)

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. Also, the data for the EP Toxicity elements in Table 2.12 for SST archive sample 102-C indicate that the Pb and total Cr could exceed the EP Toxicity threshold, making Pb analysis by ICP questionable. The toxicity threshold for both elements is 100 mg/kg based on the acid-digested sample criteria.

ICP sensitivity would be sufficient to measure all of the EP Toxicity metal ions except Se, if the U content in SST sample 102-C were lower. The U concentrations for the duplicate analyses after extraction by the EP Toxicity procedure were 430 and 356 μg/mL (Table 2.5). Even this low U concentration, however, requires spectral correction to As, Cr, Pb, Se, and Ag of between 50 and 90% of the "raw" intensities. Many of these elements will require GFAA analysis for EP Toxicity when the samples contain U. Table 2.13 is a summary of this objective.

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

As discussed previously, the ICP has low sensitivity and significant corrections are required due to U interference for 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, due to their high instrument sensitivity, these elements are still considered measurable by ICP. Table 2.14 is a summary of this objective.

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, on a 1.1005- and 1.3118-g sample. Based on 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 Raw ICP (µg/mL)	Sample 1 Corr.[a] (µg/mL)	Sample 2 Raw ICP (µg/mL)	Sample 2 Corr.[a] (µg/mL)	RPD	Spike Added (µg/mL)	Spike Recovered (µg/mL)	% Spike Recovery
Ag	-0.009	-0.010	0.008	0.009	DL[b]	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	DL[b]	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	DL[b]	1.00	1.04	104
Be	0.0004	0.0004	0.0014	0.0015	DL[b]	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	-0.31		-0.25					
Co	-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
Dy	-0.016							
Fe	0.79	0.886	1.65	1.65	60.2[c]	1.00	1.05	105
K	0.41	0.45	0.66	0.69	42.1[c]	4.00	7.15	179[d]
La	-0.025		-0.017					
Li	-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	0.012	0.014	0.017	0.018	DL[b]			
Na	113.0	149.0	164.0	172.0	14.3			
Nd	-0.11		-0.085					
Ni	0.604	0.678	1.24	1.30	62.9[c]			
P[e]	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	-0.16		-0.12					
Ru	-0.032		-0.004					
Sb[e]	0.31	-0.061	0.681	-0.020	DL[b]	1.00		(f)
Se[e]	0.32	-0.56	0.974	-1.22	DL[b]	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	-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	DL[b]	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) Values at or near ICP detection limit; defined as ±50% RSD.
(c) Values exceeding SOW 7 87 control limit of ±20%. Indication purpose only.
(d) Spike recovery exceeds SOW 7 87 limit of ±25%. Indication purpose only.
(e) Elements with poor ICP sensitivity and high U & Al spectral interference.
(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	µg/mL Element Interference from 100 µg/mL U	µg/mL Element Interference from 500 µg/mL U	Potential to Reduce Interference[a]
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) Anion with spike recovery not within the ±25% defined by the Test Plan.
(b) Values exceeding SOW 787 control limit of ±20%. Indication purpose only.
(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 Measurements			Spike Recovery Measurements		
EP Toxicity Element	Sample 1 (μg/mL)	Sample 2 (μg/mL)	RPD	Spike Added (μg/mL)	Spike Recovered (μg/mL)	% Spike Recovery
Ag	0.003	0.17	193[a]	5.0	4.63	93
As	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	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			
Ni	0.206	0.23	11	5.0	4.67	93
Pb	0.07	0.54	154[a]	5.0	4.10	82
Se	0.5	8.6	178[a]	1.0	3.90	390[b]
Tl	0.31	3.1	164[a]	5.0	6.07	121

(a) Values exceed SOW 787 limit of ±20%. Indication purposes only.
(b) Spike recovery exceed SOW 787 limit of ±25%. Indication purposes only.
(c) Hg analyses performed by CVAA.

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

Element	Sample 1 (μg/mL) Direct	Sample 1 (μg/mL) 5X Dil	Percent Difference	Sample 2 (μg/mL) Direct	Sample 2 (μg/mL) 5X Dil	Percent Difference
Ag	0.003	0.128	DL[a]	0.17	0.16	0.59
Al	17.4	18.2	4.4	9.29	9.64	3.6
As	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	DL[a]	0.02	0.02	DL[a]
Be	0.001	0.0	DL[a]	0.004		DL[a]
Ca	17.6	18.7	5.8	14.9	15.7	5.1
Cd	0.009	0.0	DL[a]	0.068	0.01	DL[a]
Ce	-0.09		DL[a]	0.41		DL[a]
Co	0.005		DL[a]	0.037		DL[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	-0.002		DL[a]	-0.027		DL[a]
Fe	-0.025		DL[a]	0.04		DL[a]
K	10.8	10.7	0.9	9.9	9.43	4.8
La	-0.009		DL[a]	0.05		DL[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	-0.001		DL[a]	0.02		DL[a]
Na	1340.0	1330.0	0.8	1210.0	1260.0	4.0
Nd	-0.01		DL[a]	0.18		DL[a]
Ni	0.206	0.216	4.6	0.23	0.15	35.0
P	3.04	2.16	29.0	4.35	2.42	44.0
Pb	0.07		DL[a]	0.54		DL[a]
Rh	-0.04		DL[a]	0.3		DL[a]
Ru	-0.04		DL[a]	0.13		DL[a]
Sb	-0.2		DL[a]	0.1		DL[a]
Se	0.5		DL[a]	8.6		DL[a]
Si	112.0	108.0	3.6	107.0	101.0	5.6
Sr	0.54	0.57	5.3	0.45	0.47	4.3
Te	0.009		DL[a]	0.15		DL[a]
Ti	0.010	0.01	0.0	0.037	0.0	DL[a]
Tl	0.31		DL[a]	3.1		DL[a]
U	430.0	392.0	8.8	356.0	364.0	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		DL[a]	0.03		DL[a]

(a) Values at or near ICP detection limit defined as ±50% RPD.
(b) Reason for large percent difference is unknown, possible borosilicate glass contamination.

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

(a) Values at or near ICP detection limit; defined as ±50% RSD.
(b) Values exceeding SOW 787 control limit of ±20%. Indication purpose only.
(c) Elements where the U correction is greater than 50% of the ICP raw data.

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)	-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)	-160	-156		93		--(d)
Se(a)	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)	51	38	29(c)	370	143	39
U	21,300	21,300	0.5			
V(a,b)	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) Elements where the U correction is greater than 50% of the ICP raw data.
(c) Values exceeding SOW 787 control limit of ±20%. Indication purpose only.
(d) Spike recoveries exceeding SOW 787 control limit of ±25%.
(e) Zr probably precipitated as a zirconium phosphate compound.
(f) Cu and P channel lost during spike analyses.

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

Element	5X Dil (µg/mL)	25X Dil (µg/mL)	Percent Difference	5X Dil (µg/mL)	25X Dil (µg/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 fusion solution required a 5X dilution in order to place the element concentrations with the calibrated ranges. The dilution study was performed by diluting this 5X solution another 5 fold.

TABLE 2.9. Comparison of KOH and Na_2O_2 Fusion of ICP Analysis for SST Sample 102-C

Element	KOH Fusion (mg/kg)	Na_2O_2 Fusion (mg/kg)	RPD
Ag	28	81	97(a,b)
Al	220,000	222,000	0.9
As	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	--	1,600	--(c)
Pb	730	3,200	126
Sb	860	990	14.0
Se	850	760	11.2
Si	75,700	73,400	3.2
Sr	80	125	43.9(a,b)
Ti	1,620	1,660	2.4
Tl	1,000	1,200	9.1
U	19,400	21,060	8.2
Zn	260	200	26.0(a,b)
Zr	940	--	--(c)

(a) Elements concentration is less than 5X the ICP detection limit.
(b) Values exceeding SOW 787 control limit of ±20%. Indication purpose only.
(c) Results for only one analysis due to the flux and crucible used.

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

	Acid Digestion [A] (mg/kg)		Acid Insol Fused [B] (mg/kg)		Total: [A]+[B] (mg/kg)	
Element	Sample 1	Sample 2	Sample 1(a)	Sample 2(b)	Sample 1	Sample 2
Ag	26.1	27				
Al	135,200	158,000	40,800	41,800	175,800	199,800
As	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	637	683	150	360	787	1,223
Sb	-160	-156	320		160	-156
Se	160	135			160	135
Si	1,245	96B	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	51	38			51	38
U	21,400	21,300	95		21,500	21,300
V	20	25			20	25
Zn	220	186	20	20	240	206
Zr	317	356			317	--(c)

(a) KOH/Ni Fusion
(b) Na_2O_2/Zr Fusion
(c) Fusion crucible contamination; only one fusion result summed.

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	180	170	2,100
Al	225,000	246,000	115,000
As	230	320	390
B	150	300	350
Ba	110	150	350
Ca	9,400	1,600	1,900
Cd	80	80	--
Ce	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	60	210	560
P	3,100	5,900	7,300
Pb	890	1,130	2,500
Sb	--	2,500	2,900
Se	--	1,000	1,400
Si	76,800	10,800	26,000
Sr	80	160	110
Ti	1,750	230	330
Tl	2,300	1,600	1,200
U	23,300	10,500	**[b]
V	90	60	--
Zn	160	--	--
Zr	1,320	710	600

(a) Additional Sample 102-C fusion sample 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 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.

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	0.0	1.7	27			
Al	1,300	266	145,000	41,300	186,300	221,000
As		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	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	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	1,220	400	1,600	1,600
Pb	17	6.2	660	250	900	2,000
Se	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		1.6				
Ti	3.1	0.5	990	425	1,420	1,640
Tl		34	44		44	
U	820	7,840	21,300		21,300	20,230
V	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.

TABLE 2.13. Summary of EP Toxicity Metal Ions by ICP

Element	Sufficient Sensitivity? With U	Without U	Element	Sufficient Sensitivity? With U	Without U
Ag	Probable	Probable	Cr	Probable	Probable
As	No	Yes	Pb	No	Probable
Ba	Yes	Yes	Se	No	No
Cd	Yes	Yes	Tl	No	No

TABLE 2.14. Summary of EPA Pollutant Metal Ions by ICP

Element	By ICP?	Element	By ICP?	Element	By ICP?
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 semivolatile organic analysis was performed on methylene chloride extracts of SST samples. Results of the analysis are described in the following discussion. A description of the experimental work followed by a discussion of the problems and some possible solutions conclude the organic analysis section.

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 SIGNIFICANCE

3.1.1 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 (this double extraction is described in Section 3.2.1). The data files and sample descriptions are as follows:

Sample Extract	Dilution	Data File
Blank	none	>WPL05
Acidified Sample	1 to 3	>WPL10
Unacidified Sample	1 to 10	>WPL11

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 (μg/kg or ppb), which are the contract required quantitation limits (CRQL). The high values for the CRQL reflect the sample dilution.

3.1.2 Tentatively Identified Compounds

There were nontarget compounds 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 μg/g (ppm) rather than the typical μg/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.

3.1.3 Surrogate and Matrix Spike Test

To test for extraction efficiency and matrix effects, all of the sample aliquots were spiked with surrogate compounds and two sets of aliquots were spiked with matrix spike compounds. However, because of the dilutions and the split of the surrogate and matrix spike compounds 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.

3.1.4 Experimental

The analyses followed the CLP SOW 288. The extraction process, described in Section 3.2.1, was sonication and was performed in the hot cells. The extract concentration process was carried out in open-faced hoods.

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.

As mentioned previously, surrogate and matrix spike recoveries were unsatisfactory because of dilutions, so the recovery criteria were not met. This will be further discussed in Section 3.2.2.

3.1.5 Screening

Two screening techniques were tested: the CLP SOW 288 GC method and the TOC method. The results of these techniques are discussed in Section 3.2.1.

3.2 PROBLEM AREAS AND CORRECTIVE ACTIONS

3.2.1 Extraction

In the first attempt to extract the sample, the low-level sample extraction process was followed with a 5-g sample. The sample was very basic, so a double extraction process was used. The sample was first extracted normally; it was then extracted after acidifying to ensure acid compound extraction (the surrogate and matrix spike compounds were added before the first 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. By this method, only 1/20 of the acid was added compared to the first method. No problems were encountered in concentrating this extract. In future work, a separate, weighed sample will be

acidified with a known amount of H_2SO_4 to the desired pH so that a good estimate of the amount of acid needed can be made. Also, pH indicator paper will not be used due to the potential of adding organic contamination to 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 the opposite is true for others of the acidic spikes.

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.

3.2.2 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. From SOW 288 screening protocol, this would indicate that the medium-level extraction procedure should be used and the results agree reasonably well with the GC results if the comparison is estimated on a molar basis.

In order 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 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.

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
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 I SV-2 1/87 Rev.

FIGURE 3.1. Semivolatile Organics Analysis Data Sheet

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
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

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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:01/28/89

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 1/87 Rev.

FIGURE 3.2. Semivolatile Organics Analysis Data Sheet

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

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg) ug/Kg	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
205-59-2	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

FORM I SV-2 1/87 Rev.

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

CAS NO.	COMPOUND	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

FORM I SV-1 1/87 Rev.

FIGURE 3.3. Semivolatile Organics Analysis Data Sheet

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

FORM I SV-2 1/87 Rev.

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-pf/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.	
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
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26.					
27.					
28.					
29.					
30.					

FIGURE 3.4. Semivolatile Organics Analysis Data Sheet Tentatively Identified Compounds

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

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

CONCENTRATION UNITS: ug/gm

Number TICs found: 14

	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.	
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

FIGURE 3.5. Semivolatile Organics Analysis Data Sheet Tentatively Identified Compounds

EPA SAMPLE NO.

89-0011

1F SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

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/gm

Number TICs found: 21

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.		Unknown	6.56	73.	
2.		Unknown	7.52	57.	
3.		Siloxane	7.76	460.	
4.		Unknown	12.03	210.	
5.		Siloxane	12.09	160.	
6.		Alkane	14.35	52.	
7.		Siloxane	15.49	200.	
8.		Alkane	16.45	1500.	
9.		Alkane	17.83	48.	
10.		Unknown	18.20	38.	
11.		Alkane	18.42	5700.	
12.		Siloxane	18.81	260.	
13.		Alkane	19.72	36.	
14.		Alkane	20.19	3600.	
15.		Alkane	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.	
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

FIGURE 3.6. Semivolatile Organics Analysis Data Sheet Tentatively Identified Compounds

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), WHC also asked that total alpha, total beta, and gamma energy analysis (GEA) be performed on both samples. The primary objectives of the radionuclide measurements 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 SIGNIFICANCE

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 (Na_2O_2/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 Na_2O_2/Zr fusion methods, was obtained for the total alpha and total beta results for sample 105-C. For sample 105-C, the total alpha and total beta results from the Na_2O_2/Zr fusion were somewhat higher than 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

Sample 105-C was fused by both the KOH/Ni and Na_2O_2/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 either a contaminated crucible or volumetric flask. Therefore, the 105-C sample fusions were repeated using new crucibles and new glassware, and then the reproducibility of the total alpha and GEA values were within acceptable limits, as reported in Table 4.1. This finding demonstrates that all 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 due to the large variation in activity levels anticipated for different samples.

Although good agreement between fusion methods was obtained for ^{137}Cs by GEA, 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.

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.

4.2.1 Radionuclides ^{227}Ac

Rather than measure 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.

4.2.2 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.

4.2.3 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.

4.2.4 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.

4.2.5 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.

4.2.6 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.

4.2.7 Radionuclide ^{210}Po

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

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

Results reported in Table 4.2 for ^{238}Pu and for $^{239+240}Pu$ 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.

4.2.9 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 are currently being made to this method that 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.

4.2.10 Radionuclide ^{151}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.

A procedure was evaluated using ^{151}Sm radioactive tracer, and 85% recovery of the Sm was obtained. 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 in order to verify that adequate separation from Eu is attainable.

4.2.11 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.

4.2.12 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.

4.2.13 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 TEST PLAN OBJECTIVES

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

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 ^{135}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

	Sample 105-C (nCi/g)		Sample 106-C (nCi/g)	
Radionuclide	KOH/Ni	Na_2O_2/Zr	KOH/Ni	Na_2O_2/Zr
Total α	1.17E3 1.15E3	1.40E3 1.30E3	4.13E3	3.99E3
Total β as $^{90}Sr/^{90}Y$	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 Activity (nCi/g)	Sample 105-C Yield (%)	Sample 106-C Activity (nCi/g)	Sample 106-C Yield (%)
^{227}Ac	<1.4	1-2	<0.9	1-2
^{241}Am	962 ± 38	22, 27	2824 ± 98	42, 26
^{243}Am	4.9 ± 1.3	"	19.2 ± 2.1	"
^{242}Cm	3.0 ± 0.3	"	10.5 ± 0.7	"
^{244}Cm	29.5 ± 1.4	"	129 ± 5	"
^{238}Pu	48 ± 5	62, 72	422 ± 11	51, 44
^{239}Pu	747 ± 126	"	2340 ± 57	"
^{242}Pu	<0.2	"	<0.4	"
^{135}Cs				
^{59}Ni	128 ± 5	61, 76	68 ± 14	87, 88
^{63}Ni	12885 ± 1804	"	7770 ± 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 percent of ^{137}Cs, ^{60}Co, and ^{154}Eu activity extracted was 0.026%, 0.076%, and 0.003%, respectively.

5.2 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 (μg/g)			NPH SST Sample (μg/g)		
	H_2O	HNO_3	Total	H_2O	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 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

Gamma Energy Analysis	(nCi/mL)
^{137}Cs	127.0
^{60}Co	0.88
^{154}Eu	0.17

Total Alpha	Total Beta (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 SIGNIFICANCE

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.

TABLE 6.1. Exposure Data Summary for Radiochemical Separations

Sample Procedure Used	Volume Removed from Hot Cell (mL)	Exposure Level Contact (mR/hr)	Exposure Level 3 feet (mR/hr)	Volume Used for Analysis (mL)	Time in Contact with Sample (est.) (min)
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 Procedure Used	Volume Removed from Hot Cell (mL)	Exposure Level Contact (mR/hr-bkgd)	Exposure Level 3 feet (mR/hr)	Volume Used for Analysis (mL)	Time in Contact with Sample (est.) (min)
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_2O_2 Fusion	10	4.0-<0.5	<0.5	10	5
Sample 102-C Fused Solids from Acid Oigestion, 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

REVISION 0
Approval Date 2-1-89

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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REVISION 0
Approval Date 2-1-89

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

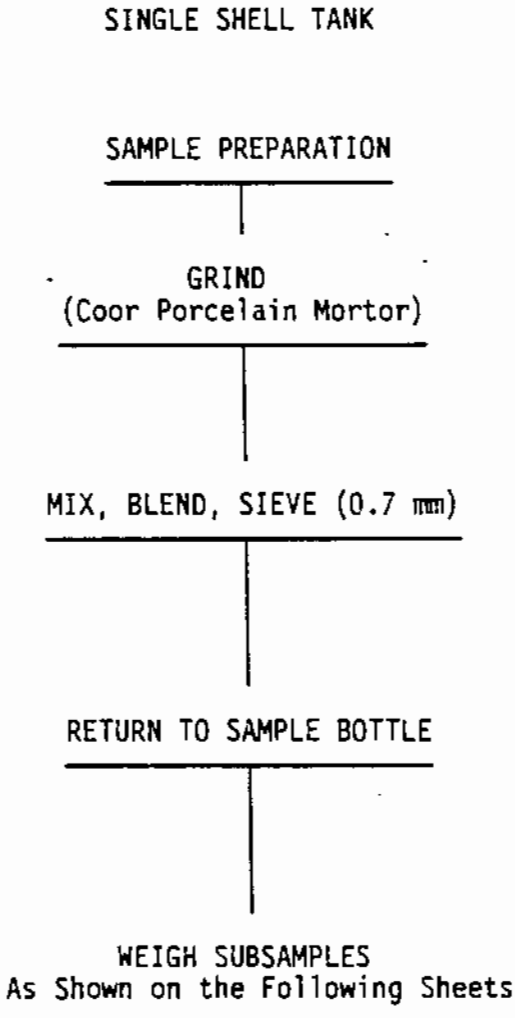
SINGLE SHELL TANK
SAMPLE PREPARATION
GRIND
(Coor Porcelain Mortor)
MIX, BLEND, SIEVE (0.7 mm)
RETURN TO SAMPLE BOTTLE
WEIGH SUBSAMPLES
As Shown on the Following Sheets

FIGURE 2

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

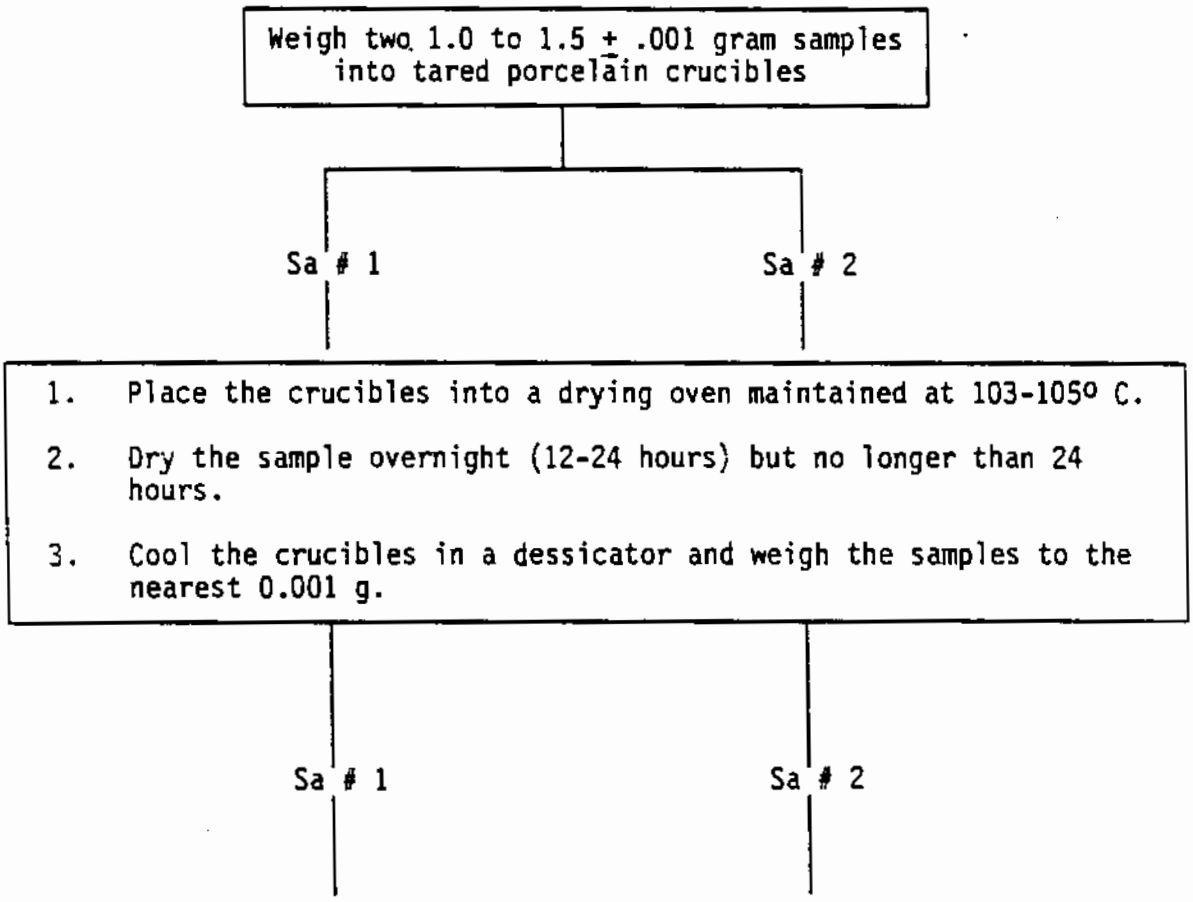

FIGURE 3

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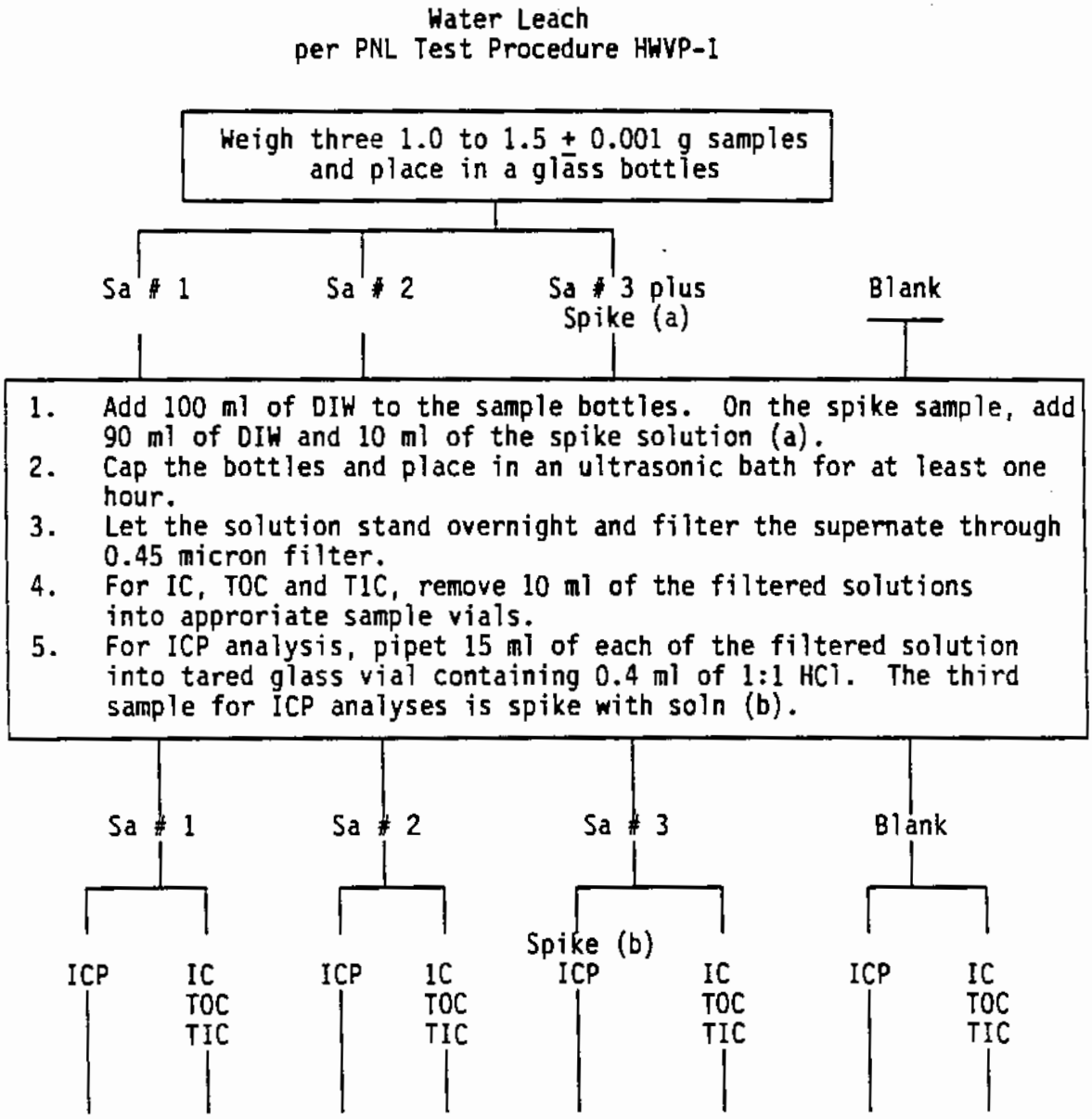
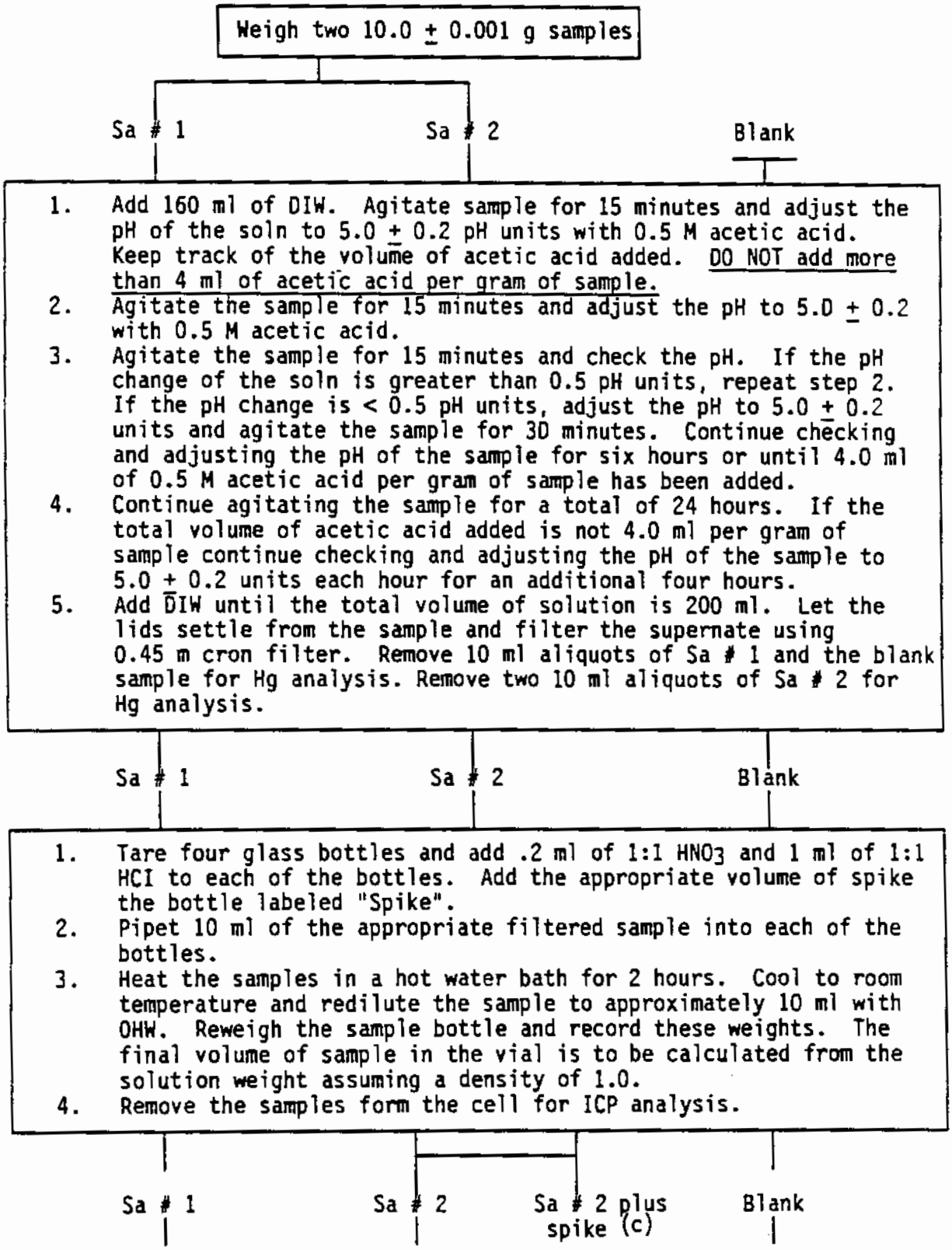


(a) Anion spike to contain 20 ug F^-, 20 ug Cl^-, 100 ug $NO3^-$, 1300 ug $NO2^-$, 100 ug $PO4^{-3}$, and 300 ug $SO4^{-2}$ per 10 ml of sample.

(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



(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

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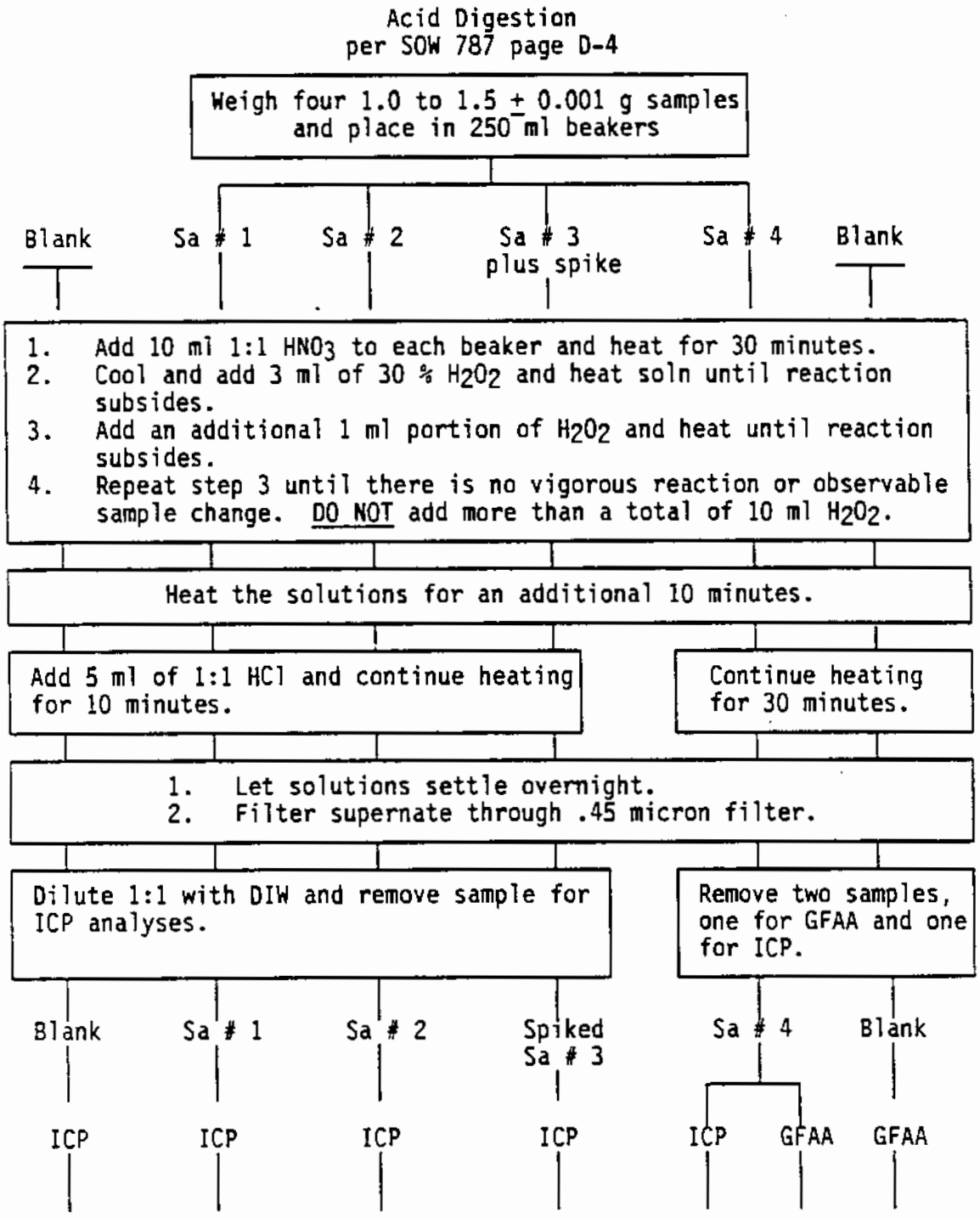

Spike to contain 20 ug Ba, 5 ug Cd, 100 ug Ca, 100 ug Cr, 5 ug Co,50 ug Pb, 20 ug Mg, 100 ug K, 10 ug Sr, 10 ug Zr, 10 ug Cu,5 ug Sb, 20 ug As,.5 ug Be,20 ug Tl, 5 ug V, and 5 ug Zn per 10 ml of sample. A second spike to contain 100 ug P and 5 ug Ag per 10 ml of sample

FIGURE 6

SINGLE SHELL TANK

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

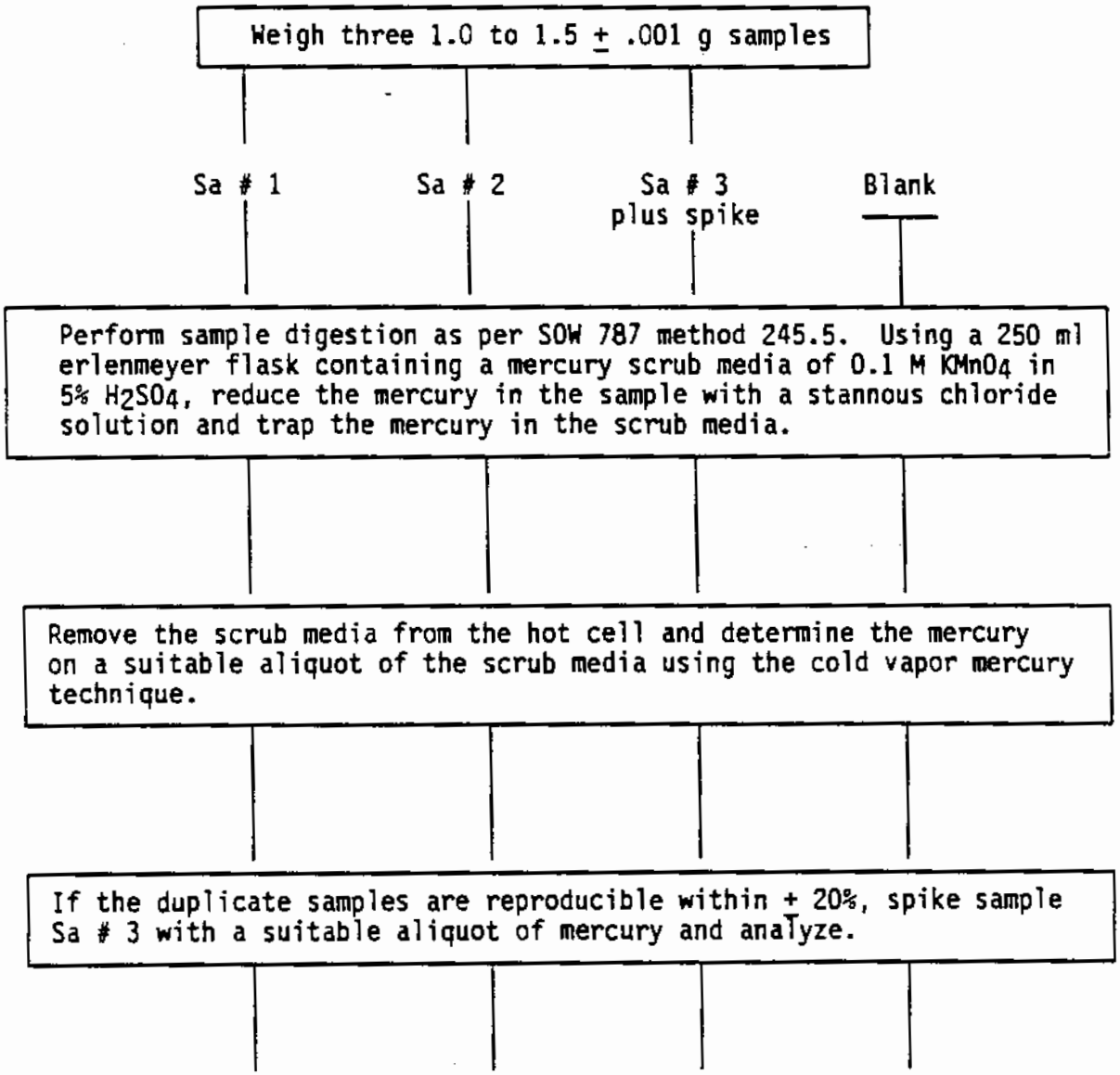

FIGURE 7

SINGLE SHELL TANK

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

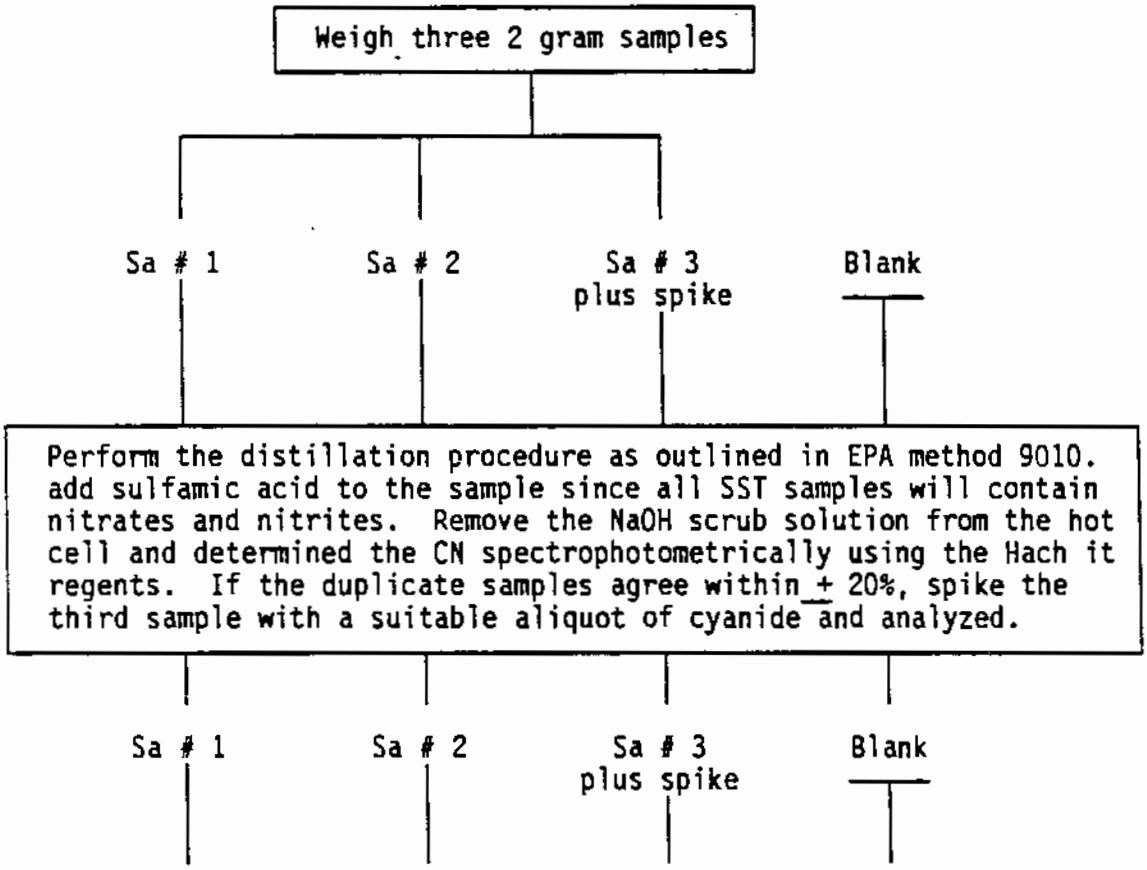

FIGURE 8

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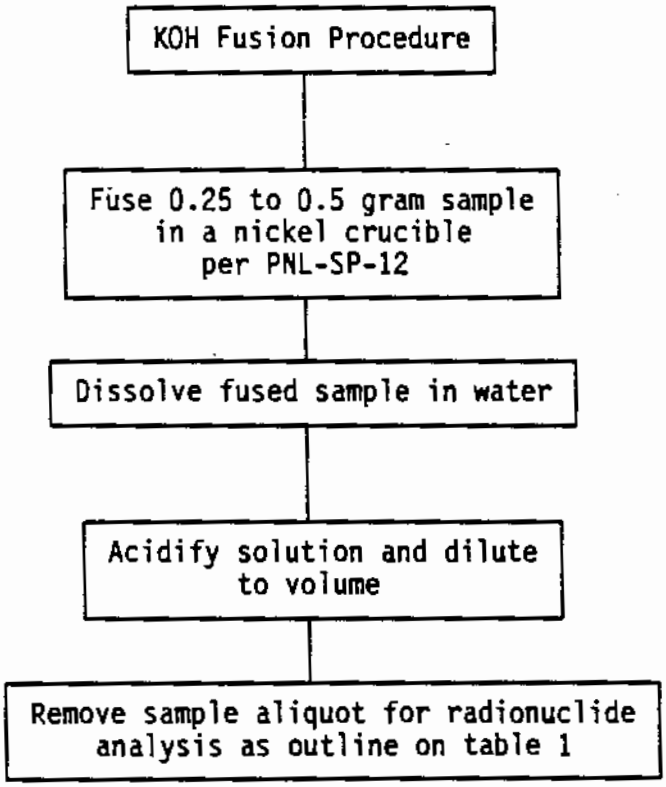

Table 1

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
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 7-4D.15
13.	^{151}Sm	PNL-Sm-01
14.	^{229}Th ^{230}Th ^{232}Th	RSD-51-DEQ-3

* May require mass spectrometer analysis

Table 1(continued)

15.	^{233}U ^{234}U ^{235}U ^{236}U ^{238}U	HTA-4-16 2-30.6 HTA-4-36
16.	^{93}Zr	PNL-Zr-01
17.	Total U Total	Included in item 15 Included in item 4 and 1D

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

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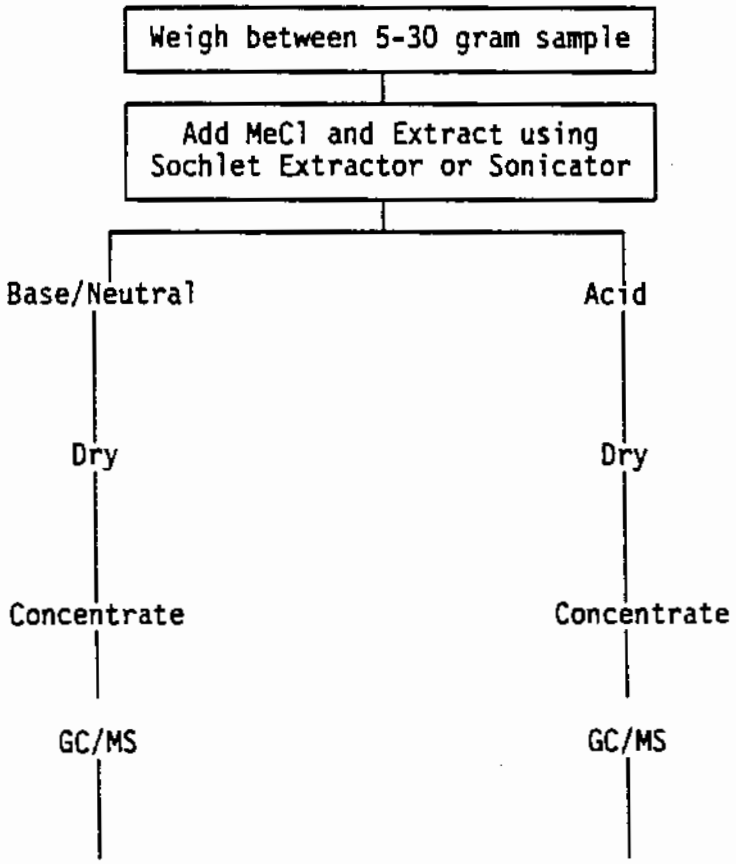
Semivolatile Organic Method
per SOW 787 Section D-2/SV



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

NPH Extractability Studies

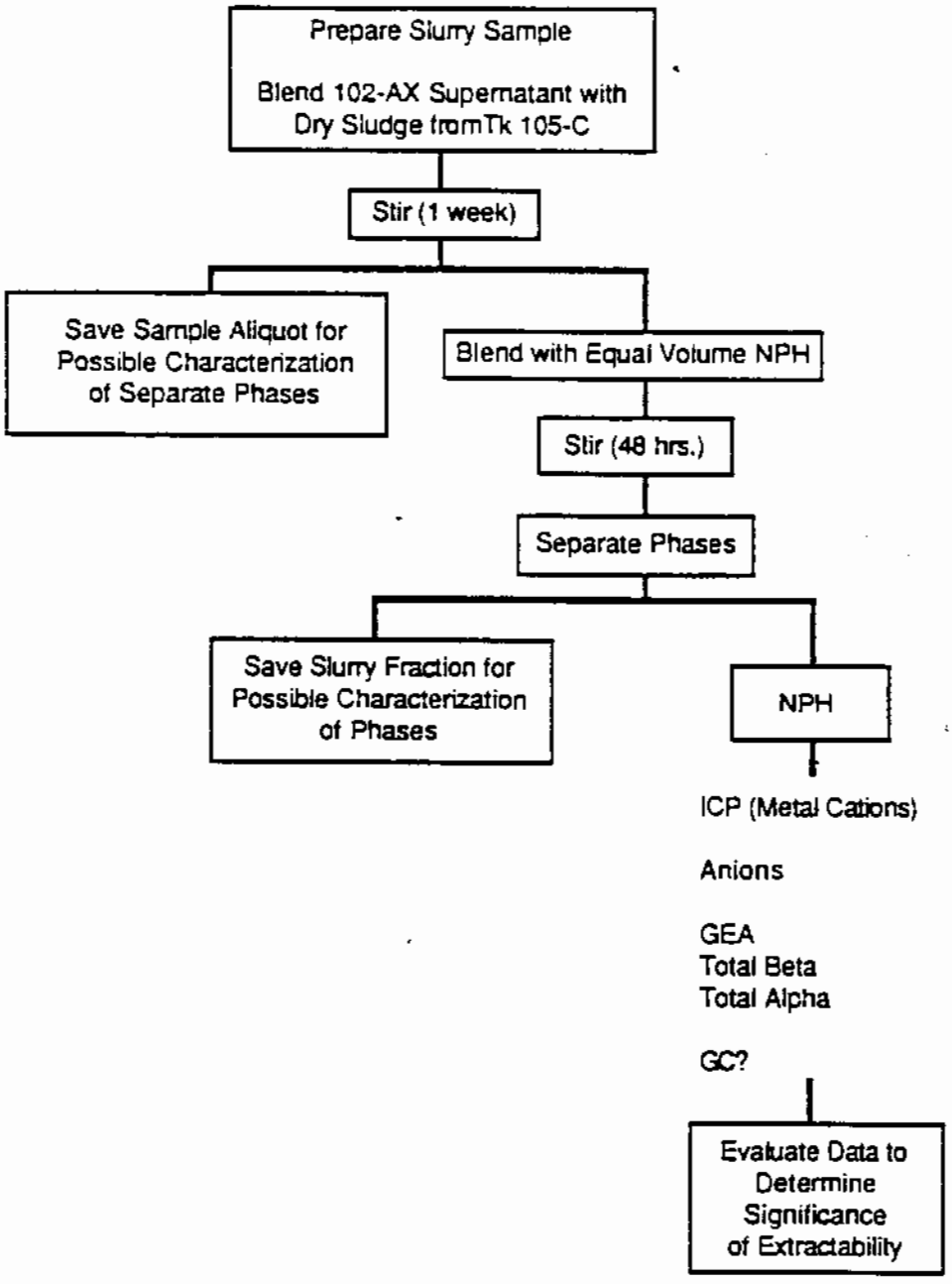


Figure 10

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 Perquisites 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 identifed 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.

PNL-7258
UC-721

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