Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Tank 40 Sludge Batch 9 Waste Acceptance Product Specifications (WAPS) Solids and Chemical Analyses (2018)

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September 2018
SRNL-STI-2018-00318, Revision 0

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Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2018-00318
Revision 0

Keywords: *Sludge Batch 9*
WAPS
Tank 40

Retention: *Permanent*

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Savannah River National Laboratory™
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PREFACE OR ACKNOWLEDGEMENTS

The authors would like to thank the staff and management of the Shielded Cells Operations at SRNL. In particular, we would like to thank Monica L. Jenkins and Phyllis U. Burkhalter for their attention to detail throughout the subsampling and digestion procedures. The authors also thank Dr. Chuck Coleman for his assistance and supervision in preparation and execution of the aqua regia and peroxide fusion digestions.

EXECUTIVE SUMMARY

A 3 L sample of sludge was collected from High Level Waste (HLW) Tank 40 (sample ID: HTF-40-18-9) at the Savannah River Site (SRS) and subsequently analyzed by the Savannah River National Laboratory (SRNL) in accordance with requirements for reporting the Waste Acceptance Product specification (WAPS) [1]. The collected sample was representative of Sludge Batch (SB) 9 that will be processed by the Defense Waste Processing Facility (DWPF) into a vitrified waste form.

The original 3 L sample was subsampled into a smaller 500 mL (approximate) bottle in the shielded cells operations (SCO) at SRNL. During the subsampling, the original 3 L sample was continuously agitated, via a mixing blade inserted into the bottle, to ensure the original sample was well-mixed. The sub-sample was then analyzed for the following properties:

- Supernate density
- Slurry density
- Weight Percent Total Solids (slurry)
- Weight Percent Calcined Solids (slurry)
- Weight Percent Dissolved Solids (supernate)
- Weight Percent Insoluble Solids (slurry)
- Weight Percent Soluble Solids (slurry)

In addition to these analyses, chemical analyses were also performed on the sub-sample to identify elemental and molecular species present in the slurry and supernate. The following chemical analyses were conducted on the respective sub-sample components:

- Supernate:
  - Anion
  - Mercury
  - Total Organic/Inorganic Carbon
  - Free OH^-
  - Other Base
  - Elemental
- Slurry:
  - Elemental
  - Mercury

The results of these analyses were consistent with previous Tank 40 analyses within the range of uncertainty specified within the Waste Qualification Report, Vol. 2, Rev. 6, "Reporting the Chemical Composition of the DWPF Product [2]." Certain notable findings of these analyses were:

- Supernate density: 1.05 g/cm^3 ; Slurry density: 1.10 g/cm^3
- Total solids: 15.14 wt.% ; Calcined solids: 11.56 wt.%
- Nitrite (supernate): 0.30 M ; Nitrate (supernate): 0.10 M ; Oxalate (supernate): 0.03 M
- Mercury (supernate): 3.42×10^{-4} M
- Sodium (supernate): 0.86 M
- Al (slurry): 6.01 wt.% ; Fe (slurry): 15.75 wt.% ; Na (slurry): 13.85 wt.%

In instances where two measurements (i.e., 2017 Tank 40 SB9 WAPS sample [3] and 2018 Tank 40 SB9 WAPS sample) have been acquired for a particular material property (e.g., slurry density) or chemical analyte (e.g., supernate Na concentration), the two measurements were averaged together and an analytical uncertainty associated with this average is reported.

The following conclusion is determined based on the work presented in this document:

- The differences observed between the 2017 and 2018 Tank 40 Sludge Batch 9 samples are within the expected range of uncertainty with respect to the criteria outlined in Volume 2 of the Waste Form Qualification Report [2]. The number of data are insufficient to determine if observed differences have any statistical significance in terms of sampling and analytical methods.

The following recommendations are based on the work presented in this document:

- SRNL work instruction, ITS-WI-0020 will be rewritten such that future 3 L tank samples are constantly agitated during the sub-sampling method. This protocol will improve the mixing of the large sample during the transfer to the smaller sample container.
- The acquisition of multiple samples based on a statistically designed experimental protocol, similar to that presented in Reference [11], would enable a more accurate determination of the uncertainty associated with a given WAPS analysis.

This report describes the method by which the subsample was obtained, the various sample analyses, and a summary of the measurements and uncertainty produced with each of the conducted analyses. The method by which certain measurements were averaged between the two WAPS samples and by which the error in this calculation was determined is also presented.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DWPF	Defense Waste Processing Facility
HLW	High-Level Waste
IC	Ion Chromatography
ICP-ES	Inductively-coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively-coupled Plasma – Mass Spectroscopy
SB9	Sludge Batch 9
SCO	Shielded Cells Operations
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TFP	Tank Farm Projection
WAPS	Waste Acceptance Product Specification
W_{cs}	Weight Percent Calcined Solids
W_{ds}	Weight Percent Dissolved Solids
W_{is}	Weight Percent Insoluble Solids
W_{ss}	Weight Percent Soluble Solids
W_{ts}	Weight Percent Total Solids

1.0 Introduction

A 3 L sludge sample (sample ID: HTF-40-18-9) was obtained from Tank 40 at the Savannah River Site (SRS) and transferred to Shielded Cells Operations (SCO) in Savannah River National Laboratory (SRNL) for solids and chemical analysis as requested via [4]. The material that was sampled comprises what is known as Sludge Batch (SB) 9 to be processed at the Defense Waste Processing Facility (DWPF) at SRS.

Once transferred to the SCO in SRNL, the 3 L sample was subsampled into an approximately 500 mL sample that is assumed to be representative of the larger, original Tank Farm sample. The 3 L sample was continuously agitated during the subsampling routine to ensure that the original sample was well mixed – this method of continuous agitation was not used to acquire a prior subsample of SB9 material that was analyzed in 2017 [5].

Smaller portions of the subsample were prepared in accordance with the appropriate procedures relative to the analysis that was to be performed. These portions were used to determine the densities of the supernate and slurry solutions, the weight percentages of various slurry and supernate solids, and certain elemental and molecular species within the Tank 40 SB9 sample. The density and solids measurements as well as the sample preparation were performed in SCO while the chemical analyses were completed in various laboratories within Analytical Development (AD) at SRNL.

2.0 Experimental Procedure

2.1 Subsampling

The subsampling of Tank Farm sample HTF-40-18-9 3 L sample was conducted in the SCO facility at SRNL. Previous SB9 analyses yielded a total weight percent solids result that was lower than the value that was projected [3, 6]. Diagnosing the specific phenomenon responsible for the discrepancy between the projected and measured values for the 2017 Tank 40 Waste Acceptance Product Specifications (WAPS) sample would require additional experimental and statistical analyses. However, the subsampling procedure was modified for the 2018 Tank 40 WAPS sample analysis to mitigate the experimental variable of sludge settling affecting the solids measurements while ensuring that the 3 L sample was well-mixed during the subsampling.

The 3 L sample was continuously agitated by mixing blades for approximately 30 minutes prior to initiating the sample transfer to the smaller, 500 mL container. The sample transfer occurs via two “dip legs” which are connected through a peristaltic pump. In addition to the continuous agitation, the well-mixed slurry was circulated through the peristaltic pump via the dip legs for approximately five minutes before the sample transfer was executed. The sample agitation continued throughout the subsample transfer, which took approximately one minute to complete.

Upon completion of the sample transfer from the 3 L container to the 500 mL container, the 500 mL container was agitated by shaking for approximately five minutes. Approximately 100 mL of the slurry sample was immediately added to a 0.45 μm filter cup – this filtrate product was representative of the Tank 40 supernate solution.

2.2 Density Measurements

The densities of the slurry and supernate materials were gravimetrically determined against the density of water at a specific temperature. Four replicates of the supernate were acquired from the filtrate solution that was produced during the subsampling. The remaining slurry subsample was agitated for approximately five minutes and four replicates of slurry material were obtained. Each of the replicate samples was

weighed and the density of the slurry and supernate was determined based on the results of these measurements. The reported density for the slurry and supernate solutions is an average of the replicate samples.

2.3 Solids Analyses

The weight percent total solids (W_{ts}) and weight percent dissolved solids (W_{ds}) were determined by drying replicate samples of the slurry and supernate materials, respectively. The supernate specimens were obtained by adding approximately 4 mL of the filtrate material to a glass beaker – four replicates of supernate material were prepared and dried for solids analysis. The slurry specimens were obtained in a similar fashion; however, the 500 mL bottle containing the slurry material was agitated for approximately five minutes prior to initiating the sample collection. The 500 mL bottle was agitated again for five minutes prior to the collection of the last two replicates. Rather than glass beakers, the slurry samples were added to Al_2O_3 crucibles that would later be used for the calcination of the specimens. The masses of the replicate samples were measured prior to further experimentation.

Each of the replicate sample vessels was loaded into a drying oven which was maintained at a constant temperature of 110 °C. The initial drying period was greater than eight hours (overnight). The dry sample weights of the replicates were measured after the initial drying. Additional dryings were performed for approximately four hours each until the dry sample weight from one drying to the next was less than or equal to 0.005 g. The reported solids values are averages of the replicate samples. In addition to the two measured values, W_{ts} and W_{ds}, two additional values were calculated based on the dry sample weights: weight percent insoluble solids (W_{is}) and weight percent soluble solids (W_{ss}) according to Equations 1 and 2[7].

$$W_{is} = \frac{W_{ts} - W_{ds}}{100 - W_{ds}} \cdot 100 \quad (1)$$

$$W_{ss} = W_{ts} - W_{is} \quad (2)$$

The weight percent calcined solids in the slurry sample was determined by heating the dry slurry replicates to approximately 1100 °C for approximately two hours. The calcined sample masses were obtained after the samples had cooled for roughly ten minutes.

It should be noted that during the drying procedure for the W_{ds} determination, three of the four replicates appeared to gain weight (~0.03 g) from the first to second drying. However, the masses measured after a third drying of all four replicates were measured to be a difference of less than or equal to 0.001 g of the weights after the first drying. At this point, the samples were assumed to be thoroughly dried, and the W_{ds} values were calculated based on the weights obtained for the four replicates after the third drying.

2.4 Chemical Analyses

Samples of the supernate and slurry materials were prepared in the shielded cells and transferred to AD for multiple chemical analyses. Four supernate replicates were diluted in water as well as an additional four replicated in 1.0 M HNO_3. Four slurry replicates were digested by aqua regia (HNO_3/HCl) and four replicates by peroxide fusion ($NaOH/Na_2O_2$). The various dilution/digestion methods facilitate the analytical techniques used to determine the elemental and molecular composition of their respective samples. The dilution/digestion method and subsequent characterization methods are given in Table 2-1 for each of the respective specimens.

Table 2-1: Chemical analyses of supernate and slurry from 2018 Tank 40 SB9 WAPS sample.

Sample	Diluent/Digestion	Analysis
Supernate	water	ion chromatography (IC), cold-vapor atomic absorption (CVHg), total carbon (organic/inorganic) (TOC, TIC), free OH^-, total base, other base
Supernate	1.0 M HNO_3	inductively coupled plasma – emission spectroscopy (ICP-ES), inductively coupled plasma – mass spectroscopy (ICP-MS)
Slurry	aqua regia	ICP-ES, ICP-MS
Slurry	peroxide fusion	ICP-ES

2.5 Combining 2017 and 2018 WAPS Sample Data

Certain analyses were performed on both the 2017 WAPS and 2018 WAPS samples resulting in two valid sets of data for some measurements. As such, these data were averaged, and the analytical error associated with the two sets was combined to give a standard error of the measurement. The calculation of the standard deviation was derived from the analytical variation associated with a given WAPS sample as demonstrated below for two sets of measurements (A and B) and the associated analytical variation of a hypothetical property, $\mathbb{X}$: $\overline{\mathbb{X}}_A \pm s_A$ *and* $\overline{\mathbb{X}}_B \pm s_B$.

For example, let $\overline{\mathbb{X}}_A$ represent the average of the measured, replicate supernate densities for the 2017 WAPS sample, s_A is the analytical variation of the replicate density measurements as represented by the sample standard deviation of the $\mathbb{X}_{A_1}, \mathbb{X}_{A_2}, \ldots, \mathbb{X}_{A_{nA}}$ results. Similarly, $\overline{\mathbb{X}}_B$ and s_B represent the average and analytical variation of the measured replicate supernate densities for the 2018 WAPS sample. Then the average of these two measurement sets and the standard deviation associated with that average are given by Equation 3 and Equation 4, respectively:

$$\overline{\mathbb{X}} = \frac{1}{2}\left(\overline{\mathbb{X}}_A + \overline{\mathbb{X}}_B\right) \tag{3}$$

$$s_{\overline{\mathbb{X}}} = \frac{1}{2}\sqrt{\left(\frac{s_A}{\sqrt{n_A}}\right)^2 + \left(\frac{s_B}{\sqrt{n_B}}\right)^2} \tag{4}$$

where $\overline{\mathbb{X}}$ is the average of the results from the 2017 WAPS sample and the 2018 WAPS sample, $s_{\overline{\mathbb{X}}}$ is the standard deviation for the average of the two combined results, and n_A and n_B are the number of replicate measurements in Sample A and Sample B, respectively. This method will be applied throughout this report to combine measurements where two data sets were available. Relative standard deviations (%RSD) of the replicate measurements are reported for the individual sample sets.

It should be noted that the reported standard deviation, as calculated by Equation 4, does not represent any confidence interval associated with Tank 40 sampling uncertainty. This error value is only representative of the analytical variation revealed in the replicated measurements. It also does not include all of the uncertainty introduced from the measurement techniques themselves. For example, the AD laboratory

reported a %RSD on their ICP-ES results of approximately 10% for most of the measurements. This %RSD was not introduced as a separate uncertainty into the calculation of the average standard variation.

2.6 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 Procedure 2.60[8]. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2[9].

3.0 Results and Discussion

3.1 Densities and Solids Analyses

The results of the individual replicate density measurements, ρ, for both the supernate and slurry were averaged, and a relative standard deviation was calculated based on the average density and the associated standard deviation according to Equation 5:

$$\%RSD = \frac{s}{\overline{\mathbb{X}}} \cdot 100 \quad (5)$$

where *%RSD* is the relative standard deviation, *s* is the standard deviation of the replicate measurements, and $\overline{\mathbb{X}}$ is the average of the replicate values. Equation 5 represents the method by which all *%RSD* values are calculated throughout this report for the combined 2017 and 2018 WAPS sample data. The 2018 Tank 40 SB9 WAPS sample densities are given in Table 3-1 along with the reported density for the 2017 Tank 40 SB9 WAPS sample [3] and the Tank Farm Projection (TFP) [6].

Table 3-1: Densities for the supernate and slurry samples from the 2018 and 2017 Tank 40 SB9 WAPS samples, combined average, and the TFP values. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

	2017 WAPS Sample	2018 WAPS Sample	Combined Average	TFP
Sample Type	$\overline{\rho}$ **(%RSD) (g/cm³)**	$\overline{\rho}$ **(%RSD) (g/cm³)**	$\overline{\rho}$ **(%$RSD_{\overline{\rho}}$) (g/cm³)**	**ρ (g/cm³)**
Supernate	1.05 (0.2) [3]	1.05 (0.5) [4]	1.05 (0.1)	1.05
Slurry	1.09 (1.9) [4]	1.10 (0.4) [4]	1.10 (0.5)	1.13

The solids measurements and calculations for the 2017 WAPS sample, 2018 WAPS sample and TFP value are given in Table 3-2 along with the calculated average and standard error for the combined 2017 and 2018 WAPS samples.

Table 3-2: Solids data for the 2017 and 2018 Tank 40 SB9 WAPS samples combined average , and the TFP values. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

	2017 WAPS Sample [4]	2018 WAPS Sample [4]	Combined Average	TFP
Type	**wt.% (%RSD)**	**wt.% (%RSD)**	**wt.% (%RSD)**	**wt.%**
Total Solids (Slurry)	14.06 (0.53)	15.14 (0.99)†	14.60 (0.26)	15.46
Calcined Solids (slurry)	10.60 (1.45)	11.56 (0.55)	11.08 (0.38)	11.63
Insoluble Solids	9.13 (1.37)	10.30 (1.54)	9.72 (0.52)	10.68
Dissolved Solids (supernate)	5.42 (1.90)	5.40 (1.32)	5.41 (0.58)	NR
Soluble Solids	4.93 (2.95)	4.84 (4.50)	4.89 (1.34)	NR
†Five replicates were used to measure the Total Solids wt.% for the 2018 WAPS Sample				

The analysis of the supernate solution included measurements of the anion, carbon and base content as well as the elemental composition of the solution. The results of these various measurements are given in Table 3-3, Table 3-4, and Table 3-5 and show the reported data for the 2017 and 2018 WAPS samples, the averaged value of these two samples and the TFP.

Table 3-3: Anion composition measured by Ion Chromatography (IC) for the 2017 and 2018 Tank 40 SB9 WAPS samples, combined average, and the TFP values. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

	2017 WAPS Sample [4]	2018 WAPS Sample [4]	Combined Average	TFP
Anion	**mol/L (%RSD)**	**mol/L (%RSD)**	**mol/L (%RSD)**	**mol/L**
NO_3^-	0.102 (2.3)	0.083 (2.7)	0.093 (0.9)	0.117
NO_2^-	0.281 (1.2)	0.296 (0.8)	0.289 (0.4)	0.274
SO_4^{2-}	0.009 (0.7)	0.010 (1.1)	0.010 (0.3)	0.012
PO_4^{3-}	<0.001	<0.001	<0.001	0.001
Br^-	<0.011	<0.001	<0.001	NR
Cl^-	<0.003	<0.003	<0.003	0.001
CHO_2^-	<0.002	<0.002	<0.002	NR
$C_2O_4^{2-}$	0.028 (5.4)	0.027 (0.4)	0.028 (1.4)	NR
F^-	<0.005	<0.005	<0.005	0.001

Table 3-4: Measured carbon and base content of the 2017 and 2018 Tank 40 SB9 WAPS samples supernate and combined average. Note there is no TFP data given in [6] for these analyses. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

Analyte	2017 WAPS Sample Measurement (%RSD) [4]	2018 WAPS Sample Measurement (%RSD) [4]	Combined Average (%RSD)
Total Carbon (µg C/mL)	1730 (1.6)	2423 (1.2)	2077 (0.4)
Inorganic Carbon (µg C/mL)	1170 (1.4)	1650 (1.5)	1410 (0.5)
Organic Carbon (µg C/mL)	563 (5.6)	772 (0.8)	668 (1.2)
Total Base (M)	0.24 (13.0)	0.25 (6.7)	0.25 (3.6)
Free OH^- (M)	0.19 (9.7)	0.11 (20.3)	0.15 (4.9)
Other Base (M)	<0.08	0.06 (42.1)	0.06 (42.1)[†]

[†]Only the 2018 WAPS sample data is included because 2017 WAPS result was below detection limit for that particular experimental analysis.

Table 3-5: The elemental composition of the 2017 and 2018 Tank 40 SB9 WAPS samples supernate solution, combined average, and TFP values. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

	2017 WAPS Sample [4]	2018 WAPS Sample [4]	Combined Average	TFP
Element	**M (%RSD)**	**M (%RSD)**	**M (%RSD)**	**M**
Al	3.08E-02 (1.8)	2.68E-02 (1.76)	2.88E-02 (0.6)	NR
B	4.69E-04 (4.9)	6.33E-04 (2.81)	5.51E-04 (1.3)	NR
Cr	5.19E-04 (2.5)	5.50E-04 (2.6)	5.35E-04 (0.9)	NR
Hg[a]	4.61E-04 (1.5)	3.42E-04 (2.5)	4.02E-04 (0.7)	NR
K	3.53E-03 (4.9)	1.10E-03 (18.1)	2.31E-03 (2.8)	NR
Mo	9.46E-05 (4.9)	7.92E-05 (4.1)	8.69E-05 (1.6)	NR
Na	8.23E-01 (1.8)	8.60E-01 (0.4)	8.42E-01 (0.4)	8.40E-01
S	1.07E-02 (1.5)	1.15E-02 (12.8)	1.11E-02 (3.3)	NR

As previously mentioned, the analysis of the slurry composition utilizes two digestion methods which complement one another in terms of dissolution efficacy. The elemental composition of the 2017 and 2018 WAPS samples, the combined average of these two samples, and the TFP are given in Table 3-6.

[a] Cold-vaper atomic absorption (CV Hg) analysis was used to determine the Hg content in the supernate solution.

Table 3-6: Elemental composition of slurry from 2017 and 2018 WAPS samples, the combined average, and the TFP values. Special circumstances are demarcated and explanations given at the beginning of the table. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

[*]Only the peroxide fusion digestion method was used in determining the concentration of these elements (Al, Si).
[†]Peroxide fusion and aqua regia digestion methods were both used in determining the concentration of these elements (Ba, Ca, Fe, Mn, Ni, U)
[§]For these particular analyses, only one WAPS sample yielded results above the instrumental detection limit. Consequently, the reported values represent that sample's measured results and the %RSD associated with those replicate measurements.
[#]Only one replicate yielded a measurement above the detection limit.

	2017 WAPS Sample	2018 WAPS Sample	Combined Average	TFP
Element	wt.% (%RSD) [4]	wt.% (%RSD) [4]	wt.% (%RSD)	wt.%
Ag	NR	<0.02	<0.02	0.01
Al[*]	6.62 (2.1)	6.06 (11.4)	6.34 (2.8)	6.37
B	<0.03	0.03 (15.5)	0.03 (15.5)[§]	0.01
Ba[†]	0.07 (7.4)	0.07 (2.9)	0.07 (0.6)	0.07
Be	<0.00	0.02 (17.6)	0.02 (17.6)[§]	0.00
Ca[†]	0.93 (6.4)	1.03 (3.0)	0.98 (0.7)	1.00
Cd	0.01 (5.5)	0.01 (0.9)	0.01 (0.3)	0.02
Ce	0.22 (0.4)	0.22 (0.7)	0.22 (0.2)	0.10
Co	0.01 (2.1)	0.01 (0.8)	0.01 (0.5)	0.01
Cr	0.09 (9.0)	0.08 (0.8)	0.09 (0.5)	0.07
Cu	0.04 (0.5)	0.03 (1.4)	0.04 (0.4)	0.05
Fe[†]	16.3 (4.4)	15.75 (2.8)	16.03 (0.5)	16.90
Gd	0.08 (2.2)	0.08 (0.0)	0.08 (0.3)	0.08
Hg	1.92 (8.8)	2.22 (2.5)	2.07 (2.15)	2.48
K	0.12 (13)	0.08 (4.3)	0.10 (4.1)	0.09
La	0.04 (1.4)	0.04 (0.8)	0.04 (0.5)	0.04
Li	0.04 (0.8)	0.04 (0.3)	0.04 (0.2)	0.05
Mg	0.22 (0.7)	0.21 (1.2)	0.22 (0.4)	0.22
Mn[†]	5.32 (1.0)	5.12 (2.8)	5.22 (0.5)	5.50
Mo	<0.02	0.01 (2.0)	0.01 (2.0)[§]	0.01
Na	15.6 (0.7)	13.85(1.6)	14.73 (0.4)	13.60
Ni[†]	1.15 (3.3)	1.04 (2.9)	1.10 (0.5)	1.19
P	0.17 (9.6)	0.14 (11.5)	0.16 (3.7)	0.15
Pb	0.03 (3.4)	0.04 (1.2)	0.04 (1.96)	0.03
S	0.26 (0.7)	0.25 (8.6)	0.26 (2.1)	0.26
Sb	<0.03	0.02	0.02[§,#]	NR
Si[*]	1.20 (4.5)	1.24 (9.8)	1.22 (2.7)	1.34
Sn	<0.02	<0.01	<0.02	0.01
Sr	0.03 (0.7)	0.02 (0.5)	0.03 (0.2)	0.03
Th	0.765 (0.6)	0.80 (0.5)	0.78 (0.2)	0.83
Ti	0.02 (1.1)	0.02 (1.0)	0.02 (0.4)	0.02
U[†]	3.00 (0.6)	2.90 (0.8)	2.95 (0.4)	3.19
V	<0.00	<0.01	<0.01	0.00
Zn	0.03 (1.0)	0.03 (0.8)	0.03 (0.3)	0.03
Zr	0.09 (20)	0.03 (80.9)	0.06 (14.6)	0.05

The aqua regia-digested slurry sample was also characterized via ICP-MS for noble metal content, and the results of this analysis are given in Table 3-7. The analysis of noble metal concentrations followed the calculations given in Bibler [10].

Table 3-7: ICP-MS results for the 2017 and 2018 Tank 40 SB9 WAPS Samples, the combined averaged, and the TFP values. Relative standard deviations are given inside the parentheses and the number of replicates is given in brackets.

	2017 WAPS Sample [4]	2018 WAPS Sample [4]	Combined Average	TFP
Element	**wt.% (%RSD)[a]**	**wt.% (%RSD)**	**wt.% (%RSD)**	**wt.%**
Ag(-107, -109)	1.10E-02 (1.0)	1.15E-02 (1.2)	1.13E-02 (0.4)	9.70E-02
Rh(-103)	1.14E-02 (1.2)	1.15E-02 (0.9)	1.14E-02 (0.4)	1.20E-02
Ru(-101,-102,-104)	5.05E-02 (0.7)	5.23E-02 (1.5)	5.14E-02 (0.4)	5.80E-02
Pd(-105, -106, -107, -108, -110)	2.33E-03 (1.6)	2.31E-03 (2.4)	2.32E-03 (0.7)	3.00E-03
Th	7.41E-01 (0.6)	7.25E-01 (0.7)	7.41E-01 (0.2)	8.27E-01
U	3.00E+00 (1.2)	3.02E+00 (0.8)	3.01E+00 (0.4)	3.19E+00

4.0 Conclusion

The following conclusion was drawn based on the analyses of the 2018 Tank 40 SB9 WAPS sample (HTF-40-18-9):

- The differences observed between the 2017 and 2018 Tank 40 SB9 samples are within the expected range of uncertainty with respect to the criteria outlined in Volume 2 of the Waste Form Qualification Report [2]. The number of data are insufficient to determine if observed differences have any statistical significance in terms of sampling and analytical methods.

5.0 Recommendations

The following recommendations are being made by SRNL in terms of Tank 40 WAPS sample analysis:

- SRNL work instruction, ITS-WI-0020 will be rewritten such that future 3 L tank samples are constantly agitated during the sub-sampling method. This protocol will improve the mixing of the large sample during the transfer to the smaller sample container.
- The acquisition of multiple samples based on a statistically designed experimental protocol, similar to that presented in Oji [11], would enable a more accurate determination of the uncertainty associated with a given WAPS analysis.

[a] These uncertainty values were determined using a different method than the values reported in [3].

6.0 References

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