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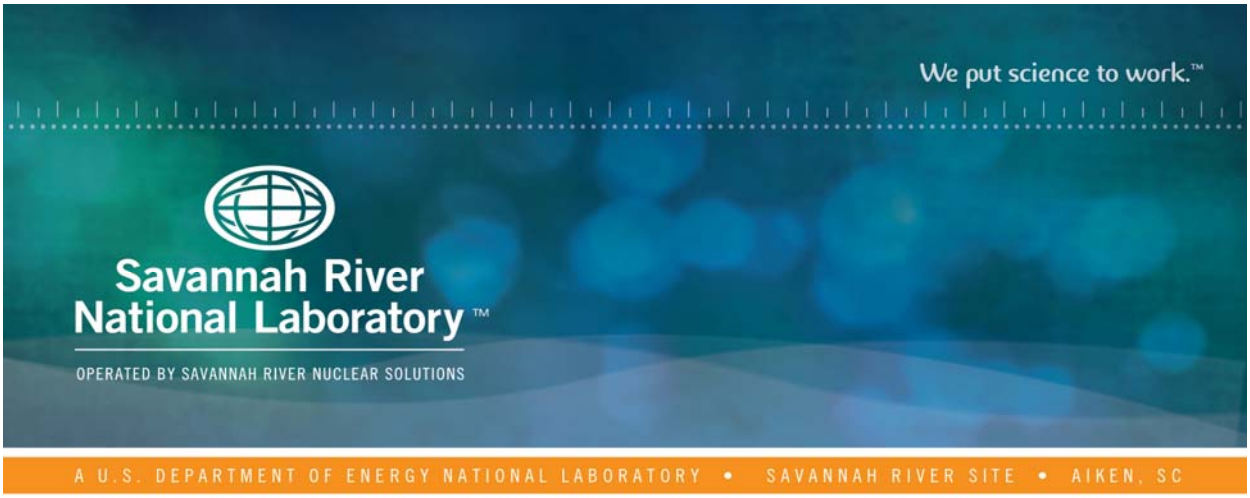

Analysis of Tank 23H (HTF-23-19-23, -24, -25) Samples for Support of the Enrichment Control and Corrosion Control Programs

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EXECUTIVE SUMMARY

SRNL analyzed samples from Tank 23H to support ECP and CCP. The results of the analysis indicate the concentrations of species in Tank 23H increase with depth in the tank. The sample obtained from the lowest level of 60" from the bottom of the tank shows the highest concentrations for most species analyzed. The surface sample and the 140" sub-surface sample show similar compositions with the sub-surface sample being slightly more concentrated, and both are more dilute than the lowest 60" sub-surface sample for most species analyzed.

The total uranium concentration in the three Tank 23H samples show a slight increase from the surface sample to the next lower sub-surface sample, but then a slight decrease in the uranium concentration in the lowest sub-surface sample. The U-235 weight fraction ranges from 0.94-1.2% in the Tank 23H samples.

The sum of the major cations versus the sum of the major anions shows a difference of ~5% or less for all three of the Tank 23H samples indicating good data quality for the non-radioactive analytes in the table. Small %RSD values for the replicate analyses with the exception of species close to the detection limit (e.g., Fe) provide another indication of good data quality for the non-radioactive species. The silicon concentrations measured in the Tank 23H samples were all below detection.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	De-ionized
CCP	Corrosion Control Program
ECP	Enrichment Control Program
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC	Total Inorganic Carbon

1.0 Introduction

The Enrichment Control Program (ECP) and the Corrosion Control Program (CCP) require periodic sampling and analysis to confirm that the waste supernate composition stays within the limits.[1,2] Savannah River Remediation (SRR) obtained samples from three different heights within Tank 23H on March 14, 2019. The samples were received by the Savannah River National Laboratory (SRNL) Shielded Cells on March 14, 2019. Analysis of these samples provides information necessary for determining compliance with the ECP and CCP. The sample characterization was requested via a Technical Task Request[3] and conducted based on a Task Technical and Quality Assurance Plan.[4]

2.0 Experimental Procedure

The samples from Tank 23H were opened in the SRNL Shielded Cells and poured into clear plastic beakers. The beakers were photographed, and the mass of each sample determined. Table 2-1 provides the sampling height and sample mass for each Tank 23H sample. Figure 2-1 shows a photograph of the samples in the clear plastic beakers. All of the samples were mostly clear and showed no visible undissolved solids when poured into the clear plastic beakers.

All three samples received the analyses required by the ECP that includes determination of uranium isotopes by inductively coupled plasma-mass spectrometry (ICP-MS) and determination of plutonium isotopes by radiochemical separation and counting methods. All three samples were also submitted for gamma spectroscopy to determine the Cs-137 concentration and inductively coupled plasma-emission spectroscopy (ICP-ES) to determine Na, Al, Si, and other metals. All three samples from Tank 23H received the analyses required by the CCP. The CCP analysis suite includes determination of free hydroxide, and ion chromatography (IC). The total inorganic carbon (TIC) was also determined on the samples to provide a concentration for the carbonate anion present in the samples.

Density measurements were made on well-mixed (unfiltered) aliquots of the samples using calibrated volumetric tubes at ambient cell temperature (21 °C).

For the samples receiving the CCP analysis suite, de-ionized (DI) water dilutions were made in triplicate from a well-mixed (unfiltered) sample and submitted to Analytical Development (AD) for analysis. A blank of the DI water was also prepared along with the samples.

Triplicate aliquots of the well-mixed (unfiltered) sample from each sample receiving the ECP analysis suite were prepared for analysis using the warm acid strike method.[5] A reagent blank and three silicon standard solutions were submitted for analysis with the samples.

Quality Assurance
Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This review meets the acceptable criteria to comply with the TTR classification for this work as safety class. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-31.

Table 2-1. Sampling Height and Sample Mass of the Tank 38H and 43H Samples

Sample ID	Sample Type	Sampling Height (inches from bottom)	Sample Mass (g)
HTF-23-19-23	Surface	surface	88.3
HTF-23-19-24	Sub-surface	140”	92.9
HTF-23-19-25	Sub-surface	60”	99.6

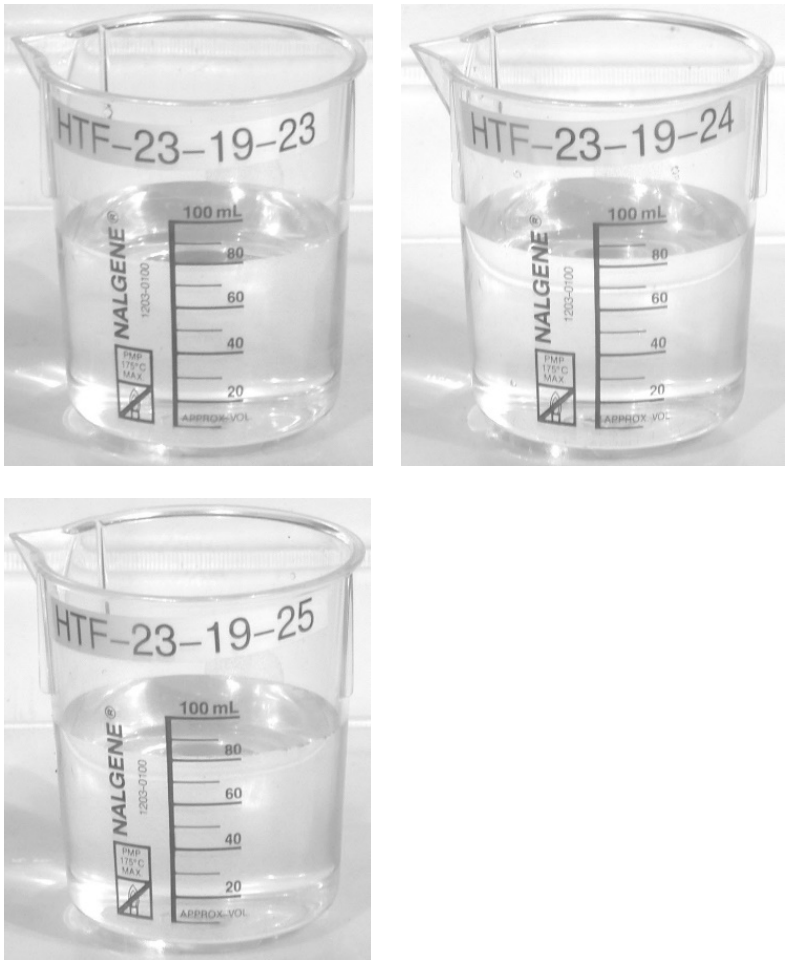

Figure 2-1. Samples from Tank 23H

3.0 Results and Discussion

The following table contains the results from the analysis of the samples. The table shows the average concentrations and the percent relative standard deviations (RSD) for the triplicate sample preparations unless otherwise noted. Results preceded by "<" indicate the analyte was below the limits of quantification for all three replicate aliquots of the sample. Results preceded by "≤" indicate that at least one of the replicates for the sample was above the limits of quantification while one or more of the replicates analyzed were below detection. The percent RSD presented in the table only includes the uncertainty associated with sub-sampling/sample preparation in the Shielded Cells and the analytical method. The estimated one sigma percent uncertainty provides an indication of the uncertainty associated with the analytical method as reported by AD. Neither of these measures of uncertainty includes the uncertainty associated with sampling a large waste tank. Previous investigations indicate the uncertainty from taking a small sample from a large waste tank can be significant.[6,7,8]

Overall, the results in Table 3-1 indicate the concentrations of species in Tank 23H increase with depth in the tank. The sample obtained from the lowest level of 60" from the bottom of the tank (HTF-23-19-25) shows the highest concentrations for most species analyzed. The sodium concentration increases from 3.14 M in the surface sample (HTF-23-19-23), to 3.23 M in the 140" sub-surface sample (HTF-23-19-24), to 5.63 M in the 60" sub-surface sample (HTF-23-19-25). The surface sample (HTF-23-19-23) and the 140" sub-surface sample (HTF-23-19-24) show similar compositions with the sub-surface sample being slightly more concentrated, and both are more dilute than the lowest 60" sub-surface sample (HTF-23-19-25) for most species analyzed.

The sum of the major cations versus the sum of the major anions shows a difference of ~5% or less for all three of the Tank 23H samples indicating good data quality for the non-radioactive analytes in the table. Small %RSD values for the replicate analyses with the exception of species close to the detection limit (e.g., Fe) provide another indication of good data quality for the non-radioactive species.

The total uranium concentrations in Table 3-1 show similar concentrations for the surface sample (HTF-23-19-23) and the next lower sub-surface sample (HTF-23-19-24), but then a slight decrease in the uranium concentration in the lowest sub-surface sample. The lower uranium concentration in the lowest sub-surface sample (HTF-23-19-25) may result from the much higher free hydroxide concentration in the lowest sample compared with the upper two samples. The U-235 weight fraction ranges from 0.94-1.2% in the Tank 23H samples.

The Pu-238 concentration in the top two samples (HTF-23-19-23 and -24) are similar while the lowest level sample (HTF-23-19-25) shows a concentration ~2.5 times higher. The Pu-239/240 results are all below detection. The Pu-241 results are near or below detection for the top two samples with a higher concentration measured in the lowest sample. The Cs-137 concentration in the top two samples is also similar with a higher concentration measured in the lowest level sample.

The silicon concentrations measured in the Tank 23H samples were all below detection. The standards used for the silicon analysis (50 mg/L silicon in the solution prepared by warm acid strike diluted to final concentrations of 0.5, 1.0, and 2.0 mg/L) were all close to the target concentrations with differences from the targeted concentrations of 3-9%. The silicon concentration was below detectable levels in the process blank.

Table 3-1. ECP, CCP, and other Analytical Data for Tank 23H. (Averages and %RSD values are of triplicate measurements)

analyte	method	units	est. 1σ	HTF-23-19-23 average	RSD	HTF-23-19-24 average	RSD	HTF-23-19-25 average	RSD
Sample Type	--	--	--	Surface		Sub-surface (140")		Sub-surface (60")	
density @ 21°C	grav.	g/mL	5%	1.15	0.1%	1.17	0.2%	1.27	0.4%
U-233	ICP-MS	mg/L	10%	<9.99E-03	--	<1.02E-02	--	<1.01E-02	--
U-234	ICP-MS	mg/L	10%	1.81E-02	0.4%	1.90E-02	0.5%	2.69E-02	1.5%
U-235	ICP-MS	mg/L	10%	1.27E-01	0.8%	1.33E-01	0.4%	1.33E-01	1.5%
U-236	ICP-MS	mg/L	10%	2.14E-02	1.0%	2.27E-02	2.0%	3.23E-02	1.3%
U-238	ICP-MS	mg/L	10%	1.33E+01	1.0%	1.39E+01	1.0%	1.06E+01	0.6%
Total U	calc.	mg/L	--	1.34E+01	1.0%	1.41E+01	1.0%	1.07E+01	0.6%
U-235 / U	calc.	%	--	0.94%	1.3%	0.95%	1.0%	1.2%	0.9%
Pu-238	PuTTA	mg/L	10%	3.77E-04	4.6%	3.57E-04	3.8%	9.00E-04	11%
		dpm/mL		1.43E+04		1.36E+04		3.42E+04	
Pu-239 [a]	PuTTA	mg/L	10%	<2.70E-03	--	<1.94E-03	--	≤7.96E-03	--
Pu-239/240	PuTTA	dpm/mL		<3.73E+02		<2.68E+02		≤1.10E+03	
Pu-241	Pu238/41	mg/L	20%	<4.92E-06	--	4.00E-06[b]	19%	1.73E-05	37%
		dpm/mL		<1.12E+03		9.14E+02[b]		3.95E+03	
Cs-137	gamma scan	dpm/mL	5%	9.64E+07	2.0%	9.77E+07	4.4%	1.55E+08	6.2%
Ba-137m				9.12E+07		9.24E+07		1.46E+08	
OH^-_{free}	titration	M	10%	3.24E-01	2.5%	3.91E-01	4.8%	7.67E-01	3.9%
F^-	IC	M	10%	<9.94E-03	--	<1.03E-02	--	<1.04E-02	--
CHO_2^-	IC	M	10%	<4.20E-03	--	<4.36E-03	--	<4.38E-03	--
Cl^-	IC	M	10%	<5.33E-03	--	<5.54E-03	--	<5.56E-03	--
NO_2^-	IC	M	10%	3.17E-01	0.7%	3.30E-01	0.7%	3.74E-01	1.5%
NO_3^-	IC	M	10%	1.63E+00	0.7%	1.74E+00	5.1%	3.23E+00	1.7%
PO_4^{3-}	IC	M	10%	<1.99E-03	--	≤2.30E-03	--	7.47E-03	1.4%
SO_4^{2-}	IC	M	10%	1.02E-01	0.2%	1.08E-01	2.3%	1.49E-01	1.5%
$C_2O_4^{2-}$	IC	M	10%	6.43E-03	1.1%	6.79E-03	1.2%	5.29E-03	0.4%
Br^-	IC	M	10%	<2.36E-03	--	<2.46E-03	--	<2.47E-03	--
CO_3^{2-}	TIC	M	10%	2.24E-01	0.3%	1.91E-01	1.8%	2.41E-01	1.5%
Al	ICP-ES	mg/L	10%	1.85E+03	0.4%	1.96E+03	0.9%	4.02E+03	1.3%
B	ICP-ES	mg/L	10%	1.61E+01	0.4%	1.81E+01	2.0%	2.33E+01	1.7%
Ca	ICP-ES	mg/L	10%	<4.33E-01	--	≤2.28E+00	--	<4.54E-01	--
Cr	ICP-ES	mg/L	10%	1.78E+01	1.3%	1.83E+01	0.7%	6.95E+01	2.4%
Fe	ICP-ES	mg/L	10%	4.52E+00	60%	3.58E+00	48%	4.11E+00	45%
K	ICP-ES	mg/L	10%	1.05E+02	2.1%	1.16E+02	2.7%	2.54E+02	0.6%
Li	ICP-ES	mg/L	10%	4.25E+00	9.7%	5.67E+00	5.6%	<2.13E+00	--
Na	ICP-ES	mg/L	10%	7.22E+04	0.9%	7.43E+04	1.4%	1.30E+05	0.1%
		M		3.14E+00		3.23E+00		5.63E+00	
P	ICP-ES	mg/L	10%	1.30E+02	1.4%	1.42E+02	4.7%	3.14E+02	1.2%
Si	ICP-ES	mg/L	10%	<1.45E+01	--	<1.48E+01	--	<1.46E+01	--
Zn	ICP-ES	mg/L	10%	<3.75E+00	--	<3.83E+00	--	1.22E+01	2.7%
Anion	sum	M	--	3.00E+00	--	3.15E+00	--	5.33E+00	--
Cation	sum	M	--	3.14E+00	--	3.23E+00	--	5.64E+00	--

calc. = calculation; est.1σ = estimated one sigma percent uncertainty as reported by AD.

[a] Pu-239 mass assumes entire Pu-239/240 activity is Pu-239 [b]Average of two values since third was below detection

4.0 Conclusions

The results of the analysis indicate the concentrations of species in Tank 23H increase with depth in the tank. The sample obtained from the lowest level of 60" from the bottom of the tank shows the highest concentrations for most species analyzed. The surface sample and the 140" sub-surface sample show similar compositions with the sub-surface sample being slightly more concentrated, and both are more dilute than the lowest 60" sub-surface sample for most species analyzed.

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5.0 Acknowledgements

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