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Analysis of Tank 38H (HTF-38-17-18, -19) and Tank 43H (HTF-43-17-20, -21) Samples for Support of the Enrichment Control and Corrosion Control Programs

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EXECUTIVE SUMMARY

SRNL analyzed samples from Tank 38H and Tank 43H to support ECP and CCP. The total uranium in the Tank 38H samples ranged from 53.7 mg/L for the surface sample to 57.0 mg/L in the sub-surface sample. The Tank 43H samples showed uranium concentrations of 46.2 mg/L for the surface sample and 45.7 mg/L in the sub-surface sample. The U-235 percentage was 0.63% in the Tank 38H samples and 0.62% in the Tank 43H samples. The total uranium and percent U-235 results appear consistent with recent Tank 38H and Tank 43H uranium measurements. The plutonium results for the Tank 38H surface sample are slightly higher than recent sample results, while the Tank 43H plutonium results are within the range of values measured on previous samples. The Cs-137 results for the Tank 38H surface and sub-surface samples are slightly higher than the concentrations measured in recent samples. The Cs-137 results for the two Tank 43H samples are within the range of values measured on previous samples. The comparison of the sum of the cations in each sample versus the sum of the anions shows a difference of 23% for the Tank 38H surface sample and 18% for the Tank 43H surface sample. The four samples show silicon concentrations somewhat lower than the previous samples with values ranging from 80.2 to 105 mg/L.

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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

Feed limits have been established for the 2H-Evaporator system to ensure nuclear criticality is not possible and corrosion is minimized.[1] These limits are protected by the Enrichment Control Program (ECP) and the Corrosion Control Program (CCP) that require periodic sampling and analysis to confirm that the waste supernate composition stays within the limits.[2,3]

Savannah River Remediation (SRR) obtained samples from two different heights within each of the two waste tanks supporting the 2H-Evaporator operations. The Tank 38H (evaporator drop tank) and Tank 43H (evaporator feed tank) samples were received by the Savannah River National Laboratory (SRNL) Shielded Cells on February 13, 2017. The 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[4] and conducted based on a Task Technical and Quality Assurance Plan.[5]

2.0 Experimental Procedure

The samples from Tank 38H and 43H were opened in the SRNL Shielded Cells and poured into clear plastic beakers. The beakers were photographed and the masses of the samples determined. Table 2-1 provides the sampling height and mass of each sample. Figure 2-1 shows a photograph of the samples in the clear beakers. Both Tank 38H samples contained only partially filled dip bottles. The surface samples from each tank (HTF-38-17-18 and HTF-43-17-20) were mostly clear and showed no visible undissolved solids when poured into the plastic beakers. The sub-surface sample from Tank 38H (HTF-38-17-19) was mostly clear while the sub-surface sample from Tank 43H (HTF-43-17-21) was mostly clear but darker in color.

All four 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 four samples were also submitted for inductively coupled plasma-emission spectroscopy (ICP-ES) to determine Na, Al, Si, and other metals. Only the two surface samples received the analyses required by the CCP. The CCP analysis suite includes determination of free hydroxide, gamma spectroscopy, and ion chromatography (IC). The total inorganic carbon (TIC) was also determined on the surface samples to provide a concentration for the carbonate present in the samples.

Density measurements were made on decanted (unfiltered) aliquots of the samples using calibrated volumetric tubes at ambient cell temperature (23 °C).

For the two surface samples, de-ionized (DI) water dilutions were made in triplicate from decanted (unfiltered) liquid and submitted to Analytical Development (AD) for analysis. A blank of the DI water was also prepared along with the samples. The water dilutions were analyzed by ion chromatography, total inorganic carbon, and free hydroxide methods. Nitric acid dilutions of decanted (unfiltered) liquid from the two surface samples were made in triplicate and submitted to AD for analysis by ICP-MS, ICP-ES, plutonium isotopics, and gamma spectroscopy. A blank of the diluting acid (2 M HNO_3) was also prepared along with the samples.

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-38-17-18	Surface	surface	36.0
HTF-38-17-19	Sub-surface	265”	46.8
HTF-43-17-20	Surface	surface	100.4
HTF-43-17-21	Sub-surface	161”	100.3

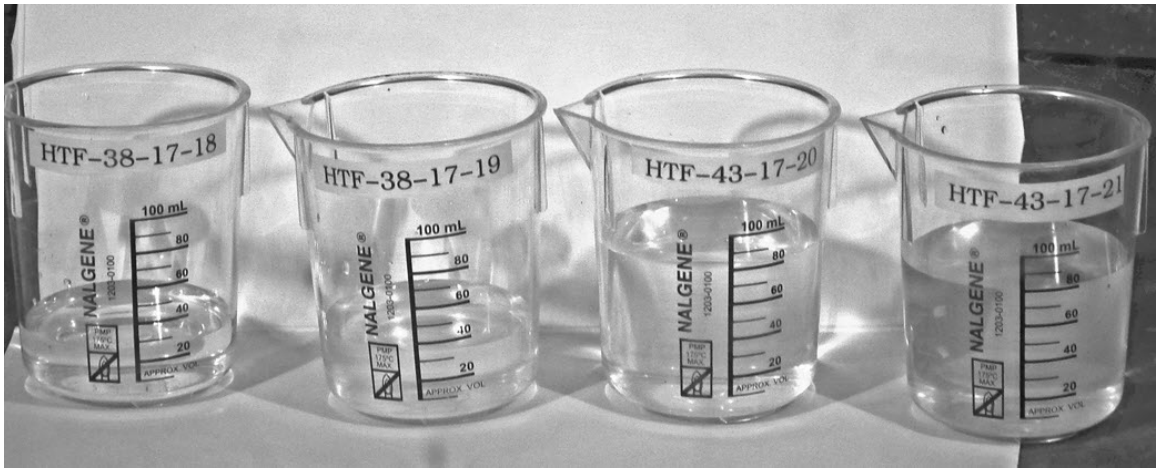

Figure 2-1. Samples from Tank 38H and 43H

Triplicate aliquots of decanted (unfiltered) liquid from each sub-surface sample were prepared for analysis using the warm acid strike method.[6] A reagent blank and three silicon standard solutions were submitted for analysis with the samples. The samples prepared by warm acid strike were submitted to AD for analysis by ICP-ES, ICP-MS, plutonium isotopics, and gamma spectroscopy.

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. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-16.

3.0 Results and Discussion

Table 3-1 contains the results from the analysis of the Tank 38H and Tank 43H samples. The tables show the average concentration and the percent relative standard deviations (%RSD) for the triplicate sample preparations. Results preceded by "<" indicate the analyte was below the limits of quantification. 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 were below detection. The %RSD presented in the table only includes the uncertainty associated with sub-sampling and sample preparation in the Shielded Cells. The %RSD does not include tank sampling uncertainty. 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.[7,8,9]

The uranium results in Table 3-1 appear consistent between the two samples from Tank 38H and the two samples from Tank 43H. The total uranium in the Tank 38H surface sample was 53.7 mg/L while the sub-surface sample was 57.0 mg/L. The Tank 43H samples contained total uranium concentrations of 46.2 mg/L in the surface sample and 45.7 mg/L in the sub-surface sample. The U-235 percentage was 0.63% for the Tank 38H samples and 0.62% in the Tank 43H samples. The total uranium and percent U-235 results in the table appear consistent with recent Tank 38H and Tank 43H uranium measurements.

The plutonium results in the table also appear consistent between the two samples from Tank 38H and the two samples from Tank 43H. The plutonium concentration in the Tank 38H samples is slightly higher than in the Tank 43H samples. The Pu-239/240 was below detection in all of the Tank 38H and Tank 43H samples. The plutonium results for the Tank 38H surface sample are slightly higher than recent sample results. The Tank 43H plutonium results are within the range of values measured on previous samples.

The Cs-137 results for the Tank 38H surface and sub-surface samples are also slightly higher than the concentrations measured in recent samples. The Cs-137 results for the two Tank 43H samples are within the range of values measured on previous samples.

The non-radioactive components of the samples such as the metals from the ICP-ES analysis and anions from the water dilutions of the samples appear consistent between the surface and sub-surface samples from each tank. However, the sum of the major cations versus the sum of the major anions shows a difference of 23% for the Tank 38H surface sample and 18% for the Tank 43H surface sample. The anion sum is low by 23% in the Tank 38H surface sample and 18% high in the Tank 43H surface sample. A single sample replicate of the water dilutions of the Tank 38H surface sample and another from the water dilutions of the Tank 43H surface sample were rerun in AD and yielded results consistent with the original analysis. Comparing the cation sum from Tank 38H with the anion sum from Tank 43H as shown in Table 3-1 produces a difference of only 7.6%. A similar comparison of the cation sum from Tank 43H with the anion sum from Tank 38H shows a difference of 2.3%. This may indicate that the water dilutions of the Tank 38H and Tank 43H surface samples were switched during sample preparation. However, the difference between the anion results from the Tank 38H and Tank 43H surface samples is only ~15%. The poor agreement between the cation/anion sums in the samples may be the result of an unfortunate confluence of analytical and sampling uncertainties. A new set of water dilutions can be prepared from the original samples to investigate the larger than normal cation/anion differences if desired.

Table 3-1. ECP, CCP, and other Analytical Data for Tank 38H and 43H Samples. (Averages and %RSD values are of triplicate measurements)

analyte	method	units	est. 1σ	HTF-38-17-18		HTF-38-17-19		HTF-43-17-20		HTF-43-17-21	
				average	RSD	average	RSD	average	RSD	average	RSD
density @ 23°C	grav.	g/mL	5%	1.33	0.5%	1.35	0.4%	1.27	0.3%	1.27	0.3%
U-233	ICP-MS	mg/L	20%	<1.24E-02	--	5.69E-03	3.4%	<1.23E-02	--	<4.95E-03	--
U-234	ICP-MS	mg/L	20%	<1.24E-02	--	1.03E-02	0.5%	<1.23E-02	--	8.35E-03	2.2%
U-235	ICP-MS	mg/L	20%	3.36E-01	1.5%	3.57E-01	0.4%	2.89E-01	0.4%	2.85E-01	1.0%
U-236	ICP-MS	mg/L	20%	2.11E-02	5.0%	2.23E-02	1.1%	1.82E-02	6.4%	1.77E-02	3.4%
U-238	ICP-MS	mg/L	20%	5.33E+01	0.3%	5.67E+01	0.2%	4.59E+01	0.3%	4.54E+01	0.4%
Total U	calc.	mg/L	--	5.37E+01	0.3%	5.70E+01	0.2%	4.62E+01	0.3%	4.57E+01	0.4%
U-235 / U	calc.	%	--	0.63%	1.2%	0.63%	0.4%	0.62%	0.4%	0.62%	0.7%
Pu-238	PuTTA	mg/L	10%	3.28E-04	3%	3.32E-04	2.5%	2.82E-04	6.2%	2.44E-04	9.7%
		dpm/mL		1.25E+04		1.26E+04		1.07E+04		9.26E+03	
Pu-239 [a]	PuTTA	mg/L	25%	≤1.16E-03	--	<1.49E-03	--	≤1.07E-03	--	<1.07E-03	--
Pu-239/240	PuTTA	dpm/mL		≤1.60E+02		<2.06E+02		≤1.48E+02		<1.48E+02	
Pu-241	Pu238/41	mg/L	20%	5.54E-06	31%	≤8.88E-06	--	4.34E-06	32%	≤7.49E-06	--
		dpm/mL		1.27E+03		≤2.03E+03		9.92E+02		≤1.71E+03	
Cs-137	gamma scan	dpm/mL	5%	2.32E+08	2.9%	2.45E+08	1.3%	1.86E+08	1.5%	1.86E+08	1.4%
Ba-137m				2.19E+08		2.32E+08		1.76E+08		1.76E+08	
OH^-	titration	M	10%	2.44E+00	5.6%	--	--	3.03E+00	1.5%	--	--
F^-	IC	M	10%	<1.33E-02	--	--	--	<1.28E-02	--	--	--
CHO_2^-	IC	M	10%	3.23E-02	0.9%	--	--	3.84E-02	2.9%	--	--
Cl^-	IC	M	10%	<7.13E-03	--	--	--	<6.85E-03	--	--	--
NO_2^-	IC	M	10%	1.74E+00	0.5%	--	--	2.05E+00	3.3%	--	--
Br^-	IC	M	10%	<3.16E-02	--	--	--	<3.04E-02	--	--	--
NO_3^-	IC	M	10%	1.10E+00	1.4%	--	--	1.29E+00	3.3%	--	--
PO_4^{3-}	IC	M	10%	<2.66E-03	--	--	--	≤2.58E-03	--	--	--
SO_4^{2-}	IC	M	10%	2.96E-02	1.0%	--	--	3.42E-02	2.7%	--	--
$C_2O_4^{2-}$	IC	M	10%	4.69E-03	0.9%	--	--	4.97E-03	2.3%	--	--
CO_3^{2-}	IC	M	10%	4.16E-01	0.3%	--	--	5.05E-01	3.5%	--	--
Al	ICP-ES	mg/L	10%	1.72E+03	0.7%	1.93E+03	0.4%	1.34E+03	0.2%	1.42E+03	0.5%
B	ICP-ES	mg/L	10%	1.66E+02	0.9%	1.86E+02	0.7%	1.31E+02	0.4%	1.39E+02	1.1%
Ca	ICP-ES	mg/L	10%	<4.81E+00	--	4.89E+00	51%	<4.75E+00	--	≤5.99E+00	--
Cr	ICP-ES	mg/L	10%	8.19E+01	0.4%	8.46E+01	0.7%	6.46E+01	0.5%	6.63E+01	0.4%
Fe	ICP-ES	mg/L	10%	8.80E+00	14%	<4.79E+00	--	<5.83E+00	--	<4.68E+00	--
K	ICP-ES	mg/L	10%	4.68E+02	3%	4.70E+02	1.2%	3.66E+02	0.6%	3.47E+02	1.7%
Li	ICP-ES	mg/L	10%	7.92E+01	1.0%	8.66E+01	0.6%	6.11E+01	0.2%	6.39E+01	0.7%
Na	ICP-ES	mg/L	10%	1.88E+05	0.1%	1.91E+05	0.4%	1.47E+05	0.1%	1.44E+05	0.5%
		M		8.16E+00		8.30E+00		6.41E+00		6.26E+00	
P	ICP-ES	mg/L	10%	1.69E+02	2%	1.84E+02	0.7%	1.32E+02	2.0%	1.36E+02	1.4%
Si	ICP-ES	mg/L	10%	9.93E+01	0.6%	1.05E+02	0.8%	8.06E+01	0.7%	8.02E+01	1.5%
Zn	ICP-ES	mg/L	10%	4.78E+00	4.0%	<1.14E+01	--	3.56E+00	1.1%	<1.11E+01	--

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

The sodium and aluminum concentrations measured in the Tank 38H surface and sub-surface samples are consistent between the samples and have increased compared with the previous samples from the tank. The Tank 43H surface and sub-surface samples show consistent concentrations for sodium and aluminum and may have increased slightly compared with the previous samples from the tank. However, the difference between recent Tank 43H samples is small and likely within expected uncertainties.

The standards used for the silicon analysis (50 mg/L silicon in the solution prepared by warm acid strike to final concentrations of 0.5, 1.0, and 2.0 mg/L) were all close to the target concentration with differences from the targeted concentrations of 0.8%, 4.1%, and 1.0% respectively. The silicon concentration was below detectible levels in the process blank. The four samples analyzed show silicon concentrations somewhat lower than the previous sample with values ranging from 80.2 to 105 mg/L.

4.0 Conclusions

SRNL analyzed samples from Tank 38H and Tank 43H to support ECP and CCP. The total uranium in the Tank 38H samples ranged from 53.7 mg/L for the surface sample to 57.0 mg/L in the sub-surface sample. The Tank 43H samples showed uranium concentrations of 46.2 mg/L for the surface sample and 45.7 mg/L in the sub-surface sample. The U-235 percentage was 0.63% in the Tank 38H samples and 0.62% in the Tank 43H samples. The total uranium and percent U-235 results in the table appear consistent with recent Tank 38H and Tank 43H uranium measurements. The plutonium results for the Tank 38H surface sample are slightly higher than recent sample results, while the Tank 43H plutonium results are within the range of values measured on previous samples. The Cs-137 results for the Tank 38H surface and sub-surface samples are slightly higher than the concentrations measured in recent samples. The Cs-137 results for the two Tank 43H samples are within the range of values measured on previous samples. The comparison of the sum of the cations in each sample versus the sum of the anions shows a difference of 23% for the Tank 38H surface sample and 18% for the Tank 43H surface sample. The four samples show silicon concentrations somewhat lower than the previous samples with values ranging from 80.2 to 105 mg/L.

5.0 Acknowledgements

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