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Analysis of Tank 38H (HTF-38-16-80, 81) and Tank 43H (HTF-43-16-82, 83) 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 surface sample was 57.6 mg/L while the sub-surface sample was 106 mg/L. The Tank 43H samples ranged from 50.0 to 51.9 mg/L total uranium. The U-235 percentage was consistent for all four samples at 0.62%. The total uranium and percent U-235 results in the table appear consistent with recent Tank 38H and Tank 43H uranium measurements. The Tank 38H plutonium results show a large difference between the surface and sub-surface sample concentrations and somewhat higher concentrations than previous samples. The Pu-238 concentration is more than forty times higher in the Tank 38H sub-surface sample than the surface sample. The surface and sub-surface Tank 43H samples contain similar plutonium concentrations and are within the range of values measured on previous samples. The four samples analyzed show silicon concentrations somewhat higher than the previous sample with values ranging from 104 to 213 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 Corrosion Control Program (CCP) that require periodic sampling and analysis to confirm 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 tanks. 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 September 8, 2016. 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] Preliminary results of the primary species of the CCP analysis were reported previously.[6]

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 and 2-2 show photographs of the samples in the clear beakers. The surface samples from each tank (HTF-38-16-80 and HTF-43-16-82) were mostly clear and showed no visible undissolved solids when poured into the plastic beakers. The sub-surface samples from both tanks were darker colored and contained some visible undissolved. The small amount of sub-surface sample from Tank 38H (HTF-38-16-81) contained a significant amount of visible undissolved solids but much less than 1 wt% based on visual examination and previous experience with samples from these tanks.

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 (24 °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-38-16-80	Surface	surface	100.8
HTF-38-16-81	Sub-surface	254”	18.8
HTF-43-16-82	Surface	surface	82.9
HTF-43-16-83	Sub-surface	161”	98.3

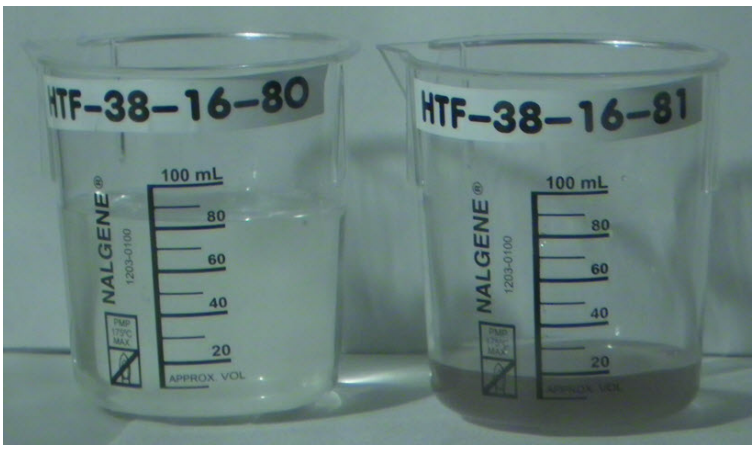

Figure 2-1. Samples from Tank 38H

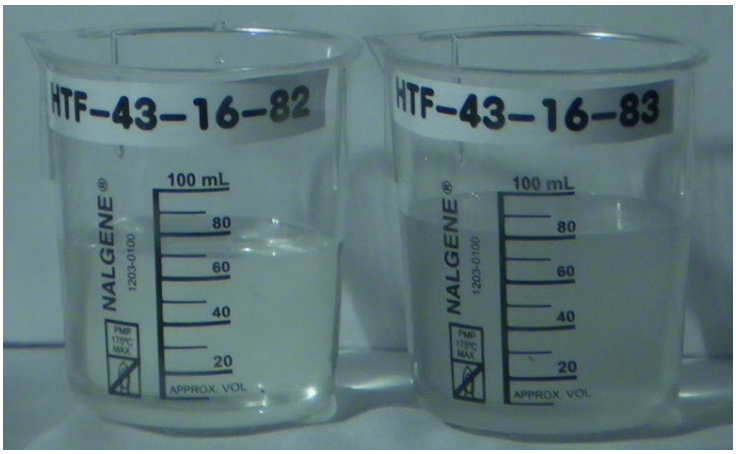

Figure 2-2. Samples from Tank 43H

Triplicate aliquots of decanted (unfiltered) liquid from each sub-surface sample were prepared for analysis using the warm acid strike method.[7] 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 Y7081-00081-13.

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.[8,9,10]

The uranium results in Table 3-1 appear consistent between the two samples from Tank 43H but differ by a factor of ~2 between the two Tank 38H samples. The total uranium in the Tank 38H surface sample was 57.6 mg/L while the sub-surface sample was 106 mg/L. The Tank 43H samples ranged from 50.0 to 51.9 mg/L total uranium. The U-235 percentage was consistent for all four samples at 0.62%. 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 show a similar large difference between the surface and sub-surface sample concentrations for Tank 38H. The Pu-238 concentration is more than forty times higher in the Tank 38H sub-surface sample than the surface sample. The surface and sub-surface Tank 43H samples contain similar plutonium concentrations and are within the range of values measured on previous samples.

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-38-16-80		HTF-38-16-81		HTF-43-16-82		HTF-43-16-8	
				average	%RSD	average	%RSD	average	%RSD	average	%R
density @26°C	grav.	g/mL	5%	1.26	0.6%	1.27	0.7%	1.25	0.1%	1.23	0.5
U-233	ICP-MS	mg/L	20%	5.77E-03	0.7%	8.76E-03	2.6%	5.12E-03	0.7%	4.83E-03	4.4
U-234	ICP-MS	mg/L	20%	9.99E-03	2.9%	6.08E-02	2.0%	8.74E-03	1.5%	8.74E-03	3.2
U-235	ICP-MS	mg/L	20%	3.56E-01	0.3%	6.65E-01	2.4%	3.23E-01	1.1%	3.12E-01	2.8
U-236	ICP-MS	mg/L	20%	2.30E-02	0.6%	5.23E-02	1.9%	2.05E-02	1.1%	1.97E-02	6.3
U-238	ICP-MS	mg/L	20%	5.73E+01	0.5%	1.06E+02	1.6%	5.16E+01	0.7%	4.97E+01	3.4
Total U	calc.	mg/L	--	5.76E+01	0.5%	1.06E+02	1.7%	5.19E+01	0.7%	5.00E+01	3.4
U-235 / U	calc.	%	--	0.62%	0.5%	0.62%	0.9%	0.62%	0.4%	0.62%	0.7
Pu-238	PuTTA	mg/L	10%	2.26E-04	3.2%	9.88E-03	11%	2.40E-04	17%	2.46E-04	17
		dpm/mL		8.59E+03		3.75E+05		9.12E+03		9.34E+03	
Pu-239 [a,b]	PuTTA	mg/L	10%	<2.55E-03	--	5.58E-02	6.4%	<5.39E-03	--	≤1.49E-03	-
Pu-239/240 [b]	PuTTA	dpm/mL		<3.52E+02		7.70E+03		<7.43E+02		≤2.06E+02	
Pu-241 [b,c]	Pu238/41	mg/L	15%	≤5.12E-06	--	2.05E-04	6.3%	5.81E-06	95%	≤2.59E-06	-
		dpm/mL		≤1.17E+03		4.68E+04		1.33E+03		≤5.93E+02	
Cs-137	gamma scan	dpm/mL	5%	1.87E+08	2.4%	1.95E+08	3.2%	1.71E+08	2.1%	1.70E+08	4.8
Ba-137m				1.77E+08		1.85E+08		1.62E+08		1.61E+08	
OH^-	titration	M	10%	2.49E+00	9.1%	--	--	2.18E+00	1.9%	--	-
F^-	IC	M	10%	<1.34E-02	--	--	--	<1.34E-02	--	--	-
CHO_2^-	IC	M	10%	3.46E-02	0.1%	--	--	3.12E-02	0.5%	--	-
Cl^-	IC	M	10%	<7.16E-03	--	--	--	<7.18E-03	--	--	-
NO_2^-	IC	M	10%	2.03E+00	0.8%	--	--	1.76E+00	4.4%	--	-
Br^-	IC	M	10%	<1.59E-02	--	--	--	<1.59E-02	--	--	-
NO_3^-	IC	M	10%	9.34E-01	0.7%	--	--	8.16E-01	4.2%	--	-
PO_4^{3-}	IC	M	10%	3.02E-03	0.4%	--	--	≤2.69E-03	--	--	-
SO_4^{2-}	IC	M	10%	3.13E-02	0.8%	--	--	3.36E-02	32%	--	-
$C_2O_4^{2-}$	IC	M	10%	8.34E-03	0.2%	--	--	8.80E-03	0.5%	--	-
CO_3^{2-}	IC	M	10%	4.39E-01	0.2%	--	--	3.97E-01	0.6%	--	-
Al	ICP-ES	mg/L	10%	1.34E+03	0.2%	1.56E+03	0.5%	1.20E+03	0.2%	1.23E+03	4.9
B	ICP-ES	mg/L	10%	1.45E+02	0.4%	1.49E+02	0.5%	1.33E+02	0.4%	1.30E+02	4.8
Ca	ICP-ES	mg/L	10%	<1.54E+00	--	<2.45E+00	--	<1.54E+00	--	<2.36E+00	-
Cr	ICP-ES	mg/L	10%	6.59E+01	0.5%	7.41E+01	1.3%	6.00E+01	0.8%	5.82E+01	5.4
Fe	ICP-ES	mg/L	10%	1.16E+01	27%	3.84E+01	2.5%	6.63E+00	18%	5.52E+00	14
K	ICP-ES	mg/L	10%	3.31E+02	0.9%	3.19E+02	5.1%	3.11E+02	1.9%	2.68E+02	4.6
Li	ICP-ES	mg/L	10%	7.18E+01	0.3%	7.14E+01	2.1%	6.45E+01	0.8%	6.27E+01	5.1
Na	ICP-ES	mg/L	10%	1.35E+05	0.3%	1.65E+05	0.4%	1.38E+05	0.5%	1.37E+05	5.2
		M		5.87E+00		7.16E+00		6.00E+00		5.97E+00	
P	ICP-ES	mg/L	10%	1.56E+02	3.5%	1.82E+02	2.5%	1.41E+02	3.0%	1.38E+02	4.2
Si	ICP-ES	mg/L	10%	1.32E+02	16%	2.13E+02	4.8%	1.12E+02	10%	1.04E+02	1.4
Zn	ICP-MS	mg/L	10%	5.37E+00	27%	5.05E+00	7.0%	4.26E+00	7.2%	3.92E+00	0.5

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 non-radioactive components of the samples such as the metals from the ICP-ES analysis and anions from the IC analysis appear self-consistent. The sum of the major cations versus the sum of the major anions shows a difference of 11% for the Tank 38H surface sample and 5% for the Tank 43H surface sample providing an indication of good data quality for the non-radioactive analytes in the table. The sodium, aluminum, and soluble anion concentrations measured in the Tank 38H surface sample have increased compared with the previous sample but fall within the range of previous analyses over the last five samples. The two Tank 43H samples and the Tank 38 sub-surface sample show sodium, aluminum, and soluble anion concentrations similar to previous samples also.

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 somewhat higher than the target concentration with differences from the targeted concentrations of 40%, 20%, and 19% respectively. The silicon concentration was below detectible levels in the process blank. The four samples analyzed show silicon concentrations somewhat higher than the previous sample with values ranging from 104 to 213 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 surface sample was 57.6 mg/L while the sub-surface sample was 106 mg/L. The Tank 43H samples ranged from 50.0 to 51.9 mg/L total uranium. The U-235 percentage was consistent for all four samples at 0.62%. The total uranium and percent U-235 results in the table appear consistent with recent Tank 38H and Tank 43H uranium measurements. The Tank 38H plutonium results show a large difference between the surface and sub-surface sample concentrations and somewhat higher concentrations than previous samples. The Pu-238 concentration is more than forty times higher in the Tank 38H sub-surface sample than the surface sample. The surface and sub-surface Tank 43H samples contain similar plutonium concentrations and are within the range of values measured on previous samples. The four samples analyzed show silicon concentrations somewhat higher than the previous sample with values ranging from 104 to 213 mg/L.

5.0 Acknowledgements

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