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Analysis of Tank 38H (HTF-38-18-43, -44) and Tank 43H (HTF-43-18-41, -42) 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 38.8 mg/L while the sub-surface sample was 35.7 mg/L. The Tank 43H samples contained total uranium concentrations of 27.5 mg/L in the surface sample and 23.4 mg/L in the sub-surface sample. The U-235 weight fraction ranged from 0.62% to 0.63% for the Tank 38H samples and Tank 43H samples. The total uranium concentrations in the table are reasonably consistent with recent Tank 38H/43H sample uranium measurements. The plutonium results in the table are consistent with the range of concentrations measured in recent samples from these tanks with the exception of the Pu-238 value measured in the Tank 43H sub-surface sample. The Pu-238 in the Tank 43H sub-surface sample is higher than any recent measurement by a factor of two. The Cs-137 results show slightly lower concentrations in the surface samples versus the sub-surface samples from each tank. The non-radioactive components of the samples show some differences between the surface and sub-surface samples for each tank.

The sum of the major cations versus the sum of the major anions shows a difference of ~28% for the Tank 38H surface sample and ~18% for the Tank 43H surface sample. The sodium concentration measured in both surface samples is lower than in the corresponding sub-surface sample by about 30%. The sodium concentration measured in both surface samples is also much lower than in recent analyses of Tank 38H/43H samples. The sodium concentration measured in both sub-surface samples agrees well with recent analyses of Tank 38H/43H samples. Additionally, the carbonate and hydroxide concentrations in the surface samples is somewhat higher than in recent analyses of Tank 38H/43H surface samples. The uranium, plutonium, and cesium measurements do not show this difference in concentrations between the surface and sub-surface samples. This may indicate a problem with the ICP-ES analysis results for the surface samples causing the sodium, silicon, and other metal concentrations to be low.

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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 on April 26, 2018. 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 May 9, 2018. 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. The surface samples from each tank were mostly clear and showed no visible undissolved solids when poured into the plastic beakers. The sub-surface samples from each tank were slightly cloudy but no visible solid particles were observed.

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 gamma spectroscopy and 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, 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 (28 °C).

For the two surface samples, 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. The water dilutions were analyzed by ion chromatography, total inorganic carbon, and free hydroxide methods. Nitric acid dilutions of a well-mixed (unfiltered) sample 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-38-18-43	Surface	surface	103.0
HTF-38-18-44	Sub-surface	265”	94.3
HTF-43-18-41	Surface	surface	97.7
HTF-43-18-42	Sub-surface	161”	102.1

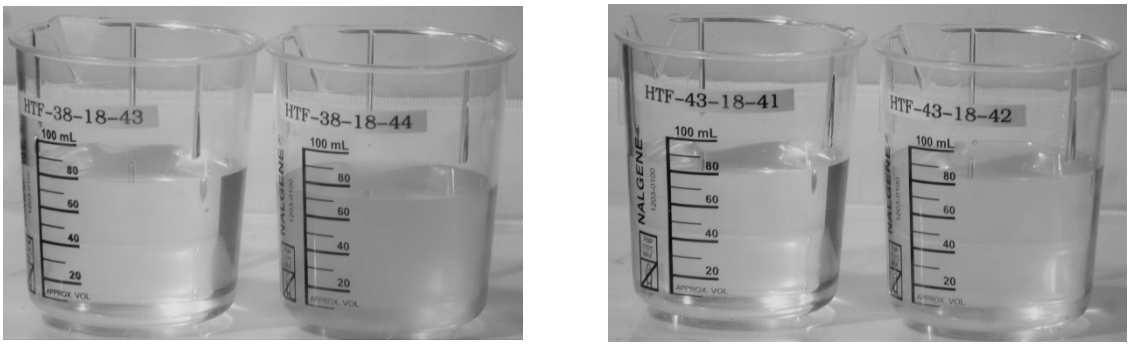

Figure 2-1. Samples from Tank 38H and 43H

Triplicate aliquots of the well mixed (unfiltered) sample 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 Y7081-00081-25.

3.0 Results and Discussion

The following tables contain 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 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 %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 concentrations in Table 3-1 appear consistent between the two samples from Tank 38H and the two samples from Tank 43H although the surface sample show slightly higher concentrations in both tanks. The total uranium in the Tank 38H surface sample was 38.8 mg/L while the sub-surface sample was 35.7 mg/L. The Tank 43H samples contained total uranium concentrations of 27.5 mg/L in the surface sample and 23.4 mg/L in the sub-surface sample. The U-235 weight fraction ranged from 0.62% to 0.63% for the Tank 38H samples and Tank 43H samples. The total uranium concentrations in the table are reasonably consistent with recent Tank 38H/43H sample uranium measurements.

The plutonium results in the table are consistent with the range of concentrations measured in recent samples from these tanks with the exception of the Pu-238 value measured in the Tank 43H sub-surface sample. The Pu-238 in the Tank 43H sub-surface sample is higher than any recent measurement by a factor of two. The high uncertainty in the Pu-239/240 results likely stems from the concentrations in the samples being close to the method detection limit.

The Cs-137 results show slightly lower concentrations in the surface samples versus the sub-surface samples from each tank but these differences fall with the estimated one sigma uncertainty of the measurement. The measured Cs-137 concentrations all fall within the range of values measured on previous samples from these tanks.

The non-radioactive components of the samples show some differences between the surface and sub-surface samples for each tank. The concentrations of the metals measured by ICP-ES in the sub-surface sample from Tank 38H are 30-40% higher than measured in the surface sample. In the Tank 43H surface and sub-surface samples, the difference is similar with metals measured by ICP-ES about 10-40% higher in the sub-surface sample.

The sum of the major cations versus the sum of the major anions shows a difference of ~28% for the Tank 38H surface sample and ~18% for the Tank 43H surface sample. The sodium concentration measured in both surface samples is lower than in the corresponding sub-surface sample by about 30%. The sodium concentration measured in both surface samples is also much lower than in recent analyses of Tank 38H/43H samples. The sodium concentration measured in both sub-surface samples agrees well with recent analyses of Tank 38H/43H samples. Additionally, the carbonate and hydroxide concentrations in the surface samples is somewhat higher than in recent analyses of Tank 38H/43H surface samples. The uranium, plutonium, and cesium measurements do not show this difference in concentrations between the surface and sub-surface

samples. This may indicate a problem with the ICP-ES analysis results for the surface samples causing the sodium, silicon, and other metal concentrations to be low.

The measured silicon concentrations are much lower in the surface samples than in the sub-surface samples. The silicon concentrations in the surface samples are also much lower than found in other recent Tank 38H/43H surface samples. The silicon concentrations measured in the sub-surface sample from Tank 38H compares well with recent Tank 38H analyses. However, the silicon concentration measured in the sub-surface sample from Tank 43H is much lower than recent Tank 43H analyses. 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 concentrations with differences from the targeted concentrations of <5%. The silicon concentration was below detectable levels in the process blanks.

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-38-18-43		HTF-38-18-44		HTF-43-18-41		HTF-43-18-42	
				average	RSD	average	RSD	average	RSD	average	RSD
density @ 23°C	grav.	g/mL	5%	1.30	0.5%	1.32	0.5%	1.22	0.4%	1.25	0.6%
U-233	ICP-MS	mg/L	10%	<4.16E-03	--	<1.04E-02	--	<4.09E-03	--	<1.07E-02	--
U-234	ICP-MS	mg/L	10%	7.87E-03	2.1%	<1.04E-02	--	5.71E-03	0.7%	<1.07E-02	--
U-235	ICP-MS	mg/L	10%	2.43E-01	1.2%	2.23E-01	0.3%	1.72E-01	0.5%	1.45E-01	1.0%
U-236	ICP-MS	mg/L	10%	1.52E-02	4.0%	1.38E-02	2.4%	1.06E-02	4.5%	<1.07E-02	--
U-238	ICP-MS	mg/L	10%	3.86E+01	1.1%	3.54E+01	0.7%	2.73E+01	0.7%	2.32E+01	0.9%
Total U	calc.	mg/L	--	3.88E+01	1.1%	3.57E+01	0.7%	2.75E+01	0.7%	2.34E+01	0.9%
U-235 / U	calc.	%	--	0.63	0.5%	0.62	0.4%	0.63	0.4%	0.62	0.3%
Pu-238	PuTTA	mg/L	15%	3.37E-04	9.5%	3.17E-04	1.4%	2.90E-04	6.0%	5.65E-04	5.3%
		dpm/mL		1.28E+04		1.21E+04		1.10E+04		2.15E+04	
Pu-239 [a]	PuTTA	mg/L	50%	≤1.31E-03	--	≤8.49E-03	--	2.08E-03	49%	≤2.25E-03	--
Pu-239/240	PuTTA	dpm/mL		≤1.80E+02		≤1.17E+03		2.87E+02		≤3.11E+02	
Pu-241	Pu238/41	mg/L	25%	7.92E-06	22%	≤9.21E-06	--	8.04E-06	38%	7.16E-06	17%
		dpm/mL		1.81E+03		≤2.11E+03		1.84E+03		1.64E+03	
Cs-137	gamma scan	dpm/mL	5%	2.85E+08	0.5%	3.01E+08	2.3%	1.94E+08	4.0%	2.04E+08	1.2%
Ba-137m				2.70E+08		2.85E+08		1.83E+08		1.93E+08	
OH^-	titration	M	10%	2.64E+00	0.8%	--	--	1.76E+00	0.8%	--	--
F^-	IC	M	10%	<1.13E-02	--	--	--	<1.13E-02	--	--	--
CHO_2^-	IC	M	10%	3.26E-02	1.1%	--	--	2.40E-02	1.3%	--	--
Cl^-	IC	M	10%	<6.03E-03	--	--	--	<6.03E-03	--	--	--
NO_2^-	IC	M	10%	1.99E+00	1.7%	--	--	1.41E+00	1.1%	--	--
Br^-	IC	M	10%	<2.68E-03	--	--	--	<2.68E-03	--	--	--
NO_3^-	IC	M	10%	1.13E+00	1.5%	--	--	7.98E-01	1.1%	--	--
PO_4^{3-}	IC	M	10%	<2.25E-02	--	--	--	<2.25E-02	--	--	--
SO_4^{2-}	IC	M	10%	5.43E-02	2.4%	--	--	3.91E-02	0.7%	--	--
$C_2O_4^{2-}$	IC	M	10%	<2.43E-02	--	--	--	<2.43E-02	--	--	--
CO_3^{2-}	TIC	M	10%	7.57E-01	0.3%	--	--	5.80E-01	1.1%	--	--
Al	ICP-ES	mg/L	10%	1.74E+03	1.3%	2.32E+03	1.2%	1.46E+03	1.1%	1.57E+03	1.2%
B	ICP-ES	mg/L	10%	1.14E+02	1.5%	1.69E+02	2.7%	1.07E+02	1.8%	1.32E+02	2.4%
Ca	ICP-ES	mg/L	10%	<4.02E+00	--	<2.58E+00	--	<3.94E+00	--	<2.65E+00	--
Cr	ICP-ES	mg/L	10%	7.50E+01	1.5%	1.05E+02	1.7%	6.71E+01	1.1%	8.60E+01	1.8%
Fe	ICP-ES	mg/L	10%	<4.93E+00	--	1.20E+01	28%	<4.84E+00	--	≤5.27E+00	--
K	ICP-ES	mg/L	10%	4.25E+02	3.3%	4.96E+02	6.8%	3.46E+02	1.5%	3.84E+02	3.5%
Li	ICP-ES	mg/L	10%	6.45E+01	1.2%	9.00E+01	1.2%	5.76E+01	2.0%	6.28E+01	1.4%
Na	ICP-ES	mg/L	10%	1.29E+05	5.7%	1.72E+05	1.2%	1.01E+05	16%	1.36E+05	0.9%
		M		5.62E+00		7.48E+00		4.40E+00		5.93E+00	
P	ICP-ES	mg/L	10%	1.49E+02	1.6%	1.90E+02	3.2%	1.22E+02	3.5%	1.48E+02	1.8%
Si	ICP-ES	mg/L	10%	1.76E+01	9.5%	1.29E+02	3.5%	1.75E+01	19%	6.44E+01	10%
Zn	ICP-ES	mg/L	10%	3.27E+00	0.9%	<4.69E+00	--	2.70E+00	3.0%	<4.83E+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

4.0 Conclusions

The total uranium in the Tank 38H surface sample was 38.8 mg/L while the sub-surface sample was 35.7 mg/L. The Tank 43H samples contained total uranium concentrations of 27.5 mg/L in the surface sample and 23.4 mg/L in the sub-surface sample. The U-235 weight fraction ranged from 0.62% to 0.63% for the Tank 38H samples and Tank 43H samples. The total uranium concentrations in the table are reasonably consistent with recent Tank 38H/43H sample uranium measurements. The plutonium results in the table are consistent with the range of concentrations measured in recent samples from these tanks with the exception of the Pu-238 value measured in the Tank 43H sub-surface sample. The Pu-238 in the Tank 43H sub-surface sample is higher than any recent measurement by a factor of two. The Cs-137 results show slightly lower concentrations in the surface samples versus the sub-surface samples from each tank. The non-radioactive components of the samples show some differences between the surface and sub-surface samples for each tank.

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