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Analysis of Tank 38H (HTF-38-16-26, 27) and Tank 43H (HTF-43-16-28, 29) Samples for Support of the Enrichment Control and Corrosion Control Programs

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EXECUTIVE SUMMARY

Savannah River National Laboratory analyzed samples from Tank 38H and Tank 43H to support Enrichment Control Program and Corrosion Control Program. The total uranium in the Tank 38H samples ranged from 20.5 to 34.0 mg/L while the Tank 43H samples ranged from 47.6 to 50.6 mg/L. The U-235 percentage ranged from 0.62% to 0.64% over the four samples. The total uranium and percent U-235 results appear consistent with previous 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 a somewhat higher concentration than previous sub-surface samples. The two Tank 43H samples show similar plutonium concentrations and are within the range of values measured on previous samples. The plutonium results may be biased high due to the presence of plutonium contamination in the blank samples from the cell sample preparations. The four samples analyzed show silicon concentrations ranging from 47.9 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.[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 April 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]

2.0 Experimental Procedure

The four samples were opened in the SRNL Shielded Cells and poured into clear plastic beakers. The beakers were photographed and the mass of the samples determined, however, some material was removed from the Tank 38H sub-surface sample (HTF-38-16-27) for the Mercury Speciation program prior to the determination of the mass. Table 2-1 provides the sampling height and mass of each sample. Figure 2-1 shows photographs of the samples. The surface samples from each tank (HTF-38-16-26 and HTF-43-16-28) were clear and showed no visible undissolved solids when poured into the plastic beakers. The sub-surface sample from Tank 43H (HTF-43-16-29) also contained no visible undissolved solids but was slightly hazy. The sub-surface sample from Tank 38H (HTF-38-16-27) contained a significant amount of visible undissolved solids. After sitting undisturbed overnight, a ~1/8" layer of dark solids settled to the bottom of the poly bottle containing HTF-38-16-27. The solids from HTF-38-16-27 were filtered through a 0.45 µm nylon filter, washed with de-ionized water, and dried to determine the weight percent insoluble solids. The measured weight percent insoluble solids for HTF-38-16-27 of 0.2 wt% indicates most of the original solids captured on the filter were water soluble. The results from the analysis of the HTF-38-16-27 insoluble solids will be reported in a separate memorandum.

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 (26 °C). For the Tank 38 sub-surface sample HTF-38-16-27, the density measurement was made on the filtered supernate due to the solids present in the sample.

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

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-38-16-26	Surface	surface	92.0
HTF-38-16-27	Sub-surface	248”	99.9
HTF-43-16-28	Surface	surface	92.3
HTF-43-16-29	Sub-surface	161”	94.1

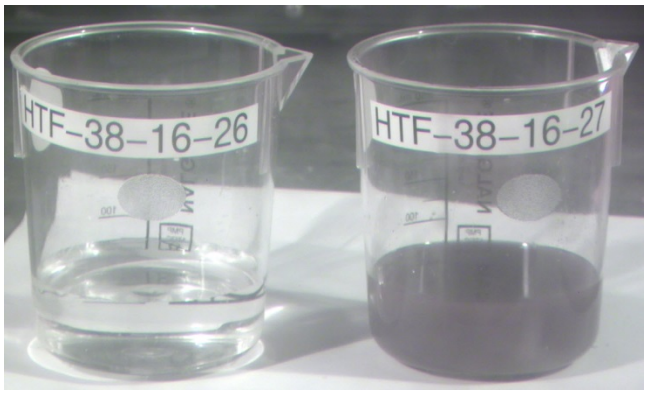

Figure 2-1. Samples from Tank 38H

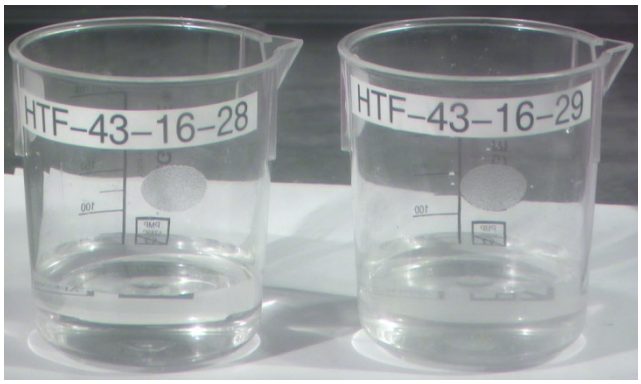

Figure 2-2. Samples from Tank 43H

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.

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 Y7081-00081-11.

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 reasonably consistent between the two samples from each tank. The total uranium in the Tank 38H samples ranged from 20.5 to 34.0 mg/L while the Tank 43H samples ranged from 47.6 to 50.6 mg/L. The U-235 percentage ranged from 0.62% to 0.64% over the four samples. The total uranium and percent U-235 results in the table appear consistent with recent Tank 38H and Tank 43H uranium measurements. Tank 38H uranium concentrations have varied from 6.55 mg/L to 112 mg/L over the course of the last five sample analysis reports. The Tank 43H uranium concentration shows less variation ranging from 47.6 mg/L to 70.2 mg/L over the last five sample analysis reports. The percent U-235 has ranged from 0.59% to 0.64% over recent samples with what appears to be one outlier at 0.94%.

The plutonium results in the table show a large difference between the surface and sub-surface sample concentrations for Tank 38H. Additionally, the Pu-238 and Pu-239/240 value measured on the Tank 38H sub-surface sample (HTF-38-16-27) is somewhat higher than measured in the last five sample analysis reports. The surface and sub-surface Tank 43H samples show 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-38-16-26		HTF-38-16-27		HTF-43-16-28		HTF-43-16-29	
				average	RSD	average	RSD	average	RSD	average	RSD
density @26°C	grav.	g/mL	5%	1.16	1.0%	1.26	1.1%	1.23	0.6%	1.22	0.7%
U-233	ICP-MS	mg/L	20%	< 1.44E-02	--	<5.04E-03	--	<1.43E-02	--	<5.08E-03	--
U-234	ICP-MS	mg/L	20%	< 1.44E-02	--	<5.04E-03	--	<1.43E-02	--	<5.08E-03	--
U-235	ICP-MS	mg/L	20%	2.17E-01	4.3%	1.29E-01	4.3%	2.93E-01	2.2%	3.16E-01	2.1%
U-236	ICP-MS	mg/L	20%	<1.44E-02	--	<5.04E-03	--	1.86E-02	5.6%	<5.08E-03	--
U-238	ICP-MS	mg/L	20%	3.37E+01	3.9%	2.04E+01	3.9%	4.73E+01	2.0%	5.03E+01	1.9%
Total U	calc.	mg/L	--	3.40E+01	3.9%	2.05E+01	3.9%	4.76E+01	2.0%	5.06E+01	1.9%
U-235 / U	calc.	%	--	0.64%	0.4%	0.63%	0.5%	0.62%	0.4%	0.62%	0.2%
Pu-238	PuTTA	mg/L	10%	1.75E-04	20%	1.66E-03	4.0%	2.45E-04	19%	2.28E-04	3.8%
		dpm/mL		6.64E+03		6.31E+04		9.33E+03		8.67E+03	
Pu-239 [a,b]	PuTTA	mg/L	25%	3.63E-03	22%	1.26E-02	17%	≤3.23E-03	--	5.88E-03	61%
Pu-239/240 [b]	PuTTA	dpm/mL		5.02E+02		1.74E+03		≤4.46E+02		8.11E+02	
Pu-241 [b,c]	Pu238/41	mg/L	20%	7.09E-06	2.0%	4.96E-05	12%	7.60E-06	31%	9.76E-06	53%
		dpm/mL		1.62E+03		1.14E+04		1.74E+03		2.23E+03	
Cs-137	gamma scan	dpm/mL	5%	1.56E+08	12%	1.40E+08	6.4%	1.13E+08	1.5%	1.07E+08	2.7%
Ba-137m				1.47E+08		1.32E+08		1.07E+08		1.01E+08	
OH^-	titration	M	10%	1.27E+00	6.2%	--	--	1.70E+00	15%	--	--
F^-	IC	M	10%	<1.54E-02	--	--	--	<1.59E-02	--	--	--
CHO_2^-	IC	M	10%	2.11E-02	2.0%	--	--	3.27E-02	0.4%	--	--
Cl^-	IC	M	10%	<8.23E-03	--	--	--	<8.53E-03	--	--	--
NO_2^-	IC	M	10%	1.12E+00	1.5%	--	--	1.47E+00	0.5%	--	--
Br^-	IC	M	10%	<1.83E-02	--	--	--	<1.89E-02	--	--	--
NO_3^-	IC	M	10%	5.79E-01	8.1%	--	--	7.41E-01	3.2%	--	--
PO_4^{3-}	IC	M	10%	<3.07E-03	--	--	--	<3.19E-03	--	--	--
SO_4^{2-}	IC	M	10%	1.58E-02	3.2%	--	--	1.36E-02	1.6%	--	--
$C_2O_4^{2-}$	IC	M	10%	1.51E-02	2.6%	--	--	6.87E-03	1.3%	--	--
CO_3^{2-}	IC	M	10%	2.60E-01	2.1%	--	--	3.27E-01	1.2%	--	--
Al	ICP-ES	mg/L	10%	1.07E+03	5.1%	1.72E+03	3.3%	7.63E+02	1.6%	9.02E+02	1.6%
B	ICP-ES	mg/L	10%	8.63E+01	6.0%	1.40E+02	3.2%	1.19E+02	1.2%	1.24E+02	1.1%
Ca [b]	ICP-ES	mg/L	10%	7.50E+00	22%	4.99E+00	19%	6.54E+00	27%	6.27E+00	30%
Cr	ICP-ES	mg/L	10%	4.10E+01	7.6%	8.62E+01	2.4%	4.81E+01	0.7%	4.80E+01	0.9%
Fe [c]	ICP-ES	mg/L	20%	5.38E+00	23%	1.20E+01	30%	7.16E+00	26%	9.08E+00	18%
K	ICP-ES	mg/L	20%	2.11E+02	10%	3.91E+02	6.2%	2.58E+02	5.3%	2.64E+02	4.3%
Li	ICP-ES	mg/L	10%	3.90E+01	4.9%	6.00E+01	3.3%	5.43E+01	0.3%	6.09E+01	1.9%
Na	ICP-ES	mg/L	10%	9.01E+04	4.5%	1.58E+05	3.7%	1.14E+05	1.4%	1.21E+05	2.2%
		M		3.92E+00		6.85E+00		4.96E+00		5.27E+00	
P	ICP-ES	mg/L	10%	8.16E+01	13%	2.71E+02	1.9%	1.20E+02	0.4%	1.21E+02	2.7%
Si	ICP-ES	mg/L	10%	7.77E+01	7.2%	4.79E+01	2.0%	9.78E+01	1.7%	1.05E+02	6.6%
Zn	ICP-MS	mg/L	10%	4.98E+00	47%	7.88E+00	17%	5.79E+00	22%	5.77E+00	30%

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] The concentration in the blank is nearly the same magnitude as the concentrations in the surface samples HTF-38-16-26 and HTF-43-16-28

[c] The concentration in the blank is nearly the same magnitude as the concentrations in the sub-surface samples HTF-38-16-27 and HTF-43-16-29

The blank for the acid dilutions of the surface samples and the warm acid strike blank associated with the sub-surface samples contained low levels of plutonium contamination from the Shielded Cells sample preparations. For the surface samples from both Tank 38H and Tank 43H, the acid dilution blank contained Pu-239/240 and Pu-241 concentrations of the same magnitude as measured in the surface samples. The Pu-238 concentration in the surface samples is an order of magnitude higher than the Pu-238 concentration in the blank. For the sub-surface samples from both Tank 38 and Tank 43H, the concentration of the Pu-241 in the warm acid strike blank is the same magnitude as measured in the sub-surface samples.

The low concentrations of plutonium in the samples and the presence of plutonium contamination in the blank samples indicate the plutonium results for the current Tank 38H and Tank 43H samples will have higher uncertainty than may be shown by the %RSD. The plutonium results may be biased high due to the plutonium contamination from the cell sample preparations for a result that is conservative with respect the enrichment calculation.

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 <10% for the two surface samples providing an indication of good data quality for the non-radioactive analytes in the table. The sodium concentration measured in the samples fall within the range of previous analyses with the exception of the Tank 38H surface sample. The sodium concentration in the Tank 38H surface samples appears to vary considerably over the last three analyses of these tank samples. However, the good cation/anion balance and the results of the density measurements support the validity of the lower sodium concentration in the current Tank 38 surface sample.

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 but within expected recovery values with differences from the targeted concentrations of 17%, 12%, and 10% respectively. The silicon concentration was below detectible levels in the process blank. The four tank samples show silicon concentrations ranging from 47.9 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 20.5 to 34.0 mg/L while the Tank 43H samples ranged from 47.6 to 50.6 mg/L. The U-235 percentage ranged from 0.62% to 0.64% over the four samples. The total uranium and percent U-235 results appear consistent with previous 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 two Tank 43H samples show similar plutonium concentrations and are within the range of values measured on previous samples. The plutonium results may be biased high due to the plutonium contamination from the cell sample preparations. The four samples analyzed show silicon concentrations ranging from 47.9 to 105 mg/L.

5.0 Acknowledgements

The contributions of Carl Black and Dan Hallman for preparing the samples, Chuck Coleman, David Diprete, Amy Ekechukwu, Mark Jones, John Young, and Tom White for providing analytical services are appreciated and acknowledged.

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