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Sample Results from the Integrated Salt Disposition Program Macrobatches 5 Tank 21H Qualification Samples

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed samples from Tank 21H in support of qualification of Macrobatch (Salt Batch) 5 for the Integrated Salt Disposition Project (ISDP). This document reports partial results of the analyses of samples of Tank 21H. No issues with the projected Salt Batch 5 strategy are identified.

A subsequent report will provide analyses related needed for the Performance Objectives Demonstration Document (PODD) as well as results from process demonstrations for the waste.

LIST OF ABBREVIATIONS

AA – Atomic Absorption
AD – Analytical Development
AMP – ammonium molybdophosphate
ARP – Actinide Removal Project
CVHg – Cold Vapor Mercury
ESS – extraction, scrub, strip
IC – Ion Chromatography
ICPES – Inductively Coupled Plasma Emission Spectroscopy
ICPMS – Inductively Coupled Plasma Mass Spectroscopy
ISDP – Integrated Salt Disposition Program
MST – monosodium titanate
PODD – Performance Objectives Demonstration Document
PuTTa – plutonium thenoyl trifluoroacetone scintillation
RSD – relative standard deviation
SRNL – Savannah River National Laboratory
SRR – Savannah River Remediation
TIC-TOC – Total Inorganic Carbon-Total Organic Carbon
TTQAP - Task Technical and Quality Assurance Plan
TTR – Technical Task Request
WAC – Waste Acceptance Criteria
% RSD – percent relative standard deviation

1.0 Introduction

This report covers the Tank 21H qualification sample results for Macrobatches (Salt Batch) 5 of the Integrated Salt Disposition Program (ISDP). A previous document covers initial characterization which includes results for a number of non-radiological analytes.¹ This work was specified by Task Technical Request² and by Task Technical and Quality Assurance Plan (TTQAP).³

Details for the work are contained in controlled laboratory notebooks.⁴

2.0 Experimental Procedure

Five Tank 21H samples (i.e., dip sample bottles HTF-21-11-114, HTF-21-11-115, HTF-21-11-116, HTF-21-11-117, and HTF-21-11-118) arrived at SRNL on October 13, 2011.

For this macrobatch, Tank 21H is used as the blend and preparation tank. This material will be transferred to Tank 49H where it will be combined with the heel from Macrobatches 4. In this qualification effort for Macrobatches 5, only samples from Tank 21H have been analyzed. In this campaign, the qualification and tank strategy⁵ indicates that analysis of Tank 49H is not needed as the material was qualified for Macrobatches 4. As long as the Tank 21H material is qualified, and the qualified Tank 49H material has not changed, then the blend of these two tanks will provide a usable composite.

All of the samples were optically clear, with no visible solids present. The researchers measured the density of the solution in each bottle to make sure that the samples pulled from each depth were relatively homogenous. Samples were well shaken before measuring. The density results were previously reported.¹ Once the density was measured, the five samples were composited with customer concurrence.

3.0 Results and Discussion

In a previous document¹, density, Inductively Coupled Plasma Emission Spectroscopy (ICPES), Ion Chromatography (IC) and ¹³⁷Cs results were reported for the Tank 21H composite. These results are also reported here for clarity (Table 1). Values in parentheses are the relative standard deviation (RSD).

Table 1. Previous Results

Analyte	Result (mg/L)	Analyte	Result (mg/L)
Density	1.301 g/mL (0.75%)	Sb	<10.7
Ag	<1.46	Si	46.8 (1.66%)
Al	7125 (0.10%)	Sn	<5.61
B	35.8 (0.40%)	Sr	<0.05
Ba	<0.52	Th	<2.68
Be	<0.08	Ti	<0.38
Ca	<0.56	U	<32.7
Cd	0.850 (1.66%)	V	<0.47
Ce	<6.03	Zn	4.40 (0.64%)
Cr	41.0 (0.34%)	Zr	>0.25
Cu	1.29 (23.7%)	F ⁻	<10
Fe	5.54 (0.64%)	Cl ⁻	<500
Gd	<2.15	Br ⁻	<500
K	324 (2.40%)	Formate	<10
La	<0.67	Nitrite	25750 (5.77%)
Li	10.4 (0.68%)	Nitrate	175000 (5.27%)
Mg	<0.15	Phosphate	485 (13.7%)
Mn	<0.53	Sulfate	7305 (4.36%)
Mo	7.79 (8.45%)	Oxalate	242 (20.5%)
Na	146000 (0.49%)	TIC	2860 (2.97%)
Ni	<1.6	TOC	220 (5.14%)
P	168 (0.84%)	Free Hydroxide	2.08 M (2.04%)
Pb	<7.16	¹³⁷ Cs	5.90E+07 (0.00%)
S	2940 (0.00%)		

The nickel (Ni) result converted into a concentration of Ni(OH)₂ is <2.53 mg/L.

3.1 Tank 21H Qualification Analyses

The tank samples were analyzed by Analytical Development (AD) by the listed non-radiological methods (Table 2) and radiological (Table 3) methods. Analyses were performed in duplicate. Averages of the individual results, with the percent relative standard deviation (RSD) in parentheses, are reported in subsequent data tables. Shaded sample results indicate calculated values.

Table 2. Non-Radiological Analyses

Method	Analyte
IC Cations	NH ₄ ⁺
TIC	total inorganic carbon
TOC	total organic carbon
AA-As	As
AA-Se	Se
CV-Hg	Hg
HPLC	tetraphenylborate, phenol
SVOA	tributylphosphate
VOA	isopropanol, butanol, isobutanol

Table 3. Radiological Analyses

Method	Analyte
Tritium	³ H
¹⁴ C	¹⁴ C
gamma scan, Cs-removed	⁶⁰ Co, ⁹⁴ Nb, ¹⁰⁶ Ru, ¹²⁵ Sb, ¹²⁶ Sn, ¹⁴⁴ Ce, ¹⁵⁴ Eu, ¹⁵⁵ Eu, ²⁴¹ Am, ²²⁶ Ra,
⁹⁰ Sr	⁹⁰ Sr
¹²⁹ I	¹²⁹ I
gamma scan	¹³⁴ Cs, ¹³⁷ Cs
²³² U	²³² U
²³⁸⁻²⁴¹ Pu (filtered and unfiltered) (Plutonium thenoyl trifluoroacetone scintillation)	²³⁸ Pu, ^{239/40} Pu, ²⁴¹ Pu
Am/Cm	²⁴¹ Am, ²⁴³ Am, ²⁴⁴ Cm, ²⁴⁵ Cm
^{59/63} Ni	^{59/63} Ni
⁹⁹ Tc	⁹⁹ Tc
¹⁴⁷ Pr/ ¹⁵¹ Sm	¹⁴⁷ Pr/ ¹⁵¹ Sm
Rad ICPMS (Inductively Coupled Plasma Mass Spectroscopy)	isotopes from mass number 81 to 209 and 230 to 252, incl. ²³³ U and above, ²³⁷ Np, ²³⁰ Th, ²³² Th
Liquid Scintillation Counting	total alpha, total beta

3.2 Tank 21H Qualification Results (non-radiological analytes)

Free Hydroxide, IC Cations and Total Inorganic Carbon/Total organic Carbon (TIC/TOC) are listed in Table 4. The analytical uncertainty for each of these methods is 10%.

Table 4. IC Cations, Free Hydroxide and TIC/TOC Results

Analyte	Result (mg/L)
NH ₄ ⁺	<50
TIC	2860 (2.97%)
TOC	220 (5.14%)
carbonate	≤ 0.238 M
Free Hydroxide	2.08 (2.04%) M

The TIC and TOC results are in terms of mg/L of carbon. If we assume that the entire TIC result is carbonate, this translates to a carbonate concentration of 0.238 M.

The results for the weight percent insoluble solids, phenol, tetraphenylborate, tributyl phosphate, isopropanol, methanol, isobutanol, butanol, arsenic, mercury, and selenium are listed in Table 5. The analytical uncertainty for all listed analyses is 20%, except for the wt% insoluble solids, which is 10%.

Table 5. Miscellaneous Results (mg/L unless otherwise noted)

Analyte	Result
wt % insoluble solids	0.32 wt% (8.84%)
phenol	<10
tetraphenylborate	<10
tributylphosphate	<1
isopropanol	<0.25
butanol	<0.75
isobutanol	<0.75
methanol	≤ 190
As	0.322 (11.2%)
Hg	88.2 (10.6%)
Se	0.201 (2.47%)

The TTR requested a TPB detection limit of 5 mg/L or less; however this resolution is not normally attainable. SRNL is in the process of trying to refine this method. The oxalate concentration is 242 mg/L, and the formate result is 317 mg/L. The oxalate result is converted to the equivalent carbon result of 66 mg/L. The formate result is converted to the equivalent carbon result of 82.7 mg/L. Subtracting this result from the TOC result gives a remainder of 71.3 mg/L of carbon. If we assume all of this remainder carbon is in the form of methanol, this gives a calculated methanol result of 190 mg/L. This methanol result should be considered an upper bound as no direct analytical method for methanol exists.

3.3 Tank 21H Qualification Results (radiological analytes)

The results of the radiological analysis are listed in Table 6. The analytical uncertainty for RADICPMS samples are 20%. Other analytical methods have varying uncertainties, typically 5-10% and are noted for single sample results.

Results given in italics indicate that one of the sample results was either below detection or quantification limits, in which case the value in the parentheses is the analytical uncertainty. Only quantifiable measured values are reported when available.

⁹⁰Y is calculated as equal to the ⁹⁰Sr result. ¹⁰⁶Rh is calculated as equal to the ¹⁰⁶Ru result. ^{137m}Ba is calculated as 94.7% of the ¹³⁷Cs result (as seen in Table 1).⁶ The ¹³⁷Cs value was previously reported.¹ ¹⁴⁴Pr is calculated as equal to the ¹⁴⁴Ce result. The ¹³⁵Cs result assumes that all of mass 135 from the ICPMS result is ¹³⁵Cs. The ²³²Th result assumes that all of mass 232 from the ICPMS result is ²³²Th. The Total Alpha value is calculated by adding all the alpha results together and treating the less-than results as real values. Thus, this value is biased high. Total gamma is calculated as the sum of the ¹³⁷Cs, ¹³⁴Cs, ¹³⁵Cs, ⁶⁰Co, ⁹⁴Nb, ¹⁰⁶Ru, ¹²⁵Sb, ¹²⁶Sn, ¹⁴⁴Ce, ¹⁴⁴Pr, ¹⁵⁴Eu, ¹⁵⁵Eu, and ²²⁶Ra. The ²³⁸Pu (soluble or total), ^{239/40}Pu, and ²⁴¹Pu results are from radiocounting, while the other Pu results are from ICPMS.

The Total Soluble Plutonium value is calculated by adding all the plutonium results together and treating the measurements less-than the method detection limits as equal to the method detection limit. Thus, this value is conservative. The Total Soluble Uranium value is calculated by adding all the uranium results together and treating the values reported as less-than the method detection limits as equal to the method detection limit. Thus, this value is conservative.

The high RSD in the ⁹⁰Sr result is due to the two disparate results (1.28E+05 and 2.58E+05 pCi/mL). This method requires an isotopic extraction and decay and can occasionally give duplicate results with high RSD. The high RSD in the ²³²U result is again due to two disparate results (7.25 and 1.42 pCi/mL) which is due to being very close to the method detection limit.

**Table 6. Radiological Results of Tank 21H Analyses for Macrobatches 5
(pCi/mL unless otherwise noted)**

Analyte	Average Result	Analyte	Average Result
^3H	9.46E+02 (12.3%)	^{232}Th	<1.10E-03
^{14}C	7.20E+02 (10%)	^{232}U	4.33E+00 (95.0%)
^{59}Ni	<2.00E+01	^{233}U	<9.68E+01
^{63}Ni	<4.06E+02	^{234}U	9.00E+01 (28.5%)
^{60}Co	<5.63E+00	^{235}U	1.94E-01 (3.46%)
^{90}Sr	1.93E+05 (47.8%)	^{236}U	1.08E+00 (6.77%)
^{90}Y	1.93E+05 (47.8%)	^{238}U	3.70E+00 (3.86%)
^{94}Nb	<6.08E+00	^{237}Np	3.39E+00 (7.93%)
^{99}Tc	2.28E+04 (5.87%)	^{238}Pu (soluble)	1.49E+04 (5.57%)
^{106}Ru	<8.19E+01	^{238}Pu (total) ^Y	1.46E+04 (4.56%)
^{106}Rh	<8.19E+01	$^{239/40}\text{Pu}$	1.49E+03 (6.00%)
^{125}Sb	<5.99E+01	^{241}Pu	<5.22E+03
^{126}Sn	1.93E+02 (3.46%)	^{242}Pu	<3.82E+01
^{129}I	1.30E+01 (6.38%)	^{244}Pu	<1.77E-01
^{134}Cs	<5.54E+03	^{241}Am	<7.6E+00
^{135}Cs	2.81E+02 (2.90%)	^{243}Am	<3.98E+00
$^{137\text{m}}\text{Ba}$	5.59E+07 (0.00%)	^{244}Cm	1.05E+01 (23.8%)
^{144}Ce	<7.70E+01	^{245}Cm	<1.13E+01
^{144}Pr	<7.70E+01	Total Alpha	<7.47E+03
^{147}Pm	<1.80E+02	Total Beta	6.55E+07 (6.32%)
^{151}Sm	<1.53E+02	Total Gamma	5.90E+07
^{154}Eu	<1.53E+01	Total Sol. Pu (mg/L)	4.18E-02
^{155}Eu	<3.62E+01	Total Sol. U (mg/L)	1.12E+01
^{226}Ra	<3.12E+02		

4.0 Conclusions

Results of the analyses of the Tank 21H samples from this report in conjunction with the findings of the previous report,¹ indicates that the material does not display any unusual characteristics.

^Y The Waste Acceptance Criteria (Tank 50 WAC) limit is for total ^{238}Pu . There is an Actinide Removal Process (ARP) limit of 7.93E+05 pCi/mL for soluble ^{238}Pu . Unlike most samples, this one was deliberately not filtered before analysis.

5.0 References

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