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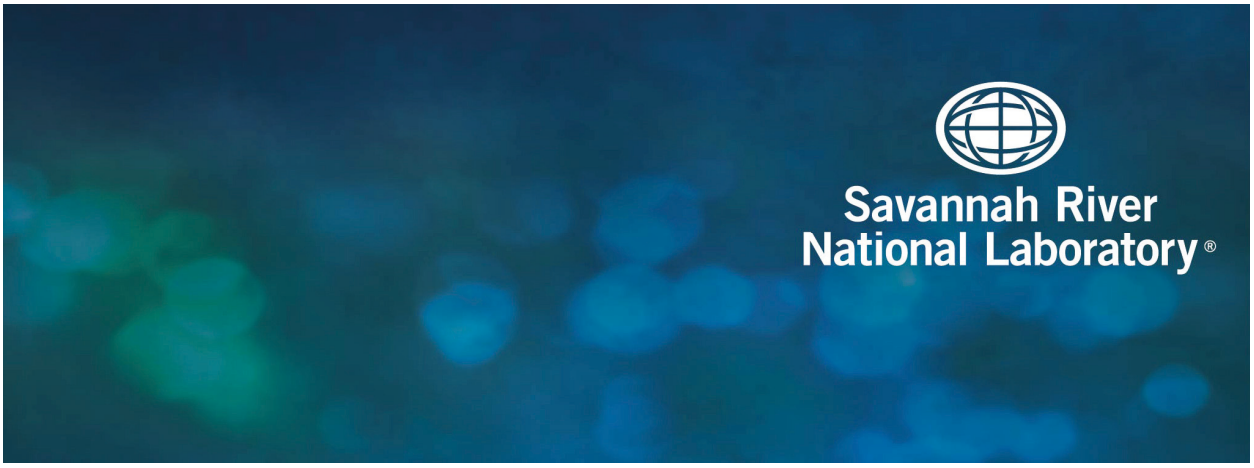

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Results for the January 2022 Semiannual Tank 50 Salt Solution Sample

C. L. Crawford

May 2022

SRNL-STI-2022-00137, Revision 0

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EXECUTIVE SUMMARY

In this Technical Report, the chemical and radionuclide contaminant results from the January 2022 Semiannual sample of Tank 50 salt solution are presented in tabulated form. The information from this characterization will be used by Savannah River Mission Completion (SRMC) for the transfer of aqueous waste from Tank 50 to the Saltstone Production Facility (SPF), where the waste will be treated and disposed in the Saltstone Disposal Facility. This Technical Report compares results, where applicable, to SPF Waste Acceptance Criteria (WAC) LIMITS and TARGETS that were established at the time the Tank 50 sample was obtained.[1] The chemical and radionuclide contaminant results from the characterization of the January 2022 semiannual sampling of Tank 50 were requested by SRMC personnel via a Task Technical Request (TTR)[2] and details of the testing are presented in the Savannah River National Laboratory (SRNL) Task Technical and Quality Assurance Plan (TTQAP).[3] This Technical Report is part of Deliverable 2 relating to Task 1 from the SRMC request.[2] Data pertaining to the regulatory limits for Resource Conservation and Recovery Act (RCRA) metals per Task 2 from the RMC request, will be obtained semiannually for the January 2022 and July 2022 Tank 50 samples.

The following facts pertaining to the WAC are drawn from the analytical results provided in this report.

- WAC TARGETS and LIMITS were met for all analyzed chemical and radioactive contaminants for which the detection limits are below the WAC TARGETS and LIMITS.[1]

- Nitrosamines were not detected in the Tank 50 salt solution sample above the instrument detection limits of <1 mg/L.

- The minimum detection limit (<1.07E-01 pCi/mL) is reported for ^{94}Nb as determined from the minimum detectable activity associated with the radiochemical method used for this radionuclide. The reported detection limit is above the requested SRMC target minimum detection limit concentration.[4] However, the minimum detection limit reported for the January 2022 semiannual Tank 50 sample for ^{94}Nb is lower than the estimated detection limit of 4.38E-01 pCi/mL initially established by SRNL in 2009.[5] Thus, per guidance from SRMC,[4] SRNL continues to achieve as low as practical detection limits for this radionuclide.

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LIST OF ABBREVIATIONS

CP&C	Chemical Processing & Characterization
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
DMA	Direct Mercury Analyzer
EDTA	ethylenediaminetetraacetate
GC/MS	Gas Chromatographic/Mass Spectrometric
HDPE	high-density polyethylene
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LSC	Liquid Scintillation Counting
MRL	Minimum Reporting Limit
NDMA-d6	N-nitrosodimethylamine-d6
P&T-TD-CVAFS	Purge & Trap, Thermal Desorption, Cold Vapor Atomic Fluorescence Spectroscopy
Pu alpha PHA	Plutonium alpha Pulse Height Analysis
RCRA	Resource Conservation and Recovery Act
SDI	Salt Disposition Integration
SDU	Saltstone Disposal Unit
SPF	Saltstone Production Facility
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TPB	tetraphenylborate
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VDS	Variable Depth Sample
VOA	Volatile Organic Analysis
WAC	Waste Acceptance Criteria

1.0 Introduction

Tank 50 aqueous waste is analyzed on a semiannual basis and the results are compared to the Waste Acceptance Criteria (WAC) of the Z-Area Saltstone Production Facility (SPF).[1] The information from this characterization will be used by Savannah River Mission Completion (SRMC) for the transfer of aqueous waste from Tank 50 to SPF, where the waste will be treated and disposed in the Saltstone Disposal Facility. This Technical Report compares results, where applicable, to SPF WAC LIMITS and TARGETS.[1] A memorandum reporting the average Cs-137 value and comparison to WAC LIMITS has been previously issued.[6] The semiannual Tank 50 analysis is to occur in January and July of each year. A reduced set of analyses will also be obtained on a planned bimonthly basis to occur in March, May, September and November of each year.[7]

2.0 Experimental

2.1 Technical

The January 2022 semiannual Tank 50 samples [a 200-mL sample obtained 6" below the surface (HTF-50-22-6) and a 1-L variable depth sample (VDS) obtained 66" from the tank bottom (HTF-50-22-7)] were obtained and received at Savannah River National Laboratory (SRNL) on January 12, 2022.[8]

The contents of the 1-L slurry in the steel variable depth sampler were initially mixed by recycling some of the slurry using the transfer pump with both ends of the transfer line submerged in the sample. After initial mixing, a 30-mL aliquot and a 15-mL aliquot of the Tank 50 sample were pumped into a Teflon® and a glass container, respectively, with zero headspace. These two samples were used for Hg speciation measurement. The remaining contents were then transferred by pumping into two different high-density polyethylene (HDPE) 1-L bottles. The transferred slurry was left to settle in the bottles and no suspended or settled solids were observed during the brief storage in the Shielded Cells. Therefore, no clear supernate was returned to the sampler for rinsing. The entire sample was promptly transferred out of the Shielded Cells on the same day as it was collected from the steel variable depth sampler and placed in a radiochemical hood. The two small zero headspace vials for Hg speciation testing were put in shrouded containers and transferred to storage in a refrigerator. All transfers out of the Shielded Cells were made on the same day as sample collection. After receipt in a radiochemical hood for processing, the 1-L bottles were agitated by hand to thoroughly disperse any extremely limited suspended solids into the supernate. These suspended solids are typically only visible as trace solids at the bottom of the container upon prolonged storage of the material under static conditions. Aliquots of slurry samples were promptly collected with slurry pipettes to minimize settling effects and placed into HDPE bottles. Samples for volatile organic analysis (VOA) and semi-volatile organic analysis (SVOA) were removed from the 200-mL surface sample from within a radiochemical hood and were transferred using glass pipettes into clean amber glass sample vials with Teflon-lined caps. Amber colored glass sample vials were used for the samples that were analyzed for nitrosamines to minimize exposure to light.

Unless otherwise stated, all concentrations presented in the tables (except upper limits) are averages based on analyses of triplicate aliquots of the January 2022 semiannual Tank 50 sample. The 1-sigma standard deviation of each average is also presented. Several of the contaminants were either not detected in the slurry samples or detected at values below the method reporting limit (MRL). For contaminants not detected or detected below the MRL, the result is preceded by a "<", which indicates the result is an upper limit based on the sensitivity of the method used to analyze the individual analyte. If only one value out of the triplicate analysis is above the detection limit, then that single value is reported and noted in the tables. Also, if only two values out of the triplicate analyses are above the detection limit, then the average of those two values is reported and noted in the tables.

All VOA, SVOA and nitrosamines analyses were performed on the surface sample and all other analyses were performed on the variable depth sample. The VOA method is performed per SRNL Chemical Processing & Characterization (CP&C) Procedure L16.1, ADS-2656.[9] This method is based upon a purge-and-trap, Gas Chromatographic/Mass Spectrometric (GC/MS) process that involves dilution of 1 mL of Tank 50 supernate with 4 mL of reagent water. The SVOA method is performed per SRNL CP&C Procedure L16.1, ADS-2657.[10] Both of these methods use discrete standards as detailed in the procedures.[9,10] The SVOA method uses organic solvents to extract SVOA analytes that are subsequently measured by GC/MS. A 3 mL dichloromethane (also known as methylene chloride, CH_2Cl_2) volume is used to initially extract 10 mL of Tank 50 supernate for phenol. The same Tank 50 supernate is then extracted with 2 additional 3-mL volumes of dichloromethane. The dichloromethane extracts are all combined and concentrated to 1 mL before analysis for phenol. Tributyl phosphate is analyzed from a 0.01 mL hexane (C_6H_{14}) extract of 10 mL of Tank 50 supernate. Isopar L[a] and Norpar 13 are analyzed from a 2.5 mL hexane extraction of 10 mL of Tank 50 supernate. Nitrosamines are analyzed by a separate SVOA method that uses 2 mL of dichloromethane as extractant and 10 mL of Tank 50 supernate with deuterated N-nitrosodimethylamine-d6 (NDMA-d6) as a standard along with a separate GC/MS analysis methodology.

Data reported for inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are derived from the digested Tank 50 supernate (1 mL supernate diluted to 50 mL total volume) by the aqua regia method.[11] The aqua regia method heats the Tank 50 supernate mixed with a 1:3 mixture of nitric acid/hydrochloric acid for 2 hours in sealed Teflon containers in an oven at 115 ºC. Anion and the ammonium cation analyses are determined from Ion Chromatography (IC). Total Inorganic Carbon/Total Organic Carbon (TIC/TOC) analysis was used to measure the TIC (carbonate) and TOC components. The tetraphenylborate (TPB) anion and ethylenediaminetetraacetate (EDTA) were analyzed using High Performance Liquid Chromatography (HPLC). The IC, TIC/TOC and HPLC methods all used undiluted samples. All the above analyses, excluding VOA and SVOA, used approximately 150 mL of the 1-L variable depth sample. Densities were measured on triplicate samples of the Tank 50 slurry by SRNL CP&C. Total and soluble weight percent solids were determined on quadruplicate portions of the Tank 50 sample, without filtration and with filtration, respectively, using the "Weight Percent Solids Determination Using a Furnace or Oven" procedure.[12] Approximately 630 mL of the VDS were used to determine all the measured radionuclide concentrations in triplicate. Radionuclides reported using the ICP-MS method are converted from a reported mass per volume basis to activity per volume units using the specific activities (Ci/g) reported from the Department of Energy 1996 Integrated Data Base Report.[13] The Cs-137 and C-134 radionuclides are determined from gamma spectroscopy. Total beta is measured from a radscreen method using Liquid Scintillation Counting (LSC). The total alpha is measured from the same method after removal of Cs-137 from the sample using ammonium phosphomolybdate. No other radiochemical species in the matrix are removed. This methodology for measuring total alpha concentrations typically results in upper limits rather than minimum detectable activities when other peaks from competing radionuclides, e.g., Sr-90, in the matrix prevent detection of the alpha emitters. Plutonium isotopes (Pu-238, Pu-239 and Pu-240) are determined from a Plutonium alpha Pulse Heigh Analysis (Pu alpha PHA) method.

Mercury analyses performed at SRNL by CP&C included Total mercury using the Direct Mercury Analyzer (DMA) method[14] and monomethyl mercury and ethyl mercury by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS).[15] Soluble elemental mercury (Hg(0)) was measured by CP&C using a Purge & Trap, Thermal Desorption, CVAFS (P&T-TD-CVAFS) method.[16] A variation of this method was also developed by CP&C to analyze for inorganic mercury (Hg(I/II)).[17] Dimethyl mercury was analyzed using a semi-quantitative CP&C VOA method that involves extraction followed by GC/MS.[9] The parent sample for all mercury analyses performed at SRNL was obtained from the original Tank 50 sample within two

[a] Isopar L is a trademark chemical (Isopar™ L) manufactured by ExxonMobil. It is a synthetic isoparaffinic hydrocarbon that is manufactured from a petroleum based raw material.

days of sample receipt. As discussed above, the parent Tank 50 sample was obtained in near zero-headspace containers that were immediately refrigerated after removal from the Shielded Cells Facility on the same day of preparation.[18] Total mercury, Monomethyl and ethyl mercury are determined from the Tank 50 parent sample obtained in the 30-mL Teflon bottle. All other species are determined from the 15-mL Tank 50 parent stored in the glass bottle. Samples of Tank 50 submitted to SRNL CP&C analytical laboratories for mercury speciation analysis were submitted without dilution. These samples were diluted within the SRNL CP&C analytical laboratories to meet the targeted calibration range of either the DMA instrument for total Hg or the CVAFS instrument for other Hg species and for VOA analysis for dimethyl mercury.

2.2 Quality Assurance

Quality Assurance requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[19] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[20] The customer requested that a Functional Classification of Safety Significant apply to this work.[2] Thus, a Design Verification technical review was performed via a document review according to the applicable elements detailed in Section 5.3.1 'Design Verification by Document Review' of E7 2.60.[19] Data collection and analysis methods used in this work comply with this requirement as detailed in the TTQAP.[3]

3.0 Results and Discussion

Analyzed nonradionuclide chemical concentrations, their 1-sigma standard deviations and their corresponding WAC LIMITS[1] are shown in Table 3-1 that correspond to the Attachment 8.1 LIMITS in the WAC.[1] Per the WAC, the LIMITS shown shall not be exceeded accounting for the analytical uncertainty in each measured concentration.[1] Analyzed nonradionuclide chemical concentrations, their standard deviations and their corresponding WAC TARGETS[1] are shown in Table 3-2 that correspond to the Attachment 8.2 TARGETS in the WAC.[1] Per the WAC, the TARGETS shown shall not be exceeded accounting for the analytical uncertainty in each measured concentration.[1] The LIMITS refer to a type of acceptance criteria that, if not satisfied, will have an adverse impact on repository requirements, whereas the TARGETS refer to a type of acceptance criteria that is set as a guideline to protect a LIMIT.[1] For the chemical contaminants and the radionuclides given in tables below, an analytical uncertainty of 2 sigma (2σ) shall be accounted for in sample analyses used to determine the analytical uncertainty vs. either the LIMIT or TARGET.[1] The standard deviations given in tables for this WAC report are taken as 1 sigma (1σ) values that are calculated from the normal 'standard deviation' function for either duplicate or triplicate values from within Excel® spreadsheets.

Comparison of the average analyzed detectable values shown in Table 3-1 to the WAC LIMITS indicates that free hydroxide and nitrate anions and total mercury are the highest analytes relative to the WAC LIMITS at 20%, 25% and 14%, respectively. Comparison of the average analyzed values shown in Table 3-2 to the WAC TARGETS indicates that aluminum is the highest analyte relative to the WAC TARGET at 61%, with average TOC at a lower ratio to WAC TARGET of 42%. No VOA analytes (butanol, propanol, benzene and toluene) were detected above the indicated method detection limits from duplicate analyses as shown in Table 3-1 and Table 3-2. Analyzed radionuclide concentrations and the respective radiochemical analysis methods, their standard deviations and their corresponding WAC[1] LIMITS and TARGETS are shown in Table 3-3 and Table 3-4, respectively. The minimum detection limit reported for Nb-94 of (<1.07E-01 pCi/mL) in Table 3-4 is above the requested SRMC TARGET minimum detection limit of 2.8E-03 pCi/mL "to meet future inventory reporting requirements"[4] but is lower than the estimated detection limit initially established by SRNL of 4.38E-01 pCi/mL in 2009.[5] All of these Nb-94 values (analyzed, 2013-requested and 2009 estimated detection limit) are orders of magnitude below the WAC TARGET for Nb-94 of 1.53E+02 pCi/mL shown in Table 3-4.

Comparison of the average analyzed detectable values shown in Table 3-3 to the WAC LIMITS[1] indicates that Tc-99 and I-129 are the highest analytes relative to the WAC LIMITS at 17% and 19%, respectively. Comparison of the average analyzed detectable values shown in Table 3-4 to the WAC TARGETS indicates that none of the radionuclides are higher than 3% of the WAC TARGETS.[1] Table 3-4 indicates that the upper limit determined in the triplicate samples analyzed for total alpha for the January 2022 semiannual sample is 8.87E+02 pCi/mL.

Table 3-1. Chemical Contaminants from January 2022 Semiannual Tank 50 Samples and SPF WAC, Attachment 8.1 LIMITS

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC LIMIT (mg/L)
Aluminate ($Al(OH)_4^-$)	ICP-AES	1.51E+04[a]	2.92E+02	**4.08E+05**
Ammonium (NH_4^+)	IC	<5.00E+01	NA	**2.12E+02**
Carbonate (CO_3^{2-})	TIC	1.38E+04[b]	1.19E+03	**1.20E+05**
Chloride (Cl^-)	IC	2.28E+02	2.52E+00	**7.95E+03**
Fluoride (F^-)	IC	<1.00E+02	NA	**4.07E+03**
Free Hydroxide (OH^-)	Total Base	3.21E+04[b]	1.02E+03	**1.58E+05**
Nitrate (NO_3^-)	IC	1.10E+05	5.77E+02	**4.37E+05**
Nitrite (NO_2^-)	IC	2.15E+04	1.53E+02	**2.14E+05**
Oxalate ($C_2O_4^{2-}$)	IC	5.00E+02	4.16E+00	**2.72E+04**
Phosphate (PO_4^{3-})	IC	2.69E+02	5.86E+00	**3.14E+04**
Sulfate (SO_4^{2-})	IC	6.83E+03	4.36E+01	**5.69E+04**
Arsenic (As)	ICP-MS	1.10E-01	5.25E-03	**1.97E+02**
Barium (Ba)	ICP-AES	< 3.72E-01	NA	**6.19E+02**
Cadmium (Cd)	ICP-AES	< 2.18E-01	NA	**3.10E+02**
Chromium (Cr)	ICP-AES	4.96E+01	1.13E+00	**1.50E+03**
Lead (Pb)	ICP-MS	2.90E-01	1.40E-02	**7.50E+02**
Total Mercury (Hg)	DMA	4.59E+01	2.65E-01	**3.25E+02**
Elemental Mercury (Hg(0))	P&T-TD-CVAFS	1.14E+01	5.69E-01	**3.25E+02**
Monomethyl Mercury (CH_3Hg)	CVAFS	2.09E+01	6.56E-01	**3.50E+02**
Ethyl Mercury (C_2H_5Hg)	CVAFS	< 1.00E+00	NA	**3.73E+02**
Ionic Mercury (Hg(I/II))[d]	P&T-TD-CVAFS	4.47E+00[d]	1.75E-01	**NA[e]**
Selenium (Se)	ICP-MS	8.74E-02	7.33E-03	**3.75E+02**
Silver (Ag)	ICP-AES	< 2.66E-01	NA	**6.19E+02**
Aluminum (Al)	ICP-AES	4.29E+03	8.29E+01	**1.16E+05**
Potassium (K)	ICP-AES	<2.96E+02	NA	**3.03E+04**
Butanol (C_4H_9OH)	VOA	<2.500E-01[c]	NA	**7.73E+00**
Propanol (C_3H_7OH)	VOA	<2.50E-01[c]	NA	**1.88E+00**
Phenol (C_6H_5OH)	SVOA	<1.00E+01[c]	NA	**7.50E+02**
Tetraphenylborate [TPB] ($B(C_6H_5)_4^-$)	HPLC	<5.00E+00	NA	**5.00E+00**
Total Organic Carbon (----)	TOC	3.14E+02[b]	8.50E+00	**4.50E+03**
Isopar L (----)	SVOA	<3.30E+01[c]	NA	**8.75E+01**

a. Result is calculated from the measured Al concentration assuming all the Al is present as the OH compound.
b. Measurement performed on filtered supernate samples.
c. Measurement performed on duplicate samples rather than triplicate samples.
d. Ionic mercury (Hg(I/II)) species is not included in the SPF WAC.[1]

Table 3-2. Chemical Contaminants from January 2022 Semiannual Tank 50 Samples and SPF WAC, Attachment 8.2 TARGETS

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC TARGET (mg/L)
Aluminum (Al)	ICP-AES	4.29E+03	8.29E+01	**7.00E+03**[e]
Boron (B)	ICP-AES	3.73E+01	8.79E-01	**7.43E+02**
Cobalt (Co)	ICP-MS[a]	3.58E-02	9.25E-04	**1.45E+02**
Copper (Cu)	ICP-AES	< 1.61E+00	NA	**7.43E+02**
Iron (Fe)	ICP-AES	4.76E+00	2.40E-01	**4.95E+03**
Lithium (Li)	ICP-AES	<5.96E+00	NA	**7.43E+02**
Manganese (Mn)	ICP-AES	<4.67E-01	NA	**7.43E+02**
Molybdenum (Mo)	ICP-AES	1.42E+01	3.07E-01	**7.43E+02**
Nickel (Ni)	ICP-AES	< 7.52E-01	NA	**7.43E+02**
Silicon (Si)	ICP-AES	< 2.35E+01	NA	**1.07E+04**
Strontium (Sr)	ICP-AES	< 2.25E-01	NA	**7.43E+02**
Zinc (Zn)	ICP-AES	< 5.93E+00	NA	**8.03E+02**
Dimethyl Mercury ($(CH_3)_2Hg$)	VOA[b]	< 2.50E-01	NA	**1.00E+00**
Benzene (C_6H_6)	VOA	<2.50E-01[c]	NA	**3.10E+02**
Methanol (CH_3OH)	VOA	d	NA	**1.88E+00**
Toluene ($C_6H_5CH_3$)	VOA	<2.50E-01[c]	NA	**3.10E+02**
Dibutylphosphate [DBP] ($C_8H_{19}O_4P$)	IC	<2.50E+02	NA	**3.47E+02**
Tributylphosphate [TBP] ($(C_4H_9O)_3PO$)	SVOA	<7.50E-01[c]	NA	**7.50E+00**
Total Organic Carbon (TOC)	TOC	3.14E+02	8.50E+00	**7.50E+02**[e]
EDTA ($C_{10}H_{12}N_2O_8^{4-}$)	HPLC	<1.00E+02	NA	**3.10E+02**
NORPAR 13 ($C_nH_{2\cdot n}$)	SVOA	<7.50E-01[c]	NA	**7.50E-01**
Formate ($CHOO^-$)	IC	<1.00E+02	NA	**6.38E+03**

a. Cobalt based on the stable Co-59 isotope.
b. This method is a semi-quantitative method due to lack of a dimethyl mercury standard.
c. Measurement performed on duplicate samples rather than triplicate samples.
d. Currently, a routine method for detecting this species does not exist in AD.
e. The WAC TARGETS for Al and TOC shown in this table are more restrictive than the corresponding WAC LIMITS shown in Table 3-1 to protect assumptions associated with thermolytic hydrogen generation.[1]

Table 3-3. Radionuclide Contaminants from January 2022 Semiannual Tank 50 Samples and SPF WAC, Attachment 8.3 LIMITS

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC LIMIT (pCi/mL)
Tritium (^{3}H)	Tritium Counting	1.51E+03	4.04E+01	**5.63E+05**
Carbon-14 (^{14}C)	C-14 Liquid Scintillation	5.47E+02	5.41E+01	**1.13E+05**
Nickel-63 (^{63}Ni)	Ni-59/63	<1.15E+01	NA	**1.13E+05**
Strontium-90 (^{90}Sr)	Sr-90 Liquid Scintillation	8.53E+03	2.90E+02	**2.62E+06**
Technetium-99 (^{99}Tc)	Tc-99 Liquid Scintillation	3.68E+04	5.37E+02	**2.11E+05**
Iodine-129 (^{129}I)	I-129 (w/ separation) Liquid Scintillation	1.89E+01	9.52E-01	**1.00E+02**
Cesium-137 (^{137}Cs)	Gamma Scan	3.32E+04	2.38E+02	**1.29E+06**
Uranium-233 (^{233}U)	ICP-MS	<3.12E+01	NA	**1.13E+04**
Uranium-235 (^{235}U)	ICP-MS	2.15E-01	4.06E-03	**1.13E+02**
Plutonium-241 (^{241}Pu)	Pu238/241 Liquid Scintillation	8.23E+02	9.47E+01	**8.38E+05**
Total Alpha	Liquid Scintillation Counting (Cs removed)	<8.87E+02	NA	**2.13E+05**

Table 3-4. Radionuclide Contaminants from January 2022 Semiannual Tank 50 Samples and SPF WAC, Attachment 8.4 TARGETS

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC TARGET (pCi/mL)
Aluminum-26 (^{26}Al)	Gamma Scan (Cs removed)	<3.78E-02	N/A	**2.88E+03**
Potassium-40 (^{40}K)	Gamma Scan (Cs removed)	<1.34E+00	NA	**1.00E+02**
Cobalt-60 (^{60}Co)	Gamma Scan (Cs removed)	<8.78E-02	NA	**9.75E+02**
Nickel-59 (^{59}Ni)	Ni-59/63	<8.11E+00	NA	**1.13E+03**
Selenium-79 (^{79}Se)	Se-79	5.45E+01	7.97E+00	**1.90E+04**
Yttrium-90 (^{90}Y)	Secular Equilibrium w/ 100% of Sr-90	8.53E+03	2.90E+02	**2.62E+06**
Zirconium-93 (^{93}Zr)	ICP-MS	<1.06E+01	NA	**1.00E+05**
Niobium-94 (^{94}Nb)	Nb-94	<1.07E-01	NA	**1.53E+02**
Rhodium-106 (^{106}Rh)	Secular Equilibrium w/ 100% of Ru-106	<1.15E+00	NA	**3.12E+05**
Ruthenium-106 (^{106}Ru)	Gamma Scan (Cs removed)	<1.15E+00	NA	**3.12E+05**
Antimony-125 (^{125}Sb)	Gamma Scan (Cs removed)	7.55E+01	1.29E+01	**7.99E+03**
Tellurium-125m (^{125m}Te)	Secular Equilibrium w/ 100% of Sb-125	7.55E+01	1.29E+01	**1.83E+03**
Tin-126 (^{126}Sn)	Gamma Scan (Cs removed)	3.94E+02	8.70E+01	**1.80E+04**
Cesium-134 (^{134}Cs)	Gamma Scan	<4.91E+01	NA	**5.93E+03**
Cesium-135 (^{135}Cs)	Cs-135	2.20E-01	1.04E-02	**2.50E+02**
Barium-137m (^{137m}Ba)	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	3.14E+04	2.25E+02	**1.22E+06**
Cerium-144 (^{144}Ce)	Gamma Scan (Cs removed)	<1.71E+00	NA	**3.12E+04**
Praseodymium-144 (^{144}Pr)	Secular Equilibrium w/ 100% of Ce-144	<1.71E+00	NA	**3.12E+04**
Promethium-147 (^{147}Pm)	Pm-147/Sm-151 Liquid Scintillation	<1.28E+02	NA	**1.57E+06**
Samarium-151 (^{151}Sm)	Pm-147/Sm-151 Liquid Scintillation	<4.45E+01	NA	**2.25E+04**
Europium-154 (^{154}Eu)	Gamma Scan (Cs removed)	<2.59E-01	NA	**1.62E+03**
Radium-226 (^{226}Ra)	Ra-226	<4.18E+00	NA	**1.00E+03**
Radium-228 (^{228}Ra)	Gamma Scan (Cs removed)	<6.26E-01	NA	**1.00E+04**
Actinium-227 (^{227}Ac)	Th-229/230	<1.29E-02	NA	**1.00E+04**
Thorium-229 (^{229}Th)	Th-229/230	<1.36E-02	NA	**1.63E+05**
Thorium-230 (^{230}Th)	Th-229/230	<1.36E-02	NA	**6.26E+03**
Thorium-232 (^{232}Th)	ICP-MS	<3.53E-04	NA	**2.88E+03**
Protactinium-231 (^{231}Pa)	Pa-231	<1.76E+01	NA	**1.00E+03**
Uranium-232 (^{232}U)	U-232	1.85E+00	6.37E-01	**2.27E+03**
Uranium-233 (^{233}U)	ICP-MS	<3.12E+01	NA	**3.12E+03**
Uranium-234 (^{234}U)	ICP-MS	5.77E+01	3.78E+00	**3.12E+03**
Uranium-236 (^{236}U)	ICP-MS	1.22E+00	3.74E-02	**3.12E+03**
Uranium-238 (^{238}U)	ICP-MS	1.54E+00	2.76E-02	**3.12E+03**

Table 3-4. Radionuclide Contaminants from January 2022 Semiannual Tank 50 Samples and SPF WAC, Attachment 8.4 TARGETS, continued

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC TARGET (pCi/mL)
Neptunium-237 (^{237}Np)	ICP-MS	<2.27E+00	NA	**1.00E+04**
Plutonium-238 (^{238}Pu)	Pu238/241 Pu alpha PHA	1.82E+03	1.48E+02	**6.67E+04**
Plutonium-239 (^{239}Pu)	Pu238/241 Pu alpha PHA	7.10E+01	9.69E+00	**6.67E+04**
Plutonium-240 (^{240}Pu)	Pu238/241 Pu alpha PHA	7.10E+01	9.69E+00	**6.67E+04**
Plutonium-242 (^{242}Pu)	ICP-MS	<1.23E+01	NA	**6.67E+04**
Plutonium-244 (^{244}Pu)	ICP-MS	<5.71E-02	NA	**7.02E+04**
Americium-241 (^{241}Am)	Am/Cm	9.39E-01[a]	1.11E-01	**6.67E+04**
Americium-242m (^{242m}Am)	Am/Cm	<1.80E-01	NA	**4.50E+05**
Americium-243 (^{243}Am)	Am/Cm	<5.77E-01	NA	**6.67E+04**
Curium-242 (^{242}Cm)	Am/Cm	<1.49E-01	NA	**1.13E+04**
Curium-244 (^{244}Cm)	Am/Cm	9.49E-01	1.12E-01	**6.67E+04**
Curium-245 (^{245}Cm)	Am/Cm	<1.41E+00	NA	**2.25E+05**
Total Alpha	Liquid Scintillation Counting (Cs removed)	<8.87E+02	NA	**6.67E+04**

a. Average and standard deviation calculated from only two detectable values

The following tables show various chemical contaminants (Table 3-5), organic species (Table 3-6) and processing constituents (Table 3-7) related to the Salt Disposal Unit (SDU) that are referred to in the WAC per Tables 2, 4 and 5, respectively.[1] The reported detection limit for Isopar L of <2.72E+01 ppm in Table 3-5 is lower than the current Isopar LIMIT of 87.5 ppm associated with SDU flammability for the Salt Disposition Integration (SDI) WAC.[1] The pH value shown in Table 3-7 is calculated from the pH equation for water (pH + pOH = 14) with the measured [OH^-] from Table 3-1 used in the calculation.

Table 3-5. Chemical Contaminants Impacting Saltstone Disposal Unit (SDU) Flammability from January 2022 Semiannual Tank 50 Samples and WAC Table 2 LIMITS and TARGETS

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC LIMIT/TARGET
Isopar L (----)	SVOA	<2.71E+01 ppm[a,b]	NA	**8.75E+01 ppm (LIMIT)**
Tetraphenylborate [TPB] ($B(C_6H_5)_4^-$)	HPLC	<5.00E+00	NA	**5.00E+00 mg/L (LIMIT)**
Ammonium (NH_4^+)	IC	<5.00E+01	NA	**2.12E+02 mg/L (LIMIT)**
Total Mercury (Hg)	DMA	4.59E+01	2.65E-01	**3.25E+02 mg/L (LIMIT)**
Monomethyl Mercury (CH_3Hg)	CVAFS	2.09E+01	6.56E-01	**3.50E+02 mg/L (LIMIT)**
Dimethyl Mercury ($(CH_3)_2Hg$)	VOA[c]	<2.50E-01	NA	**1.00E+00 mg/L (TARGET)**

a. Measurement performed on duplicate samples rather than triplicate samples.
b. Result is calculated from the reported concentration of <33 mg/L and the density of the slurry sample listed in Table 3-8.
c. This method is a semi-quantitative method due to lack of a dimethyl mercury standard.

Table 3-6. Other Organics Impacting SDU Flammability from January 2022 Semiannual Tank 50 Samples and WAC Table 4 Concentrations

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC Concentrations (mg/L)
Butanol (C_4H_9OH)[a]	VOA	<2.500E-01	NA	**0.75**
Tributylphosphate[TBP] ($(C_4H_9O)_3PO$)[a]	SVOA	<7.50E-01	NA	**1.0**
Propanol (C_3H_7OH)[a]	VOA	<2.50E-01	NA	**0.25**
Methanol (CH_3OH)	b	NA	NA	**0.05**
NORPAR 13 ($C_nH_{2.n}$)[a]	SVOA	<7.50E-01	NA	**0.75**

a. Measurement performed on duplicate samples rather than triplicate samples.
b. Currently, a routine method for detecting this species does not exist in AD.

Table 3-7. Processing Constituents from January 2022 Semiannual Tank 50 Samples and WAC Table 5 LIMITS

Processing Constituents	Method	Value	Std. Dev.	WAC LIMIT
pH	Calculated	>13	NA	**> 10**
Sodium Concentration	ICP-AES	4.58 M	1.11E-01	**2.5 M < [Na^+] < 7.0 M**
Total Insoluble Solids	Calculated[a]	~0 wt %	NA	**< 15 wt %**

a. Error propagation performed on the measured total solids and dissolved solids gives no credible calculated insoluble solids value, i.e., there is no statistical difference in the two measured values.

Table 3-8 contains additional measured constituents per the TTQAP.[3] There were no detectable nitrosamine species in the Tank 50 surface sample via the SVOA analyses shown in Table 3-8.

Table 3-8. Additional Measured Constituents

Constituent	Method	Average Value	Std. Dev.
Density (slurry)	Measured (18.4ºC)	1.219 g/mL	<0.001 g/mL
Specific Gravity	a	1.220	<0.001
Total Solids	Measured	25.38 wt %	0.29 wt %
Total Beta	LSC	1.20E+05 pCi/mL	1.07E+04 pCi/mL
Total Gamma	b	3.24E+04 pCi/mL	7.19E+01 pCi/mL[c]
Beryllium (Be)	ICP-AES	< 1.67E-01 mg/L	NA
N-Nitrosodimethylamine ($C_2H_6N_2O$)	SVOA[d]	<1 mg/L	NA
N-Dioctylnitrosamine ($C_{16}H_{34}N_2O$)	SVOA[d]	<1 mg/L	NA

a. Calculated from the measured density of slurry and density of water at 18.8 °C.[21]
b. Calculated from the sum of gamma emitters (Sb-126, Sn-126, Sb-125, Eu-154, Am-241, Co-60 and Ba-137m).
c. Value is the "standard error of the mean" rather than the standard deviation of the measurements since its calculation involves multiple radionuclides.
d. Measurement performed on duplicate samples rather than triplicate samples

4.0 Conclusions

The following conclusions pertaining to the WAC are drawn from the analytical results provided in this report.

- WAC TARGETS and LIMITS were met for all analyzed chemical and radioactive contaminants for which the detection limits are below the WAC TARGETS and LIMITS.[1]

- Nitrosamines were not detected in the Tank 50 salt solution sample above the instrument detection limits of <1 mg/L.

- The minimum detection limit (<1.07E-01 pCi/mL) is reported for ^{94}Nb as determined from the minimum detectable activity associated with the radiochemical method used for this radionuclide. The reported detection limit is above the requested SRMC target minimum detection limit concentration.[4] However, the minimum detection limit reported for the January 2022 semiannual Tank 50 sample for ^{94}Nb is lower than the estimated detection limit of 4.38E-01 pCi/mL initially established by SRNL in 2009.[5] Thus per guidance from SRMC,[4] SRNL continues to achieve as low as practical detection limits for this radionuclide.

5.0 References

[1] Harrington, S. J., “Waste Acceptance Criteria for Transfers to the Z-Area Saltstone Production Facility During Salt Disposition Integration (SDI) (U)”, Savannah River Remediation, X-SD-Z-00004, Rev. 4, March 2021.

[2] M. Brown., "Routine Saltstone Support for Salt Solution and Grout Analyses ", Savannah River Remediation, X-TTR-Z-00025, Rev. 0, August 2021.

[3] Crawford, C. L., Hill, K. A., "Task Technical and Quality Assurance Plan for Salt Solution Analyses and Grout Sample Preparation and Analyses", Savannah River National Laboratory, SRNL-RP-2021-04610, Rev. 0, December 2021.

[4] Dixon, D. B., "Minimum Detection Limits for Saltstone Quarterly WAC Analyses", Savannah River Remediation, SRR-WSE-2013-00005, Rev. 1, January 2013.

[5] DiPrete, C. C., "Overview of Capability to Measure Radionuclides of Interest for Saltstone", Savannah River National Laboratory, SRNL-L4000-2009-00028, Rev. 0, June 2009.

[6] Crawford, C. L., “Results for the January 2022 Semiannual Tank 50 Salt Solution Sample: Cs-137”, Savannah River National Laboratory, SRNL-L3100-2022-00002, Rev.0, February 2022.

[7] Crawford, C. L. and Hill, K. A., “Task Technical and Quality Assurance Plan for Bimonthly Saltstone Support for Salt Solution Performance Assessment Analyses”, SRNL-RP-2021-04577, Rev. 0, September 2021.

[8] Crawford, C. L., “January 2022 Semiannual Tank 50 WAC Characterization”, B9108-00327-20, SRNL E-Notebook (Production), Savannah River National Laboratory, February 2022.

[9] “Gas Chromatography/Mass Spectrometry for Volatile Organics: Contract Laboratory Program Methods”, Manual L16.1, Procedure ADS-2656, Rev. 9, October 2016.

[10] “Gas Chromatography/Mass Spectrometry for Semivolatile Organics Including Polychlorinated Biphenyls”, Manual L16.1, Procedure ADS-2657, Rev. 7, May 2016.

[11] “Aqua Regia Dissolution of Sludge for Elemental Analysis”; Savannah River National Laboratory, Manual L16.1, Procedure ADS-2226, Rev. 10, July 2013.

[12] “Weight Percent Solids Determination Using a Furnace or Oven”, Savannah River National Laboratory, Manual L29, Procedure ITS-0078, Rev. 1, October 2012.

[13] “Integrated Data Base Report – 1996: U.S. Spent Nuclear Fuel and Radioactive Waste Inventories, Projections, and Characteristics”, Oak Ridge National Laboratory, DOE/RW-0006, Rev. 13, December 1997. https://www.nrc.gov/docs/ML1028/ML102850100.pdf (accessed April 28, 2022).

[14] White, T. L., Brown, L. W., Looney, B. B. and Jones, M. A., “Total Mercury Analysis Comparison Deployment of Analytical Method for the Savannah River Site Liquid Waste System”, Savannah River National Laboratory, SRNL-STI-2019-00056, Rev. 0, July 2019.

[15] Boggess, A. J., Bannochie, C. J., White, T. L., Jones, M. A. and Edwards, T. B., “Methylmercury and Ethylmercury Analytical Performance in SRR Samples Measured by SRNL and Eurofins Frontier Global Sciences”, Savannah River National Laboratory, SRNL-STI-2018-00250, Rev. 0, July 2019.

[16] Boggess, A. J., White, T. L., Jones, M. A., Edwards, T. B. and Harris, S. P., "Development and Comparison of Purgeable Mercury Values in SRR Samples Measured by SRNL and Eurofins FGS", Savannah River National Laboratory, SRNL-STI-2019-00300, Rev. 0, September 2019.

[17] Boggess, A. J., Jones, M. A., White, T. L., "Analysis of Ionic Mercury Species in SRR Samples Measured by SRNL and Eurofins FGS", Savannah River National Laboratory, SRNL-STI-2020-00081, Rev. 0, May 2020.

[18] "Best Handling Practices for Elemental Mercury, Organo-Mercury Compounds, and Inorganic Mercury Compounds", SRNL-TR-2019-00243, Rev. 1, June 2020.

[19] "Technical Reviews", Savannah River Site, Manual E7, Procedure 2.60, Latest Revision.

[20] "Savannah River National Laboratory Technical Report Design Check Guidelines", Westinghouse Savannah River Company, WSRC-IM-2002-00011, Rev. 2, August 2004.

[21] *CRC Handbook of Chemistry and Physics,* 102nd Print Edition, Internet Version 2021; Section 6: Fluid Properties. Edited by Rumble, J. R., CRC Press Taylor and Francis Group, Boca Raton, FL, Internet Version 2021. http://hbcponline.com/faces/contents/ContentsSearch.xhtml (accessed March 28, 2022).

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