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Results for the Fourth Quarter 2013 Tank 50 WAC Slurry Sample

Chemical and Radionuclide Contaminants

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April 2014

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EXECUTIVE SUMMARY

This report details the chemical and radionuclide contaminant results for the characterization of the 2013 Fourth Quarter sampling of Tank 50 for the Saltstone Waste Acceptance Criteria (WAC) in effect at that time.¹ Information from this characterization will be used by DWPF & Saltstone Facility Engineering (DSFE) to support the transfer of low-level aqueous waste from Tank 50 to the Salt Feed Tank in the Saltstone Facility in Z-Area, where the waste will be immobilized. This information is also used to update the Tank 50 Waste Characterization System.

The following conclusions are drawn from the analytical results provided in this report:

- SRR WAC targets or limits were met for all analyzed chemical and radioactive contaminants unless noted in this section.
- ⁵⁹Ni, ⁹⁴Nb, ²⁴⁷Cm, ²⁴⁹Cf, and ²⁵¹Cf are above the requested SRR target concentrations². However, they are below the detection limits established by SRNL³.
- Norpar 13 and Isopar L have higher detection limits⁴ compared with the Saltstone WAC¹. The data provided in this report is based upon the concentrations in the sub-sample, and due to the limited solubility of these materials in aqueous solution, may not represent the concentrations of the analytes in Tank 50.
- The low insoluble solids content increases the measurement uncertainty for insoluble species.

The semivolatile organic analysis (SVOA) method employed in the measurement of Norpar 13 and tributyl phosphate (TBP) has resulted in the erroneous reporting of a variety of small chain alcohols, including 4-methyl-3-hexanol and 5-methyl-3-hexanol, in previous quarterly sample reports^{5,6}. It has now been determined that these alcohols are an artifact of the sample preparation. Further work is being conducted in SRNL to delineate the conditions that produce these alcohols, and these findings will be reported separately.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption (spectroscopy)
AD	Analytical Development
ARP/MCU	Actinide Removal Process/Modular CSSX Unit
CLFL	Composite Lower Flammability Limit
CSSX	Caustic Side Solvent Extraction
CVAA	Cold Vapor Atomic Absorption
DSFE	DWPF & Saltstone Facility Engineering
ETP	Effluent Treatment Project
GC/MS	Gas Chromatograph/Mass Spectrometer
HDPE	High Density Polyethylene
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
L	Liter
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
MRL	Method Reporting Limit
mg	Milligram
mL	Milliliter
NA	Not Applicable
pCi/mL	Picocurie per Milliliter
PHA	Pulse Height Analysis
pK _a	Acid Dissociation Constant
RSD	Relative Standard Deviation
SC	Shielded Cells (Facility)
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
TCLP/UHC	Toxicity Characterization Leaching Procedure/Underlying Hazardous Constituent
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TTR	Technical Task Request
VOA	Volatile Organic Analysis

WAC Waste Acceptance Criteria
WT % Weight Percent

1.0 Introduction

The Saltstone Facility is designed and permitted to treat low-level radioactive and hazardous liquid waste (salt solution) remaining from the processing of radioactive material at the Savannah River Site. Low-level waste (LLW) streams from the Effluent Treatment Project (ETP), H-Canyon, and the decontaminated salt solution product from the Actinide Removal Process/Modular Caustic Side Solvent Extraction (CSSX) Unit (ARP/MCU) process are stored in Tank 50 until the LLW can be transferred to the Saltstone Facility for treatment and disposal. The LLW must meet the specified waste acceptance criteria (WAC) before it is processed into saltstone.¹ The specific chemical and radionuclide contaminants and their respective WAC limits are in the current^a Saltstone WAC.

DWPF Saltstone Facility Engineering (DSFE) requested that the Savannah River National Laboratory (SRNL) perform quarterly analysis on saltstone samples.⁷ The concentrations of chemical and radionuclide contaminants are measured to ensure the saltstone produced during each quarter complies with the current WAC.^{1, 7, 8} This report documents the concentrations of chemical and radionuclide contaminants and discusses those results for the 2013 Fourth Quarter samples collected from Tank 50 on October 29, 2013^b.

2.0 Experimental

2.1 Technical

On October 29, 2013, one 1-L sampler (HTF-50-13-177) and one 200-mL sampler (HTF-50-13-178) were collected from Tank 50 for the Fourth Quarter 2013 (4Q13) WAC analyses and delivered the same day to the SRNL Shielded Cells (SC). The 200 mL sampler is a dip sample taken six inches below the surface and the 1-L sampler was pulled 66 inches from the bottom of the tank with one agitator pump running.

At SRNL, slurry samples (~15 mL each) from HTF-50-13-178 were transferred with glass pipettes to glass vials with Teflon-lined caps. The vials were completely filled to minimize the void space and the volatilization of organics. The aliquots were transferred to the Analytical Development (AD) Organic Analysis Laboratory for semi-volatile and volatile organic analysis (SVOA and VOA, respectively). Two additional 15-mL aliquots were used for SVOA analysis to determine the concentration of Isopar L and Norpar 13, respectively, in the sample.

After the samples for organic analyses were obtained, the slurries in the steel samplers were combined into a 2-L high-density polyethylene (HDPE) bottle. The 200 mL steel sampler was agitated to disperse any solids in the slurry and poured into the 2-L bottle. The transferred slurry was left to settle in the 2-L bottle. Visual inspection of the inside of each sampler indicated there were no visible solids remaining in the samplers, so no clear supernate was returned to either sampler for rinsing. The total weight of the transferred slurry was 1615.66 g.

The 2-L HDPE bottle was agitated to disperse thoroughly the extremely limited suspended solids into the supernate. Aliquots of slurry samples were promptly collected with slurry pipettes to minimize settling effects and placed into HDPE bottles. A 3-mL sample of the slurry was used to determine the density of the slurry using an Anton-Paar DMA 35n portable density meter.

^a This report references the Saltstone WAC revision in effect when the sample is pulled for analysis and/or that which was referenced during initial data reporting. This may or may not be the latest revision when this report receives its final approval signature.

^b Collection of the 4th Quarter sample was delayed by the U. S. Federal Government shutdown and resulting contractor furloughs.

Slurry samples were submitted in triplicate to SRNL laboratories for the following analyses:

- Six-mL aliquots to the AD Ion Chromatography (IC) Laboratory for soluble anion and cation analyses.
- Three-mL aliquots to the AD Organic Analysis Laboratory for measurement of tetraphenylborate and ethylenediaminetetraacetate by high performance liquid chromatography (HPLC).
- Six-mL aliquots to the AD Wet Chemistry Laboratory for Total Inorganic Carbon/ Total Organic Carbon (TIC/TOC) analyses.
- Two sets of 70-mL aliquots to AD Radiochemistry Laboratory for radiochemical separations and analyses.
- Twelve-mL aliquots of filtered supernate were prepared by filtering aliquots of supernate using a 0.45 micron syringe filter. The filtered supernate samples were then submitted to the AD Wet Chemistry Laboratory for TIC/TOC analyses and Total Base analyses.
- Twelve-mL aliquots were sent to the AD Dissolution Laboratory for digestion using an aqua regia method⁹. Visual inspection of the digested sample by the AD Task Supervisor indicated that all the solids had dissolved. Aliquots of dissolved slurries were analyzed using inductively coupled plasma – atomic emission spectroscopy (ICP-AES), inductively coupled plasma – mass spectrometry (ICP-MS), atomic absorption spectroscopy (AA) for As, K, Na, and Se, and cold vapor atomic absorption spectroscopy (CVAA) for Hg.

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 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.

3.0 Results and Discussion

The following tables contain the results for the 4Q13 WAC analyses. Each table provides the analyte of interest, the method used for measuring that analyte, the average concentration of the analyte based on triplicate samples (unless otherwise noted), the standard deviation of the average, and, if applicable, the WAC target or limit for the analyte concentration. Several of the contaminants were either not detected in the slurry samples or detected at values below the method-reporting limit (MRL). For those analytes, the result is preceded by a “<” which indicates the result is an upper limit based on the sensitivity of the method/equipment used to analyze the individual analyte.

Tables 3-1, 3-2, 3-3 and 3-4 are based directly on attachments 8.1, 8.2, 8.3, and 8.4, respectively, of the WAC.¹

Table 3-1. Results for the 4th Quarter 2013 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.1 of the Saltstone WAC, Revision 12

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit (mg/L)</u>
Aluminate (Al(OH) ₄ ⁻)	ICP-ES	1.62E+04 ^e	1.90E+02	4.08E+05
Ammonium (NH ₄ ⁺)	IC	<1.00E+02	NA	2.12E+02
Carbonate (CO ₃ ²⁻)	TIC	1.31E+04 ^a	1.73E+02	1.20E+05
Chloride (Cl)	IC	1.71E+02	1.15E+00	7.95E+03

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit (mg/L)</u>
Fluoride (F ⁻)	IC	<1.00E+02	NA	4.07E+03
Free Hydroxide (OH ⁻)	Total base	3.59E+04 ^a	1.96E+02	1.58E+05
Nitrate (NO ₃ ⁻)	IC	1.43E+05	1.15E+03	4.37E+05
Nitrite (NO ₂ ⁻)	IC	2.27E+04	6.03E+02	2.14E+05
Oxalate (C ₂ O ₄ ²⁻)	IC	4.63E+02	4.04E+00	2.72E+04
Phosphate (PO ₄ ³⁻)	ICP-ES	4.19E+02	5.80E+00	2.94E+04
Sulfate (SO ₄ ²⁻)	IC	5.44E+03	8.72E+01	5.69E+04
Arsenic (As)	AA	<9.11E-02	NA	1.50E+02
Barium (Ba)	ICP-ES	<1.16E+00	NA	6.19E+02
Cadmium (Cd)	ICP-ES	<2.31E+00	NA	3.10E+02
Chromium (Cr)	ICP-ES	3.44E+01	2.14E-01	1.24E+03
Lead (Pb)	ICP-MS	2.26E-01	3.93E-02	6.19E+02
Mercury (Hg)	CVAA	6.30E+01	7.56E-01	3.25E+02
Selenium (Se)	AA	<1.82E-01	NA	4.46E+02
Silver (Ag)	ICP-ES	<2.24E+00	NA	6.19E+02
Aluminum (Al)	ICP-ES	4.60E+03	5.39E+01	1.16E+05
Potassium (K)	AA	1.13E+02	1.05E+00	3.03E+04
Nickel Hydroxide	ICP-ES	<3.13E+01 ^d	NA	1.17E+03
n-Butanol	VOA	<5.00E-01 ^b	NA	7.73E+00
i-Butanol	VOA	<5.00E-01 ^b	NA	7.73E+00
i-Propanol	VOA	<2.50E-01 ^b	NA	1.88E+00
Phenol	SVOA	<1.00E+01 ^b	NA	7.50E+02
Isopar L	SVOA	<2.67E+01 ppm ^{b,c}	NA	1.10E+01 ppm
Total organic carbon	TOC	2.75E+02 ^a	4.62E+00	5.00E+03
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00

a. Measurement performed on filtered supernate samples.

b. Measurement performed on duplicate samples rather than triplicate samples.

c. Result is calculated from the reported concentration of < 33 mg/L and the density of the slurry sample listed in Table 3-8.

d. Result is calculated from the measured Ni concentration assuming all of the Ni is present as the hydroxide compound.

e. Result is calculated from the measured Al concentration assuming all of the Al is present as the hydroxide compound.

Table 3-2. Results for the 4th Quarter 2013 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.2 of the Saltstone WAC, Revision 12

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC TARGET (mg/L)</u>
Boron (B)	ICP-ES	4.20E+01	8.92E-01	7.43E+02
Cobalt (Co)	ICP-MS	<8.28E-02 ^c	NA	7.43E+02
Copper (Cu)	ICP-ES	4.42E+01	2.58E-01	7.43E+02
Iron (Fe)	ICP-ES	1.05E+01	1.53E+00	4.95E+03
Lithium (Li)	ICP-ES	3.42E+01	1.05E+00	7.43E+02
Manganese (Mn)	ICP-ES	2.06E+00	1.20E-01	7.43E+02
Molybdenum (Mo)	ICP-ES	<2.48E+01	NA	7.43E+02
Nickel (Ni)	ICP-ES	<1.98E+01	NA	7.43E+02

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC TARGET (mg/L)</u>
Silicon (Si)	ICP-ES	2.83E+01	5.72E-01	1.07E+04
Strontium (Sr)	ICP-ES	<2.46E+01	NA	7.43E+02
Zinc (Zn)	ICP-ES	7.62E+00	6.82E-02	8.03E+02
Benzene	VOA	<1.50E-01 ^a	NA	3.10E+02
Methanol	VOA	b	NA	1.88E+00
Toluene	VOA	<1.50E-01 ^a	NA	3.10E+02
Dibutylphosphate (DBP)	IC	<2.75E+02	NA	3.47E+02
Tributyl Phosphate (TBP)	SVOA	<7.50E-01 ^a	NA	7.50E+00
EDTA	HPLC	<1.00E+02	NA	3.10E+02
Norpar 13	SVOA	<7.50E-01 ^a	NA	1.00E-01

a. Measurement performed on duplicate samples rather than triplicate samples.

b. Currently, a routine method for detecting this species does not exist in SRNL.

c. Blank is of comparable magnitude, so there may be little or no Co in the sample.

As indicated in Tables 3-1 and 3-2, all of the contaminants are within the WAC limits or targets with the exception of Isopar L and Norpar 13. In October 2010, SRNL reviewed the MRLs for the organic constituents in Tank 50. All of the MRLs are at or below the WAC targets for the organics with the exception of Norpar 13, which has an MRL of 0.75 mg/L, which is above the WAC target.¹ Additionally, the MRL for Isopar L, <26.7 ppm, is above the WAC limit.¹ Isopar L and Norpar 13 have negligible solubility in aqueous solutions, which makes it difficult to obtain reliable sub-samples of the original sample. The values reported in these tables are the concentrations as detected by the gas chromatography – mass spectrometry (GC/MS) but may not necessarily be an accurate representation of the concentrations of these analytes in Tank 50.

Table 3-3. Results for 4th Quarter 2013 Tank 50 Slurry Samples and WAC Limits for Radionuclide Contaminants Listed in Attachment 8.3 of the Saltstone WAC, Revision 12

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>	<u>WAC LIMIT (pCi/mL)</u>
Tritium (³ H)	Tritium counting	5.46E+02	5.11E+01	5.63E+05
Carbon-14 (¹⁴ C)	C-14 Liquid scintillation	5.68E+02 ^a	4.46E+01	1.13E+05
Nickel-63 (⁶³ Ni)	Ni-59/63	<1.20E+01	NA	1.13E+05
Strontium-90 (⁹⁰ Sr)	Sr-90 Liquid scintillation	3.33E+03	2.06E+02	3.15E+06
Technetium-99 (⁹⁹ Tc)	Tc-99 Liquid scintillation	1.65E+04	1.00E+03	NA
Iodine-129 (¹²⁹ I)	I-129 (w/ separation) Liquid scintillation	1.18E+01	7.87E-01	3.80E+02
Cesium-137 (¹³⁷ Cs)	Gamma Scan	1.79E+06	3.38E+04	3.96E+06
Uranium-233 (²³³ U)	ICP-MS	<1.61E+02	NA	1.13E+04
Uranium-235 (²³⁵ U)	ICP-MS	1.90E-01	9.64E-03	1.13E+02
Plutonium-241 (²⁴¹ Pu)	Pu238/241 Liquid scintillation	2.87E+02	3.59E+01	8.38E+05
Total Alpha	Liquid Scintillation Counting (LSC)	<5.27E+02	NA	2.13E+05

a. Measurement derived from duplicate samples rather than triplicate samples.

As shown in Table 3-4, none of the radionuclide contaminants exceeds the targets listed in the latest revision of the WAC. In a memo from Savannah River Remediation (SRR), the requested detection limits for several radionuclides were lowered in order to accommodate future inventory reporting requirements.² The reported detection limits of ⁵⁹Ni and ⁹⁴Nb are above the limits requested by SRR (6.59E+00 and 2.00E-03 pCi/mL, respectively)² but below the quantification limits established by SRNL (2.00E+01 and 4.38E-01 pCi/mL, respectively).³

The radionuclide ^{137m}Ba is the radioactive daughter of 94.6% of the beta decay of ¹³⁷Cs. 5.4% of the ¹³⁷Cs decays to stable ¹³⁷Ba. The half-life of the parent radionuclide, ¹³⁷Cs, is six million times longer than its daughter, ^{137m}Ba, therefore the two radionuclides are in secular equilibrium. Radionuclides in secular equilibrium have the same activity associated with their decay. Thus, the activity of ^{137m}Ba is 94.6% of the activity of the ¹³⁷Cs or 1.69E+06 pCi/mL.

The concentration of ¹³⁵Cs is calculated by assigning all of the mass at 135 to cesium. It is assumed all the mass detected at mass 244 is ²⁴⁴Pu. The Pu alpha Pulse Height Analysis (PHA) method does not resolve the alpha activities of ²³⁹Pu and ²⁴⁰Pu. To determine the maximum concentration of each radionuclide, the total activity is assigned to each radionuclide separately. As shown in Table 3-4, the reported activity is below the WAC target for each radionuclide.

Table 3-4. Results for the 4th Quarter 2013 Tank 50 Slurry Samples and WAC Targets for Radionuclide Contaminants Listed in Attachment 8.4 of the Saltstone WAC, Revision 12

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC TARGET (pCi/mL)
Aluminum-26 (²⁶Al)	Gamma scan (Cs removed)	<1.53E-01	NA	2.88E+03
Cobalt-60 (⁶⁰Co)	Gamma scan (Cs removed)	3.16E-01	4.95E-02	9.747E+02
Potassium-40 (⁴⁰K)	Gamma scan (Cs removed)	<2.69E+00	NA	1.00E+02
Nickel-59 (⁵⁹Ni)	Ni-59/63	<1.08E+01	NA	1.13E+03
Selenium-79 (⁷⁹Se)	Se-79	<1.49E+01	NA	1.90E+04
Yttrium-90 (⁹⁰Y)	Secular Equilibrium w/ Sr-90	3.33E+03	2.06E+02	3.15E+06
Zirconium-93 (⁹³Zr)	ICP-MS	<6.25E+01	NA	1.00E+05
Niobium-94 (⁹⁴Nb)	Gamma scan (Cs removed)	<4.20E-01	NA	1.53E+02
Rhodium-106 (¹⁰⁶Rh)	Secular Equilibrium w/ Ru-106	<4.02E+00	NA	1.13E+06
Ruthenium-106 (¹⁰⁶Ru)	Gamma scan (Cs removed)	<4.02E+00	NA	1.13E+06
Antimony-125 (¹²⁵Sb)	Gamma scan (Cs removed)	1.41E+01	3.75E-01	7.988E+03
Tellurium-125m (^{125m}Te)	Secular Equilibrium w/ Sb-125	1.41E+01	3.75E-01	1.828E+03
Tin-126 (¹²⁶Sn)	Gamma scan (Cs removed)	1.48E+02	3.38E+00	1.80E+04
Cesium-134 (¹³⁴Cs)	Gamma Scan	<1.41E+02	NA	1.82E+04
Cesium-135 (¹³⁵Cs)	ICP-MS	<3.82E+01	NA	1.50E+03
Barium-137m (^{137m}Ba)	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	1.69E+06	3.20E+04	3.75E+06
Cerium-144 (¹⁴⁴Ce)	Gamma scan (Cs removed)	<4.55E+00	NA	1.13E+05
Promethium-147 (¹⁴⁷Pm)	Pm-147/Sm-151 Liquid scintillation	<4.04E+01	NA	5.63E+06
Samarium-151 (¹⁵¹Sm)	Pm-147/Sm-151 Liquid scintillation	<3.68E+01	NA	2.25E+04

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC TARGET (pCi/mL)
Europium-154 (¹⁵⁴Eu)	Gamma scan (Cs removed)	4.18E+00	1.07E-01	1.615E+03
Europium-155 (¹⁵⁵Eu)	Gamma scan (Cs removed)	<2.15E+00	NA	1.13E+04
Radium-226 (²²⁶Ra)	Ra-226	<6.62E+00	NA	1.00E+03
Radium-228 (²²⁸Ra)	Gamma scan (Cs removed)	<1.55E+00	NA	1.00E+04
Actinium-227 (²²⁷Ac)	Th-229/230	<4.32E-02	NA	1.00E+04
Thorium-229 (²²⁹Th)	Th-229/230	<8.74E-02	NA	1.63E+05
Thorium-230 (²³⁰Th)	Th-229/230	<6.85E-02	NA	6.26E+03
Thorium-232 (²³²Th)	ICP-MS	<1.82E-03	NA	2.88E+03
Protactinium-231 (²³¹Pa)	Pa-231	<2.78E+01	NA	1.00E+03
Uranium-232 (²³²U)	U-232	4.38E+00	4.43E-01	9.06E+03
Uranium-234 (²³⁴U)	ICP-MS	<1.04E+02	NA	1.13E+04
Uranium-236 (²³⁶U)	ICP-MS	<1.07E+00	NA	1.13E+04
Uranium-238 (²³⁸U)	ICP-MS	4.03E+00	1.14E-01	1.13E+04
Neptunium-237 (²³⁷Np)	ICP-MS	<1.17E+01	NA	1.00E+04
Plutonium-238 (²³⁸Pu)	Pu238/241 Pu alpha PHA	9.35E+02	4.51E+01	2.13E+05
Plutonium-239 (²³⁹Pu)	Pu238/241 Pu alpha PHA	6.70E+01	5.37E+00	2.13E+05
Plutonium-240 (²⁴⁰Pu)	Pu238/241 Pu alpha PHA	6.70E+01	5.37E+00	2.13E+05
Plutonium-242 (²⁴²Pu)	ICP-MS	<6.33E+01	NA	2.13E+05
Plutonium-244 (²⁴⁴Pu)	ICP-MS	<2.94E-01	NA	7.02E+04
Americium-241 (²⁴¹Am)	Am/Cm	1.16E+01	4.60E-01	2.13E+05
Americium-242m (^{242m}Am)	Am/Cm	<2.41E-02	NA	4.50E+05
Americium-243 (²⁴³Am)	Am/Cm	<3.22E-01	NA	2.13E+05
Curium-242 (²⁴²Cm)	Am/Cm	<1.99E-02	NA	1.13E+04
Curium-244 (²⁴⁴Cm)	Am/Cm	2.72E+01	7.44E+00	2.13E+05
Curium-245 (²⁴⁵Cm)	Am/Cm	<8.11E-01	NA	2.25E+05

Tables 3-5 and 3-6 list the chemical contaminants that affect vault flammability. These chemicals must be monitored to ensure flammable gases do not contribute more than 10% of the Composite Lower Flammability Limit (CLFL).¹ A substituted alcohol, 4-methyl-3-hexanol, was initially thought to have been detected in both replicates of the surface dip sample and measured at levels above the detection limit, 7.85E+00 mg/L, STDEV = 7.07E-02. Subsequent investigation (to be documented fully by SRNL in a future report) using the 1Q14 Tank 50 WAC surface sample (no additional 4Q13 Tank 50 WAC surface sample existed for this work) revealed that this substituted alcohol, as well as a previously reported alcohol, 5-methyl-3-hexanol, were artifacts of the acidification phase of the sample preparation. The SVOA procedure acidifies the tank sample to ensure that phenolate ions are protonated and can be extracted into the methylene chloride organic phase and detected as the phenol by GC/MS. It was found that this acidification process was producing the alcohols, but the exact pH which the sample must reach for these materials to appear is still under investigation. No alcohol actually present in the tank sample would require acidification in order to be extracted into methylene chloride due to the very high proton dissociation constant, or pK_a , of an alcohol, -OH, functional group.

The pK_a is the acid dissociation constant for a molecule. The larger the value, the lower the potential or ease of removing an acidic proton. The only marginally "acidic" proton on an alcohol is the hydrogen on the oxygen. The hydrogen atoms that are covalently bonded to the carbons are not thought of as acidic, though they can be removed by other chemical manipulations. In water, alcohols are not ionized into H^+ and RO^- (where R is an organic chain), hence they are not ionic species. Alcohols gain their solubility in water due to hydrogen bonding between the oxygen and the hydrogen in a water molecule. Long chain alcohols, unlike ethanol, have limited solubility in water. Phenol, a benzene ring with an -OH functional group in place of one hydrogen in benzene has a pK_a of ~10. Hence at pH 10, a simple phenol is 50% ionized into $C_6H_5O^-$ and H^+ . The pK_a of a phenol is lower than that of an alcohol because the pi cloud of the benzene ring withdraws electron density from the oxygen, making the oxygen hydrogen more acidic. In concentrated caustic solution, like a SRS tank sample, phenol is converted to phenolate anions which are water soluble and will not extract into a highly non-polar solvent like methylene chloride. The phenolate anions must be protonated (converted back to the phenol) to be sufficiently non-polar to extract into methylene chloride. At pH 6, 99.99% of the phenolate will be converted to phenol, but there is some indication that the acidification step of the SVOA preparation was going to a much lower (unnecessarily low) pH. The alcohols reported are sufficiently lipophilic that they would extract into the methylene chloride regardless of the pH of the sample, but they don't extract unless the pH is made very low. Neutral pH extractions of the Tank 50 material do not show the alcohols in the GC/MS analysis. This would seem to indicate that these alcohols are not present in the sample, but are being created during the acidification of the sample. SRNL is attempting to determine the starting constituents from which they are forming and will address this in a future report.

To address the uncertainty caused by this situation in future quarterly tank analyses, several modifications to our sampling and analysis methodology have been implemented. First, a second set of surface sample sub-samples will be collected prior to combining the surface and dip samples, or alternatively, the entire dip sample will be reserved for organic analyses; this additional sample material will be held in reserve for later analysis pending the outcome of the first set of samples. Secondly, the cell prepared blank will be pH adjusted (made basic) and processed for analysis in the same manner as the actual tank samples to better detect contaminants introduced to the sample. Finally, the caustic used to adjust the blank pH will be analyzed for contaminants.

Table 3-5. Results for the 4th Quarter 2013 Tank 50 Slurry Samples for Acceptance Criteria Limits for Chemical Contaminants Impacting Vault Flammability, Listed in Table 3 of the Saltstone WAC, Revision 12

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit</u>
Isopar L	SVOA	<2.67E+01 ppm ^{a,b}	NA	1.10E+01 ppm
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00 mg/L
Ammonium (NH ₄ ⁺)	IC	<1.00E+02	NA	2.12E+02 mg/L

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.

Table 3-6. Results for the 4th Quarter 2013 Tank 50 Slurry Samples for Concentrations of "Other Organics" Affecting Vault Flammability, Listed in Table 4 of the Saltstone WAC, Revision 12

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Concentrations</u>
n-Butanol	VOA	<5.00E-01	NA	0.75 mg/L

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Concentrations</u>
Tributylphosphate	SVOA	<7.50E-01	NA	1.0 mg/L
i-Propanol	VOA	<2.50E-01	NA	0.25 mg/L
Methanol	a	NA	NA	0.05 mg/L
Norpar 13	SVOA	<7.50E-01	NA	0.1 mg/L

a. Currently, a routine method for detecting this species does not exist in SRNL.

Isopar L and Norpar 13 are the only species considered in Tables 3-5 or 3-6 with reported values above the WAC limit. It should be noted that the detection limit for Isopar L was expected based on current SRNL capabilities.⁴ The reported detection limit for Norpar is above the WAC limit for both accident analysis (Table 3-2) and vault flammability (Table 3-6), but it is the lowest achievable MRL for this analyte.⁴ As previously discussed, the insolubility of Isopar L and Norpar 13 makes sub-sampling difficult, therefore the reported results are not necessarily representative of the concentration of these analytes in the Tank 50 sample received by SRNL.

Table 3-7 provides results for the processing criteria for transfers into the Saltstone Facility. All of the results contained in Table 3-7 fall within the general processing criteria. The pH was calculated using the free base concentration (OH⁻). The low insoluble solids content makes sub-sampling difficult.

Table 3-7. Results for the 4th Quarter 2013 Tank 50 Slurry Samples for Saltstone Processing Criteria WAC Limits, Listed in Table 5 of the Saltstone WAC, Revision 12

<u>Processing Criterion</u>	<u>Method</u>	<u>Value</u>	<u>Std. Dev.</u>
pH > 10	Calculated	>13	NA
2.5 M < [Na ⁺] < 7.0 M	ICP-ES	5.44 M	0.0963
Total Insoluble Solids <15 wt%	Calculated	~0 wt%	NA

Table 3-8 provides constituents listed in the Technical Task Request (TTR) but not contained in the WAC.

Table 3-8. Requests for Constituents for TCLP/UHC Support as well as from the TTR for the 4th Quarter 2013 Tank 50 Slurry Samples; Results Not Contained in Previous Tables

<u>Constituent</u>	<u>Method</u>	<u>Average Value (mg/L, unless stated otherwise)</u>	<u>Std. Dev.</u>
Antimony (Sb)	ICP-ES	2.68E+01	9.45E-01
Beryllium (Be)	ICP-ES	<1.66E-01	NA
Cyanide (CN)	a	NA	NA
Thallium (Tl)	ICP-MS	<1.12E-01 ^b	NA
Density (slurry)	Measured (18.7°C)	1.2376 g/mL	0.0007
Total Beta	LSC	1.94E+06 pCi/mL	9.79E+04
Total Solids	Measured	28.32 wt%	0.065

a. Currently, a routine method for detecting this species does not exist in SRNL.

b. Blank value was of comparable magnitude indicating that there may be little to no Tl in the sample.

The results from Table 3-8 are used to support the toxicity characterization leaching procedure/underlying hazardous constituents (TCLP/UHC) testing by a certified laboratory.¹⁰ The density of the slurry was measured at 18.7 °C. Natural Tl is composed of two isotopes, ²⁰³Tl and ²⁰⁵Tl with fractional abundances of 0.295 and 0.705, respectively. The concentration of each isotope was divided by its fractional abundance, and the reported concentration of Tl is that determined from averaging the five values determined from two replicates for the mass 203 isotope and the three replicates for the mass 205 isotope.

As has been previously observed and reported for these Tl masses, as well as those for Pb (206 – 208), the blank often gives a signal of the same magnitude.¹¹ In the past when this situation was observed, the samples were analyzed a second time, but the same result was found. The digestion acids were also examined.¹¹ The concentrated nature of these samples, which are diluted to 1:4 during measurement, versus a more typical 1:100 or even 1:400 dilution, is allowing these small values to be above the detection limit of the instrument. In light of the previous observations,¹¹ the value for Tl is given as a detection limit since there is likely little or no Tl in these samples.

The tank corrosion species listed in Table 3-9 were requested by DSFE.¹² Specific gravity was calculated by dividing the measured density of the slurry (given in Table 3-8 at 18.7 °C) by the density of water at the same temperature.¹³

**Table 3-9. Requests from the SFE for Corrosion Species from the 4th Quarter 2013
Tank 50 Slurry Samples (Results Not Contained in Previous Tables)**

<u>Constituent</u>	<u>Method</u>	<u>Average Value</u>	<u>Std. Dev.</u>
Specific Gravity	a	1.2395	0.0007
Total Gamma	b	1.69E+06 pCi/mL	1.85E+04 ^c

- a. Calculated from the measured density of slurry and density of water at 18.7 °C¹³.
 b. Calculated from the sum of measured gamma emitters.
 c. Value is the “standard error of the mean” rather than the standard deviation of the measurements since its calculation involves multiple radionuclides.

The activities calculated for total gamma and ^{137m}Ba are expected to be close for this sample because the total gamma activity is dominated by ^{137m}Ba, the radioactive daughter of ¹³⁷Cs. The total gamma activity was calculated by summing the measured gamma activity of the major gamma emitters: ⁶⁰Co, ¹²⁵Sb, ¹²⁶Sb, ¹²⁶Sn, ^{137m}Ba, ¹⁵⁴Eu, and ²⁴¹Am.

Table 3-10 provides results for additional radionuclides not listed in the WAC but which now require quantification in order to support inventory-reporting requirements.

**Table 3-10. Additional Radionuclides Requested for Inventory Reporting Requirements
or Based on Recommended Concentration for 2009 PA Implementation**

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>
Niobium-93m (^{93m} Nb)	ICP-MS	<6.09E+01	NA
Silver-108m (^{108m} Ag)	Gamma scan (Cs removed)	<6.98E-01	NA
Barium-133 (¹³³ Ba)	Gamma scan (Cs removed)	<1.17E+00	NA

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.
Bismuth-207 (²⁰⁷Bi)	Gamma scan (Cs removed)	<4.36E-01	NA
Thorium-228 (²²⁸Th)	Gamma scan (Cs removed)	<1.59E+01	NA
Curium-247 (²⁴⁷Cm)	Am/Cm	<1.23E+00	NA
Californium-249 (²⁴⁹Cf)	Am/Cm	<1.28E+00	NA
Californium-251 (²⁵¹Cf)	Am/Cm	<9.59E-01	NA

4.0 Conclusions

The following conclusions are drawn from the analytical results provided in this report:

- SRR WAC targets or limits were met for all analyzed chemical and radioactive contaminants unless noted in this section.
- ⁵⁹Ni, ⁹⁴Nb, ²⁴⁷Cm, ²⁴⁹Cf, and ²⁵¹Cf are above the requested SRR target concentrations². However, they are below the detection limits established by SRNL³.
- Norpar 13 and Isopar L have higher detection limits⁴ compared with the Saltstone WAC¹. The data provided in this report is based upon the concentrations in the sub-sample, and due to the limited solubility of these materials in aqueous solution, may not represent the concentrations of the analytes in Tank 50.
- The low insoluble solids content increases the measurement uncertainty for insoluble species.

The semivolatile organic analysis (SVOA) method employed in the measurement of Norpar 13 and tributyl phosphate (TBP) has resulted in the erroneous reporting of a variety of small chain alcohols, including 4-methyl-3-hexanol and 5-methyl-3-hexanol, in previous quarterly sample reports.^{5,6} It has now been determined that these alcohols are an artifact of the sample preparation. Further work is being conducted in SRNL to delineate the conditions that produce these alcohols, and these findings will be reported separately.

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