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Dead-End Filtration and Crystalline Silicotitanate Cesium Ion Exchange with Hanford Tank Waste AW-102

July 2019

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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Executive Summary

The Direct Feed Low-Activity Waste (DFLAW) flowsheet provides for the initial production of immobilized low-activity waste (ILAW) by feeding low-activity waste (LAW) directly from tank farms to the Hanford Tank Waste Treatment and Immobilization Plant (WTP) LAW facility for immobilization. Prior to the transfer of feed to the WTP LAW facility, tank supernatant waste will be pretreated by the Tank Side Cesium Removal (TSCR) system to meet the WTP LAW waste acceptance criteria (<3.18E-5 Ci 137Cs/mole of Na). This pretreatment facility will filter the waste to remove suspended solids and remove cesium from the waste stream through ion exchange.

Bench-scale filtration testing of 7.4 liters of diluted of AW-102 supernate was conducted using dead-end filtration in the hot cells of the Radiochemical Processing Laboratory at Pacific Northwest National Laboratory. A Mott 70-mm disc filter (media grade 5) was used to capture solids. The filter area was adjusted to 2.2 in^2 to match the planned TSCR supernate process volume to surface area ratio. There was no indication of filter fouling and no recoverable solids were observed on the filter.

Ion exchange testing with the filtered, diluted AW-102 supernatant was conducted using crystalline silicotitanate (CST) ion exchange media. The IONSIV R9140-B CST was provided by Honeywell UOP, LLC in 2018 (Lot number 2002009604). The column testing operations were prototypic to the intended Low-Activity Waste Pretreatment System operations in a lead-lag column format, although on a small-scale basis with 10-mL CST beds. The feed was processed downflow through the lead column and then through the lag column at ~1.8 bed volumes per hour (BV/h). After 88.6 BVs of feed processing, the volume in the feed bottle dropped below the inlet tube and the lead column fluid headspace was displaced with air. Feed processing was suspended while a new column was prepared and installed into the lead position. A total of 450 BVs of diluted AW-102 feed were processed through the new lead column; only 4.3% Cs breakthrough was achieved. This volume of feed was insufficient to generate useful Cs loading information without extrapolation. A straight-line extrapolation was used to determine the 50% breakthrough of the lead column and contract limit breakthrough from the lag. The values were found to be 1200 BVs and 930 BVs, respectively. Table ES.1 summarizes the observed column performance and relevant Cs loading characteristics.

Table ES.1. AW-102 Column Performance Summary with CST

		Lead Column		Lag Column	
Loading Range (BVs)	Flowrate (BV/h)	Extrapolated 50% Cs Breakthrough (BVs)	µCi ^{137}Cs Loaded	Contract Limit Breakthrough (BVs)	µCi ^{137}Cs Loaded
0-88	1.82	NA	93,200	NA	5.35
0-451	1.81	1200[(a)]	470,000	930[(b)]	3,740

(a) Based on a straight-line extrapolation from 4.3% to 50% breakthrough on a probability-log plot.
(b) Based on a straight-line extrapolation from 1.08E-3% to 0.176% breakthrough on a probability-log plot.
NA = not applicable

The Cs exchange kinetics and capacity were also examined using batch contact testing. Kinetic testing showed that the Cs reached equilibrium loading onto CST between 46 and 92 h contact time. At the equilibrium Cs concentration of 6.21 µg Cs/mL (4.63E-5 M), the equilibrium Cs loading corresponded to 0.051 mmole Cs per g dry CST.

The AW-102 feed and effluent were characterized. Resource Conservation and Recovery Act (RCRA) element Cr partitioned almost exclusively to the effluent. As, Ba, and Cd were detected in the feed (with concentration errors likely to exceed 15%) but were below the method detection limit (MDL) in the effluent. Pb and Se were below the MDL in both the feed and the effluent; therefore, partitioning could not be assessed. In addition to Cs removal, large fractions of Ca, U, ^{90}Sr, Np, and Pu were also significantly removed by the CST. Cr partitioned almost exclusively to the effluent. Concentrations and recoveries of selected analytes are summarized in Table ES.2; those with low recovery were assumed to be adsorbed onto CST.

Table ES.2. Selected Analyte Recovery in the AW-102 Effluent

	Analyte	Feed Concentration (µg/mL)	Effluent 1 Concentration (µg/mL)	Effluent Composite Concentration (µg/mL)	Effluent 1 Recovery	Effluent Composite Recovery
Selected RCRA metals	Ag	[1.0]	--	--	--	--
	Ba	[0.51]	--	--	--	--
	Cd	[1.9]	--	[1.5]	--	[77%]
	Cr	592	513	554	93%	92%
Other analytes of interest	Ca	[24]	[19]	[9.1]	[83%]	[37%]
	U	[22]	[22]	[20]	[105%]	[89%]
	^{238}U	178.0	17.1	124.5	10%	68%
		µCi/mL	µCi/mL	µCi/mL		
	^{90}Sr	3.44E-01	5.81E-03	8.33E-04	0.28%	0.20%
	^{99}Tc	8.98E-02	7.43E-02	7.51E-02	13.7%	69.1%
	^{237}Np	1.03E-05	1.21E-06	5.50E-06	1.9%	44.1%
	^{238}Pu	8.40E-05	1.69E-05	2.93E-05	3.3%	28.8%
	$^{239+240}$Pu	5.66E-04	1.08E-04	1.81E-04	3.2%	26.4%

Notes:
"--" indicates the value was < MDL and effluent recovery could not be calculated.
Values in brackets [ ] were ≥ MDL but < EQL, with errors likely to exceed 15%.
EQL = estimated quantitation limit.

This report describes the filtration along with the Cs ion exchange batch contact and column test results with the AW-102 tank waste.

Acknowledgments

The authors gratefully acknowledge the Shielded Facilities Operations staff Jarrod Turner and Michael Rojas for in-cell sample handling and systems manipulations. We thank the Analytical Support Operation (ASO) count room staff Truc Trang-Le and Mike Cantaloub for rapid ^{137}Cs analysis for the column load and batch contact sample analyses. We thank the ASO staff Karl Pool, Lori Darnell, Jenn Carter, Denis Cherkasov, Sam Morrison, Chuck Soderquist, and Deborah Coffey for the sample analysis processing and reporting. We thank Renee Russell for reviewing the ion exchange calculation files, test data packages, and this technical report. We also thank Matt Wilburn for technical editing of this report.

Acronyms and Abbreviations

AEA	alpha energy analysis
ASO	Analytical Support Operation
BET	Brunauer-Emmett-Teller
BV	bed volume
CST	crystalline silicotitanate
CWF	clean water flux
DEF	dead-end filtration
DF	decontamination factor
DFLAW	Direct Feed Low-Activity Waste
DI	deionized (water)
EQL	estimated quantitation limit
FD	feed displacement
GEA	gamma energy analysis
ID	identification (number) or internal diameter, see context
ICP-MS	inductively coupled plasma mass spectrometry ICP-OES inductively coupled plasma optical emission spectroscopy
ILAW	immobilized low-activity waste
IC	ion chromatography
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
MDL	method detection limit
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
PTFE	polytetrafluoroethylene
QA	quality assurance
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
TIC	total inorganic carbon
TOC	total organic carbon
TSCR	Tank Side Cesium Removal
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The U.S. Department of Energy (DOE) Hanford Site contains over 55 million gallons of radioactive waste, generated as a by-product of plutonium production and reprocessing operations. The waste, now in underground storage tanks at the Hanford Site, will be pretreated by the Tank Side Cesium Removal (TSCR) system to filter the waste to remove suspended solids and remove cesium from the waste stream through ion exchange. The waste in its final form is to be vitrified in borosilicate glass for permanent storage. The Low-Activity Waste Pretreatment System (LAWPS) provides for the initial production of immobilized low-activity waste (ILAW) by feeding low-activity waste (LAW) directly from tank farms to the Hanford Tank Waste Treatment and Immobilization Plant (WTP) LAW facility for immobilization. Prior to the transfer of feed to the WTP LAW facility, tank supernatant waste will be pretreated by the TSCR system to meet the WTP LAW waste acceptance criteria (<3.18E-5 Ci ^{137}Cs/mole of Na).

At the time of this testing, the TSCR facility was planned to pretreat Hanford tank waste supernate by filtering solids in a dead-end filter apparatus and processing through two ion exchange columns to remove cesium (Cs). Hanford tank AW-102 is within the feed sequence for TSCR (albeit after evaporation and subsequent dilution) and was chosen to be sampled to gain filtration and ion exchange process knowledge.

Dead-end filtration and ion exchange tests were conducted at the small-scale test platform level using approximately 5.8 liters of decanted AW-102 tank waste supernate. The as-received tank waste was diluted from 6.3 M Na to 5.8 M Na to better compare to previously reported data with AP-107 at 5.6 M Na (Geeting et al. 2018; Rovira et al. 2018). The purpose of filtration testing was to demonstrate dead-end filtration of AW-102 using a grade 5 Mott filter. The grade 5 filter has the same pore size planned for TSCR processing and has an available surface area that was adjusted to match the planned TSCR process volume to surface area ratio. Any recoverable solids were to be characterized and compared to previously collected AP-105 and AP-107 tank waste solids. The filtrate provided feed to the ion exchange system.

The ion exchange ^{137}Cs removal flowsheet includes the use of crystalline silicotitanate (CST), manufactured in a spherical (engineered) form by Honeywell UOP LLC (UOP; Des Plaines, IL). Previous column testing with 5.6 M Na simulant at 12% and full TSCR bed heights indicated 27-cm-tall column testing can reasonably predict full-height column test results. The efficacy of the 6-cm-tall CST beds to predict full-height column performance has not been established. The use of the small (10-mL CST bed volume [BV]) bench-scale columns helps reduce costs and is necessary for actual waste processing due to sample volume limitations. Batch contact and dual small-column testing on CST was conducted using the 5.8 M Na AW-102 filtered supernate using 10-mL CST columns in a lead/lag format.

The objectives of this work were to:

1. Dilute the AW-102 waste to nominally 5.6 M Na.
2. Filter the AW-102 diluted waste in a dead-end filtration apparatus representative of the planned TSCR filtration pore size and process volume to surface area ratio.
3. Conduct ion exchange processing of the filtered AW-102 diluted waste to establish Cs breakthrough performance.
4. Measure the fractionation of Pu, Np, Fe, Ca, Ba, K, Zn, ^{99}Tc, and ^{90}Sr as a result of processing the filtered AW-102 diluted waste through the CST.
5. Compare the filtration and ion exchange performances of the diluted AW-102 tank waste to those of the AP-107 tank waste.

6. Conduct batch contact testing of the filtered AW-102 diluted waste to establish Cs load capacity and kinetic load behavior.
7. Provide loaded CST from the AW-102 diluted waste column processing for characterization and crucible vitrification.

2.0 Quality Assurance

The work described in this report was conducted with funding from Washington River Protection Solutions (WRPS) contract 36437/273, *Radioactive Waste Test Platform (child of 68326)*. This contract was managed under Pacific Northwest National Laboratory (PNNL) Project 73312. All research and development (R&D) work at PNNL is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the PNNL's WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2008), and NQA-1a-2009, *Addenda to ASME NQA-1-2008* (ASME 2009). These are implemented through the *WWFTP Quality Assurance Plan* (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research" and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, Scientific Investigation for Applied Research. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

3.0 Experimental

This section describes the AW-102 tank waste sample, sample dilution, dead-end filtration (DEF) filtration, and Cs ion exchange through batch contact testing and column testing.

3.1 As-Received AW-102 Tank Waste

Twenty 250-mL (~5-L total) samples of AW-102 tank waste supernatant were sampled on October 24, 2018, ~135 in. below the tank surface level. The AW-102 tank waste samples were delivered directly to PNNL's Radiochemical Processing Laboratory Shielded Analytical Laboratory. The first and last samples (2AW-18-04 and 2AW-18-23) were subsampled and measured for density, ^{137}Cs, Al, Na, and K concentrations to assess homogeneity for the entire sample set (see Table 3.1). Cesium was isolated from aliquots with the aid of spherical resorcinol formaldehyde resin; the Cs eluates were submitted for Cs isotopic analysis. Because the results agreed within 4% relative percent difference (RPD), the sample suite was assumed to be homogenous.

Table 3.1. As-Received AW-102 Tank Waste Analysis

Analyte	Units	Method	2AW-18-04	2AW-18-23	RPD
Density	g/mL	Gravimetric[(a)]	1.290	1.288	0.16
Al	M	ICP-OES	0.557	0.561	0.59
Cr	M	ICP-OES	0.0124	0.0126	1.7
K	M	ICP-OES	0.177	0.182	3.0
Na	M	ICP-OES	6.36	6.32	0.58
^{137}Cs	µCi/mL	GEA	125	130	3.5
^{133}Cs	µg/mL	ICP-MS	5.85	5.84	0.22
^{133}Cs	Wt%	ICP-MS	63.4	63.5	0.16
^{135}Cs	Wt%	ICP-MS	17.1	17.1	0.00
^{137}Cs	Wt%	ICP-MS	19.4	19.5	0.51

(a) The densities were measured using 10-mL A grade volumetric flasks and an analytical balance.
ICP-MS = inductively coupled plasma mass spectrometry
ICP-OES = inductively coupled plasma optical emission spectrometry
GEA = gamma energy analysis

3.2 Sample Handling and Dilution

Dilution of the feed material received from Tank AW-102 was based on the average measured Na concentration (6.34 M) and density (1.289 g/mL) and the target end point Na concentration (5.6 M) and density (1.266 g/mL). Dilution was performed using 0.01 M NaOH. The contents of two AW-102 sample jars were combined and diluted with 0.01 M NaOH at a volume ratio of nominally 500:65 to achieve a dilution factor of 1.13. Actual AW-102 and 0.01 M NaOH combinations were determined and controlled by mass and density corrected to establish process volumes.

The diluted AW-102 samples were checked for density to assess the dilution. The densities were measured using 10-mL A grade volumetric flasks and an analytical balance and ranged from 1.271 to 1.281 g/mL at an ambient cell temperature of 22.5 °C. The Na concentration was not measured after dilution but was measured after filtration (which would not affect Na concentration). Table 3.2 shows the filtered and diluted AW-102 (ion exchange feed) analysis. The final Na concentration of the diluted AW-102 was 5.8 M. Both the density and Na molarity slightly exceeded the targeted values but were considered close enough to proceed with testing.

Table 3.2. ASR 0731 for Filtered and Diluted AW-102 Tank Waste

Analysis Method	Analyte	Ion Exchange Feed (M)
ICP-OES	Al	4.93E-01
	Ba	3.71E-06
	Ca	5.99E-04
	Cr	1.14E-02
	Fe	1.52E-04
	K	1.53E-01
	Na	5.83E+00
	P	2.89E-02
	Ti	1.32E-05
	Zn	3.38E-04
Hot Persulfate Oxidation	TOC	1.92E-01
	TIC	5.87E-01
ICP-MS	Cs-133	3.69E-05
	U	7.48E-04
IC-Anions	NO_2^-	1.16E+00
	SO_4^{2-}	2.51E-02
	$C_2O_4^{2-}$	3.57E-03
	NO_3^-	2.21E+00
	PO_4^{3-}	2.30E-02

3.3 Dead-End Filtration Testing

The test filter for dead-end filtration (DEF) was a Mott Corp. (Farmington, CT) 70-mm-diameter disc test filter, which is a commercial off-the-shelf dead-end filter selected for feasibility studies at the laboratory bench scale. Figure 3.1 shows the configuration of the disc filter. The disc filter is a barrier type filter with an available filter area of approximately 4.4 in^2. This area was adjusted to 2.2 in^2 by blinding[1] in order to match the planned TSCR supernate process volume to surface area ratio. The Mott filter media is 316L stainless steel porous metal with a 5-µm media grade pore size. The Mott filter is fitted into a filter housing also provided by the Mott Corp.

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[1] Clear coat nail polish was recommended by the manufacturer to blind over surface pores. After the coat was applied, the filter was soaked in 5.6 M Na simulant for 4 hours to verify high caustic would not dissolve the coat.

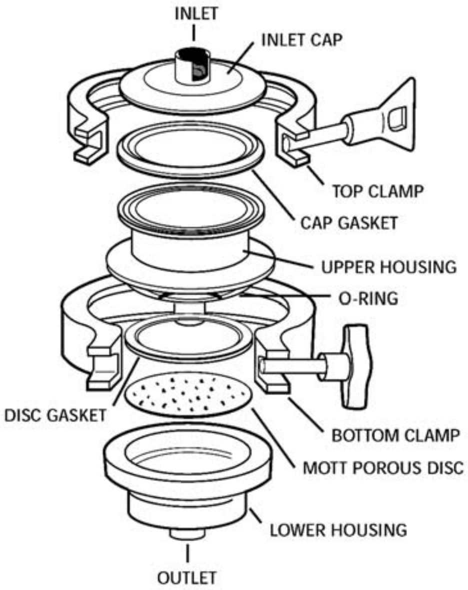

Figure 3.1. Mott 70-mm Disc Test Filter Assembly from https://mottcorp.com

Figure 3.2 shows a schematic of the DEF test apparatus. The components above the filter assembly was constructed in house. The dilute slurry feed was introduced to the filter assembly through the feed reservoir. Compressed air may be supplied to the top of the reservoir to push the feed through the test filter, or if the filter has high permeability, filtrate may pass through the filter due to pressure from its own weight (ρgh). Filtrate passes through the filter and the transmembrane pressure (TMP) and filtrate mass are measured as a function of time.

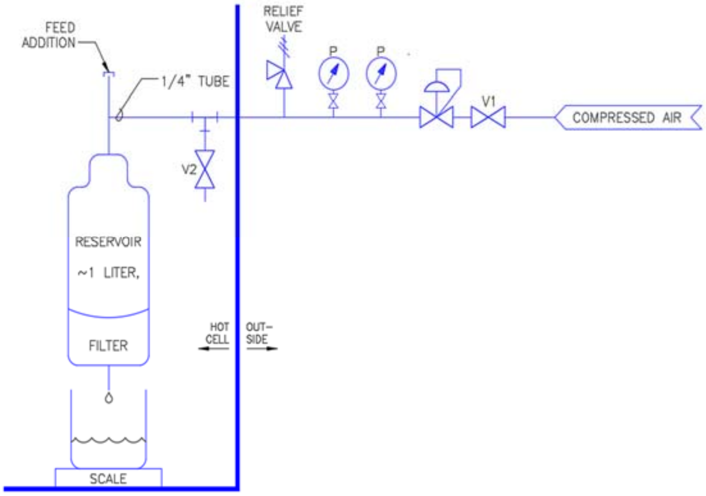

Figure 3.2. Schematic of Dead-End Filtration Test Apparatus

The evolutions used to test the AW-102 diluted tank waste in the DEF are outlined below:

1. Performed CWF (clean water flux) test gravity filtered
2. Added AW-102 in 10 batches and gravity filtered for 25-30 minutes then pressurized to ~1.5 psig until fluid volume passed through the filter; pressurization of the DEF apparatus concluded prior to all feed being passed through the filter to ensure the filter never went dry between evolutions
3. Removed filter and visually inspected filter for solids collection, air dried the filter and weighed.
4. Rinsed DEF system.

Table 3.3 provides a mass balance for DEF testing. A total of 8941.9 g of material was added to the DEF. A total of 8932.1 g was accounted. That left 9.8 g of material unaccounted; this is material that either evaporated or remained wetted inside of the DEF.

Table 3.3. Mass Balance-DEF

Evolution	Description	IN (g)	OUT (g)	
		Fed to DEF	Filtrate Collected	Solids Recovered
1	Clean Water Flux	741.5	727.2	--
2	Filtration of AW-102 (Batch 1)	733.1	720.7	--
3	Filtration of AW-102 (Batch 2)	725.3	722.1	--
4	Filtration of AW-102 (Batch 3)	728.7	702.8	--
5	Filtration of AW-102 (Batch 4)	732.2	751.1	--
6	Filtration of AW-102 (Batch 5)	739.5	736.9	--
7	Filtration of AW-102 (Batch 6)	744.9	749.5	--
8	Filtration of AW-102 (Batch 7)	737.6	746.1	--
9	Filtration of AW-102 (Batch 8)	754.5	769.1	--
10	Filtration of AW-102 (Batch 9)	765.4	737.7	--
11	Filtration of AW-102 (Batch 10)	741.4	774.0	--
12	Wet Solids Recovered from Filter			0
13	System Rinse	797.8	794.9	
	Totals	8941.9	8932.1	0

3.4 CST Media

The CST material utilized was IONSIV™ R9140-B[1], Lot number 2002009604, obtained from UOP LLC, Des Plaines, IL. The material was procured by WRPS in eleven 5-gallon buckets (149 kg). The UOP particle size specification of this material was 18 x 50 mesh and was provided in the sodium form. The media was delivered in a series of 5-gallon buckets. One 5-gallon sample was subdivided using a riffle type splitter as described in Fiskum et al. 2019. Properties of the full particle size distribution (PSD) and <25 mesh sieve cut CST media have been previously reported (Fiskum et al. 2019) and are reproduced in Table 3.4.

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[1] R9140-B is provided in the sodium form by the vendor.

Table 3.4. Physical Properties of Pretreated R9140-B, Lot 2002009604 CST

	Full PSD		<25 mesh	
Parameter	Sample 1	Sample 2	Sample 1	Sample 2
Bulk dry density, g/mL	1.02	1.01	1.03	1.01
Wet bed density, g/mL	1.00	1.00	1.01	1.01
Settled bed void fraction, %	68.5	66.7	64.7	67.7
Particle density, g/mL	3.32	3.34	4.13	3.41

The CST surface area was measured to complement the previously reported CST physical properties (Fiskum et al. 2019). The CST was pretreated by first rinsing with 0.1 M NaOH to float off fines. A quick rinse with deionized (DI) water was conducted to remove the bulk interstitial NaOH, the water was removed, and the CST was allowed to air dry. This pretreatment process was repeated on a <25 mesh sieved fraction of CST. The air-dried CST was prepared for surface area analysis by degassing at 105 °C under vacuum for ~24 h using a Quantachrome FloVac Degasser (Quantachrome Instruments, Boynton Beach, FL). The multi-point nitrogen Brunauer, Emmett, and Teller (BET) surface area of duplicate aliquots of each CST sieve cut was measured using a QuadraSorb SI surface area analyzer. Results of the surface area analysis are shown in Table 3.5.

Table 3.5. Nitrogen BET Surface Area Analysis of Pretreated R9140-B, Lot 2002009604 CST

	Full PSD		<25 mesh	
Parameter	Sample 1	Sample 2	Sample 1	Sample 2
Surface area, m^2/g	102	105	109	106

The uncertainty of the measurements was expected to be around 5%. The difference between the average full-size PSD CST and the average <25 mesh CST surface areas was small (4 m^2/g) and was within the overall uncertainty of the measurement. Huckman and Latheef (1999) showed no relationship between particle size and surface area, which is consistent with porous media. The measured surface areas in CST Lot 2002009604 were nearly twice as high as those previously reported for CST. Bostick and Steele (1999) reported 33 ± 2 m^2/g (sample preparation at 60 °C for several days), Wester et al. (2003) reported 66.2 m^2/g (sample preparation 8 hours at 90 °C), and Latheef (1999) reported 21.1 to 41.4 m^2/g (sample preparation conditions were not reported). The reason for the increased surface area reported herein relative to previously reported results is not understood at this time. It is possible there are differences in UOP's manufacturing processes and likely that the different sample preparation methods used for the degassing of the materials prior to analysis are important factors; incomplete degassing could result in lower surface area values. Optimization of sample preparation conditions prior to BET surface area determinations may in part resolve these observed differences.

3.4.1 CST Pretreatment

The initial CST preparations were performed by aliquoting 50 mL of the CST and passing it through a 25-mesh (ASTM E11 specification) sieve to remove >710-µm diameter particles. Removal of large particles was necessary to accommodate the small column diameter (1.43 cm inside diameter) and mitigate wall effects for fluid transfer through the column, which in turn leads to channeling. The sieved CST was then soaked in ~150 mL of 0.1 M NaOH with gentle agitation. The supernatant was decanted, and fresh 0.1 M NaOH was added to remove CST colloidal fines. This cycle was repeated four times. A 10-mL aliquot of the wetted CST (colloidal fines removed) was set aside for batch contact testing. Two 10-mL wet settled CST volumes were measured in graduated cylinders and quantitatively transferred into the ion exchange columns using additional 0.1 M NaOH to aid the transfer.

3.4.2 CST F-factor

The F-factor is the ratio of the dry mass of exchanger to the initial mass of the exchanger and was determined at the same time the batch contact samples and column media fractions were weighed. The F-factor was obtained by drying approximately 0.5 g CST, under vacuum, at 100 °C to constant mass (<1% difference in 4 h). The CST subsamples that were dried to 100 °C were further dried at 200 °C; an additional 5.5% mass loss was obtained as shown in Figure 3.3, where CST mass (% of starting mass) is plotted as a function of time for both tested temperatures (100 °C and 200 °C). The extra mass loss associated around 200 C is likely water associated with the decomposition of the Zr(OH)4 binder to ZrO2 and two waters. For all the experiments described below, the mass corrected to dry weight at 100 °C is used in the calculations.

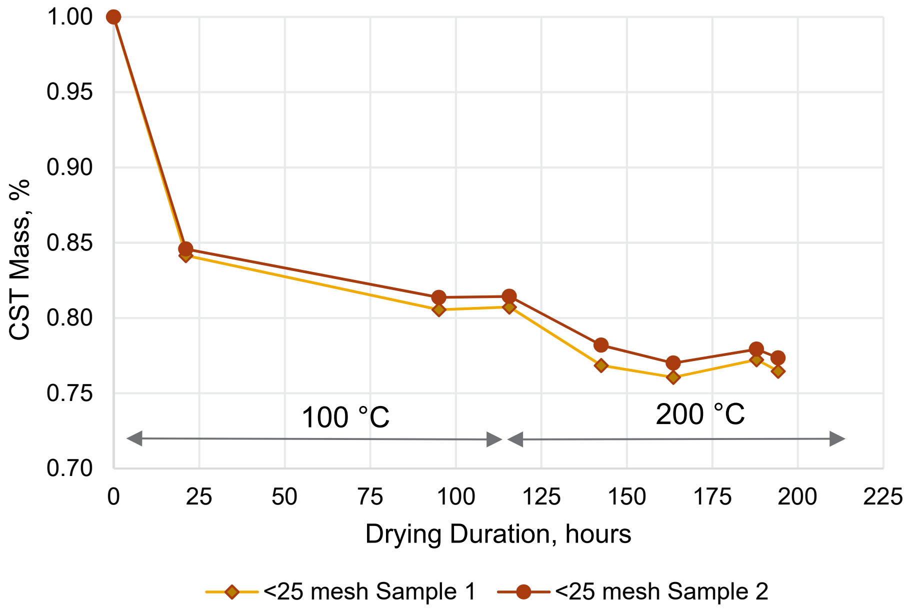

Figure 3.3. CST Mass Loss Profiles to Determine F-factors

3.5 Batch Contact Testing

Batch contact testing was conducted to assess Cs loading kinetics and capacity for the AW-102 diluted tank waste. The batch contact processing activities were conducted according to a test instruction (internally prepared and reviewed).[1]

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[1] Fiskum SK. TI-TCT-010, *Batch Contact Testing with Crystalline Silicotitanate and AW-102 Tank Waste*. Pacific Northwest National Laboratory, Richland Washington. Issued January 2019. This document is internal to PNNL and is not publicly available.

3.5.1 Cs Kinetic Load Behavior

To assess Cs kinetic load behavior, batch contacts were performed using AW-102 diluted tank waste in duplicate. A ~50-mL aliquot of AW-102 diluted tank waste was spiked with 1.05 M $CsNO_3$ to obtain a concentration of ~40 µg/mL Cs; actual $CsNO_3$ and AW-102 diluted tank waste masses transferred were determined by mass and density corrected to establish volumes and exact concentrations (see Table 3.6). The spiked solutions were sampled to establish the initial ^{137}Cs concentrations.

Table 3.6. Batch Contact Kinetic Test Matrix

Solution	Initial [Cs], µg/mL	Initial AW-102 Volume, mL	Dry CST Mass, g
Sample, K1	40.0	47.55	0.2214
Duplicate, K2	37.3	51.60	0.2246

Nominal 0.27-g aliquots of pretreated and air-dried CST were weighed into 60-mL polyethylene bottles (0.275 g air-dried CST corresponded to 0.223 g dry mass basis at 100 °C; actual F-factor corrected CST masses are shown in Table 3.6). The spiked AW-102 diluted tank waste was added to the bottles containing CST and the contact time clock was immediately started. The samples were placed upright on an orbital shaker table and set to mix at ~400 rpm. Small samples (~0.6 mL) were collected after contacting for nominally 0.5, 2.0, 6, 23, 47, and 92, and 165 h; a brief CST settling period was incorporated with each sampling time. After sampling, the main batch contact solutions were placed back on the orbital shaker table. The batch contact solutions were maintained at ambient temperatures, ranging from 20 to 22 °C. Each ~0.6-mL sample was transferred directly to a syringe fitted with a syringe filter, 45-µm pore size, 25-mm diameter (Puradisc^{TM} 25NYL, Whatman). The sample was passed through the filter and the filtrate was collected for analysis. Duplicate aliquots were collected from K1 sample at the 2-h contact time; duplicate aliquots were collected from the K2 sample at the 6-h contact time. After all sampling was complete, the final batch contact solution volumes were 42.43 mL (K1) and 46.81 mL (K2). Thus, the batch contact solution volume to dry CST mass phase ratio ranged from 230 to 192 over the course of the test.

3.5.2 Cs Load Capacity

To assess Cs load capacity, batch contacts were performed using diluted, filtered AW-102 tank waste (hereafter termed AW-102) at four different Cs concentrations in duplicate. Aliquots of the AW-102 subsamples were tested without spiking; additional aliquots were spiked with 1.05 M $CsNO_3$ to obtain stock AW-102 solutions nominally 40 mg/L, 240 mg/L, and 1500 mg/L. To this end, spiked stock solutions were prepared by first adding $CsNO_3$ solution to centrifuge tubes. Aliquots of AW-102 were transferred by pouring to a 33-mL mark in centrifuge tubes; the actual volumes transferred were determined by mass difference and solution density. The initial Cs concentrations in the AW-102 stock contact solutions are given in Table 3.7.

Table 3.7. Batch Contact Capacity Test Matrix

Solution	Initial [Cs], µg/mL
Un-spiked	6.21
Cs spike 1	39.4
Cs spike 2	242
Cs spike 3	1520

The batch contact tests targeted a phase ratio of approximately 200 mL/g (liquid volume to exchanger mass). Nominal 0.088-g aliquots of pretreated and air-dried CST were placed into glass liquid scintillation counting vials (0.088 g air-dried CST corresponded to 0.073 g dry mass basis at 100 °C). A 15-mL aliquot of a stock solution was added to a sample vial. Each Cs concentration solution was tested in duplicate.

Samples were agitated in an orbital shaker for 93 to 97 h, as confirmed from kinetic testing to reach equilibrium conditions. The temperature was not controlled but was generally constant at 26 ± 1°C during the 4 days of contact. Process temperature was assessed from a sentinel consisting of 15 mL water in a glass vial placed in the shaker assembly alongside the samples. An aliquot of each sample was transferred directly to a syringe fitted with a syringe filter, 45 μm pore size, 25 mm diameter (Puradisc$^{\text{TM}}$ 25NYL, Whatman). The sample was passed through the filter and the filtrate was collected for analysis and removed from the hot cell.

3.5.3 Sample Analysis

All batch-distribution measurements were determined by measuring ^{137}Cs on both the stock solution (initial concentration) and the contacted solution (final concentration). Each sample was measured by gamma energy analysis (GEA). The samples were counted as long as needed to achieve a ≤1% count uncertainty. The ^{137}Cs concentration in solution directly correlated to the total Cs concentration. Thus, the distribution coefficient (K_d, mL/g) was directly assessed from the ^{137}Cs concentration. All fluid transfers were tracked by mass; thus, the overall uncertainty in the K_d measurements was estimated to be about ±2%.

The batch distribution coefficient, K_d (with units of mL/g), was determined using the following relationship:

$$K_d=\frac{(C_0-C_1)}{C_1}*\frac{V}{M*F} \tag{3.1}$$

where:

C_0 = initial ^{137}Cs concentration
C_1 = final ^{137}Cs concentration
V = volume of the liquid sample (mL)
M = mass of the ion exchanger (g)
F = dried ion exchanger mass divided by the initial ion exchanger mass.

The Cs λ value (column distribution ratio) is a function of the feed condition batch distribution coefficient and the dry bed density and is obtained as shown in Eq. (3.2).

$$\lambda=K_d*\rho \tag{3.2}$$

3.6 Ion Exchange Column Testing

A schematic of the ion exchange system is shown in Figure 3.4. The system consisted of two small 1.44-cm-inside diameter by 20-cm-high columns containing 10 mL CST media, a small metering pump, three valves mounted on a manifold, a pressure gauge, and a pressure relief valve. Valves 1, 2, and 3 were three-way valves that could be turned to the flow position, sample position, or no-flow position. Valve 1 was placed at the outlet of the pump and was used to eliminate air from the system lines, purge the initial volume of the system, or isolate the columns from the pump. Valves 2 and 3 were primarily used for obtaining samples and could also be used to isolate the columns from the rest of the system.

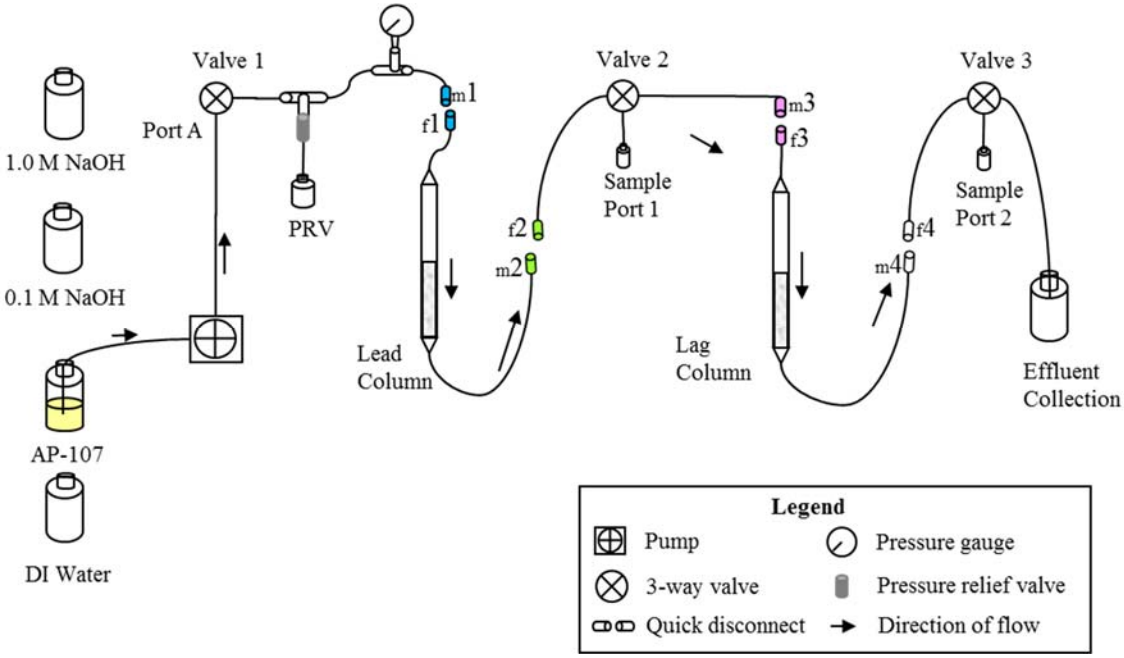

Figure 3.4. Cesium Ion Exchange Column System

The columns were prepared by Spectrum Chromatography (Houston, TX), part number 125009. The column assembly included the column plus the top and bottom end fittings. Column fittings were composed of polytetrafluoroethylene (PTFE) and Teflon endplates and ferrule fittings for 1/8 in. outside diameter tubing. A stainless steel, 200-mesh screen supported the CST bed. A decal millimeter scale affixed to the column allowed for measurement of CST bed height. The connecting tubing was 1/8-in. outside diameter, 1/16-in. inside diameter polyethylene. Valved quick-disconnects were installed in-line to allow for column switching. An FMI QVG50 pump (Fluid Metering, Inc.) equipped with a ceramic low-flow piston pump head was used for all fluid introduction. The pump head was set to a given low stroke length. The flow rate was controlled with a remotely operated FMI stroke-rate controller. The pump was calibrated with the stroke-rate controller and could provide pumping rates from 0.28 to 0.72 mL/min. The volume pumped was determined using the mass of the collected fluid and the fluid density. The total holdup volume of the Cs ion exchange system was the summed volume of all fluid-filled parts and was estimated to be 37 mL.

As a reminder, the BV corresponded to the initial settled CST media BV was measured in a graduated cylinder prior to transferring the media into the ion exchange column. The reference CST BVs were 10.0 mL for both the lead and lag columns. A photograph of the AW-102 in-cell system after processing concluded is shown in Figure 3.5.

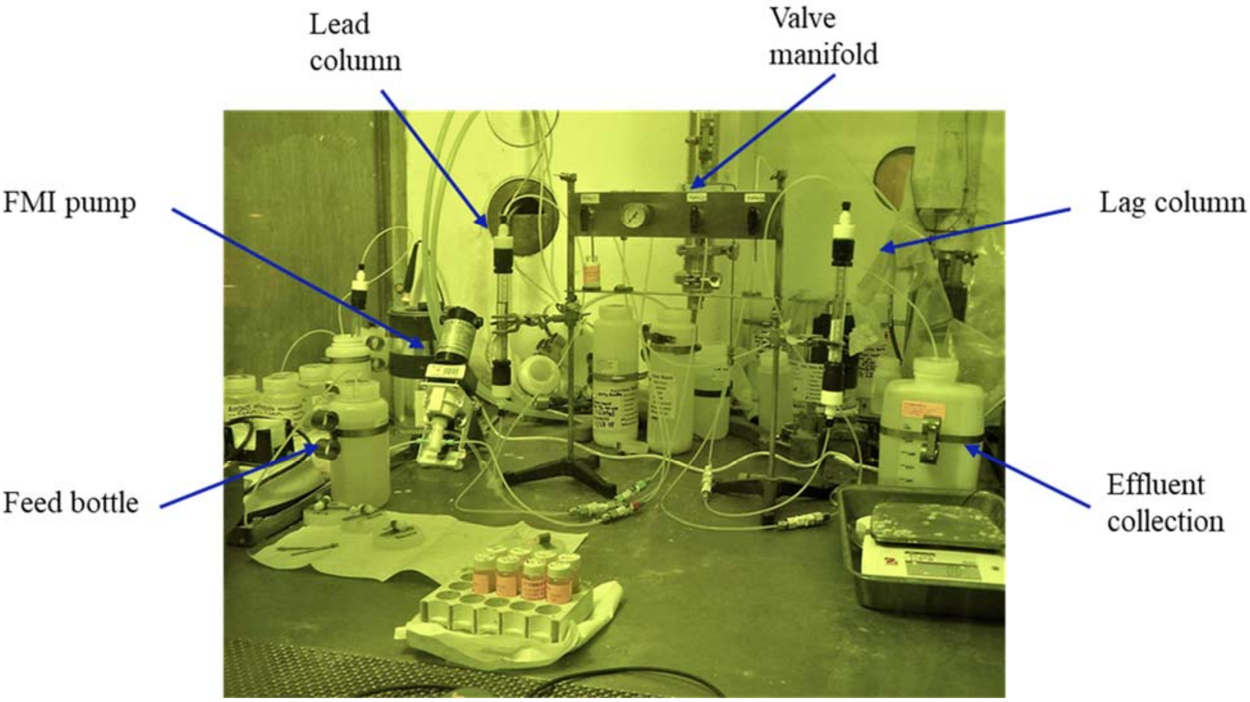

Figure 3.5. Column Assembly in the Hot Cell

Processing was performed downflow from lead to lag at ambient cell temperature (21 to 23 °C). Specific processing details are provided in Table 3.8. Samples were collected in nominal 25-BV increments during the feed processing to evaluate Cs breakthrough behavior. Effluents were collected in ~1- to 1.5-L increments and removed from the hot cell.

Table 3.8. System Flow Description Summary

Step	Feed Material	Volume, BV	Flowrate, BV/h	Dates	Duration, h
Caustic Rinse	0.1 M NaOH	As needed	Established pump calibration	1/22	
Column A/B Feed processing	AW-102	88.6	1.82	1/28-1/30	48
Column C/B Feed processing	AW-102	450.3	1.81	2/4-2/8 2/19-2/25	98 154
Feed displacement (FD)	0.1 M NaOH	6.1	3.17	2/26	2
Water rinse (fdi)	Deionized water	12.8	4.31	2/26	3

BV = bed volume, ~10 mL

On January 30, after processing ~88 BVs of feed, the AW-102 volume in the feed bottle dropped below the inlet tube and the lead column fluid headspace was displaced with air. This necessitated the replacement of the lead column (column A); feed processing was suspended for 120 h while a new column was prepared and installed on 2/4/19. The lag column (column B) remained stagnant with feed during this interval. The test was restarted with a new lead column (column C) and processing re-started on 2/4/19. The AW-102 feed ceased flowing again after processing 170 BVs (on 2/8/19). The system pump head had failed. During the pump head replacement, the manipulator broke. Due to these factors, compounded with imminent adverse weather conditions, the system was placed in standby and the lead and lag columns remained in static contact with the AW-102 for 11 days. The pump and head were replaced, and the manipulator was repaired on 2/19/19, and then the AW-102 feed processing resumed until the conclusion of testing at 450 BVs processed (on 2/25/19).

Figure 3.6 shows flowrate vs time data points collected during the duration of testing. The gaps in data reflect the cease flow conditions. From 2/4/19 to 2/8/19 the flowrate is seen decreasing over time. The declining flowrate was indicative of a pump head problem and salt buildup was observed at the inlet port to the pump head, indicating a slow leak and likely abrasion of the piston in the pump head from the salts. The flowrate jumped slightly above the target flowrate of 1.9 BV/h when the stroke rate was increased. It was eventually decided to replace the pump and head altogether. On 2/20/19, flow was resumed; the initial flowrates were low while the pump control setting was readjusted to the new pump and pump head.

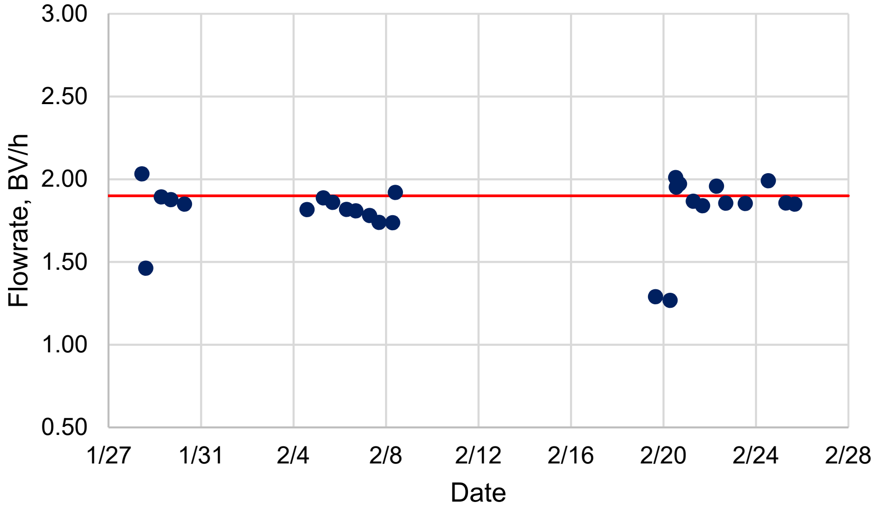

Figure 3.6. Flowrate vs. Time for AW-102 Ion Exchange Processing

3.7 Sample Analysis

A composite feed sample was prepared by sampling 2 mL from each DEF filtered sample bottle into one plastic vial. Duplicate effluent composite samples were generated by collecting a pro-rated volume from each effluent bottle and combining in plastic vials.

Table 3.9 summarizes the sample collections and analyses from the testing conducted according to Analytical Services Request (ASR) 0647 along with the cross references to Radiochemical Processing Laboratory sample identifications (IDs). PNNL's Analytical Support Operations (ASO) organization was responsible for the preparation and analysis of appropriate analytical batch and instrument quality control samples and for providing any additional processing to the sub-samples that might be required (e.g., acid digestion, radiochemical separations, dilutions).

All analyses were conducted by the ASO according to standard operating procedures, the ASO QA Plan, and the ASR. Samples were analyzed directly (no preparation) for ^{137}Cs analysis by GEA.

Table 3.9. Analytical Scope for ASR 0647

Sample ID	ASO Sample ID	Analysis Scope
TCT008-COMP-FEED	19-1107	GEA, ^{99}Tc, IC, TOC/TIC, free OH, ICP-MS, ICP-OES, AEA, ^{90}Sr, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-EFF-1	19-1108	GEA, ^{99}Tc, ICP-MS, ICP-OES, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-COMP-EFF	19-1109	GEA, ^{99}Tc, ICP-MS, ICP-OES, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-L-F5-A (11 BVs)	19-1110	GEA, ICP-OES, ICP-MS, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-L-F9-A (104 BVs)	19-1111	GEA, ICP-OES, ICP-MS, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-L-F15-A (206 BVs)	19-1112	GEA, ICP-OES, ICP-MS, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-L-F19-A (298 BVs)	19-1113	GEA, ICP-OES, ICP-MS, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu
TCT008-L-F23-A (434 BVs)	19-1114	GEA, ICP-OES, ICP-MS, AEA, ^{237}Np, ^{238}Pu, $^{239+240}$Pu

IC = ion chromatography; TIC = total inorganic carbon; TOC = total organic carbon.

4.0 Results

This section describes the results from dead-end filtration, batch-contact, and column testing of AW-102.

4.1 DEF Filtration Results

The diluted AW-102 tank waste was filtered in 10 (~575-mL) batches with no external pressure[1] applied for the first 25 to 28 minutes and then pressurizing to 1.5 psig. Pressurization of the DEF apparatus concluded prior to all feed being passed through the filter to ensure the filter never went dry between evolutions. Figure 4.1 shows the volume of feed accumulated as a function of time for the 10 batches of AW-102 feed for the first 25 minutes of this testing. It is apparent that as additional material was being filtered, filter performance was retained throughout all 10 batches. This indicated no cake buildup of solids on the filter.

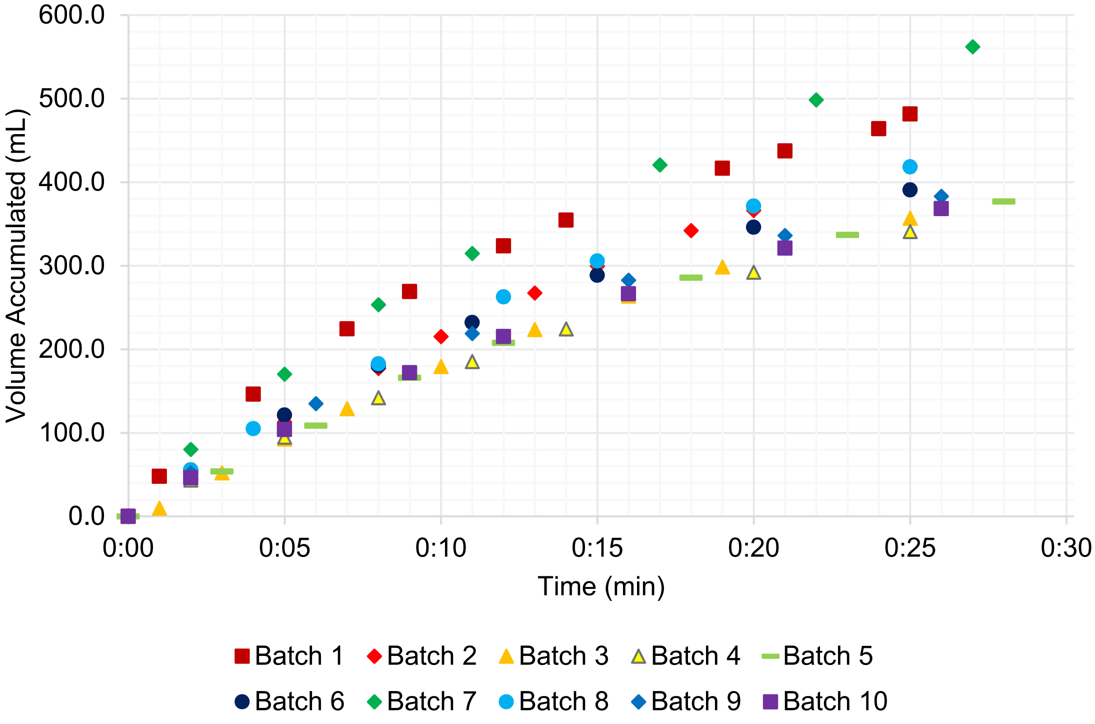

Figure 4.1 AW-102 DEF Mass Chart

Figure 4.2 plots filtration resistance as a function of volume filtered through the filter area for the first 25 minutes of filtering the DEF batches. Filtration resistance was determined using the following relationship shown in Eq. (4.1) (Chen et al. 1996).

$$R_m = \frac{p_m}{\mu q} \tag{4.1}$$

where R_m is medium resistance (1/m), p_m is filtration pressure (Pa), μ is liquid viscosity (kg/m-s), and q is equal to filtration rate ($m^3/m^2/s$). A liquid viscosity of 0.005 kg/m-s was used based on previously measured AP-105 and AP-107 tank viscosities.

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[1] Pressure for filtration was from the hydrostatic head (ρgh) of the feed inside the DEF, see Section 3.3.

The intercept of Figure 4.2plot represents the media resistance of the new clean filter. As the AW-102 is filtered, the resistance increases slightly, the slight increase in resistance is indicative of solids forming on the filter surface. A flow curve provided by Mott at ambient conditions indicates a new filter factory resistance of 1E+9 (1/m). This is slightly higher than what was found for the CWF and Batch 1 but falls directly in line with resistances calculated for Batches 2, 6, and 7. The zero slope of the resistance graph was maintained throughout all 10 batches, signifying the increase in solids during the duration of the batch was minimal. The lower resistance for the CWF is due to lower viscosity of the liquid.

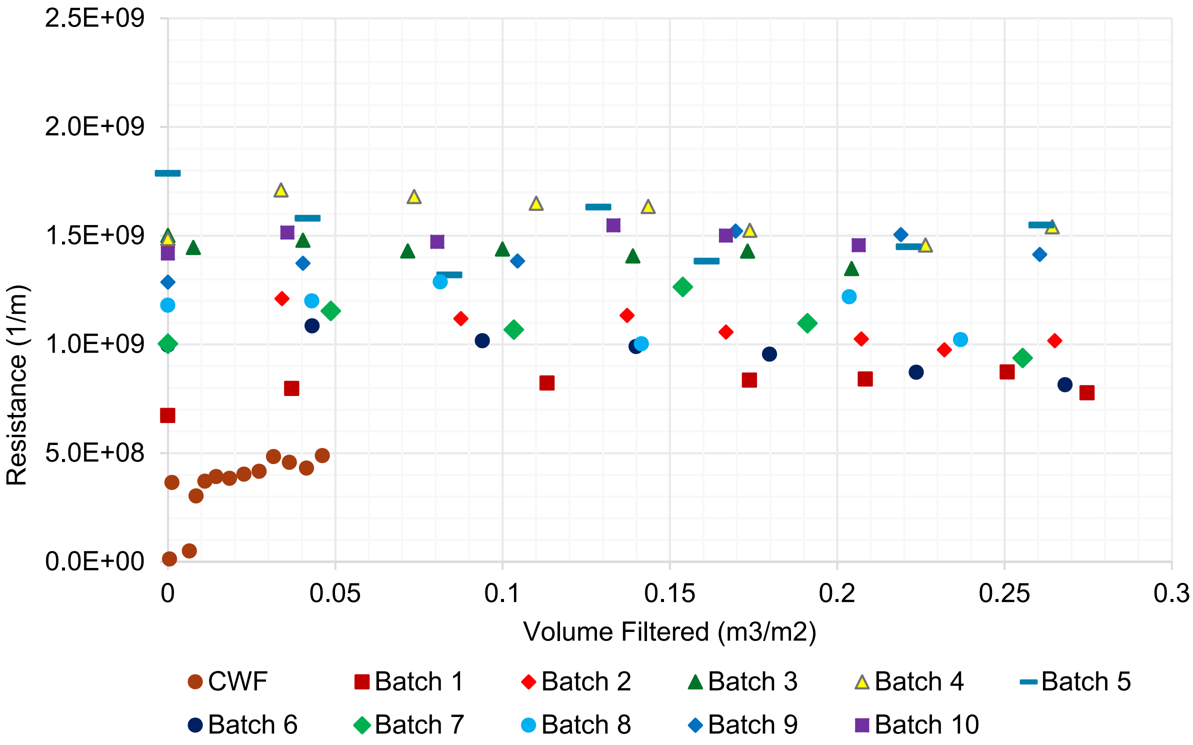


Figure 4.2. Resistance vs. Process Volume for DEF of AW-102 Batches 1-10

After the 10 batches of AW-102 were filtered through the DEF, the filter housing was disassembled, and the filter was inspected. No visual solids appeared on the filter despite the slight increase in resistance throughout the 10 batch runs. The filter was air dried and weighed; there was no accumulation in mass from the initial filter weight.

4.2 Batch Contact Results

This section provides the batch contact kinetic and capacity results for the <25-mesh CST contacted with AW-102. The K_d values were calculated using Eq. (3.1) and are based on the ^{137}Cs concentrations as measured by GEA. The equilibrium Cs concentrations were based on the measured ^{137}Cs concentrations and the ratio of ^{137}Cs:total Cs determined for the un-spiked and spiked solutions.

4.2.1 Kinetic Testing Results

Table 4.1 identifies the initial Cs concentration, contact time, contact volumes, final Cs concentration, K_d values, and Cs loading onto the CST for testing in AW-102. Note that duplicate aliquots were collected at the 1.95 and 5.65 h contact times (K1 and K2 tests, respectively). The duplicate K_d values varied within

±2 and were indicative of overall experimental uncertainty. The difference in K_d values between the 92- and 165-h contact times was within the overall experimental uncertainty indicating that equilibrium was achieved between 45- and 92-h contact times.

Table 4.1. Kinetic Batch Contact Testing Results for Batch Contact Samples in AW-102

Sample ID	Initial [Cs], µg/mL	Contact Time, h	AW-102 volume, mL	Final [Cs], µg/mL	K_d, mL/g	Eq. Cs in CST, mmole Cs/g CST (Q)
TCT010-K1-2A	40.1	0.50	47.5	27.1	103	2.09E-02
TCT010-K1-3A		1.95	46.9	17.1	286	3.66E-02
TCT010-K1-4A		1.95	46.9	16.9	291	3.69E-02
TCT010-K1-5A		5.65	45.4	14.3	368	3.97E-02
TCT010-K1-6A		23.4	44.7	7.82	833	4.90E-02
TCT010-K1-7A		46.8	44.0	7.49	864	4.87E-02
TCT010-K1-8A		92.5	43.5	6.35	1042	4.98E-02
TCT010-K1-1A		165.3	42.4	6.42	1004	4.85E-02
TCT010-K2-2A	37.30	0.50	51.6	34.5	19	4.81E-03
TCT010-K2-3A		1.95	51.0	19.1	217	3.11E-02
TCT010-K2-4A		5.65	50.3	16.2	292	3.56E-02
TCT010-K2-5A		5.65	50.3	16.2	292	3.56E-02
TCT010-K2-6A		23.4	49.1	8.13	785	4.80E-02
TCT010-K2-7A		46.8	48.4	7.23	897	4.88E-02
TCT010-K2-8A		92.5	47.9	6.52	1006	4.94E-02
TCT010-K2-1A		165.3	46.8	6.32	1022	4.86E-02

The calculated ^{137}Cs K_d values are plotted as a function of time in Figure 4.3 for CST in contact with AW-102 and 5.6 M Na simple simulant. Similarly, Figure 4.4 plots the data from Figure 4.3 as Q versus time on a linear-linear scale. The Cs exchange rate was rapid from 0 to 25 h. The exchange rate after 25 h leveled off with the K_d rate still gradually increasing until 95 h. The Fiskum et al. (2019) kinetic study was conducted at significantly different scale (1.1 g CST in 342 mL simulant and a different shaker table).However, the solution/CST phase ratios were similar at 200 and the two studies tracked well. The AW-102 results mirror those previously reported (Fiskum et al. 2019; King et al. 2018), where the Cs concentration loading in the CST solids was essentially complete after 24 h yet the K_d values continue to change significantly up to 96 h contact time. The 15-mL capacity test (see Section 4.2.2, 92-h contact time with 39.4 µg/mL Cs) where an average K_d value of 997 mL/g was attained (Table 4.2) can also be compared to the kinetic study test where an average K_d value of 1024 mL/g was attained. The capacity study K_d value is 97% of the average of the two 92-h kinetic study K_d values, indicating very little bias in the kinetic study test design and results where multiple samplings were collected relative to a single point sampling test.

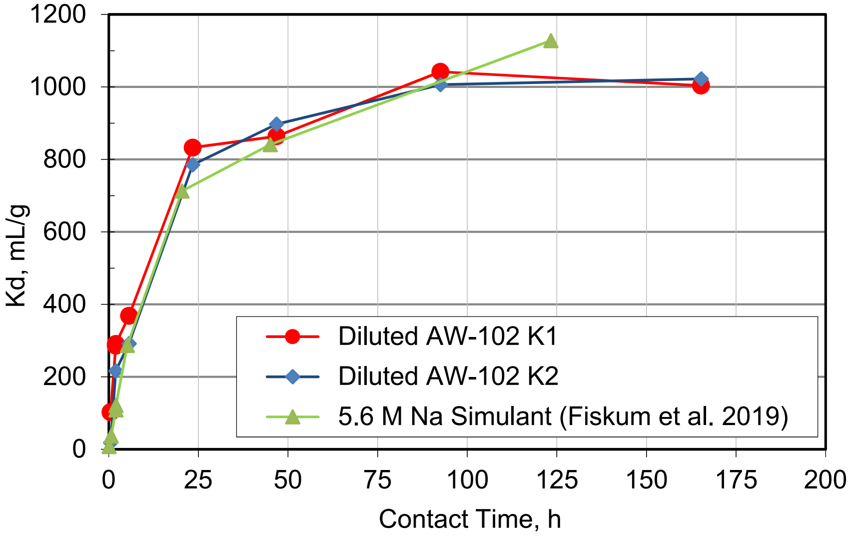


Figure 4.3. K_d as Function of Time for AW-102 and 5.6 M Na Simulant

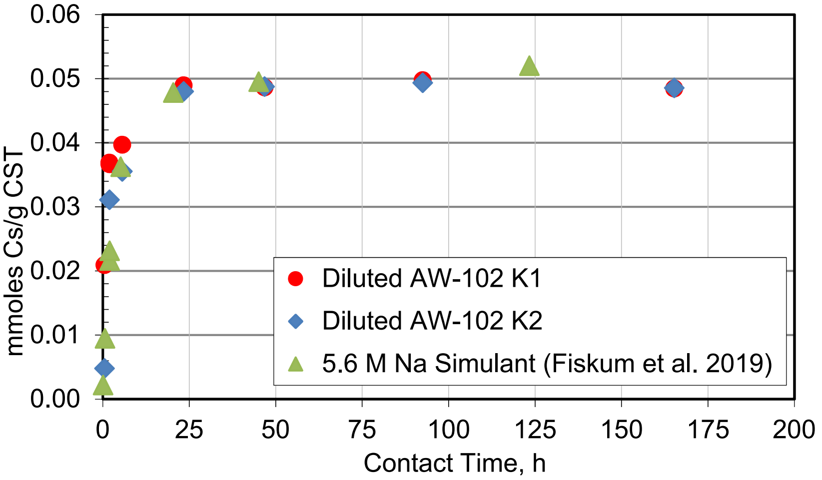


Figure 4.4. Cs Loading as a Function of Time in AW-102 and 5.6 M Na Simulant

4.2.2 Capacity Testing Results

Equilibrium Cs concentrations and K_d results for the batch contacts are provided in Table 4.2; the K_d values are plotted versus Cs concentrations in Figure 4.5 on a log-log scale.

Table 4.2. Equilibrium Results for Batch Contact Samples in AW-102

Sample ID	Initial [Cs] (µg/mL)	Final [Cs] (µg/mL)	Δ Time (h)	K_d (mL/g)	Equilibrium Cs in CST (mg Cs/g)	Equilibrium Cs in CST, mmoles Cs/g
TCT010-S0-CST	6.21	1.14	93	930	1.06	7.91E-03
TCT010-S1-CST	39.4	6.87	93	982	6.80	5.12E-02
TCT010-S2-CST	242	50.6	93	740	37.5	2.82E-01
TCT010-S3-CST	1520	1093	93	81	88.5	6.66E-01
TCT010-S0-D-CST	6.21	1.12	97	935	1.05	7.86E-03
TCT010-S1-D-CST	39.4	6.60	97	1012	6.69	5.03E-02
TCT010-S2-D-CST	242	55.1	97	685	37.9	2.85E-01
TCT010-S3-D-CST	1520	1097	97	77	85.1	6.40E-01

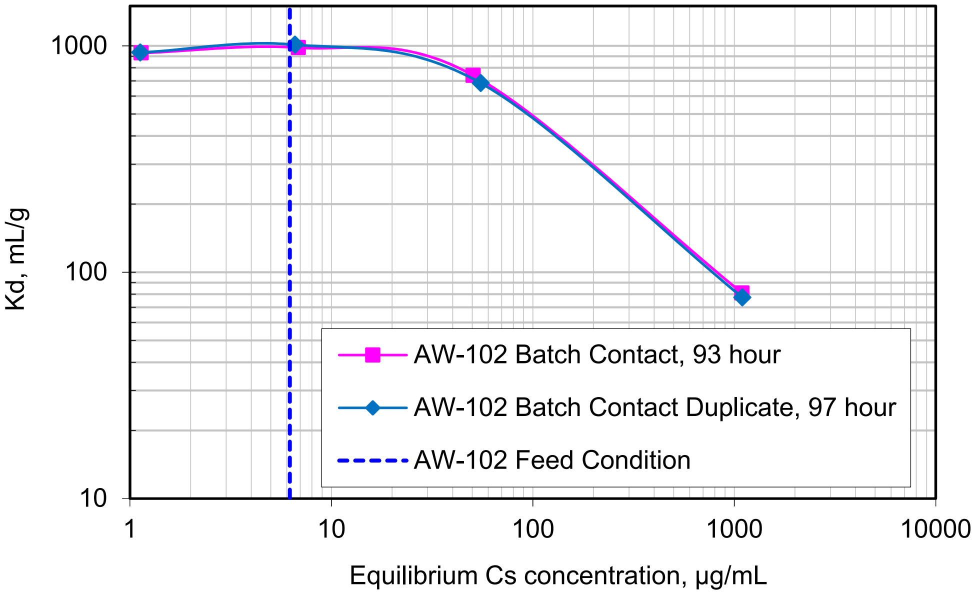
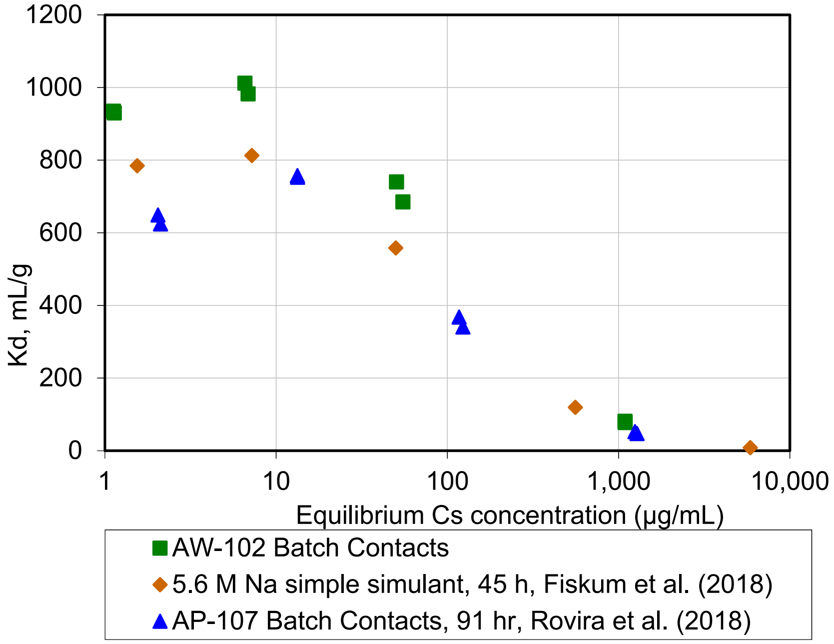


Figure 4.5. Equilibrium Cs K_d Curve for AW-102 with CST

The K_d vs. the log of the Cs equilibrium concentration was fit to a second order polynomial equation to calculate the K_d at the feed concentration of 6.21 µg Cs/mL: 953 mL AW-102/g CST. The theoretical 50% Cs breakthrough on the ion exchange column (λ) can be predicted from the product of the K_d value and the ion exchanger bed density (ρ_b) according to Eq. (3.2). The CST bed density is the dry CST mass divided by the volume in the column. Assuming a constant CST bed density of 1.00 g/mL, the theoretical 50% breakthrough (λ) for AW-102 with 6.21 µg/mL Cs is 953 BVs.

Figure 4.6 compares the K_d values obtained with AW-102 batch contacts with the 45-h 5.6 M Na simple simulant batch contacts (Fiskum et al. 2018) and with those reported by Rovira et al. (2018), who used CST Batch 2081000057 in AP-107 tank waste. The AW-102 results show higher K_d values at lower Cs concentrations than those found for 5.6 M Na simulant and AP-107 tank waste. This is consistent with the overall higher Cs loading limit in the current Lot 2002009604. However, this evaluation doesn't include effects of K, hydroxide, and other potential competitors such as Ca for ion exchange onto the CST so a high Cs capacity cannot be fully concluded.



Feed	K, M	OH, M	Cs, M
5.6 M Na Sim.	0.122	2.07	3.02E-4
AP-107	0.097	0.92	6.39E-5
AW-102	0.18	0.98	4.63E-5

Figure 4.6. Comparison of AW-102 Test Data with 5.6 M Na Simple Simulant (Fiskum et al. 2018) and Rovira et al. (2018) Test Data

Figure 4.7 provides the isotherm for the AW-102 and AP-107 batch contact test samples. In this case, the equilibrium Cs concentration is expressed in terms of molarity (as opposed to µg/mL in Figure 4.5). The isotherm was fit to the Freundlich/Langmuir Hybrid equilibrium isotherm model (see Hamm et al. 2002) according to Eq. (4.2). The expected Cs loading onto the CST at a given Cs concentration can be determined from the isotherm.

$$\frac{a_i \times [\mathrm{Cs}]}{(\beta + [\mathrm{Cs}])} = \mathrm{Cs}_{\mathrm{IX}} \qquad (4.2)$$

where:

[Cs] = equilibrium Cs concentration, mmole Cs per mL
$\mathrm{Cs}_{\mathrm{IX}}$ = equilibrium Cs loading on the CST, mmole Cs per g CST
α_i = isotherm parameter constant (mmole Cs per g CST)
β = isotherm parameter constant (mmole Cs per mL)

Hamm et al. (2002) computed the α_i parameter for the engineered CST to be 0.39 mmoles/g. Testing with the newer CST production batch (Lot 2002009604) resulted in a higher Cs capacity where the α_i parameter was calculated to be 0.70 mmoles/g, an 80% increase relative to 0.39 mmoles/g. The β parameter contains the selectivity coefficients, making it dependent upon temperature and liquid composition of all the ionic species in solution; the larger the beta parameter, the less favorable (and lower loadings) an isotherm will be (Hamm et al. 2002). The AW-102 test resulted in a β value of 5.84E-4 mmoles Cs/mL. This β parameter was a factor of two higher than reported by Hamm et al. (2002) (average β value of 2.8552E-04 mmoles Cs /mL Cs for Envelope A tank waste). This indicated that Lot 2002009604 CST was more negatively affected by the salt composition in AW-102 relative to the CST production batches evaluated by Hamm et al. (2002). The higher Cs capacity was nearly counterbalanced by the negative Cs exchange effect from the matrix constituents at the feed Cs concentration. Testing with

AP-107, CST Batch 2081000057, resulted in Cs loading parameter α_i at 0.50 mmole Cs/g and β value of 5.3E-4 mmoles Cs/mL (Rovira et al. 2018). Despite the different matrices between AP-107 and AW-102, the CST Lot 2002009604 demonstrated 40% higher Cs capacity than that of Batch 2081000057 but with similar matrix effects (similar β parameters). Figure 4.7 graphs the AW-102 and AP-107 isotherms with the isotherm derived from α_i and β parameters reported by Hamm et al. (2002).

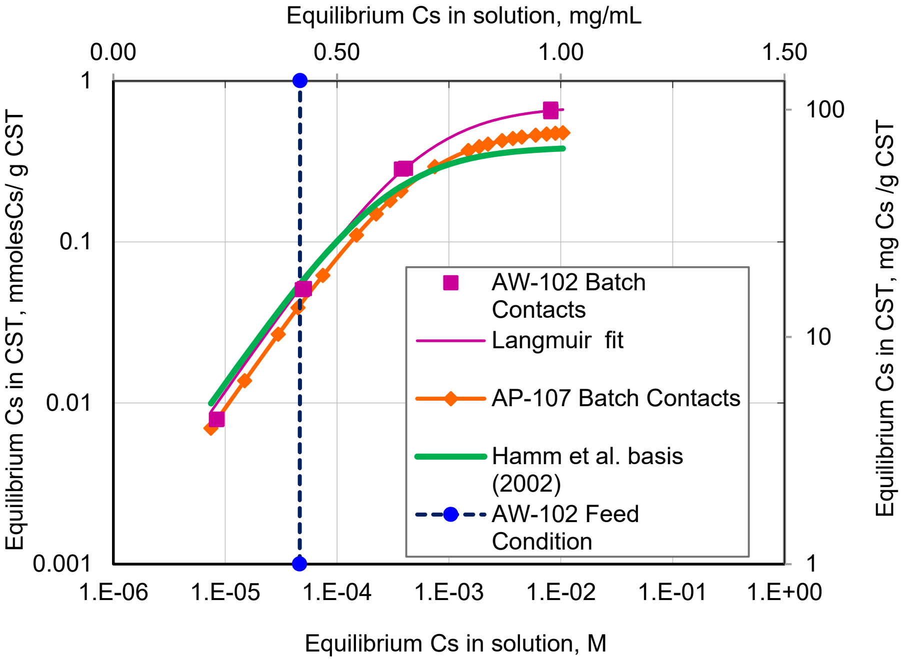


Figure 4.7. Isotherms for AW-102, AP-107 and Hamm et al. 2002 with CST

4.3 Ion Exchange Testing Results

The Cs load behavior was evaluated with the AP-107 tank waste. This section discusses the load, FD, water rinse, and Cs mass balance results. Raw data are provided in Appendix A.

4.3.1 Cs Load, Feed Displacement, and Water Rinse Results

The AW-102 feed was processed at nominally 1.8 BV/h through the lead and lag columns. Figure 4.8 shows a linear-linear plot of the Cs load profile for feed processed through each column. The x-axis shows the BVs processed and the y-axis shows the effluent Cs concentration (C) relative to the feed concentration (C_0) in terms of % C/C_0. The C_0 value for ^{137}Cs was determined to be 105.2 µCi/mL which corresponded to a contract limit of 0.170 % C/C_0 based on the waste acceptance limit.[1] In this graphing layout, the Cs breakthrough from the lead column started at 188 BVs and continued to 450 BVs (a range of 262 BVs) by the completion of testing. Lag column Cs breakthrough is not perceptible.

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[1] The contract limit was derived from the allowed curies of ^{137}Cs per mole of Na in the pretreated LAW—3.18E-5 Ci ^{137}Cs/mole Na. At 5.6 M Na and 105.2 µCi ^{137}Cs/mL in the feed, the contract limit is 1.70E-3 C/C_0; 0.170% C/C_0.

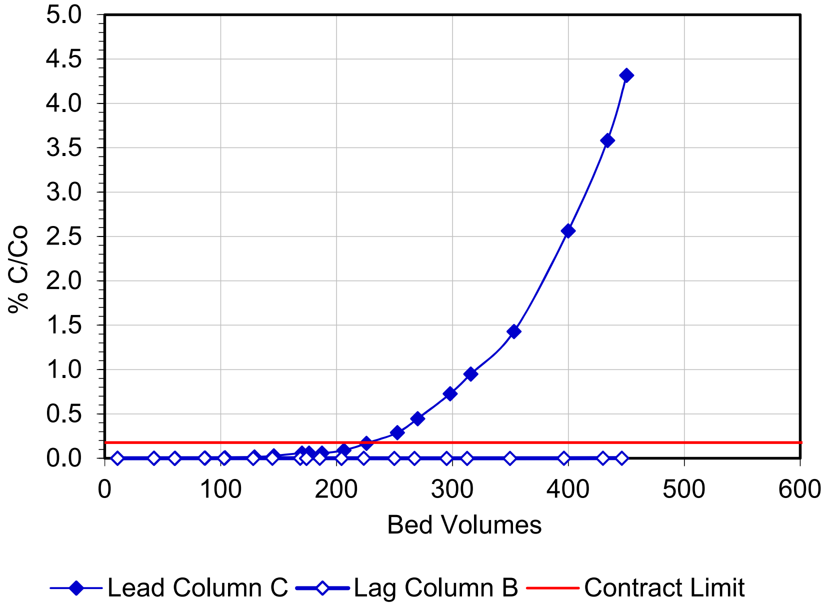

Figure 4.8. Lead and Lag Column Cs Load Profiles of AW-102 at 1.8 BV/h, Linear-Linear Plot

Figure 4.9 shows the same Cs load data from Figure 4.8, but with the ordinate % C/C_0 on a probability scale and the abscissa on a log scale. The data from the 88 BVs with column A (prior to the columns running dry) were added along with the FD and water rinse results following AW-102 loading. Examining data on this scale tends to provide a relatively straight-line breakthrough curve under ideal load conditions and provides greater fidelity of load characteristics at low and high % C/C_0 values. In this graphing configuration, breakthrough from the lead column is observed nearly immediately at ~40 BVs. Lag column B breakthrough appears to begin just past 300 BVs. The circled area in Figure 4.9 shows a leveling in the Cs load profile. This was attributed to the system being placed in standby during adverse weather and the lead and lag columns being in static contact with the AW-102 for 11 days. The stop flow condition allowed for greater Cs exchange onto the CST with the contact fluid and indicates that the residence time (pore diffusion limitation), not the superficial velocity (film diffusion limitation), dominates Cs exchange into the CST. There appeared to be no detriment to column performance as a result of this unexpected pause. Flow was easily re-established through both CST beds and the Cs exchange continued along the established breakthrough trajectory.

Following the AW-102 load, 6 BVs of 0.1 M NaOH solution were passed through the system as FD. The FD was bulk collected off the lag column and sampled for GEA. The FD sample Cs concentration was equivalent to that of the last sample collected from the lag column; this was consistent with previous testing with AP-107 (Rovira et al. 2018). The DI water rinse was also collected in bulk; its Cs concentration showed a 2.4x increase in Cs concentration above the FD. The increased Cs concentration in the DI water rinse was also seen in full-height column testing with 5.6 M Na simulant (Fiskum et al. 2019). Following water rinse, the system was flushed by pumping air through the system to displace all the fluid. The collected flush fluid exceeded the contract limit. The increasing Cs concentration in the DI water effluent and flush fluids indicated that some Cs had not remained bound to the CST in the presence of DI water or that small/colloidal CST particles containing Cs escaped the system.

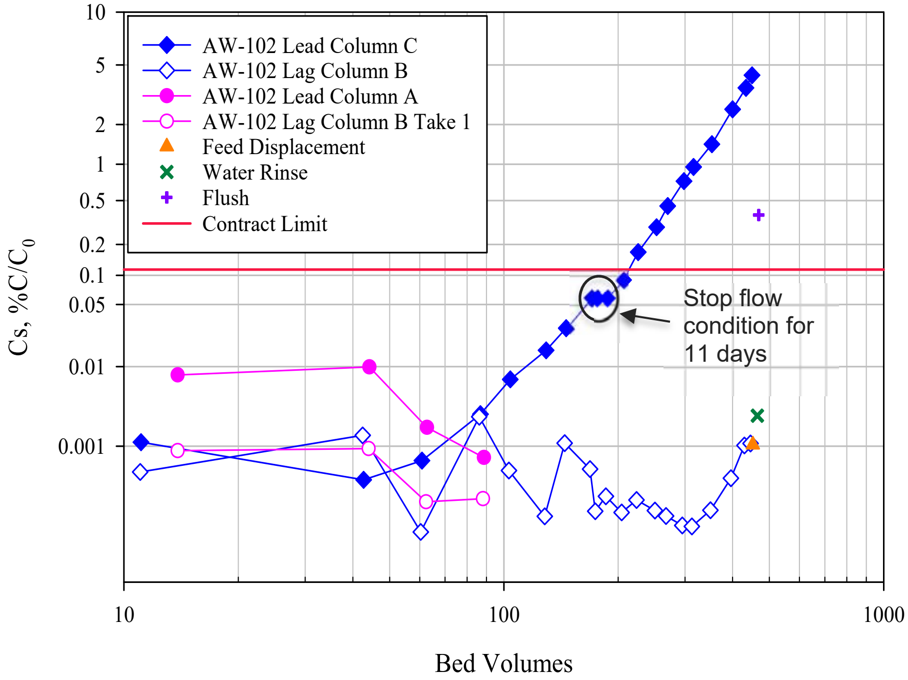

Figure 4.9. Lead and Lag Column Cs Load Profiles of AW-102 at 1.8 BV/h, Probability-Log Plot

The lead column data from Figure 4.9 are plotted in Figure 4.10 to estimate the 50% Cs breakthrough point. The 50% Cs breakthrough value is the point at which the C/C$_0$ is 50% (0.5) and is normally a direct indicator of the effective capacity of the ion exchanger. A straight-line extrapolation to 50% breakthrough from 4.3 % BT to 50% C/C$_0$ is inherently prone to error. With this caveat, the 50% Cs breakthrough extrapolated to about 1190 BVs for the lead column. This value is about 20% higher than the predicted Cs λ value of 953 BVs determined with batch-contact tests. The lag column was similarly extrapolated from1.08E-3 % C/C$_0$ to the contract limit of 0.176% C/C$_0$ and was found to be 930 BVs.

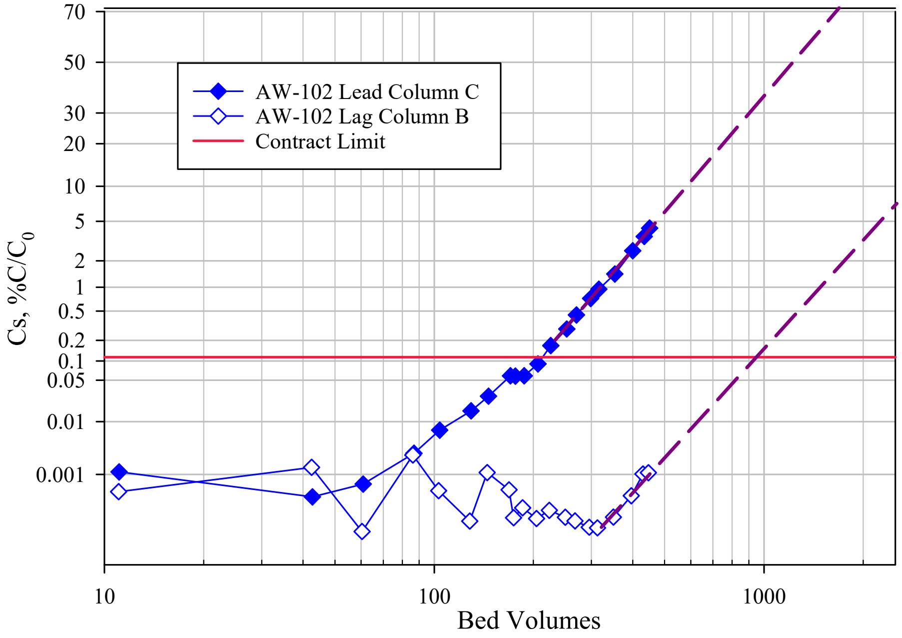

Figure 4.10 Lead and Lag Column Cs Breakthrough Profile for Breakthrough Extrapolation

Table 4.3 provides the Cs-decontaminated effluent composite results in terms of ^{137}Cs concentration and overall decontamination factor (DF). A DF of 589 was needed to meet the waste acceptance criteria.

Table 4.3. AW-102 Effluent Composites ^{137}Cs Content and Decontamination Factor

Effluent Container	^{137}Cs (µCi/mL)	Decontamination Factor
Effluent-1 (0-89 BVs)	1.17E-4	9.01E+05
Effluent-2[1] (0-129 BVs)	1.33E-4	7.89E+05
Effluent-3[2] (130-253 BVs)	1.13E-4	9.31E+05
Effluent-4 (254-353 BVs)	1.05E-4	1.00E+06
Effluent-5 (354-451 BVs)	5.54E-4	1.90E+05

[1] Start of new test with replaced lead column C.

[2] After processing 176 BVs: replaced pump, manipulator broke in the process and required repair, system was placed on standby for 11 days due to weather issues.

4.3.2 AW-102, AP-107, and 5.6 M Na Simulant Loading Comparison

The Cs load and breakthrough profiles are compared in Figure 4.11 for processing with 5.6 M Na simulant (Fiskum et al. 2019), AP-107 tank waste (Rovira et al. 2018), and diluted AW-102 tank waste. The AP-107 testing with CST from the 2012 CST production batch 2081000057 is shifted left relative to the 5.6 M Na simulant and AW-102 tests, indicative of a decreased Cs loading capacity. The simulant and AW-102 tests both used CST from production lot 2002009604 and appear to have similar Cs breakthrough profiles with the exception that the simulant test resulted in the most delayed onset for Cs breakthrough. The breakthrough slopes for all three tests appear similar, indicating the Cs exchange kinetics for both batches are similar.

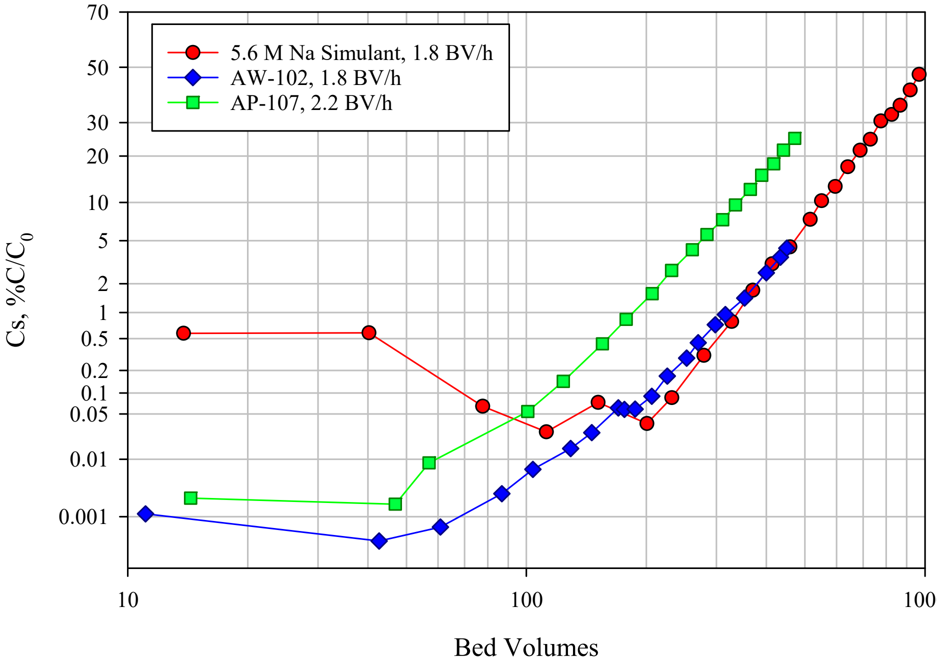

Figure 4.11. Lead Column Cs Load Profiles of 5.6 M Na Simulant, AP-107 and AW-102

4.3.3 Activity Balance for ^{137}Cs

An activity balance for the ^{137}Cs fractionation was determined to compare the ^{137}Cs recovered in various process streams to the ^{137}Cs present in the feed sample. The quantities of Cs loaded onto the lead and lag columns were determined by subtracting the Cs recovered in the samples and effluents from the Cs fed to the column. Table 4.4 summarizes the ^{137}Cs fractions found in the various effluents as well as the calculated ^{137}Cs column loading. About 16% of the total Cs loaded onto lead column A, 83% loaded onto lead column C, and less than 1% loaded onto lag column B. Sample and effluent collection amounted to less than 1% of the input Cs indicating 99% Cs removal by the CST.

Table 4.4. ^{137}Cs Activity Balance for AW-102

Input	µCi	%
Feed sample	5.67E+05	100.0
Output		
Effluent-1 (0-89 BVs)	1.02E-01	1.79E-05
Effluent-2 (0-129 BVs)	1.70E-01	2.99E-05
Effluent-3 (130-253 BVs)	1.36E-01	2.40E-05
Effluent-4 (254-353 BVs)	1.04E-01	1.83E-05
Effluent-5 (354-451 BVs)	5.31E-01	9.37E-05
Load samples	3.60E+01	6.35E-03
Feed displacement and water rinse	4.03E-01	7.10E-05
Total ^{137}Cs recovery	3.75E+01	6.61E-03
Total ^{137}Cs Column Loading		
Lead A column Cs loading	9.32E+04	16.44
Lead C column Cs loading	4.70E+05	82.90
Lag B column Cs loading	3.74E+03	0.66
Column total	5.67E+05	100.0

The total Cs loaded onto each column was determined and is shown in Table 4.5. The total µCi ^{137}Cs loaded per gram CST was also calculated by dividing the total µCi loaded onto the column by the grams of CST in the bed.

Table 4.5. Total Cs Loaded

Column	Total Cs Loaded onto Column (mg Cs)	Total µCi ^{137}Cs/g CST
A	5.51	9,320
C	27.76	47,000
B	0.22	374

4.3.4 Chemical and Radiochemical Composition

The compositions of the AW-102 ion exchange feed and effluents were evaluated to understand analyte mass fractionations to the effluent and by difference to CST through the ion exchange process. FD and water rinse effluents were not analyzed. Effluent 1 was collected prior to the new lead column (column C) installation and was analyzed separately from the subsequent effluent bottles. Effluent 1 was slightly diluted by the ~43 mL 0.1 M NaOH fluid filled apparatus volume (~1.05x dilution factor). The composite effluent was created by collecting a pro-rated volume from each effluent collection bottle after the installation of column C and combining it in a polyethylene vial. No processing dilution was applied to it.

Table 4.6 summarizes the feed and effluent radioisotopic concentrations and fractionations to the effluent. Table 4.7 summarizes the metals fractionations to the effluent. The analyte fractionations were calculated as ratios of the total analyte measured in the feed processed through the columns and the total analyte collected in the Cs-decontaminated effluents according to Eq. (4.3):

$$\frac{C_{Da} \times V_D}{C_{Fa} \times V_F} = F_{Da} \tag{4.3}$$

where:

C_{Da} = concentration of analyte *a* in the Cs-decontaminated effluent
V_D = volume of Cs-decontaminated effluent (828 mL for EFF-1; 4520 mL for EFF-Comp mL)
C_{Fa} = concentration of analyte *a* in the AW-102 feed
V_F = volume of AW-102 feed (885 mL for EFF-1; 4420 mL for EFF-Comp)
F_{Da} = fraction of analyte *a* in the Cs-decontaminated effluent

Analyte results shown in brackets in Table 4.6 through Table 4.8 indicate that the analytical result was less than the estimated quantitation limit (EQL) but greater than the method detection limit (MDL) and the associated analytical uncertainty could be higher than ±15%. The fractionation result was placed in brackets, where it was calculated with one or more bracketed analytical value(s) to highlight the higher uncertainty. The opportunistic analyte results measured by ICP-OES are also shown in Table 4.7; these analytes are part of the ICP-OES data output but have not been fully evaluated for quality control performance. The composite feed sample results in Table 4.6 and Table 4.7 were compared to the initial characterization sample results (Table 3.1).

Table 4.6. AW-102 Feed and Effluent ASR 0731, Radionuclides

Analysis Method	Analyte	TCT008-Comp-Feed (µCi/mL)	TCT008-EFF-1 (µCi/mL)	TCT008-EFF-COMP (µCi/mL)	Fraction in Effluent 1 (%)	Fraction in Comp Effluent (%)
Gamma energy analysis (GEA)[(a)]	^{60}Co	<0.00071	4.00E-04	4.22E-04	--	--
	^{126}Sn	<0.031	2.16E-04	2.58E-04	--	--
	^{126}Sb	<0.0027	2.43E-04	2.94E-04	--	--
	^{137}Cs	1.14E+02	1.37E-04	2.00E-04	0.0%	0.0%
	^{152}Eu	<0.002	<0.000005	2.35E-06	--	--
	^{154}Eu	<0.0029	4.06E-05	4.59E-05	--	--
	^{241}Am	<0.19	9.82E-05	1.23E-04	--	--
Separations/ Alpha energy analysis (AEA)[(b)]	^{237}Np	1.03E-05	1.21E-06	5.50E-06	11.7%	52.8%
	^{238}Pu	8.40E-05	1.69E-05	2.93E-05	20.1%	34.5%
	$^{239+240}$Pu	5.66E-04	1.08E-04	1.81E-04	19.0%	31.7%
Separations/ Beta counting[(b)]	^{90}Sr	3.44E-01	5.81E-03	8.33E-04	1.7%	0.2%
	^{99}Tc	8.98E-02	7.43E-02	7.51E-02	82.6%	82.7%
Calculated from AEA results[(b)]	Sum of alpha[(c)]	4.07E-04	1.11E-04	1.98E-04	27.2%	48.2%
Proportional counting[(b)]	Total beta	1.42E+02	8.69E-02	9.69E-02	0.1%	0.1%

(a) Reference date is March 6, 2019.
(b) Reference date range is April 4-30, 2019
(c) This is the summation of alpha-emitting isotopes concentrations (Am, Cm, Np, and Pu isotopes) as measured by AEA.
"--" = not applicable; value not reported, or fractionation cannot be calculated with a less-than value.

Table 4.7. AW-102 Feed and Effluent Compositions ASR 0731, Cation Analytes

Analysis Method	Analyte	TCT008-Comp-Feed (µg/mL)	TCT008-EFF-1 (µg/mL)	TCT008-EFF-COMP (µg/mL)	Fraction in Effluent 1 (%)	Fraction in Comp Effluent (%)
ICP-MS[(a)]	^{238}U	178	171	124.5	103	68
ICP-OES	Al	13,300	11,656	12,550	87%	93%
	As	--	--	--	--	--
	Ba	[0.51]	--	--	--	--
	Ca	[24]	[19]	[9.1]	[77%]	[38%]
	Cd	[1.9]	--	[1.5]	--	[78%]
	Cr	592	513	554	87%	93%
	Fe	[8.5]	[5.1]	[3.9]	[60%]	[45%]
	K	5,990	4,964	5655	83%	93%
	Na	134,000	118,000	125,500	88%	93%
	P	894	776	825	87%	91%
	Pb	--	--	--	--	--
	S	1,220	1,085	1115	89%	90%
	Sr	--	--	--	--	--
	Ti	[0.41]	[0.40]	[0.45]	[98%]	[107%]
	Zn	22.1	[2.9]	--	[13%]	--
	Zr	--	[2.2]	[2.35]	--	--

(a) Reference date is March 28, 2019.

Table 4.7 (cont.)

Analysis Method	Analyte	TCT008-Comp-Feed (µg/mL)	TCT008-EFF-1 (µg/mL)	TCT008- EFF-COMP (µg/mL)	Fraction in Effluent 1 (%)	Fraction in Comp Effluent (%)
ICP-OES opportunistic analytes	Ag	[1.0]	--	--	--	--
	B	41.2	[26]	[26]	[63%]	[62%]
	Be	[0.19]	[0.08]	[0.15]	[43%]	[78%]
	Bi	--	--	--	--	--
	Ce	--	--	--	--	--
	Co	--	--	--	--	--
	Cu	--	--	--	--	--
	Dy	--	--	--	--	--
	Eu	--	--	--	--	--
	La	--	--	--	--	--
	Li	[0.64]	[0.69]	--	[107%]	
	Mg	--	--	--	--	--
	Mn	--	--	--	--	--
	Mo	38.9	35.9	37.4	92%	95%
	Nd	--	--	--	--	--
	Ni	[23]	[19]	[22]	[83%]	[93%]
	Pd	--	[6.1]	--	--	--
	Rh	--	--	--	--	--
	Ru	[7.5]	--	[4.9]	--	[32%]
	Sb	--	--	--	--	--
	Se	--	--	--	--	--
	Si	[59]	[62]	[47]	[105%]	[79%]
	Sn	[19]	--	[19]	--	[49%]
	Ta	--	--	--	--	--
	Te	--	--	--	--	--
	Th	--	--	--	--	--
	Tl	--	--	[53]	--	--
	U	[22]	[22]	[20]	[98%]	[45%]
	V	--	--	--	--	--
	W	[69]	[60]	[64]	[88%]	[91%]
	Y	--	--	--		

Bracketed values indicate the associated sample results were less than the EQL but greater than the MDL. Analytical uncertainty for these analytes is > ±1—.
"--" = not detected or not applicable.

Consistent with previous AP-107 testing on CST, the CST appears to sorb many transuranic elements. A large amount of the Pu was assumed to have partitioned to the CST (~80%), with nominally 20% found in in EFF-1. The ^{237}Np results were similar to the Pu results where 11% of the processed ^{237}Np was accounted for in EFF-1, resulting in 90% remaining on the CST.

The recovery of Pu and ^{237}Np in EFF-COMP found 30% of the Pu and 53% of the ^{237}Np recovered in the effluent. These results indicate that we have saturated the ability to uptake both Pu and ^{237}Np onto the ion exchanger as indicated by the increasing recovery in the effluent with additional BVs processed. An 83% recovery of ^{99}Tc was found in both EFF-1 and EFF-COMP. About 90% of the U fractionated to the CST from EFF-1 and 30% for EFF-COMP. Nominally all ^{90}Sr partitioned to the CST with only 1.7% and 0.2% recovery in EFF-1 and EFF-COMP, respectively. Based on ^{90}Sr results, a nominal Sr DF of ~400 was obtained through the both the lead and lag columns (based on the composite effluent result). This is about a factor of 5 less than what was seen with AP-107 testing on CST.

The ICP-OES results for metals showed that nominally all the Al, Cr, K, Na, P, and S reported to the effluent. Both Ca and Fe recovered higher in EFF-1 than in EFF-Comp. Fe recovery in the composited effluent was consistent with what was seen with AP-107. U recovered 100% in effluent 1 but over time the average uranium recovery dropped to 68% in the effluent composite. It's difficult to ascertain loading behavior from the average. Cr partitioned almost exclusively to the effluent. As, Ba, and Cd were detected in the feed (with concentration errors likely to exceed 15%) but were below the MDL in the effluent. Pb and Se were below the MDL in both the feed and the effluent; therefore, partitioning could not be assessed.

Selected lead column C samples were also analyzed by ICP-OES. The fractionation summary of selected analytes is shown in Table 4.8. Fraction results shown in brackets represent analytical results that were less than the EQL but greater than the MDL with associated analytical uncertainty ±15%. The load behaviors were examined to explore partitioning behaviors to the CST over time. Ca and Fe increased by 25% and 13%, respectively, from 11 to 430 BVs. A nominal ~50% uptake of Ca and Fe is consistent with what was seen with previous AP-107 testing on CST (Rovira et al. 2018). Al, Cr, K, Mo, Na, P, and S all remained at nominally the same concentration in the samples with increased loading.

Table 4.8. Selected Analyte Percentage with Loading

BVs:	11.1 BV	103.9 BV	206.5 BV	298.1 BV	433.8 BV
(Analyte)	TCT008-L-F5-A	TCT008-L-F9-A	TCT008-L-F15-A	TCT008-L-F19-A	TCT008-L-F23-A
Ca	[42%]	[46%]	[50%]	[63%]	[67%]
Cd	--	[58%]	--	[63%]	[68%]
Fe	[45%]	[51%]	[53%]	[53%]	[58%]
Ti	[115%]	[149%]	[144%]	[122%]	[163%]
Al	96%	99%	98%	96%	100%
B	138%	121%	83%	83%	[78%]
Be	[27%]	[111%]	[95%]	[90%]	[95%]
Cr	97%	99%	97%	95%	99%
K	100%	101%	100%	100%	104%
Mo	104%	103%	94%	96%	103%
Na	97%	99%	96%	96%	98%
Ni	[87%]	[96%]	[91%]	[87%]	[91%]
P	95%	97%	94%	93%	95%
S	100%	99%	92%	95%	100%
Si	[232%]	[186%]	[120%]	[105%]	[98%]
U	[105%]	[86%]	[82%]	[114%]	[114%]
W	[106%]	[103%]	[99%]	[88%]	[101%]

Radioisotopic concentrations for the selected lead column C samples were also examined. Table 4.9 shows the fractionation summary of selected analytes. Consistent with the Cs breakthrough load profile, Np increased from 30% to 98% in the effluent from 11 BVs to 434 BVs. The Pu breakthrough increased by 30% over the 420 BV range. Np and Pu appear to be fully saturated onto the CST by 11 BVs as shown by an increasing recovery in the effluent with subsequent processing. In this same loading interval, ^{137}Cs breakthrough increased by 3.6%.

Table 4.9. Selected Radionuclide Percentage with Loading

BVs:	11.1 BV	103.9 BV	206.5 BV	298.1 BV	433.8 BV
(Analyte)	TCT008-L-F5-A	TCT008-L-F9-A	TCT008-L-F15-A	TCT008-L-F19-A	TCT008-L-F23-A
^{137}Cs	0.0%	0.0%	0.1%	0.7%	3.6%
Gross Alpha	34.6%	52.3%	49.9%	75.4%	77.9%
^{237}Np	26.8%	71.0%	81.8%	94.1%	98.1%
^{238}Pu	32%	50%	35%	56%	63%
$^{239/240}$Pu	29%	47%	35%	58%	63%

5.0 Conclusions

The objectives for filtration and ion exchange testing were met: 1) Diluted AW-102 to nominally 5.6 M Na, 2) filtered the diluted AW-102 in a dead-end filtration apparatus representative of the planned TSCR filtration pore size and surface area to volume ratio, 3) conducted batch contact testing of the diluted AW-102 to establish Cs load capacity and kinetic behavior, 4) conducted ion exchange processing of the filtered AW-102 to establish Cs breakthrough performance, 5) compared the filtration and ion exchange performances of the diluted AW-102 tank waste to those of the AP-107 tank waste, and 6) provide CST from diluted AW-102 column processing for characterization and crucible vitrification. The AW-102 feed and column processing effluent underwent characterization to better define waste characteristics and assess fractionation to the CST.

5.1 Dilution

AW-102 tank waste was diluted 1.12x with 0.1 M NaOH on individual 500-mL aliquots. A nominal density of 1.27 g/mL was and achieved with a Na molarity of 5.8.

5.2 Dead-End Filtration

Diluted AW-102 supernatant was filtered through a single grade Mott 5 70-mm disc filter (DEF) in 10 discrete ~0.74-L batches. The DEF filter exhibited no measurable filtration resistance increase over the testing. No solids were observed on the filter at the completion of testing.

5.3 Batch Contact Testing

Batch contact testing with CST was conducted to determine the AW-102 Cs K_d values during kinetics and load capacity testing. The calculated ^{137}Cs K_d of 953 mL AW-102/g CST at Cs equilibrium condition of 6.21 µg Cs/mL corresponded to a predicted 50% Cs breakthrough of 953 BVs. This value was 20% lower than the extrapolated column test results. The newer CST production batch (Lot 2002009604) resulted in a higher capacity by nearly 20% than the 2012 production batch 2081000057 and indicated that the Cs effective capacity was slightly higher for the newer CST production batch.

Kinetic testing showed that Cs exchange was essentially complete between 46 and 95 h. Evaluation of the K_d values showed that residual Cs continued to be removed from solution up to 165-h contact time.

5.4 Column Testing

A total of 5 L of diluted AW-102 tank waste, consisting of 5.8 M Na and 105 µCi/mL ^{137}Cs, was processed through the Cs ion exchange system. The feed flowrate was set to 1.8 BV/h. After processing 88 BVs of feed, the lead column fluid head ran dry. A new lead column was prepared and installed. An additional 451 BVs of feed was processed through this column and resulted in a C/C_0 value of 4.3% breakthrough. Processing continued with 0.1 M NaOH FD and water rinse flowrates set to 3 and 4 BV/h, respectively. The following conclusions were made as a result of this work.

1. An 11-day stop after processing 176 BVs of AW-102 did not have an adverse effect on the functionality of the column dynamics or Cs exchange onto the CST.

2. Straight-line extrapolation on the probability-log plot from 4.3% Cs breakthrough indicated 1190 BVs would have been processed to 50% Cs breakthrough if sufficient feed was available.

3. Actual AW-102 waste Cs loading results with CST production lot 2002009604 were similar to simulant test results (Fiskum et al. 2019) with respect to the system flowrates vs. volume processed to contract limit. However, compared to AP-107 processing (Rovira et al. 2018) where CST Batch 2081000057 was used, the newer CST production lot 2002009604 demonstrated enhanced Cs retention, despite the differences in feed chemistry

4. Within analytical uncertainty, >99% of the Cs processed through the ion exchange system was collected on the CST in the columns.

5.5 Sample Analysis

1. Nominally all the Al, Cr, K, Na, P and S partitioned to the effluent. Cr partitioned almost exclusively to the effluent. As, Ba, and Cd were detected in the feed (with concentration errors likely to exceed 15%) but were below the method detection limit (MDL) in the effluent. Pb and Se were below the MDL in both the feed and the effluent; therefore, partitioning could not be assessed. U recovered 100% in effluent 1 but dropped to 68% recovery in the effluent composite. The ^{90}Sr analysis indicated nearly complete Sr removal with a DF of ~400. Only ~30% of the Pu partitioned to the composite effluent, indicating that ~70% sorbed onto the CST. Recovery of ^{99}Tc in the composite effluent showed 30% partitioned to the CST.

2. Selected lead column C samples were analyzed to examine analyte loading as a function of process volume. Both Ca and Fe increased in effluent recovery by 25% and 13%, respectively, from 11 BVs to 430 BVs. In this same loading interval, ^{137}Cs breakthrough increased by 3.5%. Al, Cr, K, Mo, Na, P, and S all remained at nominally the same concentration in the samples with increased loading.

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Appendix A – Column Load Data

The AW-102 column loading, feed displacement, and water rinse raw data are provided in Table A.1.

Table A.1. AW-102 Test Cs Load, Feed Displacement, Water Rinse, and Flush Results

Lead Column A				Lead Column C				Lag Column B				Feed Displacement and Water Rinse			
BV	µCi ^{137}Cs/ mL	% C/C$_0$	DF	BV	µCi ^{137}Cs/ mL	% C/C$_0$	DF	BV	µCi ^{137}Cs/ mL	% C/C$_0$	DF	BV	µCi ^{137}Cs/ mL	% C/C$_0$	DF
13.8	8.36E-3	7.95E-3	1.26E+04	11.1	1.18E-3	1.12E-3	8.90E+04	13.8	9.13E-4	8.67E-4	1.15E+05	FD			
44.3	1.04E-2	9.92E-3	1.01E+04	42.7	3.63E-4	3.45E-4	2.90E+05	44.1	9.75E-4	9.27E-4	1.08E+05	6.1	1.10E-3	1.04E-3	95,832
62.7	1.85E-3	1.76E-3	5.68E+04	60.8	6.71E-4	6.38E-4	1.57E+05	62.4	1.76E-4	1.67E-4	5.98E+05	DI rinse			
88.6	7.37E-4	7.00E-4	1.43E+05	86.8	2.74E-3	2.60E-3	3.84E+04	88.0	1.95E-4	1.86E-4	5.39E+05	12.8	2.62E-3	2.49E-3	40,117
				103.9	7.42E-3	7.05E-3	1.42E+04	11.0	4.66E-4	4.43E-4	2.26E+05	Flush			
				129.3	1.63E-2	1.55E-2	6.47E+03	42.5	1.46E-3	1.38E-3	7.22E+04	3.6	3.92E-1	3.72E-1	269
				146.0	2.90E-2	0.028	3.63E+03	60.4	6.32E-5	6.01E-5	1.66E+06				
				170.3	6.20E-2	0.059	1.70E+03	86.1	2.54E-3	2.41E-3	4.14E+04				
				176.2	6.13E-2	0.058	1.72E+03	103.1	4.88E-4	4.64E-4	2.15E+05				
				187.5	6.19E-2	0.06	1.70E+03	128.2	1.08E-4	1.03E-4	9.71E+05				
				206.5	9.45E-2	0.09	1.11E+03	144.7	1.15E-3	1.09E-3	9.17E+04				
				225.8	1.78E-1	0.17	5.93E+02	168.7	5.13E-4	4.87E-4	2.05E+05				
				252.5	3.04E-1	0.29	3.46E+02	174.1	1.28E-4	1.22E-4	8.19E+05				
				270.0	4.70E-1	0.45	2.24E+02	185.5	2.12E-4	2.02E-4	4.96E+05				
				298.1	7.66E-1	0.73	1.37E+02	204.3	1.23E-4	1.17E-4	8.53E+05				
				315.8	9.99E-1	0.95	1.05E+02	223.5	1.87E-4	1.78E-4	5.61E+05				
				353.2	1.50E+0	1.43	6.99E+01	249.9	1.32E-4	1.25E-4	7.99E+05				
				400.0	2.70E+0	2.56	3.90E+01	267.2	1.10E-4	1.04E-4	9.59E+05				
				433.8	3.77E+0	3.58	2.79E+01	295.1	7.91E-5	7.52E-5	1.33E+06				
				450.3	4.54E+0	4.32	2.32E+01	312.6	7.65E-5	7.27E-5	1.38E+06				
								349.7	1.33E-4	1.26E-4	7.94E+05				
								396.2	3.83E-4	3.64E-4	2.75E+05				
								429.9	1.07E-3	1.02E-3	9.80E+04				
								446.1	1.14E-3	1.08E-3	9.22E+04				

BV = bed volume; DI = deionized; DF = decontamination factor; FD = feed displacement; C$_0$ = 105.2 µCi ^{137}Cs/ mL.

Appendix B – Analytical Reports

Analytical reports provided by Analytical Support Operation are included in this appendix. In addition to the analyte results, they define the procedures used for chemical separations and analysis, as well as quality control sample results, observations during analysis, and overall estimated uncertainties. The analyses are grouped according to Analytical Service Request (ASR) number.

Table of Contents

Appendix C -Analyte Concentrations with Loading

The AW-102 load behaviors of selected load samples from the lead column are provided in Table C.1.

Table C.1. Analyte Concentrations of Selected Samples from the Lead Column

	Feed	11.1 BV	103.9 BV	206.5 BV	298.1 BV	433.8 BV
Sample ID>>	TCT008-COMP-FEED	TCT008-L-F5-A	TCT008-L-F9-A	TCT008-L-F15-A	TCT008-L-F19-A	TCT008-L-F23-A
Analyte			µg/mL			
Ca	[24]	[10]	[11]	[12]	[15]	[16]
Cd	[1.9]	--	[1.1]	--	[1.2]	[1.3]
Fe	[8.5]	[3.8]	[4.3]	[4.5]	[4.5]	[4.9]
Ti	[0.41]	[0.47]	[0.61]	[0.59]	[0.50]	[0.67]
Zr	--	[3.2]	[3.3]	[2.2]	[2.4]	[2.4]
Analyte			µg/mL			
^{137}Cs	1.05E+02	1.18E-03	7.42E-03	9.45E-02	7.66E-01	3.77E+00
^{238}Pu	8.40E-05	2.67E-05	4.16E-05	2.91E-05	4.71E-05	5.27E-05
$^{239+240}$Pu	5.66E-04	1.66E-04	2.66E-04	1.98E-04	3.26E-04	3.55E-04
^{237}Np	1.03E-05	2.76E-06	7.31E-06	8.43E-06	9.69E-06	1.01E-05

BV = bed volume; Bracketed values indicate the associated sample results were less than the estimated quantitation limit but greater than the method detection limit (MDL). Analytical uncertainty for these analytes is >±15%.
"--" = analyte was <MDL.
Additional analyte concentrations may be found in Appendix B.

**Pacific Northwest
National Laboratory**

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

www.pnnl.gov

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature Sandra Fiskum
Print Name SANDRA FISKUM
Phone 375-5677 MSIN ____

Project Number: 72335
Work Package: NC2504

Matrix Type Information

- **Liquids:** ☑ Aqueous ☐ Organic ☐ Multi-phase
- **Solids:** ☐ Soil ☐ Sludge ☐ Sediment
  ☐ Glass ☐ Filter ☐ Metal
  ☐ Smear ☐ Organic ☐ Other
- **Other:** ☐ Solid/Liquid Mixture, Slurry
  ☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

Disposal Information

- **Disposition of Virgin Samples:**
  Virgin samples are returned to requestor unless archiving provisions are made with receiving group!
  If archiving, provide:
  Archiving Reference Doc: ____
- **Disposition of Treated Samples:**
  ☑ Dispose ☐ Return

QA/Special Requirements

- **QA Plan:**
  ☑ ASO-QAP-001 (Equivalent to HASQARD)
  ☐ Additional QA Requirements, List Document Below:
  Reference Doc Number: ____
- **Field COC Submitted?** ☑ No ☐ Yes
- **Lab COC Required?** ☑ No ☐ Yes
- **Sample/Container Inspection Documentation Required?**
  ☑ No ☐ Yes
- **Hold Time:** ☑ No ☐ ***Yes***
  ***If Yes,* Contact ASO Lead before submitting Samples**
  ☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)
  ☐ Other? Specify: ____
- **Special Storage Requirements:**
  ☐ None ☐ Refrigerate ☐ Other, Specify: ____
- **Data Requires ASO Quality Engineer Review?** ☑ No ☐ Yes

Data Reporting Information

- **Is Work Associated with a Fee-Based Milestone?** ☑ No ☐ Yes
  If yes, milestone due date: ____
- **Preliminary Results Requested, As Available?** ☐ No ☑ Yes
- **Data Reporting Level**
  ☑ ASO-QAP-001 (Equivalent to HASQARD).
  ☐ Minimum data report.
  ☐ Project Specific Requirements: Contact ASO Lead or List Reference Document: ____
- **Requested Analytical Work Completion Date:** ____
  (Note: Priority rate charge for < 10 business day turn-around time)
- **Negotiated Commitment Date:** 11/27/18
  (To be completed by ASO Lead)

Waste Designation Information

- **ASO Sample Information Check List Attached?** ☐ No ☑ Yes
  If no, Reference Doc Attached: ____
  or, Previous ASR Number: ____
  or, Previous RPL Number: ____

Does the Waste Designation Documentation Indicate Presence of PCBs?
☑ **No** ☐ **Yes**

Send Report To: SK Fiskum **MSIN** ____
AM Rovira **MSIN** ____

Additional or Special Instructions ____

Receiving and Login Information *(to be completed by ASO staff)*

Date Delivered: S. Fiskum 11/1/18
Delivered By (optional) ____
Time Delivered: 12:40
Group ID (optional) ____
CMC Waste Sample? ☒ No ☐ Yes

Received By: S. Morrison
ASR Number: 0647 Rev.: 00
RPL Numbers: 19-0481 - 19-0482
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** 11/5/18

Note: Cs Isotopic Samples delivered to Lab 405 on 11/5/18

Analytical Service Request (ASR)

(REQUEST PAGE ----- Information Specific to Individual Samples)

Provide Analytes of Interest and Required Detection limits - ☐ Below ☐ Attached

ASO Staff Use Only RPL Number	Customer Sample ID	Sample Description (& Matrix, if it varies)	Analysis Requested	ASO Staff Use Only Test	ASO Staff Use Only Library
19-0481	2AW-18-04	AW102 diluted 0.5 to 10.5	GEA, ICP-OES (Na, K, Al, Cr)		
			ICP-MS (Cs-133)		
19-0482	2AW-18-23	↓	ICP-MS (Cs isotopic		

GEA sample supplied as separate aliquot w/ "GEA" extension to ID

ICP-MS (Cs-133) and ICP-OES supplied as samples with "A" extension to ID

ICP-MS (Cs isotopic) supplied w/ "Cs" extension to sample ID

Diluent is 0.5M HNO_3

Report uCi/ml + ug/ml based on the diluted sample, as-received.

ASR # ____________ Rev.: ______

Page ________ of ________

Exhibit 1. Example ASO Sample Information Checklist (SICL) Form

Sample Location, Owner and Hazard Description Information
To be completed by the sample custodian relinquishing the sample(s) and based on best available information.

ASO Customer Information:

Company: PNNL
Project #: 72335
Point of Contact (name. telephone#): Fiskum 375-5677

Comments:

Sample Description (medium, collection location, known contaminants, purpose of sample collection):

Sample Collection Date: 10/24/18 Sample Collection Time: —

Is the sample known to be radioactive? ☑ Yes ☐ No

Comments *(list known isotopes)*: AW-102 Hanford tank waste, F-listed

Is the sample known to contain or have come in contact with PCBs? ☐ Yes ☑ No

List any hazardous sample constituents known to be present:

Constituent/Chemical	**Concentration**	**Comment**

Are any other comments applicable to sample receipt, storage, handling, or disposition?

Sample diluted: 0.5 mL added to 10 mL 0.5M HNO_3.

Checklist Prepared By:

SANDRA Fiskum Sandra Fiskum 10/30/18
Printed Name Signature Date

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename 19-0481 Fiskum
12/5/2018

Client: Fiskum Project: 72335
ASR 0647 NC2504

Prepared by: LR Greenwood 12/5/18

Technical Reviewer: T Trang-le 12/5/18

Procedures:	RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS) Spectrometry
M&TE:	Gamma detectors T
Count dates:	1-Nov-18

Measured Activity, µCi/mL ± 1s

RPL ID: Sample ID: **Isotope**	19-0481 2AW-18-04		19-0482 2AW-18-23	
Cs-137	1.25E+02	± 1%	1.28E+02	± 1%

Battelle PNNL/RPL/Inorganic Analysis ... ICP-MS Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#:	72335 / NC2504
ASR#:	0647.00
Client:	S. Fiskum
Total Samples:	2 (Aqueous)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
19-0481	2AW-18-04	AW 102 diluted 0.5 to 10.5	NA
19-0482	2AW-18-23	AW 102 diluted 0.5 to 10.5	NA

Sample Preparation: Sample dilution in 2% v/v HNO_3 performed by S. Morrison on 11/09/18.

Procedure: RPG-CMC-292, Rev. 1, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)."

Analyst:	S. Morrison	**Analysis Date:**	11/09/2018	**ICP File:**	M0107

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE:				
	☒	PerkinElmer NexION™ 350X ICP-MS	SN: 85VN4070702	RPL 405
	☒	Ohaus PA224C	SN: B725287790	RPL 405
	☒	Mettler AT400 Balance	SN: M19445	RPL 405 FH
	☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☐	Ohaus EX324 Balance	SN: 8033311209	SAL Cell 2
	☐	Sartorius BA3105 Balance	SN: 10803210	RPL 309
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH

Report Preparer

11/12/2018
Date

Review and Concurrence

11/19/18
Date

Two aqueous samples submitted under Analytical Service Request (ASR) 0647.00 were analyzed by ICP-MS. Prior to analysis all samples were diluted in 2% HNO_3. None of the samples were filtered.

All results are reported on a mass per unit volume basis (ng/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-MS Data Report. Cesium-133, Cesium-135, and Cesium-137 were the AOI. The quality control (QC) results for the AOI have been evaluated and are presented below.

Calibration of the ICP-MS was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards were used to verify acceptance of the six-point calibration curve and for initial and continuing calibration verification (ICV/CCV).

The controlling document was procedure RPG-CMC-292, Rev 1, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-digestion spike, duplicate, blank spike, and serial dilution were conducted during the analysis run.

Internal Standard (IS):

All solutions (blanks, standards, QC checks, and samples) were mixed in-line with a solution containing 10 ppb of Tb-159 as the internal standard (IS). The AOI (m/z 133, 135, and 137) data were normalized using the data for the closest IS mass (e.g., Tb-159). The Tb-159 IS recoveries ranged from 94.7% to 108.8% for the entire analysis sequence, which were within the acceptance criterion of 30% to 120%.

Preparation Blank (PB):

A diluent blank from the ICP-MS laboratory (2% HNO_3) was analyzed as a preparation blank. Results for the diluent blank were within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank spike (BS) sample was prepared by spiking a 2% HNO_3 blank with an equivalent volume of the CCV-71A-2ppb standard (1:1 ratio). The recovery for the m/z 133 (98%), 135 (96%), 137 (98%) were within the acceptance criteria of 80% to 120% recovery.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

Replicates of sample 19-0482 were prepared and analyzed. RPD are listed for all analytes that were measured at or above the EQL. RPD for the m/z 133, 135, and 137 were 1%, 1%, 1%, respectively; which were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

The sample was analyzed "as received" and diluted as appropriate for analyses of the target analytes. A matrix spike sample is not generated as no sample preparation was performed. A post spike sample was analyzed and recovery results reported.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution was analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (2% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <5% of sample.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB. The recovery for m/z 133, 135, and 137 were 104%, 104%, and 104% respectfully; all within the acceptance criteria of 75% to 125%.

Interference Check Standard (ICS):

The ICS solution was analyzed immediately after the LLS solution and immediately after the final CCV solution. The recoveries for m/z 133 (100%, 98%), m/z 135 (99%, 99%), and m/z 137 (101%, 99%) which were within the acceptance criteria of 80% to 120%.

Serial Dilution (SD):

Five-fold serial dilution was conducted on samples 19-0481. Percent differences (%D) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %D for the AOI m/z 133 (2%), m/z 135 (2%), and m/z 137 (1%) were within the acceptance criterion of ≤10%, when analytes were at >10xEQL.

Post-Digestion Spike (PS-71A)/Analytical Spike (AS-71A) - Sample (71A Component):

Because no MS sample was required to be prepared, a post-digestion spike (PS-71A) was conducted on samples 19-0481. The recovery is listed for all analytes in the spike that was measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for m/z 133 and 137 were 89% and 80% respectively, and were within the acceptance criterion of 75% to 125%. Recovery value for m/z 135 was not reported.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike 71A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, and Zn. Analytes included in the spike 71B component are; Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr. Analytes included in the spike 71C component are; Ir, Os, Pd, Pt, Re, Rh, and Ru. Analytes included in the spike 71D component are; Bi, In, Li, Sc, Tb, and Y. Analytes included in the spike Hg component are; Hg.

Battelle PNNL/RPG/Inorganic Analysis ... ICP-MS Data Report

		Run Date >	09/11/18	09/11/18	09/11/18	09/11/18
		Process Factor >	1.00	125.0	125.0	125.0
		RPL/LAB >	2% HNO3 Lab Blank	19-0481	19-0481 (Dup)	19-0482
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	2AW-18-04		2AW-18-23
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
0.0003	0.0034	Cs 133	--	6.03E+02	6.08E+02	5.99E+02
0.0001	0.0006	Cs 135	--	1.63E+02	1.64E+02	1.61E+02
0.0001	0.0012	Cs 137	--	1.85E+02	1.86E+02	1.84E+02

Internal Standard % Recovery

Tb 159 (IS)	104%	103%	107%	104%

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

QC Performance 09/11/2018

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	≤ 10%
QC ID >	19-4801	BS/LCS	MS (None)	19-0481 + CCV71A	19-0481 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Diff
Cs 133	0.8%	98%		89%	2.3%
Cs 135	0.7%	96%		*nr*	2.0%
Cs 137	0.5%	98%		80%	1.2%

Internal Standard % Recovery

Tb 159 (IS)	103%	101%		105%	104%

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

na = not applicable; KOH flux and Ni crucible or Na2O2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

NM = Not measured. The isotope was not measure due to method or molecular interference limitations.

N:\Inorganic Analyses\ICP-MS NexION 350\Analysis Data\M0100-M0199\M0107 ASR-0647 Fiskum, Cs isotopes SSM 181109.xlsx

Battelle PNNL/RPL/Inorganic Analysis … ICP-MS Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#:	72335 / NC2504
ASR#:	0647.00
Client:	S. Fiskum
Total Samples:	2 (Aqueous)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
19-0481	2AW-18-04	AW 102 diluted 0.5 to 10.5	NA
19-0482	2AW-18-23	AW 102 diluted 0.5 to 10.5	NA

Sample Preparation: Sample dilution in 2% v/v HNO_3 performed by S. Morrison on 11/01/18.

Procedure: RPG-CMC-292, Rev. 1, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)."

Analyst:	S. Morrison	**Analysis Date:**	11/01/2018	**ICP File:**	M0104

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:				
	☒	PerkinElmer NexION^{TM} 350X ICP-MS	SN: 85VN4070702	RPL 405
	☒	Ohaus PA224C	SN: B725287790	RPL 405
	☒	Mettler AT400 Balance	SN: M19445	RPL 405 FH
	☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☐	Ohaus EX324 Balance	SN: 8033311209	SAL Cell 2
	☐	Sartorius BA3105 Balance	SN: 10803210	RPL 309
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH

Report Preparer — 11/05/2018
Date

Denis Cherkasov
Review and Concurrence — 11/05/18
Date

Two aqueous samples submitted under Analytical Service Request (ASR) 0647.00 were analyzed by ICP-MS. Prior to analysis all samples were diluted in 2% HNO_3. None of the samples were filtered.

All results are reported on a mass per unit volume basis (ng/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-MS Data Report. Cesium-133 was the only AOI. The quality control (QC) results for the AOI have been evaluated and are presented below.

Calibration of the ICP-MS was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards were used to verify acceptance of the six-point calibration curve and for initial and continuing calibration verification (ICV/CCV).

The controlling document was procedure RPG-CMC-292, Rev 1, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-digestion spike, duplicate, blank spike, and serial dilution were conducted during the analysis run.

Internal Standard (IS):

All solutions (blanks, standards, QC checks, and samples) were mixed in-line with a solution containing 10 ppb of Tb-159 as the internal standard (IS). The AOI (Cs-133) data were normalized using the data for the closest IS mass (e.g., Tb-159). The Tb-159 IS recoveries ranged from 93.6% to 101.9% for the entire analysis sequence, which were within the acceptance criterion of 30% to 120%.

Preparation Blank (PB):

A diluent blank from the ICP-MS laboratory (2% HNO_3) was analyzed as a preparation blank. Results for the diluent blank were within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank spike (BS) sample was prepared by spiking a 2% HNO_3 blank with an equivalent volume of the CCV-71A-2ppb standard (1:1 ratio). The recovery for the AOI was 100.4%, which is within the acceptance criteria of 80% to 120% recovery.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

Replicates of sample 19-0482 were prepared and analyzed. RPD are listed for all analytes that were measured at or above the EQL. RPD for the AOI meeting this requirement was 0.8%, which was within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

The sample was analyzed "as received" and diluted as appropriate for analyses of the target analytes. A matrix spike sample is not generated as no sample preparation was performed. A post spike sample was analyzed and recovery results reported.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution was analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (2% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB. The recovery for Cs-133 (101.0%) was within the acceptance criteria of 75% to 125%.

Interference Check Standard (ICS):

The ICS solution was analyzed immediately after the LLS solution and immediately after the final CCV solution. The recoveries for Cs-133 (100.9% and 101.1%) were within the acceptance criteria of 80% to 120%.

Serial Dilution (SD):

Five-fold serial dilution was conducted on samples 19-0482. Percent differences (%D) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %D for the AOI meeting this requirement was 1.3% and was within the acceptance criterion of ≤10%, when analytes at >10xEQL.

Post-Digestion Spike (PS-71A)/Analytical Spike (AS-71A) - Sample (71A Component):

Because no MS sample was required to be prepared, a post-digestion spike (PS-71A) was conducted on samples 19-0482. The recovery is listed for all analytes in the spike that was measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOI meeting this requirement was 99.7%, respectively, and were within the acceptance criterion of 75% to 125%.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be

quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".

3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike 71A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, and Zn. Analytes included in the spike 71B component are; Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr. Analytes included in the spike 71C component are; Ir, Os, Pd, Pt, Re, Rh, and Ru. Analytes included in the spike 71D component are; Bi, In, Li, Sc, Tb, and Y. Analytes included in the spike Hg component are; Hg.

		Run Date >	09/11/18	09/11/18	09/11/18	09/11/18
		Process Factor >	1.00	900.0	900.0	900.0
		RPL/LAB >	2% HNO3 Lab Blank	19-0481	19-0482	19-0482 (Dup)
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	2AW-18-04	2AW-18-23	
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
0.0002	0.0020	Cs 133	--	2.77E+02	2.73E+02	2.75E+02

Internal Standard % Recovery

Tb 159 (IS)	101%	95%	96%	97%

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

QC Performance 09/11/2018

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	≤ 10%
QC ID >	19-4802	BS/LCS	MS (None)	19-0482 + CCV71A	19-0482 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Diff
Cs 133	0.8%	100%		100%	1.3%

Internal Standard % Recovery

Tb 159 (IS)	96%	98%		98%	94%

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

na = not applicable; KOH flux and Ni crucible or Na2O2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

NM = Not measured. The isotope was not measure due to method or molecular interference limitations.

Battelle PNNL/RPL/Inorganic Analysis ... ICP-OES Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#:	72335 / NC2504
ASR#:	0647
Client:	S. Fiskum
Total Samples:	2 (liquids)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
19-0481	2AW-18-04	AW102 diluted 0.5 to 10.5	NA
19-0482	2AW-18-23	AW102 diluted 0.5 to 10.5	NA

Sample Preparation: Dilution of the "as received" samples in 5% v/v HNO_3 was performed by J. Carter on 11/09/18.

Procedure: RPG-CMC-211, Rev. 4, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)."

Analyst:	J. Carter	**Analysis Date:**	11/09/2018	**ICP File:**	C0775

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:			
	☒	PerkinElmer 5300DV ICP-OES	SN: 077N5122002
	☐	Sartorius ME414S Balance	SN: 22406373
	☐	Mettler AT400 Balance	SN: 1113292667
	☐	Sartorius R200D Balance	SN: 39080042
	☐	Mettler AT201 Balance	SN: 192720-92
	☒	Ohaus Pioneer PA224C	SN: B725287790
	☐	SAL Cell 2 Balance	SN: 8033311209
	☐	Lab 309 Balance	SN: 10803210

Report Preparer

11/12/18
Date

Review and Concurrence

11/28/18
Date

Two aqueous samples submitted under Analytical Service Request (ASR) 0647 were analyzed by ICP-OES. All samples were diluted in 5% HNO_3 prior to analysis. None of the samples were filtered.

All sample results are reported on a mass per unit volume basis (µg/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-OES Data Report. The quality control (QC) results for the AOI have been evaluated and are presented below. Analytes other than the AOI are reported in the bottom section of the report, but have not been fully evaluated for QC performance.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte and for continuing calibration verification.

The controlling documents were procedures RPG-CMC-211, Rev 4, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)*, and ASO-QAP-001, Rev. 11, *Analytical Support Operations (ASO) Quality Assurance Plan.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-digestion spikes, duplicate, blank spike, and serial dilution were conducted during the analysis run.

Preparation Blank (PB):

No preparation blank was required to be prepared for the samples. The ICP-OES laboratory diluent (5% HNO_3) was analyzed as a blank. All AOI were within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples

Blank Spike (BS)/Laboratory Control Sample (LCS):

A 50:50 mixture of the MCVA and MCVB solutions was analyzed as the blank spike. Recovery values are listed for all analytes included in the BS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement ranged from 100% to 102%, and were within the acceptance criterion of 80% to 120%.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

Replicates of samples 19-0481 was prepared and analyzed. RPD are listed for all analytes that were measured at or above the EQL. RPD for the AOI meeting this requirement ranged from 0.3% to 3.0% and were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

The sample was analyzed "as received" and diluted as appropriate for analyses of the target analytes. A matrix spike sample is not generated as no sample preparation was performed. A post spike sample was analyzed and recovery results reported.

Initial/Continuing Calibration Verification (ICV/CCV):

MCVA and MCVB solutions were analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (5% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL, with the exception of the two final CCB solutions that exhibited carryover sodium concentrations (0.133 and 0.120 µg/mL) slightly above EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130% recovery.

Interference Check Standard (ICS/SST):

The ICS solution was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCV solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-0481. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %Ds for the AOI meeting this requirement ranged from 1.0% to 12.2% and were within the acceptance criterion of ≤10%, with the exception of potassium (12.2%).

Post-Digestion Spike (PS-A)/Analytical Spike (AS-A) - Sample (A Component):

In addition to the BS sample, a post-digestion spike (A Component) was conducted on sample 19-0481. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOI meeting this requirement ranged from 103% to 114%, and were within the acceptance criterion of 80% to 120%.

Post-Digestion Spike (PS-B)/Analytical Spike (AS-B) - Sample (B Component):

In addition to the BS sample, a post-digestion spike (B Component) was conducted on sample 19-0481. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. There were no AOI included in the spike B Component.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 5% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	11/9/2018	11/9/2018	11/9/2018	11/9/2018
		Process Factor >	1.0	20.0	20.0	20.0
			405 diluent	19-0481 @ 20x	19-0481 @ 20x rep	19-0482 @ 20x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	2AW-18-04	2AW-18-04	2AW-18-23
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0038	0.038	Al	--	721	703	710
0.0016	0.016	Cr	--	30.6	30.5	30.8
0.0262	0.262	K	--	338	328	335
0.0075	0.075	Na	[0.029]	6,930	6,910	6,820
Other Analytes						
0.0014	0.014	Ag	--	--	--	[0.043]
0.0383	0.383	As	--	--	--	[0.85]
0.0032	0.032	B	[0.020]	1.52	1.56	1.49
0.0001	0.001	Ba	--	0.0405	0.0389	0.0392
0.0001	0.001	Be	--	[0.0086]	[0.0095]	[0.0099]
0.0220	0.220	Bi	[0.028]	--	--	--
0.0054	0.054	Ca	--	2.39	2.41	1.84
0.0016	0.016	Cd	--	[0.12]	[0.11]	[0.11]
0.0052	0.052	Ce	--	[0.18]	[0.14]	[0.20]
0.0033	0.033	Co	--	--	--	--
0.0023	0.023	Cu	--	[0.12]	[0.11]	[0.083]
0.0012	0.012	Dy	--	--	--	--
0.0006	0.006	Eu	--	--	--	--
0.0033	0.033	Fe	[0.0042]	[0.44]	[0.54]	[0.41]
0.0010	0.010	La	--	--	--	[0.021]
0.0010	0.010	Li	--	[0.028]	--	[0.024]
0.0014	0.014	Mg	--	--	--	--
0.0003	0.003	Mn	--	--	[0.0069]	[0.0068]
0.0048	0.048	Mo	--	1.98	1.98	1.95
0.0095	0.095	Nd	--	--	--	--
0.0040	0.040	Ni	--	1.16	1.15	1.21
0.0369	0.369	P	--	46.8	46.8	46.9
0.0144	0.144	Pb	--	[1.1]	[0.57]	[0.69]
0.0082	0.082	Pd	--	--	--	--
0.0108	0.108	Rh	--	[0.33]	--	[0.28]
0.0068	0.068	Ru	--	[0.24]	[0.27]	[0.25]
0.0898	0.898	S	--	64.7	65.9	63.2
0.0569	0.569	Sb	--	--	--	--
0.0876	0.876	Se	--	--	--	--
0.0043	0.043	Si	[0.0083]	2.55	2.65	2.69
0.0195	0.195	Sn	--	[0.52]	--	[0.52]
0.0001	0.001	Sr	[0.0001]	[0.0065]	[0.0075]	[0.0063]
0.0109	0.109	Ta	--	--	--	--
0.0155	0.155	Te	--	--	--	--
0.0057	0.057	Th	--	--	--	--
0.0004	0.004	Ti	[0.0004]	[0.010]	--	--
0.0310	0.310	Tl	--	--	--	--
0.0312	0.312	U	--	[1.2]	[1.2]	[0.98]
0.0016	0.016	V	--	[0.043]	--	[0.041]
0.0187	0.187	W	--	[3.2]	[3.0]	[3.1]
0.0003	0.003	Y	--	--	--	--
0.0023	0.023	Zn	--	1.12	1.13	0.966
0.0013	0.013	Zr	[0.0015]	[0.062]	[0.069]	[0.061]

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

QC Performance 11/9/2018

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	19-0481 Dup	LCS/BS	MS (none)	19-0481 + PS-A	19-0481 + AS-B	19-0481 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	2.5	102		105		1.0
Cr	0.4	102		103		3.5
K	3.0	100		114		12.2
Na	0.3	101		103		1.2
Other Analytes						
Ag		100		98		
As		105		106		
B	2.7	105		105		
Ba	4.1	101		101		
Be		99		99		
Bi		92		99		
Ca	0.9	105		111		
Cd		99		104		
Ce		102			103	
Co		101		102		
Cu		102		106		
Dy		100			102	
Eu		98			101	
Fe		101		103		
La		97			101	
Li		112		116		
Mg		102		105		
Mn		104		105		
Mo	0.0	99		101		
Nd		100			101	
Ni	1.0	104		104		
P	0.1	103		104		0.4
Pb		101		101		
Pd		92			96	
Rh		101			102	
Ru		98			100	
S	1.9	98			99	
Sb		107		108		
Se		101		104		
Si	3.8	100		110		
Sn		101		104		
Sr		101		99		
Ta		99		102		
Te		98			100	
Th		98			103	
Ti		101		102		
Tl		95		96		
U		104			106	
V		97		100		
W		103		105		
Y		98		100		
Zn	1.6	98		103		
Zr		100		102		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature Sandra Fiskum
Print Name SANDRA A FISKUM
Phone ______ MSIN ______

Project Number: 73325
Work Package: NC2504

Matrix Type Information

- **Liquids:** ☑ Aqueous ☐ Organic ☐ Multi-phase
- **Solids:** ☐ Soil ☐ Sludge ☐ Sediment
  ☐ Glass ☐ Filter ☐ Metal
  ☐ Smear ☐ Organic ☐ Other
- **Other:** ☐ Solid/Liquid Mixture, Slurry
  ☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

Disposal Information

- **Disposition of Virgin Samples:**
  Virgin samples are returned to requestor unless archiving provisions are made with receiving group!
  If archiving, provide:
  Archiving Reference Doc: ______
- **Disposition of Treated Samples:**
  ☑ Dispose ☐ Return

QA/Special Requirements

- **QA Plan:**
  ☑ ASO-QAP-001 (Equivalent to HASQARD)
  ☐ Additional QA Requirements, List Document Below:
  Reference Doc Number: ______
- **Field COC Submitted?** ☑ No ☐ Yes
- **Lab COC Required?** ☑ No ☐ Yes
- **Sample/Container Inspection Documentation Required?**
  ☑ No ☐ Yes
- **Hold Time:** ☑ No ☐ *Yes*
  If *Yes*, Contact ASO Lead before submitting Samples
  ☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)
  ☐ Other? Specify: ______
- **Special Storage Requirements:**
  ☑ None ☐ Refrigerate ☐ Other, Specify: ______
- **Data Requires ASO Quality Engineer Review?** ☑ No ☐ Yes

Data Reporting Information

- **Is Work Associated with a Fee-Based Milestone?** ☑ No ☐ Yes
  If yes, milestone due date: ______
- **Preliminary Results Requested, As Available?** ☐ No ☑ Yes

- **Data Reporting Level**
  ☑ ASO-QAP-001 (Equivalent to HASQARD).
  ☐ Minimum data report.
  ☐ Project Specific Requirements:
  Contact ASO Lead or List Reference Document: ______

- **Requested Analytical Work Completion Date:** 4/3/2019
  (Note: Priority rate charge for < 10 business day turn-around time)
- **Negotiated Commitment Date:** 4/18/19
  (*To be completed by ASO Lead*)

Waste Designation Information

- **ASO Sample Information Check List Attached?** ☑ No ☐ Yes
  If no, Reference Doc Attached: ______
  or, Previous ASR Number: 0707
  or, Previous RPL Number: ______

Does the Waste Designation Documentation Indicate Presence of PCBs?
☑ **No** ☐ **Yes**

Send Report To: SK Fiskum **MSIN** ______
AM Rovira **MSIN** ______
Additional or Special Instructions ______

Receiving and Login Information (*to be completed by ASO staff*)

Date Delivered: 2/27/19
Delivered By (optional) S. Fiskum
Time Delivered: 09:35
Group ID (optional) ______
CMC Waste Sample? ☒ No ☐ Yes

Received By: L. P. Darnell
ASR Number: 0731 Rev.: 00
RPL Numbers: 19-1107-7 19-1114
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** 3/1/19

Analytical Services Request (ASR)

(REQUEST PAGE ---- Information Specific to Individual Samples)

ASO Staff Use Only	Provide Analytes of Interest and Required Detection limits - ☐ Below ☐ Attached			ASO Staff Use Only	
RPL Number	Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	**Test**	**Library**
19-1107	TCT008-COMP-FEED	AW-102 Tank Waste	1) GEA - All samples (Cs-137 and any other observed gamma emitting isotopes) 2) Tc-99 3) IC-Anions - NO_2, NO_3, PO_4, C_2O_4 and SO_4 4) TOC/TIC - Hot Pursulfate 5) OH 7) Acid Digestion- 128 - Prep Lab a) ICP/OES - Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, P, Pb, S, Sr, Ti, Zn, Zr b) ICP/MS - Cs-133 and Total U c) Sr-90 d) Np-AEA, Np-237 e) Pu-AEA, Pu-238, Pu-239/240		
19-1108	TCT008-EFF-1	AW-102 Tank Waste - Cs Removed	1) GEA - All samples (Cs-137 and any other observed gamma emitting isotopes) 2) Tc-99 3) Acid Digestion- 128 - Prep Lab a) ICP/OES - Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, P, Pb, S, Sr, Ti, Zn, Zr b) ICP/MS - Total U c) Pu-AEA, Pu-238, Pu-239/240 d) Np-AEA, Np-237		
19-1109	TCT008-COMP-EFF				

ASR: 0731 Rev: 00

Analytical Services Request (ASR)

(REQUEST PAGE ---- Information Specific to Individual Samples)

Provide Analytes of Interest and Required Detection limits - ☐ **Below** ☐ **Attached**

ASO Staff Use Only **RPL Number**	Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	ASO Staff Use Only **Test**	ASO Staff Use Only **Library**
19-1110	TCT008-L-F5-A	AW-102 Tank Waste - Cs Removed	1) Acid Digest - 128 - Prep Lab a) ICP/OES - Ca, Cd, Fe, Ti, Zr b) ICP/MS - Total U c) Pu-AEA, Pu-238, Pu-239/240 d) Np-AEA, Np-237		
19-1111	TCT008-L-F9-A				
19-1112	TCT008-L-F15-A				
19-1113	TCT008-L-F19-A				
19-1114	TCT008-L-F23-A				

Page 2 of 2

ASR: 0731 Rev: 00

Gamma Energy Analysis (GEA)

Project / WP#:	73325/ NC2504
ASR#:	0731.00
Client:	SK Fiskum
Total Samples:	3

RPL ID	Client Sample ID
19-1107	**TCT008-COMP-FEED**
19-1108	**TCT008-EFF-1**
19-1109	**TCT008-COMP-EFF**

Analysis Type:	GEA- for all positively measured or non-detected isotopes
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-129, Rev. 0 *HNO_3-HCl Acid Extraction of Solids Using a Dry Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other: Preparation may also involve attaining a GEA geometry that is compatible with the calibration geometry.
Analysis Procedure:	RPG-CMC-450, Rev. 3 *Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)*
Reference Date:	3/6/2019
Analysis Date or Date Range:	March 6-7, 2019
Technician/Analyst:	T Trang-Le
Rad Chem Electronic Data File:	*19-1107 Fiskum.xls*
ASO Project 98620 File:	*File Plan 5872, Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and standard certificates and preparation. Also, balance calibration and performance check records.*
M&TE Number(s):	*Detectors L,M,T*

T Trang-le / 3/19/19
Prepare **Date**

/ 3/19/19
Reviewer **Date**

SAMPLE RESULTS

Activities for all gamma emitters detected in these samples are presented in an attached Excel spreadsheet for 0731.00. Cs-137 was the only detectable activity in sample TCT008-COMP-FEED. The effluent samples also showed the presence of Co-60, Sn/Sb-126, Eu-152, Eu-154, and Am-241.

ASO Project File, ASR 0731.00 has been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form, standard certificates, laboratory bench records, Shielded Analytical Laboratory Bench Sheet, and Gamma Energy Analysis printouts. Detector calibration records, control charts and balance calibration records can be found in the ASO Records.

Sample Preparation, Separation, Mounting and Counting Methods

The quality control (QC) sample results for each of the isotopes measured above background have been evaluated and are discussed below. A summary of the GEA analysis results, including QC sample performance, is given in the attached Data Report.

QUALITY CONTROL RESULTS

Tracer:

Tracers are not used for ASO Gamma Energy Analysis (GEA) methods.

Process Blank (PB):

No process blank was prepared for gamma counting.

Required Detection Limits

There are no required detection limit requirements for these samples.

Blank Spike (BS)/Laboratory Control Sample (LCS)/ Matrix Spike (MS):

There are no BS, LCS or MS QC samples analyzed for ASO GEA analyses. Instrument performance is assessed by the analyses of daily control counts and weekly background counts, as discussed below.

Duplicate Relative Percent Difference (RPD):

No duplicate samples were provided for gamma counting.

Instrument Calibration and Quality Control

Gamma detectors are calibrated using multi-isotope standards that are NIST-traceable and prepared in the identical counting geometry to all samples and detectors, if possible. Counter control sources containing Am-241, Cs-137 and Co-60 are analyzed daily before the use of each detector. Procedure RPG-CMC-450 requires that a counter control source is checked daily and must be within ±3 sigma or ±3% of the control value, whichever is greater. Gamma counting was not performed unless the control counts were within the required limits. Background counts are performed on all gamma detectors at least weekly for either an overnight or weekend count within operational limits, and/or when system background is thought to have changed. The most recent background is subtracted from all sample counts.

The samples were prepared in a 2 mL geometry in lab 420.

Assumptions and Limitations of the Data

None

Interferences/Resolution

None.

Uncertainty

For gamma counting, the uncertainty in the counting data, photon abundance and the nuclear half-life, and efficiency are included in the calculation of the total uncertainty along with a systematic uncertainty for sample prep. The Canberra Genie software includes both random and systematic uncertainties in the calculation of the total uncertainties which are listed on the report. We conservatively estimate that 2% is the lowest uncertainty possible for our GEA measurements taking into account systematic uncertainties in gamma calibration standards. This uncertainty assumes the sample geometry matches the calibration geometry, and is undoubtedly larger when the sample geometry does not match a calibration geometry.

Comments

None.

Attachment: Data Report Sample Results for ASR 0731.00.

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
3/15/2019

Client: Fiskum	Project: 73325	Prepared by: T Trang-le 3/15/19
ASR 0731	NC2504	
		Technical Reviewer: LRGreenwood 3/19/19

Procedures: RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS) Spectrometry

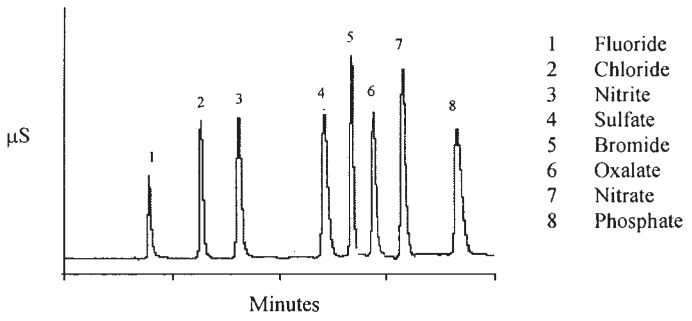
M&TE: Gamma detectors L,M,T
Reference dates: 3/6/2019 @ 9:00 am

Measured Activity, µCi per mL ± 1s

RPL ID:	19-1107		19-1108		19-1109	
Sample ID:	TCT008-COMP-FEED		TCT008-EFF-1		TCT008-COMP-EFF	
Isotope						
Co-60	<7.1E-04		**4.00E-04**	**± 2%**	**4.22E-04**	**± 2%**
Sn-126	<3.1E-02		**2.16E-04**	**± 9%**	**2.58E-04**	**± 4%**
Sb-126	<2.7E-03		**2.43E-04**	**± 2%**	**2.94E-04**	**± 2%**
Cs-137	**1.15E+02**	**± 2%**	**1.37E-04**	**± 2%**	**2.00E-04**	**± 2%**
Eu-152	<2.0E-03		<5.0E-06		**2.35E-06**	**± 15%**
Eu-154	<2.9E-03		**4.06E-05**	**± 2%**	**4.59E-05**	**± 2%**
Am-241	<1.9E-01		**9.82E-05**	**± 13%**	**1.23E-04**	**± 4%**

Battelle - Pacific Northwest National Laboratory
Analytical Support Operations – IC Report
PO Box 999, Richland, Washington 99352

Common Inorganic Anions
Dionex AS18 Column; Hydroxide Gradient



Client: S. Fiskum
ASR #: 0731
Project #: 73325
 # Samples: 1 liquids
Charge Code: NC2504

*** RPL Number: 19-1107 ***

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPG-CMC-212 Rev.2, "Determination of Common Anions by Ion Chromatography"
Prep Procedure	NA
Analyst	JC Carter
Analysis Dates	03-18-19 through 03-27-19
Calibration Date	03-18-19
Cal/Ver Stds Prep Date	03-18-19
Excel Data File	IC 0242 Fiskum ASR 0731 Results.xls
M&TE Numbers	IC System (M&TE) WD81499
	Balance: 39080042
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0242)

Prepared By 3/29/19
Date

Reviewed By 5/2/19
Date

IC Report

Sample Results

See Attachment: Sample Results ASR 0731

Sample Analysis/Results Discussion

One liquid sample was submitted to the Analytical Support Operations (ASO) laboratory for ion chromatography analysis under ASR 0731. The results are discussed in this report. The analytes of interest include sulfate, nitrite, nitrate, oxalate and phosphate. The dilutions were prepared using deionized water and the water was analyzed as the 'Dilution Blank" sample. The sample results are reported in µg/mL and have been adjusted for analytical dilutions.

The estimated method detection limits (MDL) are provided for each analyte of interest measured and the MDLs have been adjusted for all analytical dilutions and processing factors. The MDLs are set at one-tenth the lowest calibration standard, which is defined as the estimated quantitation limit (EQL).

Data Limitations

The oxalate result was below the acceptance criteria in the laboratory control sample. This is indicative of oxalate instability specific to this solution. The oxalate results passed for all continuing calibration verification standards for this batch. All other QC requirements were met.

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by the Analytical Support Operations QA Plan ASO-QAP-001 and in procedure, RPG-CMC-212 Rev.2.

IC Workstation QC Results

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001 and in procedure, RPG-CMC-212 Rev.2.

Process Blank (Dilution Blank): No analytes of interested were detected, thus meeting the ASO's QA Plan acceptance criteria of all analytes being <EQL.

Duplicate: All samples were analyzed in duplicate. The relative percent difference (RPD) is reported for all analytes which were measured at or above the EQL. The reported RPDs ranged from 1 to 6% for all analytes of interest, which meets the ASO's QA Plan acceptance criteria of ≤20% for liquid samples.

Laboratory Control Sample (LCS): A routine instrument LCS was analyzed with recoveries, except oxalate, ranging from 89% to 93%, meeting the QA Plan acceptance criteria of 80% to 120%. The oxalate instrument LCS recovered at 33%. (See data limitations above)

Analytical Spike (AS) (Accuracy): Analytical spikes were prepared using all prepared dilutions of the one liquid sample by adding a known concentration of mid-range multi-mix standard, "CCV 031819". The results for the spiked 15606x dilutions are reported. Where the spiking concentration exceeds 20% of the sample concentration, the AS recoveries meet the QA Plan acceptance criteria of 75% to 125%.

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed each run day. Results for the IC System QC samples (that bound the reported results for each analyte of interest) are within acceptance criteria of the ASO's QA Plan (i.e., verification standard recoveries from 90% to 110% and verification blank results <EQL or ≤5% of reported sample result).

Deviations from Procedure

None

General Comments

- The reported "Final Results" have been corrected for all dilutions performed on the sample during processing or analysis.
- For each anion, the instrument EQL is defined as the concentration of the lowest calibration standard and the instrument MDL is set at one-tenth of the EQL. The MDLs and EQLs reported for each sample are adjusted for the sample dilution factors (processing and analysis) and assume non-complex aqueous matrices. Matrix-specific MDLs or EQLs may be determined, when requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference.

Sample Results ASR-0731

		NO_2			SO_4			C_2O_4			NO_3			PO_4		
RPL Number	**Client Sample ID**	**MDL µg/mL**	**Result µg/mL**	**DF**	**MDL µg/mL**	**Result µg/mL**	**DF**	**MDL µg/mL**	**Result µg/mL**	**DF**	**MDL µg/mL**	**Result µg/mL**	**DF**	**MDL µg/mL**	**Result µg/mL**	**DF**
Diltution Blank	Dilution Blank	0.1	0.1	U	0.15	0.15	U	0.1	0.1	U	0.2	0.2	U	0.12	0.12	U
19-1107	TCT008-COMP-FEED	780	53400		31	2400		20	324		1600	108000		25	2210	

Sample QC Results ASR-0731

Sample/Replicate Precision Results

		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	**Sample ID**	**µg/mL**	**RPD**	**µg/mL**	**RPD**	**µg/mL**	**RPD**	**µg/mL**	**RPD**	**µg/mL**	**RPD**
19-1107	Sample	53400	--	2400	--	324	--	108000	--	2210	--
	Duplicate | RPD	53200	<1	2430	1	304	6	109000	1	2150	3

Sample Spike Results - At IC Workstation

		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	**Sample ID**	**µg/mL**	**%Rec**	**µg/mL**	**%Rec**	**µg/mL**	**%Rec**	**µg/mL**	**%Rec**	**µg/mL**	**%Rec**
19-1107	Sample	53400	--	2400	--	324	--	108000	--	2210	--
		5.4	100	2.9	90	1.8	91	10.3	97	2.4	90

LCS/Blank Spike Results

Run ID	**Sample ID**	**F % Rec**	**Cl % Rec**	**NO_2 % Rec**	**SO_4 % Rec**	**Br % Rec**	**C_2O_4 % Rec**	**NO_3 % Rec**	**PO4 % Rec**
3/26/2019 18:20	LCS 031819	95.3	90.6	92.5	90.0	84.4	33%	87.1	89.7

AS = Analytical Spike: Spike performed at IC Workstation on Liquid Samples.
LCS = Laboratory Control Sample (or Blank Spike)
RPD = Relative Percent Difference
%Rec = Percent Recovery
DF = Data Quality Flag
U = Not Detected Above Method Detection Limit (MDL)
J = Detected, Result are Qualitative: Result >MDL but <EQL (Estimated Quantitation Limit)
-- = Value Not Calculated or Place Holder for Blank Cell

Project / WP#:	73325 / NC2504
ASR#:	0731
Client:	S. Fiskum
Total Samples:	8 (Aqueous)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
19-1107	TCT008-COMP-FEED	AW-102 Tank Waste	NA
19-1108	TCT008-EFF-1	AW-102 Tank Waste Cs Removed	NA
19-1109	TCT008-COMP-EFF	AW-102 Tank Waste Cs Removed	NA
19-1110	TCT008-L-F5-A	AW-102 Tank Waste Cs Removed	NA
19-1111	TCT008-L-F9-A	AW-102 Tank Waste Cs Removed	NA
19-1112	TCT008-L-F15-A	AW-102 Tank Waste Cs Removed	NA
19-1113	TCT008-L-F19-A	AW-102 Tank Waste Cs Removed	NA
19-1114	TCT008-L-F23-A	AW-102 Tank Waste Cs Removed	NA

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater", performed by L. Darnell on 3/7/2019 & 3/8/2019, dilution of Sample 17-1242 in deionized water performed by L. Grow on 8/17/17, and ICP-MS bench dilution in 2% v/v HNO_3 performed by S.S. Morrison on 3/15/19 & 3/28/19, respectively.

Procedure: RPG-CMC-292, Rev. 1, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)."

Analyst:	S.S. Morrison	**Analysis Date:**	03/28/2019	**ICP File:**	M0141

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:				
	☒	PerkinElmer NexION^{TM} 350X ICP-MS	SN: 85VN4070702	RPL 405
	☒	Ohaus PA224C Balance	SN: B725287790	RPL 405
	☒	Mettler AT400 Balance	SN: M19445	RPL 405 FH
	☒	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☒	Ohaus EX324 Balance	SN: 8033311209	SAL Cell 2
	☒	Sartorius BA3105 Balance	SN: 10803210	RPL 309
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH
	☐			

SSM — 04/02/2019

Report Preparer — Date

03-Apr-2019

Review and Concurrence — Date

Eight aqueous samples submitted under Analytical Service Request (ASR) 0731 were analyzed by ICP-MS. Sample 19-1109 was prepared in duplicate following RPL procedure RPG-CMC-128 by diluting 1 mL to approximately 25 mL. Prior to analysis all samples were further diluted in 2% HNO_3. None of the samples were filtered.

All results are reported on a mass per unit volume basis (ng/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-MS Data Report. Total U was the analyte of interest for samples 19-1107 to 19-1114; Cs was the analyte of interest for sample 19-1107 only. For the total Uranium analysis U-238 was used with a correction for isotopic abundance, standards were depleted Uranium and samples 19-1107 to 19-1114 were natural Uranium isotopics. The quality control (QC) results for the AOI have been evaluated and are presented below.

Calibration of the ICP-MS was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards were used to verify acceptance of the six-point calibration curve and for initial and continuing calibration verification (ICV/CCV).

The controlling document was procedure RPG-CMC-292, Rev 0, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)* and ASO-QAP-001, Rev. 11, *Analytical Support Operations (ASO) Quality Assurance Plan.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-digestion spike, duplicate, blank spike, and serial dilution were conducted during the analysis run.

Internal Standard (IS):

All solutions (blanks, standards, QC checks, and samples) were mixed in-line with a solution containing 10 ppb each of Li-6, Sc-45, Y-89, In-115, Tb-159, and Bi-209 as the internal standard (IS). The AOI data were normalized using the IS mass (e.g., Bi-209). The Bi-209 IS recoveries ranged from 73.1% to 108.1%, which were within the acceptance criterion of 30% to 120%.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the dissolution process. The concentration of Cs and U were within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples. The concentration of Cs was below the IDL (10%EQL) and the U concentration was below the EQL but above the IDL.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank spike (BS) sample was during dissolution with 1 mL of BPNL-QC-1A. The recovery for U was 106%, which is within the acceptance criteria of 80% to 120% recovery. An additional blank spike was prepared with 2% HNO_3 acid and 1 mL of CCV-

71A, the recovery of Cs was 92% and the recovery of U was 98%, which is within the acceptance criteria of 80% to 120% recovery.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

A duplicates of sample 19-1109 was prepared. No RPD was listed for Cs since the Cs was below EQL. The RPD for U was 1.2% which is within the acceptance criterion of ≤20% RPD for liquid samples.

Matrix-Spike (MS) Sample:

A matrix spike was prepared during dissolution with 1 mL of BPNL-QC-1A. There is no Cs present in the BPNL-QC-1A spike solution and therefore, the Cs was below EQL in the sample solution. The recovery of Uranium was 98% which is within the acceptance criterion of 75% to 125% recovery.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution was analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (2% HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130% recovery.

Interference Check Standard (ICS):

The ICS solution was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCV solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-1109. Percent differences (%D) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The Cs was below the EQL. The percent difference was 0.4% for the Uranium; which is within the acceptance criterion of ≤10%.

Post-Digestion Spike (PS-71)/Analytical Spike):

A post spike sample was prepared for sample 19-1109 with the addition of CCV-71A. The recovery of Cs was 96%, and for U was 101% which met the acceptance criterion of 80% to 120%.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 50 µg/mL (0.005 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike 71A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, and Zn. Analytes included in the spike 71B component are; Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr. Analytes included in the spike 71C component are; Ir, Os, Pd, Pt, Re, Rh, and Ru. Analytes included in the spike 71D component are; Bi, In, Li, Sc, Tb, and Y. Analytes included in the spike Hg component are; Hg.

		Run Date >	03/28/19	03/28/19	03/28/19	03/28/19	03/28/19	03/28/19	03/28/19	03/28/19	03/28/19	03/28/19
		Process Factor >	745.07	3782.21	748.02	3695.21	3755.04	733.64	3698.89	3750.57	3726.14	3740.09
		RPL/LAB >	19-1107 BLK	19-1107	19-1108	19-1109	19-1109 DUP	19-1110	19-1111	19-1112	19-1113	19-1114
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	19-1107 BLK	TCT008-COMP-FEED	TCT008-EFF-1	TCT008-COMP-EFF		TCT008-L-F5-A	TCT008-L-F9-A	TCT008-L-F15-A	TCT008-L-F19-A	TCT008-L-F23-A
(ug/mL)	(ug/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
6.23E-07	6.23E-06	Cs	--	4.9E+00	--	--	--	--	--	--	--	--
9.18E-07	9.18E-06	U	2.95E-03	1.78E+01	1.71E+00	1.23E+01	1.26E+01	3.28E+00	1.50E+01	1.44E+01	1.78E+01	1.86E+01

Internal Standard % Recovery

Bi 209 (IS)	106%	103%	87%	102%	104%	73%	90%	90%	94%	95%

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

QC Performance 3/28/2019

Criteria >	≤ 20%	80%-120%	80%-120%	75%-125%	75%-125%	≤ 10%
QC ID >	19-1109 DUP	19-1107 Reagent Spike	Blank Spike 71-A	19-1107 Matrix Spike	19-1109 + CCV 71-A	19-1109 Serial Dilution (5x)
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Cs	--	--	92%	--	96%	--
U	1.2%	106.3%	98.4%	97.7%	100.7%	0.4%

Internal Standard % Recovery

Bi 209 (IS)	104%	97%	100%	102%	100%	103%

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

na = not applicable; KOH flux and Ni crucible or Na2O2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

NM = Not measured. The isotope was not measure due to method or molecular interference limitations.

Battelle PNNL/RPL/Inorganic Analysis ... ICP-OES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 73325 / NC2504
ASR#: 0731
Client: S. Fiskum
Total Samples: 8 (liquids)
Sample Description AP-107 Tank Waste

ASO Sample ID	Client Sample ID	Sample Weight (g)
19-1107	TCT008-COMP-FEED	NA
19-1108	TCT008-EFF-1	NA
19-1109	TCT008-COMP-EFF	NA
19-1110	TCT008-L-F5-A	NA
19-1111	TCT008-L-F9-A	NA
19-1112	TCT008-L-F15-A	NA
19-1113	TCT008-L-F19-A	NA
19-1114	TCT008-L-F23-A	NA

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater", performed by L. Darnell on 03/07/19 and 03/08/19. Simple dilution of "as received" samples in 5% v/v HNO_3 performed by J. Carter on 04/02/19.

Procedure: RPG-CMC-211, Rev. 4, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)."

Analyst:	J. Carter	**Analysis Date:**	04/02/19	**ICP File:**	C0787

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:	☒	PerkinElmer 5300DV ICP-OES	SN: 077N5122002
	☒	Mettler AT400 Balance	SN: 1113292667
	☒	Ohaus PA224C Balance	SN: B725287790
	☐	Sartorius R200D Balance	SN: 39080042
	☐	SAL Cell 2 Balance	SN: 8033311209

Report Preparer — Date: 4/8/19

Review and Concurrence — Date: 4/9/2019

Eight aqueous samples submitted under Analytical Service Request (ASR) 0731 were analyzed by ICP-OES. The samples were prepared following RPL procedure RPG-CMC-128, Rev. 1, "*HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*". All samples were diluted in 5% HNO_3 prior to analysis. None of the samples were filtered.

All sample results are reported on a mass per unit volume basis (μg/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-OES Data Report. There were two analyte lists requested. Samples were divided between those two lists and a separate data report is provided for each. The quality control (QC) results for the AOI have been evaluated and are presented below. Analytes other than the AOI are reported in the bottom section of the report but have not been fully evaluated for QC performance.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte and for continuing calibration verification.

The controlling documents were procedures RPG-CMC-211, Rev. 4, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)*, and ASO-QAP-001, Rev. 11, *Analytical Support Operations (ASO) Quality Assurance Plan.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), matrix spike, post-digestion spikes, duplicate, reagent spike, blank spike, and serial dilution were conducted during the analysis run.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the extraction process. Two analytes (Ba and Zn) were above EQL. Remaining analytes were within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤10% of the concentration in the samples. The lab diluent passed these criteria.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A reagent spike (RS) sample (reagents and spikes) was prepared for the extraction process. Recovery values are listed for all analytes included in the RS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement and within the acceptance criterion of 80% to 120%, ranged from 90% to 114%. Zn failed at 137%. The reason for Za failure is unknown.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

A duplicate of sample 19-1107 was prepared and analyzed. RPDs are listed for all analytes that were measured at or above the EQL. RPDs for the AOI meeting this requirement ranged from 0.1% to 4.6% and were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

A matrix spike (MS) of sample 19-1109 was prepared for the extraction process. Recovery values are listed for all analytes included in the MS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement ranged from 99% to 115% and were within the acceptance criterion of 75% to 125%, with the exception of K (126%).

Initial/Continuing Calibration Verification (ICV/CCV):

MCVA and MCVB solutions were analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery, with the exception of strontium (115%) in the final CCV solution. Strontium was not present in any of the samples submitted.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (5% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130% recovery.

Interference Check Standard (ICS/SST):

The ICS solution was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCV solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-1107. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %Ds for the AOI meeting this requirement ranged from 0.7% to 3.6% and were within the acceptance criterion of ≤10%.

Post-Digestion Spike (PS-A) - Sample (A Component):

In addition to the BS sample, a post-digestion spike (A Component) was conducted on sample 19-1107. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOI meeting this requirement ranged from 100% to 109% and were within the acceptance criterion of 80% to 120%.

Post-Digestion Spike (PS-B) - Sample (B Component):

In addition to the MS sample, a post-digestion spike (B Component) was conducted on sample 19-1107. The recovery value is listed for the analyte in the spike that was measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. The recovery value for the AOI meeting this requirement 94% for sulfur and was within the acceptance criterion of 80% to 120%.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 5% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	4/3/2019	4/3/2019	4/3/2019	4/3/2019	4/3/2019	4/3/2019
		Process Factor >	1.0	24.8	504.2	498.6	492.6	500.6
			405 diluent	BLK-1107	19-1107 @ 20x	19-1108 @ 20x	19-1109 @ 20x	Dup-1109 @ 20x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagents Only	TCT008-COMP-FEED	TCT008-EFF-1	TCT008-COMP-EFF	
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0122	0.122	Al	[0.019]	[1.9]	13,300	11,656	12,500	12,600
0.0529	0.529	As	--	--	--	--	--	--
0.0003	0.003	Ba	--	0.0984	[0.51]	--	--	--
0.0177	0.177	Ca	--	[0.62]	[24]	[19]	[9.2]	[9.0]
0.0022	0.022	Cd	--	--	[1.9]	--	[1.7]	[1.3]
0.0025	0.025	Cr	--	[0.081]	592	513	554	554
0.0052	0.052	Fe	[0.0098]	[0.50]	[8.5]	[5]	[3.5]	[4.3]
0.0240	0.240	K	[0.031]	[5.4]	5,990	4,964	5,610	5,700
0.0246	0.246	Na	--	[1.1]	134,000	117,787	125,000	126,000
0.0554	0.554	P	--	--	894	776	808	842
0.0162	0.162	Pb	--	--	--	--	--	--
0.1186	1.186	S	--	--	1,220	1,085	1,120	1,110
0.0005	0.005	Sr	--	--	--	--	--	--
0.0004	0.004	Ti	--	[0.011]	[0.41]	[.4]	[0.45]	[0.44]
0.0043	0.043	Zn	--	2.17	22.1	[3]	--	--
0.0019	0.019	Zr	[0.0019]	--	--	[2]	[2.0]	[2.7]
Other Analytes								
0.0019	0.019	Ag	--	[0.086]	[1.0]	--	--	--
0.0067	0.067	B	[0.044]	[1.6]	41.2	[26]	[26]	[26]
0.0001	0.001	Be	--	[0.0018]	[0.19]	[0.08]	[0.14]	[0.16]
0.0494	0.494	Bi	--	--	--	--	--	--
0.0069	0.069	Ce	--	[0.25]	--	--	--	--
0.0035	0.035	Co	--	--	--	--	--	--
0.0016	0.016	Cu	--	--	--	--	--	--
0.0029	0.029	Dy	--	--	--	--	--	--
0.0013	0.013	Eu	--	--	--	--	--	--
0.0022	0.022	La	--	--	--	--	--	--
0.0009	0.009	Li	[0.0011]	[0.12]	[0.64]	[.69]	--	--
0.0068	0.068	Mg	--	--	--	--	--	--
0.0002	0.002	Mn	[0.0004]	[0.010]	--	--	--	--
0.0045	0.045	Mo	--	--	38.9	36	36.2	38.6
0.0086	0.086	Nd	--	--	--	--	--	--
0.0049	0.049	Ni	--	--	[23]	[19]	[22]	[21]
0.0077	0.077	Pd	--	--	--	[6]	--	--
0.0165	0.165	Rh	--	--	--	--	--	--
0.0097	0.097	Ru	--	--	[7.5]	--	[4.9]	--
0.0518	0.518	Sb	--	--	--	--	--	--
0.1595	1.595	Se	--	--	--	--	--	--
0.0237	0.237	Si	--	[3.0]	[59]	[62]	[45]	[49]
0.0313	0.313	Sn	--	--	[19]	--	--	[19]
0.0217	0.217	Ta	--	--	--	--	--	--
0.0311	0.311	Te	--	--	--	--	--	--
0.0189	0.189	Th	--	--	--	--	--	--
0.0530	0.530	Tl	--	[1.7]	--	--	[53]	--
0.0360	0.360	U	--	--	[22]	[22]	--	[20]
0.0021	0.021	V	--	--	--	--	--	--
0.0216	0.216	W	--	--	[69]	[60]	[66]	[61]
0.0012	0.012	Y	--	--	--	--	--	--

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

QC Performance 4/3/2019

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	19-1107 Dup	LCS/BS	19-1109 MS	19-1107 + PS-A	19-1107 + PS-B	19-1107 5-fold Serial Dil
Analytes	**RPD (%)**	**%Rec**	**%Rec**	**%Rec**	**%Rec**	**%Diff**
Al	3.1	100	nr	101		0.7
As				100		
Ba		102	101	100		
Ca		100	106	105		
Cd		101	101	102		
Cr	0.1	107	nr	104		2.9
Fe		107	103	101		
K	4.6	90	126	109		3.6
Na	0.7	nr	nr	104		0.7
P	3.6	101	100	100		
Pb		105	104	101		
S	3.2	103	99		94	
Sr		114	115	107		
Ti		102	101	100		
Zn		137	105	102		
Zr		104	104	101		
Other Analytes						
Ag				96		
B	9.8	103	95	104		
Be		106	105	103		
Bi				97		
Ce		94	91		95	
Co				102		
Cu		103	101	105		
Dy					94	
Eu					92	
La		94	94		93	
Li		103	124	114		
Mg		104	102	103		
Mn		103	100	100		
Mo	2.4	104	101	103		
Nd		95	92		94	
Ni		104	102	104		
Pd					93	
Rh					100	
Ru					90	
Sb				102		
Se				100		
Si			58	104		
Sn				100		
Ta				101		
Te					99	
Th		93	92		91	
Tl				95		
U		100	98		101	
V		96	97	94		
W			105	102		
Y				96		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	4/3/2019	4/3/2019	4/3/2019	4/3/2019	4/3/2019	4/3/2019	4/3/2019
		Process Factor >	1.0	24.8	489.0	493.2	500.0	496.8	498.6
			405 diluent	BLK-1107	19-1110 @ 20x	19-1111 @ 20x	19-1112 @ 20x	19-1113 @ 20x	19-1114 @ 20x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagents Only	TCT008-L-F5-A	TCT008-L-F9-A	TCT008-L-F15-A	TCT008-L-F19-A	TCT008-L-F23-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0177	0.177	Ca	--	[0.62]	[10]	[11]	[12]	[15]	[16]
0.0022	0.022	Cd	--	--	--	[1.1]	--	[1.2]	[1.3]
0.0052	0.052	Fe	[0.0098]	[0.50]	[3.8]	[4.3]	[4.5]	[4.5]	[4.9]
0.0004	0.004	Ti	--	[0.011]	[0.47]	[0.61]	[0.59]	[0.50]	[0.67]
0.0019	0.019	Zr	[0.0019]	--	[3.2]	[3.3]	[2.2]	[2.4]	[2.4]
Other Analytes									
0.0019	0.019	Ag	--	[0.086]	--	--	--	--	--
0.0122	0.122	Al	[0.019]	[1.9]	12,800	13,200	13,000	12,800	13,300
0.0529	0.529	As	--	--	--	--	--	--	--
0.0067	0.067	B	[0.044]	[1.6]	56.7	50.0	34.4	34.3	[32]
0.0003	0.003	Ba	--	0.0984	--	--	--	[0.17]	--
0.0001	0.001	Be	--	[0.0018]	[0.052]	[0.21]	[0.18]	[0.17]	[0.18]
0.0494	0.494	Bi	--	--	--	--	--	--	--
0.0069	0.069	Ce	--	[0.25]	--	[5.3]	--	--	--
0.0035	0.035	Co	--	--	--	--	--	--	--
0.0025	0.025	Cr	--	[0.081]	572	584	577	561	584
0.0016	0.016	Cu	--	--	--	--	--	--	--
0.0029	0.029	Dy	--	--	--	--	--	--	--
0.0013	0.013	Eu	--	--	--	--	--	--	--
0.0240	0.240	K	[0.031]	[5.4]	5,970	6,070	6,000	5,970	6,210
0.0022	0.022	La	--	--	--	--	--	--	--
0.0009	0.009	Li	[0.0011]	[0.12]	--	--	[0.60]	--	[0.49]
0.0068	0.068	Mg	--	--	--	--	--	--	--
0.0002	0.002	Mn	[0.0004]	[0.010]	--	--	--	--	--
0.0045	0.045	Mo	--	--	40.3	40.1	36.7	37.4	39.9
0.0246	0.246	Na	--	[1.1]	130,000	132,000	128,000	129,000	131,000
0.0086	0.086	Nd	--	--	--	--	--	--	--
0.0049	0.049	Ni	--	--	[20]	[22]	[21]	[20]	[21]
0.0554	0.554	P	--	--	847	868	841	828	845
0.0162	0.162	Pb	--	--	--	--	--	--	--
0.0077	0.077	Pd	--	--	--	--	--	--	--
0.0165	0.165	Rh	--	--	--	--	--	--	--
0.0097	0.097	Ru	--	--	--	[5.7]	--	--	[5.1]
0.1186	1.186	S	--	--	1,220	1,210	1,120	1,160	1,220
0.0518	0.518	Sb	--	--	--	--	--	--	--
0.1595	1.595	Se	--	--	--	--	--	--	--
0.0237	0.237	Si	--	[3.0]	137	[110]	[71]	[62]	[58]
0.0313	0.313	Sn	--	--	--	--	--	--	--
0.0005	0.005	Sr	--	--	--	--	--	--	--
0.0217	0.217	Ta	--	--	--	--	--	--	--
0.0311	0.311	Te	--	--	--	--	--	--	--
0.0189	0.189	Th	--	--	--	--	--	--	--
0.0530	0.530	Tl	--	[1.7]	--	--	--	[29]	--
0.0360	0.360	U	--	--	[23]	[19]	[18]	[25]	[25]
0.0021	0.021	V	--	--	--	--	--	--	--
0.0216	0.216	W	--	--	[73]	[71]	[68]	[61]	[70]
0.0012	0.012	Y	--	--	--	--	--	--	--
0.0043	0.043	Zn	--	2.17	--	[2.1]	--	--	--

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

QC Performance 4/3/2019

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	19-1107 Dup	LCS/BS	19-1109 MS	19-1107 + PS-A	19-1107 + PS-B	19-1107 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Ca		100	106	105		
Cd		101	101	102		
Fe		107	103	101		
Ti		102	101	100		
Zr		104	104	101		
Other Analytes						
Ag				96		
Al	3.1	100	nr	101		0.7
As				100		
B	9.8	103	95	104		
Ba		102	101	100		
Be		106	105	103		
Bi				97		
Ce		94	91		95	
Co				102		
Cr	0.1	107	nr	104		2.9
Cu		103	101	105		
Dy					94	
Eu					92	
K	4.6	90	126	109		3.6
La		94	94		93	
Li		103	124	114		
Mg		104	102	103		
Mn		103	100	100		
Mo	2.4	104	101	103		
Na	0.7	nr	nr	104		0.7
Nd		95	92		94	
Ni		104	102	104		
P	3.6	101	100	100		
Pb		105	104	101		
Pd					93	
Rh					100	
Ru					90	
S	3.2	103	99		94	
Sb				102		
Se				100		
Si			58	104		
Sn				100		
Sr		114	115	107		
Ta				101		
Te					99	
Th		93	92		91	
Tl				95		
U		100	98		101	
V		96	97	94		
W			105	102		
Y				96		
Zn		137	105	102		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

Hydroxide Analysis by Titration

Project / WP#:	73325/NC2504 73312/NC4189
ASR#:	0731.00 & 0787.01
Client:	SK Fiskum
Total # of Samples:	2

RPL ID	Client Sample ID
19-1107	TCT008-COMP-FEED
19-1773	TI061-COMP-FEED

Analysis Type:	Hydroxide
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-128, Rev.1, *HNO_3-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other:
Pre-dilution Prior to Radiochemical Processing?	☒ No ☐ Yes
Analysis Procedure:	RPG-CMC-228, Rev. 0.1, *Determination of Hydroxyl (OH^-) and Alkalinity of Aqueous Solutions, Leachates & Supernates*
Analysis Date or Date Range:	5/30/19
Technician/Analyst:	KN Pool & AM Carney
Electronic Data File:	ASR 0731 & 0787.01_Fiskum.xls
ASO Project 98620 File:	File Plan 5872: Sample preparation and analysis records; LSC 3100 TR calibration, daily checks, and maintenance records; and standard certificates and preparation. Also, balance calibration and performance check records.
M&TE Number(s):	Beckman Coulter pH Meter, SN: 110650046

Karl N. Pool / 6/2/19
Preparer **Date**

Andrew Carney / 6/4/19
Reviewer **Date**

SAMPLE RESULTS

See attached data report, Sample Results for ASR's 0731.00 and 0787.01. All sample data are molarity of hydroxide at each end point.

ASO Project Files, ASR 0731.00 and 0787.01 have been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form and laboratory bench records, and records associated with hydroxide analysis. Standard certificates and balance calibration records can be found in the ASO Records.

Sample preparation and analysis

Hydroxide analysis was performed for diluted sample aliquots of 2 aqueous samples (19-1107 and 19-1773). Samples were analyzed by manual titration for the base constituents content following procedure RPG-CMC-228, Rev. 0.1, *Determination of Hydroxyl (OH^-) and Alkalinity of Aqueous Solutions, Leachates & Supernates*.

A sample size of 0.100 mL was added to 2.5 mL of DI water. The titrant used was 0.0887 M HCl. Standardized HCl was prepared on 5/6/19 and documented on Chem_Rec 238. Titration pH measurements were obtained using a Beckman Coulter 560 pH meter with serial number (SN) 110650046. The pH meter was calibrated using 3 buffers, pH 4, 7 and 10 and the calibration verified using an independent pH 7 buffer.

The customer requested target MDL of 0.1M was achieved for all samples. The titrant used for the sample analyses is 0.0887M HCl along with a pH meter accurate to within 0.05 pH units. The low concentration of the titrant along with the sensitivity of the pH meter provides the detection capability to meet this requirement.

The initial diluted pH is reported on the attached Report Summary along with the free hydroxide molarity. pH measured at each inflection point are provided below.

Sample ID	1st Inflection point	2nd Inflection point	3rd Inflection point
19-1107	10.9	8.3	4.8
19-1773	10.9	7.9	4.8

Included in the data package is a report summary and the sample results calculated from the raw data. A copy of the titration curve data for each sample is also included with this report.

QUALITY CONTROL RESULTS

This analysis has limited quality control (QC) samples that are prepared. There are no laboratory blanks (LB), matrix spikes or reagent spikes analyzed.

Instrument Calibration Control

The pH meter was calibrated using 3 buffers, pH 4, 7 and 10 and the calibration verified using an independent pH 7 buffer.

Assumption and Limitations of the Data

Generally ASO analysis methods are associated with reported uncertainty. Titrations are not amenable to calculations of uncertainty.

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.

Attachment: Data Report -- Sample Results for ASR 0731.00 and 0787.01

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group
Chemical Measurements Center

ASR # 731.00 & 0787.01

WP# NC2504 & NC4189

Hydroxide and Alkalinity Determination
Procedure: RPG-CMC-228, Rev 0.1

Equip # Beckman Coulter 560, SN#110650046

Report Summary for ASR # -- 731.00 & 0787.01

Revision # **Rev-00 & 01**

Report Date: 6/2/2019
Analysis Date: 5/30/2019

				Concentration, moles / Liter		
				First Point	**Second Point**	**Third Point**
RPG #	**Client ID**	**Diluted Initial pH**	**OH conc ug/mL**	**Molarity**	**Molarity**	**Molarity**
19-1107	**TCT008-COMP-FEED**	**12.39**	1.66E+04	**0.98**	**1.24**	**0.71**
19-1773	**TI061-COMP-FEED**	**12.42**	1.51E+04	**0.89**	**1.15**	**0.71**

OH conc (mg/L) = M (g/L) * 17,000

Note: Results are presented for the first, second, and third inflection points on the titration curves for the hydroxide titration, as applicable. The first inflection point is generally associated with the free hydroxide concentration. The second inflection point generally represents total hydroxide, or carbonate or a combination of aluminate and carbonate. The third inflection point is usually indicative of bicarbonate or other weak acids or possibly the continued protonation of alumina.

Analyst: andrew Carey 6/4/19

Reviewer: Karl N. Pool 6/2/19

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group

ASR # and Rev # 731.00 & 0787.0 Rev-00 & 01
Client: S. Fiskum
Project: 71274 WP# NC2504
NC4189

Report Date: 6/2/2019
Analysis Date: 5/30/2019

Procedure: **RPG-CMC-228, Rev 0.1** Determination of Hydroxyl (OH-) and
Alkalinity of Aqueous Solutions, Leachates and Supernates

Spreadsheet: OH-TemplateLocked07.xls 4/1/2007

By Manual Titration

Equip # 110650046 Lab Loc. 420

Analyst: andrew Cary

Titrant	Molarity	Chem Rec#
HCl	**0.0887**	**238**

									OH			
RPG #	Sample ID		Dilution Factor	Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Titrator Routine #	**Diluted** Initial pH reading	**1st Equivalence** Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
19-1107	TCT008-COMP-FEED		NA	0.105	NA	NA	NA	12.39	1.15	10.86	0.102	0.976
19-1773	TI061-COMP-FEED		NA	0.105	NA	NA	NA	12.42	1.05	10.89	0.093	0.887

Instrument Calibration

Buffer	Vendor	Lot Number	Expire Date
4	Inorganic Ventures	N2-WCS673492	30-May-20
7	Inorganic Ventures	N2-WCS674708	30-May-20
10	Inorganic Ventures	P2-WCS675599	30-May-19

2-nd Verif	Vendor	Lot Number	Expire Date
7	Spex	1-53MJX	23-May-20

Slope
NA

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group

ASR # and Rev # 31.00 & 0787.0 Rev-00 & 01

WP# NC2504
NC4189

Procedure:

Alkalinity of Aqueous Solutions, Leachates and Supernates

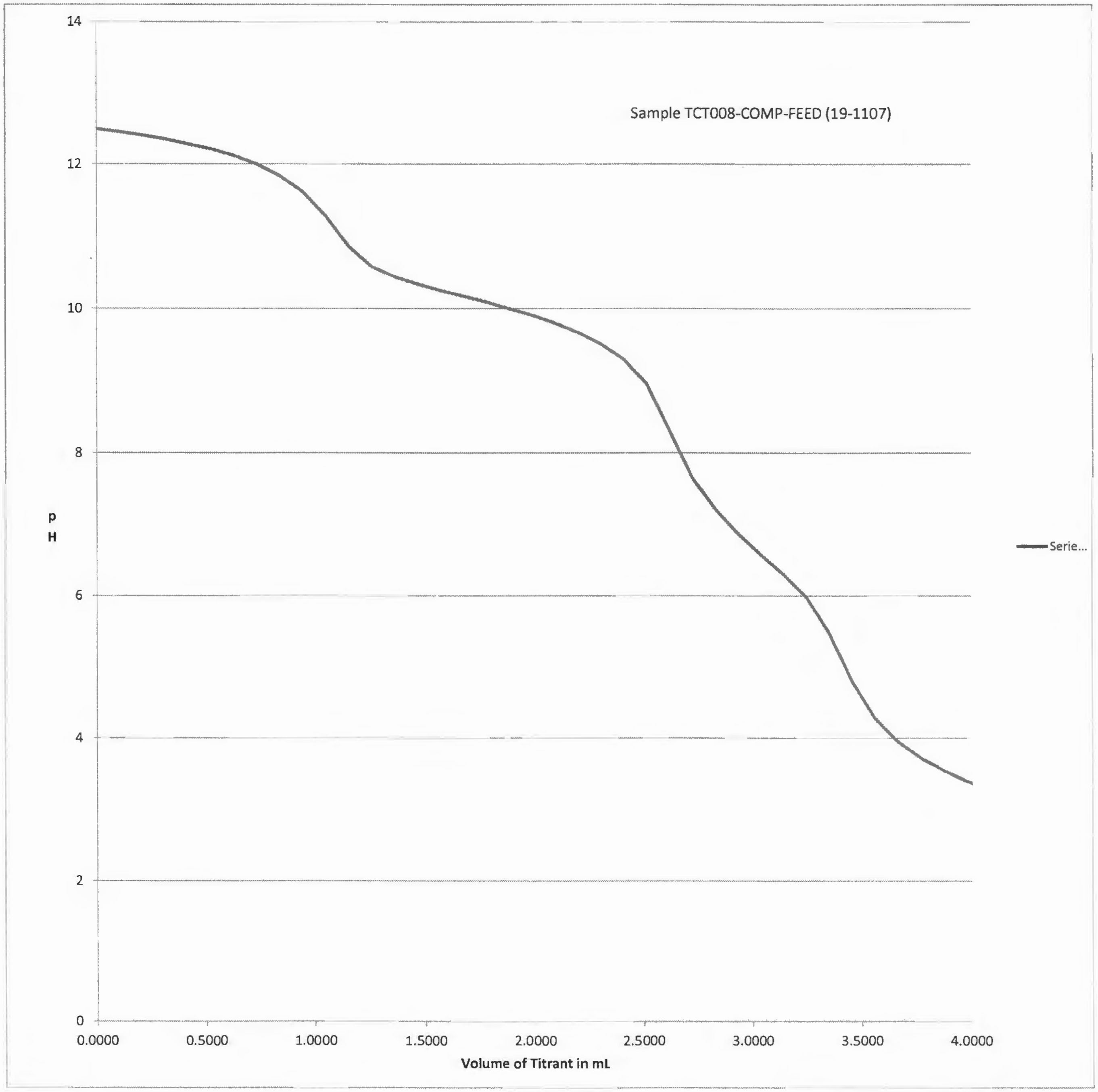
By Manual Titration

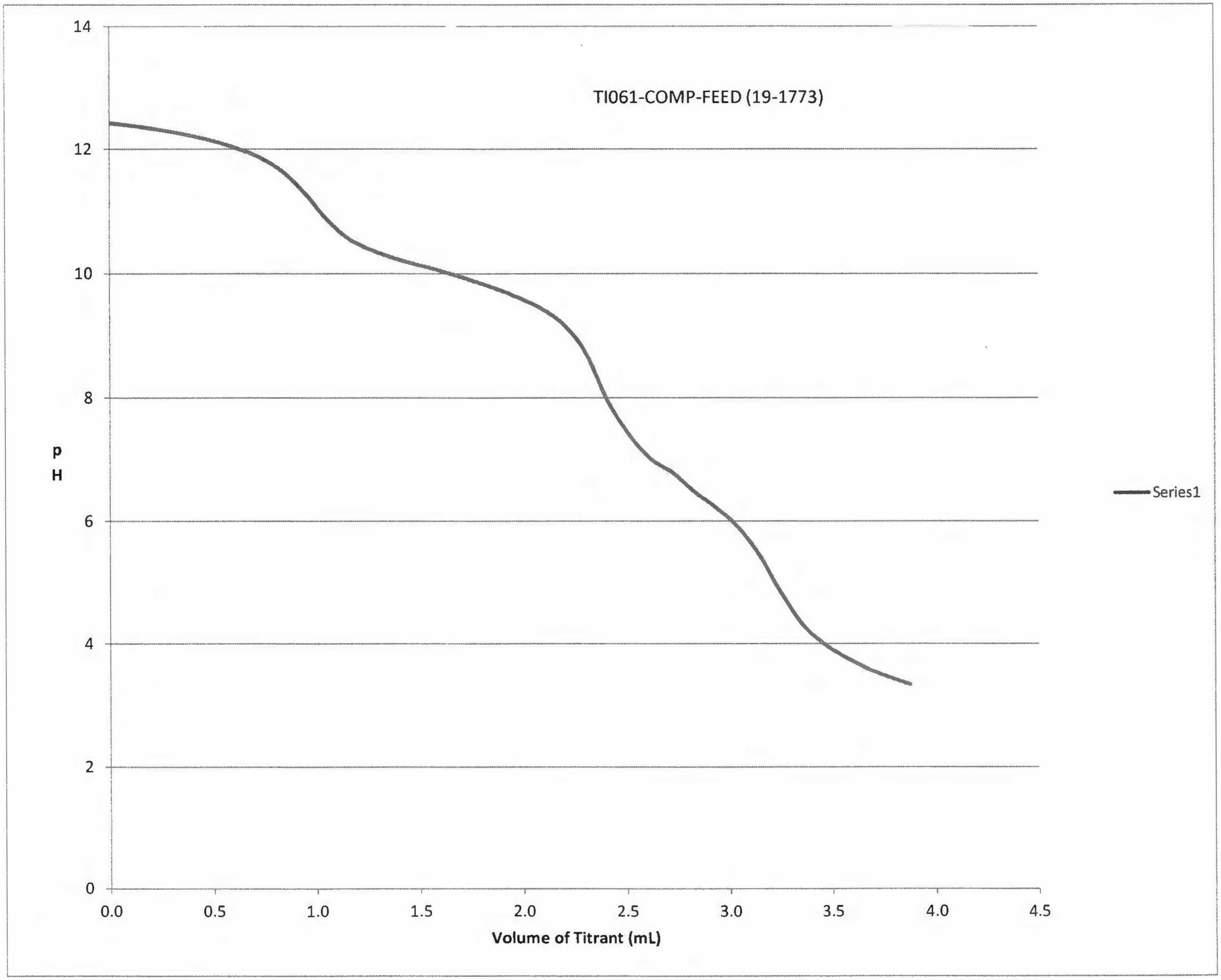
Equip # Beckman Coulter 560, SN#110650046

Titrant	Molarity
HCl	0.0887

RPG #		Sample Vol. (mL)	**2nd Equivalence** Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
19-1107		0.105	2.618	8.310	0.130	1.242
19-1773		0.105	2.408	7.940	0.121	1.153

3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
3.455	4.790	0.074	0.710
3.246	4.840	0.074	0.710


Sample TCT008-COMP-FEED (19-1107)
14
12
10
8
6
4
2
0
p
H
0.0000
0.5000
1.0000
1.5000
2.0000
2.5000
3.0000
3.5000
4.0000
Volume of Titrant in mL
Serie...


TI061-COMP-FEED (19-1773)
p
H
14
12
10
8
6
4
2
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Volume of Titrant (mL)
Series1

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Sr-90 by Liquid Scintillation Spectrometry

Project / WP#:	73325/NC2504
ASR#:	0731
Client:	SK Fiskum
Total # of Samples:	3

RPL ID	Client Sample ID
19-1107	TCT008-COMP-FEED
19-1108	TCT008-EFF-1
19-1109	TCT008-COMP-EFF

Analysis Type:	Sr-90
Sample Processing Prior to Radiochemical Processing/Analysis	☐ None ☒ Digested as per RPG-CMC-128, Rev.1, *HNO_3-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other:
Pre-dilution Prior to Radiochemical Processing?	☐ No ☐ Yes
Total Alpha and Beta Preparation Procedure:	RPG-CMC-4001, Rev. 1, *Source Preparation For Gross Alpha and Gross Beta Analyses.*
Technician/Analyst:	LP Darnell, (03/19/2019)
Spike Standard ID's	R-693-b-10 (Sr-90)
Analysis Procedure	RPG-CMC-408, Rev. 2, *Total Alpha and Beta Analysis*
Technician/Analyst:	LP Darnell and T. Trang-Le 03/21/19
Separation Procedure:	RPG-CMC-476, Rev. 0, *Strontium Separation Using Eichrom Strontium Resin*
Spike Standard ID:	R-693-b-10 (Sr-90)
Separation Date:	03/28/2019 @ 14:40
Technician/Analyst:	L. Darnell
Analysis Procedure:	RPG-CMC-474, Rev. 1, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*
Reference Date:	03/28/19
Analysis Date or Date Range:	03/29/19 (first count), 04/01/19 (second count)
Technician/Analyst:	LP Darnell & CZ Soderquist
Rad Chem Electronic Data File:	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1107 Fiskum.xls
ASO Project 98620 File:	File Plan 5871: T 73325: Sample preparation and analysis records; T-4.4 LSC 3100 calibration, daily checks, and maintenance records; and T3 standard certificates and preparation. Also, balance calibration and performance check records.
M&TE Number(s):	Perkin Elmer Tri-Carb 3100, Serial # DG08061340, RPL 425, Tri-Carb 2700TR software version 1.04 dated 9/99.

/ 5/16/19 / 21 MAY 2019

Preparer **Date** **Reviewer** **Date**

SAMPLE RESULTS

See attached data report, Sample Results for ASR 0731. All sample data are reported in µCi/mL with a 1-σ uncertainty (see Comments).

Sample preparation, separation, mounting, and counting

All three samples submitted under Analytical Service Request (ASR) 0731 were analyzed for Sr-90 by chemical separation and liquid scintillation counting. All the samples were prepared in RPL/420. Aliquots of the acid digestions were used for radioanalytical analyses; only Sr-90 data are presented in this report.

QUALITY CONTROL RESULTS

Quality control (QC) samples include a laboratory preparation blank (PB) and sample duplicate. Additional laboratory QC samples were prepared prior to separations; these include a reagent blank spike (RS), and a matrix spike (MS), each made with the addition of Sr-90 standard to an aliquot of the samples.

Laboratory Preparation Blank (PB) and :

The activity level of Sr-90 present in the laboratory separation blank (-3.6E-6 µCi/mL) is both below the activity present in the samples (8.07E-4 µCi/mL or higher) and less than sample MDC (2.3 E-4 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Blank Spike (BS) – Reagent Spike (RS):

The RS recovery of 105% meets the procedure acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

The MS recovery of 106% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared “after” digestion (see comments), by adding a known Sr-90 standard quantity to an aliquot of 19-1107 (TCT008-COMP-FEED).

Duplicate -- Relative Percent Difference (RPD):

Duplicate results are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be >5 times the MDA or have individual uncertainties <20%. The duplicate result was 6% RPD; thus meeting the ≤20% requirement.

Instrument Quality Control

The liquid scintillation counter is calibrated for tritium and C-14 using quenched standard sets that are purchased from the vendor. Daily control counts are then performed using a tritium, C-14, and a background count sample. The instrument software assesses the performance of the control counts and provides control charts to ensure the continuing calibration of the instrument. If the daily performance check fails, then the instrument is not used. Preventative maintenance and repairs are performed by the vendor under our service contract. The counting efficiency for Sr-90 is assumed to be 100%; therefore, no specific Sr-90 calibration is performed. The LSC system calibration and performance is verified by assessing the recovery of a reagent spike and a matrix spike that are included in every batch of samples.

A preparation blank (i.e., digestion blank) and a laboratory separations blank are also included with every batch of samples; the instrument background is subtracted from all results and the preparation and separation blanks are used to assess sample contamination during sample processing steps.

Assumption and Limitations of the Data

None

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.
2. The stated 1-σ uncertainty represents the total propagated error associated with processing and counting operations and includes weighing errors, volume uncertainties, and counting error. Generally, errors are set at 2% to provide a

Attachment: Data Report -- Sample Results for ASR 0731

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Client: S. Fiskum
ASR 0731

Project: 73325

Prepared by: C Soderquist 5-2 2019

Technical Reviewer: LR Greenwood 5-2-19

Procedures:	RPG-CMC-4001, Rev 1, Source Preparation for Gross Alpha and Gross Beta Counting RPG-CMC-408, Rev 2, Gross Alpha and Gross Beta Counting RPG-CMC-476, Rev 0, Strontium Separation using Eichrom Strontium Resin RPG-CMC-432, Rev 0, Technetium-99 Analysis RPG-CMC-474, Rev 1, Liquid Scintillation Spectrometry
M&TE:	LB4100 proportional counters, Ludlum alpha counters, Perkin Elmer TriCarb model 3100 TR
Reference dates:	Mar 19 2019 (gross alpha, gross beta), Mar 28 2019 (Sr-90), April 17 2019 (Tc-99)

	Lab	**Measured Activity, µCi per mL ± 1s**							
Sample	ID	Gross alpha		Gross beta		Strontium-90		Technetium-99	
TCT008-COMP-FEED	19-1107	4.07E-4	± 9%	1.42E+2	± 3%	3.44E-1	± 1%	8.98E-2	± 3%
TCT008-EFF-1	19-1108	1.11E-4	± 19%	8.69E-2	± 3%	5.81E-3	± 2%	7.43E-2	± 3%
TCT008-COMP-EFF	19-1109	1.78E-4	± 15%	9.72E-2	± 3%	8.58E-4	± 6%	7.34E-2	± 3%
	19-1109 Dup	2.18E-4	± 13%	9.66E-2	± 3%	8.07E-4	± 6%	7.67E-2	± 3%
	RPD	--		0.6%		6%		4%	
TCT008-L-F5-A	19-1110	1.41E-4	± 16%	1.41E-1	± 3%	--		--	
TCT008-L-F9-A	19-1111	2.13E-4	± 13%	9.81E-2	± 3%	--		--	
TCT008-L-F15-A	19-1112	2.03E-4	± 14%	1.85E-1	± 3%	--		--	
TCT008-L-F19-A	19-1113	3.07E-4	± 11%	8.28E-1	± 3%	--		--	
TCT008-L-F23-A	19-1114	3.17E-4	± 11%	4.29E+0	± 3%	--		--	
	Lab blank	-1.2E-6	± 44%	1.1E-5	± 39%	-3.5E-6	± 119%	1.7E-6	± 72%
	Reagent spike	109%		120%		105%		92%	
	Matrix spike	52%		--		106%		--	

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Procedures: RPG-CMC-4017, Rev 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry
RPG-CMC-422, Rev 2, Alpha Spectrometry
M&TE: Alpha spectrometry counting system
Count date: April 23, 2019 (plutonium), April 20, 2019 (neptunium)

Sample	Lab ID	**Measured Activity, µCi per mL ± 1s**					
		Neptunium-237		Plutonium-238		Plutonium-239+240	
TCT008-COMP-FEED	19-1107	1.03E-5	± 6%	8.40E-5	± 4%	5.66E-4	± 2%
TCT008-EFF-1	19-1108	1.21E-6	± 18%	1.69E-5	± 5%	1.08E-4	± 2%
TCT008-COMP-EFF	19-1109	5.91E-6	± 8%	2.88E-5	± 4%	1.79E-4	± 2%
	19-1109 Dup	5.08E-6	± 8%	2.97E-5	± 4%	1.83E-4	± 2%
	RPD	15%		3%		2%	
TCT008-L-F5-A	19-1110	2.76E-6	± 11%	2.67E-5	± 4%	1.66E-4	± 2%
TCT008-L-F9-A	19-1111	7.31E-6	± 7%	4.16E-5	± 3%	2.66E-4	± 2%
TCT008-L-F15-A	19-1112	8.43E-6	± 6%	2.91E-5	± 4%	1.98E-4	± 2%
TCT008-L-F19-A	19-1113	9.69E-6	± 6%	4.71E-5	± 3%	3.26E-4	± 2%
TCT008-L-F23-A	19-1114	1.01E-5	± 6%	5.27E-5	± 3%	3.55E-4	± 2%
	Lab blank	6.6E-8	± 109%	4.5E-9	± 356%	-5.3E-9	± 114%
	Reagent spike	98%		--		93%	
	Matrix spike	98%		--		92%	

The gross alpha results are biased low because of solids on the counting plate. Data shaded in grey are at or below detection limit. The gross beta and technetium-99 matrix spikes were too small for the accompanying sample activity (sample TCT008-COMP-EFF).

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Tc-99 Analysis

Project / WP#:	73325/NC2504
ASR#:	0731.00
Client:	SK Fiskum
Total # of Samples:	3

RPL ID	Client Sample ID
19-1107	TCT008-COMP-FEED
19-1108	TCT008-EFF-1
19-1109	TCT008-COMP-EFF

Analysis Type:	Tc-99
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per PNL-ALO-106, Rev. 1, *Acid Digestion of Waters, Soils, and Sludges for Subsequent Radiochemical Sample Analyses* ☐ Fusion as per RPG-CMC-115 Rev. 0, *Solubilization of Metals from Solids Using a KOH-KNO$_3$ Fusion* ☐ Digested as per RPG-CMC-128, Rev.1, *HNO$_3$-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater*
Pre-dilution Prior to Radiochemical Processing?	☒ No ☐ Yes
Total Alpha and Beta Preparation Procedure:	RPG-CMC-4001, Rev. 1, *Source Preparation For Gross Alpha and Gross Beta Analyses.*
Technician/Analyst:	LP Darnell, (03/19/2019)
Spike Standard ID's	R-687-a-7 (Pu-239), R-693-b-10 (Sr-90)
Analysis Procedure	RPG-CMC-408, Rev. 2, *Total Alpha and Beta Analysis*
Technician/Analyst:	LP Darnell and T. Trang-Le 03/21/2019
RadioChemical Preparation Procedure:	RPG-CMC-432, Rev. 0, *Technicium-99 Analysis*
Technician/Analyst:	LP Darnell, (4/11/19)
Spike and Tracer Standard ID's:	R-714-b-1 (10/25/19) (Tc-99)
Analysis Procedure:	RPG-CMC-474, Rev. 1, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*
Reference Date:	Not applicable
Analysis Date(s) or Date Range:	4/15/19
Technician/Analyst:	LP Darnell
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1107 Fiskum.xls
CMC Project 98620 File:	File Plan 5872: T 73325: Sample preparation and analysis records; T-4.4 Alpha Detector calibration, calibration verification checks, and maintenance records; and T3 Standard certificates and preparation. Also balance calibration and instrument performance checks.
M&TE Number(s):	Perkin Elmer 3100 TR Liquid scintillation spectrometer– See attached M&TE list

Karl N. Pool / 5/16/19 / 21 MAY 2019

Preparer **Date** **Reviewer** **Date**

Sample Results

See attached data report, Sample Results for ASR 0731.00. All data are reported in units of µCi/mL with a 1-σ uncertainty (see comments).

Sample Preparation, Separation, Mounting and Counting Methods

Three samples submitted under ASR 0731.00 were analyzed for Tc-99. All the samples were prepared in Laboratory 420. A direct aliquot of each of the parent samples was processed using procedure RPG-CMC-432, Rev. 0, *Technicium-99 Analysis*.

The samples were counted on April 15, 2019; no decay corrections were made.

QUALITY CONTROL RESULTS

Quality control (QC) samples prepared in laboratory 420 include a laboratory blank and sample duplicate, matrix spike sample and reagent spike sample.

The QC sample results for Tc-99 have been evaluated and are discussed below. A summary of the Tc-99 analysis results, including QC sample performance, is given in the attached data report.

Tracer:

There is no tracer for Tc-99 analysis.

Laboratory Separation Blank (LB):

The activity level of Tc-99 present in the laboratory separation blank (1.74E-6 µCi/mL) is both below the activity present in the samples (7.34E-2 µCi/mL or higher) and less than sample MDC (4.0 E-6 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Reagent Spike (RS):

The RS recovery of 92% (Tc-99) meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

A matrix spike sample was prepared using sample 19-1109 (TCT008-COMP-EFF). The sample activity was significantly higher (~150x) than the activity of spike added for the matrix spike. The matrix spike is not calculated in this case.

Laboratory Duplicate - Relative Percent Difference (RPD):

Duplicate results for 19-1109 (TCT008-COMP-EFF) are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be > 5 times the MDC or have individual uncertainties < 20%. Duplicate results were 4% RPD, thus meeting the ≤ 20% requirement.

Instrument Quality Control

LSC counters receive initial calibration with NIST traceable sources to determine the counter efficiency. When internal tracers are not used, the counter efficiency is used in calculation of final results.

The liquid scintillation counter (LSC) is calibrated for tritium and C-14 using quenched standard sets that are purchased from the vendor. Daily control counts are then performed using a tritium, C-14, and a background count sample. The instrument software assesses the performance of the control counts and provides control charts to ensure the continuing calibration of the instrument. If the daily performance check fails, then the instrument is not used. Preventative maintenance and repairs are performed by the vendor under our service contract. The counting efficiency for Tc-99 is assumed to be 100%; therefore no specific Tc-99 calibration is performed. The LSC system calibration and performance is verified by assessing the recovery of a reagent spike and a matrix spike that are included in every batch of samples. A laboratory separation blank is also included with every batch of samples; the instrument background is subtracted from all results and separation blanks are used to assess sample contamination during sample processing steps.

Assumption and Limitations of the Data

None

Attachment: Data Report -- Sample Results for ASR 0731.00.

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Client: S. Fiskum
ASR 0731

Project: 73325

Prepared by: C. Soderquist 5-2 2019

Technical Reviewer: L R Greenwood 5-2-19

Procedures:	RPG-CMC-4001, Rev 1, Source Preparation for Gross Alpha and Gross Beta Counting RPG-CMC-408, Rev 2, Gross Alpha and Gross Beta Counting RPG-CMC-476, Rev 0, Strontium Separation using Eichrom Strontium Resin RPG-CMC-432, Rev 0, Technetium-99 Analysis RPG-CMC-474, Rev 1, Liquid Scintillation Spectrometry
M&TE:	LB4100 proportional counters, Ludlum alpha counters, Perkin Elmer TriCarb model 3100 TR
Reference dates:	Mar 19 2019 (gross alpha, gross beta), Mar 28 2019 (Sr-90), April 17 2019 (Tc-99)

	Lab	Measured Activity, µCi per mL ± 1s							
Sample	ID	Gross alpha		Gross beta		Strontium-90		Technetium-99	
TCT008-COMP-FEED	19-1107	4.07E-4	± 9%	1.42E+2	± 3%	3.44E-1	± 1%	8.98E-2	± 3%
TCT008-EFF-1	19-1108	1.11E-4	± 19%	8.69E-2	± 3%	5.81E-3	± 2%	7.43E-2	± 3%
TCT008-COMP-EFF	19-1109	1.78E-4	± 15%	9.72E-2	± 3%	8.58E-4	± 6%	7.34E-2	± 3%
	19-1109 Dup	2.18E-4	± 13%	9.66E-2	± 3%	8.07E-4	± 6%	7.67E-2	± 3%
	RPD	--		0.6%		6%		4%	
TCT008-L-F5-A	19-1110	1.41E-4	± 16%	1.41E-1	± 3%	--		--	
TCT008-L-F9-A	19-1111	2.13E-4	± 13%	9.81E-2	± 3%	--		--	
TCT008-L-F15-A	19-1112	2.03E-4	± 14%	1.85E-1	± 3%	--		--	
TCT008-L-F19-A	19-1113	3.07E-4	± 11%	8.28E-1	± 3%	--		--	
TCT008-L-F23-A	19-1114	3.17E-4	± 11%	4.29E+0	± 3%	--		--	
	Lab blank	-1.2E-6	± 44%	1.1E-5	± 39%	-3.5E-6	± 119%	1.7E-6	± 72%
	Reagent spike	109%		120%		105%		92%	
	Matrix spike	52%		--		106%		--	

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Procedures: RPG-CMC-4017, Rev 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry
RPG-CMC-422, Rev 2, Alpha Spectrometry
M&TE: Alpha spectrometry counting system
Count date: April 23, 2019 (plutonium), April 20, 2019 (neptunium)

	Lab	**Measured Activity, µCi per mL ± 1s**					
Sample	ID	Neptunium-237		Plutonium-238		Plutonium-239+240	
TCT008-COMP-FEED	19-1107	1.03E-5	± 6%	8.40E-5	± 4%	5.66E-4	± 2%
TCT008-EFF-1	19-1108	1.21E-6	± 18%	1.69E-5	± 5%	1.08E-4	± 2%
TCT008-COMP-EFF	19-1109	5.91E-6	± 8%	2.88E-5	± 4%	1.79E-4	± 2%
	19-1109 Dup	5.08E-6	± 8%	2.97E-5	± 4%	1.83E-4	± 2%
	RPD	15%		3%		2%	
TCT008-L-F5-A	19-1110	2.76E-6	± 11%	2.67E-5	± 4%	1.66E-4	± 2%
TCT008-L-F9-A	19-1111	7.31E-6	± 7%	4.16E-5	± 3%	2.66E-4	± 2%
TCT008-L-F15-A	19-1112	8.43E-6	± 6%	2.91E-5	± 4%	1.98E-4	± 2%
TCT008-L-F19-A	19-1113	9.69E-6	± 6%	4.71E-5	± 3%	3.26E-4	± 2%
TCT008-L-F23-A	19-1114	1.01E-5	± 6%	5.27E-5	± 3%	3.55E-4	± 2%
	Lab blank	6.6E-8	± 109%	4.5E-9	± 356%	-5.3E-9	± 114%
	Reagent spike	98%		--		93%	
	Matrix spike	98%		--		92%	

The gross alpha results are biased low because of solids on the counting plate. Data shaded in grey are at or below detection limit. The gross beta and technetium-99 matrix spikes were too small for the accompanying sample activity (sample TCT008-COMP-EFF).

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Neptunium 237 Analysis

Project / WP#:	73325/NC2504
ASR#:	0731.00
Client:	SK Fiskum
Total # of Samples:	8

RPL ID	Client Sample ID	RPL ID	Client Sample ID
19-1107	TCT008-COMP-FEED	19-1111	TCT008-L-F9-A
19-1108	TCT008-EFF-1	19-1112	TCT008-L-F15-A
19-1109	TCT008-COMP-EFF	19-1113	TCT008-L-F19-A
19-1110	TCT008-L-F5-A	19-1114	TCT008-L-F23-A

Analysis Type:	AEA – Np-237
Sample Processing Prior to Radiochemical Processing/Analysis	☐ None ☐ Digested as per PNL-ALO-106, Rev. 1, *Acid Digestion of Waters, Soils, and Sludges for Subsequent Radiochemical Sample Analyses* ☐ Fusion as per RPG-CMC-115, Rev0, *Solubilization of Metals from Solids Using a KOH-KNO$_3$ Fusion* ☒ Digested as per RPG-CMC-128, Rev.1, *HNO$_3$-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater*
Pre-dilution Prior to Radiochemical Processing?	☐ No ☒ Yes -- *example 2 mL to 100 mL; 50x dilution*
Total Alpha and Beta Preparation Procedure:	RPG-CMC-4001, Rev. 1, *Source Preparation For Gross Alpha and Gross Beta analyses.*
Technician/Analyst:	LP Darnell, (03/19/2019)
Spike Standard ID's	R-687-a-7 (Pu-239), R-693-b-10 (Sr-90)
Analysis Procedure	RPG-CMC-408, Rev. 2, *Total Alpha and Beta Analysis*
Technician/Analyst:	LP Darnell and T. Trang-Le 03/21/19
Neptunium Separation Procedure:	RPG-CMC-4017, Rev. 0, *Analysis of Environmental Water Samples for Actinides and Strontium- 90*
Technician/Analyst:	LP Darnell, (03/29/2019)
Spike Standard ID's:	R-686-a-39 (Np-237)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, *Coprecipitation Mounting of Actinides for Alpha Spectroscopy*
Technician/Analyst:	LP Darnell, (04/05/2019)
Analysis Procedure:	RPG-CMC-422, Rev. 2, *Solutions Analysis: Alpha Spectrometry*
Reference Date:	Same as counting dates
Analysis Date or Date Range:	April 24 - 30, 2019
Technician/Analyst:	CS Soderquist
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1107 Fiskum.xls
CMC Project 98620 File:	File Plan 5871: T 73325: Sample preparation and analysis records; T-4.4 Alpha Detector calibration, calibration verification checks, and maintenance records; and T3 Standard certificates and preparation. Also balance calibration and instrument performance checks.
M&TE Number(s):	Ortec AEA counters – 32 counters – See attached M&TE list

	5/21/19		21 MAY 2019
Preparer	**Date**	**Reviewer**	**Date**

Sample Results

See attached data report, Sample Results for ASR 0731. All data are reported in units of µCi per mL with a 1-σ uncertainty unless noted otherwise (see Comments).

Sample Preparation, Separation, Mounting and Counting Methods

All eight samples submitted under Analytical Service Request (ASR) 0731 were analyzed for neptunium by Alpha Spectrometry. All the samples were prepared in RPL/420, only Np-AEA is presented in this report.

Following the digestion process of samples, the Np was separated from the aqueous samples using anion exchange chromatography using procedure RPG-CMC-4017. The separated Np fraction was mounted for alpha spectrometry by co-precipitation using procedure RPG-CMC-496, and then counted by alpha spectrometry using procedure RPC-CMC-422. The samples were counted on April 24-30, 2019; no decay corrections were made.

Alpha and beta analyses were performed on each sample to determine appropriate aliquot sizes for the chemical separations needed for the alpha and beta emitters of interest. Gross alpha and gross beta activity were measured by evaporating small aliquots of leachate onto counting planchets per procedure RPG-CMC-4001 and counting per procedure RPG-CMC-408.

QUALITY CONTROL RESULTS

Quality control (QC) samples include a laboratory preparation blank and sample duplicate. Additional QC samples were prepared prior to separations; these include a reagent spike (RS), and a matrix spike (MS) made by adding Np-237 standard to a diluted sample.

Tracer:

Tracer is not used for analyses of Np.

Laboratory Preparation Blank (PB)):

The activity level of Np-237 present in the laboratory preparation blank (6.6E-8 µCi/mL) is both below the activity present in the samples (1.21E-6 µCi/mL or higher) and less than lowest sample MDC (4.1 E-5 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Blank Spike (BS) – Reagent Spike (RS):

The RS recovery of 98% meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

The MS recovery of 98% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared "after" digestion, by adding a known Np-237 standard quantity to an aliquot of the leachate. Sample number 19-1109 (TCT008-COMP-EFF) was selected as the matrix spike sample.

Duplicate -- Relative Percent Difference (RPD):

Duplicate results are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be >5 times the MDA or have individual uncertainties <20%. The duplicate result was 15% RPD; thus meeting the ≤20% requirement.

Instrument Quality Control

Alpha counters undergo calibration annually to determine the counter's efficiency over the normal calibration range of 3 to 6 MeV. The vendor software determines a constant detector efficiency for this energy range. Np samples are counted and results calculated using the established detector efficiency.

Detector backgrounds are determined every 4 weeks or after the last analytical run, whichever is longer. Detector background counts are subtracted from all subsequent sample counts. A process blank is analyzed with each analytical batch to evaluate for contamination in the sample preparation process.

Assumption and Limitations of the Data

None.

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.
2. The 1-sigma uncertainty represents the total propagated error associated with processing and counting operations and include; weighing errors, volume uncertainties, and counting error.

Attachment: Data Report -- Sample Results for ASR 0731.

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Client: S. Fiskum
ASR 0731

Project: 73325

Prepared by: C Soderquist 5-2 2019

Technical Reviewer: L R Greenwood 5-2-19

Procedures:	RPG-CMC-4001, Rev 1, Source Preparation for Gross Alpha and Gross Beta Counting
	RPG-CMC-408, Rev 2, Gross Alpha and Gross Beta Counting
	RPG-CMC-476, Rev 0, Strontium Separation using Eichrom Strontium Resin
	RPG-CMC-432, Rev 0, Technetium-99 Analysis
	RPG-CMC-474, Rev 1, Liquid Scintillation Spectrometry
M&TE:	LB4100 proportional counters, Ludlum alpha counters, Perkin Elmer TriCarb model 3100 TR
Reference dates:	Mar 19 2019 (gross alpha, gross beta), Mar 28 2019 (Sr-90), April 17 2019 (Tc-99)

Sample	Lab ID	**Measured Activity, µCi per mL ± 1s**							
		Gross alpha		Gross beta		Strontium-90		Technetium-99	
TCT008-COMP-FEED	19-1107	4.07E-4	± 9%	1.42E+2	± 3%	3.44E-1	± 1%	8.98E-2	± 3%
TCT008-EFF-1	19-1108	1.11E-4	± 19%	8.69E-2	± 3%	5.81E-3	± 2%	7.43E-2	± 3%
TCT008-COMP-EFF	19-1109	1.78E-4	± 15%	9.72E-2	± 3%	8.58E-4	± 6%	7.34E-2	± 3%
	19-1109 Dup	2.18E-4	± 13%	9.66E-2	± 3%	8.07E-4	± 6%	7.67E-2	± 3%
	RPD	--		0.6%		6%		4%	
TCT008-L-F5-A	19-1110	1.41E-4	± 16%	1.41E-1	± 3%	--		--	
TCT008-L-F9-A	19-1111	2.13E-4	± 13%	9.81E-2	± 3%	--		--	
TCT008-L-F15-A	19-1112	2.03E-4	± 14%	1.85E-1	± 3%	--		--	
TCT008-L-F19-A	19-1113	3.07E-4	± 11%	8.28E-1	± 3%	--		--	
TCT008-L-F23-A	19-1114	3.17E-4	± 11%	4.29E+0	± 3%	--		--	
	Lab blank	-1.2E-6	± 44%	1.1E-5	± 39%	-3.5E-6	± 119%	1.7E-6	± 72%
	Reagent spike	109%		120%		105%		92%	
	Matrix spike	52%		--		106%		--	

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Procedures: RPG-CMC-4017, Rev 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry
RPG-CMC-422, Rev 2, Alpha Spectrometry
M&TE: Alpha spectrometry counting system
Count date: April 23, 2019 (plutonium), April 20, 2019 (neptunium)

Sample	Lab ID	Measured Activity, µCi per mL ± 1s					
		Neptunium-237		Plutonium-238		Plutonium-239+240	
TCT008-COMP-FEED	19-1107	1.03E-5	± 6%	8.40E-5	± 4%	5.66E-4	± 2%
TCT008-EFF-1	19-1108	1.21E-6	± 18%	1.69E-5	± 5%	1.08E-4	± 2%
TCT008-COMP-EFF	19-1109	5.91E-6	± 8%	2.88E-5	± 4%	1.79E-4	± 2%
	19-1109 Dup	5.08E-6	± 8%	2.97E-5	± 4%	1.83E-4	± 2%
	RPD	15%		3%		2%	
TCT008-L-F5-A	19-1110	2.76E-6	± 11%	2.67E-5	± 4%	1.66E-4	± 2%
TCT008-L-F9-A	19-1111	7.31E-6	± 7%	4.16E-5	± 3%	2.66E-4	± 2%
TCT008-L-F15-A	19-1112	8.43E-6	± 6%	2.91E-5	± 4%	1.98E-4	± 2%
TCT008-L-F19-A	19-1113	9.69E-6	± 6%	4.71E-5	± 3%	3.26E-4	± 2%
TCT008-L-F23-A	19-1114	1.01E-5	± 6%	5.27E-5	± 3%	3.55E-4	± 2%
	Lab blank	6.6E-8	± 109%	4.5E-9	± 356%	-5.3E-9	± 114%
	Reagent spike	98%		--		93%	
	Matrix spike	98%		--		92%	

The gross alpha results are biased low because of solids on the counting plate. Data shaded in grey are at or below detection limit. The gross beta and technetium-99 matrix spikes were too small for the accompanying sample activity (sample TCT008-COMP-EFF).

Plutonium 238, 239+240 Analysis

Project / WP#:	73325/NC2504
ASR#:	0731.00
Client:	SK Fiskum
Total # of Samples:	8

RPL ID	Client Sample ID	RPL ID	Client Sample ID
19-1107	TCT008-COMP-FEED	19-1111	TCT008-L-F9-A
19-1108	TCT008-EFF-1	19-1112	TCT008-L-F15-A
19-1109	TCT008-COMP-EFF	19-1113	TCT008-L-F19-A
19-1110	TCT008-L-F5-A	19-1114	TCT008-L-F23-A

Analysis Type:	AEA – Pu-238, Pu-239+240
Sample Processing Prior to Radiochemical Processing/Analysis	☐ None ☐ Digested as per PNL-ALO-106, Rev. 1, *Acid Digestion of Waters, Soils, and Sludges for Subsequent Radiochemical Sample Analyses* ☐ Fusion as per RPG-CMC-115, Rev0, *Solubilization of Metals from Solids Using a KOH-KNO₃ Fusion* ☒ Digested as per RPG-CMC-128, Rev.1, *HNO₃-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater*
Pre-dilution Prior to Radiochemical Processing?	☐ No ☒ Yes -- *example 2 mL to 100 mL; 50x dilution*
Total Alpha and Beta Preparation Procedure:	RPG-CMC-4001, Rev. 1, *Source Preparation For Gross Alpha and Gross Beta analyses.*
Technician/Analyst:	LP Darnell, (03/19/2019)
Spike Standard ID's	R-687-a-7 (Pu-239), R-693-b-10 (Sr-90)
Analysis Procedure	RPG-CMC-408, Rev. 2, *Total Alpha and Beta Analysis*
Technician/Analyst:	LP Darnell and T. Trang-Le 03/21/19
Plutonium Separation Procedure:	RPG-CMC-4017, Rev. 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
Technician/Analyst:	LP Darnell, (03/29/2019)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, Coprecipitation Mounting of Actinides for Alpha Spectroscopy
Technician/Analyst:	LP Darnell, (04/04/2019)
Spike and Tracer Standard ID's:	R-687-a-7 (Pu-239), R-700-a-2 (Pu-242 tracer)
Analysis Procedure:	RPG-CMC-422, Rev. 2, *Solutions Analysis: Alpha Spectrometry*
Reference Date:	Same as counting dates
Analysis Date or Date Range:	April 4 - 23, 2019
Technician/Analyst:	CS Soderquist
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1107 Fiskum.xls
CMC Project 98620 File:	File Plan 5871: T 73325: Sample preparation and analysis records; T-4.4 Alpha Detector calibration, calibration verification checks, and maintenance records; and T3 Standard certificates and preparation. Also balance calibration and instrument performance checks.
M&TE Number(s):	Ortec AEA counters – 32 counters – See attached M&TE list

/ 5/21/19		/ 21 MAY 2019	
Preparer	**Date**	**Reviewer**	**Date**

Sample Results

See attached data report, Sample Results for ASR 0731. All data are reported in units of µCi per mL with a 1-σ uncertainty unless noted otherwise (see Comments).

Sample Preparation, Separation, Mounting and Counting Methods

All eight samples submitted under Analytical Service Request (ASR) 0731 were analyzed for plutonium isotopes by Alpha Spectrometry. All the samples were prepared in RPL/420, only Pu-AEA is presented in this report.

Following the digestion process of the samples, the Pu was separated from the aqueous samples by anion exchange chromatography using procedure RPG-CMC-4017. The separated Pu fraction was mounted for alpha spectrometry by co-precipitation using procedure RPG-CMC-496, and then counted by alpha spectrometry using procedure RPC-CMC-422. The samples were counted on April 4-23, 2019; no decay corrections were made.

Alpha and beta analyses were performed on each sample to determine appropriate aliquot sizes for the chemical separations needed for the alpha and beta emitters of interest. Gross alpha and gross beta activity were measured by evaporating small aliquots of leachate onto counting planchets per procedure RPG-CMC-4001 and counting per procedure RPG-CMC-408.

QUALITY CONTROL RESULTS

Quality control (QC) samples include a laboratory preparation blank and sample duplicate. Additional QC samples were prepared prior to separations; these included a reagent spike (RS) and a matrix spike (MS) made by adding Pu-239 standard to a diluted sample.

Tracer:

The Pu-242 tracer is added to every sample after appropriate dilution and prior to plutonium separations. The use of a Pu-242 tracer corrects for radiochemical yield and mathematically removes the detector counting efficiency from the results calculations. Tracer recovery is required to be high enough to provide acceptable counting statistics. The Pu-242 tracer counting statistics were acceptable for all samples. The tracer recoveries ranged from 100% to 109%.

Laboratory Preparation Blank (PB):

The activity levels of Pu-239/240 and Pu-238 present in the laboratory preparation blank (-5.3E-9 µCi/mL, Pu-239/240 and 4.5E-9 µCi/mL, Pu-238) are both below the activities present in the samples (1.08E-4 µCi/mL Pu-239/240 and 1.69E-5 µCi/mL Pu-238 or higher) and less than lowest sample MDC (3.9E-7 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Blank Spike (BS) – Reagent Spike (RS):

The RS recovery of 93% meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

The MS recovery of 92% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared "after" digestion, by adding a known Pu-239 standard quantity to an aliquot of the leachate. Sample number 19-1109 (TCT008-COMP-EFF) was selected as the matrix spike sample.

Duplicate -- Relative Percent Difference (RPD):

Duplicate results are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be >5 times the MDA or have individual uncertainties <20%. The duplicate results were ≤3% RPD for Pu-238 and Pu-239/240; thus meeting the ≤20% requirement.

Instrument Quality Control

Alpha counters receive initial calibration with NIST traceable sources to determine the counter efficiency. When internal tracers are not used, the counter efficiency is used in calculation of final results.

Detector backgrounds are determined every 4 weeks or after the last analytical run, whichever is longer. Detector background counts are subtracted from all subsequent sample counts. A process blank is analyzed with each analytical batch to evaluate for contamination in the sample preparation process.

Assumption and Limitations of the Data

None

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.
2. The 1-sigma uncertainty represents the total propagated error associated with processing and counting operations and include; weighing errors, volume uncertainties, and counting error.

Attachment: Data Report -- Sample Results for ASR 0731.

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Client: S. Fiskum
ASR 0731

Project: 73325

Prepared by: C Soderquist 5-2 2019

Technical Reviewer: L R Greenwood 5-2-19

Procedures:	RPG-CMC-4001, Rev 1, Source Preparation for Gross Alpha and Gross Beta Counting
	RPG-CMC-408, Rev 2, Gross Alpha and Gross Beta Counting
	RPG-CMC-476, Rev 0, Strontium Separation using Eichrom Strontium Resin
	RPG-CMC-432, Rev 0, Technetium-99 Analysis
	RPG-CMC-474, Rev 1, Liquid Scintillation Spectrometry
M&TE:	LB4100 proportional counters, Ludlum alpha counters, Perkin Elmer TriCarb model 3100 TR
Reference dates:	Mar 19 2019 (gross alpha, gross beta), Mar 28 2019 (Sr-90), April 17 2019 (Tc-99)

	Lab	**Measured Activity, µCi per mL ± 1s**							
Sample	ID	Gross alpha		Gross beta		Strontium-90		Technetium-99	
TCT008-COMP-FEED	19-1107	4.07E-4	± 9%	1.42E+2	± 3%	3.44E-1	± 1%	8.98E-2	± 3%
TCT008-EFF-1	19-1108	1.11E-4	± 19%	8.69E-2	± 3%	5.81E-3	± 2%	7.43E-2	± 3%
TCT008-COMP-EFF	19-1109	1.78E-4	± 15%	9.72E-2	± 3%	8.58E-4	± 6%	7.34E-2	± 3%
	19-1109 Dup	2.18E-4	± 13%	9.66E-2	± 3%	8.07E-4	± 6%	7.67E-2	± 3%
	RPD	--		0.6%		6%		4%	
TCT008-L-F5-A	19-1110	1.41E-4	± 16%	1.41E-1	± 3%	--		--	
TCT008-L-F9-A	19-1111	2.13E-4	± 13%	9.81E-2	± 3%	--		--	
TCT008-L-F15-A	19-1112	2.03E-4	± 14%	1.85E-1	± 3%	--		--	
TCT008-L-F19-A	19-1113	3.07E-4	± 11%	8.28E-1	± 3%	--		--	
TCT008-L-F23-A	19-1114	3.17E-4	± 11%	4.29E+0	± 3%	--		--	
	Lab blank	-1.2E-6	± 44%	1.1E-5	± 39%	-3.5E-6	± 119%	1.7E-6	± 72%
	Reagent spike	109%		120%		105%		92%	
	Matrix spike	52%		--		106%		--	

Pacific Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1107 Fiskum
5/1/2019

Procedures: RPG-CMC-4017, Rev 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry
RPG-CMC-422, Rev 2, Alpha Spectrometry
M&TE: Alpha spectrometry counting system
Count date: April 23, 2019 (plutonium), April 20, 2019 (neptunium)

	Lab	**Measured Activity, µCi per mL ± 1s**					
Sample	ID	Neptunium-237		Plutonium-238		Plutonium-239+240	
TCT008-COMP-FEED	19-1107	1.03E-5	± 6%	8.40E-5	± 4%	5.66E-4	± 2%
TCT008-EFF-1	19-1108	1.21E-6	± 18%	1.69E-5	± 5%	1.08E-4	± 2%
TCT008-COMP-EFF	19-1109	5.91E-6	± 8%	2.88E-5	± 4%	1.79E-4	± 2%
	19-1109 Dup	5.08E-6	± 8%	2.97E-5	± 4%	1.83E-4	± 2%
	RPD	15%		3%		2%	
TCT008-L-F5-A	19-1110	2.76E-6	± 11%	2.67E-5	± 4%	1.66E-4	± 2%
TCT008-L-F9-A	19-1111	7.31E-6	± 7%	4.16E-5	± 3%	2.66E-4	± 2%
TCT008-L-F15-A	19-1112	8.43E-6	± 6%	2.91E-5	± 4%	1.98E-4	± 2%
TCT008-L-F19-A	19-1113	9.69E-6	± 6%	4.71E-5	± 3%	3.26E-4	± 2%
TCT008-L-F23-A	19-1114	1.01E-5	± 6%	5.27E-5	± 3%	3.55E-4	± 2%
	Lab blank	6.6E-8	± 109%	4.5E-9	± 356%	-5.3E-9	± 114%
	Reagent spike	98%		--		93%	
	Matrix spike	98%		--		92%	

The gross alpha results are biased low because of solids on the counting plate. Data shaded in grey are at or below detection limit. The gross beta and technetium-99 matrix spikes were too small for the accompanying sample activity (sample TCT008-COMP-EFF).

Project Number:	73325
Charge Code:	NC2504
ASR Number:	0731
Client:	S. Fiskum
Total Samples:	1 liquid

	Sample
RPL Numbers	19-1107
Client IDs	TCT008-COMP-FEED

Analysis Procedure	RPG-CMC-386 Rev. 1, "Carbon Measured in Solids, Sludge, and Liquid Matrices"
Prep Procedure	None
Analyst	A. Carney
Analysis Date	March 18, 2019
CCV Standards	TIC/TOC CMS # 543144 and 543143
BS/LCS/MS Standards	TIC/TOC CMS # 542973 and 533456
Excel Data File	ASR-0731-Fiskum.xlsx
M&TE Numbers	Carbon System (WD36639, RPL/701)
	Balance : Sartorius R200D, S/N 30809774
All Analysis Records	5015_01-01-2003-004350.CSV

Andrew Carny 5/7/19

Prepared By Date

5/9/19

Reviewed By Date

Table 1: TOC/TIC Results for ASR 0731

TIC in Sample **19-1107** (mg C/L):	7150
MDL (mg C/L):	314
EQL:	1569
TOC in Sample **19-1107** (mg C/L):	2249
MDL (mg C/L):	314
EQL:	1569
TIC in Sample **19-1107-Dup** (mg C/L):	6929
MDL (mg C/L):	314
EQL:	1569
TOC in Sample **19-1107-Dup** (mg C/L):	2365
MDL (mg C/L):	314
EQL:	1569
19-1107 TIC RPD:	3.1%
19-1107 TOC RPD:	5.0%

Sample Analysis/Results Discussion

One liquid sample was submitted under Analytical Service Request (ASR) 0731 for total inorganic and total organic carbon analysis. The analysis was performed by the hot persulfate wet oxidation method, with the results summarized in Table 1. The TIC is measured first with additions of heated sulfuric acid followed by the addition of a silver catalyzed acidic potassium persulfate solution for oxidation at 92-95 °C for TOC. The analyses were performed following procedure RPG-CMC-386, Rev. 1, *Carbon Analyses in Solids, Sludge and Liquid Matrices*

The sample was analyzed with one duplicate for each TIC and TOC. An analytical spike was also run for TIC and TOC on the sample. The sample results are corrected for the contribution from the system blank, as per procedure RPG-CMC-386, Rev. 1. All data are reported as µg C/mL of sample.

Data Limitations

None

Quality Control Discussion

The calibration and QC sample standards for the TOC initial/continuing calibration verification check (ICV/CCV) sample is a 1000 µg/mL solution of total organic carbon standard. The calibration and QC sample standards for the TIC initial/continuing calibration verification check (ICV/CCV) sample is a 1000 µg/mL total inorganic standard. The identification of the standards and their Chemical Management System (CMS) numbers are included on the raw data bench sheets for traceability.

The QC samples analyzed as part of the method include initial and continuing calibration verification samples (ICV/CCV), initial and continuing calibration blanks (ICB/CCB), laboratory duplicate for the sample, a laboratory control sample/blank spike (LCS/BS), and an analytical spike (AS). The work was performed in one batch.

Two blanks are run at the beginning of each batch and a blank is run after ICV/CCV. The blanks must be <EQL. The blanks run in the batch are <EQL.

Initial Calibration Check and Continuing Calibration Verification Standards:

> The calibration of the coulometer analysis system was checked by calibration verification standards analyzed at the beginning and end of the analysis run. TOC results for the two ICVs were 100.3% and 99.5% recovery, and for the two TIC ICVs the results were 92.4% and 92.3% recovery, within the acceptance criterion of 90% to 110%. The TOC result for the CCV was 100.3% recovery and the TIC CCV was 100.3% recovery, within the acceptance criterion of 85% to 115%.

Laboratory Control Sample/Blank Spike: One TIC and TOC LCS/BS was analyzed. The TIC LCS/BS result was 101.2% recovery and the TOC LCS/BS result was 100.0% recovery, meeting the acceptance criteria of 75% to 125%.

Duplicate/Replicate: Precision of the carbon measurements is demonstrated by the relative percent difference (RPD) between sample and duplicate/replicate. Sample 19-1107 TIC RPD was 3.1% and TOC was 5.0%. Both samples meet the acceptance criteria of ≤20%.

Analytical Spike (AS): The accuracy of the carbon measurements can be estimated by the recovery from the AS. The results for the analytical spike for TIC is 101.1% recovery and for the TOC, 95.9% recovery. The AS recovery for the TOC and TIC results meets the acceptance criterion of 75% to 125%.

Deviation from Procedure:

None

General Comments

1) Routine precision and bias are typically ±15% or better for non-complex samples that are free of interferences.
2) For the TIC/TOC, the analysis MDL is calculated by dividing the batch IDL by the sample mass and is therefore dependent on sample size. The estimated quantitation limit (EQL) is defined as 5x the MDL. Results <5x MDL have higher uncertainties and RPDs are not calculated if the results are <5x MDL.
3) Where applicable, the reported "Final Results" have been corrected for any dilution performed on the sample prior to analysis.