PNNL-32911, Rev. 0
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Reduced Temperature Cesium Removal from AP-101 Using Crystalline Silicotitanate

June 2022

AM Westesen
EL Campbell
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

The Tank Side Cesium Removal (TSCR) system, currently operational under Washington River Protection Solutions LLC (WRPS), sends initial low-activity Hanford waste tank supernate feed to the Hanford Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) Facility. In addition to entrained solids removal from the supernate, the primary goal of TSCR is to remove cesium-137 (^{137}Cs) by ion exchange, allowing contact handling of the liquid effluent product at the WTP. Crystalline silicotitanate (CST) ion exchange media, manufactured by Honeywell UOP, LLC (product IONSIV™ R9140-B), was selected as the ion exchange media at TSCR.

Laboratory-scale ion exchange processing using TSCR prototypic unit operations continues to contribute toward WRPS establishing accurate process flowsheets for the individual feed campaigns planned for TSCR. This report describes the small-scale ion exchange testing with 14.0 L of diluted and filtered supernate from tank 241-AP-101 (AP-101DF) at 16 °C (62 °F) to demonstrate processing at temperature conditions that are more prototypic of what the TSCR system could experience during colder seasons of the year. Since CST Cs capacity increases with decreasing contact temperature, testing at the lower operating temperature will help to predict the maximum ^{137}Cs loading onto the CST in the TSCR system.

One of the waste acceptance criteria (WAC) for the WTP Low-Activity Waste Facility is that the waste must contain less than 3.18×10^{-5} Ci ^{137}Cs per mole of Na.[1] For the AP-101DF tank waste to meet this criterion, only 0.144% of the influent ^{137}Cs concentration may be delivered to the WTP; this requires a Cs decontamination factor of 694. Testing with AP-101DF matched TSCR prototypic operations where a lead-lag configuration was used until the lag column reached the WAC limit, then a polish column was brought online for continued processing in a lead-lag-polish column configuration. Feed was processed at 1.9 bed volumes (BVs) per hour; the flowrate, in terms of contact time with the CST bed, matched the expected flowrate at TSCR. The Cs-decontaminated product was retained for vitrification testing (to be reported separately).

The lead column reached 62% Cs breakthrough after processing ~1400 BVs of feed; the 50% Cs breakthrough occurred at 1250 BVs. Testing compared to previous AP-107 testing at 16 °C showed ~80 BV increases in volume processed to reach the WAC limit for both lead and lag columns. A similar slope in breakthrough curves for both tests indicates similar kinetic behavior, with variations in feed matrices (Na and Cs concentrations) likely responsible for the deviations in reaching the WAC limit. The Cs effluent from the lag column reached the WAC limit after processing 875 BVs. Anticipating this breakthrough point, the polish column was preemptively installed at 770 BVs. Cs breakthrough from the lag column began at 300 BVs, reaching 5.32×10^{0} µCi/mL, or 5.6 % Cs breakthrough, after processing all 1400 BVs of feed. Table S.1 and Figure S.1 summarize the observed column performance and relevant Cs loading characteristics.

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[1] 24590-WTP-ICD-MG-01-030, Rev. 1. 2021. *ICD 30 – Interface Control Document for DFLAW Feed*. Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

Table S.1. AP-101 Column Performance Summary with CST at 16 °C

Column	WAC Limit Breakthrough (BVs)	50% Cs Breakthrough (BVs)	^{137}Cs Loaded (µCi)	Cs Loaded (mg/g CST)
Lead	275	1250	1.35E+06	7.14
Lag	875	2134(a)	2.64E+05	1.60
Polish	1543(a)	NA	8.09E+03	0.32

(a) Extrapolated value.
BV = bed volume, 10.0 mL
The time-weighted average flowrate was 1.90 BV/h.

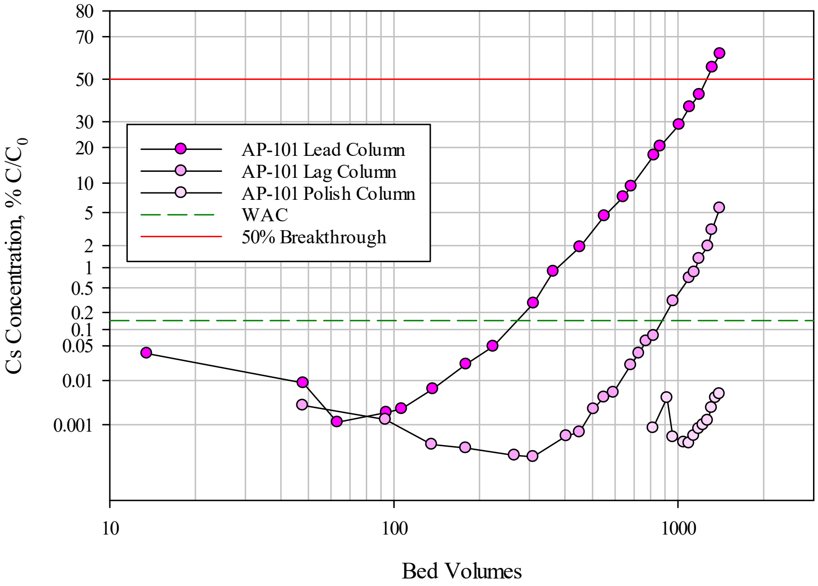

Figure S.1. Lead, Lag, and Polish Column Cs Load Profiles for AP-101 at 16 °C

The AP-10DF composite feed and composite effluent were characterized to understand the fractionation of selected metals and radionuclides. Concentrations and recoveries of the selected analytes are summarized in Table S.2; those with low recovery were assumed to be adsorbed onto CST. Lead (Pb) and barium (Ba) were detected in the feed (with concentration errors likely to exceed 15%) but were below the method detection limit (MDL) in the effluent; this was indicative of uptake by the CST. In addition to Cs removal, measurable fractions of calcium (Ca), iron (Fe), strontium (Sr), uranium (U), ^{237}Np, ^{238}Pu, and $^{239+240}$Pu also partitioned to the CST.

Table S.2. Recoveries of Analytes of Interest in the AP-101DF Effluent

	Analyte	Feed Concentration (M)	Effluent Concentration (M)	Fraction in Effluent
Metals / Non-metals	Al	3.39E-01	3.41E-01	99%
	Ba	3.52E-06	<5.3E-07	--
	Ca	7.93E-04	5.17E-04	64%
	Cd	[5.2E-06]	5.72E-06	109%
	Cr	9.53E-03	9.44E-03	98%
	Fe	3.25E-05	2.36E-05	72%
	K	9.81E-02	9.73E-02	98%
	Na	5.21E+00	5.22E+00	99%
	Ni	2.62E-04	2.38E-04	90%
	P	1.48E-02	1.44E-02	96%
	Pb	[8.0E-05]	<7.9E-05	--
	S	5.00E-02	[4.8E-02]	95%
	Sr	[1.4E-06]	2.12E-07	15%
	Ti	1.58E-06	7.23E-06	451%
	U	5.22E-05	3.43E-05	65%
	Zn	<2.5E-05	4.35E-05	--
	Zr	4.90E-06	1.69E-05	341%
	Analyte	Feed Concentration (µCi/mL)	Effluent Concentration (µCi/mL)	Fraction in Effluent
Radioisotopes	^{137}Cs	1.17E+02	4.45E-03	0.004%
	^{237}Np	1.99E-05	1.44E-05	71%
	^{90}Sr	3.04E-01	2.48E-04	0.1%
	^{238}Pu	1.62E-05	9.50E-06	58%
	$^{239+240}$Pu	1.27E-04	7.12E-05	55%
	^{241}Am	1.32E-04	1.05E-04	78%

Notes:
"<" values were < MDL, sample-specific MDL provided in Appendix C.
"--" indicates effluent recovery could not be calculated.
Values in brackets [ ] were ≥ MDL but < EQL, with errors likely to exceed ±15%.
EQL = estimated quantitation limit.

Batch contact tests were performed with the AP-101DF tank waste at four Cs concentrations and four temperatures (13, 16, 21, and 35 °C), each at a phase ratio of 200 (liquid volume to dry CST mass). The 16 °C distribution coefficient (K_d) at the equilibrium condition of 4.64E-5 M Cs (AP-101DF feed condition) was 1236 mL AP-101DF/g CST. With a CST bed density of 1.00 g/mL (<30 mesh CST), this K_d corresponded to a predicted 50% Cs breakthrough of 1384 BVs. The observed column performance 50% Cs breakthrough (1250 BVs) fell within 10% of the predicted performance (1384 BVs). The batch contact testing predicted a Cs load capacity of 0.0642 mmoles Cs/g dry CST at the equilibrium Cs concentration. The Cs breakthrough from the lead column at the 50% breakthrough point was used to determine full loading onto the CST at 100% C/C_0 and resulted in 0.0580 mmoles Cs/ g CST — 90.3% of the maximum Cs loading at feed condition based on prediction from batch contact testing.

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Acronyms and Abbreviations

AEA	alpha energy analysis
ASO	Analytical Support Operations
ASR	Analytical Service Request
BV	bed volume
CST	crystalline silicotitanate
DF	diluted feed
DI	deionized
EQL	estimated quantitation limit
erf	error function
FD	feed displacement
GEA	gamma energy analysis
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
ID	identification
LAW	low-activity waste
MDL	method detection limit
NA	not applicable
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RPL	Radiochemical Processing Laboratory
RSD	relative standard deviation
SRF	spherical resorcinol-formaldehyde
SV	system volume
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
TSCR	Tank Side Cesium Removal
WAC	waste acceptance criteria
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The Tank Side Cesium Removal (TSCR) system, developed by Washington River Protection Solutions (WRPS), removes cesium from Hanford tank waste supernate. The treated supernate is sent to the Low-Activity Waste (LAW) Facility at the Hanford Waste Treatment and Immobilization Plant (WTP) for vitrification. The TSCR system uses a non-elutable ion exchange medium, crystalline silicotitanate (CST) produced by Honeywell UOP, LLC (Des Plaines, IL) under the product name IONSIV™ R9140-B. The TSCR system processing will implement a lead-lag-polish column operational format. Each column will contain 596 L (157.5 gal) of CST media with a 234-cm (92-inch) bed height (Siewert 2019).

Decanted tank waste supernatant will be pretreated using TSCR to meet the WTP LAW Facility waste acceptance criteria (WAC).[2] The TSCR unit uses a filter to remove entrained solids and then a CST ion exchanger capable of retaining up to 141.6 kCi of ^{137}Cs on each column within the unit.[3] The TSCR WAC requires supernate temperatures be less than 35 °C (95 °F), with normal operations occurring around current tank temperatures of 16 to 20 °C. Zheng et al. (1997) showed that CST Cs capacity decreased as contact temperature increased. Figure 1.1 shows the temperature profile of the Hanford AP-101 tank waste for the two-year period from early January 2020 to late December 2021; the temperature averaged 19.1 °C with a range of 16.2 to 22.3 °C. Testing at the lower operating range will help to predict the maximum ^{137}Cs loading onto the CST in the TSCR system and guide the appropriate operating restrictions to ensure the column loading limit will not be exceeded.

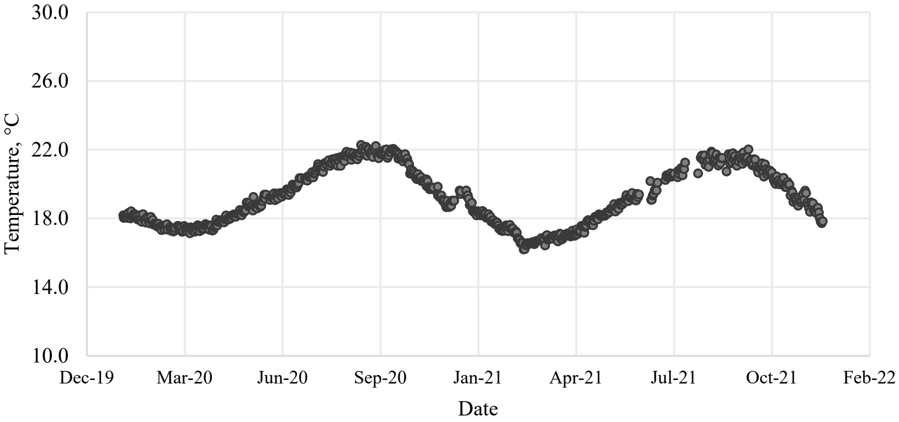

Figure Notes: Data collected from 241-AP-101 Location Riser 4 18.
Data downloaded from Tank Waste Information Network System on February 18, 2022.

Figure 1.1. AP-101 Tank Waste Temperatures from January 7, 2020 to December 31, 2021

The primary objective of the work described in this report was to test Cs removal using TSCR prototypic hybrid column processing at an operating temperature of 16 °C and establish Cs load profiles. For this testing, a lead-lag column system was used, and once the lag column effluent reached the WAC limit, a

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[2] 24590-WTP-ICD-MG-01-030, Rev. 1. 2021. *ICD 30 – Interface Control Document for DFLAW Feed*. Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

[3] RPP-RPT-61030, Rev. 1. 2019. *Process Operations Description*. AVANTech Incorporated, Richland, Washington.

polish column was positioned after the lag column and processing continued in a lead-lag-polish configuration. Additional objectives of the current study are as follows:

1. Conduct batch contact testing with CST at 13, 16, 21, and 35 °C to determine the Cs load capacity of diluted and filtered AP-101 (AP-101DF).
2. Compare the 16 °C AP-101DF Cs load profile to the previously reported 16 °C AP-107 load curve (Westesen et al. 2021b).
3. Analyze the AP-101DF ion exchange feed and effluent to derive the fates of key analytes (^{90}Sr, ^{137}Cs, $^{239+240}$Pu, ^{237}Np, Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr, Ti, U, Zn, Zr).
4. Provide Cs-decontaminated AP-101DF for vitrification (conducted in early 2022 and addressed in a separate report).

The efficacy of loading higher amounts of Cs onto the lead column CST while maintaining a product below the WTP LAW WAC limit from the polish column was of prime interest to support the evolving WRPS TSCR design. The design of the tests reported herein exposed the CST to higher feed volumes through the individual column beds, allowing for a more representative assessment of the fractionations of analytes of interest.

WRPS funded Pacific Northwest National Laboratory (PNNL) to conduct testing with AP-101 tank waste under the statement of work presented in Requisition #351656, "FY 22 Radioactive Waste Test Platform," Rev. 0, dated September 7, 2021.

2.0 Quality Assurance

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), and consists of 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 Test Conditions

This section describes the CST media, AP-101 tank waste, column ion exchange conditions, sample analysis, batch contact conditions. All testing was conducted in accordance with a test plan prepared by PNNL and approved by WRPS.[4]

3.1 CST Media

The CST used in this testing was procured by WRPS as ten 5-gallon buckets (149 kg total) of IONSIV™ R9140-B,[5] lot number 2002009604, from Honeywell UOP, LLC. The CST was transferred to PNNL for use in laboratory testing described herein. Details of the procurement and material properties can be found elsewhere (Fiskum et al. 2019b). Before use in column and batch contact testing, the <30-mesh CST fraction was first pretreated by contacting with 0.1 M NaOH successively until fines were no longer overserved.

3.2 AP-101 Tank Waste Sample

WRPS collected multiple samples (36 each at nominally 250 mL) from the AP-101 Hanford tank in October 2021. The first and last samples collected, 1AP-21-08 and 1AP-21-43, were subsampled for a limited analysis suite to confirm density and Na, K, OH, and Cs concentrations. The density was measured in a PNNL hot cell using a 10-mL volumetric flask. All other measurements were conducted by PNNL's Analytical Support Operations (ASO) laboratory according to Analytical Service Request (ASR) 1386.00; results are provided in Table 3.1. The results of the two samples agreed well, indicating the 36 samples were likely homogenous.

Table 3.1. Characterization of Samples 1AP-21-08 and 1AP-21-43 Collected from Hanford Tank AP-101 (ASR 1386.00)

Analyte	1AP-21-08 Result	1AP-21-43 Result	Result Units	Analysis Method
Al	0.591	--	M	ICP-OES
K	0.150	--	M	ICP-OES
Na	8.888	--	M	ICP-OES
^{133}Cs	6.04	6.09	µg/mL	ICP-MS
^{137}Cs	202$^{(a)}$	192$^{(a)}$	µCi/mL	GEA
^{137}Cs	2.15$^{(a)}$	2.19$^{(a)}$	µg/mL	GEA
Density	1.3981$^{(b)}$	--	g/mL	Volumetric flask

(a) Reference date is November 2, 2021.
(b) Measured at 25.0 °C using a 10-mL volumetric flask.
ASR 1386.00, sample 22-0010 and 22-0011, see Appendix C.
GEA = gamma energy analysis; ICP-MS = inductively coupled plasma mass spectrometry; ICP-OES = inductively coupled plasma optical emission spectroscopy

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[4] Westesen AM. 2021. Test Plan TP-DFTP-123, Rev. 0.0. *FY22 Cesium Ion Exchange Testing with AP-101 Tank Waste Using Crystalline Silicotitanate*. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available.

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

The Cs isotopic composition of the AP-101 samples was measured to determine the total Cs concentration in the AP-101 tank waste. Except for ^{133}Cs, direct analysis of AP-101 for the ^{135}Cs and ^{137}Cs isotopes can result in isobaric interferences. Therefore, subsamples (first and last AP-101 tank samples collected, 1AP-21-08 and 1AP-21-43 of AP-101) were processed to isolate Cs. Aliquots (1.5 mL) of AP-101 were batch contacted with 2 mL Na-form spherical resorcinol-formaldehyde (SRF) resin suspended in 8 mL 1 M NaOH. The slurries were mixed for ~24 hours on a shaker at room temperature. The aqueous phase was decanted and the SRF was washed three times with 6 mL 0.1 M NaOH, then rinsed three times with 6 mL deionized water. Cs was eluted from the SRF resin with 0.45 M HNO_3. Quantitative recovery was not required because only the Cs isotope ratios were needed, and isotope fractionation does not occur in Cs uptake to, or elution from, SRF resin. The elution aliquots were measured by ICP-MS for Cs isotopic distribution; results are provided in Table 3.2. The total Cs concentration was calculated from the GEA-measured ^{137}Cs and the ICP-MS-measured isotopic composition. The calculated ^{133}Cs concentration agreed within 4% of the ICP-MS-measured ^{133}Cs concentration (shown in Table 3.2). These values aligned within 1% of isotopic ratios measured for tank AP-107.

Table 3.2. 1AP-21-08 and 1AP-21-43 Average Cs Isotopic Composition (ASR 1386)

Analyte[(a)]	1AP-21-08 Results	1AP-21-43 Results	Units
Cs isotopic mass ratio[(a,b,c)]	61.1	61.8	wt% ^{133}Cs
	17.1	17.6	wt% ^{135}Cs
	21.9	20.6	wt% ^{137}Cs
Total Cs	10.66		µg/mL Cs

(a) The Cs eluate samples (1AP-21-08-Cs and 1AP-21-43-Cs) were analyzed for the Cs isotopic mass distribution by ICP-MS per ASR 1386 samples 22-0010 and 22-0011, see Appendix C.
(b) Reference date is November 5, 2021.
(c) ^{134}Cs, a fission product, was not detected by GEA; with a 2.065-year half-life, it was assumed to be decayed to extinction.

The AP-101 tank waste samples were composited and diluted to achieve a targeted 1.25 g/mL density and 5.50 M Na concentration as described in Allred et al. 2022. Nominally 1 L of AP-101 tank waste was combined with 0.553 L of Columbia River process water. The AP-101 and water were mixed, and density was measured to verify the target dilution had been achieved. Density was measured via 10-mL Class A volumetric flask and an analytical balance and was recorded at 1.259 g/mL at an ambient cell temperature of 25.2 °C. The Na concentration was not measured after dilution but was measured after filtration (which should not affect Na concentration). The diluted AP-101, hereafter referred to as AP-101DF (where the "DF" suffix designates diluted feed), was chilled to 16 °C before being filtered with a media grade 5 filter (Allred et al. 2022). After filtration, 11 bottles of AP-101DF, containing nominally 1.3 L each, were made available for ion exchange testing.

The densities and ^{137}Cs concentrations of each of the 11 bottles of AP-101DF were measured. The density average was 1.242 g/mL [1.13% relative standard deviation (RSD)] and the ^{137}Cs average was 115.0 µCi/mL (2.9% RSD; reference date December 2021). Therefore, AP-101DF feeds in all containers were considered uniform. The total Cs concentration for the diluted waste was calculated from the ^{137}Cs concentration (in terms of µg/mL with unit conversion per the specific activity) and ^{137}Cs mass fraction (average 21.2 wt%). The total Cs concentration in the AP-101DF was 6.23 µg/mL or 4.64E-5 M. This Cs concentration is notably lower than tank AP-107, which measured 8.57 µg/mL, but aligns with the differing Na concentrations of the two feeds.

3.3 Ion Exchange Processing at 16 °C

This section describes the ion exchange column system and AP-101DF process conditions. The preparations and column testing were conducted in accordance with a test instruction.[6]

3.3.1 Ion Exchange Column System

Figure 3.1 provides a piping and instrumentation diagram of the ion exchange process system. The columns were housed in a 12-inch × 6-inch × 15-inch (W×D×H) insulated box, previously used for AP-107 testing at 16 °C and described in Westesen et al. 2021b. Heat exchange was conducted with ethylene glycol from a chilled circulating bath flowing through copper tubing on the inner panels of the box. The internal temperature was monitored with a thermocouple seated inside a vial of water adjacent to the columns.

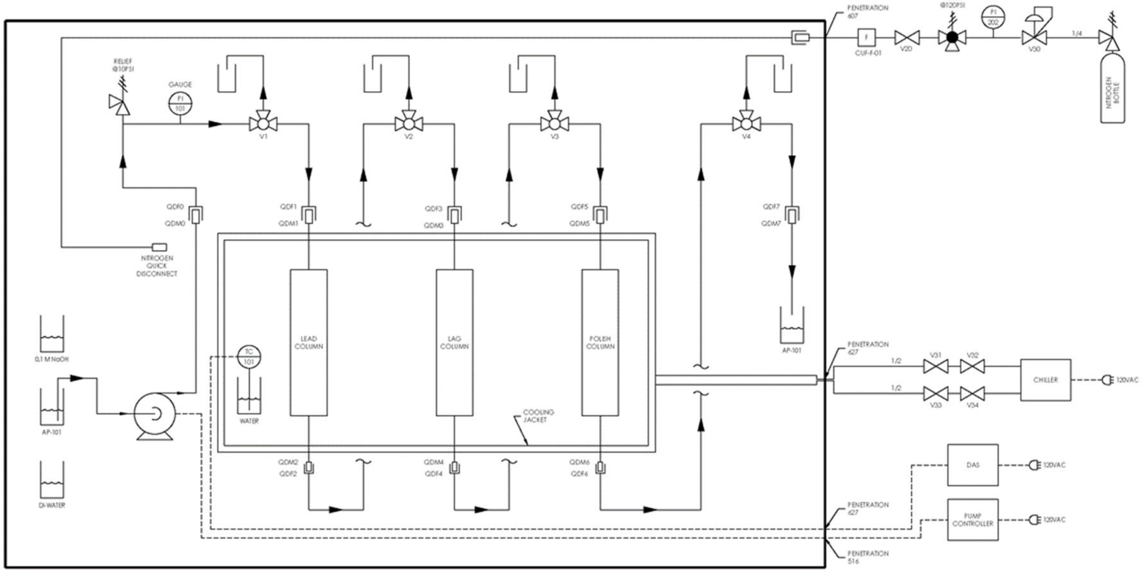

Figure 3.1. Chilled Ion Exchange Piping and Instrumentation Diagram

Figure 3.2 shows a photograph of the system heat exchanger after installation in the hot cell. The heat exchanger housed all three columns. A 10-inch × 3-inch front window was installed for visual monitoring of the columns during processing. Tubing preceding each column was coiled within the heat exchanger to ensure the temperature of the feed entering the columns was within the operating range of 16 ± 2.2 °C.

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[6] Westesen AM. 2021. Test Instruction TI-DFTP-126. *Reduced Temperature Cesium Removal from AP-101 Using Crystalline Silicotitanate in a Two and Three-Column Format.* Pacific Northwest National Laboratory, Richland, Washington. Implemented December 2021. Not publicly available.

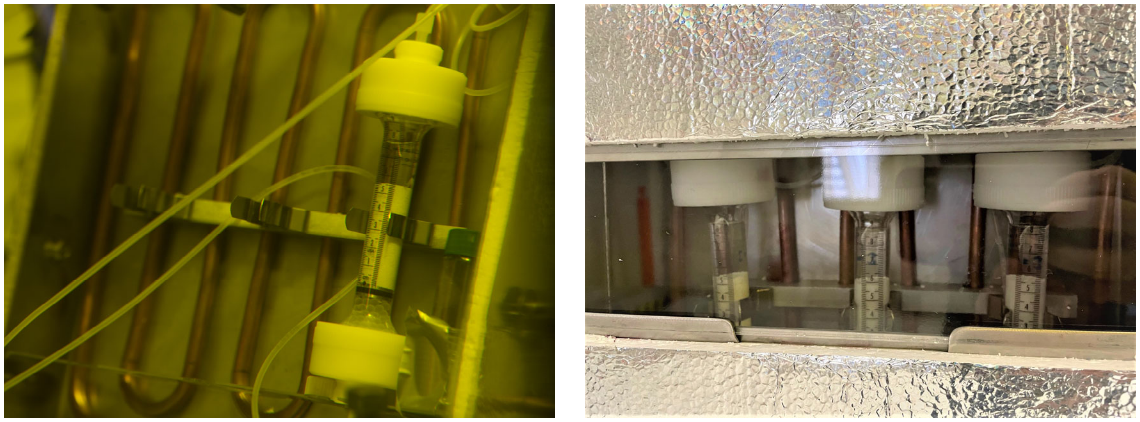

Figure 3.2. Photographs of Insulated Box and Ion Exchange System Inside of the Hot Cell

Flow through the system was controlled with a Fluid Metering Inc. positive displacement pump. Fluid was pumped past an Ashcroft pressure gage and a Swagelok pressure relief valve with a 10-psi trigger point. The 1/8-inch outside diameter / 1/16-inch inside diameter polyethylene tubing was purchased from Polyconn (Plymouth, MN). The 1/8-inch outside diameter / 1/16-inch inside diameter stainless steel tubing was used in conjunction with the valve manifold. Valved quick disconnects (QDM/QDF in Figure 3.1) were purchased from Cole Parmer (Vernon Hills, IL). Use of the quick disconnects enabled easy disassembly and re-assembly for installation in the hot cell. Multiple quick disconnects were used such that columns could be isolated (required for system install and reserved polish column) or replaced as needed. Also, recovery from upset conditions could be accommodated by allowing access to a column either downflow or upflow.

Chromaflex® column assemblies were custom-ordered from Kimble Chase (www.kimble-chase.com). Each column assembly included the column plus the standard top and bottom end fittings. Each column was made of borosilicate glass; the straight portion of the column was 9 cm tall with an inside diameter of 1.5 cm (corresponding to a CST volume of 1.77 mL/cm). The 1.5-cm inside diameter columns are not commercial-off-the-shelf items. The columns are flared at each end to support the off-the-shelf column fittings and tubing connectors that were composed of polytetrafluoroethylene. The CST was supported by an in-house-constructed support consisting of a 200-mesh stainless steel screen tack welded onto a stainless-steel O-ring. With a rubber O-ring, the bed support was snug-fit into place in the column (as previously described by Fiskum et al. 2019b). The flared cavity at the bottom of each column was filled to the extent possible with 4-mm-diameter glass beads to minimize the mixing volume below the CST bed. An adhesive centimeter scale with 1-mm divisions (Oregon Rule Co., Oregon City, OR) was affixed to each column with the 0-point coincident with the top of the support screen.

The valve manifold was the same that had been used previously for AP-107 processing reported in Westesen et al. (2021b). Four Swagelok valves (V1 through V4 in Figure 3.1) were installed on the valve manifold. Valve 1 was placed at the outlet of the pressure gage and used to isolate the columns from the pump (when in the closed position) and purge the tubing from the inlet to valve 1 (when placed in the sampling position). Lead column samples were collected at valve 2, the lag column samples were collected at valve 3, and the polish column samples were collected at valve 4. The gross AP-101DF effluent, feed displacement (FD), water rinse, and flushed fluid were collected at the effluent line.

Three 10.0-mL aliquots of settled CST (pretreated, <30 mesh) were measured using a graduated cylinder and then quantitatively transferred, one aliquot each, to the three columns. The CST was allowed to settle through the 0.1 M NaOH solution, thus mitigating gas bubble entrainment. The columns were tapped with a rubber bung until the CST height no longer changed.

The CST bed volume (BV) corresponded to the settled CST media volume as measured in the graduated cylinder prior to transferring the media into the ion exchange column. The reference CST BV was 10.0 mL; each of the three columns contained 10.0 mL CST. The settled CST bed heights in the columns were nominally 5.5 cm. This small column bed height corresponded to 2.4% of the full-height TSCR column (234 cm or 92 inches) and the BV corresponded to 0.0017% of the full-scale column (596 L) (Siewert 2019).

The entire fluid-filled volume of the assembly was calculated for the two-column system at ~54 mL, and for the three-column system at ~76 mL. The bed void volume was assigned 66% (Westesen et al. 2020). Therefore, each CST bed held 6.6 mL of fluid and the CST only comprised ~30% of the fluid-filled bed volume. The TSCR system platform may have a much larger fluid fraction associated with the CST bed. The fluid-filled mixing space above each CST bed averaged 6 mL and the fluid mixing volume below each CST bed ranged from 2.2 to 2.5 mL. Thus, ~60% of the total fluid holdup volume was unavoidably associated with the geometry of the two-column system. These scales of fluid mixing volume fractions are not likely to be representative of plant-scale operations. Figure 3.3 is a photograph of the chilled ion exchange system in-cell during AP-101DF processing.

Figure 3.3. Ion Exchange Assembly in the Hot Cell Post Processing

3.3.2 AP-101DF Tank Waste Process Conditions

Once the ion exchange columns were installed within the chiller box, a flow of 0.1 M NaOH was used to verify system integrity and calibrate the pump. The AP-101DF contained in various 1.5-L polyethylene containers from the filtration process (Allred et al. 2022) was used as the ion exchange feed. To provide stability, bottles were positioned in a bottle stand with the feed line inserted through the lid. When the contents in a feed bottle decreased to ~300 mL, the next bottle in line was moved to the feed position and the residual contents were poured into the new feed bottle. The AP-101DF feed was processed downflow through the ion exchange media beds, lead to lag. Effluent was collected in ~1.3-L increments. This volume limitation allowed for safe transfer out of cell in 1.5-L polyethylene bottles. The lag column effluent Cs concentration was closely monitored. When the WAC limit was reached, the polish column was placed in-line and the run continued.

After the AP-101DF processing (also “loading” in subsequent discussion) was completed, ~12 BVs of 0.1 M NaOH FD followed by ~12 BVs of deionized water were passed downflow through the system to rinse residual feed out of the columns and process lines. The 12 BVs was equivalent to ~1.7 times the fluid-filled system volume (SV).

Figure 3.4 provides a daily temperature profile of the AP-101DF processing as it went through the columns. Temperature was measured using a thermocouple placed inside a vial of water that sat within the exchanger. The exchanger temperature averaged 16.1 °C throughout the duration of testing, with min/max temperatures of 15.6 and 16.6 °C, respectively. Test parameters, including process volumes, flowrates, and CST contact times, are summarized in Table 3.3. The stroke rate was adjusted throughout testing to maintain the flowrate to the targeted 1.90 BV/h.

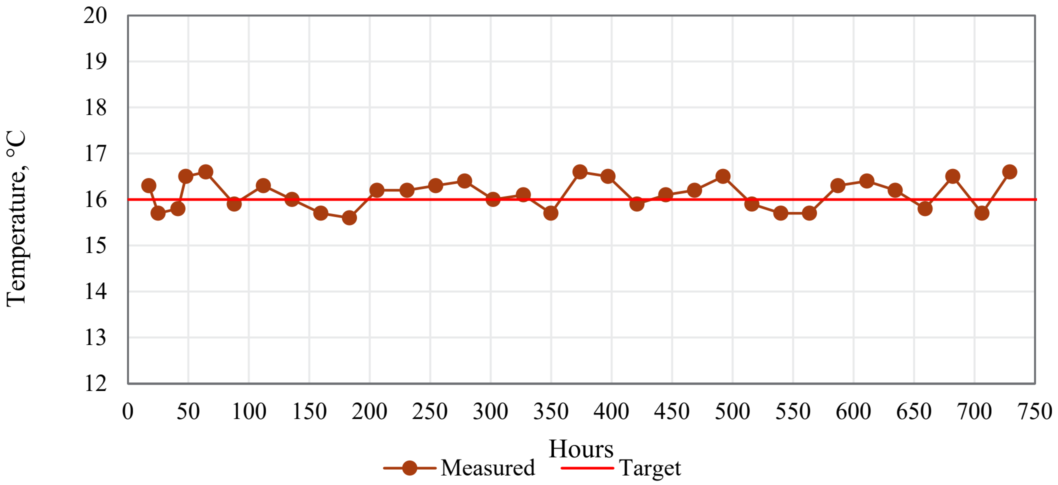

Figure 3.4 AP-101DF Daily Column Temperature during Testing

Table 3.3. Experimental Conditions for AP-101DF Column Processing at 16 °C, January 10 to February 10, 2022

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(SV)	(mL)	(BV/h)	(mL/min)	(h)
Loading lead column	AP-101DF	1407.0	NA	14070	1.89	0.316	745
Loading lag column[(a)]	AP-101DF	1402.5	NA	14025	1.89	0.316	745
Loading polish column[(b)]	AP-101DF	1397.7	NA	13977	1.89	0.316	335
Feed displacement	0.1 M NaOH	12.7	1.65	126.5	3.30	0.550	4.0
Water rinse	DI water	12.8	1.67	127.7	3.30	0.550	4.0
Flush with compressed air[(c)]	NA	6.3	0.86	63.2	NA	NA	NA

(a) The feed volume through the lag column was reduced relative to that of the lead column because samples collected from the lead column did not enter the lag column.
(b) The feed volume through the polish column was lower relative to that of the lead and lag columns because it was placed in position after 817 BVs were processed.
(c) The flush occurred on February 14, 2022, after the system sat in static contact with water rinse for 4 days.
BV = bed volume (10.0 mL as measured in graduated cylinder).
DI = deionized.
SV = system volume (estimated 76 mL).
NA = not applicable.

The total cumulative volume of AP-101DF processed was 14.1 L (1407 BVs). The AP-101DF process cycle mimicked, as best as possible, the current process flow anticipated at the TSCR facility in terms of BV/h (i.e., contact time), FD, and water rinse as defined in the test plan. It was understood that the feed linear flow velocity in this small-column configuration (0.18 cm/min) could not begin to match that of the full-height processing configuration (7.3 cm/min, Fiskum et al. 2019b). The objective was to match contact time in the bed.

During the loading phase, nominal 2-mL samples were collected from the lead, lag, and polish columns at the sample collection ports (see Figure 3.1, valves 2, 3, and 4). Sampling from the columns necessitated brief (~7-minute) interruptions of flow to the downstream columns. Samples were collected after the first 13 BVs were processed and again at nominal 12- to 145-BV increments. Only brief (~5-min) interruptions were associated with changing the feed bottles.

The feed displacement (FD) effluent was collected in a series of 6 vials in ~20-mL increments. The water rinse was similarly collected. The fluid-filled volume was expelled with compressed air connected at the first quick disconnect in the system, *QDF0* (see Figure 3.1), in ~4 minutes. The collected volume (63.2 mL) did include the interstitial fluid space between the CST beads but was not expected to include fluid in the CST pore space. Hours of additional gas flow were required to dry the CST enough to be free-flowing such that it would effectively pour out of the columns into specially designed shielded containment for later examination (not addressed in this report). The recovered CST was 10.28 g, 10.31 g, and 10.41 g for the lead, lag, and polish columns, respectively. With a CST bed density is 1.00 g/mL, quantitative recovery of the CST from the columns was estimated, with slight increases in mass on subsequent columns potentially due to CST fines carried over during air drying.

After settling for a couple of days, solids were observed in FD samples with “-3”, and “-4” designators as well as the flush solution, pictured in Figure 3.5. The aqueous phase was decanted and the solid slurry at the bottom of the sample was removed from the hot cell for better visualization. Solids in gas-flushed fluid had been previously noted for AP-105DF processing, reported in Fiskum et al. (2021b), and were found to be primarily Ca, Si, and Al with fractions of Ba, Sr, Ti, and Zr, indicative of some amount of CST fines.

Figure 3.5 Settled FD Solids

3.4 Sample Analysis

Cesium load performance was determined from the ^{137}Cs measured in the collected samples relative to the native ^{137}Cs in AP-101DF feed. The collected samples were analyzed directly to determine the ^{137}Cs concentration using GEA. Cesium loading breakthrough curves for both the lead and lag columns were generated based on the feed ^{137}Cs concentration (C_0) and the effluent Cs concentration (C) in terms of % C/C_0.

A composite feed sample was prepared by collecting a pro-rated volume from each feed bottle and combining in a polyethylene vial; a composite effluent sample was similarly collected. Selected effluent samples from the lead column were measured for selected radionuclides and cations to assess the exchange behavior for these analytes. Table 3.4 summarizes the specific sample collections and targeted analytes along with the cross-reference to the ASO sample identification (ID).

The ASO 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 their standard operating procedures, the ASO QA Plan, and the ASR. Samples were analyzed directly (no preparation) by GEA; longer count times were used to assess isotopes other than ^{137}Cs.

Table 3.4. Analytical Scope Supporting Column Processing, ASR 1420

Sample ID	ASO Sample ID	Analysis Scope
TI126-Comp-FEED	22-0512	GEA (^{137}Cs, ^{60}Co, ^{154}Eu) ICP-OES (Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr, Ti, U, Zn, Zr) ICP-MS (Ba, Nb, Pb, Sr, ^{238}U) Radioanalytical (^{90}Sr, ^{99}Tc, ^{237}Np, ^{238}Pu, $^{239+240}$Pu, ^{241}Am)
TI126-Comp-EFF	22-0513	GEA (^{60}Co, ^{137}Cs, ^{154}Eu) IC anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, $C_2O_4^{2-}$, SO_4^{2-}) Hot pursulfate (TIC, TOC) Acid titration (free OH) ICP-OES (Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr, Ti, U, Zn, Zr) ICP-MS (Ba, Nb, Pb, Sr, ^{238}U) Radioanalytical (^{90}Sr, ^{99}Tc, ^{237}Np, ^{238}Pu, $^{239+240}$Pu, ^{241}Am)
TI126-L-F4	22-0514	ICP-OES (Al, Ca, Cd, Fe, K) ICP-MS (Ba, Pb, ^{238}U) Radioanalytical (^{90}Sr, ^{237}Np, ^{238}Pu, $^{239+240}$Pu)
TI126-L-F11	22-0515	
TI126-L-F15	22-0516	
TI126-L-F18	22-0517	
TI126-L-F21	22-0518	

ICP-OES = inductively coupled plasma optical emission spectroscopy
ICP-MS = inductively coupled plasma mass spectrometry
IC = ion chromatography
TIC = total inorganic carbon
TOC = total organic carbon

3.5 Batch Contact Conditions

Batch contact experiments with AP-101 effluent following ion exchange processing were conducted to evaluate Cs loading at four different temperatures. Stock solutions of 0.75 and 0.085 M $CsNO_3$ were prepared by dissolving the nitrate salt in a volumetric flask with DI water and adjusting to 0.01 M HNO_3. Calculated volumes of Cs stock solutions were delivered to poly bottles and the mass of the spike was measured. The AP-101 effluent was spiked with ^{137}Cs and nominally 120 mL was transferred into each poly bottle to achieve Cs concentrations of 1.2E-4, 3.4E-4, 8.8E-4, and 1.7E-4 M Cs. Solutions were prepared gravimetrically, and exact volumes were calculated from mass and density measurements.

Nominal 0.075-g (dry mass basis) aliquots of CST were measured into 20-mL vials. F-factor samples were collected in duplicate, bracketing batch contact sample collection, and used to determine the dry mass of the exchanger. The F-factor was measured at 105 and 427 °C with average values of 0.923 and 0.846, respectively. The F-factor at 105 °C was used to calculate the dry mass of CST for the batch contact tests.

Aliquots (15-mL) of the AP-101 Cs stock solutions were added to the appropriate vials (in duplicate) and the exact solution volume transferred was calculated from net solution mass and density. The solution-to-mass phase ratio ranged from 174 to 202.

The 13 and 21 °C batch contact tests were done concurrently. The 21 °C (ambient) samples were contacted on a Cole-Parmer (Vernon Hills, Illinois) large orbital shaker set to 240 rpms. The remaining three temperatures (13, 16, and 35 °C) were sequentially contacted in a Benchmark (Sayreville, New Jersey) Incu-Shaker™ refrigerated/heated orbital shaker set to 200 rpms. A vial of water co-located with each sample set was used to monitor the temperature over the ~ 240-hour contact time. The resulting temperature fluctuations are shown in Figure 3.6 with error bars representative of the 2.2 °C measurement uncertainty of a Type K thermocouple. The weighted mean temperature for each set of batch contacts is provided in Table 3.5.

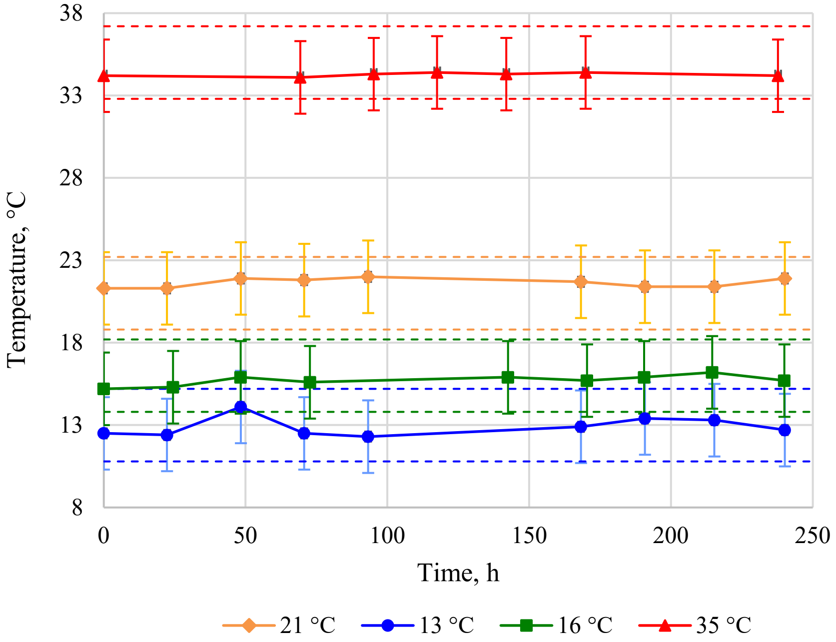

Figure 3.6 . Temperature Profiles of Batch Contact Testing with AP-101 Tank Waste Supernate

Table 3.5. Average Contact Temperature

Target Temperature (°C)	Weighted Mean Temperature (°C)
13	12.9
16	15.7
21	21.7
35	34.3

After contact, 2 mL of the supernate was removed and filtered through a 0.45-micron pore size nylon syringe filter and transferred to a glass vial for gamma energy analysis (GEA). The ^{137}Cs activity measured by GEA in pre- and post-contacted solutions was used to determine the total Cs exchange. Analysis and data reduction were conducted using the methods previously reported (Fiskum et al. 2019a). The isotherm data were fitted to a Freundlich/Langmuir hybrid equilibrium fit (Hamm et al. 2002).

The batch distribution coefficients were calculated according to Eq (3.1).

$$\frac{(A_0 - A_1)}{A_1} \times \frac{V}{M \times F} = K_d \qquad (3.1)$$

where A_0 = initial ^{137}Cs concentration (µCi/mL)
A_1 = final (equilibrium) ^{137}Cs concentration (µCi/mL)
V = volume of the batch contact liquid (mL)
M = measured mass of CST (g)
F = F-factor, mass of the 105 °C dried CST divided by the mass of the undried CST
K_d = batch-distribution coefficient (mL/g)

Final (equilibrium) Cs concentrations (C_{Eq}) were calculated relative to the tracer recovered in the contacted samples (A_1) and the initial metal concentration (C_0) according to Eq. (3.2)

$$C_0 \times \left(\frac{A_1}{A_0}\right) = C_{Eq} \qquad (3.2)$$

where C_0 = initial Cs concentration in solution (µg/mL or M)
C_{Eq} = equilibrium Cs concentration in solution (µg/mL or M)

The equilibrium Cs concentrations loaded onto the CST (Q in units of mmoles Cs per gram of dry CST mass) were calculated according to Eq. (3.3)

$$\frac{C_0 \times V \times \left(1 - \frac{A_1}{A_0}\right)}{M \times F \times 1000 \times FW} = Q \qquad (3.3)$$

where Q = equilibrium Cs concentration in the CST (mmole/g CST)
1000 = conversion factor to convert µg to mg
FW = Cs formula weight

4.0 Results

This section discusses the Cs exchange behavior during column and batch contact testing with AP-101 tank waste. Ion exchange process raw data are provided in Appendix A. Batch contact raw data are provided in Appendix D.

4.1 Ion Exchange Processing

The AP-101DF feed was processed at nominally 1.90 BV/h through the lead and lag columns for 770 BVs, at which time a polish column was plumbed into position in preparation for the lag column effluent reaching the WAC limit. The polish column processed a total of 580 BVs. Figure 4.1 shows a linear-linear plot of the cesium 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 115 µCi/mL (average of the seven filter product bottle feeds, RSD of 2.9%). In this graphing layout, the Cs breakthrough from the lead column appeared to start at ~350 BVs and continued to 62% C/C_0 after processing 1407 BVs when the last sample was collected from the lead column. Similarly, the lag column Cs breakthrough appeared to start at ~1190 BVs and increased to 6% breakthrough when the last sample was collected from the column. The polish column Cs breakthrough performance is not discernable at this linear scale.

Figure 4.2 shows the same Cs load data provided in Figure 4.1, but with the ordinate % C/C_0 on a probability scale and the abscissa BVs processed on a log scale. Under normal load processing conditions, these scales provide a predictable straight-line Cs breakthrough curve and provide greater fidelity of load characteristics at low and high % C/C_0 values (Buckingham 1967). In contrast to Figure 4.1, the Cs breakthrough from the lead column was observed to occur at around 90 BVs processed and breakthrough from the lag column started just after 275 BVs of processing. In addition to the 50% C/C_0 indication line, the WAC limit, set at 0.144% C/C_0, is also apparent (dashed green line).[7] The WAC Cs breakthrough for the lead column occurred at 275 BVs and lag column at 880 BVs.

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[7] The WAC limit was derived from the allowed curies of ^{137}Cs per mole of Na in the effluent to support contact handling of the final vitrified waste form: 3.18×10^{-5} Ci ^{137}Cs/mole Na. At 5.6 M Na and 162 µCi ^{137}Cs/mL in the feed, the WAC limit translates to 0.114% C/C_0.

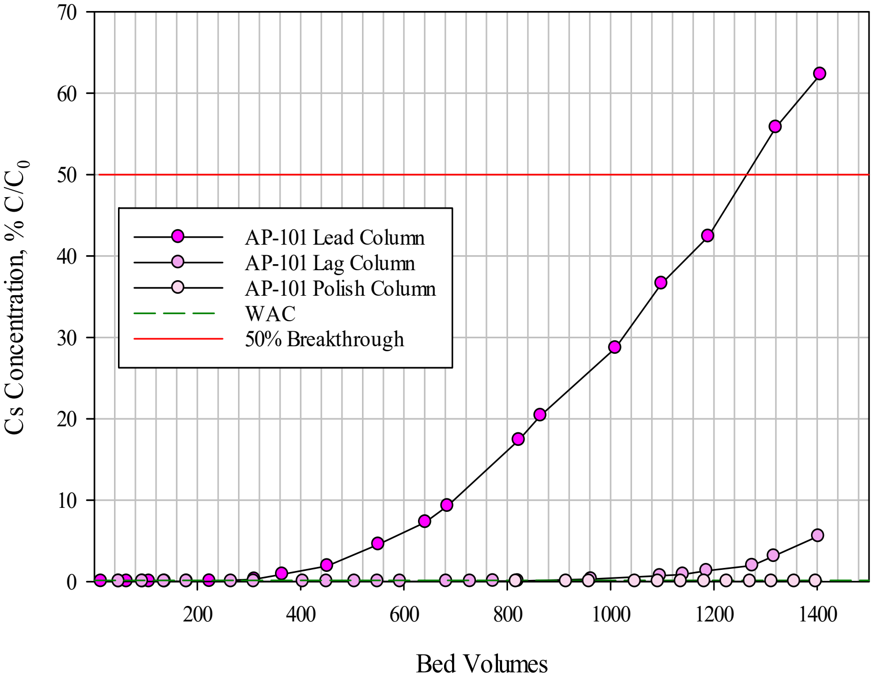

Figure 4.1. Lead, Lag, and Polish Column Cs Load Profiles of AP-101DF at 1.90 BV/h, Linear-Linear Plot

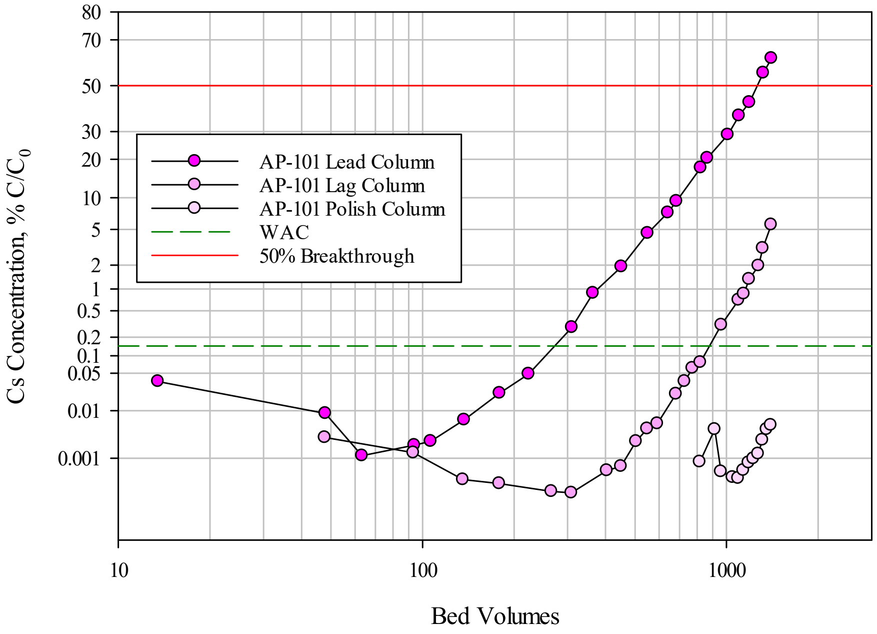

Figure 4.2 Lead, Lag and Polish Column Cs Load Profiles of AP-101DF at 1.90 BV/h, Probability-Log Plot

The Cs breakthrough curves were modeled by the error function (erf) (Hougen and Marshall 1947; Klinkenberg 1948), as shown in Eq. (4.1):

$$\frac{C}{C_0} = \frac{1}{2}\left(1 + \operatorname{erf}\left(\sqrt{k_1 t} - \sqrt{k_2 z}\right)\right) \tag{4.1}$$

where:

k_1 and k_2 = parameters dependent on column conditions and ion exchange media performance
t = time (or BVs processed)
z = column length

Using this model, fits were generated to the lead and lag column experimental data (see Figure 4.3 and Figure 4.4). Previous testing with AP-105 and AP-107 (Fiskum et al. 2021b and Westesen et al. 2021b) showed deviations from the fit at C/C_0 values above 0.7; however, this high of loading was not achieved for this test and the fit for the collected data agrees well.

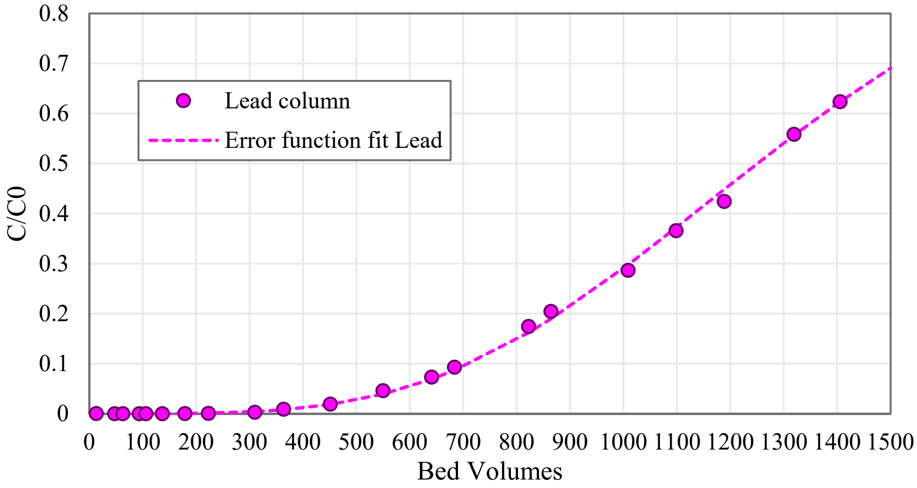

Figure 4.3 AP-101DF Lead Column Cs Breakthroughs with Error Function Fit

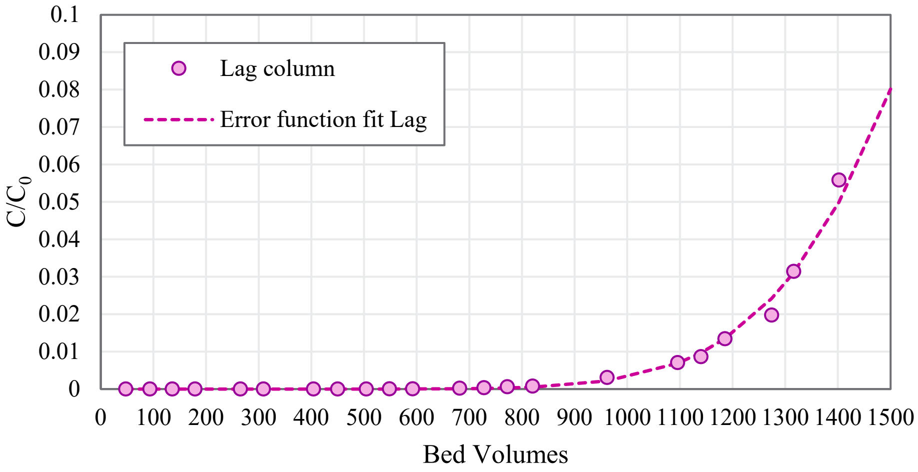

Figure 4.4 AP-101DF Lag Column Cs Breakthroughs with Error Function Fit

The 50% Cs breakthroughs for the lead and lag columns were estimated from the error function fit at 1250 BVs and 2134 BVs, respectively. 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. (4.5) (Bray et al. 1993). The CST bed density is the dry CST mass divided by the volume in the column:

$$K_d \times \rho_b = \lambda \tag{4.2}$$

The lead column 50% Cs breakthrough value was within 10% of the 1384 BVs Cs λ value predicted from batch contact studies and shows excellent agreement between the two measurements.

The WAC limit Cs breakthroughs were interpolated for each column by curve fitting the BVs processed as a function of the log % C/C_0 values (see Figure 4.5). The curves were fitted to a second-order polynomial function ($R^2 \geq 0.98$) and the WAC limit breakthroughs were then calculated, resulting in the following:

- Lead column: 275 BVs
- Lag column: 875 BVs
- Polish Column*: 1543 BVs (*=largely extrapolated)

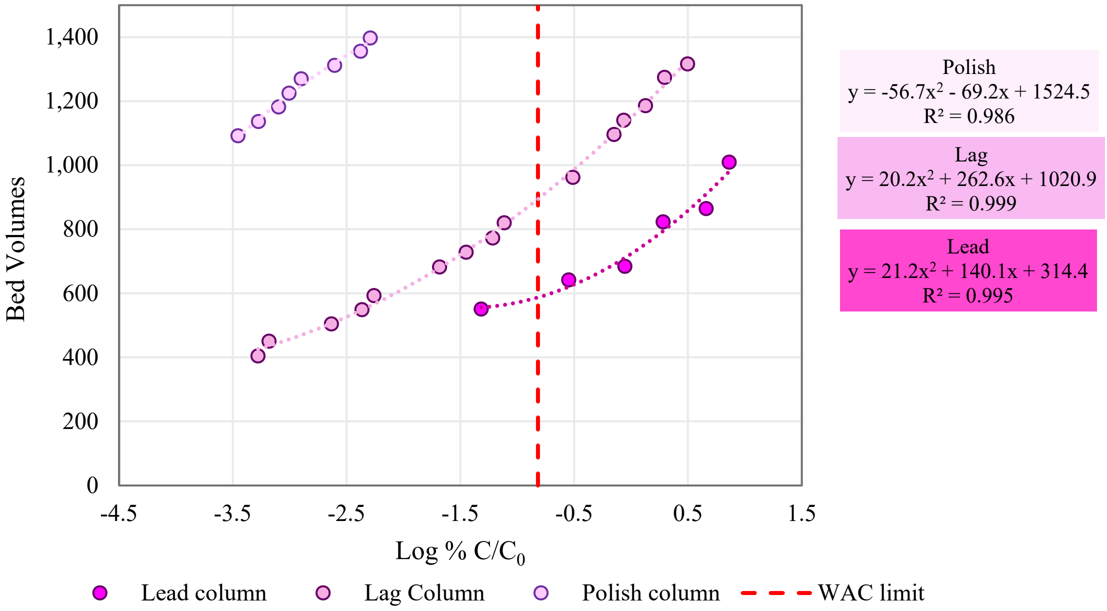

Figure 4.5. Curve Fits to Interpolate WAC Limit Breakthroughs from Lead, Lag, and Polish Columns

Figure 4.6 shows the end of the Cs breakthrough profile from the polish column with the feed displacement (FD), water rinse, and final flushed fluid from the column system on a probability-linear plot. The linear x-axis scale provides better Cs concentration resolution of the various effluent solutions relative to graphing on a log scale. A steep jump is seen in the first three FD samples (~6 BVs) before the Cs concentration began to drop and continue on a downward trajectory. A large amount of solids was found in FD sample #3 (see Section 3.3.2), which also volumetrically aligns with the displacement of the residual feed from the system. Unlike previous tests with AP-107 and AW-102 where Cs concentrations increased in the water rinse (Fiskum et al. 2019a; Westesen et al. 2021a; Westesen et al. 2021b), the Cs concentration in the AP-101DF test water rinse continued to drop until the last three samples, which remained relatively static at ~1.7E-4 %C/C_0. As observed previously (Fiskum et al. 2019a; Westesen et al. 2021a; Westesen et al. 2021b), the Cs concentration in the solution expelled with compressed air bumped up past the WAC limit. No effort was made to filter this solution prior to ^{137}Cs analysis, so it's not clear if this increased Cs concentration was associated with suspended fines or if a small amount of Cs had exchanged back into the solution during the weekend-long contact period with the water rinse.

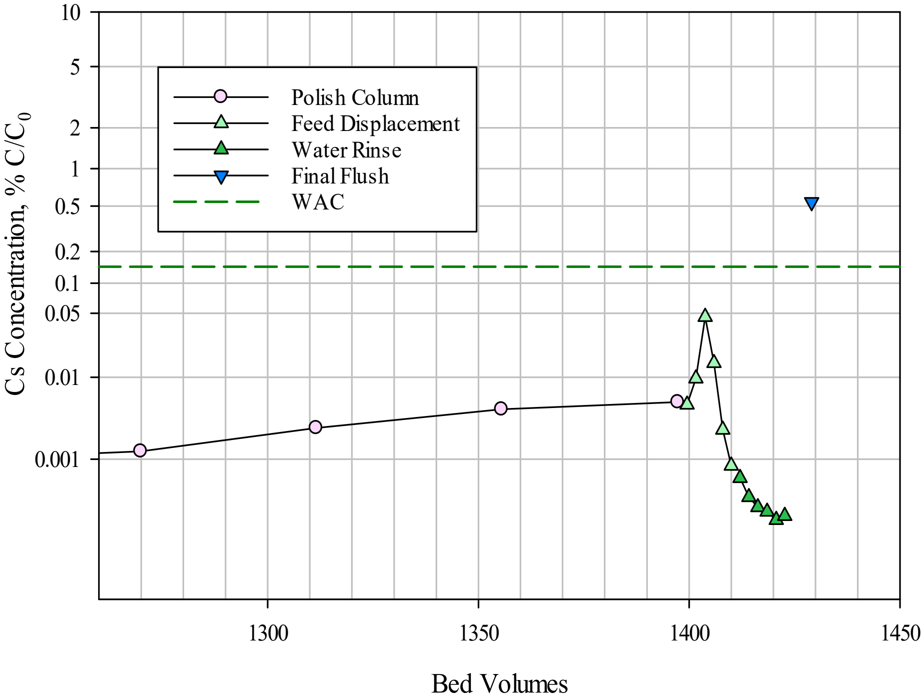

Figure 4.6. AP-101DF Polish Column Cs Load Profile with Feed Displacement, Water Rinse, and Column Flush Solution

Figure 4.7 compares AP-101DF Cs load profiles with AP-107 from FY21 testing conducted at 16 °C (Westesen et al. 2021b). CST Lot 2002009604 sieved to <30-mesh was used in both tests. Initial breakthrough from both AP-101DF and AP-107 lead and lag columns happened simultaneously; however, AP-107 reached the WAC limit nominally 80 BVs before AP-101DF for both the lead and lag columns. The increased AP-101DF loading was not kinetically driven, based on similar shapes in load curves. This effect was consistent with the β parameter for AP-101DF being lower than that of AP-107 at 2.92E-4 vs. an AP-107 value of 5.53E-04 (see Section 4.2.1). It is noted that Na and Cs concentrations in AP-101DF were lower (5.2 M Na, 4.64E-5 M Cs) than in AP-107 (6.2 M Na, 6.91E-5 M Cs).

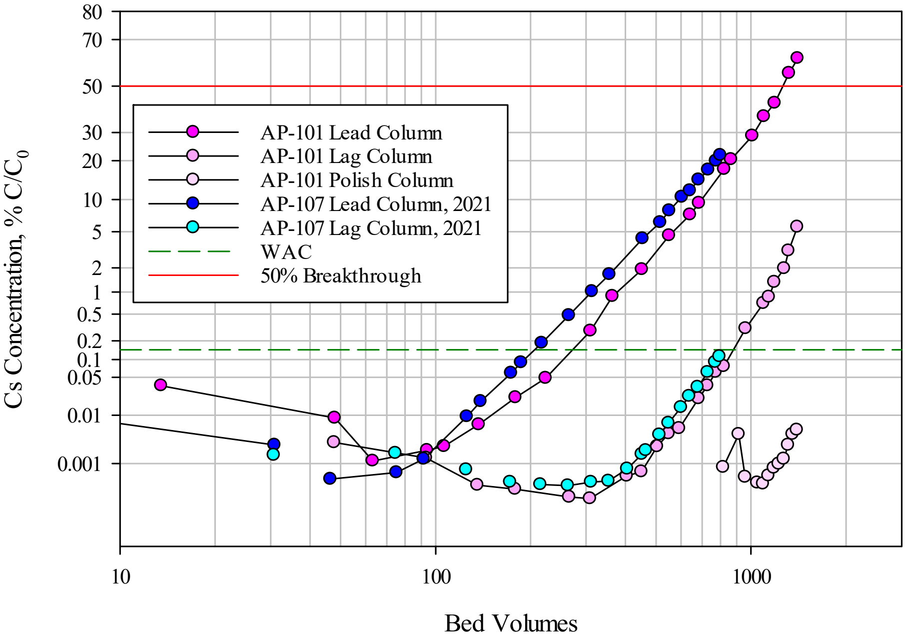

Figure Notes:

	AP-101DF	AP-107
Configuration	Lead-Lag Lead-Lag-Polish	Lead-Lag
Flowrate, BV/h	1.90	1.90
Process Temp. °C	16.0	16.0
Cs, M	4.64E-05	6.99E-05
Na, M	5.2	6.2
K, M	0.098	0.101
OH, M	1.58	0.89
TIC, M	0.51	0.65

Figure 4.7. Load Profile Comparisons: AP-101DF and AP-107 (Westesen et al. 2021b), at 16 °C, CST Lot 2002009604

4.1.1 Cesium Activity Balance

The Cs fractionations to the effluents and the columns were determined based on the input ^{137}Cs and the measured ^{137}Cs in the various effluent streams. The quantities of Cs loaded onto the lead, lag, and polish columns were determined by subtracting the Cs recovered in the samples and effluents from the Cs fed to each column. Table 4.1 summarizes the ^{137}Cs fractions found in the various effluents as well as the calculated ^{137}Cs column loadings. Approximately 81.3 % of the total Cs loaded onto the lead column (previous testing with AP-107 at 16 °C found 94% of total Cs loaded onto the lead column, Westesen et al. 2021b), 18.3% loaded onto the lag column, and only 0.4% onto the polish column. Sample and effluent collection amounted to only ~0.004% of the input Cs.

Table 4.1. ^{137}Cs Activity Balance for AP-101DF

Input		
	µCi	%
Feed sample	1.62E+06	100
Output		
Effluent-1 (0-135 BVs)	0.85	5.21E-05
Effluent-2 (135-264 BVs)	0.10	6.25E-06
Effluent-3 (264-403BVs)	0.21	1.26E-05
Effluent-4 (403-502 BVs)	1.0	6.34E-05
Effluent-5 (502-636 BVs)	9.8	6.03E-04
Effluent-6 (636-769 BVs)	47.3	2.91E-03
Effluent-7 (769-914 BVs)	0.93	5.71E-05
Effluent-8 (914-1046 BVs)	0.14	8.52E-06
Effluent-9 (1046-1180 BVs)	0.53	3.28E-05
Effluent-10 (1180-1309 BVs)	1.5	9.13E-05
Effluent-11 (1309-1395 BVs)	3.1	1.92E-04
Load samples	730	4.49E-02
Feed displacement, water rinse, and flush	41.1	2.53E-03
Total ^{137}Cs recovered in effluents	836	5.15E-02
Total ^{137}Cs column loading		
Lead column Cs loading	1.35E+06	83.2
Lag column Cs loading	2.64E+05	16.3
Polish column loading	8.09E+03	0.5
Column total	1.62E+06	100.0

The total Cs loaded per g CST was calculated from the total Cs loaded onto the lead column and the dry CST mass loaded into the lead column according to Eq. (4.3):

$$\frac{A_{Cs} \times CF}{M} = C \tag{4.3}$$

where

A_{Cs} = activity of ^{137}Cs, µCi on the lead column
CF = conversion factor, mg Cs/µCi ^{137}Cs
M = mass of dry CST (10.0 g)
C = capacity, mg Cs/g CST

A total of 7.15 mg Cs/g CST (0.0533 mmoles Cs/g CST) was loaded onto the lead column and was consistent with previous AP-107 and 5.6 M Na simulant studies (see Table 4.2). Since 50% breakthrough on the lead column was achieved, the total load capacity can be determined and was calculated to be 7.78 mg Cs/g CST (0.058 mmoles Cs/g CST). This represented 90.3% of the predicted Cs load capacity found from batch contact testing (see Section 4.2.1) and shows good agreement between batch contacts and column flowthrough measurements. The documented safety analysis developed for TSCR limits a single column curie loading to 141,600 Ci, which equates to 0.10 mmole Cs/g CST. The total load capacity determined for the column testing only represented 57% of this limit and indicates that the WAC limit on the polish column should be reached before the curie loading limit is reached on the lead column.

Table 4.2. Cs CST Column Loading Comparison

Test	Sieve Fraction	CST Cs loading (mg Cs/g CST)	Reference
AP-101 chilled, 2.4% full height	<30 mesh	7.31	Current report
AP-107 chilled, 2.4% full height	<30 mesh	7.08	Westesen et al. 2021b
AP-105, 2.4% full height	<30 mesh	5.39	Fiskum et al. 2021b
5.6 M Na simulant, 2.5% full height	<30 mesh	7.63	Westesen et al. 2021a
5.6 M Na simulant, 12% full height	<25 mesh	6.95	Fiskum et al. 2019a
5.6 M Na simulant, 100% full height	As received	6.60	Fiskum et al. 2019a

See Russell et al. (2017) for the 5.6 M Na simulant formulation.

4.1.2 Metals and Radionuclide Analysis

The AP-101DF composite feed and composite effluent samples underwent extensive characterization to better define waste characteristics and assess analyte fractionation to the CST. Five lead column samples (collected after processing 94.0, 451.5, 822.7, 1099, and 1406 BVs) were also selected for metals and radionuclide analysis to assess analyte load characteristics.

Table 4.4 summarizes the feed and effluent metals concentrations and fractionations to the effluent. The anions, free hydroxide, inorganic carbon, and organic carbon concentrations in the effluent are provided in Table 4.5; they were not measured in the feed because it was shown that their concentrations were not affected by the CST processing (Westesen et al. 2021a). Further, bench handling of the effluent was safer for the analysts from a radiological dose perspective. Analytical reports along with result uncertainties and quality control discussions are provided in Appendix C.

By inference, the analytes present in the feed and not found in the effluent were assumed to be retained on the CST. Analyte fractionation was calculated as the ratio of the total analyte measured in the feed processed through the columns and the total analyte collected in the Cs-decontaminated effluent according to Eq. (4.4):

$$\frac{C_{Da} \times V_D}{C_{Fa} \times V_F} = F_{Da} \tag{4.4}$$

where:

C_{Da} = concentration of analyte *a* in the Cs-decontaminated effluent
V_D = volume of Cs-decontaminated effluent
C_{Fa} = concentration of analyte *a* in the AP-101DF feed
V_F = volume of AP-101DF feed
F_{Da} = fraction of analyte *a* in the Cs-decontaminated effluent

The analyte results shown in brackets indicate the result was less than the instrument estimated quantitation limit (EQL) but greater than or equal to the method detection limit (MDL); 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 values to highlight the higher uncertainty. The opportunistic analyte results measured by ICP-OES are also shown in Table 4.4; these analytes are part of the ICP-OES data output but have not been fully evaluated for quality control performance.

Table 4.3. AP-101DF Feed and Effluent Radionuclide Concentrations and Fractionations (ASR 1420)

Analysis Method	Analyte	Feed Conc. TI126-Comp-Feed (µCi/mL)	Effluent Conc. TI126-Comp-Eff (µCi/mL)	Fraction in Effluent (%)
Gamma energy analysis (GEA)[(a)]	^{60}Co	<1.72E-3	2.38E-04	--
	^{126}Sn	<5.96E-3	2.32E-04	--
	^{126}Sb	1.02E+01	1.92E-04	0.002%
	^{137}Cs	1.17E+02	4.45E-03	0.004%
	^{154}Eu	<7.1E-3	1.41E-05	--
Separations/ Alpha energy analysis (AEA)[(a)]	^{237}Np	1.99E-05	1.44E-05	71%
	^{238}Pu	1.62E-05	9.50E-06	58%
	$^{239+240}$Pu	1.27E-04	7.12E-05	55%
	^{241}Am	1.32E-04	1.05E-04	78%
Separations/ Beta counting[(a)]	^{90}Sr	3.04E-01	2.48E-04	0.1%
	^{99}Tc	9.38E-02	9.32E-02	98.0%

(a) Reference date is March 2022.

"--" = not applicable; value not reported, or fractionation cannot be calculated with a less-than value.

The recovered fractions are calculated with values containing more significant figures than shown; using listed values may result in a slight difference due to rounding.

Table 4.4. AP-101DF Feed and Effluent Inorganic Analyte Concentrations and Fractionation (ASR 1420)

Analysis Method	Analyte	Feed Conc. TI126-Comp-Feed (M)	Effluent Conc. TI126-Comp-Eff (M)	Fraction in Effluent
ICP-OES	Al	3.39E-01	3.41E-01	99%
	Ba	3.52E-06	<5.3E-07	--
	Ca	7.93E-04	5.17E-04	64%
	Cd	[5.2E-06]	5.72E-06	109%
	Cr	9.53E-03	9.44E-03	98%
	Fe	3.25E-05	2.36E-05	72%
	K	9.81E-02	9.73E-02	98%
	Na	5.21E+00	5.22E+00	99%
	Ni	2.62E-04	2.38E-04	90%
	P	1.48E-02	1.44E-02	96%
	Pb	[8.0E-05]	<7.9E-05	--
	S	5.00E-02	[4.8E-02]	95%
	Sr	[1.4E-06]	2.12E-07	15%
	Ti	1.58E-06	7.23E-06	NA
	U	5.22E-05	3.43E-05	65%
	Zn	<2.5E-05	4.35E-05	--
	Zr	4.90E-06	1.69E-05	NA
ICP-MS	Ba	5.54E-07	3.43E-07	61%
	Nb	2.12E-07	1.12E-05	NA
	Pb	3.01E-05	1.61E-05	53%
	Sr	1.54E-06	4.24E-07	27%
	^{238}U	5.41E-05	4.18E-05	76%

Table 4.4 (cont.)

Analysis Method	Analyte	Feed Conc. TI082-Comp-Feed (M)	Effluent Conc. TI082-Comp-Eff (M)	Fraction in Effluent
ICP-OES Opportunistic Analytes	Ag	<1.1E-05	2.18E-06	--
	Au	<1.8E-05	<1.8E-05	--
	B	5.90E-03	2.43E-03	41%
	Be	[1.1E-05]	9.13E-06	79%
	Cu	1.70E-05	1.44E-05	84%
	Ga	7.12E-05	5.76E-05	80%
	Li	5.55E-05	4.01E-05	71.30%
	Lu	3.41E-07	3.25E-07	94%
	Mg	4.60E-05	<4.4E-05	--
	Mn	8.59E-07	1.08E-06	124%
	Mo	[3.8E-04]	[3.7E-04]	96%
	Pd	[3.2E-05]	2.85E-05	89%
	Rh	[3.7E-05]	3.30E-05	87%
	Ru	5.77E-05	6.06E-05	103%
	Sb	<3.0E-04	7.31E-05	--
	Si	5.35E-03	1.61E-03	30%
	Sn	5.75E-05	5.52E-05	95%
	Th	4.39E-06	<1.9E-05	--
	V	9.75E-06	1.24E-05	125%
	W	3.93E-04	3.71E-04	93%

Bracketed values indicate the associated sample results were less than the EQL but greater than or equal to the MDL. Analytical uncertainty for these analytes was > ±15%.

“--” indicates the recovery could not be calculated.

NA = not applicable; Nb, Ti, and Zr are components of CST.

The recovered fractions are calculated with values containing more significant figures than shown; using listed values may result in a slight difference due to rounding.

Table 4.5. AP-101DF Feed and Effluent Anions and Carbon Composition (ASR 1420)

Analysis Method	Analyte	Diluted Feed* (M)	Effluent TI126-Comp-Eff (M)
Titration	Free Hydroxide	NA	1.58
Ion Chromatography	F^-	2.33E-03	2.21E-03
	Cl^-	8.51E-02	7.71E-02
	NO_2^-	1.07E+00	9.83E-01
	NO_3^-	2.46E+00	1.98E+00
	PO_4^{3-}	1.43E-02	1.06E-02
	$C_2O_4^{2-}$	3.74E-03	3.41E-03
	SO_4^{2-}	3.10E-02	2.61E-02
Hot persulfate oxidation*	Total organic C	5.12E-01	NA
	Total inorganic C(a)	1.51E-01	NA

NA= not analyzed

* Diluted values calculated based on as-received AP-101 analysis.

(a) Assumed to be carbonate.

In addition to Cs removal, the CST removed 99.9% of the ^{90}Sr with a ^{90}Sr decontamination factor of 1243. The reduced Sr decontamination (72.9%) measured by ICP-MS may have been confounded with Sr isobaric interferences. The radiochemical analysis was considered more reliable with specificity for ^{90}Sr, and stable Sr and ^{90}Sr were expected to behave similarly. About 29% of the Np and 45% of the Pu were also removed. The Np and Pu removal factors were slightly higher but relatively consistent with what was found for AP-107 processing at 16 °C, however were significantly less than previous testing with AP-105, AW-102, and AP-107 tank waste at ambient conditions (see analyte recovery summary in Table 4.6). This indicates potential temperature impacts on radionuclide removal by the CST.

Table 4.6. Np and Pu Effluent Recovery Comparisons

Tank	Process Temp., °C	BVs	^{237}Np	^{238}Pu	$^{239+240}$Pu
AP-101DF	16	1402	71	58	55
AP-107(a)	16	799	80	70	67
AP-105DF(b)	28	1091	18	41	39
AW-102(c)	22	450	53	35	32
AP-107(d)	26	855	43	37	36

(a) Westesen et al. 2021b

(b) Fiskum et al. 2021b

(c) Westesen et al. 2021a

(d) Fiskum et al. 2019a

NA = not applicable; the analyte was not detected in the effluent.

About 22% of Am was calculated to be removed during processing; the chemistry involved in Am removal by CST is not known. Assuming the difference in total Am, Np, and Pu µCi content between the feed and effluent remained solely on the lead column CST (10 g), the CST would contain 138 nCi/g of transuranic (TRU) isotopes, which moderately exceeds the threshold 100 nCi/g defining TRU waste. If evenly distributed between the lead and lag columns, only 69 nCi/g TRU isotopes would be loaded onto each column. Most of ^{99}Tc, 98% (likely present as anionic pertechnetate), was found in the effluent, showing minimal Tc interaction with the CST.

The ICP-OES results for the feed composite and effluent composite showed that the majority of analytes remained in the effluent (see Table 4.4 and Appendix C for analytical reports). The Al, Cd, Cr, K, Na, P (phosphate), and S (sulfate) partitioned exclusively to the effluent (>95% recovery). Recoveries of Ca, Fe, and U showed nominally ~30% was removed by the CST.

The load behaviors of selected analytes were examined as a function of BVs processed through the lead column. (Raw data are provided in Appendix B.) Figure 4.8 shows the Al, Ca, Pb, and U breakthrough results along with the Cs breakthrough profile. The Al breakthrough serves as an "internal standard" for comparison of the ICP-OES analysis results; its breakthrough remained at 105% ± 4% throughout the analytical run.

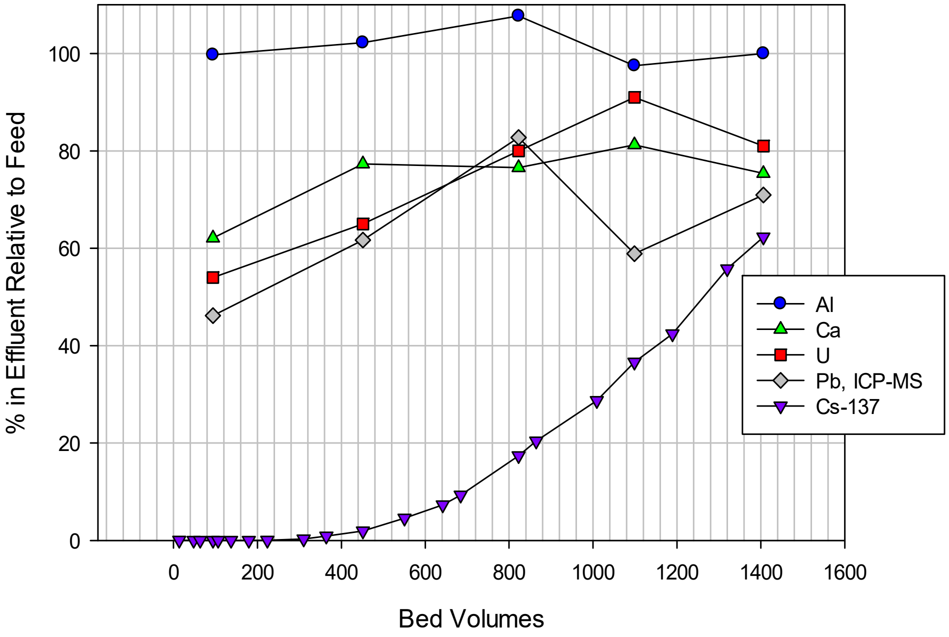

Figure 4.8. Al, Ca, Cs, Pb, and U Load Profiles from the Lead Column

The breakthrough profiles showed a slow gradual rise in effluent concentration from ~50% to ~80% over the duration of the BVs processed. Based on these results, it appears that only up to 50% of the Ca, Pb, and U are available for removal by the CST, with the remainder experiencing minimal interaction and passing through to the effluent.

Selected lead column effluent samples were also analyzed for ^{237}Np, ^{238}Pu, $^{239+240}$Pu, and ^{90}Sr. Figure 4.9 compares their load profiles with that of ^{137}Cs. Somewhat sporadic breakthrough was exhibited by ^{237}Np and ^{238}Pu but demonstrated nominally 30% of these radionuclides are of a form that can be removed by the CST and indicated early saturation of the available forms of each analyte. A gradual breakthrough of $^{239+240}$Pu was seen from 40% to 15% removal by the CST over the duration of the BVs processed. A variation of oxidation states for Pu in the tank waste could be causing a complexation of soluble Pu that cannot be removed by CST.

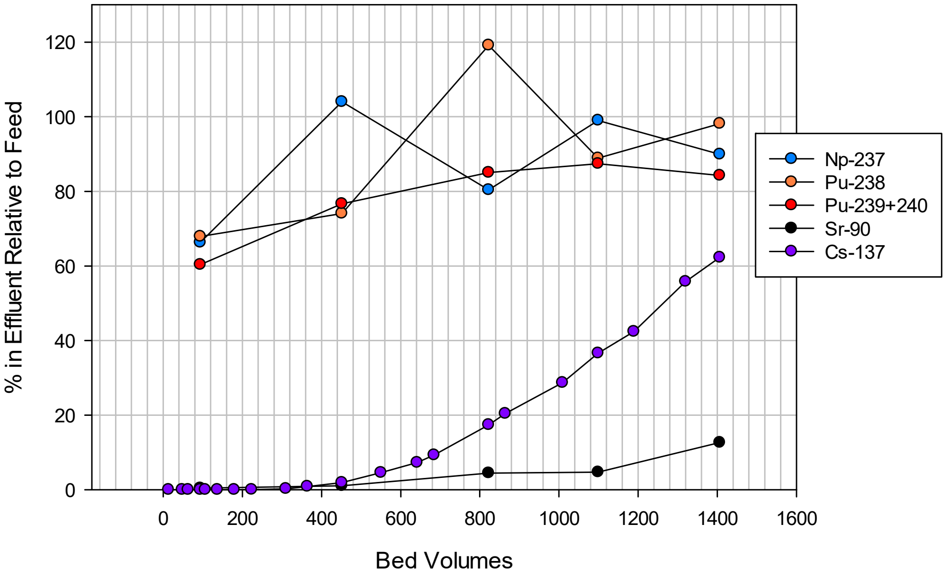

Figure 4.9. ^{237}Np, ^{238}Pu, ${}^{239+240}$Pu, and ^{90}Sr Load Profiles from the Lead Column

Strontium breakthrough was first observed at approximately 500 BVs and resulted in a fractional breakthrough of only 12.6% after processing 1400 BVs. The breakthrough data were used to construct a logarithmic probability plot of ^{90}Sr and ^{137}Cs breakthrough vs. column throughput, shown in Figure 4.10. Displaying the data in this way allows an estimation of sorption ratios to be determined, which are approximately equal to the number of BVs at 50% breakthrough. Although a 50% breakthrough for ^{90}Sr was not achieved, it can be estimated by the error function (erf) using Eq. (4.1) described earlier in Section 4.1. Using this relationship, the 50% breakthrough value for Sr was determined to occur at around 3225 BVs. This shows CST's selectivity of Sr over Cs, where Sr breakthrough occurs nearly 2000 BVs later than Cs.

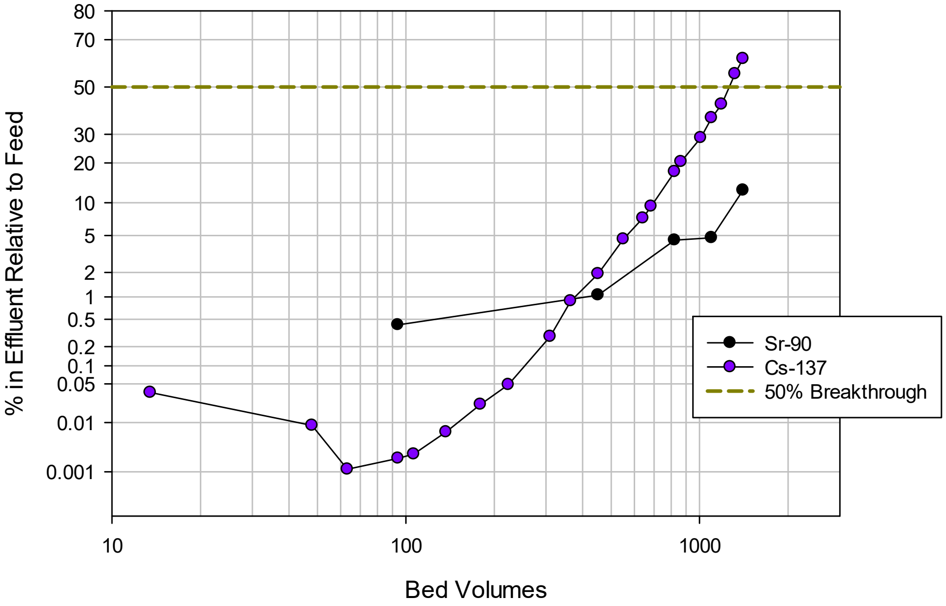

Figure 4.10. ^{90}Sr and ^{137}Cs Breakthrough Profiles

4.1.3 Predicted TSCR Performance

Westesen et al. (2020) demonstrated that the impact of residence time (flowrate through the CST column in terms of BV/h or contact time) directly influenced the volume that can be processed before reaching the WAC limit, as a linear relationship. An evaluation of 1-, 2-, and 3-column systems can be determined collectively in terms of system volumes (SVs). The SV/h in the lead column was, by definition, equivalent to the BV/h flowrate. The combined lead-lag column system, with two sequential 10-mL CST beds, corresponded to half this flowrate. The 3-column system, with three sequential 10-mL CST beds, corresponded to a third of this flowrate. The AP-101DF SVs, adjusted flowrate, and SVs to WAC limit are provided in Table 4.7. These data are then evaluated in terms of the square root of BVs to WAC and the square root of SV/h to develop a linear relationship to project the volume of waste that can be processed through the TSCR facility before reaching the WAC limit. Figure 4.11 plots these data alongside data from AP-107 (Westesen et al. 2021b), processed in a lead-lag configuration at 16 °C, AP-105 (Fiskum et al. 2021b), which was processed in a lead-lag-polish configuration at 25 °C, and two full-height column tests (Fiskum et al. 2019b) using tank waste simulant processed in a lead-lag configuration at 25 °C. Using this relationship, the volume projection for AP-101 tank waste processed before WAC Cs breakthrough on the polish column is 242,000 gallons.

Table 4.7. Bed Volumes Processed to Reach WAC Limit for Cesium

AP-101DF Systems	SV (mL)	Flowrate (SV/h)	SVs to WAC Limit
Lead column	10	1.90	272
Lead-lag columns	20	0.95	434
Lead-lag-polish columns	30	0.63	514[(a)]

(a) The polish column was only in position during second half of processing interval from 775 BV to 1407 BV and did not reach the WAC limit. An extrapolated value is used here but may not be truly representative of the 30-mL CST bed (3-column system) configuration.

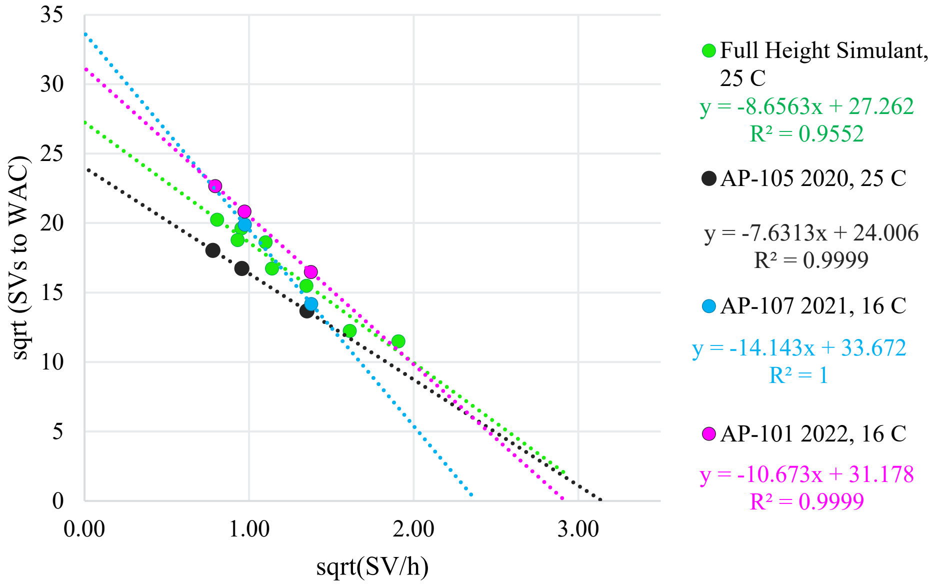

Figure 4.11 Projected Breakthrough Results for AP-101, AP-107, AP-105, and 5.6 M Na Simulant

A further evaluation of the impact of kinetics on Cs exchange can be made by graphing the percentage of capacity used to reach the WAC limit vs. the residence time (SV/h) for each testing condition. Figure 4.12 shows reasonable linear fits over the range of interest and accentuates the impact on kinetics with varying temperature. The testing at 16 °C for AP-101 and AP-107 shows a lower capacity use when compared to the room temperature AP-105 and simulant tests. This is due to the slower kinetics of the exchange as a result of the decreased temperature. This analysis can also be used to estimate the BVs to breakthrough on the polish column and results in a value of 239,000 gallons.

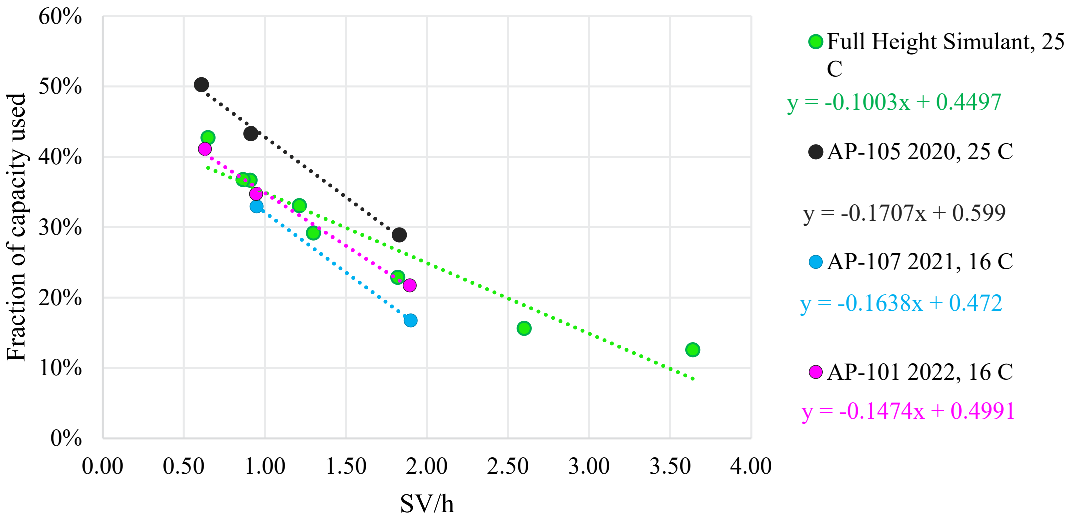

Figure 4.12. Percentage of CST Capacity Used vs. Residence Time for AP-101, AP-107, AP-105, and 5.6 M Na Simulant

4.2 Batch Contact Results

This section provides the K_d and isotherm curves for AP-101 tank waste at the four process test temperatures, and a comparison of AP-101 tank waste with AP-107 and AP-105 temperature-dependent isotherm results. Input data supporting the various isotherms and figures are provided in Appendix D.

4.2.1 K_d and Isotherm Results for AP-101

Figure 4.13 shows the K_d dependence on Cs concentration at 13, 16, 21, and 35 °C. The K_d increased with decreasing temperature, consistent with AP-107 and AP-105 tank waste batch contact testing (Fiskum et al. 2021a). The K_d for the lowest Cs concentration (1.2E-4 M) is the lowest of the K_d across the three lower Cs concentrations (1.2E-4, 3.4E-4, and 8.8E-4 M). This behavior, although not inherently clear, was also observed for the K_d values calculated with AP-107 and AP-105 temperature studies (Fiskum et al. 2021a).

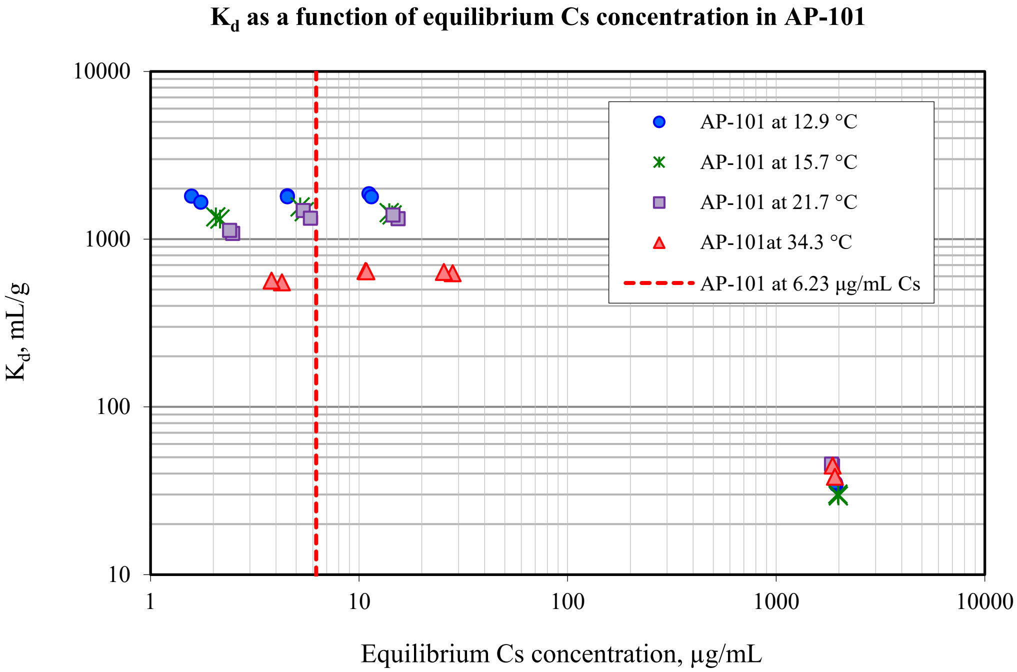

Figure 4.13. Cs K_d vs. Cs Concentration, AP-101 Tank Waste, Four Temperatures

Figure 4.13 shows the corresponding isotherms and Q (mmoles Cs/g dry CST) values versus Cs molarity at all four test temperatures with AP-101 tank waste. Also provided are the curve fits to the Freundlich/Langmuir hybrid equilibrium model as given in Eq. (4.5) (Hamm et al. 2002).

$$Q = \frac{\alpha_i \times [Cs]}{(\beta + [Cs])} \tag{4.5}$$

where [Cs] = equilibrium Cs concentration, mmoles/mL or M
Q = equilibrium Cs loading on the CST, mmole Cs per g CST
α_i = isotherm parameter constant (mmoles/g), equivalent to total capacity in the matrix
β = isotherm parameter constant (mmoles/mL or M), selectivity coefficient, dependent on matrix and temperature; the larger the value, the less selective the CST is for Cs (Hamm et al. 2002)

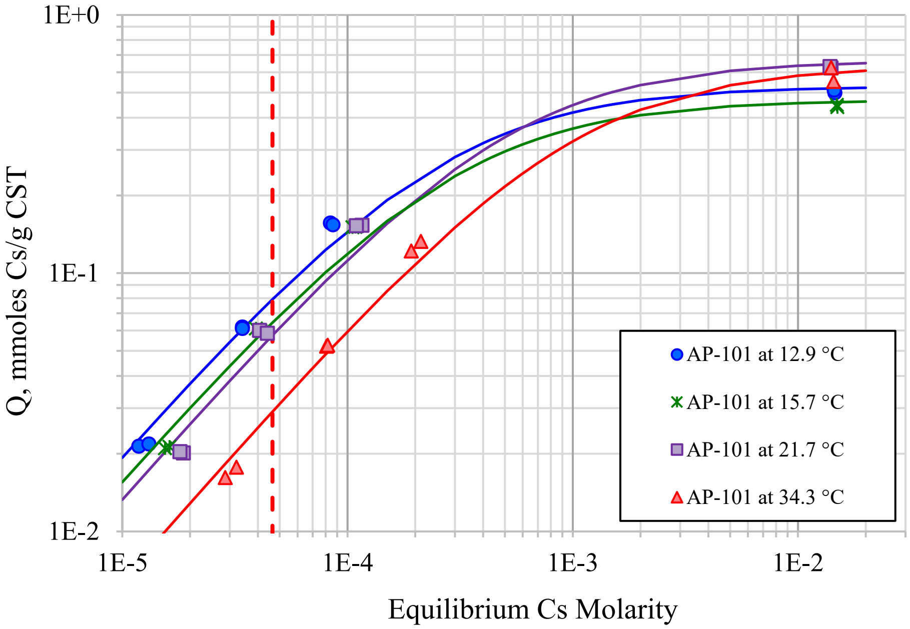

Figure 4.14. Q vs. Cs Equilibrium Concentration, AP-101 Tank Waste with Freundlich/Langmuir Hybrid Equilibrium Fits, Four Temperatures. The dashed red line represents the Cs concentration (4.64E-5 M) in AP-101 feed adjusted to 5.2 M Na.

The Freundlich/Langmuir hybrid equilibrium model does not fit the experimental data exceptionally well at the lower Cs concentrations. The 16 and 21 °C experimental Q and K_d are nearly indistinguishable, but the 13 and 16 °C results show a larger difference in the measured values. A plot of Q (mmoles Cs/g CST) vs. temperature (Figure 4.15) indicates that the loading decreases linearly as temperature increases. This is consistent with the data collected for both AP-107 and AP-101 tank waste (Fiskum et al. 2021a). In fact, the slope of -0.0022 matches that of simple simulant (1 M NaOH/4.6 M $NaNO_3$) identically and is in excellent agreement with the slope obtained for AP-107 waste at -0.0025 (Fiskum et al. 2021a).

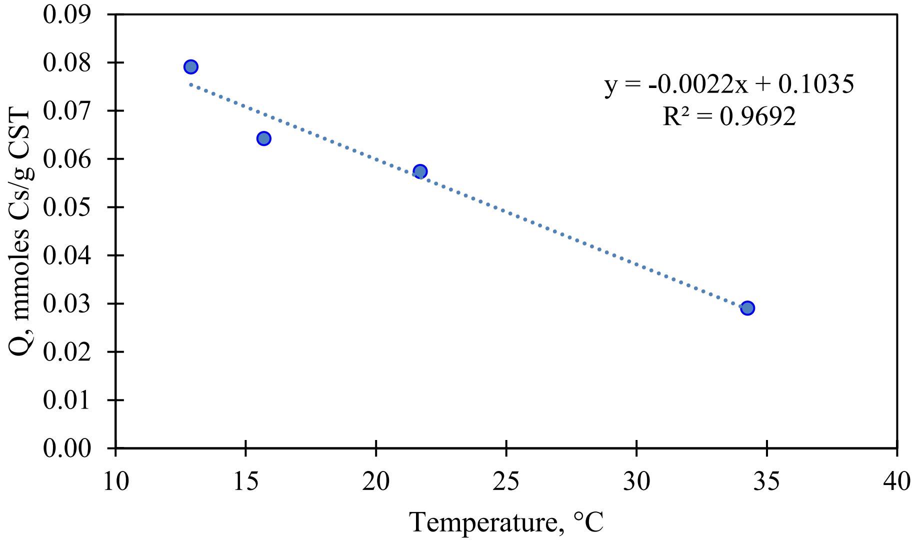

Figure 4.15. Q Dependence on Temperature for AP-101 Tank Waste

To evaluate the Cs loading near the feed condition, the log of Q was plotted against the log of the equilibrium Cs concentration consistent with the linear Freundlich isotherm approach as shown in Figure 4.16. A comparison of the loading calculated using the Freundlich/Langmuir hybrid model and the linear Freundlich approach is shown in Figure 4.16. The loadings predicted by both isotherm models are in excellent agreement at the AP-101 feed condition of 4.64E-5 M Cs; however, the Freundlich/Langmuir hybrid model overpredicts the loading at the lowest Cs concentration and underpredicts Cs loading at 8.76E-4 M Cs.

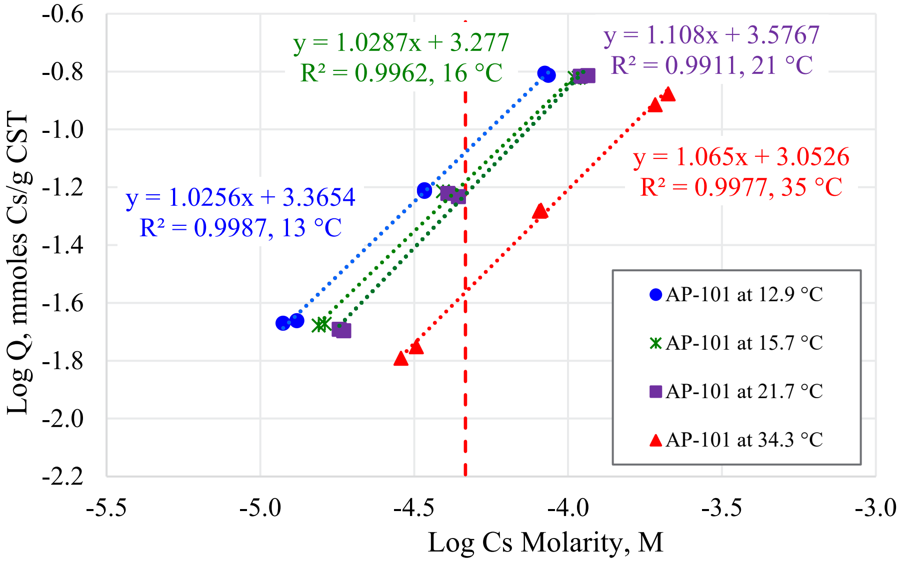

Figure 4.16. Linear Fits for Log Q vs. Log [Cs] at Four Test Temperatures

Table 4.8. Cs loading (Q, mmoles Cs/g CST) for the Freundlich/Langmuir Hybrid and Linear Freundlich Isotherm Model at AP-101 Feed Condition of 4.64E-5 M Cs

Process Temperature (°C)	Q (mmoles Cs/g) F/L Hybrid model	Q (mmoles Cs/g) Linear Freundlich model
12.9	0.079	0.083
15.7	0.064	0.066
21.7	0.057	0.060
34.3	0.029	0.027

4.2.2 Tank Waste Comparisons

The alpha parameter in the Freundlich/Langmuir hybrid model represents the maximum Cs loading that can be achieved under the corresponding matrix conditions. Excel Solver was used to calculate the α_i and β parameters using a generalized reduced gradient nonlinear method and the results are shown in Table 4.9. The highest α_i values were calculated from AP-107 tank waste where $\alpha_i > 0.7$ mmoles Cs/g CST. The calculated capacities of AP-105 and AP-101 were lower and more in line with the α_i of 0.55 mmoles Cs/g CST calculated for simple simulant (Campbell et al. 2021).

More importantly, the β values, or selectivity coefficient, can be used to compare Cs selectivity in the different tank waste matrices. The β values linearly increased with temperature, which is expected as increasing temperature inhibits Cs loading. The smaller the β value, the more favorable the exchange. The β values for AP-101 were the smallest of the waste series measured, which coincides with the ion exchange performance.

Table 4.9 Freundlich/Langmuir Hybrid Equilibrium Model α_i and β Parameter Summary

Matrix	Process Temperature (°C)	α_i, (mmoles Cs/g CST)	β, (Cs M)	Reference
AP-101 Tank Waste 4.64×10^{-5} M Cs	12.9	0.529	2.64E-4	Current testing
	15.7	0.469	2.92E-4	Current testing
	21.7	0.667	4.93E-4	Current testing
	34.3	0.639	9.74E-4	Current testing
AP-105 Tank Waste 6.91×10^{-5} M Cs	12.7	0.477	3.29E-4	Fiskum et al. 2021a
	15.9	0.475	4.05E-4	Fiskum et al. 2021a
	21.0	0.510	4.75E-4	Fiskum et al. 2021a
	34.5	0.503	9.11E-4	Fiskum et al. 2021a
AP-107 Tank Waste 5.65×10^{-5} M Cs	12.7	0.703	4.00E-4	Fiskum et al. 2021a
	15.9	0.782	5.53E-4	Fiskum et al. 2021a
	21.0	0.817	6.45E-4	Fiskum et al. 2021a
	34.5	1.05	1.48E-3	Fiskum et al. 2021a

A comparison of the K_d values vs. temperature is shown in Figure 4.17 for AP-107, AP-105, and AP-101 tank waste. The K_d values increased from AP-105<AP-107<AP-101, which is consistent with ion exchange performance (see Figure 4.11). The K_d calculated from ion exchange processing (1250) is included in the plot for reference and falls within 10% of K_d measured from batch contact testing.

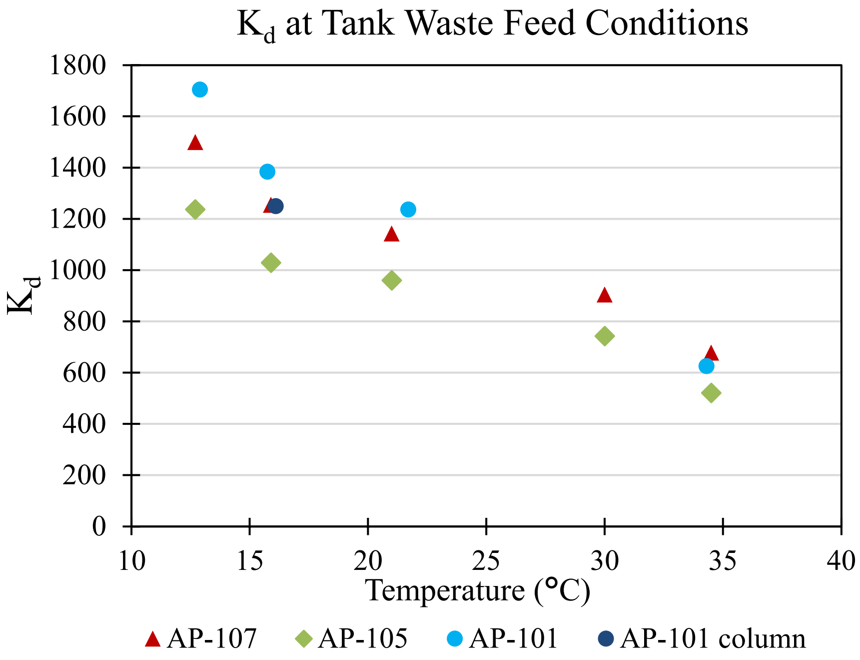

Figure 4.17. Cs K_d vs. Temperature for AP-107, AP-105, and AP-101 Tank Waste at Corresponding Feed Conditions.

The Q loading vs. temperature at Cs feed concentrations for AP-101 is compared to previous batch contact results from AP-107 and AP-105 in Figure 4.18. It is important to note that several matrix effects can impact the Cs loading and that none of the batch contact results were normalized to one another. What can be learned from the plot is that the loading decreases with increasing temperature across all tank waste matrices. Additionally, using the 50% breakthrough inflection point from the AP-101 lead column processed at 16 °C, a maximum load capacity of 0.058 mmoles Cs/g CST was calculated, which is in excellent agreement with the 0.064 mmoles Cs/g CST measured from batch contact testing.

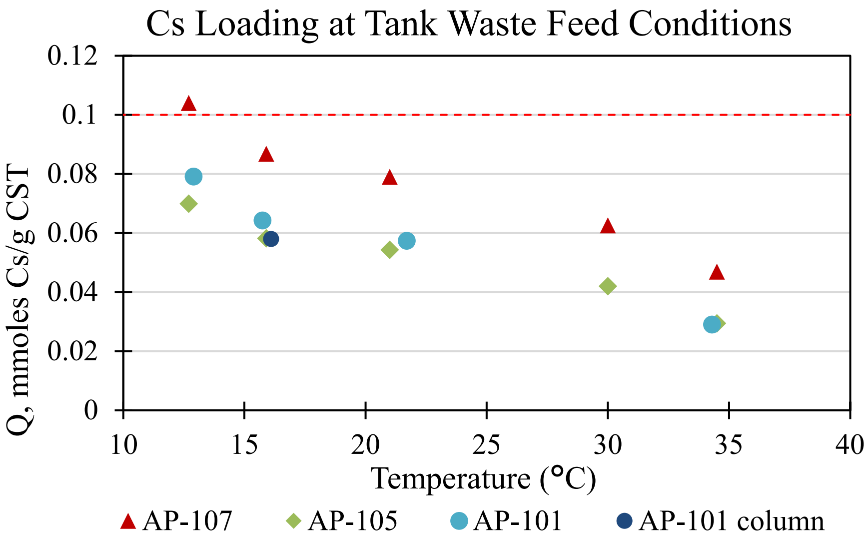

Figure 4.18. Q vs. temperature for AP-107, AP-105, and AP-101 tank waste as corresponding feed conditions. The Q calculated from AP-101 column processing is included for reference. The dashed red line indicates the DSA loading limit of 0.10 mmoles Cs/g CST.

4.2.3 Impact of Na Concentration on Ion Exchange Performance

A series of batch contacts were conducted on AP-107 (post ion exchange processing) to measure Cs distribution (K_d) from six Na concentrations at 25 °C.[8] A plot of the distribution coefficients vs. the Na molarity is shown in Figure 4.19. Included on this graph is the AP-101DF K_d at 21 °C, which shows excellent agreement with the AP-107 data. The batch distribution coefficient (K_d) is an equilibrium measure of the ability of CST to remove Cs from solution and can be directly related to the theoretical 50% breakthrough value (described above in Eq.(4.5)). This graph shows that the performance deviation between AP-101DF and AP-107 is in direct relation to the differing Na concentrations. A lower Na concentration favors Cs exchange, so at 6.2 M Na, AP-107 is expected to demonstrate fewer BVs processed before reaching the WAC limit compared to 5.2 M Na in AP-101DF.

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[8] Westesen AM. 2022. Calculation Package CALC-DFTP-094. *LRB BNW-62643 Batch Contact Calculations with AP-107 at Variable Na Molarities.* Pacific Northwest National Laboratory, Richland, Washington. Not publicly available.

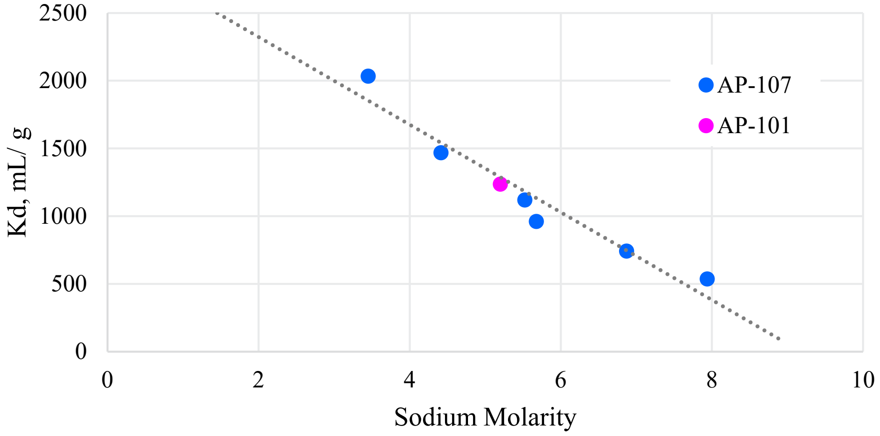

Figure 4.19 Cs distribution vs. Na Molarity for AP-107 and AP-101DF

5.0 Conclusions

Cesium ion exchange column testing was conducted with CST Lot 2002009604 sieved to <30 mesh to assess Cs ion exchange performance with AP-101DF tank waste at 16 °C. Column testing was conducted at a small scale in PNNL's Radiochemical Processing Laboratory (RPL) hot cells to accommodate the high radiological dose rate of the Hanford tank waste matrix. The results summary is provided below.

5.1 Column Testing

AP-101DF tank waste was processed through two columns sequentially positioned in a lead-lag format; after processing 775 BVs, a polish column was places in line. Each column was filled with 10.0 mL of CST ion exchanger. A total of 14.1 L of AP-101DF tank waste, consisting of 5.2 M Na and 115 µCi/mL ^{137}Cs, was processed through the Cs ion exchange system at 1.90 BV/h and 16 °C. Effluent samples were collected periodically from each column during the load process and measured for ^{137}Cs to establish the Cs load curves. The flowrate was increased to 3.0 BV/h to process 12.0 BVs each of 0.1 M NaOH feed displacement solution and water rinse. The following conclusions were drawn from the results of this work:

1. Testing showed that at 16 °C, 1250 BVs of AP-101DF tank waste, processed at 1.90 BV/h, can be treated before reaching 50% Cs breakthrough on the lead column. The WAC limit was reached on the lag column when 775 BVs of AP-101DF feed was processed. A polish column was installed and reached 0.005% breakthrough after processing 580 BVs of feed.
2. The WTP LAW WAC limit for the AP-101DF lead and lag columns was reached nearly 100 BVs later than respective column breakthrough with AP-107 at 16 °C (Westesen et al. 2021b). Although the overall breakthrough slopes between the two tests were the same; indicative of similar kinetic behavior, variations in feed matrices (Na and Cs concentrations) may be responsible for the deviations in reaching the WAC limit.
3. The total Cs loading onto the lead column (7.15 mg Cs/g CST) was similar to that seen in previous AP-107 testing (7.08 mg Cs/g CST) at the same processing flowrate and temperature.

5.1.1 Analyte Fractionation

1. Major components Al, K, Na, P (phosphate), and S (sulfate) partitioned exclusively to the effluent. Minor components Cd and Cr also portioned to the effluent (>95% recovery). Recoveries of Ca, Fe, and U showed nominally ~30% was removed by the CST.
2. Nb, Ti and Zr, components of CST, were detected at elevated levels in the composite effluent and the selected lead column effluent samples, indicating that a small amount of CST components leached into solution.
3. The effluent contained 70% of the feed Np, 55% of the feed Pu, and 77% of the feed Am. The balances of these isotopes were assumed to remain on the CST. Assuming the retained isotopes were bound only to the lead column CST bed, the CST would contain 138 nCi/g TRU, which is above the 100 nCi/g threshold defining TRU waste.
4. In addition to Cs removal, the CST removed 99.9% of the ^{90}Sr with a ^{90}Sr decontamination factor of 1243.

5.2 Batch Contact Testing

Cs isotherms were developed for AP-101 tank waste at 12.9, 15.7, 21.7, and 34.3 °C using decontaminated effluent post ion exchange processing with nonradioactive Cs concentrations of 1.2E-4, 3.4E-4, 8.8E-4, and 1.7E-4 M. Batch contacts were conducted in duplicate with 0.075 g dry CST (lot 2002009604) per 15 mL of solution and agitated in a temperature-controlled box for ~240 hours. The isotherm data were fit to the Freundlich/Langmuir hybrid equilibrium model and the linear Freundlich model (for the lowest three Cs concentrations) to calculate K_d and Q values at AP-101 feed condition of 4.64E-5 M. Results of AP-101 batch contact testing were compared to AP-107 and AP-105 temperature studies. The following conclusions were made from this testing:

1. A linear relationship for Q versus temperature was established in AP-101, where Q decreased as temperature increased.
2. The Freundlich/Langmuir hybrid model overpredicts Cs loading at the lowest (1.2E-4 M) Cs concentration, underpredicts loading at 8.8E-4 M Cs, but accurately predicts the loading near the AP-101 feed condition. The linear Freundlich isotherm predicts loading with $R^2 > 0.99$ for the three lowest Cs concentrations at all temperatures.
3. The β values are smallest for AP-101 waste testing, which is consistent with greater selectivity for Cs in the AP-101 matrix. This agrees with the results of ion exchange processing where breakthrough of the AP-101 lead column was shifted later (more BV) in comparison to AP-107 at 16 °C.
4. The K_d values increase in the following order: AP-105 < AP-107 < AP-101.
5. The Cs loading at the AP-101 feed condition as calculated from batch contact testing at 16 °C was 0.064 mmoles Cs/g CST, which was in excellent agreement with the predicted loading of 0.058 mmoles Cs/g CST as calculated from the 50% breakthrough projection of the AP-101 lead column.

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Appendix A – Column Load Data

The AP-101DF lead, lag, and polish column loading raw data are provided in Table A.1. The feed displacement, water rinse, and final fluid expulsion raw data are provided in Table A.2. The raw data include the processed bed volumes (BVs) and corresponding ^{137}Cs concentration in the collected sample, % C/C$_0$, and the Cs decontamination factor (DF).

Table A.1. Lead, Lag, and Polish Column Cs Breakthrough Results with AP-101DF

Lead Column				Lag Column				Polish Column			
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
13.5	4.36E-2	3.54E-2	2,823	47.7	3.48E-3	2.83E-3	35,384	816.9	1.03E-3	8.29E-4	120,579
47.9	1.08E-2	8.81E-3	11,357	93.3	1.60E-3	1.33E-3	75,466	914.1	5.19E-3	4.19E-3	23,887
63.2	1.38E-3	1.14E-3	87,600	135.8	3.93E-4	3.26E-4	307,138	958.4	5.12E-4	5.01E-4	199,776
94.0*	2.34E-3	1.94E-3	51,606	179.0	3.20E-4	2.65E-4	377,091	1047.3	3.79E-4	3.70E-4	270,288
106.3	2.85E-3	2.36E-3	42,387	265.4	2.04E-4	1.72E-4	582,478	1091.9	3.90E-4	3.52E-4	284,002
137.0	7.91E-3	6.55E-3	15,261	309.0	1.88E-4	1.58E-4	632,799	1136.2	5.91E-4	5.33E-4	187,653
179.5	2.62E-2	2.17E-2	4,612	404.2	6.22E-4	5.28E-4	189,405	1181.6	8.87E-4	8.00E-4	124,974
223.5	5.75E-2	4.83E-2	2,069	449.9	7.77E-4	6.60E-4	151,450	1224.8	9.42E-4	9.89E-4	101,158
310.2	3.38E-1	2.84E-1	352	504.2	2.62E-3	2.33E-3	42,910	1269.9	1.20E-3	1.26E-3	79,234
364.3	1.04E+0	8.82E-1	113	548.5	4.87E-3	4.32E-3	23,136	1311.5	2.37E-3	2.49E-3	40,214
451.5*	2.26E+0	1.92E+0	52	592.3	6.56E-3	5.51E-3	18,146	1355.5	4.00E-3	4.20E-3	23,788
550.3	5.16E+0	4.58E+0	22	681.8	2.47E-2	2.08E-2	4,816	1397.3	4.88E-3	5.12E-3	19,524
641.3	8.70E+0	7.30E+0	14	727.8	4.30E-2	3.56E-2	2,811				
684.1	1.11E+1	9.30E+0	11	772.4	7.37E-2	6.09E-2	1,642				
822.7*	2.16E+1	1.74E+1	6	820.1	9.52E-2	7.69E-2	1,301				
864.6	2.53E+1	2.04E+1	5	961.9	3.15E-1	3.08E-1	324				
1009.3	2.93E+1	2.87E+1	3	1095.6	7.85E-1	7.08E-1	141				
1098.8*	4.05E+1	3.66E+1	3	1140.2	9.57E-1	8.63E-1	116				
1189.2	4.70E+1	4.24E+1	2	1185.7	1.49E+0	1.34E+0	75				
1319.9	5.32E+1	5.58E+1	2	1274.3	1.88E+0	1.97E+0	51				
1406.1*	5.94E+1	6.23E+1	2	1316.1	2.99E+0	3.14E+0	32				
				1402.1	5.32E+0	5.58E+0	18				

BV = bed volume, 10 mL/BV
DF = decontamination factor
C$_0$ = 115 µCi ^{137}Cs/ mL (reference date December 2021)
* = samples submitted for additional analysis to assess selected constituent breakthrough profiles

Table A.2. Feed Displacement, Water Rinse, and Final Flush Results Following AP-101DF Processing

Feed Displacement				Water Rinse				Final Fluid Flush			
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
2.2	5.51E-3	4.79E-3	2.09E+4	2.2	6.50E-4	5.65E-4	1.77E+5	6.3	6.20E-1	5.39E-1	1.86E+2
4.3	1.11E-2	9.69E-3	1.03E+4	4.2	3.59E-4	3.12E-4	3.21E+5				
6.4	5.27E-2	4.58E-2	2.18E+3	6.4	2.61E-4	2.27E-4	4.41E+5				
8.6	1.67E-2	1.45E-2	6.90E+3	8.6	2.26E-4	1.96E-4	5.09E+5				
10.6	2.73E-3	2.37E-3	4.22E+4	10.7	1.72E-4	1.50E-4	6.68E+5				
12.7	9.45E-4	8.21E-4	1.22E+5	12.8	1.96E-4	1.71E-4	5.86E+5				

BV = bed volume, 10.0 mL
DF = decontamination factor
C$_0$ = 115 µCi ^{137}Cs/mL (reference date December 2021)

Appendix B – Analyte Concentrations as a Function of Loading

The load behaviors of selected analytes in AP-101DF were evaluated from selected samples collected from the lead column. Analysis results of these samples are summarized in Table B.1.

Table B.1. Analyte Concentrations of Selected Samples from the Lead Column during AP-101DF 16 °C Processing

BV Processed>	NA	94.0	451.5	822.7	1098.8	1406.1
Sample ID>	TI126-Comp-Feed	TI126-L-F4-A	TI126-L-F11-A	TI126-L-F15-A	TI126-L-F18-A	TI126-L-F21-A
Analyte	ICP-OES, M					
Al	3.39E-01	2.83E-01	2.90E-01	3.05E-01	2.76E-01	2.84E-01
Ba	3.52E-06	1.60E-7	<4.4E-05	<4.4E-05	<4.5E-05	<4.5E-05
Ca	7.93E-04	[4.9E-4]	4.89E-4	5.19E-4	4.82E-4	3.97E-4
Cd	[5.2E-06]	[4.9E-6]	5.07E-6	5.69E-6	3.56E-6	6.58E-6
Cr	9.53E-03	7.77E-3	7.98E-3	7.40E-3	7.17E-3	8.00E-3
Fe	3.25E-05	1.75E-5	2.42E-5	2.47E-5	2.15E-5	2.33E-5
K	0.09813	8.18E-2	8.36E-2	7.44E-2	7.26E-2	8.34E-2
Na	5.21E+00	4.09E+0	4.19E+0	3.79E+0	3.65E+0	4.09E+0
Ni	2.62E-04	2.11E-4	2.10E-4	1.70E-4	1.65E-4	2.08E-4
P	1.48E-02	1.17E-2	1.21E-2	1.15E-2	1.09E-2	1.19E-2
Pb	[8.0E-05]	<2.9E-05	1.45E-5	<3.0E-05	<3.0E-05	<2.9E-05
S	5.00E-02	3.99E-2	[3.9E-2]	3.77E-2	[3.6E-2]	3.96E-2
Sr	[1.4E-06]	<6.9E-05	<6.9E-05	<7.0E-05	1.60E-7	2.51E-7
Ti	1.58E-06	5.22E-6	5.85E-6	3.55E-6	2.71E-6	7.72E-6
U	5.22E-05	2.73E-5	3.36E-5	3.82E-5	3.40E-5	2.27E-5
Zn	<2.5E-05	<9.2E-05	<9.2E-05	8.57E-6	2.60E-5	<9.3E-05
Zr	4.90E-06	1.32E-5	1.10E-5	7.45E-6	6.80E-6	1.53E-5
Analyte	ICP-MS, M					
Sr	5.54E-07	4.25E-7	2.56E-7	4.22E-7	5.03E-7	5.65E-7
Nb	2.12E-07	1.26E-5	5.06E-6	3.75E-6	2.12E-6	1.64E-6
Ba	3.01E-05	3.35E-7	2.89E-7	2.63E-7	9.92E-7	5.05E-7
Pb	1.54E-06	1.38E-5	1.85E-5	2.48E-5	1.77E-5	2.13E-5
U	5.41E-05	4.26E-5	3.07E-5	5.60E-5	4.85E-5	5.36E-5
Analyte	Radiochemistry, µCi/mL					
^{137}Cs	1.17E+02	2.34E-03	2.26E+00	2.16E+01	4.05E+01	5.94E+01
Total Alpha	2.52E-04	1.58E-04	2.01E-04	1.22E-04	2.08E-04	2.17E-04
^{237}Np	1.99E-05	1.32E-05	2.07E-05	1.60E-05	1.97E-05	1.79E-05
^{238}Pu	1.62E-05	1.10E-05	1.20E-05	1.93E-05	1.44E-05	1.59E-05
$^{239+240}$Pu	1.27E-04	7.67E-05	9.74E-05	1.08E-04	1.11E-04	1.07E-04
^{90}Sr	3.04E-01	1.27E-03	3.21E-03	1.36E-02	1.44E-02	3.84E-02

BV = bed volume, 10.0 mL

Bracketed values indicate the associated sample results were less than the estimated quantitation limit (EQL) but greater than or equal to the method detection limit (MDL). Analytical uncertainties for these analytes are > ±15%.

Additional analyte concentrations may be found in Appendix C, ASR 1420.

Appendix C – Analytical Reports

Analytical reports provided by PNNL's Analytical Support Operations (ASO) laboratory 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. Cross-references of ASO sample IDs to test description are provided in the body of the report (see Table 3.4 of the main report).

Appendix C Table of Contents

ASR 1386, Initial Characterization of AP-101, As-Received

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- IC, Anions C.13
- TIC/TOC C.18
- ICP-OES, Metals C.22
- ICP-MS, ^{99}Tc C.28

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- OH^{-} C.41
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  - ^{99}Tc and ^{90}Sr C.43
- ICP-OES, Metals C.44
- ICP-MS, Ba, Nb, Pb, Sr, ^{238}U C.54
- IC, Anions C.61

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 amywestesen
Print Name Amy Westesen
Phone 371-7908 MSIN

Project Number: 79156
Work Package: NK4633

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)

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

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

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:** 1/14/22
(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: Am Westesen **MSIN**
MSIN

Additional or Special Instructions

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

Date Delivered: 11/1/21
Delivered By (optional)
Time Delivered: Noon
Group ID (optional)
CMC Waste Sample? ☒ No ☐ Yes

Received By: T Trang-Le
ASR Number: 1386 Rev.: 00
RPL Numbers: (22-0010) → (22-0014)
(first and last)

ASO Work Accepted By: **Signature/Date:** David Blanchard

11-3-2021

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				ASO Staff Use Only	
RPL Number	**Customer Sample ID**	**Sample Description** (& Matrix, if it varies)	**Analysis Requested**	**Test**	**Library**
22-0010	1AP-21-08-Cs	Cs component from AP-101 tank	ICP-MS mass fractionation of Cs		
22-0011	1AP-21-43-Cs	waste in 0.45 M HNO_3	(^{133}Cs, ^{135}Cs, ^{137}Cs)		
22-0012	1AP-21-08-GEA	0.1 mL AP-101 tank waste in 1.9 mL	GEA for ^{137}Cs, ^{241}Am		
22-0013	1AP-21-43-GEA	0.1 M NaOH			
22-0014	1AP-21-08	AP-101 tank waste supernate	1) IC-Anions: F, Cl, NO_2, NO_3, PO_4, C_2O_4, and SO_4		
			2) TIC/TOC- hot pursulfate		
			3) Acid Digestion-128		
			a) ICP-OES: Al, K and Na		
			b) ICP-MS for ^{99}Tc		

ASR # 1386 Rev.: 00

Page 1 of 1

Battelle PNNL/RPL/Inorganic Analysis … ICP-MS Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#: 79156 / NK4635 **ASR#:** 1386.00
Client Name: A. Westensen **Total Samples:** 2 (Aqueous)
Client Sample Description: Cs Component from AP-101 tank waste in 0.45 HNO_3

ASO Sample ID	Client Sample ID
22-0010	1AP-21-08-Cs
22-0011	1AP-21-43-Cs

Sample Preparation: Simple dilution of samples in 2% v/v HNO_3 performed by A.W. Getz on 11/04/21.

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:**	11/05/2021	**ICP File:**	M0318

See Chemical Measurement Center 98620 file: ICP-MS-325-405-1 (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: 1113162654	RPL 420 FH
	☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH

Samuel S Morrison
Report Preparer

11/08/2021
Date

Review and Concurrence

11/11/2021
Date

Two aqueous samples submitted under Analytical Service Request (ASR) 1386.00 were analyzed by ICP-MS. The samples were diluted prior to analysis, 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 as m/z 133, 135, and 137 listed in the upper section of the attached ICP-MS Data Report. 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 (natural abundance) 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 curves and for initial and continuing calibration verification (ICV/CCV). The data have been corrected from the natural abundance calibration solutions to report total isobaric results (ng/mL) at each m/z.

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 each of Tb-159 and Bi-209 as the internal standard (IS). The AOI data were normalized to the Tb-159 IS and were within the acceptance criterion of 30% to 120% recovery.

Preparation Blank (PB):

One preparation blank was prepared, the 2% HNO_3 Lab Blank was the diluent used to prepare the samples for ICP-MS analysis. The concentrations of the AOI in the 2% HNO_3 lab diluent blank was within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤5% of the concentration in the samples.

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

Blank spike samples for AOI were within the acceptance criteria of 80% to 120% recovery.

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

A replicate of sample 22-0010 was analyzed, and the results were within the acceptance criterion of ≤25% for liquid samples.

Matrix-Spike (MS) Sample:

No matrix spike sample was analyzed for this sample set. In lieu of the matrix spike a post spike analysis was performed of each sample.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution (71A) 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 that bracket the reported results were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solutions (2% v/v HNO_3) were analyzed immediately after each respective ICV solution and after each respective CCV solution (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.

Post-Digestion Spike (PS)/Analytical Spike (AS) - Sample (P1 Component):

Instead of a MS sample, post-digestion spike (71A) was conducted on sample 22-0010. 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. All results were within the acceptance criterion of 75% to 125% recovery.

Low-Level Standard (LLS):

The LLS solution (71A) was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130%.

Interference Check Standard (ICS):

The ICS solution (71A) 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 22-0010. Percent differences (%D) 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 were within the acceptance criterion of ≤10%

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. Analyte included in the spike Hg component is Hg.
5) Isotopic abundances values were obtained from Nuclides and Isotopes: Chart of the Nuclides. 16th Edition, Revised 2002. Ed Baum, Harold Knox, Tom Miller
6) Analytes included in P1 solution are Ag, Cd, In, Mo, Nb, Pd, Rh, Ru, Sn, Zr.

Results

		Run Date >	11/05/21	11/05/21	11/05/21	11/05/21
		Process Factor >	1.00	886	886	892
		RPL/LAB >	Blank #8	22-0010	22-0010 rep	22-0011
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	1AP-21-08-Cs		1AP-21-43-Cs
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
0.0003	0.0028	m/z 133		6.04E+02	6.09E+02	6.47E+02
0.0002	0.0016	m/z 135		1.68E+02	1.71E+02	1.84E+02
0.0002	0.0017	m/z 137		2.15E+02	2.19E+02	2.16E+02

Internal Standard % Recovery

Tb 159 (IS)	97%	98%	100%	102%

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 11/5/2021

Criteria >	≤ 35%	80%-120%	75%-125%	≤ 10%
QC ID >	22-0010 Rep	BS71A	22-0010 Post Spike CCV71A	22-0010 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Diff
m/z 133	1%	108%	105%	1%
m/z 135	2%	106%	105%	1%
m/z 137	2%	106%	106%	1%

Internal Standard % Recovery

Bi 159 (IS)	100%	98%	100%	95%

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.

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.

Gamma Energy Analysis (GEA)

Project / WP#: 79156/NK4633
ASR#: 1386.00
Client: A. Westesen
Total Samples: 2

RPL ID	Client Sample ID
22-0012	1AP-21-08-GEA
22-0013	1AP-21-43-GEA

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:	None
Analysis Date or Date Range:	November 2, 2021
Technician/Analyst:	T Trang-Le
Rad Chem Electronic Data File:	*22-0012 Westesen.xlsx*
ASO Project 98620 File:	*File Plan 5872, T4.4 Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and T3 standard certificates and preparation. Also, balance calibration and performance check records.*
M&TE Number(s):	*Detectors T*

____________________ / ____________ ____________________ / ____________

Prepare **Date** **Reviewer** **Date**

SAMPLE RESULTS

Activities for all gamma emitters detected in these samples are presented in an attached Excel spreadsheet for ASR 1386.00. All sample results for target isotopes are reported in units of µCi/sample with estimates of the total propagated uncertainty reported at the 1-sigma level. Due to the high activity of Cs-137, Am-241 could not be detected in these samples. MDA (minimum detectable activity) values are reported for Am-241.

ASO Project File, ASR 1386.00 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

2 mL samples were sent to the counting room for GEA.

The quality control (QC) steps for direct GEA are discussed below.

QUALITY CONTROL RESULTS

Tracer:

Tracers are not used for ASO GEA methods.

Process Blank (PB):

No process blank was prepared by ASO for gamma counting.

Required Detection Limits

There are no required detection limits for these samples.

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

There are no BS, LCS or MS 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. 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.

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 considering systematic uncertainties in gamma calibration standards.

Comments

None

Attachment: Data Report Sample Results for ASR 1386.00.

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

filename 22-0012
11/4/2021

Client: A. Westesen	Project: 79156	Prepared by: ____________________
ASR 1386	WP#: NK4633	
		Technical Reviewer: ____________________

Procedures:	RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS) Spectrometry
M&TE:	Gamma detectors T
Count dates:	2-Nov-21

Measured Activity, uCi/sample ± 1s

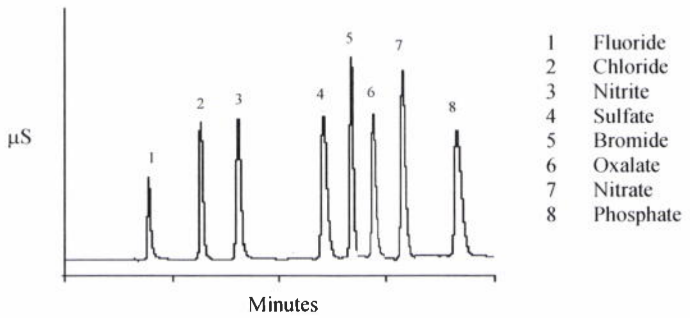
RPL ID:	22-0012		22-0013	
Sample ID:	**1AP-21-08-GEA**		**1AP-21-43-GEA**	
Isotope				
Cs-137	**2.02E+01**	**± 2%**	**1.92E+01**	**± 2%**
Am-241	<3.63E-2		<1.67E-2	

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:	A. Westesen	***ASR #:***	1386
Project #:	79156	***# Samples:***	1 liquid
Charge Code:	NK4633		

*** RPL Number: 21-0014 ***

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPG-CMC-212 Rev.2, "Determination of Common Anions by Ion Chromatography"
Prep Procedure	None
Analyst	AW Getz
Analysis Dates	12/15/21
Calibration Date	08/23/21
Cal/Ver Stds Prep Date	Cal 08/24/21 and Ver 11/03/21
Excel Data File	IC-0253 ASR-1386.00 Westesen.xls
M&TE Numbers	IC System (M&TE) WD81129
	Balance: B725287790
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0253)

12/21/2021

Prepared By — Date

1-19-2022

Reviewed By — Date

IC Report

Sample Results

See Attachment: Sample Results IC ASR-1386

Sample Analysis/Results Discussion

One liquid sample was submitted to the Analytical Support Operations (ASO) laboratory for ion chromatography analysis under ASR 1386. The results are discussed in this report. The analytes of interest for the sample includes fluoride, chloride, nitrite, sulphate, nitrate, oxalate and phospate. Multiple sample dilutions were required. The best result for each anion was chosen based on that which yielded the best quality control (QC) results, and were still within the IC System QC Sample requirements listed below. The sample results are reported in µg/mL.

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

There are no limitations regarding this data. All QC requirements were met.

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

IC Workstation QC Results

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

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: The sample was analyzed in duplicate. The relative percent difference (RPD) is reported for all analytes which were measured at or above the EQL. The reported RPDs for analytes meeting this requirement were between 0% - 1%, meeting the ASO's QA Plan acceptance criteria of <20% for liquid samples.

Laboratory Control Sample (LCS): A routine instrument LCS was analyzed with recoveries ranging from 95.1% to 109.0%, meeting the acceptance criteria of 80% to 120%.

Analytical Spike (AS) (Accuracy): Analytical spikes were prepared using all of the prepared dilutions of the two liquid samples by adding a known concentration of mid-range multi-mix standard, "CCV 110321". Where the spiking concentration exceeds 20% of the sample concentration, the AS recoveries ranged from 93.5% to 109% meeting the QA Plan acceptance criteria of 75% to 125%.

IC Report

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed with each run. The 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-1386

			F			Cl			NO$_2$			SO$_4$			Br			C$_2$O$_4$			NO$_3$			PO$_4$		
RPL Number	Client Sample ID	Ext. Dil.	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	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF
22-0014	1AP-21-08	1	70	70	U ✓	84	4760	✓	1200	77500	✓	1900	4700	J ✓	99	99	U ✓	110	520	J ✓	2500	214000	✓	140	2150	✓
Dilution Blank	N/A	1	0.062	0.062	U	0.075	0.075	U	0.1	0.1	U	0.15	0.15	U	0.088	0.088	U	0.1	0.1	U	0.2	0.2	U	0.12	0.12	U

Sample QC Results ASR 1386

Sample/Replicate Precision Results

		F		Cl		NO$_2$		SO$_4$		Br		C$_2$O$_4$		NO$_3$		PO$_4$	
RPL Number	Sample ID	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD
22-0014 @ 12375	Sample	U	--	J	–	77500	--	J	--	U	--	U	--	214000	--	J	–
	Duplicate | RPD	U	N/A	J	N/A	77400	0.13	J	N/A	U	N/A	U	N/A	216000	0.93	J	N/A
22-0014 @ 1125	Sample	U	--	4760	–	OvrRng	–	U	--	U	--	J	--	OvrRng	–	2150	–
	Duplicate | RPD	U	N/A	4770	0.21	OvrRng	N/A	U	N/A	U	N/A	J	N/A	OvrRng	N/A	2140	0.47

Sample Spike Results - At IC Workstation

		F		Cl		NO$_2$		SO$_4$		Br		C$_2$O$_4$		NO$_3$		PO$_4$	
RPL Number	Sample ID	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
22-0014 @ 12375	Sample	U	--	4900	--	77500	--	4700	--	U	--	U	--	214000	--	9300	--
	MS Sample	1.2	96.8	1.7	102.8	5.2	100.9	3.2	100.0	1.9	96.4	1.9	93.5	12.3	104.4	2.8	96.2
22-0014 @ 1125	Sample	U	--	4760	–	OvrRng	–	U	–	U	--	520	–	OvrRng	–	2150	–
	MS Sample	1.2	99.2	3.8	109.0	OvrRng	N/A	3.1	102.3	2.0	99.9	2.2	98.9	OvrRng	N/A	3.5	103.4

LCS/Blank Spike Results

Run ID	Sample ID	F % Rec	Cl % Rec	NO$_2$ % Rec	SO$_4$ % Rec	Br % Rec	C$_2$O$_4$ % Rec	NO$_3$ % Rec	PO4 % Rec
LCS 110321	LCS 110321	98.3	101.3	101.7	100.8	95.1	105.8	105.2	109.0

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

Sample Results ASR-1386

			F			Cl			NO_2			SO_4			Br			C_2O_4			NO_3			PO_4		
RPL Number	Client Sample ID	Ext. Dil.	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	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF
22-0014 @ 1125	1AP-21-08	1	70	70	U	84	4760		110	OvrRng		170	170	U	99	99	U	110	520	J	230	OvrRng		140	2150	
22-0014 @ 12375	1AP-21-08	1	770	770	U	930	4900	J	1200	77500		1900	4700	J	1100	1100	U	1200	1200	U	2500	214000		1500	9300	J
Dilution Blank	N/A	1	0.062	0.062	U	0.075	0.075	U	0.1	0.1	U	0.15	0.15	U	0.088	0.088	U	0.1	0.1	U	0.2	0.2	U	0.12	0.12	U

Sample QC Results ASR 1386

Sample/Replicate Precision Results

		F		Cl		NO_2		SO_4		Br		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	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD
22-0014 @ 12375	Sample	U	--	J	--	77500	--	J	--	U	--	U	--	214000	--	J	--
	Duplicate | RPD	U	N/A	J	N/A	77400	0.13	J	N/A	U	N/A	U	N/A	216000	0.93	J	N/A
22-0014 @ 1125	Sample	U	–	4760	–	OvrRng	–	U	–	U	–	J	–	OvrRng	–	2150	–
	Duplicate | RPD	U	N/A	4770	0.21	OvrRng	N/A	U	N/A	U	N/A	J	N/A	OvrRng	N/A	2140	0.47

Sample Spike Results - At IC Workstation

		F		Cl		NO_2		SO_4		Br		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	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
22-0014 @ 12375	Sample	U	--	4900	--	77500	--	4700	--	U	--	U	--	214000	--	9300	--
	MS Sample	1.2	96.8	1.7	102.8	5.2	100.9	3.2	100.0	1.9	96.4	1.9	93.5	12.3	104.4	2.8	96.2
22-0014 @ 1125	Sample	U	–	4760	–	OvrRng	–	U	–	U	--	520	–	OvrRng	–	2150	–
	MS Sample	1.2	99.2	3.8	109.0	OvrRng	N/A	3.1	102.3	2.0	99.9	2.2	98.9	OvrRng	N/A	3.5	103.4

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
LCS 110321	LCS 110321	98.3	101.3	101.7	100.8	95.1	105.8	105.2	109.0

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 Number:	79156
Charge Code:	NK4633
ASR Number:	1386
Client:	A. Westesen
Total Samples:	1 liquid

	RPL Numbers	**Client IDs**
Samples	22-0014	1AP-21-08

Analysis Procedure	RPG-CMC-386 Rev. 1, "Carbon Measured in Solids, Sludge, and Liquid Matrices"
Prep Procedure	None
Analyst	A. Carney
Analysis Date	February 15, 2022
CCV Standards	TIC/TOC CMS # 579388 and 578209
BS/LCS/MS Standards	TIC/TOC CMS # 577892 and 566865
Excel Data File	ASR-1386-Westesen.xlsx
M&TE Numbers	Carbon System (WD36639, RPL/701)
	Balance : Sartorius R200D, S/N 30809774
All Analysis Records	5015_02-15-2022-111118.CSV

Prepared By Date

Reviewed By Date

Table 1: TIC/TOC Results for ASR 1386

TIC in Sample **22-0014** (mg C/L):	9332
MDL (mg C/L):	181
EQL (mg C/L):	903
TOC in Sample **22-0014** (mg C/L):	2981
MDL (mg C/L):	181
EQL (mg C/L):	903
TIC in Sample **22-0014-Dup**:	10053
MDL (mg C/L):	181
EQL (mg C/L):	903
TOC in Sample **22-0014-Dup**:	2724
MDL (mg C/L):	181
EQL (mg C/L):	903
22-0014 TIC RPD:	7.43%
22-0014 TOC RPD:	9.02%

Sample Analysis/Results Discussion

One liquid sample was submitted under Analytical Service Request (ASR) 1386 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 determined first by acidifying with heated sulfuric acid, converting inorganic carbonates to CO_2 (i.e., TIC analysis), then the persulfate solids and silver-catalyst solution are added and the remaining organic carbon converted to CO_2 (i.e., TOC analysis). 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 mg C/L 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 all <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. TIC results for the two ICVs were 98.4% and 99.7% recovery, and for the two TOC ICVs the results were 97.2% and 99.3% recovery, within the acceptance criterion of 90% to 110%. The TIC result for the CCV was 98.9% recovery and the TOC CCV was 97.9% 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 101.6% recovery, and the TOC LCS/BS result was 97.4% 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 22-0014 TIC RPD was 7.34% and TOC was 9.02%. Both TIC and TOC 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 98.9% recovery and for the TOC, 91.2% 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 volume 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.

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

Project / WP#:	79156 / NK4633
ASR#:	1386.00
Client:	A.Westesen
Total Samples:	1 (liquid)

ASO Sample ID	**Client Sample ID**
22-0014	1AP-21-08

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater" using Nitric Acid only, performed by L. Darnell on 11/23/21. Simple dilution of "as received" samples in 5% v/v HNO3 performed by A. Getz on 12/20/21.

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

Analyst:	A. Getz	**Analysis Date:**	12/20/2021	**ICP File:**	C0885

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: 1113162654
	☐	Sartorius R200D Balance	SN: 39080042
	☐	Mettler AT201 Balance	SN: 192720-92
	☒	Ohaus Pioneer PA224C	SN: B725287790
	☐	SAL Cell 2 Balance	SN: 8033311209

Andrew W. Getz — **12/22/2021**
12/22/2021
Report Preparer — Date

Samuel S Morrison — 01/10/2022
Review and Concurrence — Date

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

One aqueous sample was submitted under Analytical Service Request (ASR) 1386 was analyzed by ICP-OES. The sample was prepared following RPL procedure RPG-CMC-128, Rev. 1, "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". This process was conducted without the use of HCl. All samples were diluted in 5% HNO3 prior to analysis. None of the samples were filtered.

All sample results are reported on a mass per mass of sample prior to dissolution basis (µg/g) 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):

A process blank was included with the sample set. 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.

Reagent Spike (BS):

A reagent spike sample was prepared with samples and processed through the dissolution process. 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 were 98% - 99.9% and are all within the acceptance criterion of 80% to 120%.

Duplicate(Dup) Relative Percent Difference (RPD):

Duplicates of sample 22-0034 was prepared along with the samples and analyzed. The RPD ranged from 0.7% - 2.0% and were within the acceptance criterion of ≤20% for solid samples.

Matrix-Spike (MS) Sample:

A matrix spike was prepared using sample 22-0014. 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 were 100% - 102% and are all within the acceptance criterion of 75% to 125%.

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%.

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 22-0014. The percent difference (%D) for the AOIs ranged from 2.3% - 3.3% meeting the acceptance criteria 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 22-0014. The recovery for the AOIs ranged from 93% - 106% meeting the acceptance criterion of 99.8% to 100.2%.

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

In addition to the BS sample, a post-digestion spike (B Component) was conducted on sample 22-0014. There were no AOIs in the B Component, all non-AOI recoveries 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:

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

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, Eu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sm, 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 >	12/20/2021	12/20/2021	12/20/2021	12/20/2021
		Process Factor >	1.0	24.2	605.7	616.4
			405 diluent	BLK-0014	22-0014	
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagent Blank	1AP-21-08	
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg)	(µg/g)	(µg/g)
0.0101	0.101	Al	--	--	11,456	11,368
0.0312	0.312	K	--	[1.4]	4,242	4,157
0.0073	0.073	Na	--	--	146,688	145,611
Other Analytes						
0.0019	0.019	Ag	--	--	[1.91]	--
0.0619	0.619	As	--	--	--	--
0.0060	0.060	B	[0.021]	[0.42]	[26]	[15]
0.0001	0.001	Ba	--	--	[0.68]	[0.50]
0.0001	0.001	Be	--	--	[0.084]	--
0.0245	0.245	Bi	--	--	--	--
0.0056	0.056	Ca	--	[0.42]	[22]	[24]
0.0014	0.014	Cd	[0.0026]	[0.047]	[1.63]	--
0.0103	0.103	Ce	--	--	--	--
0.0043	0.043	Co	--	--	--	--
0.0020	0.020	Cr	--	--	607	598
0.0023	0.023	Cu	--	[0.095]	[8.17]	[8.73]
0.0023	0.023	Dy	--	--	--	--
0.0006	0.006	Eu	--	--	--	--
0.0014	0.014	Fe	--	--	--	--
0.0019	0.019	La	--	--	--	--
0.0007	0.007	Li	[0.0010]	[0.043]	[0.73]	[1.43]
0.0018	0.018	Mg	--	[0.044]	--	--
0.0002	0.002	Mn	--	[0.0079]	[0.94]	[1.02]
0.0044	0.044	Mo	--	--	47.6	[37]
0.0088	0.088	Nd	--	--	--	--
0.0022	0.022	Ni	--	--	19.5	[15]
0.0905	0.905	P	--	--	[554]	[565]
0.0269	0.269	Pb	--	--	--	--
0.0054	0.054	Pd	--	[0.14]	[4.93]	--
0.0211	0.211	Rh	--	--	--	--
0.0063	0.063	Ru	--	--	[6.25]	[12.52]
0.1262	1.262	S	--	--	1,823	1,861
0.0598	0.598	Sb	--	--	--	--
0.1656	1.656	Se	--	--	[144]	--
0.0086	0.086	Si	--	[0.57]	[49]	[39]
0.0291	0.291	Sn	--	--	--	--
0.0001	0.001	Sr	--	--	[0.101]	[0.113]
0.0246	0.246	Ta	--	--	--	--
0.0197	0.197	Te	--	--	--	--
0.0071	0.071	Th	--	--	--	--
0.0006	0.006	Ti	--	--	--	--
0.0814	0.814	Tl	--	--	--	--
0.0410	0.410	U	--	--	[39]	--
0.0013	0.013	V	[0.0015]	--	[1.37]	--
0.0161	0.161	W	--	[0.47]	[102]	[100]
0.0006	0.006	Y	--	--	--	--
0.0027	0.027	Zn	--	0.726	--	--
0.0014	0.014	Zr	[0.0024]	--	--	--

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%.
na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations, o

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

QC Performance 12/20/2021

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	DUP-0014	Reagent Spike	MS-0014	22-0014 + PS-A	22-0014 + AS-B	22-0014 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	0.8	99.9	100	100		3.1
K	2.0	98.0	102	100		2.3
Na	0.7	98.0	nr	100		3.3
Other Analytes						
Ag				93		
As				102		
B				101		
Ba		98.4	101	99		
Be		99.5	100	97		
Bi		99.7		96		
Ca		100.1	101	102		
Cd		98.1	102	98		
Ce		93.4	96		92	
Co				98		
Cr	1.5	96.8	nr	99		3.9
Cu		102.9	110	105		
Dy					96	
Eu					94	
Fe		98.8	98	100		
La		95.5	97		94	
Li		104.0	103	104		
Mg		99.7	103	101		
Mn		97.6	101	100		
Mo				95		
Nd		97.7	95		96	
Ni		97.7	101	99		
P				97		
Pb		97.4	103	97		
Pd					88	
Rh					92	
Ru					94	
S	2.1				94	
Sb				98		
Se				99		
Si				102		
Sn				95		
Sr		97.6	100	97		
Ta				96		
Te					92	
Th		97.8	100		95	
Ti				99		
Tl				90		
U		97.5	98		95	
V		99.6	101	97		
W				105		
Y				97		
Zn		93.6	86	97		
Zr				99		

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 Na_2O_2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

r Si for HF assisted digests.

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

filename 22-0012
2/1/2022

Client: A. Westesen
ASR 1386

Project: 79156
WP#: NK4633

Prepared by: C Soderquist 2-1-2022

Technical Reviewer: T Trang-Le 2/2/22

Procedures: RPG-CMC-432 Rev 0, Technetium-99 Analysis
RPG-CMC-474 Rev 1, Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry
M&TE: Perkin Elmer TriCarb model 3100 TR liquid scintillation spectrometer
Count date: 1-Feb-22

Sample	lab ID	**Measured Activity, µCi/mL ± 1s** Tc-99	
1AP-21-08	22-0014	**1.59E-01**	**± 2%**
	22-0014 Dup	**1.60E-01**	**± 2%**
	Matrix spike	104%	
	Reagent spike	96%	
	Lab blank	-1E-04	± 100%

This sample was received in the analytical lab on Nov 1, 2021. Technetium was chemically separated from the raw sample by cation exchange followed by solvent extraction. The separated technetium was measured by liquid scintillation counting. The LSC beta spectra showed no other radionuclides except technetium.

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

Project / WP#:	79156 / NK4635	**ASR#:**	1386.00
Client Name:	A. Westesen	**Total Samples:**	1 (Aqueous)

Client Sample Description: Cs Component from AP-101 tank waste supernate

ASO Sample ID	**Client Sample ID**
22-0014	1AP-21-08

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater" using Nitric Acid only, performed by L. Darnell on 11/23/21. Simple dilution of samples in 2% v/v HNO_3 performed by A.W. Getz on 12/07/21.

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:**	12/07/2021	**ICP File:**	M0319

See Chemical Measurement Center 98620 file: ICP-MS-325-405-1
(Calibration and Maintenance Records)

M&TE:	☒	PerkinElmer NexION™ 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: 1113162654	RPL 420 FH
	☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH

Samuel S Morrison
Report Preparer

01/11/2022
Date

Review and Concurrence

01/14/2022
Date

One aqueous sample submitted under Analytical Service Request (ASR) 1386.00 was analyzed by ICP-MS. The sample was prepared following RPL procedure RPG-CMC-128, Rev. 1, "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". This process was conducted without the use of HCl. The sample was diluted prior to analysis in 2% HNO_3, the sample was not filtered.

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

Analytes of interest (AOI) were specified in the ASR as m/z 99 listed in the upper section of the attached ICP-MS Data Report. Note that additional Ruthenium isotopes m/z 101, 102, and 104 were analyzed to assess the presence of natural Ruthenium that has an isobaric interference with Tc-99 (12.76%). 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 (natural abundance) 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 curves and for initial and continuing calibration verification (ICV/CCV). The data have been corrected from the natural abundance calibration solutions to report total isobaric results (ng/mL) at each m/z.

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 each of Tb-159 and Bi-209 as the internal standard (IS). The AOI data were normalized to the Tb-159 IS and were within the acceptance criterion of 30% to 120% recovery.

Preparation Blank (PB):

A process blank was prepared with this sample and processed through the RPL procedure RPG-CMC-128, Rev. 1, "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". This process was conducted without the use of HCl. The concentrations of the AOI in the 2% HNO_3 lab diluent blank was within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤5% of the concentration in the samples.

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

Blank spike samples for AOI were within the acceptance criteria of 80% to 120% recovery.

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

A replicate of sample 22-0014 was analyzed, and the results were within the acceptance criterion of ≤25% for liquid samples.

Matrix-Spike (MS) Sample:

No matrix spike sample was analyzed for this sample set. In lieu of the matrix spike a post spike analysis was performed of each sample.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution (71C) 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 that bracket the reported results were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solutions (2% v/v HNO_3) were analyzed immediately after each respective ICV solution and after each respective CCV solution (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.

Post-Digestion Spike (PS)/Analytical Spike (AS) - Sample (P1 Component):

Instead of a MS sample, post-digestion spike (71C) was conducted on sample 22-0014. 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. All results were within the acceptance criterion of 75% to 125% recovery.

Low-Level Standard (LLS):

The LLS solution (71A) was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130%.

Interference Check Standard (ICS):

The ICS solution (71C) 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 22-0014. Percent differences (%D) 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 were within the acceptance criterion of ≤10%

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. Analyte included in the spike Hg component is Hg.
5) Isotopic abundances values were obtained from Nuclides and Isotopes: Chart of the Nuclides. 16th Edition, Revised 2002. Ed Baum, Harold Knox, Tom Miller
6) Analytes included in P1 solution are Ag, Cd, In, Mo, Nb, Pd, Rh, Ru, Sn, Zr.

Final Report

		Run Date >	12/07/21	12/07/21	12/07/21	12/07/21	12/07/21
		Process Factor >	1.00	789	34020	34020	33907
		RPL/LAB >	Blank #8	Prep Blank	22-0014	22-0014 REP	22-0014 DUP
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	Process Blank	1AP-21-08		1AP-21-08
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng)	(ng/g)	(ng/g)	(ng/g)
0.0001	0.0008	m/z 99		2.1E-01	1.02E+04	1.04E+04	9.85E+03

Internal Standard % Recovery

Tb 159 (IS)	101%	101%	101%	102%	101%

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 12/7/2021

Criteria >	≤ 35%	≤ 35%	80%-120%	75%-125%	≤ 10%
QC ID >	22-0014 Rep	22-0014 Dup	BS71A	22-0014 Post Spike CCV71A	22-0014 5-fold Serial Dil
Analytes	RPD (%)	RPD (%)	%Rec	%Rec	%Diff
m/z 99	2%	2%	106%	105%	1%

Internal Standard % Recovery

Tb 159 (IS)	100%	100%	98%	100%	95%

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.

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.

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 amywestesen
Print Name Amy Westesen
Phone 371-7908 MSIN

Project Number: 79156
Work Package: NK4633

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)

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

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

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:**
  (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: A. Westesen MSIN
E. Campbell MSIN
Additional or Special Instructions

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

Date Delivered:
Delivered By (optional)
Time Delivered:
Group ID (optional)
CMC Waste Sample? ☒ No ☐ Yes

Received By:
ASR Number: 1420 Rev.: 00
RPL Numbers: (22-0512) → (22-0523)
(first and last)

ASO Work Accepted By: **Signature/Date:**

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**
22-0512	TI126-COMP-FEED	AP-101 Diluted Feed	1) GEA - All samples (Cs-137, Co-60 and Eu-154 and any other observed gamma emitting isotopes) 2) Tc-99 3) Sr-90 4) Np-AEA, Np-237 5) Pu-AEA, Pu-238, Pu-239/240 6) Am-AEA, Am-241 7) Acid Digestion- 128 - Prep Lab a) ICP/OES - Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr,Ti, U, Zn, Zr b) ICP/MS - Ba, Nb, Pb, Sr, U-238		
22-0513	TI126-COMP-EFF	AP-101 Tank Waste - Cs Removed	1) GEA - All samples (Cs-137, Co-60 and Eu-154 and any other observed gamma emitting isotopes) 2) IC-Anions - F, Cl, NO_2, NO_3, PO_4, C_2O_4 and SO_4 3) TOC/TIC - Hot Pursulfate 4) OH 5) Sr-90 6) Tc-99 7) Np-AEA, Np-237 8) Pu-AEA, Pu-238, Pu-239/240 9) Am-AEA, Am-241 10) Acid Digestion- 128 - Prep Lab 11) ICP/OES - Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr,Ti, U, Zn, Zr 12) ICP/MS - Ba, Nb, Pb, Sr, U-238		

ASR: 1420

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**
22-0514	TI126-L-F4-A	AP-101 Tank Waste - Cs Removed	1) Sr-90 2) Pu-AEA, Pu-238, Pu-239/240 3) Np-AEA, Np-237 4) Acid Digest - 128 - Prep Lab a) ICP/OES - Al, Ca, Cd, Fe, K b) ICP/MS - Ba, Pb, U-238		
22-0515	TI126-L-F11-A				
22-0516	TI126-L-F15-A				
22-0517	TI126-L-F18-A				
22-0518	TI126-L-F21-A				

ASR: 1420

Gamma Energy Analysis (GEA)

Project / WP#:	79156/NK4633
ASR#:	1420.00
Client:	A. Westesen
Total Samples:	2

RPL ID	Client Sample ID
22-0512	TI126-COMP-FEED
22-0513	TI126-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:	None
Analysis Date or Date Range:	February 24, 2022
Technician/Analyst:	T Trang-Le
Rad Chem Electronic Data File:	*22-0512 Westesen.xlsx*
ASO Project 98620 File:	*File Plan 5872, T4.4 Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and T3 standard certificates and preparation. Also, balance calibration and performance check records.*
M&TE Number(s):	*Detectors G,T*

_________________________ / _____________ _________________________ / _____________

Prepare **Date** **Reviewer** **Date**

SAMPLE RESULTS

Activities for all gamma emitters detected in these samples are presented in an attached Excel spreadsheet for ASR 1420.00. All sample results for target isotopes are reported in units of µCi/mL with estimates of the total propagated uncertainty reported at the 1-sigma level.

ASO Project File, ASR 1420.00 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

2 mL samples were sent to the counting room for GEA.

The quality control (QC) steps for direct GEA are discussed below.

QUALITY CONTROL RESULTS

<u>Tracer:</u>

Tracers are not used for ASO GEA methods.

<u>Process Blank (PB):</u>

No process blank was prepared by ASO for gamma counting.

<u>Required Detection Limits</u>

There are no required detection limits for these samples.

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

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

<u>Duplicate Relative Percent Difference (RPD):</u>

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. 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.

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 considering systematic uncertainties in gamma calibration standards.

Comments

None

Attachment: Data Report Sample Results for ASR 1420.00.

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

filename 22-0512
3/1/2022

Client: A. Westesen
ASR 1420

Project: 79156
WP#: NK4633

Prepared by: ____________________

Technical Reviewer: ____________________

Procedures: RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS) Spectrometry
M&TE: Gamma detectors G,T
Count dates: 24-Feb-22

Measured Activity, uCi/mL ± 1s

RPL ID:	22-0512		22-0513	
Sample ID:	**TI126-COMP-FEED**		**TI126-COMP-EFF**	
Isotope				
Co-60	<1.72E-03		**2.38E-04**	**± 2%**
Sb-126	<5.96E-03		**2.32E-04**	**± 2%**
Sn-126	**1.02E-01**	**± 12%**	**1.92E-04**	**± 16%**
Cs-137	**1.17E+02**	**± 1%**	**4.45E-03**	**± 2%**
Eu-154	<7.05E-03		**1.41E-05**	**± 14%**
Am-241	<4.48E-01		**1.05E-04**	**± 10%**

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

filename Hydroxide (22-0513)
4/12/2022

Client: A. Westesen
ASR 1420

Prepared by: C Soderquist 4-13-22

Concur: C.Arndt 4·13·22

Hydroxide Titration of Tank Waste Sample

Sample **TI126-COMP-EFF** (lab ID 22-0513) was titrated using dilute hydrochloric acid to measure the total base. The titration was done manually, using a 50-mL buret and a pH probe. The titrant was previously standardized against sodium hydroxide, which in turn was standardized against NIST potassium hydrogen phthalate. The concentration of the titrant was confirmed by titrating an accurately weighed amount of dry sodium carbonate.

The sample was measured using a pipet, then mixed with 30 mL of water for the titration. The diluted sample was titrated against 0.0351M hydrochloric acid.

Two inflection points were found - one indistinct around pH 10.5, and a well-defined inflection point around pH 8. The observed pH of 8.0 suggests that the primary base in this sample is carbonate.

The uncertainty in the measured total hydroxide is probably 2-3% at 1s, judging from the sodium carbonate titrations. Sodium carbonate 2 more closely matches the amount of hydroxide in the tank samples.

Sample	Volume Titrated	First inflection point	Second inflection point	**Total hydroxide, to second inflection point**	
TI126-COMP-EFF	0.100 mL	10.12	7.94	**1.60**	**molar**
	0.300 mL	10.75	8.17	**1.56**	**molar**

	known	measured	
Sodium carbonate 1	0.3820 g	0.3768 g	99% of expected
Sodium carbonate 2	0.0914 g	0.0880 g	96% of expected

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

filename 22-0512 Westesen
3/30/2022

Client: A. Westesen
ASR 1420

Project: 90051
WP#: NG1143

Prepared by: C Soderquist 4-11-2022

Technical Reviewer: T Trang-Le 4/11/22

Procedures:	RPG-CMC-408, Rev 2, Total Alpha and Beta Analysis RPG-CMC-4001, Rev 1, Source Preparation for Gross Alpha and Gross Beta Analysis RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectroscopy RPG-CMC-422, Rev 2, Solutions Analysis: Alpha spectrometry
M&TE:	Ludlum alpha counters, alpha spectrometry counting system

		Measured Activity, µCi/mL ± 1s uncertainty											
Sample	Lab ID	**Gross alpha**		**Np-237**		**Pu-238**		**Pu-239+240**		**Am-241**		**Cm-243+244**	
TI126-COMP-FEED	22-0512	2.52E-4	± 34%	1.99E-5	± 3%	1.62E-5	± 5%	1.27E-4	± 2%	1.32E-4	± 2%	3.38E-6	± 10%
TI126-COMP-EFF	22-0513	1.90E-4	± 42%	1.46E-5	± 3%	9.71E-6	± 6%	7.38E-5	± 3%	1.05E-4	± 2%	3.20E-6	± 10%
	22-0513 Dup	--		1.42E-5	± 3%	9.29E-6	± 6%	6.86E-5	± 3%	1.05E-4	± 2%	2.66E-6	± 11%
RPD				3%		4%		7%		0%		19%	
TI-126-L-F4-A	22-0514	5.75E-5	± 109%	1.32E-5	± 3%	1.10E-5	± 6%	7.67E-5	± 3%	--		--	
	22-0514 Dup	2.59E-4	± 34%	--		--		--		--		--	
TI-126-L-F11-A	22-0515	2.01E-4	± 44%	2.07E-5	± 3%	1.20E-5	± 6%	9.74E-5	± 3%	--		--	
TI-126-L-F15-A	22-0516	1.22E-4	± 58%	1.60E-5	± 3%	1.93E-5	± 5%	1.08E-4	± 3%	--		--	
TI-126-L-F18-A	22-0517	2.08E-4	± 40%	1.97E-5	± 3%	1.44E-5	± 5%	1.11E-4	± 3%	--		--	
TI-126-L-F21-A	22-0518	2.17E-4	± 38%	1.79E-5	± 3%	1.59E-5	± 5%	1.07E-4	± 3%	--		--	
	Reagent spike	93%		91%		--		96%		104%		--	
	Matrix spike	75%		84%		--		97%		108%		--	
	Lab blank	3.0E-7	± 190%	4.74E-9	± 285%	3.5E-7	± 70%	7.4E-7	± 28%	5.9E-7	± 43%	-2.8E-7	± 115%

Northwest National Laboratory
Richland, WA
Radiochemical Sciences and Engineering Group

filename 22-0512 Westesen
4/4/2022

Client: A. Westesen
ASR 1420

Project: 90051
WP#: NG1143

Prepared by: C. Soderquist 4-11-2022

Technical Reviewer: T Trang-le 4/11/22

Procedures:	RPG-CMC-408, Rev 2, Total Alpha and Beta Analysis RPG-CMC-4001, Rev 1, Source Preparation for Gross Alpha and Gross Beta Analysis RPG-CMC-4017, Rev 0, Analysis of Environmental Water Samples for Actinides and Strotium-90
M&TE:	Perkin Elmer TriCarb model 3100 TR liquid scintillation spectrometer

		Measured Activity, µCi/mL ± 1s uncertainty					
Sample	Lab ID	**Gross Beta**		**Sr-90**		**Tc-99**	
TI126-COMP-FEED	22-0512	1.17E+2	± 4%	3.04E-1	± 1%	9.38E-2	± 2%
TI126-COMP-EFF	22-0513	9.79E-2	± 4%	2.53E-4	± 1%	9.24E-2	± 2%
	22-0513 Dup			2.43E-4	± 1%	9.40E-2	± 2%
RPD				4%		2%	
TI-126-L-F4-A	22-0514	1.05E-1	± 4%	1.27E-3	± 1%	--	
TI-126-L-F11-A	22-0515	2.37E+0	± 4%	3.21E-3	± 1%	--	
TI-126-L-F15-A	22-0516	2.13E+1	± 4%	1.36E-2	± 1%	--	
TI-126-L-F18-A	22-0517	3.87E+1	± 4%	1.44E-2	± 1%	--	
TI-126-L-F21-A	22-0518	5.71E+1	± 4%	3.84E-2	± 2%	--	
	Reagent spike	116%		101%		94%	
	Matrix spike	96%		96%		78%	as too small for the sample activity]
	Lab blank	-1.3E-6	± 97%	2.3E-6	± 217%	-1.8E-5	± 87%

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

Project / WP#:	79156 / NK4633
ASR#:	1420
Client:	A.Westesen
Total Samples:	7 (liquids)

ASO Sample ID	Client Sample ID	Client Sample Description
22-0512	TI126-COMP-FEED	AP-101 Diluted Feed
22-0513	TI126-COMP-EFF	AP-101 Tank Waste - Cs Removed
22-0514	TI126-L-F4-A	AP-101 Tank Waste - Cs Removed
22-0515	TI126-L-F11-A	AP-101 Tank Waste - Cs Removed
22-0516	TI126-L-F15-A	AP-101 Tank Waste - Cs Removed
22-0517	TI126-L-F18-A	AP-101 Tank Waste - Cs Removed
22-0518	TI126-L-F21-A	AP-101 Tank Waste - Cs Removed

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater" using Nitric Acid only, performed by L. Darnell on 03/07/22. Simple dilution of "as received" samples in 5% v/v HNO3 performed by SRBaum on 03/17/22.

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

Analyst:	SRBaum	**Analysis Date:**	03/17/2022	**ICP File:**	C0887

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: 21308482
	☐	Mettler AT400 Balance	SN: 1113162654
	☐	Sartorius R200D Balance	SN: 39080042
	☐	Mettler AT201 Balance	SN: 192720-92
	☒	Ohaus Pioneer PA224C	SN: B725287790
	☐	SAL Cell 2 Balance	SN: 8033311209

Steven Baum / Steven Baum
Report Preparer

4-26-22
Date

Samuel S Morrison / Sam S
Review and Concurrence

4-27-2022
Date

Seven aqueous samples submitted under Analytical Service Request (ASR) 1420 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". This process was conducted without the use of HCl. All samples were diluted in 5% HNO3 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, one being a shortened version. Samples were reported using the most extensive analyte list. 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):

A process blank was included with the sample set. 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.

Reagent Spike (BS):

A reagent spike sample was prepared with samples and processed through the dissolution process. Recovery values are listed for all analytes included in the BS that were measured at or above the EQL. Recovery values for the AOI were within the acceptance criterion of 80% to 120%.

Duplicate/Replicate Relative Percent Difference (RPD):

Replicates of sample 22-0513 was prepared and analyzed. The RPD were within the acceptance criterion of ≤20% for solid samples.

Matrix-Spike (MS) Sample:

A matrix spike was prepared using sample 22-0513. Recovery values are listed for all analytes included in the MS that were measured at or above the EQL. Recovery values for the AOI were within the acceptance criterion of 75% to 125%.

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% except for Sr which was 111%-123% 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 except for Sodium (Na) which had carry-over issues with the 5x dilution samples. The 5x data for Sodium (Na) was not reported.

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 22-0513. The percent difference (%D) for the AOI met the acceptance criteria of $\leq$ 10%.

Post-Digestion Spike (PS):

A post-digestion spike was conducted on sample 22-0513. The recovery for the AOI met the acceptance criterion of 80% to 120%, except for K (124%).

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, Eu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sm, 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.

		Run Date >	3/17/2022	3/17/2022	3/17/2022	3/17/2022	3/17/2022	3/17/2022
		Process Factor >	1	25.04	24.81	494.4	499.8	490.4
		RPL/LAB >	405 Diluent	BLK-0512 @1x	RS-0512 @1x	22-0512	22-0513	DUP-0513
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagent Blank	Reagent Spike	TI126-COMP-FEED	TI126-COMP-EFF	TI126-COMP-EFF
(µg/mL)	(µg/mL)	(Analyte)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.0101	0.101	Al	--	--	2570	7,360	7,380	7,520
0.0619	0.619	As	--	--	501	--	--	--
0.0001	0.001	Ba	--	--	128	0.389	--	--
0.0056	0.056	Ca	--	0.98	518	25.60	16.60	16.90
0.0014	0.014	Cd	--	0.038	52.1	[.47]	0.48	0.56
0.0020	0.020	Cr	0.0024	--	52.8	399.0	394.0	400.0
0.0014	0.014	Fe	0.0034	0.928	128	1.46	0.83	1.30
0.0312	0.312	K	--	1.8	5050	3,090	3,060	3,090
0.0073	0.073	Na	--	0.42	511	96,500	97,200	96,700
0.0022	0.022	Ni	--	--	128	12.40	11.30	11.30
0.0905	0.905	P	--	--	523	370.0	364.0	359.0
0.0269	0.269	Pb	--	--	511	--	--	--
0.1262	1.262	S	--	--	1490	1,290	1,260	1,240
0.0001	0.001	Sr	--	0.0073	14.2	[0.100]	--	[0.015]
0.0006	0.006	Ti	--	--	129	0.06	0.29	0.27
0.0410	0.410	U	--	--	3240	10.0	4.50	8.70
0.0027	0.027	Zn	--	--	50	--	--	2.30
0.0014	0.014	Zr	--	--	50.6	0.36	1.30	1.20

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%.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations

BLUE Process blank failure (>EQL or >5%)
🟩 3*IDL>MRQ and sample concentration >3*IDL
▨ 3*IDL>MRQ and sample concentration <3*IDL

Other Analytes

0.0019	0.019	Ag	--	--	4.28	--	0.19	--
0.0058	0.058	Au	--	0.35	8.33	--	--	--
0.0060	0.060	B	0.012	0.45	262	51.40	21.60	20.80
0.0001	0.001	Be	--	--	12.9	[0.08]	0.07	0.07
0.0245	0.245	Bi	--	--	32.2	--	--	--
0.0103	0.103	Ce	--	--	120	--	--	--
0.0043	0.043	Co	--	--	0.26	--	--	--
0.0023	0.023	Cu	--	--	65.1	0.90	0.75	0.78
0.0023	0.023	Dy	--	--	0.864	--	--	--
0.0006	0.006	Eu	--	0.02	0.505	--	--	--
0.0089	0.089	Ga	--	--	--	4.00	3.40	3.10
0.0056	0.056	Hf	--	--	14.1	--	--	--
0.0019	0.019	La	--	--	128	--	--	--
0.0007	0.007	Li	--	0.045	54.3	.31	0.30	0.15
0.0003	0.003	Lu	--	--	0.182	0.05	--	0.05
0.0018	0.018	Mg	--	0.686	1300	0.90	--	--
0.0002	0.002	Mn	--	0.0061	129	0.04	--	0.05
0.0044	0.044	Mo	--	--	122	[29.4]	[28.6]	[29.0]
0.0028	0.028	Nb	0.003	0.2	719	--	--	--
0.0088	0.088	Nd	--	0.25	257	--	--	--
0.0054	0.054	Pd	--	--	13.6	[2.70]	2.50	2.40
0.0211	0.211	Rh	--	--	0.53	[3.10]	2.30	3.20
0.0063	0.063	Ru	--	--	--	4.70	5.10	4.80
0.0598	0.598	Sb	--	--	--	--	--	7.20
0.0003	0.003	Sc	--	--	0.398	--	--	--
0.1656	1.656	Se	--	--	--	--	--	--
0.0086	0.086	Si	0.039	2.93	490	121.0	37.40	35.60
0.0091	0.091	Sm	--	0.31	2.78	--	--	--
0.0291	0.291	Sn	--	--	--	5.50	--	5.30
0.0246	0.246	Ta	--	--	1.5	--	--	--
0.0045	0.045	Tb	--	--	0.82	--	--	--
0.0197	0.197	Te	--	--	2.5	--	--	--
0.0071	0.071	Th	--	--	1060	0.82	--	--
0.0814	0.814	Tl	--	--	--	--	--	--
0.0018	0.018	Tm	--	--	17	--	--	--
0.0013	0.013	V	0.0047	0.082	51.4	0.40	0.52	0.50
0.0161	0.161	W	--	--	65.9	58.20	54.20	56.10
0.0006	0.006	Y	--	--	0.11	--	--	--

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%.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations.

BLUE	Process blank failure (>EQL or >5%)
🟩	3*IDL>MRQ and sample concentration >3*IDL
▨	3*IDL>MRQ and sample concentration <3*IDL

		Run Date >	3/17/2022	3/17/2022	3/17/2022	3/17/2022	3/17/2022
		Process Factor >	493.7	487.4	488.0	499.2	498.2
		RPL/LAB >	22-0514	22-0515	22-0516	22-0517	22-0518
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	TI126-L-F4-A	TI126-L-F11-A	TI126-L-F15-A	TI126-L-F18-A	TI126-L-F21-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.0101	0.101	Al	7,630	7,490	7,760	7,460	7,170
0.0619	0.619	As	--	--	--	--	--
0.0001	0.001	Ba	0.022	--	--	--	--
0.0056	0.056	Ca	15.90	19.80	19.60	20.80	19.30
0.0014	0.014	Cd	0.74	[.55]	0.6	0.64	0.4
0.0020	0.020	Cr	416.0	404.0	415.0	385.0	373.0
0.0014	0.014	Fe	1.30	0.98	1.35	1.38	1.20
0.0312	0.312	K	3,260	3,200	3,270	2,910	2,840
0.0073	0.073	Na	101,000	100,000	104,000	94,300	92,800
0.0022	0.022	Ni	12.20	12.40	12.30	10.00	9.71
0.0905	0.905	P	369.0	362.0	374.0	356.0	337.0
0.0269	0.269	Pb	--	--	[3.00]	--	--
0.1262	1.262	S	1,270	1,280	1,260	1,210	1,160
0.0001	0.001	Sr	[0.022]	--	--	--	[0.014]
0.0006	0.006	Ti	0.37	0.25	0.28	0.17	0.13
0.0410	0.410	U	5.40	6.5	8.00	9.10	8.10
0.0027	0.027	Zn	--	--	--	0.56	1.70
0.0014	0.014	Zr	1.40	1.20	1.00	0.68	0.62

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%.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations

BLUE	Process blank failure (>EQL or >5%)
🟩	3*IDL>MRQ and sample concentration >3*IDL
▨	3*IDL>MRQ and sample concentration <3*IDL

Other Analytes							
0.0019	0.019	Ag	--	--	--	--	--
0.0058	0.058	Au	--	--	--	--	--
0.0060	0.060	B	53.60	47.30	35.00	25.40	24.00
0.0001	0.001	Be	0.08	[0.08]	0.08	0.08	0.07
0.0245	0.245	Bi	--	--	--	--	--
0.0103	0.103	Ce	1.10	--	--	--	--
0.0043	0.043	Co	--	.44	[0.58]	--	--
0.0023	0.023	Cu	0.47	0.87	1.00	1.10	1.10
0.0023	0.023	Dy	--	--	--	--	--
0.0006	0.006	Eu	--	--	--	--	--
0.0089	0.089	Ga	3.00	3.00	2.90	2.60	2.50
0.0056	0.056	Hf	--	--	--	--	--
0.0019	0.019	La	--	--	--	--	--
0.0007	0.007	Li	0.14	.11	0.08	0.16	0.12
0.0003	0.003	Lu	--	0.05	--	--	0.04
0.0018	0.018	Mg	0.36	--	--	--	0.43
0.0002	0.002	Mn	0.05	0.04	0.04	0.02	0.02
0.0044	0.044	Mo	30.10	[29.90]	[30.70]	27.70	[27.400]
0.0028	0.028	Nb	--	--	--	--	--
0.0088	0.088	Nd	--	--	--	--	--
0.0054	0.054	Pd	2.10	[2.60]	2.80	2.80	2.20
0.0211	0.211	Rh	[3.10]	[3.00]	2.60	[2.80]	--
0.0063	0.063	Ru	5.30	5.40	5.40	4.70	4.30
0.0598	0.598	Sb	--	7.40	--	--	--
0.0003	0.003	Sc	--	--	--	--	--
0.1656	1.656	Se	--	--	--	--	--
0.0086	0.086	Si	134.0	108.0	82.10	45.00	41.50
0.0091	0.091	Sm	--	--	--	--	--
0.0291	0.291	Sn	4.90	--	5.40	4.50	8.30
0.0246	0.246	Ta	--	--	--	--	--
0.0045	0.045	Tb	--	--	--	--	--
0.0197	0.197	Te	--	--	--	--	--
0.0071	0.071	Th	--	--	0.96	--	--
0.0814	0.814	Tl	--	--	--	--	--
0.0018	0.018	Tm	--	--	--	--	--
0.0013	0.013	V	0.47	0.44	0.51	0.45	0.44
0.0161	0.161	W	55.40	57.10	60.20	55.00	53.20
0.0006	0.006	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%.

na = not applicable; KOH flux and Ni crucible or Na_2O_2 flux and Zr crucible for fusion preparations.

BLUE	Process blank failure (>EQL or >5%)
🟩	3*IDL>MRQ and sample concentration >3*IDL
▨	3*IDL>MRQ and sample concentration <3*IDL

QC Performance 3/17/2022

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	≤ 10%
QC ID >	DUP-0513	LCS/BS	MS-0513	22-0513 + Post Spike	22-0513 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Diff
Al	2.0	103	95	nr	5.2
As		100	98	105	
Ba		102	100	97	
Ca	1.9	104	103	98	
Cd		104	107	98	
Cr	1.5	105	nr	nr	5.4
Fe		101	102	96	
K	1.1	101	110	124	4.5
Na	0.4	102	nr	nr	6.5
Ni	0.1	103	103	96	8.1
P	1.4	105	95	88	
Pb		102	103	105	
S	1.4	99	96	85	9.7
Sr		114	115	103	
Ti			94	98	
U			101	97	
Zn			107	105	
Zr			100	98	

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

Other Analytes					
Ag				148	
Au					
B	3.6	104	101	92	
Be		103	101	97	
Bi		64	66	89	
Ce		96	95	90	
Co				97	
Cu		130	121	110	
Dy				97	
Eu				94	
Ga					
Hf					
La		103	101	97	
Li		109	109	112	
Lu					
Mg		104	102	97	
Mn		103	101	98	
Mo	1.5	98	95	90	5.0
Nb		144	41	90	
Nd		102	100	96	
Pd				89	
Rh				89	
Ru				89	
Sb				100	
Sc					
Se				93	
Si	4.8	39	89	122	
Sm					
Sn				91	
Ta				97	
Tb					
Te				94	
Th		106	104	99	
Tl				83	
Tm					
V			102	93	
W	3.4		29	119	
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.

na = not applicable; KOH flux and Ni crucible or Na2O2 flux and Zr crucible for fusion preparations

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

Project / WP#:	79156 / NK4633	**ASR#:**	1420.00
Client Name:	A. Westesen	**Total Samples:**	7 (Aqueous)

Client Sample Description: Cs Component from AP-101 tank waste supernate

ASO Sample ID	Client Sample ID
22-0512	TI126-COMP-FEED
22-0513	TI126-COMP-EFF
22-0514	TI126-L-F4-A
22-0515	TI126-L-F11-1
22-0516	TI126-L-F15-A
22-0517	TI126-L-F18-A
22-0518	TI126-L-F21-A

Sample Preparation: RPG-CMC-128, Rev. 1. “HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater” using Nitric Acid only, performed by L. Darnell on 03/07/22. Simple dilution of samples in 2% v/v HNO_3 performed by S.S. Morrison on 4/01/22.

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:**	4/12/2022	**ICP File:**	M0324

See Chemical Measurement Center 98620 file: ICP-MS-325-405-1
(Calibration and Maintenance Records)

M&TE:				
	☒	PerkinElmer NexION™ 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: 1113162654	RPL 420 FH
	☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH

Samuel S Morrison
Digitally signed by Samuel S Morrison
Date: 2022.04.28 14:15:31 -07'00'

Report Preparer

Date

Review and Concurrence

04-May-2022
Date

Seven aqueous sample submitted under Analytical Service Request (ASR) 1420.00 was analyzed by ICP-MS. The sample was prepared following RPL procedure RPG-CMC-128, Rev. 1, "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". This process was conducted without the use of HCl. The sample was diluted prior to analysis in 2% HNO_3, the sample was not filtered.

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

Analytes of interest (AOI) were specified in the ASR as Sr, Nb, Ba, Pb, and U listed in the upper section of the attached ICP-MS Data Report. 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 (natural abundance) 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 curves and for initial and continuing calibration verification (ICV/CCV). The data have been corrected from the natural abundance calibration solutions to report total isobaric results (ng/mL) at each m/z.

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 each of Tb-159 and Bi-209 as the internal standard (IS). The AOI data were normalized to the Tb-159 IS and were within the acceptance criterion of 30% to 120% recovery.

Preparation Blank (PB):

A process blank was prepared with this sample and processed through the RPL procedure RPG-CMC-128, Rev. 1, "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". The concentrations of the AOI in the 2% HNO_3 lab diluent blank was within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤5% of the concentration in the samples, with the exception of Sr, and Ba for the process blank BLK-0512, which were greater than EQL and greater than 5% the concentration of the samples. An instrument blank was run on the ICP-MS, for all analytes of interest values were below EQL. For this reason, the Sr and Ba detected in the process blank sample was most likely acquired during the dissolution process.

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

Blank spike samples for AOI were within the acceptance criteria of 80% to 120% recovery.

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

A replicate of sample 22-0014 was analyzed, and the results were within the acceptance criterion of ≤25% for liquid samples.

Matrix-Spike (MS) Sample:

No matrix spike sample was analyzed for this sample set. In lieu of the matrix spike a post spike analysis was performed of each sample.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution (71C) 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 that bracket the reported results were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solutions (2% v/v HNO_3) were analyzed immediately after each respective ICV solution and after each respective CCV solution (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 Ba which was roughly 1.6x-2x EQL and was less than 5% the sample concentrations. The instrument operator's suggestion would be to adjust the EQL to 3x the reported EQL level. The change in the EQL level has no impact on the results reported herein.

Post-Digestion Spike (PS)/Analytical Spike (AS) - Sample (P1 Component):

Instead of a MS sample, post-digestion spike (71A, 71B) was conducted on sample 22-0513. 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. All results were within the acceptance criterion of 75% to 125% recovery.

Low-Level Standard (LLS):

The LLS solution (71A) was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130%. Unfortunately, the autosampler bumped the sampling rack out of alignment prior to the analysis of the 71B LLS solution. The solution was therefore not analyzed in this dataset.

Interference Check Standard (ICS):

The ICS solution (71A, 71B) 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. Unfortunately, the sample rack was bumped prior to the analysis of the initial 71-B ICS solution and the vial was not aligned for sampling for the initial 71B standard. A final 71B standard was analyzed and the recovery for Nb was within the acceptance criteria.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 22-0513. Percent differences (%D) 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 were within the acceptance criterion of ≤10%

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. Analyte included in the spike Hg component is Hg.
5) Isotopic abundances values were obtained from Nuclides and Isotopes: Chart of the Nuclides. 16th Edition, Revised 2002. Ed Baum, Harold Knox, Tom Miller
6) Analytes included in P1 solution are Ag, Cd, In, Mo, Nb, Pd, Rh, Ru, Sn, Zr.

Final Report

		Run Date >	04/12/22	04/12/22	04/12/22	04/12/22	04/12/22	04/12/22	04/12/22	04/12/22
		Process Factor >	1	749	17100; 571	17290; 577	17290; 577	17290; 578	17055; 570	16853; 561
		RPL/LAB >	Blank-8	BLK-0512	22-0512	22-0513	22-0513 Rep	22-0513 DUP	22-0514	22-0515
Instr. Det. Limit (IDL)	**Est. Quant. Limit (EQL)**	**Client ID >**	**2% HNO3 Lab Blank**	**Process Blank**	**TI126-Comp-Feed**	**TI-126-Comp-EFF**	**TI-126-Comp-EFF Rep**	**TI-126-Comp-EFF DUP**	**TI123-L-F4-A**	**TI123-L-F11-A**
(ng/mL)	**(ng/mL)**	**(Analyte)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**
8.46E-04	**8.46E-03**	**Sr**	--	4.00E+01	1.09E+02	3.13E+01	2.94E+01	2.94E+01	3.01E+01	1.81E+01
3.99E-04	**3.99E-03**	**Nb**	--	3.52E-01	1.59E+01	8.45E+02	8.31E+02	8.51E+02	9.49E+02	3.80E+02
5.22E-04	**5.22E-03**	**Ba**	--	3.93E+01	6.13E+01	3.78E+01	3.79E+01	3.85E+01	3.72E+01	3.20E+01
6.07E-03	**6.07E-02**	**Pb**	--	6.98E+01	5.02E+03	2.74E+03	2.69E+03	2.69E+03	2.32E+03	3.10E+03
2.60E-04	**2.60E-03**	**U**	--	6.55E-01	1.04E+04	8.16E+03	7.97E+03	7.99E+03	8.19E+03	5.91E+03

Internal Standard % Recovery

Tb 159 (IS)	98%	98%	98%; 95%	98%; 98%	100%; 98%	100%, 97%	99%; 96%	99%; 90%

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.

Final Report

		Run Date >	04/12/22	04/12/22	04/12/22	04/12/22	04/12/22
		Process Factor >	1	749	16958 ; 564	17267 ; 575	17262 ; 576
		RPL/LAB >	Blank-8	BLK-0512	22-0516	22-0517	22-0518
Instr. Det. Limit (IDL)	**Est. Quant. Limit (EQL)**	**Client ID >**	**2% HNO3 Lab Blank**	**Process Blank**	**TI123-L-F15-A**	**TI126-L-F18-A**	**TI126-L-F21-A**
(ng/mL)	**(ng/mL)**	**(Analyte)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**	**(ng/g)**
8.46E-04	**8.46E-03**	**Sr**	--	4.00E+01	2.99E+01	3.56E+01	4.00E+01
3.99E-04	**3.99E-03**	**Nb**	--	3.52E-01	2.82E+02	1.60E+02	1.23E+02
5.22E-04	**5.22E-03**	**Ba**	--	3.93E+01	2.92E+01	1.10E+02	5.60E+01
6.07E-03	**6.07E-02**	**Pb**	--	6.98E+01	4.16E+03	2.96E+03	3.57E+03
2.60E-04	**2.60E-03**	**U**	--	6.55E-01	1.08E+04	9.33E+03	1.03E+04

Internal Standard % Recovery

Tb 159 (IS)	98%	98%	97% ; 99%	102% ; 100%	99% ; 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 04/12/2022

Criteria >	≤ 35%	≤ 35%	80%-120%	80%-120%	75%-125%	75%-125%	≤ 10%
QC ID >	**Rep 22-00513**	**DUP 22-00513**	**BS71A**	**BS71B**	**22-0513 + CCV71A**	**22-0513 + CCV71B**	**21-1080 (5x) Serial Dil**
Analytes	**RPD (%)**	**RPD (%)**	**%Rec**	**%Rec**	**%Rec**	**%Rec**	**%Diff**
Sr	6%	4%	99%	na	102%	na	nr
Nb	2%	3%	na	109%	na	95%	0%
Ba	0%	4%	101%	na	102%	na	nr
Pb	2%	0%	103%	na	99%	na	2%
U	2%	0%	104%	na	96%	na	1%

Internal Standard % Recovery

Bi 209 (IS)	98%	97%	97%	97%	100%	95%	98%

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.

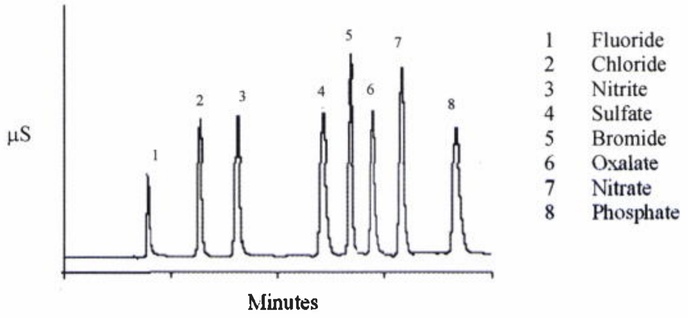
IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

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

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

Common Inorganic Anions

Dionex AS18 Column; Hydroxide Gradient



Client:	A. Westesen	***ASR #:***	1420
Project #:	79156	***# Samples:***	1 Liquid(s)
Charge Code:	NK4633		

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPG-CMC-212 Rev.2, "Determination of Common Anions by Ion Chromatography"
Prep Procedure	None
Analyst	SR Baum
Analysis Dates	03/23/2022
Calibration Date	03/23/2022
Cal/Ver Stds Prep Date	03/23/2022
Excel Data File	IC-0254 ASR-1420 Westesen
M&TE Numbers	IC System (M&TE) WD81129 Balance: B725287790
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0254)

Steven Baum 4-6-22
Prepared By **Date**

David J. Blanchard 5-18-2022
Reviewed By **Date**

IC Report

Sample Results

See Attachment: Sample Results ASR 1420

Sample Analysis/Results Discussion

One liquid sample was submitted to the Analytical Support Operations (ASO) laboratory for ion chromatography analysis under ASR 1420. The results are discussed in this report. The analytes of interest for the sample includes fluoride, chloride, nitrite, nitrate, oxalate, sulphate, and phosphate. All samples were diluted 10,000x and 1,000x prior to analysis. The sample results are reported in µg/mL.

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

Data limitations, if any, for this data set will be determined by the Cognizant Scientist due to the LCS issue as noted in the "Deviations from Procedure" section.

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

IC Workstation QC Results

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

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: The sample was analyzed in duplicate. The relative percent difference (RPD) is reported for all analytes which were measured at or above the EQL. The reported RPDs for analytes meeting this requirement were between 2% - 8%, meeting the ASO's QA Plan acceptance criteria of <20% for liquid samples.

Laboratory Control Sample (LCS): A routine instrument LCS was **not** analyzed (see "Deviations from Procedure" section). Instead, the LCV was substituted for the LCS post-analysis. The LCV had recoveries ranging from 67% to 100%. Sulfate (SO4), Oxalate (OXA), and Phosphate (PO4) had recoveries of 67% which were below the acceptance criteria of 80% to 120%.

Analytical Spike (AS) (Accuracy): Analytical spikes were prepared using all of the prepared dilutions of the one liquid sample by adding a known concentration of a multi-mix standard. The AS recoveries ranged from 83% to 107% meeting the QA Plan acceptance criteria of 75% to 125%.

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed with each run. The 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

Due to a procedural misunderstanding by the analyst an LCS was not analyzed as part of the analysis. Instead, the LCV was substituted for the LCS during data processing (i.e., post-analysis). The under-recovery of the three analytes for the "LCS" analysis is attributed to this change to the usual protocol. Given that all other QC samples met acceptance criteria, the low recoveries observed for the substitute LCV are deemed to not add any uncertainty to the sample results reported.

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

			F			Cl			NO_2			SO_4		
RPL Number	**Client Sample ID**	**Ext. Dil.**	**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**
22-0513 @10000x	TI126-COMP-EFF	1	100	100	U	250	1,700	J	500	43,500		750	3,600	J
22-0513 @1000x	TI126-COMP-EFF	1	10	42	J	25	2,660		50	OvrRng		75	2,540	

			Br			C_2O_4			NO_3			PO_4		
RPL Number	**Client Sample ID**	**Ext. Dil.**	**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**
22-0513 @10000x	TI126-COMP-EFF	1	500	500	U	300	390	J	500	119,000		750	1,100	J
22-0513 @1000x	TI126-COMP-EFF	1	50	50	U	30	210	J	50	OvrRng		75	1,020	

Sample QC Results ASR

Sample/Replicate Precision Results

		F		Cl		NO_2		SO_4		Br		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**	**μg/mL**	**RPD**	**μg/mL**	**RPD**	**μg/mL**	**RPD**
22-0513 @10000x	Sample	U	--	J	--	43,500	--	J	--	U	--	J	--	119,000	--	J	--
	Duplicate | RPD	U	N/A	J	N/A	46,900	7.52	J	N/A	U	N/A	J	N/A	126,000	5.71	J	N/A
22-0513 @1000x	Sample	J	--	2,660	--	OvrRng	--	2,540	--	U	--	J	--	OvrRng	--	1,020	--
	Duplicate | RPD	J	N/A	2,810	5.48	OvrRng	N/A	2,470	2.79	U	N/A	J	N/A	OvrRng	N/A	993	2.68

Sample Spike Results - At IC Workstation

		F		Cl		NO_2		SO_4		Br		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**	**μg/mL**	**%Rec**	**μg/mL**	**%Rec**	**μg/mL**	**%Rec**
22-0513 @10000x	Sample	U	--	1700	--	43500	--	3600	--	U	--	390	--	119000	--	1100	--
	AS Sample	0.762	101.6	2.16	106.1	8.45	109.3	6.07	101.5	3.69	98.4	3.04	100.0	15.9	106.7	5.64	98.3
22-0513 @1000x	Sample	42	--	2660	--	OvrRng	--	2540	--	U	--	210	--	OvrRng	--	1020	--
	AS Sample	0.666	83.2	4.54	100.3	OvrRng	N/A	6.54	71.1	3.75	100.0	3.05	94.7	OvrRng	N/A	6.52	97.8

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**
LCS 032322	HL2 LCV 032322	100	80	80	67	80	67	80	67

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

Appendix D – Batch Contact Results

Table D.1 provides the experimental results used to produce the AP-101 Cs distribution coefficient (K_d) curves and isotherms at four contact temperatures (Figure 4.13 and Figure 4.14 in the body of this report). The dry crystalline silicotitanate (CST) masses were based on F-factor of 0.923 at the 105 °C drying temperature.

Table D.1. AP-101 Tank Waste Isotherm Data

Sample ID	Dry CST Mass (g)	AP-101 Vol. (mL)	Initial Cs Conc. (M)	Equil. Cs Conc. (M)	K_d (mL/g)	Q (mmoles Cs/g)
12.9 °C						
TI127-S1-13	0.0765	14.9000	1.22E-4	1.19E-05	1804	2.14E-02
TI127-S1-13-d	0.0742	14.9211	1.22E-4	1.31E-05	1659	2.18E-02
TI127-S2-13	0.0740	14.8794	3.42E-4	3.42E-05	1810	6.18E-02
TI127-S2-13-d	0.0748	14.8305	3.42E-4	3.42E-05	1787	6.10E-02
TI127-S3-13	0.0755	14.9085	8.76E-4	8.41E-05	1861	1.56E-01
TI127-S3-13-d	0.0762	14.8561	8.76E-4	8.63E-05	1786	1.54E-01
TI127-S4-13	0.0760	14.8432	1.71E-2	1.46E-02	34	4.99E-01
TI127-S4-13-d	0.0771	14.8403	1.71E-2	1.45E-02	35	5.12E-01
15.7 °C						
TI127-S1-16	0.0740	14.9439	1.22E-4	1.62E-05	1316	2.13E-02
TI127-S1-16-d	0.0754	14.9217	1.22E-4	1.55E-05	1358	2.10E-02
TI127-S2-16	0.0738	14.9047	3.42E-4	3.92E-05	1557	6.11E-02
TI127-S2-16-d	0.0749	14.8722	3.42E-4	4.11E-05	1458	5.97E-02
TI127-S3-16	0.0753	14.8363	8.76E-4	1.08E-04	1393	1.51E-01
TI127-S3-16-d	0.0761	14.8648	8.76E-4	1.05E-04	1438	1.51E-01
TI127-S4-16	0.0753	14.8708	1.71E-2	1.49E-02	30	4.48E-01
TI127-S4-16-d	0.0742	14.8439	1.71E-2	1.49E-02	29	4.40E-01
21.7 °C						
TI127-S1-21	0.0761	14.8859	1.22E-4	1.87E-05	1081	2.01E-02
TI127-S1-21-d	0.0759	14.9119	1.22E-4	1.80E-05	1127	2.03E-02
TI127-S2-21	0.0743	14.8123	3.42E-4	4.07E-05	1478	6.00E-02
TI127-S2-21-d	0.0759	14.9042	3.42E-4	4.41E-05	1330	5.85E-02
TI127-S3-21	0.0737	14.8858	8.76E-4	1.16E-04	1323	1.53E-01
TI127-S3-21-d	0.0749	14.9071	8.76E-4	1.10E-04	1390	1.53E-01
TI127-S4-21	0.0740	14.8421	1.71E-2	1.40E-02	44	6.23E-01
TI127-S4-21-d	0.0765	14.8093	1.71E-2	1.39E-02	45	6.31E-01
34.3 °C						
TI127-S1-35	0.0762	15.1177	1.22E-4	3.21E-05	553	1.77E-02
TI127-S1-35-d	0.0759	13.2053	1.22E-4	2.86E-05	566	1.62E-02
TI127-S2-35	0.0756	15.1090	3.42E-4	8.07E-05	646	5.22E-02
TI127-S2-35-d	0.0744	15.0363	3.42E-4	8.16E-05	643	5.26E-02
TI127-S3-35	0.0756	15.1143	8.76E-4	2.11E-04	627	1.33E-01
TI127-S3-35-d	0.0742	13.2267	8.76E-4	1.92E-04	638	1.22E-01
TI127-S4-35	0.0752	15.0879	1.71E-2	1.40E-02	45	6.26E-01
TI127-S4-35-d	0.0742	14.8866	1.71E-2	1.44E-02	38	5.53E-01

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