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Characterization of CST Post-Processing AP-105 Hanford Tank Waste

September 2021

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Prepared for
the U.S. Department of Energy
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Summary

The primary goal of the Tank Side Cesium Removal (TSCR) system, under development by Washington River Protection Solutions, LLC (WRPS), is to remove entrained solids and ^{137}Cs from the Hanford tank waste supernate to expedite production of low-activity waste. Ion exchange (IX) testing of 10.9 L of waste from Hanford tank 241-AP-105 (AP-105), performed by Pacific Northwest National Laboratory, used a lead-lag-polish column format, with a bed volume of 10 mL per column, to decontaminate tank waste supernate using crystalline silicotitanate (CST) as the IX media.¹

The AP-105 Cs IX processing test, discussed elsewhere, resulted in a shorter transition zone (i.e., steeper load curve) than those defined by wastes from tanks 241-AP-107 and 241-AW-102.¹ The shorter transition zone was indicative of a matrix effect retarding Cs capacity. Therefore, aliquots of spent CST from the lead, lag, and polish columns were subjected to a digestion protocol to quantify analytes retained by the CST and extrapolate the impact on Cs capacity. The spent CST was digested using a combination of 5 M HNO_3 and H_2O_2 with vigorous heating and stirring. Due to the radiation dose accompanying the ^{137}Cs on the CST columns, a secondary Cs separation by ammonium molybdophosphate embedded in polyacrylonitrile (AMP-PAN) was performed to separate the ^{137}Cs from the CST so the samples could be contact-handled for analysis outside of a shielded facility.

A summary of the inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) results is shown in Table S.1, reporting selected analytes retained by the CST. Resource Conservation and Recovery Act hazardous metals, including Ba and Pb, were retained by the spent CST. Additionally, it was observed that the transition metals that likely occur in the tank waste as divalent ions, including Cd, Ca, Pb, Sr, and potentially Fe, are retained by the CST by IX and/or other mechanisms (e.g., precipitation/filtration by the CST bed). The loading of these analytes decreased from the lead to lag to polish column, with the highest concentration found on the lead column. The same phenomenon was not observed for K, which was the second-most prevalent analyte retained by CST, behind Ca. The K loaded uniformly across the three columns.

Small amounts of Al were quantified in the CST digestate solutions. The mechanism of Al retention is likely due to formation of the zeolitic aluminosilicates on the surface of CST. The spent CST also retained a portion of the uranium from the IX feed.

Compositional integrity of the CST was assessed by calculating the recovery of the main CST components (Ti, Nb, and Zr) quantified in spent CST compared to the initial concentrations reported for pre-treated CST. No discernable leaching of CST components was observed in AP-105 effluent, which was validated by the quantitative recovery of the CST components in the digested CST from AP-105 processing.

¹ Fiskum SK, AM Westesen, AM Carney, TT Trang-Le, and RA Peterson. 2021. *Ion Exchange Processing of AP-105 Hanford Tank Waste through Crystalline Silicotitanate in a Staged 2- then 3-Column System*. PNNL-30712, Rev. 0; RPT-DFTP-025, Rev. 0. Pacific Northwest National Laboratory, Richland, Washington.

Table S.1. Chemical Composition (mmol/g dry CST) of Spent CST Post-Processing AP-105 Hanford tank Waste

Analysis Method	AP-105-1 (lead)					AP-105-2 (lag)	AP-105-3 (polish)
	Analyte	Primary	Duplicate	Average	RPD	Primary	Primary
ICP-OES	Al	0.056	0.051	0.053	7%	0.052	0.050
	Ba	0.003	0.003	0.003	1%	0.001	0.000
	Ca	0.215	0.206	0.211	3%	0.195	0.163
	Cd	[5.2E-04]	[4.4E-04]	[4.8E-04]	NA	[3.5E-04]	[3.9E-04]
	Fe	0.015	0.015	0.015	1%	0.011	0.008
	K	0.148	0.141	0.145	3%	0.146	0.145
	Na	4.21	4.05	4.13	3%	4.32	4.44
	Nb	1.45	1.40	1.42	2%	1.41	1.42
	Ni	[0.001]	[0.001]	[0.001]	NA	[0.001]	[0.001]
	Pb	0.027	0.026	0.027	3%	0.023	0.020
	Si	1.81	0.833	1.32	52%	1.81	1.91
	Sr	1.89E-03	2.12E-03	2.00E-03	8%	2.91E-04	5.91E-05
	Ti	3.70	3.58	3.64	2%	3.63	3.68
	Zr	1.15	1.11	1.13	2%	1.15	1.17
ICP-MS	Sr	2.07E-03	5.21E-03	3.64E-03	61%	4.03E-04	2.37E-04
	Ba	8.26E-04	6.44E-04	7.35E-04	17%	4.92E-04	3.78E-04
	Pb	2.56E-02	2.11E-02	2.33E-02	14%	2.16E-02	1.79E-02
	U	3.01E-03	3.10E-03	3.05E-03	2%	3.01E-03	2.42E-03
Dry Mass CST, g		9.42				9.92	9.77

Values in brackets [] were $\geq$ the method detection limit but $<$ the estimated quantitation limit, with errors likely to exceed 15%.

Italicized values indicate a relative percent difference (RPD) $>15\%$ between duplicate samples of the AP-105 lead column.

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Acronyms and Abbreviations

AMP-PAN	ammonium molybdophosphate embedded in polyacrylonitrile
ASO	Analytical Support Operations
ASR	Analytical Service Request
CST	crystalline silicotitanate
DIW	deionized water
EQL	estimated quantitation limit
ICP-OES	inductively coupled plasma optical emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
IX	ion exchange
MDL	method detection limit
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
QA	quality assurance
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
SAL	Shielded Analytical Laboratory
TSCR	Tank Side Cesium Removal
WRPS	Washington River Protection Solutions, LLC
WWFTP	WRPS Waste Form Testing Program
ZAM	Zheng-Anthony-Miller (model)

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1.0 Introduction

The primary goal of the Tank Side Cesium Removal (TSCR) system, under development by Washington River Protection Solutions LLC (WRPS), is to remove entrained solids and ^{137}Cs from the Hanford tank waste supernate to expedite production of low-activity waste. Pacific Northwest National Laboratory (PNNL) has been tasked with laboratory-scale demonstration of the filtration and subsequent ion exchange (IX) processes toward this goal. Crystalline silicotitanate (CST), product UOP-IONSIV™ R9140-B, manufactured by Honeywell UOP, LLC (Des Plaines, IL) has been selected to support the TSCR pretreatment flowsheet for Cs removal from tank waste supernatant. To date, PNNL has processed supernate from tanks 241-AP-107, 241-AW-102, and 241-AP-105 (hereafter AP-107, AW-102, and AP-105) with CST media to understand bounding processing conditions ranging from particle size to temperature impacts on Cs removal (Westesen et al. 2021; Rovira et al. 2019; Fiskum et al. 2021). Two process flow designs have been tested: (1) a lead-lag column format executed for AP-107 and AW-102 IX processing and (2) a lead-lag-polish column format, which was tested on AP-105. The lead-lag-polish column format boasted 81% Cs load capacity on the lead column, which was significantly greater than the ~52% Cs capacity on the lead column in a two-stage format with AP-107 and AW-102 processing (Fiskum et al. 2021).

Characterization of spent CST following IX processing of Hanford tank wastes from AW-102 and AP-107 was conducted using a two-step digestion/separation protocol (Campbell et al. 2019). The authors found measurable retention of Ba, Ca, Cd, Fe, Pb, Sr, U, Np, and Pu on the CST. The uptake of these analytes was thought to impact Cs uptake. Later batch contact testing indicated high selectivity and uptake capacities of Ca, Pb, Ba, and Sr, but the presence of these analytes, apart from Ba, had limited to no effect on Cs exchange capacity (Campbell et al. 2020b).

Testing with diluted feed from Hanford tank AP-105 incorporated a nuanced change to the lead-lag-polish column system where the polish column was inserted when the lag column effluent reached the waste acceptance criteria limit² for ^{137}Cs . A 10.9-L volume of AP-105 (diluted with Columbia River water to 5.6 M Na) was processed through the Direct Feed Test Platform system, established at PNNL. The columns consisted of 10-mL CST beds (CST Lot 2002009604, sieved to screen out >30-mesh particles) placed in 1.5-cm-inner-diameter IX columns. Feed was processed at 1.83 bed volumes per hour; the flowrate, in terms of contact time with the CST bed, matched the expected flowrate of the full-size TSCR system. The <30-mesh CST sieve cut was expected to provide appropriate performance scaling to a full-height column. (Fiskum et al. 2019, 2021).

Analytical characterization of the feed and effluent from AP-105 was previously reported (Fiskum et al. 2021) and is reproduced in Table 1.1. Partitioning of Pb, a Resource Conservation and Recovery Act (RCRA) metal, toward CST was evident, as indicated by the 29% recovery of Pb in the effluent (i.e., most was retained on the CST). Assessment of Ba, Fe, and Cd was not achieved due to limitations with the detection limit of the method in correlation to the complexity of the tank waste matrix. Feed and effluent results indicated quantitative removal of Sr from the feed, which had been observed post-processing AP-107 and AW-102 tank waste as well (Westesen et al. 2021; Rovira et al. 2019; Campbell et al. 2020a). Radionuclides, including ^{237}Np , ^{238}U , ^{90}Sr , and several isotopes of Pu, also partitioned to the CST to some extent.

² 24590-WTP-ICD-MG-01-030, Rev. 0. 2015. *ICD 30 – Interface Control Document for Direct LAW Feed*. Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

Table 1.1. Analyte Concentrations in AP-105 Feed in Comparison to Select Analyte Recoveries in AP-105 Effluent

	Analyte	Feed	Effluent	Fraction in Effluent
		Concentration (M)	Concentration (M)	
Metals / Nonmetals	Al	5.26E-01	5.23E-01	99%
	As	<5.5E-04	[9.7E-04]	--
	Ba	<1.06E-06	<1.3E-06	--
	Ca	1.03E-03	1.02E-03	99%
	Cd	[2.4E-05]	[2.0E-05]	--
	Cr	6.43E-03	6.56E-03	101%
	Fe	[2.0E-05]	<1.6E-05	--
	K	1.02E-01	1.02E-01	100%
	Na	5.92E+00	6.00E+00	101%
	Nb	2.74E-07	2.89E-05	NA
	P	1.27E-02	1.44E-02	113%
	Pb	9.00E-05	2.67E-05	29%
	S	4.66E-02	4.65E-02	99%
	Sr	1.82E-06	1.64E-07	9%
	Ti	<5.9E-06	[2.3E-05]	NA
	U	2.46E-05	1.99E-05	80%
	Zn	[4.6E-05]	[4.7E-05]	--
	Zr	<9.4E-06	[4.5E-05]	NA
	Analyte	Feed	Effluent	Fraction in Effluent
		Concentration (μCi/mL)	Concentration (μCi/mL)	
Radionuclides ^(a)	⁹⁰ Sr	6.90E-01	7.23E-04	0.10%
	⁹⁹ Tc	1.13E-01	1.05E-01	93%
	¹³⁷ Cs	1.13E+02	5.36E-02	0.047%
	²³⁷ Np	6.69E-06	1.22E-06	18%
	²³⁸ Pu	6.37E-06	2.64E-06	41%
	²³⁹⁺²⁴⁰ Pu	3.94E-05	1.56E-05	39%
	²⁴¹ Am	2.66E-04	2.30E-04	86%

(a) Reference date is December 2020.

Notes:

“<” values were < method detection limit (MDL).

“--” indicates effluent recovery could/should not be calculated; feed and/or effluent result was < estimated quantitation limit (EQL).

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

NA = not applicable; analytes are CST components.

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.

The AP-105 Cs IX processing test resulted in a shorter transition zone (i.e., steeper load curve) than those defined by AP-107 and AW-102 (Fiskum et al. 2021). The shorter transition zone was indicative of a matrix effect retarding Cs capacity. Therefore, an examination of the post-processed CST was warranted to try to understand if other tank waste components present in AP-105 tank waste had consumed Cs exchange sites. A general understanding of matrix impacts on Cs IX performance will help the execution of Cs exchange at the TSCR platform. In addition, assessment of the capacity of the IX media for alternative metals will help define potential alternative disposition pathways.

The direct analytical characterization of the Cs-loaded CST digestate is not feasible due to the high dilution required to reduce ^{137}Cs radiation dose (for personnel safety), which would in turn bring concentrations of the retained tank waste constituents below analytical detection limits. The analytical method developed for the selective removal of Cs from the digested CST (Campbell et al. 2019) was applied.

The objectives of the work described in this report were as follows:

1. Following the previously developed method, digest subsamples of CST that had been used for processing of AP-105 tank waste supernate.
2. Separate Cs from the digestates following the developed method.
3. Quantify concentrations of Ba, Ca, Cd, Fe, Ni, Pb, Sr, and U on CST processed with AP-105 tank waste supernate.
4. Compare analyte loading with previously tested CST from AP-107 and AW-102 waste processing (Campbell et al. 2019).

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 Experimental

The acid digestion and Cs separation protocol developed in 2019 by Campbell et al. was implemented for spent CST post-processing AP-105 Hanford tank waste. The goal of this method is to minimize sample dilution and eliminate the high radiation dose from ^{137}Cs to enable analytical determination of analytes retained by CST. Processing and characterization of the spent CST is depicted in Figure 3.1. The analytical method is composed of three major steps: (1) digestion of CST in 5 M HNO_3 + 3% H_2O_2 , (2) separation of Cs using ammonium molybdophosphate embedded in polyacrylonitrile (AMP-PAN) IX resin, and (3) analytical characterization of the Cs-depleted aqueous fraction by inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

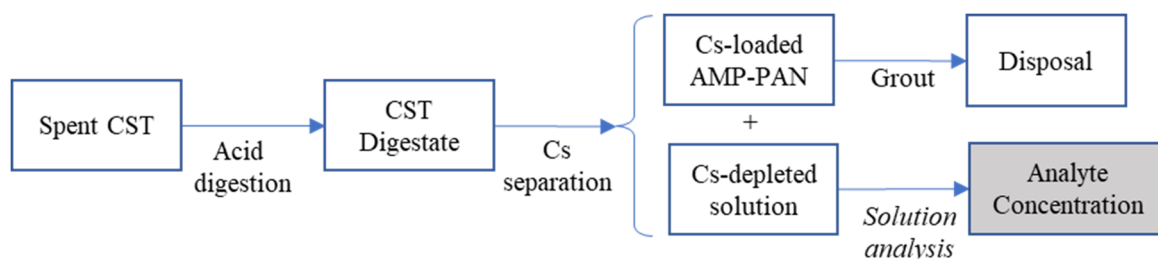


Figure 3.1. Schematic of the Analytical Method for Determination of CST Loading Characteristics

Targeted analytes included Ba, Ca, Cd, Fe, Ni, Pb, Sr, and U to compare with previous CST loading results. CST compositional materials Na, Nb, Si, Ti, and Zr were measured to assess effects on chemical integrity of the CST as a result of tank waste processing. A matrix spike was included to assess matrix effects of the digestion solution on quantification of select analytes.

3.1 CST Media

CST is manufactured by Honeywell UOP, LLC as IONSIV™. WRPS purchased CST product R9140-B,³ 18 × 50 mesh, lot number 2002009604. PNNL received a sample from WRPS on September 20, 2018, for testing. Delivery and initial subsampling were described previously (Fiskum et al. 2019).

A 34.5-g aliquot of the as-received, full particle size distribution (PSD) CST was collected and rinsed with ~100 mL of 0.1 M NaOH three times to remove colloidal fines. The CST was then rinsed once with 80 mL of deionized water (DIW) to remove the salt solution. The rinsed CST was set aside to dry at ambient temperature (~20 °C) for 13 days, at which point it essentially reached constant mass. Before subsampling, the CST was mixed by hand-tumbling the container.

The spent CST media from AP-105 processing was stored for nearly 8 months in three stainless-steel “thimbles,” labeled AP-105-1, AP-105-2, and AP-105-3, corresponding to the lead, lag, and polish columns, respectively. The total masses of free-flowing, air-dried CST for AP-105-1, AP-105-2, and AP-105-3 were 10.0201, 10.2845, and 10.3823 g, respectively.

³ Product R9140-B is provided in the sodium form and did not require conversion from the hydrogen form to the sodium form prior to testing.

Each stainless-steel “thimble” was opened and inspected prior to aliquoting. The CST from all columns was free-flowing and free of agglomeration. The CST was gently swirled to mix the contents prior to F-factor measurements.

3.1.1 CST F-factor

The F-factor (dry CST mass per sampled CST mass) was determined for the uncontacted (blank) CST after heating at ~105 °C. CST of full PSD, rinsed with 0.1 M NaOH, was used as a blank in the digestion experiments. A small aliquot of the CST was placed into each of two tared glass vials, which were then placed into an Isotemp oven (Fisher Scientific Model 280A) set to 105 °C. The vials were periodically removed from the oven, allowed to cool, then capped and the gross masses were measured. The net CST masses were calculated. Typically, mass measures were collected every 4 to 12 hours until the mass changes were <1% between successive drying-weighing events. The F-factors for this duplicate pair (0.9129 and 0.9094) averaged 0.9111 with a relative percent difference of 0.39%.

The F-factors of the spent CST were measured in the Shielded Analytical Laboratory (SAL) hot cells in PNNL’s Radiochemical Processing Laboratory using a compact oven (Thermo Scientific Model 3511); values are shown in Table 3.1. A 0.8-g aliquot of AP-105-1 CST (from the lead column) was transferred from the stainless-steel “thimble” to a tared 40-mL glass vial and the mass of CST was measured. Additionally, 0.6-g aliquots of AP-105-2 (from the lag column) and AP-105-3 (from the polish column) CST were transferred to tared 40-mL glass vials and the gross masses were recorded. The three spent CST F-factor samples were placed in the oven set to 105 °C. The vials were removed from the oven after 4 hours and the gross masses were measured. The vials were heated another ~18 hours and reweighed. The net CST masses were calculated, and the mass changes for all three CST samples were <1%. The dried CST aliquots were used for digestion.

The dry mass basis of the CST recovered from the columns was calculated using the F-factors from the lead, lag, and polish columns in Table 3.1. The masses of free-flowing, air-dried CST were multiplied by the F-factor to get dry masses of 9.42, 9.92, and 9.77 g for lead, lag, and polish columns, respectively.

Table 3.1. F-factors of CST from Lot 2002009604 and Post-processing AP-105 Hanford Tank Waste

Sample Description	F-factor
Full PSD, rinsed with 0.1 M NaOH	0.9111
Lead column (AP-105-1)	0.9400
Lag column (AP-105-2)	0.9648
Polish column (AP-105-3)	0.9411

3.2 Digestion of CST from AP-105 Processing

Precisely weighed aliquots (targeting 0.3 g) of dried CST from the F-factor vials were transferred to pre-weighed 40-mL glass vials containing a stir bar. The lead column CST, from AP-105-1, was digested in duplicate. Digestion of spent CST was accomplished by transferring 25 mL of 5 M HNO₃ to the glass vial and placing it on a stir plate/hot plate with the vial loosely capped. The stir speed was adjusted to medium with the heat set to “high.” Heating and stirring of the slurry continued until the liquid turned a milky white color and was on the verge of boiling. At this point, the vials were removed from the hot plate and 2.5 mL of H₂O₂ was added. Immediately upon addition of H₂O₂, the liquid turned a deep red color, due to formation of the Ti(IV)•hydrogen peroxide complexes (Kuchmii et al. 1988), and bubbles were observed rising from the bottom of the vial. The temperature dial of the hot plate was turned off and the digestate solution was placed back on the hot plate/stir plate with vigorous stirring for ~15 minutes. The vial was

removed from stirring, gently swirled, and inspected for complete dissolution of the CST media. After at least 10 minutes of cooling, the post-digestion mass was recorded.

In addition, two ~0.3-g aliquots (primary and duplicate) of CST (lot 2002009604), pre-treated with 0.1 M NaOH, and a process blank, underwent the same digestion protocol. The CST blanks served as a control with previously reported digestion data for this lot of CST and the process blank was necessary to assess any cross-contamination in the hot cell.

3.3 Cs Removal Using AMP-PAN

Outside of SAL, aliquots of nominally 0.6 g of AMP-PAN resin (TRISKEM International, lot FHCM180523) were measured into seven 50-mL centrifuge tubes. A volumetric pipet was used to deliver 20 mL of DIW to each centrifuge tube and the gross mass was recorded. Optimum performance of AMP-PAN for Cs removal was observed from an aqueous phase of ~1 M HNO₃; thus, the DIW was added to the AMP-PAN to dilute the ~5 M HNO₃ digestate solution (Todd et al. 2002).

The centrifuge tubes were transferred to SAL where 5.0 mL of the CST digestion solution was pipetted to the appropriate AMP-PAN centrifuge tube. The gross masses were recorded, and the centrifuge tubes were secured to a RotoFlex Plus end-over-end rotary device (Argos Technologies, Inc., Vernon Hills, IL). AMP-PAN contacts were rotated at 30 rpm for ~2 hours under ambient temperature (29 °C.)

The AMP-PAN in the samples was allowed to settle and then the supernate was filtered using an acid-washed 0.7-µm pore size polypropylene filter. The diluted, Cs-removed CST digestion solutions were removed from the hot cell and the mass of 1 mL of each solution was measured in duplicate. The mass per unit volume was used to calculate the analyte loading per gram of dry CST from the ICP-OES and ICP-MS mass/volume results.

3.4 Matrix Spike

A matrix spike with target analytes was prepared to evaluate the effect of the CST digestion matrices on ICP-OES and ICP-MS analysis. The nitrate salts of Ba, Sr, Pb, Ca, Fe, and Ni were measured and combined into a 25-mL volumetric flask as defined in Table 3.2. The metal salts were dissolved in ~15 mL of DIW and 0.5 mL of concentrated HNO₃ was added. The volumetric flask was diluted to the line with DIW, which resulted in a 2% (v/v) HNO₃ matrix. A 200-µL aliquot of the metal salt stock solution was pipetted into a 10-mL volumetric flask and diluted to the line with the pre-treated CST digestate solution (primary blank).

Table 3.2. Preparation of Metal Salt Stock Solution for Matrix Spike

Compound	Target Metal Concentration (µg/mL)	Salt Mass Added (g)
Ba(NO ₃) ₂	2500	0.0624
Sr(NO ₃) ₂	750	0.0198
Pb(NO ₃) ₂	45,000	1.1258
Ca(NO ₃) ₂ ·4H ₂ O	45,000	1.1230
Fe(NO ₃) ₃ ·9H ₂ O	8,750	0.2179
Ni(NO ₃) ₂ ·6H ₂ O	750	0.0204

4.0 Results

Analyte concentrations were obtained by both ICP-OES and ICP-MS analysis. The composition of analyte, C_{CSTa} in mmol/g for all digestion solutions was calculated using the following equation:

$$C_{CSTa} = \frac{(C_{Da} \times D) \times m_d}{d \times m_{CST} \times FW} \quad (4.1)$$

where:

- D = dilution factor (diluted digestate (g)/digestate (g))
- C_{Da} = concentration of analyte *a* in the digestate solution
- m_d = mass of digestate solution
- d = density of the diluted digestate solution (g/mL)
- m_{CST} = dry mass of CST digested
- FW = formula weight

4.1 Verification of Analysis Method

Results from the matrix spike analysis are shown in Table 4.1 for the selected analytes. The target concentration, in $\mu\text{g/mL}$, is that predicted from mass measurements made during dissolution of metal salts and subsequent dilution in the CST digestate solution. The measured concentration refers to the concentration reported by ICP-OES analysis for that sample. The percent recovery for all analytes of interest are 11% to 35% high, but within analytical error for all but Sr. The Sr value is biased high for the recovery in the matrix, but overall the matrix spike verified that the analysis method was suitable for a matrix with high Si, Ti, and Nb components.

Table 4.1. Recovery of Select Analytes in CST Digestate

Compound	Target Concentration ($\mu\text{g/mL}$)	Measured Concentration ($\mu\text{g/mL}$)	% recovery
Ba(NO ₃) ₂	49.92	29.3	112%
Sr(NO ₃) ₂	15.84	8.89	135%
Pb(NO ₃) ₂	900.6	624	111%
Ca(NO ₃) ₂ ·4H ₂ O	898.4	171	112%
Fe(NO ₃) ₃ ·9H ₂ O	174.3	27.7	115%
Ni(NO ₃) ₂ ·6H ₂ O	16.32	3.84	117%

4.2 Chemical Composition of CST

Analytical results for the digestion of CST from lot 2002009604, full particle size, and rinsed with 0.1 M NaOH are shown in Table 4.2.

Table 4.2. Chemical Composition (mmol/g of dry CST) of Full Particle Size CST after Pretreatment with 0.1 M NaOH

Analysis Method	Analyte	Blank	Blank-duplicate	Average	RPD
ICP-OES	Al	[0.022]	[0.018]	[0.020]	--
	Ca	0.096	0.100	0.098	3%
	Cd	--	--	ND	--
	Fe	0.003	0.003	0.003	5%
	K	--	--	ND	--
	Na	4.93	4.91	4.92	0%
	Nb	1.46	1.47	1.46	1%
	Ni	--	--	ND	--
	Pb	--	--	ND	--
	Si	1.28	1.97	1.62	30%
	Sr	8.0E-05	7.2E-05	7.6E-05	8%
	Ti	3.73	3.76	3.75	1%
ICP-MS	Zr	1.18	1.21	1.19	2%
	Sr	2.56E-04	2.47E-04	2.51E-04	3%
	Ba	5.57E-04	5.08E-04	5.33E-04	6%
	Pb	[4.2E-06]	[4.5E-06]	[4.4E-06]	--
	U	[9E-07]	2.E-06	1.5E-06	53%

Values in brackets [] were $\geq$ MDL but $<$ EQL, with errors likely to exceed 15%.
"--" and ND = not detected.

The Nb content in the full particle size CST (lot 2002009604), rinsed with 0.1 M NaOH, was 13.6 wt%. This is in agreement with the Nb content of 12.5 wt% previously reported for lot 2002009604 by Campbell et al. (2020a). The Ti content of 17.9 wt% was identical to that quantified previously (Campbell et al. 2020a). The Ti:Nb ratio was calculated to be 2.6. Increasing Nb content and decreasing the Ti:Nb molar ratio correlates with enhanced selectivity of the CST for Cs (Tripathi et al. 2003).

The Na concentration, or theoretical IX capacity, on the pretreated CST was calculated to be 4.92 mmol/gram on average, which is slightly higher than the reported value (Zheng et al. 1996; Walker Jr. et al. 1998). Ca is the only other analyte present in sufficient quantity that does not exist in the CST framework. Initially suspected as a competitor for Cs exchange, recent studies have shown that Ca does not impact Cs uptake in a caustic matrix (Campbell et al. 2020b).

4.3 Characterization of CST Post-Processing Actual Tank Waste from AP-105

Concentrations of analytes retained by CST post-processing of AP-105 Hanford tank waste are shown in Table 4.3. At the conclusion of IX processing, the spent CST from the three columns underwent feed displacement, followed by a water rinse, and were then dried to free-flowing with compressed air prior to transfer into stainless steel "thimbles." The mass of the "thimbles" was recorded before and after spent CST was transferred; therefore, the net mass of CST for each container was calculated. The total masses of free-flowing, air-dried CST for AP-105-1, AP-105-2, and AP-105-3 were 10.0201, 10.2845, and 10.3823 g, respectively.

Table 4.3. Chemical Composition (mmol/g dry CST) of Spent CST Post-Processing AP-105 Hanford Tank Waste

CST Source →		AP-105-1 (lead)				AP-105-2 (lag)	AP-105-3 (polish)
Analysis Method	Analyte	Primary	Duplicate	Average	RPD	Primary	Primary
ICP-OES	Al	0.056	0.051	0.053	7%	0.052	0.050
	Ca	0.215	0.206	0.211	3%	0.195	0.163
	Cd	[5.2E-04]	[4.4E-04]	[4.8E-04]	NA	[3.5E-04]	[3.9E-04]
	Fe	0.015	0.015	0.015	1%	0.011	0.008
	K	0.148	0.141	0.145	3%	0.146	0.145
	Na	4.21	4.05	4.13	3%	4.32	4.44
	Nb	1.45	1.40	1.42	2%	1.41	1.42
	Ni	[0.001]	[0.001]	[0.001]	NA	[0.001]	[0.001]
	Pb	0.027	0.026	0.027	3%	0.023	0.020
	Si	1.81	0.833	1.32	52%	1.81	1.91
	Sr	1.89E-03	2.12E-03	2.00E-03	8%	2.91E-04	5.91E-05
	Ti	3.70	3.58	3.64	2%	3.63	3.68
	Zr	1.15	1.11	1.13	2%	1.15	1.17
ICP-MS	Sr	2.07E-03	5.21E-03	3.64E-03	61%	4.03E-04	2.37E-04
	Ba	8.26E-04	6.44E-04	7.35E-04	17%	4.92E-04	3.78E-04
	Pb	2.56E-02	2.11E-02	2.33E-02	14%	2.16E-02	1.79E-02
	U	3.01E-03	3.10E-03	3.05E-03	2%	3.01E-03	2.42E-03
Dry Mass CST, g		9.42				9.92	9.77

Values in brackets [] were $\geq$ the MDL but $<$ the EQL, with errors likely to exceed 15%.

Italicized values indicate a relative percent difference (RPD) $>15\%$ between duplicate samples of the AP-105 lead column.

Compositional integrity of the CST can be assessed by calculating the recovery of the main CST components (Ti, Nb, and Zr) quantified in spent CST compared to the initial concentrations reported for pretreated CST. Si is reported in Table 4.3; however, it was excluded from recovery due to potentially biased Si results from digestion in glass. The recovery of each component, as shown in Table 4.4 for the three columns, is simply a ratio of concentrations in Table 4.3 vs. Table 4.2 for the corresponding analytes. Contrary to previous digestion results (Campbell et al. 2020a), there does not appear to have been any leaching of CST components during AP-105 IX testing, as indicated by the near-quantitative recovery for the CST framework.

Table 4.4. Recoveries of Select CST Components in AP-105 Spent CST

Analyte	AP-105-1	AP-105-2	AP-105-3
Ti	99%	95%	97%
Nb	99%	95%	96%
Zr	96%	93%	97%

Aside from the main components of CST (Si, Ti, Nb, and Zr), analytes in the feed co-retained with Cs on the CST include Al, Ba, Ca, Fe, K, Pb, Sr, and U. The Al distribution was uniform across all three columns, and the likely mechanism of Al retention is formation of the zeolitic aluminosilicates such as cancrinite on the CST surface (Taylor and Mattus 2001). Ca, the analyte with the highest molar retention by CST, loaded most heavily on the lead column and steadily decreased to the polish column. The lead column contained 0.211 mmol Ca/g dry CST, which decreased to 0.163 mmol Ca/g dry CST on the polish column. As described in the documents cited in the next sentence, extensive batch contact testing has been conducted with Ca in a caustic matrix to investigate competition with Cs and the results indicate

that CST is highly selective for Ca; however, Cs uptake is not heavily impacted by the presence of Ca. One hypothesis is that Ca forms wollastonite, CaSiO_3 (Rashid et al. 2014), CaTiO_3 (Ueda et al. 1999), and/or CaTiSiO_5 (Speer and Gibbs 1976) when contacted with CST.

Fe and Pb were also found on the spent CST. The Pb concentration on the lead column was 0.027 mmoles/g and decreased incrementally from lag to polish at 0.023 to 0.020 mmoles Pb/g dry CST. A similar observation was made for Fe partitioning, where nominally 0.015 mmoles/g was quantified on the lead column, followed by 0.011 mmoles/g and 0.008 mmoles/g on the lag and polish columns, respectively. This trend indicates the mechanism for uptake may be similar to that of Cs and is in agreement with Pb results previously reported with the same lot of CST for AW-102 tank waste testing (Campbell et al. 2019).

Interestingly, K was more uniformly distributed on the CST, with nominally 0.145 mmoles K/g dry CST quantified on all three columns. Of all the analytes reported, K was the only analyte of interest observed to follow this behavior. This may be indicative of a different mechanism by which K is partitioning to the CST. There is very limited data available in the literature regarding K exchange with CST; however, from this data, K uptake does not appear to follow Cs loading.

The total mass balance of select analytes is presented in Table 4.5. The contributions of analytes inherent to CST were calculated by multiplying the analyte concentration (mmol/g) in conditioned CST (Table 4.3) by the total dry mass (30 g) of CST loaded in the three columns. To calculate the analyte contribution on spent CST, the concentration of analyte (mmoles/g in Table 4.4) was multiplied by the dry CST mass of the corresponding column (10 g each column). The mmole analyte sum from the three columns was thus the total analyte loaded on CST, which should make up the difference between the feed and effluent concentrations.

Table 4.5. Mass Balance of Select Analytes Partitioned to the Feed, Effluent, and CST from AP-105 Waste Processing

Analyte	AP-105 IX Feed (mmoles)	Analyte Intrinsic to 30 g CST (mmoles)	AP-105 Effluent (mmoles)	Analyte Loaded on 30 g CST (mmoles)	Fraction in Effluent	Mass Balance
Al	5.76E+03	0.601	5.70E+03	1.51	99%	99%
Ba	[0.053]	0.016	[0.014]	0.02	--	43%
Ca	11.2	2.94	11.2	5.52	99%	118%
Cd	[0.26]	--	[0.22]	0.01	--	91%
Fe	[0.22]	0.092	<0.17 ^(a)	0.33	--	163%
K	1.11E+03	--	1.11E+03	4.23	100%	100%
Pb	0.985	--	0.291	0.68	29%	98%
Sr	0.0200	0.002	0.0018	0.02	9%	108%
U	0.269	--	0.217	0.08	80%	111%

(a) Value <MDL, so MDL was used as the bounding value.

Values in brackets [] were $\geq$ MDL but < EQL, with errors likely to exceed 15%.

Bolded, italicized values represent analysis by ICP-MS.

The three analytes with the lowest detectable fraction in the effluent were Pb, Sr, and U. When assessing the total analyte fractionation between the feed, effluent, and CST, there is near-complete mass balance for these analytes. While Sr is quantitatively removed by the CST, digestion of the spent CST confirms

that the Sr partitions to the CST. Additionally, nearly all the Pb is accounted for when the concentration of Pb portioned to the CST is combined with the small amount that travels through the column into the effluent. Initially, Pb was a concern due to RCRA environmental regulations and potential competition for Cs exchange sites. Both have been further investigated, and a Toxicity Characteristic Leaching Procedure (EPA 1992) test on spent CST from AW-102 and AP-107 showed that RCRA metal leaching was less than the regulatory levels (Campbell et al. 2020a). Additionally, a series of batch contacts with Pb alone and in combination with Cs did not show competitive interference with Cs exchange, even at high Pb loading (Campbell et al. 2020b).

A comparison of analyte loading on the lead columns from AP-107, AW-102, and AP-105 is shown in Table 4.6. Note that AP-107 did use a different lot of CST, 2081000057, and inconsistencies in the manufacturing and subsequent performance of CST from lot to lot has been observed in the past (Pease et al. 2019; Campbell et al. 2020a). The concentration of Al was the highest for AP-107 processing. The concentration of Ca found on CST that had processed AP-105 waste was the highest for the three tanks studied; this may be a direct correlation to the highest Ca concentration in AP-105 feed as compared to the other two tanks. Batch contact studies with Ca-loaded CST confirmed that the presence of Ca on CST had no effect on Cs exchange capacity at nominally 7.5×10^{-4} M equilibrium Cs in a 1.0 M NaOH/4.6 M NaNO₃ simulant (Fiskum et al. 2020).

Potassium, the second most prevalent analyte loaded on CST, was found to be 0.145 mmol/g dry CST (AP-105 processing). The K uptake mechanism is not fully understood, and additional data are necessary to extrapolate the impact of K on Cs exchange. The K loading predicted by the Zheng-Anthony-Miller (ZAM) model is significantly larger than the concentration of K found on spent CST. Additional efforts are underway to assess this discrepancy and provide a better estimation of K impact on Cs exchange (Campbell et al. 2021).

Table 4.6. CST Lead Column Analyte Loading from AW-102, AP-107, and AP-105 Waste Processing

CST Lot →	AW-102 ^(a) (2002009604)	AP-107 ^(a) (2081000057)	AP-105 (2002009604)
Analyte	mmol/g		
Al	0.027	0.155	0.053
Ba	0.001	0.002	7.35E-4
Ca	0.147	0.124	0.211
Cd	0.001	0.002	[0.0005]
Cu	0.029	0.020	--
Fe	0.012	0.017	0.015
K	0.221	0.108	0.145
Pb	0.014	0.026	0.027
Sr	0.001	0.001	0.002
U	0.005	0.006	0.003
CST Components, mmol/g			
Na	3.51	3.49	4.13
Nb	1.46	1.17	1.42
Si	1.77	1.23	1.32
Ti	3.31	2.99	3.64
Zr	0.947	0.979	1.13

(a) Campbell et al. 2020a

Values in brackets [] were $\geq$ MDL but $<$ EQL, with errors likely to exceed 15%.

All three tank waste tests quantitatively removed Sr, and the CST digestions proved that Sr partitions to the CST with Cs. Small amounts of Cd, Fe, and U were also found on the CST. The summations of total

mmoles of exchanged analytes were within 12% of the predicted mmoles lost due to Na exchange for AP-105.

Overall, the integrity of the CST post-processing AP-105 was maintained. The same was not observed for the CST digested post-processing AW-102 and AP-107 tank wastes. Again, the CST lot used in AP-107 processing was slightly different than that used in AW-102 and AP-105 processing, with the most notable distinction being the Nb content near 10% lower concentration and much less Ca inherent in the manufactured product used for processing AP-107.

5.0 Conclusions

The digestion protocol developed in 2019 by Campbell et al. was used to dissolve CST and remove ^{137}Cs from the aqueous matrix to support analyte analysis.

1. The spent CST, post feed displacement, water flush, and purged with compressed air, remained free-flowing, and free of agglomeration after nearly 8 months of storage.
2. Ca loading on the CST progressively decreased from lead to lag to polish column. The concentration of Ca on the lead column post-processing AP-105 waste was 0.211 mmol/g dry CST, which is the highest Ca loading to-date for the analyzed spent CST samples. This aligns with AP-105 IX feed solution containing the highest Ca concentration (1.03×10^{-3} M Ca) relative to AW-102 and AP-107 tank waste feeds. Extensive batch contact tests with increasing Ca concentrations to 1.3×10^{-4} M had no effect on the Cs exchange selectivity or capacity at the nominal equilibrium tank waste supernate condition of 6.7×10^{-5} M Cs (Fiskum et al. 2020).
3. A majority of Pb was removed from AP-105 IX feed and 0.027 mmol/g of dry CST was quantified on the lead column. The Pb concentration decreased incrementally through the lag to polish columns, 0.023 to 0.020 mmol/g dry CST, respectively. A similar observation was made for Fe partitioning, where nominally 0.015 mmol/g was quantified on the lead column, followed by 0.011 and 0.008 mmol/g on the lag and polish columns, respectively.
4. Feed and effluent results indicated quantitative removal of Sr from AP-105 processing. Sr was quantified in the CST digestate solutions, with the concentration of Sr decreasing from lead to polish columns. The lead, lag, and polish concentrations were 2.00×10^{-3} , 2.91×10^{-4} , and 5.91×10^{-5} mmol/g dry CST, respectively. The mass balance of Sr during processing increased to 108% when Sr quantified on the CST was included in the calculation.
5. Interestingly, K was more uniformly distributed on the CST, with nominally 0.145 mmol/g dry CST quantified on all three columns. Of all the analytes reported, K was the only analyte of interest observed to follow this behavior. There is very limited data available in the literature regarding K exchange with CST; however, from this data, K uptake does not appear to follow Cs loading.
6. Contrary to previous digestion results, there did not appear to be any leaching of CST components during AP-105 IX testing, as indicated by the near quantitative recovery for analytes comprising the CST framework (Campbell et al. 2020a).
7. In comparison to the AP-107 and AW-102 digestion results, the AP-105 digestion results had significantly more Ca loaded on the lead column (0.221 mmol/g CST). This is likely not the reason for the steeper Cs load curve for AP-105, however, as Ca did not compete with Cs for exchange sites in 4.6 M NaNO_3 /1.0 M NaOH (Campbell et al. 2020b).

6.0 References

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Appendix A – Analytical Reports

Samples were submitted to the Pacific Northwest National Laboratory Analytical Support Operations (ASO) laboratory according to Analytical Service Request (ASR) 1275. Analytical reports provided by ASO are included in this appendix. In addition to the analyte results, they define the procedures for analysis, as well as quality control sample results, observations during analysis, and overall estimated uncertainties.

Table of Contents

ASR 1275, Rev. 0: Analysis of CST digestates from AP-105 processing

- ASR 1275 describing samples and analyses requested.....A.2
- ICP-MS (Ba, Pb, Sr, U)A.4
- ICP-OES, Metals (Al, Ca, Cd, Fe, K, Na, Nb, Ni, Pb, Si, Sr, Ti, Zr)A.11

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 <u>Emily Campbell</u> Print Name <u>Emily Campbell</u> Phone <u>(509)375-4579</u> MSIN <u> </u>	Digitally signed by Emily Campbell Date: 2021.04.13 11:54:56 -07'00' Project Number: <u>77636</u> Work Package: <u>NH0144</u>
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Matrix Type Information

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

(If sample matrices vary, specify on Request Page)

Disposal Information

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

QA/Special Requirements

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

Data Reporting Information

◆ Is Work Associated with a Fee-Based Milestone? ☒ No ☐ Yes If yes, milestone due date: <u> </u> ◆ 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: <u> </u>	◆ Requested Analytical Work Completion Date: <u>5/14/21</u> (Note: Priority rate charge for < 10 business day turn-around time) ◆ Negotiated Commitment Date: <u>5/14/21</u> (To be completed by ASO Lead)
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Waste Designation Information

◆ ASO Sample Information Check List Attached? ☐ No ☒ Yes If no, Reference Doc Attached: <u> </u> or, Previous ASR Number: <u> </u> or, Previous RPL Number: <u> </u>	Does the Waste Designation Documentation Indicate Presence of PCBs? ☒ No ☐ Yes
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 Send Report To: emily.campbell@pnnl.gov
sandy.fiskum@pnnl.gov
MSIN MSIN Additional or Special Instructions **Receiving and Login Information (to be completed by ASO staff)**

Date Delivered: <u>4/13/21</u> Delivered By: <u> </u> Time Delivered: <u>1:00 pm</u> Group ID: <u> </u> CMC Waste Sample? ☒ No ☐ Yes	Received By: <u>T Trang-le</u> ASR Number: <u>1275</u> Rev.: <u>00</u> RPL Numbers: <u>(21-1080) → (21-1087)</u> (first and last)
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ASO Work Accepted By: KN Pool Signature/Date: Karl N Pool 4/15/21

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

Page of

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

Project / WP#: 77636/NH0144
ASR#: 1275.00
Client: E. Campbell
Total Samples: 8 (Aqueous)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
21-1080	TI112-AP-1-A	1 M HNO ₃	NA
21-1081	TI112-AP-1d-A	1 M HNO ₃	NA
21-1082	TI112-AP-2-A	1 M HNO ₃	NA
21-1083	TI112-AP-3-A	1 M HNO ₃	NA
21-1084	TI112-Blank-A	1 M HNO ₃	NA
21-1085	TI112-Blankd-A	1 M HNO ₃	NA
21-1086	TI112-PB-A	1 M HNO ₃	NA
21-1087	TI112-CST-MS-A	1 M HNO ₃	NA

Sample Preparation: Samples were diluted in 2% nitric acid on 4/28/2021 by Sam Morrison.

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:	04/29/2021	ICP File:	M0310
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See Chemical Measurement Center 98620 file: ICP-325-405-3
 (Calibration and Maintenance Records)

M&TE:	☒	PerkinElmer NexION™ 350X ICP-MS	SN: 85VN4070702	RPL 405
	☒	Ohaus PA224C Balance	SN: B725287790	RPL 405
	☒	Mettler AT400 Balance	SN: M19445	RPL 405 FH

Samuel S Morrison
 Report Preparer

June 10 2021
 Date

[Signature]
 Review and Concurrence

6/10/2021
 Date

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

Eight aqueous samples were submitted under Analytical Service Request (ASR) 1275.00 were analyzed by ICP-MS. Prior to analysis all samples were diluted by Sam Morrison on 4/28/2021 in lab 405 with 2% HNO₃ gravimetrically. None of the solutions were filtered.

All results are reported on a mass (ng/g) for each detected analyte. The results have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-MS Data Report. The isotope Strontium-88 was utilized to quantify the Strontium in the sample, Barium-138 was utilized to quantify the Barium in the sample, Lead-208 was used to quantify the Lead in the sample, and Uranium-238 was used to quantify the Uranium in the sample. The quality control (QC) results for the AOI have been evaluated and are presented below.

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

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

Internal Standard (IS):

All solutions (blanks, standards, QC checks, and samples) were mixed in-line with a solution containing 10 ppb each of Tb-159 as the internal standard (IS). The AOI data were normalized using the data for the Tb-159 IS mass. The Tb-159 IS recoveries were within the acceptance criterion of 30% to 120%.

Preparation Blank (PB):

A laboratory diluent, blank #8 (2% HNO₃) was analyzed as a blank. All AOI were within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples.

Blank Spike (BS-71A)/Laboratory Control Sample (LCS):

A single blank spike (Blank Spike 71A) sample prepared from a dilution of the 2% HNO₃ blank with an equivalent volume of each 2 ppb standard CCV-71A (1:1 ratio). The recovery for the all AOI were within the acceptance criteria of 80% to 120% recovery.

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

A duplicate of sample 21-1080 was analyzed. RPD are listed for all analytes, that were above the EQL, were ≤20% RPD, and within the acceptance criteria.

*Battelle PNNL/RPL/Inorganic Analysis ... ICP-MS Analysis Report*Matrix-Spike (MS) Sample:

No matrix spike sample was required to be prepared.

Initial/Continuing Calibration Verification (ICV/CCV):

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

Initial/Continuing Calibration Blank (ICB/CCB):

ICB/CCB solutions (2% v/v HNO₃) were analyzed immediately after each ICV solution and after each respective CCB 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.

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% recovery.

Interference Check Standard (ICS):

The ICS solution (71A) was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCB 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 21-1080. Percent differences (%D) are listed for all analytes that had a concentration at or above the 10x EQL in the diluted sample. The percent difference was within the acceptance criterion of ≤10%.

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

Because no MS sample was required to be prepared, a post-digestion spike (PSA) was conducted on sample 21-1080. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery value for the AOI meeting this requirement was within the acceptance criterion of 80% to 120%.

Other QC:

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

*Battelle PNNL/RPL/Inorganic Analysis ... ICP-MS Analysis Report***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 $\pm 15\%$ or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations $> \text{EQL}$ up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than $5000 \mu\text{g/mL}$ (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 $< \text{MDL}$ are listed as "-". Note, that calibration and QC standard samples are validated to a precision of $\pm 10\%$.
- 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.

		Run Date >	04/29/21	04/29/21	04/29/21	04/29/21	04/29/21
		Process Factor >	1	2640.2, 884.8	2640.2, 884.8	147.5, 880.3, 4413.8	148.7, 890.3, 4478.1
		RPL/LAB >	Blank-8	21-1080	21-1080 Rep	21-1081	21-1082
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO ₃ Lab Blank	TI112-AP-1-A	TI112-AP-1-A Rep	TI112-AP-1d-A	TI112-AP-2-A
(ng/mL)	(ng/mL)	(Analyte)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
5.66E-03	5.66E-02	Sr	--	391.1	368.0	1085.1	75.0
9.36E-03	9.36E-02	Ba	--	244.6	248.3	210.2	143.6
8.09E-03	8.09E-02	Pb	--	11437.7	10727.4	10375.9	9513.9
5.85E-04	5.85E-03	U	--	1547.3	1569.2	1749.8	1522.2

Internal Standard % Recovery

Tb 159 (IS)	105%	102%	101%	101%	100%
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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 $\geq$ EQL is estimated to be within $\pm 15\%$.

2) Values in brackets [] are $\geq$ 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.

		Run Date >	04/29/21	04/29/21	04/29/21	04/29/21	04/29/21
		Process Factor >	148.0, 885.9, 4400.1	147.7	147.7	29.5	147.7, 4413.1, 26355.1
		RPL/LAB >	21-1083	21-1084	21-1085	21-1086	21-1087
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	TI112-AP-3-A	TI112-Blank-A	TI112-Blankd-A	TI112-PB-A	TI112-CST-MS-A
(ng/mL)	(ng/mL)	(Analyte)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
5.66E-03	5.66E-02	Sr	50.5	43.278	43.1	7.8	6951.4
9.36E-03	9.36E-02	Ba	126.2	147.7	139.3	146.2	26777.0
8.09E-03	8.09E-02	Pb	9031.2	1.7	1.9	5.3	548308.4
5.85E-04	5.85E-03	U	1399.1	0.4	1.0	0.5	0.4

Internal Standard % Recovery

Bi 209 (IS)	101%	103%	107%	110%	109%
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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 $\geq$ EQL is estimated to be within $\pm 15\%$.

2) Values in brackets [] are $\geq$ 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 04/29/2021

Criteria >	≤ 35%	80%-120%	75%-125%	75%-125%	≤ 10%
QC ID >	Rep 21-1080	BS71A	MS (None)	21-1080 + CCV71A	21-1080 (5x) Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Diff
Sr	6.1%	103%		103%	NR
Ba	1.5%	106%		97%	NR
Pb	4.3%	103%		97%	0.8%
U	1.4%	109%		104%	0.1%

Internal Standard % Recovery

Bi 209 (IS)	106%	103%		108%	108%
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Shaded results are outside the acceptance criteria.

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

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

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

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

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

Project / WP#: 77636 / NH0144
ASR#: 1275.00
Client: E. Campbell
Total Samples: 8 (Aqueous)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
21-1080	TI112-AP-1-A	1M HNO ₃ , digested silicotitanate, contacted with AMP-PAN resin.	NA
21-1081	TI112-AP-1d-A		NA
21-1082	TI112-AP-2-A		NA
21-1083	TI112-AP-3-A		NA
21-1084	TI112-Blank-A		NA
21-1085	TI112-Blankd-A		NA
21-1086	TI112-PB-A		NA
21-1087	TI112-CST-MS-A		NA

Sample Preparation: Simple dilution of "as received" samples in 5% v/v HNO₃ performed by J. Carter on 04/23/2021.

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

Analyst:	J. Carter	Analysis Date:	04/23/2021	ICP File:	C0873
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See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE:	☒	PerkinElmer 5300DV ICP-OES	SN: 077N5122002	RPL 405 Bench
	☐	Sartorius ME414S Balance	SN: 22406373	RPL 405 Bench
	☒	Ohaus Pioneer PA224C	SN: B725287790	RPL 405 Bench

Jennifer C (Jenn) Carter

Digitally signed by Jennifer C (Jenn) Carter
Date: 2021.05.25 12:25:23 -07'00'

Report Preparer

Date

Samuel S Morrison

Review and Concurrence

5/25/2021

Date

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

Eight liquid samples were submitted under Analytical Service Request (ASR) 1275 and analyzed by ICP-OES. The sample was analyzed after dilution of the “as received” liquid in 5% v/v HNO₃. Neither the samples nor any of the dilutions were filtered.

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

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

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

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

Preparation Blank (PB):

No preparation blank was required. The ICP-OES laboratory diluent (5% HNO₃) was analyzed as a blank. All AOI were within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples.

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

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

Replicate Relative Percent Difference (RPD):

A duplicate of sample 21-1080 was prepared and analyzed. RPDs are listed for all analytes that were measured at or above the EQL. RPD for the AOIs meeting this requirement were between 0.1% and 4.2%, within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

No matrix spike was required.

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

Initial/Continuing Calibration Verification (ICV/CCV):

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

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (5% v/v HNO₃) was analyzed immediately after the ICV solutions and after the CCB 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 CCB solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Analytical Spike (AS-A) - Sample (A Component):

An analytical spike (A Component) was conducted on sample 21-1080. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration $\geq 25\%$ of that in the sample. Recovery values for the AOIs meeting this requirement were between 105% and 110%, which is within the acceptance criterion of 80% to 120%.

Analytical Spike (AS-B) - Sample (B Component):

There were no AOIs requested that are present in the B spike component.

Analytical Spike (AS-3A) - Sample (3A Component):

There were no AOIs requested that are present in the 3A spike component.

Analytical Spike (AS-3B) - Sample (3B Component):

An analytical spike (3B Component) was conducted on sample 21-1080. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration $\geq 25\%$ of that in the sample. Recovery value for the AOI meeting this requirement was 96%, which is within the acceptance criterion of 80% to 120%.

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

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 21-1080. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %D for the AOIs meeting this requirement were between 0.3% and 2.7%, meeting the acceptance criterion of $\leq 10\%$.

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 $\pm 15\%$ or better for samples in dilute, acidified water (e.g. 5% v/v HNO₃ 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 $\mu\text{g/mL}$ (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 $\pm 10\%$.
- 4) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

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

		Run Date >	4/23/2021	4/23/2021	4/23/2021	4/23/2021	4/23/2021	4/23/2021	4/23/2021	4/23/2021	4/23/2021	4/23/2021
		Process Factor >	1.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	1.0	10.0
		RPL/LAB >	405 Diluent	21-1080		21-1081	21-1082	21-1083	21-1084	21-1085	21-1086	21-1087
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	T112-AP-1-A		T112-AP-1d-A	T112-AP-2-A	T112-AP-3-A	T112-Blank-A	T112-Blankd-A	T112-PB-A	T112-CST-CS-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0276	0.276	Al	--	3.37	3.23	3.35	3.07	3.36	[1.2]	[0.99]	0.836	[1.9]
0.0233	0.233	Ca	--	19.2	19.4	20.2	17.1	16.4	7.68	8.28	1.73	179
0.0027	0.027	Cd	--	[0.13]	[0.14]	[0.12]	[0.087]	[0.11]	--	--	[0.0041]	--
0.0017	0.017	Fe	[0.0030]	1.84	1.84	2.00	1.40	1.08	0.327	0.366	0.0476	28.0
0.0500	0.500	K	[0.075]	12.9	12.8	13.5	12.5	14.2	--	--	[0.39]	--
0.0171	0.171	Na	[0.029]	216	220	227	217	256	226	233	15.1	227
0.0030	0.030	Nb	--	300	306	317	286	331	270	282	[0.026]	268
0.0074	0.074	Ni	--	[0.15]	[0.11]	[0.16]	[0.13]	[0.12]	--	--	--	3.84
0.0399	0.399	Pb	--	12.6	12.5	13.3	10.3	10.6	--	--	--	624
0.0136	0.136	Si	--	113	115	57.0	111	134	71.4	114	8.04	71.4
0.0014	0.014	Ti	--	395	393	418	379	442	356	372	0.0605	352
0.0022	0.022	Zr	--	233	237	248	230	267	214	228	[0.013]	213
Other Analytes												
0.0030	0.030	Ag	--	--	--	--	--	--	--	--	--	--
0.1576	1.576	As	--	--	--	--	--	--	--	--	--	--
0.0078	0.078	Au	--	--	--	--	--	--	--	--	--	--
0.0120	0.120	B	--	6.37	6.31	4.96	4.24	3.66	6.62	4.60	6.40	9.97
0.0002	0.002	Be	--	[0.016]	[0.016]	[0.017]	[0.011]	[0.013]	--	[0.0033]	--	--
0.0546	0.546	Bi	--	--	--	--	--	--	--	--	--	--
0.0448	0.448	Ce	--	--	--	--	--	--	--	--	--	--
0.0071	0.071	Co	--	--	--	--	--	--	--	--	[0.0099]	--
0.0047	0.047	Cr	--	0.527	0.508	0.558	[0.27]	[0.25]	--	--	--	--
0.0036	0.036	Cu	--	2.69	2.62	2.67	2.47	2.76	1.87	1.98	[0.026]	2.13
0.0034	0.034	Dy	[0.0040]	--	[0.066]	[0.040]	[0.050]	--	--	[0.054]	[0.0060]	--
0.0010	0.010	Eu	--	[0.015]	--	--	--	--	[0.010]	--	--	--
0.0152	0.152	Ga	--	--	--	--	--	--	--	--	[0.081]	--
0.0048	0.048	Hf	--	4.21	4.22	4.37	4.12	5.04	4.32	4.66	--	4.20
0.0030	0.030	La	--	[0.045]	[0.064]	[0.034]	--	--	--	--	--	[0.27]
0.0028	0.028	Li	--	[0.15]	[0.17]	[0.15]	[0.086]	[0.094]	[0.078]	[0.085]	[0.0096]	[0.16]
0.0008	0.008	Lu	--	--	--	--	--	--	--	--	--	--
0.0023	0.023	Mg	[0.0060]	1.06	1.05	1.04	0.948	0.992	0.811	0.825	0.180	0.821
0.0009	0.009	Mn	--	0.154	0.155	0.164	0.0885	0.0892	[0.072]	[0.072]	[0.0060]	0.132
0.0094	0.094	Mo	--	55.6	55.7	74.3	75.0	71.1	93.2	53.7	74.4	92.4
0.0188	0.188	Nd	--	--	--	--	--	--	--	--	--	--
0.1021	1.021	P	--	[1.7]	[1.9]	[1.8]	[2.0]	[2.0]	[2.1]	[2.0]	2.39	[2.6]
0.0170	0.170	Pd	--	--	--	[0.19]	--	[0.27]	[0.64]	--	--	--
0.0162	0.162	Rh	--	--	--	--	[0.17]	--	--	--	[0.041]	--
0.0158	0.158	Ru	--	--	--	--	--	--	--	--	--	--
0.1773	1.773	S	--	--	--	--	--	--	--	--	--	--
0.0919	0.919	Sb	--	--	--	--	--	--	--	--	--	--
0.0007	0.007	Sc	--	--	--	--	--	--	[0.0086]	[0.0076]	--	--
0.2271	2.271	Se	--	--	--	--	--	--	--	--	--	--
0.0212	0.212	Sm	--	--	--	--	--	--	--	--	--	--
0.0446	0.446	Sn	--	--	--	--	--	--	--	--	--	--
0.0003	0.003	Sr	--	0.369	0.377	0.453	0.0556	[0.013]	[0.014]	[0.013]	0.0048	8.90
0.0242	0.242	Ta	--	[0.59]	[0.61]	[0.53]	[0.34]	[0.71]	[0.55]	[0.53]	--	[0.37]
0.0110	0.110	Tb	--	--	--	--	--	--	--	--	--	--
0.0412	0.412	Te	--	--	--	--	--	--	--	--	--	--
0.0120	0.120	Th	--	[0.21]	[0.20]	[0.19]	[0.17]	[0.17]	[0.24]	[0.21]	[0.029]	[0.25]
0.0885	0.885	Tl	--	--	--	--	--	--	--	--	--	--
0.0046	0.046	Tm	--	[0.050]	--	[0.14]	[0.061]	--	[0.073]	[0.11]	--	--
0.0676	0.676	U	--	[1.6]	[1.7]	[1.9]	[1.3]	[1.4]	--	--	--	--
0.0032	0.032	V	--	--	--	--	--	--	--	--	--	--
0.0249	0.249	W	--	--	--	--	--	--	--	--	[0.15]	--
0.0006	0.006	Y	--	--	--	--	--	--	--	--	--	--
0.0066	0.066	Zn	--	--	--	--	--	--	--	--	[0.025]	[0.12]

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%.

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QC Performance 04/23/2021

Criteria >	≤ 20%	80%-120%	80%-120%	80%-120%	80%-120%	80%-120%	≤ 10%
QC ID >	21-1080 Dup	LCS/BS	21-1080 + AS-A	21-1080 + AS-B	21-1080 + AS-A (Tor)	21-1080 + AS-B (Tor)	21-1080 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Rec	%Diff
Al	4.2	107	109				
Ca	0.9	106	108				0.9
Cd		105	107				
Fe	0.1	108	110				0.8
K	1.3	101	105				
Na	1.7	106	108				1.0
Nb	1.9					96	0.3
Ni		107	107				
Pb	1.2	105	105				
Si	1.7	105	106				2.7
Ti	0.4		nr				1.6
Zr	1.6		nr				0.9
Other Analytes							
Ag		96	95				
As		105	105				
Au						101	
B	0.9	103	102				
Be		105	105				
Bi		96	100				
Ce		98		102			
Co		104	106				
Cr	3.6	103	104				
Cu	2.4	111	109				0.1
Dy		108		109			
Eu		105		107	108		
Ga					108		
Hf	0.2					106	2.4
La		104		108			
Li		113	113				
Lu					108		
Mg	0.5	107	110				
Mn	0.4	110	111				
Mo	0.3	102	92				1.5
Nd		107		109			
P		104	105				
Pd		96		100			
Rh		97		101			
Ru		103		106			
S		105		106			
Sb			104				
Sc					111		
Se		102	104				
Sm					108		
Sn		99	101				
Sr	2.2	117	120		128		2.2
Ta		103	103				
Tb					105		
Te		101		103			
Th		106		107			
Tl			95				
Tm					104		
U				108			
V			102				
W			103				
Y			102		105		
Zn			103				

Shaded results are outside the acceptance criteria.

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

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