

Fluoride Analysis by Ion Chromatography in Support of Fast Critical Assembly (FCA) Spent Nuclear Fuel Processing

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Introduction

The Savannah River Site (SRS) is currently processing Fast Critical Assembly (FCA) fuel received from the Japan Atomic Energy Agency (JAEA) for disposition. Stainless steel-clad plate and rods in stainless steel containers are dissolved using electrolysis with a solution mixture of nitric acid (HNO₃), potassium fluoride (KF), and gadolinium (Gd). An ion chromatography (IC) was developed and vetted to monitor fluoride at various sampling points of the process. To finalize the method, FCA test solution was analyzed to qualify the analytical method followed by real FCA process solution analysis using two different analytical columns. This presentation summarizes the development and vetting of the IC method.

Methods

The FCA samples were 500-fold diluted in deionized water prior to analysis. Other FCA samples were 500-fold diluted in 5 mM NaOH and passed through 2.5 cc OnGuard II Na SPE cartridge to remove transition and alkaline earth metals prior to analysis. Deionized blanks are analyzed between each FCA sample, and a 5-point calibration curve is created each day with opening/closing QC standards. Standards are controlled to + or - 10%.

Date	System	# of FCA samples	# of FCA samples with spikes	Total daily samples	Spike Average % Recovery	Comment
12/6/2024	1	4	4	8	102	6.3D Batch 6 AS11 HC column
12/6/2024	2	4	4	8	107	6.3D Batch 6 AS19 column
12/9/2024	1	6	6	12	102	6.3D Batch 6 AS11 HC column
12/9/2024	2	6	6	12	105	6.3D Batch 6 AS19 column
12/10/2024	1	4	4	8	101	6.3D Batch 6 AS11 HC column
12/10/2024	2	4	4	8	104	6.3D Batch 6 AS19 column
2/6/2025	1	4	4	8	104	6.3D Batch 8 OnGuard II Na SPE treated AS11 HC column
2/6/2025	2	4	4	8	107	6.3D Batch 8 OnGuard II Na SPE treated AS19 column

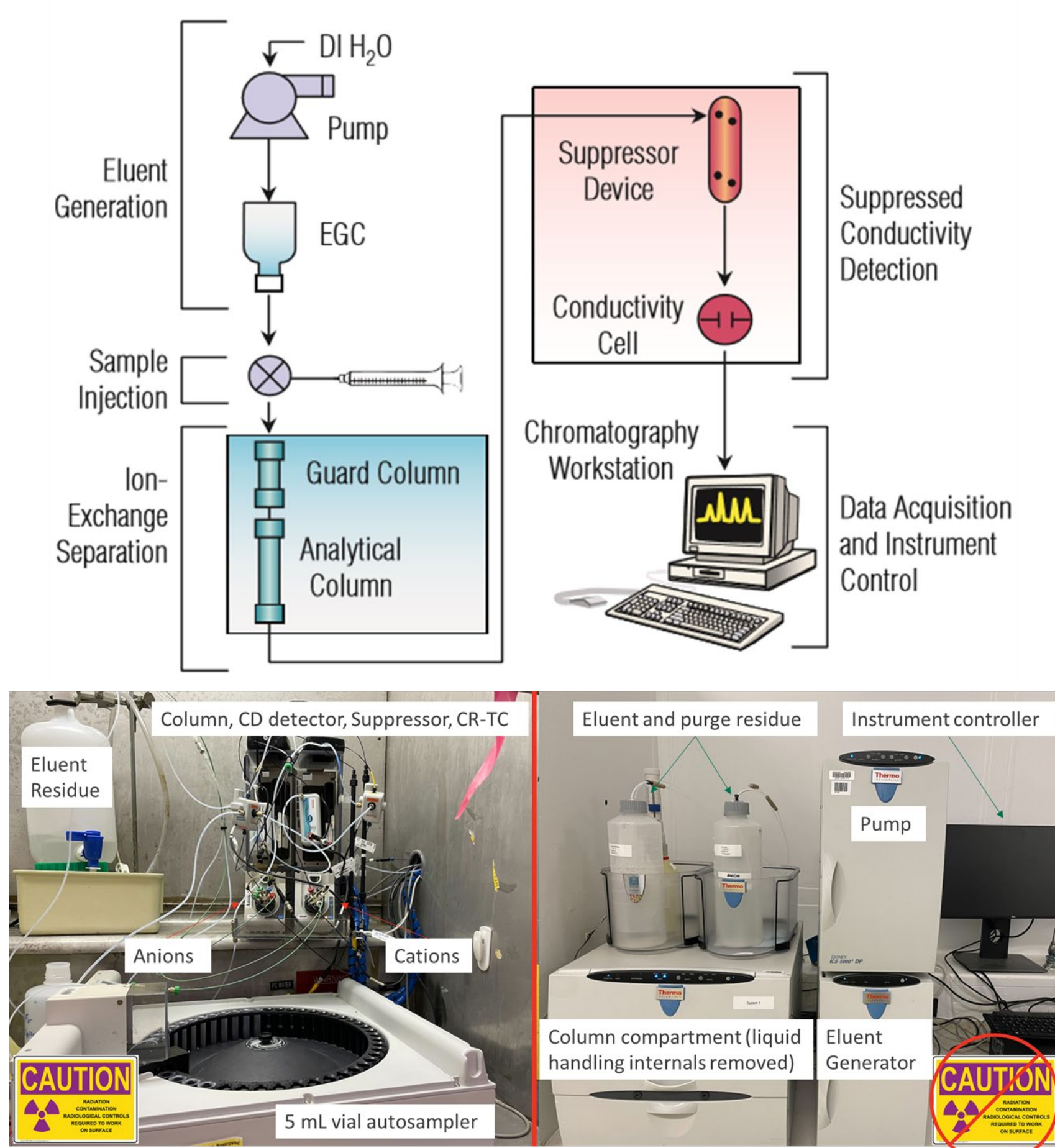
System 1 equipped with AS-11HC Column

Date	Sample	System	F-, mg/L
12/6/2024	QC 10	1	9.46
12/6/2024	QC 10	1	9.44
12/9/2024	QC 10	1	10.0
12/9/2024	QC 10	1	10.0
12/10/2024	QC 10	1	9.60
12/10/2024	QC 10	1	9.61
2/6/2025	QC 10	1	9.38
2/6/2025	QC 10	1	9.40

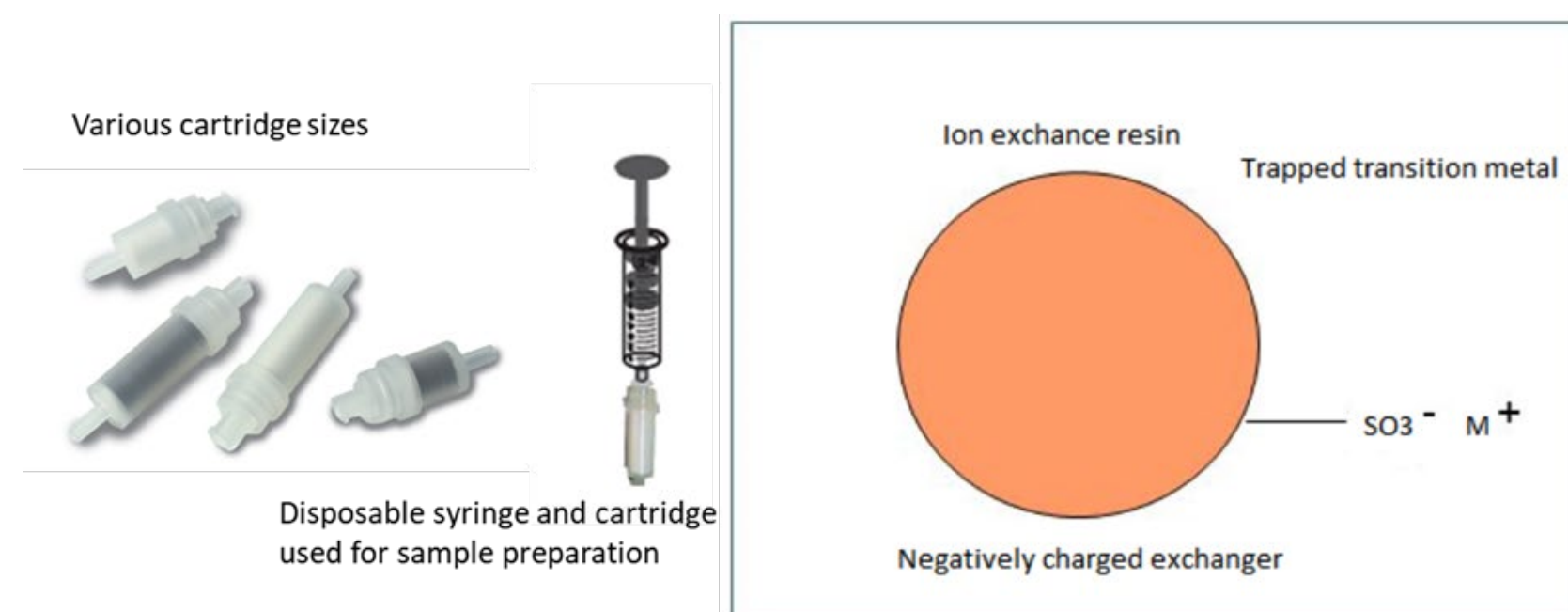
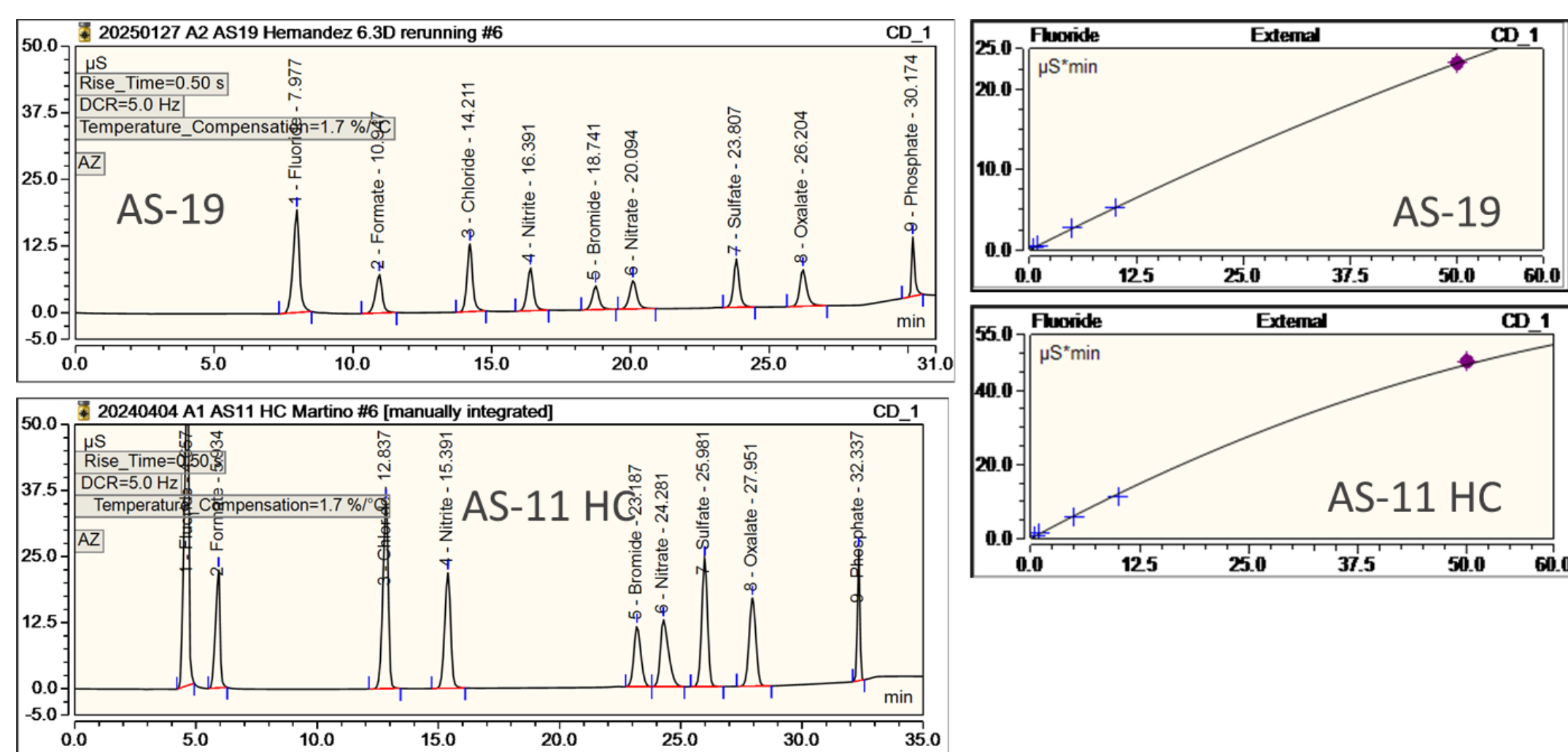
System 2 equipped with AS-19 Column

Date	Sample	System	F-, mg/L
12/6/2024	QC 10	2	10.1
12/6/2024	QC 10	2	10.1
12/9/2024	QC 10	2	10.0
12/9/2024	QC 10	2	10.0
12/10/2024	QC 10	2	10.0
12/10/2024	QC 10	2	9.99
2/6/2025	QC 10	2	9.97
2/6/2025	QC 10	2	10.1

Contained Ion Chromatography



Anion Method AS-19 column	
Injection	20 µL
Flow rate	1.0 mL/min
Stop Time	31 min
Guard Column	IonPac AG-19 4x50 mm P/N 062887
Analytical Column	IonPac AS-19 4x250 mm P/N 062885
Suppressor	Anion Dynamically Regenerated Suppressor (DRS) 600 P/N 088666 4 mm
Mobile Phase, Time min.	5-60 mM KOH Gradient P/N 074532, mM
0-7	5
7-16	20
16-25	30
25-27	60
27-29.7	60
29.7-30	5
30-31	5
Calibration Curve	1 mg/L to 50 mg/L, $r^2 = >0.995$
Temperature	30 °C
Retention Time of Fluoride	7.9 min
Retention Time of Formate	10.8 min
Retention Time of Chloride	14.2 min
Retention Time of Nitrite	16.4 min
Retention Time of Bromide	18.7 min
Retention Time of Nitrate	20.1 min
Retention Time of Sulfate	23.8 min
Retention Time of Oxalate	26.2 min
Retention Time of Phosphate	30.1 min
Anion Method AS-11 HC column	
Injection	20 µL
Flow rate	1.0 mL/min
Stop Time	35 min
Guard Column	IonPac AG-11 HC 4x50 mm P/N 052962
Analytical Column	IonPac AS-11 HC 4x250 mm P/N 052960
Suppressor	Anion Dynamically Regenerated Suppressor (DRS) 600 P/N 088666 4 mm
Mobile Phase, Time min.	5-60 mM KOH Gradient P/N 074532, mM
0-7	5
7-25	20
25-29	40
29-29.5	60
29.5-32.5	60
32.5-35	5
Calibration Curve	1 mg/L to 50 mg/L, $r^2 = >0.995$
Retention Time of Fluoride	4.6 min
Retention Time of Formate	5.9 min



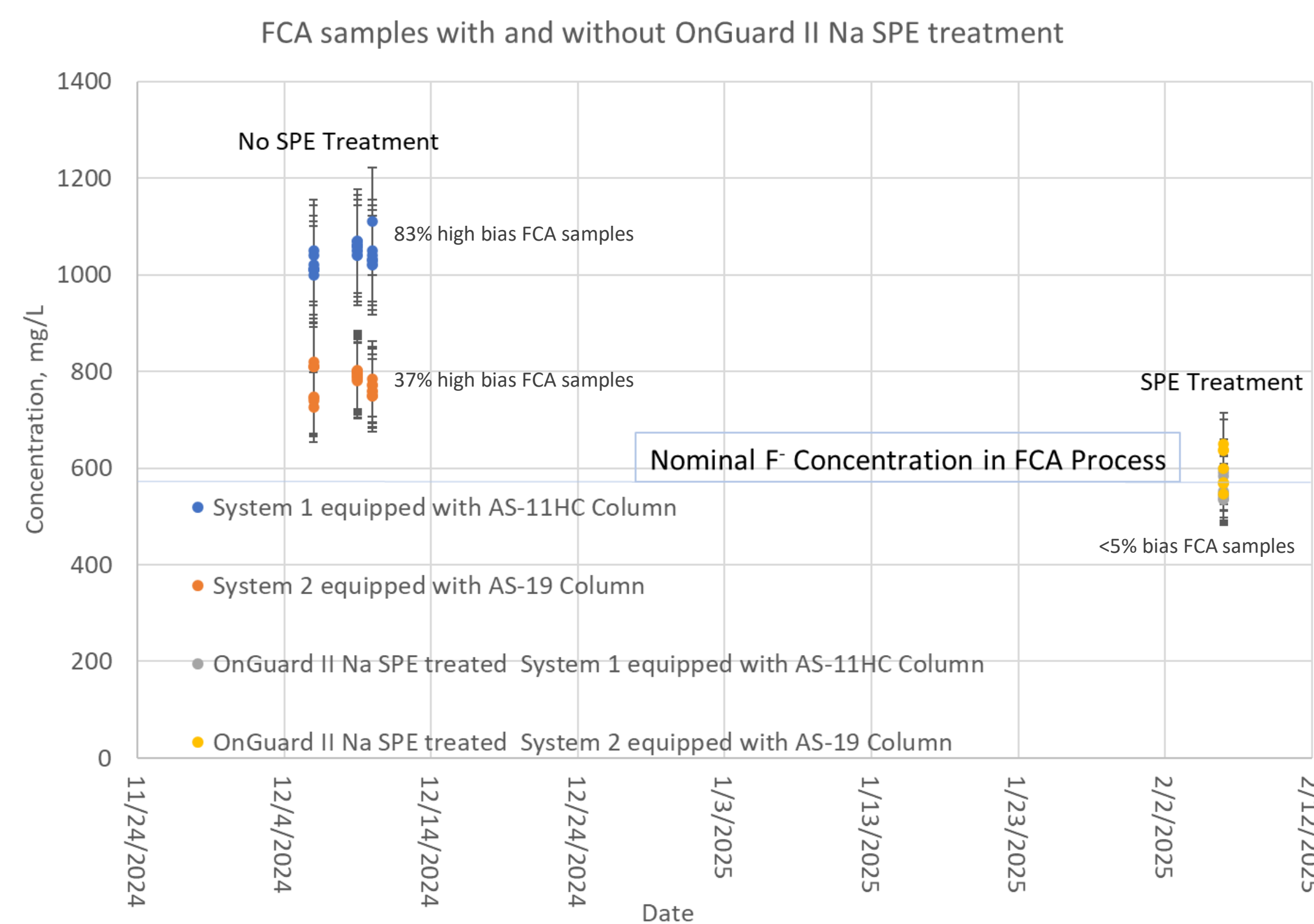
Simulated Waste Qualification

High and Low Fluoride Concentration on AS-11 HC column						
FCA Simulated Waste Initial Testing				2 Sigma Limits (Case I)		% Difference
Spikes, mg/L	Target	Measured	Uncertainty 1 Sigma	Lower Limit	Upper Limit	Target vs Measured
High F	1130	1010	10%	907	1360	10.6%
Low F	524	500	10%	419	629	4.60%

Real Waste Qualification

Date	LIMS #	System	%R
12/6/2024	39665s	1	101
12/6/2024	39665s	1	103
12/6/2024	39665s	1	100
12/6/2024	39665s	1	103
12/9/2024	39665s	1	100
12/9/2024	39665s	1	99
12/9/2024	39666s	1	99
12/9/2024	39666s	1	98
12/9/2024	39666s	1	98
12/9/2024	39666s	1	98
12/9/2024	39666s	1	97
12/10/2024	39665s	1	101
12/10/2024	39665s	1	99
12/10/2024	39666s	1	109
12/10/2024	39666s	1	102
	mean		101
	std dev		3.03
	%std dev		3.01
Matrix Spike Recovery (%R) = (SSR-SR)/SA *100			
SSR = concentration of target analyte in spike sample (spiked)			
SR = Concentration of target analyte in sample (unspiked)			
SA = Concentration of spiked added			
SPE treated			
Date	LIMS #	System	%R
2/6/2025	39665s	1	102
2/6/2025	39665s	1	106
2/6/2025	39665s	1	105
2/6/2025	39666s	1	104
	mean		104
	std dev		1.89
	%std dev		1.81
SPE treated			
Date	LIMS #	System	%R
2/6/2025	39665s	2	108
2/6/2025	39665s	2	107
2/6/2025	39665s	2	107
2/6/2025	39666s	2	107
	mean		107
	std dev		0.79
	%std dev		0.74

Results



Sys 1 3-day batch 6 duplicates		Fluoride	Sys 2 3-day batch 6 duplicates		Fluoride
(Sys 1 AS 11 HC)	mean	1042	(Sys 2 AS 19)	mean	780
	1sigma st dev	24.8		1sigma st dev	25.6
	2sigma st dev	49.6		2sigma st dev	51.3
	67% % stdev (1s)	2.38%		0.67 % stdev (1s)	3.29%
	n	28		n	28
	95% % stdev (2s)	4.76%		95% % stdev (2s)	6.57%
Sys 1 1-day batch 8 duplicates		Fluoride	Sys 2 1-day batch 8 duplicates		Fluoride
OnGuard II Na SPE treatment		OnGuard II Na SPE treatment			
(Sys 1 AS 11 HC)	mean	561	(Sys 2 AS 19)	mean	597
	1sigma st dev	26.3		1sigma st dev	39.2
	2sigma st dev	52.7		2sigma st dev	78.5
	67% % stdev (1s)	4.69%		0.67 % stdev (1s)	6.57%
	n	8		n	8
	95% % stdev (2s)	9.92%		95% % stdev (2s)	13.1%

The results of analysis without SPE are biased high due to the presence of transition metals. Removal of the metals corrects the bias (<5%) while maintaining consistent values on either analytical column (4.69% one sigma for AS-11 HC and 6.67% one sigma AS-19).

- Hernandez-Jimenez, A. M. SRNL Analytical Program Readiness Review for Support of H-Canyon's Fast Critical Assembly Campaign; Technical Report for Savannah River National Laboratory SRNL-TR-2024-00011; Aiken, SC, January 2024.
- Harris et. al. Statistical Analysis of Fluoride Chromatography Data in Support of Fast Critical Assembly Spent Nuclear Fuel Processing by H-Canyon; Technical Report for Savannah River National Laboratory SRNL-TR-2025-00011; Aiken, SC, February 2025.

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Acknowledgements



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