

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 (HNO_3), 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.

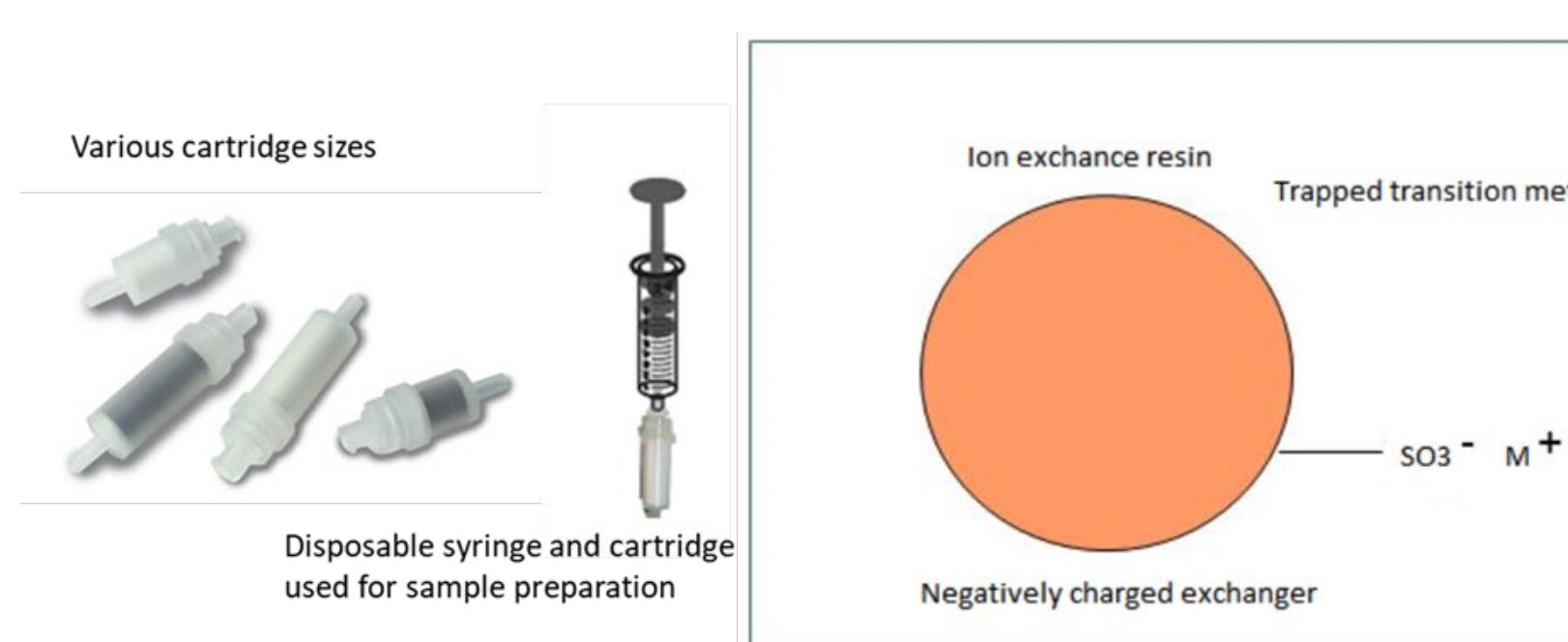
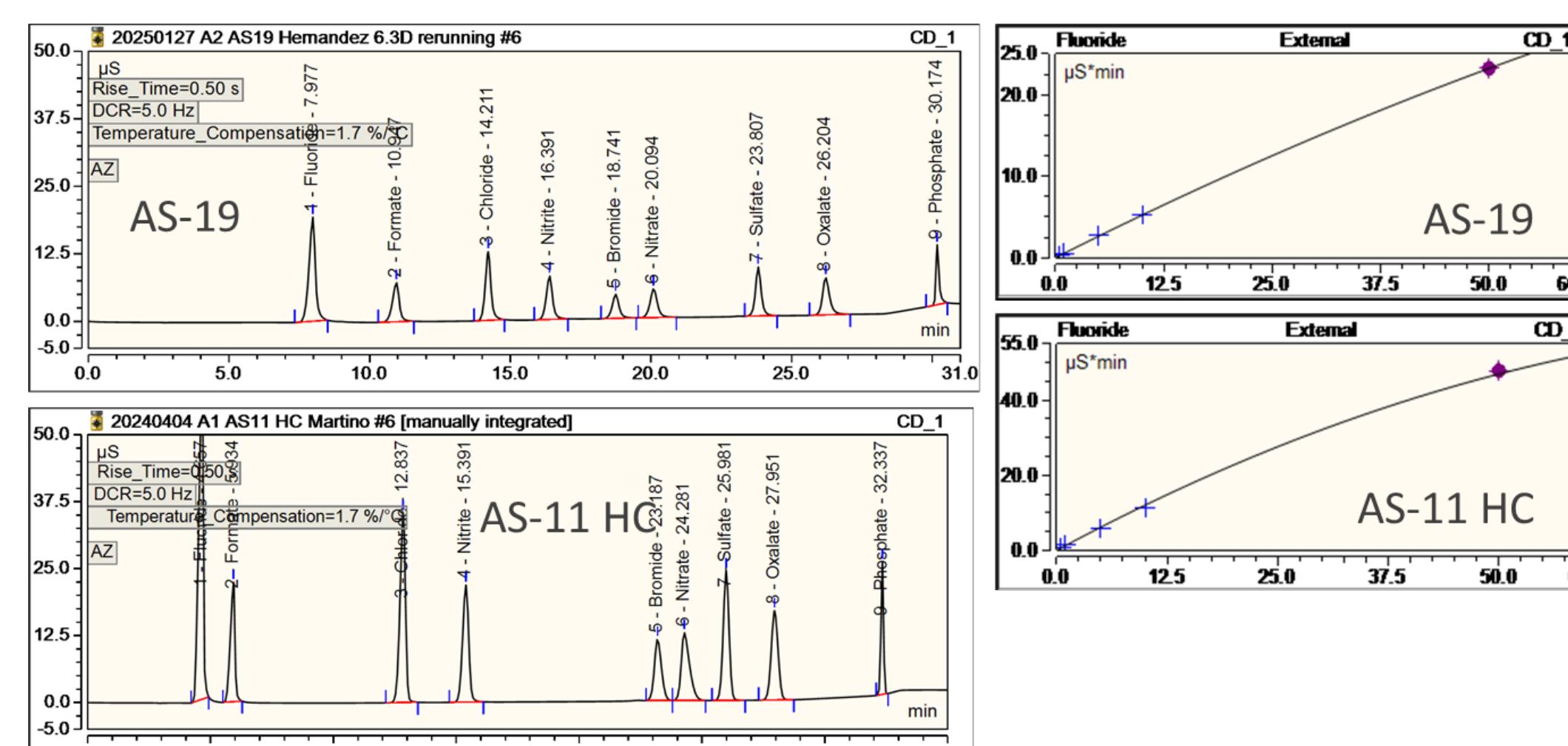
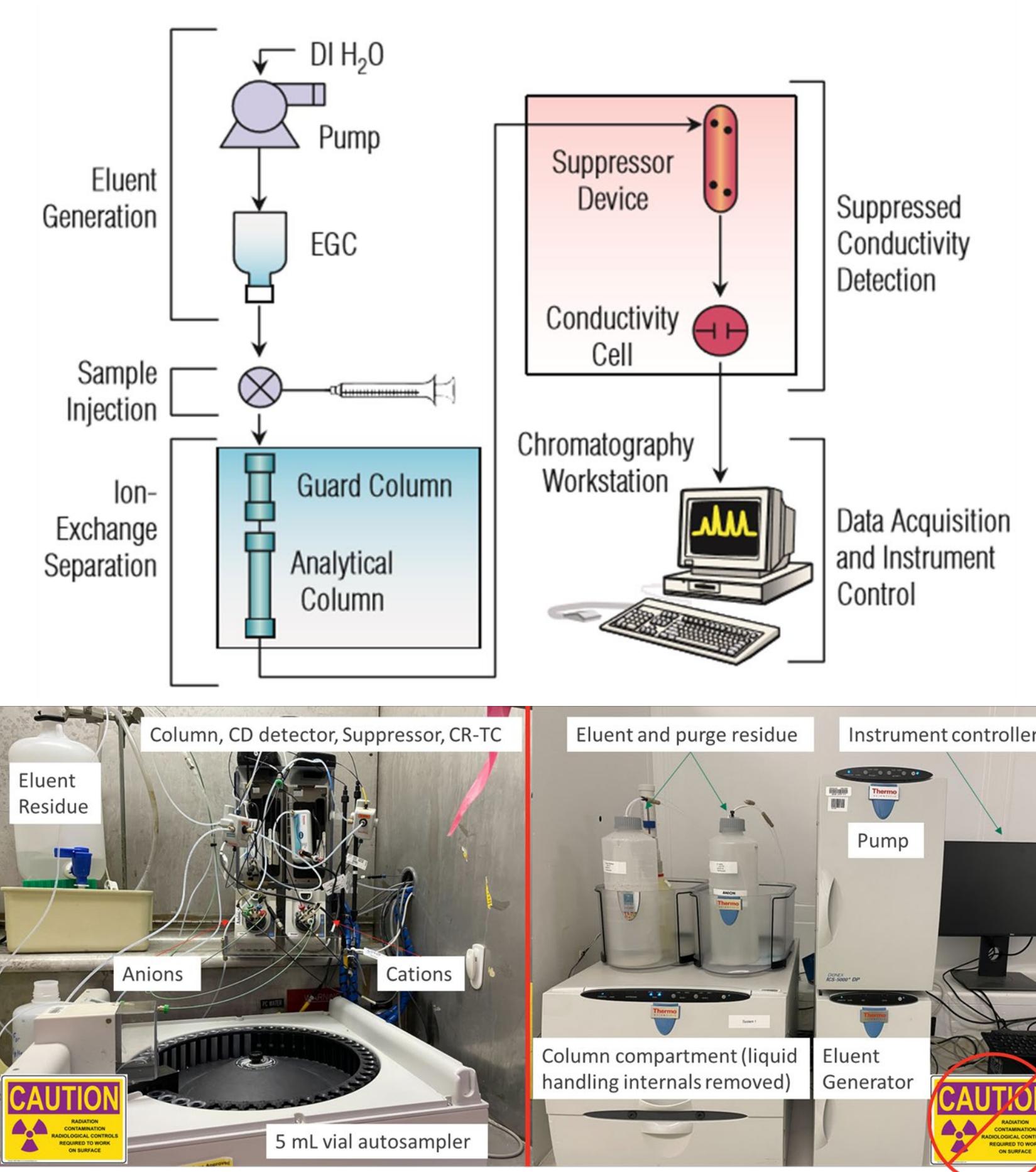
Methods

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 with spikes	# of FCA samples	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							System 2 equipped with AS-19 Column						
Date	Sample	System	F-, mg/L	Date	Sample	System	F-, mg/L						
12/6/2024	QC 10	1	9.46	12/6/2024	QC 10	2	10.1						
12/6/2024	QC 10	1	9.44	12/6/2024	QC 10	2	10.1						
12/9/2024	QC 10	1	10.0	12/9/2024	QC 10	2	10.0						
12/9/2024	QC 10	1	10.0	12/9/2024	QC 10	2	10.0						
12/10/2024	QC 10	1	9.60	12/10/2024	QC 10	2	10.0						
12/10/2024	QC 10	1	9.61	12/10/2024	QC 10	2	9.99						
2/6/2025	QC 10	1	9.38	2/6/2025	QC 10	2	9.97						
2/6/2025	QC 10	1	9.40	2/6/2025	QC 10	2	10.1						

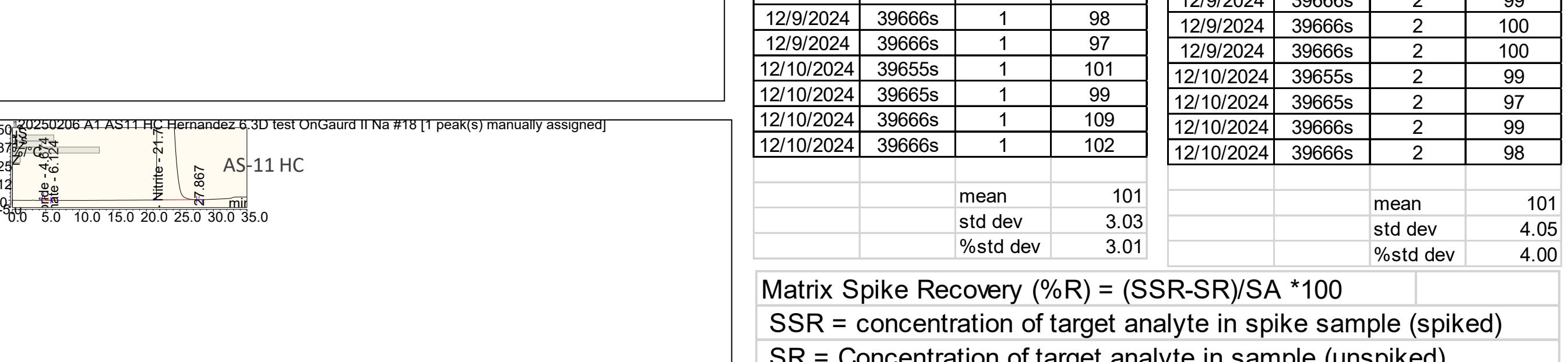
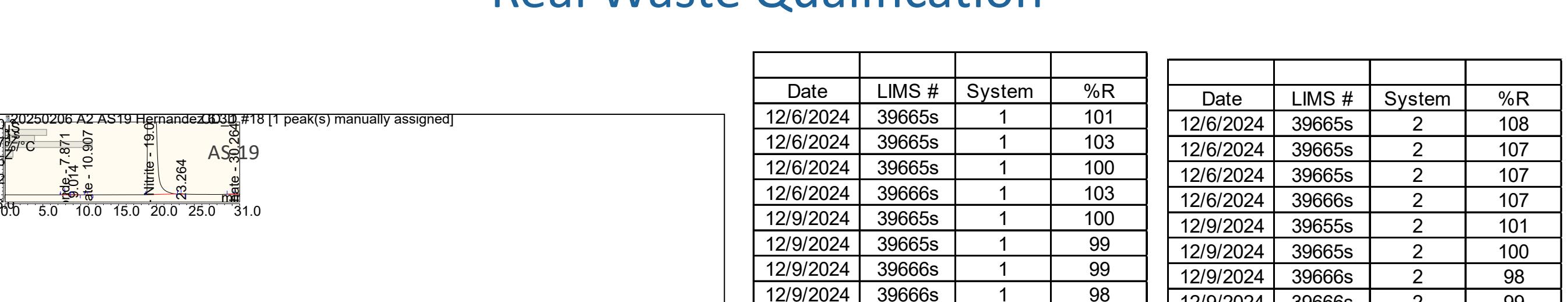
Contained Ion Chromatography



Simulated Waste Qualification

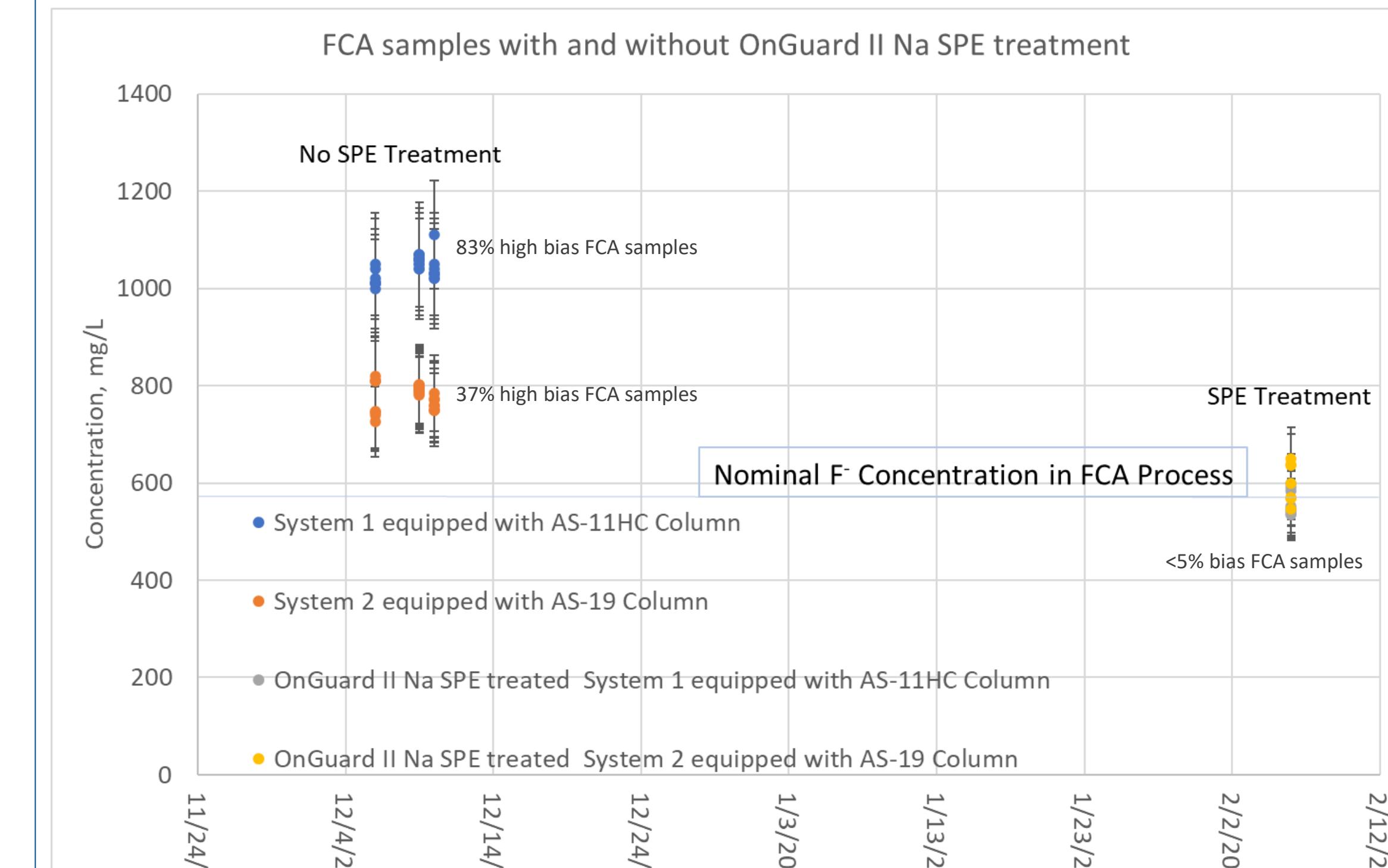
FCA Simulated Waste Initial Testing		2 Sigma Limits (Case I)		% Difference		
Spikes, mg/L	Target	Measured	Uncertainty 1 Sigma	Lower Limit	Upper Limit	Target vs Measured
High F	1130	1010	10%	907	1360	10.6%
Low F	524	500	10%	419	629	4.60%

Real Waste Qualification



SPE treated				SPE treated			
Date	LIMS #	System	%R	Date	LIMS #	System	%R
2/6/2025	39665s	1	102	2/6/2025	39665s	2	108
2/6/2025	39665s	1	100	2/6/2025	39665s	2	107
2/6/2025	39665s	1	103	2/6/2025	39666s	2	107
2/9/2024	39665s	1	100	12/9/2024	39656s	2	101
2/9/2024	39665s	1	99	12/9/2024	39656s	2	100
2/9/2024	39665s	1	99	12/9/2024	39666s	2	98
2/9/2024	39665s	1	98	12/9/2024	39666s	2	99
12/9/2024	39665s	1	98	12/9/2024	39666s	2	100
12/9/2024	39665s	1	97	12/9/2024	39666s	2	100
12/10/2024	39655s	1	101	12/10/2024	39655s	2	99
12/10/2024	39655s	1	99	12/10/2024	39665s	2	97
12/10/2024	39666s	1	109	12/10/2024	39666s	2	99
12/10/2024	39666s	1	102	12/10/2024	39666s	2	98

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	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).

1. 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.

2. 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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