

## **Inorganic and Radiochemical Analysis of AW-101 and AN-107 “Diluted Feed” Materials**

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September 1999

Prepared for BNFL, Inc. under  
Project 29952/29953  
Battelle, Richland, Washington, 99352

PNWD-2463

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## Summary

Thirty jars of waste material from tank AW-101 and seventeen jars of waste material from tank AN-107 were received by Battelle. The contents of all jars of AW-101 were mixed to provide a single composite, as were the contents of all jars of AN-107. Each composite was sub-sampled for organic, radiochemical and inorganic regulatory analyses: reports BNFL-RPT-001 (PNWD-2461) and BNFL-RPT-008 (PNWD-2462). Following sub-sampling for regulatory analyses, each composite was diluted to specific sodium molar concentrations to provide the diluted feed materials for all subsequent process testing and characterization.

The characterization analyses of the diluted feed material for AW-101 and AN-107 include:

- Inductively-coupled plasma spectrometry for Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, U, Zn, and Zr
- Radiochemical analyses for total alpha and total beta activity, Am-241, Cs-137, Cm-243+244, Eu-154, Eu-155, Sr-90
- Kinetic Phosphorescence for total uranium
- Ion chromatography for  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$
- Inductively-coupled plasma mass spectrometry for Tc-99
- Free hydroxide determination
- Total inorganic and organic carbon
- pH measurements

Besides the analytes of interest above that are specified by the governing test plan, As, Ce, Cs, Nd, P, Sr, Y, Co-60, Cs-134, Pu-238, Pu-239+240, Cm-242, Br,  $\text{NO}_2^-$ , and  $\text{C}_2\text{O}_4^{2-}$  were measured and the results included in this report for information only.

Only a limited quantity of diluted feed sample for either AW-101 or AN-107 was available for characterization analysis. Due to the very low solids content of the diluted feeds, the entire suite of analyses for the solids was conducted on less than four grams of wet solids material. From such small quantities, representative sub-sampling is very difficult; therefore, the results are considered a "best effort". However, with the exception of only a few analytes, the characterization results for both the supernatant and solids met or exceeded the quality control requirements established by the governing quality assurance plan, and met or exceeded the minimum reportable quantity requirements specified by BNFL.

## Terms and Abbreviations

ALARA	as low as reasonably achievable
BNFL	BNFL, Inc; subsidiary of British Nuclear Fuels, Ltd.
EQL	estimated quantitation level
GEA	gamma energy analysis
HLRF	High Level Radiation Facility
IC	ion chromatography
ICP	inductively coupled plasma/atomic emission spectrometry
ICP/MS	inductively coupled plasma/mass spectrometry
MDL	method detection limit
MRQ	minimum reportable quantity
QA	quality assurance
QC	quality control
RPD	relative percent difference
SAL	Shielded Analytical Laboratory
TC	total carbon
TIC	total inorganic carbon
TIMS	thermal ionization mass spectrometry
TOC	total organic carbon
TRU	transuranic

## Units

°C	degrees Centigrade
g	gram
g/mL	gram per milliliter
μg/g - μg/mL	microgram per gram / microgram per milliliter
μCi/g - μCi/mL	microcurie per gram / microcurie per milliliter
mL	milliliter
mmole/mL	millimole per milliliter
Vol%	volume percent
Wt%	weight percent

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## 1.0 Introduction

This report presents the inorganic and radiochemical analytical results for AW-101 and AN-107 diluted feed materials. The analyses were conducted in support of the BNFL Proposal No. 29952/29953 Task 2.1. The inorganic and radiochemical analysis results obtained from the diluted feed materials are used to provide initial characterization information for subsequent process testing. Quality Assurance (QA) Plan MCS-033 provides the operational and quality control protocols for the analytical activities.

The inorganic and radiochemical analytes of interest and recommended methods are defined in the BNFL Proposal No. 29552/29953 and Test Plan BNFL-29953-6 Revision 0. All analytes of interest defined by these documents are reported, with estimated method detection limits (MDL) provided where analytes of interest are not detected. Per the QA Plan analysis protocols, process blanks, samples, duplicates, blank spikes (or lab control standards) and matrix spikes (or post spikes) were analyzed, as appropriate. This report presents only the results for the process blanks, samples, and duplicates. Recoveries for quality control samples (such as matrix spikes and blank spikes) are discussed in this report and evaluated for effect on reported results if they fail to meet the acceptance criteria of QA Plan MCS-033. Matrix spike, post spike, and lab control standard/blank spike results, as well as calibration verification standards data, are included in the Project File 29953 (Record Inventory and Disposition Schedule, Technical Support to BNFL for Phase 1B, T2.1).

The AW-101 and AN-107 as received materials were diluted per Test Plan BNFL-29953-1, Revision 0. The resulting diluted feeds were sub-sampled for physical testing, ion exchange batch contact testing, solubility testing, caustic leaching testing, and radiochemical and inorganic characterization per Test Plan BNFL-29953-6. Figures 1.1 and 1.2 provide sample flow diagrams for the preparation of the AW-101 and AN-107 diluted feed materials, respectively.

The AN-107 and AW-101 diluted feeds were prepared in separate four liter glass kettles. A bladed impeller was used to homogenize the material. While the diluted feeds were being stirred, a 1/4-inch (outside diameter) stainless steel probe was used to vacuum transfer sub-samples of the homogenized slurry to 125 ml glass jars. This sampling method was shown under Test Plan 29953-1 to provide sub-samples with representative solids content for the "as received" tank materials. Under Test Plan 29953-1, a minimum of five as received sub-samples, with a volume of approximately 125 ml each, were collected using this technique from different locations in the kettle during mixing. These sub-samples were then settled for approximately 12 hours. After this settling period all sub-samples had a similar volume of settled solids (i.e., 19-21% for AW-101 and 18-22% for AN-107). A similar comparison was not made for the sub-samples of diluted feed since these sub-samples were small (generally less than 70 ml) making an accurate measurement of the settled solids volume difficult.

The diluted feed sub-sampling for radiochemical and inorganic characterization was performed in the High Level Radiation Facility (HLRF). For each diluted feed, one 125-mL glass jar containing 60 to 70 mL of diluted feed slurry was sub-sampled and transferred to the Shielded Analytical Laboratory (SAL) hot cells for analysis preparations and distributions.



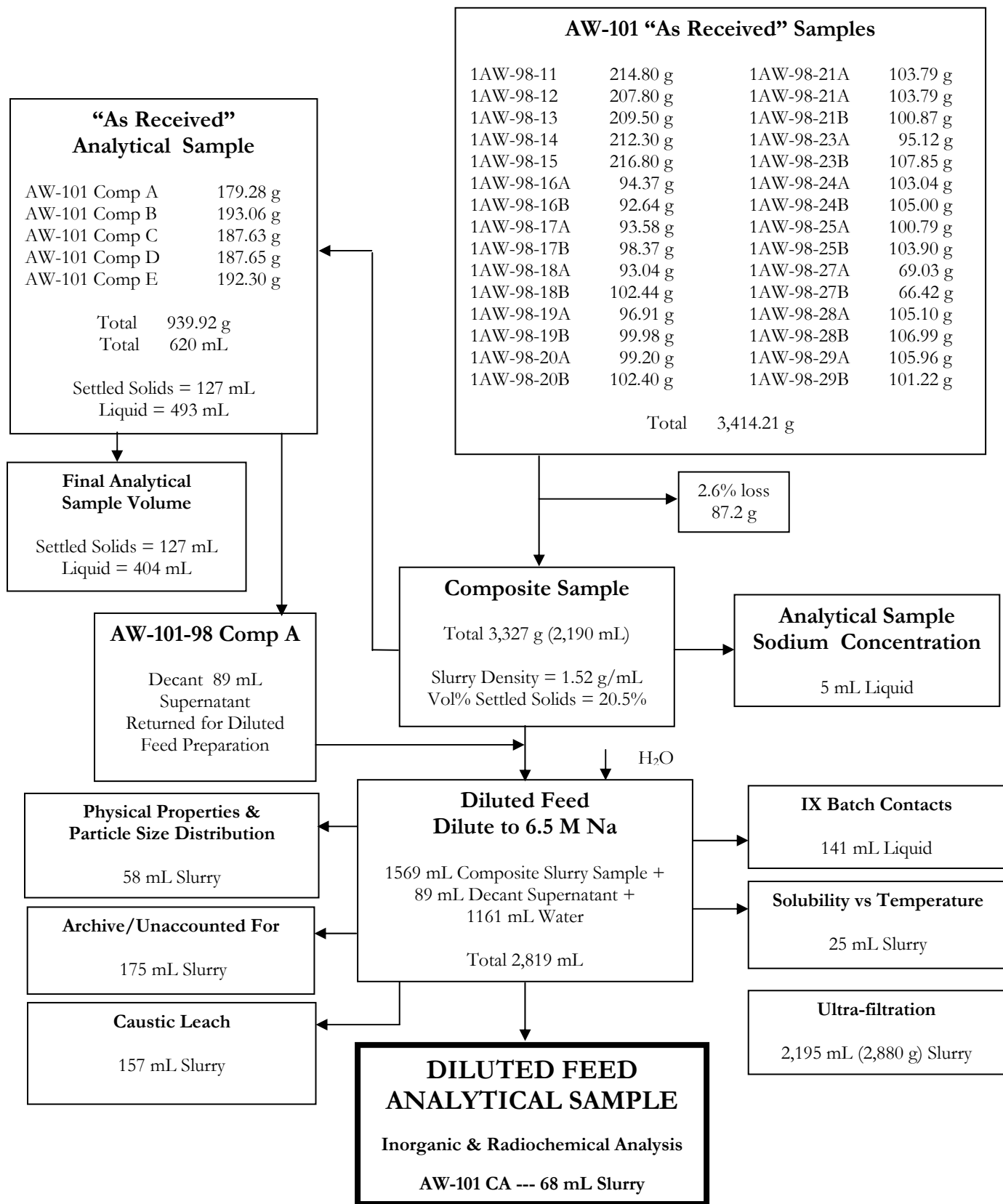


Figure 1.1 Flow Diagram for AW-101 Diluted Feed Analytical Sample

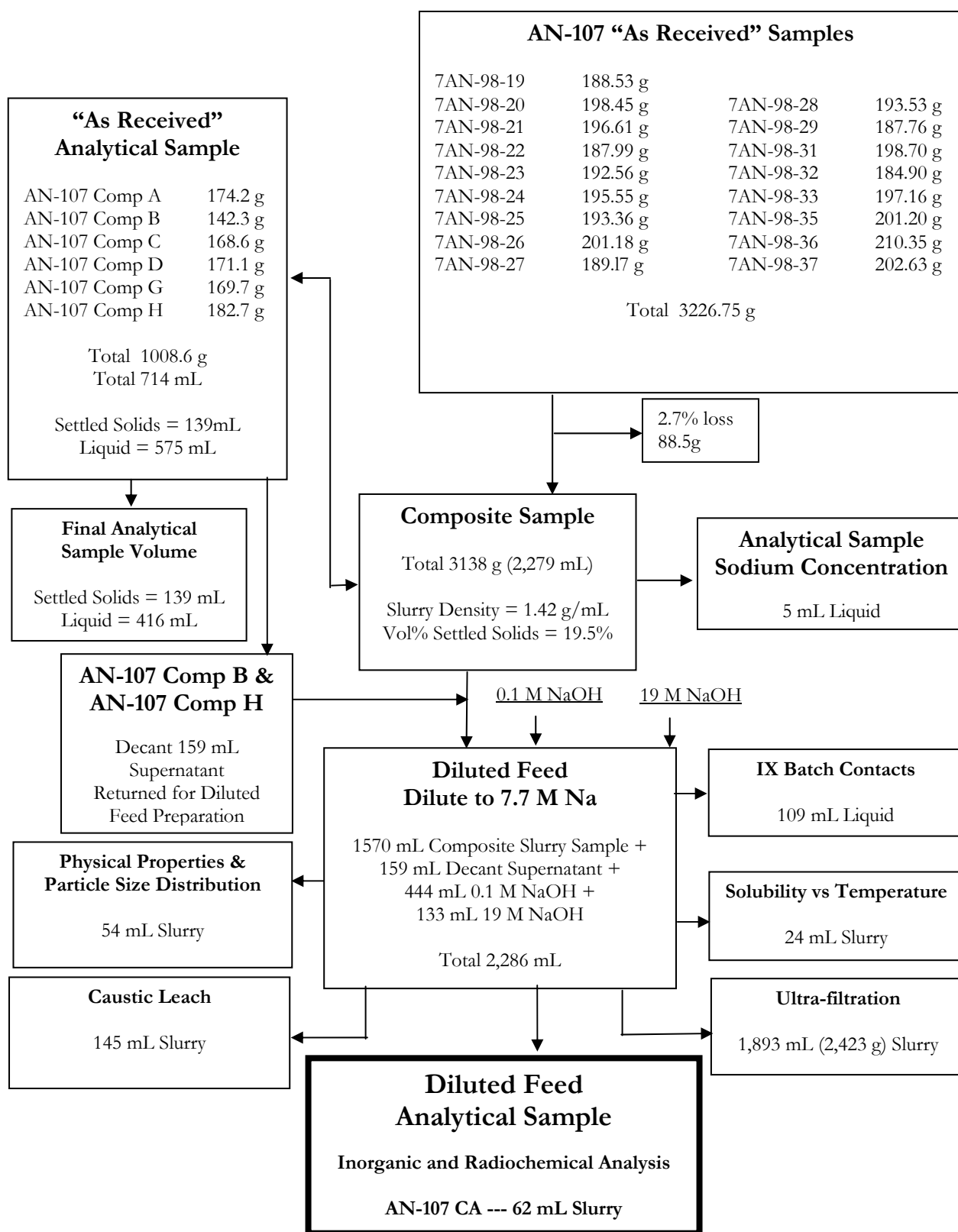


Figure 1.2 Flow Diagram for AN-107 Diluted Feed Analytical Sample

## 2.0 Sample Preparation

### 2.1 Phase Separation

The AW-101 and AN-107 diluted feed sub-samples were phase separated in the SAL so that inorganic and radiochemical analyses could be performed on each phase (i.e., supernatant and solids). The phase separation was performed by centrifuging and decanting the supernatant, since previous experience indicated that filtering of the samples would be extremely difficult. Each sample was centrifuged in its original jar, and following centrifuging, the supernatant was decanted to pre-labeled teflon bottles (i.e., the wet solids remained in the original jar). Table 2.1 details the quantity of supernatant and centrifuged wet solids collected from each sub-sample. There were insufficient solids from either diluted feed to perform weight percent solids (dried at 105 °C) measurements. Table 5.2 of Report BNFL-RPT-002, Ultrafiltration and Characterization of AW-101 Supernatant and Entrained Solids, presents additional weight percent and volume percent data for AW-101. Additional data for AN-107 is not yet available.

**Table 2.1 Supernatant and Solids Masses after Phase Separation of Diluted Feed Materials**

Jar/Bottle ID <sup>(1)</sup>	Lab ID	Total Mass (g) <sup>(2)</sup>	Supernatant		Centrifuged Wet Solids	
			Mass (g)	Wt%	Mass (g)	Wt%
AW-101 CA	99-0644/0646	89.19	86.92	97.5%	2.27	2.5%
AN-107 CA	99-0645/0647	81.81	77.61	94.9%	4.20	5.1%

<sup>(1)</sup> Jar/Bottle ID: CA = for Chemical Analysis Diluted Feed

<sup>(2)</sup> Total mass remaining following phase separation activities in the SAL.

### 2.2 Supernatant Density Measurements

Due to the viscous nature of the diluted feed supernatants, all supernatant samples were processed by weight (i.e., analytical sub-samples for processing were taken by weight instead of by volume). The density of each diluted feed supernatant was determined using method PNL-ALO-501. The resulting densities are used to convert reported supernatant results from mass/mass to mass/volume. Table 2.2 provides the density results obtained on AW-101 and AN-107 diluted feed supernatants following phase separation. Table 5.1 of Report BNFL-RPT-002, Ultrafiltration and Characterization of AW-101 Supernatant and Entrained Solids, present additional density data for AW-101. Additional data for AN-107 is not yet available.

**Table 2.2 Density Results for AW-101 and AN-107 Diluted Feed Supernatants**

Jar/Bottle ID <sup>(1)</sup>	Lab ID	Sample Density (g/mL)	Duplicate Density (g/mL)	Average Density (g/mL)
AW-101 CA	99-0644	1.318	1.323	1.32
AN-107 CA	99-0645	1.368	1.360	1.36

<sup>(1)</sup> Jar/Bottle ID: CA = for Chemical Analysis Dilute Feed

### 2.3 Supernatant Sample Preparations

Diluted feed supernatant samples were prepared for metals analysis (by inductively coupled plasma spectrometry [ICP]), radiochemical analysis, Tc-99 (by inductively coupled plasma – mass spectrometry [ICP/MS]), and cesium isotopic (by thermal ionization mass spectrometry [TIMS]) by

procedure PNL-ALO-128 ( $\text{HNO}_3$ -HCl acid digestion). The resulting digestion solutions from AW-101 were clear and those from AN-107 were slightly colored (brown). The acid digestion solutions from both supernatants had no visible residue or precipitate. All other analyses, except pH, were performed on a prepared 10-fold water dilution of the supernatant. Measurement of pH was performed directly on the supernatants.

## **2.4 Solids Sample Preparations**

Three preparative methods, PNL-ALO-129 ( $\text{HNO}_3$ -HCl acid digestion), PNL-ALO-115 (KOH- $\text{KNO}_3$  fusion), and PNL-ALO-103 (water leach), were performed on the wet centrifuged solids (including interstitial liquid) to provide analysis solutions for determining the analytes of interest. The acid digestion and fusion preparations were analyzed for metals by ICP, and the fusion preparations were used for all radiochemical analyses and Tc-99 by ICP/MS). All acid digestion and fusion preparations produced clear solutions with no visible residue.

Aliquots from the water leaching of the solids were analyzed for soluble anions by ion chromatography (after filtering) and cesium isotopic by TIMS. The carbon analyses (total organic carbon and total inorganic carbon) were performed directly on solids samples.

### 3.0 Analysis Results for Analytes of Interest

Tables 3.1 through 3.4 provide the results for all inorganic and radiochemical analyses performed on the AW-101 and AN-107 diluted feed materials. Results for samples and duplicates (where analyzed) are reported. Although the supernatant samples were processed by weight, the density of the supernatants has been used to provide the results in µg/mL or µCi/mL, as appropriate. Solids are reported in µg/g or µCi/g, as appropriate.

**Table 3.1 AW-101 Diluted Feed --- ICP Results**

<b>Tank Material</b> <b>Matrix</b> <b>Dissolution</b> <b>Lab ID</b> <b>Sample ID</b> <b>Units</b>	AW 101 Diluted Feed <sup>(1)</sup>									
	Supernatant					Centrifuged Wet Solids				
	Acid Digest				<sup>(3)</sup>	KOH-KNO <sub>3</sub> Fusion				Acid Digest <sup>(2)</sup>
	99-0648-pb	99-0644	99-0644-d			99-0646-pb	99-0646	99-0646-d		99-0646-pb 99-0646
	Proc Blnk	Sample	Duplicate	RPD		Proc Blnk	Sample	Duplicate	RPD	Proc Blnk Sample
	µg/mL	µg/mL	µg/mL	(%)		µg/g	µg/g	µg/g	(%)	µg/g µg/g
<b>BNFL List</b>										
<b>Ag</b>	< 3	< 3	< 3			< 24	[90]	[89]		< 4 81
<b>Al</b>	< 7	17,800	14,900	18		[91]	14,700	14,300	3	< 10 14,500
<b>Ba</b>	< 1	< 1	< 1			< 9	[25]	[25]		< 2 24
<b>Ca</b>	< 31	< 32	< 32			< 235	[1,700]	[1,700]		< 41 1,160
<b>Cd</b>	< 2	< 2	< 2			< 14	[34]	[35]		< 2 32
<b>Co</b>	< 6	< 6	< 6			< 47	< 48	< 44		< 8 < 10
<b>Cr</b>	< 2	61.1	51.1	18		< 19	1,640	1,600	2	< 3 1,610
<b>Cu</b>	< 3	< 3	< 3			< 24	< 24	< 22		< 4 [10]
<b>Fe</b>	< 3	[5.1]	[4.3]			[91]	1,350	1,430	6	< 4 1,430
<b>K</b>	< 247	25,200	20,800	19		n/a	n/a	n/a		< 326 17,200
<b>La</b>	< 6	< 6	< 6			< 47	< 48	< 44		< 8 [28]
<b>Mg</b>	< 12	< 13	< 13			< 94	[260]	[250]		< 16 314
<b>Mn</b>	< 6	< 6	< 6			[56]	1,390	1,440	4	< 8 1,300
<b>Mo</b>	< 6	< 6	< 6			< 47	< 48	< 44		< 8 < 10
<b>Na</b>	[41]	163,000	134,000	20		[1,300]	128,000	127,000	1	[140] 128,000
<b>Ni</b>	< 4	[5.4]	[4.2]			n/a	n/a	n/a		< 5 215
<b>Pb</b>	< 12	[45]	[37]			< 94	[120]	[120]		< 16 [119]
<b>Si</b>	[72]	[145]	[115]			< 470	[2,200]	[2,200]		[230] 2,300
<b>Ti</b>	< 3	< 3	< 3			< 24	< 24	< 22		< 4 [7.6]
<b>U</b>	< 247	< 257	< 259			< 1,882	[5,800]	[5,700]		< 326 5,400
<b>Zn</b>	[7.6]	[14]	[13]			< 47	< 48	< 44		< 8 [16]
<b>Zr</b>	< 6	[8.2]	[6.9]			< 47	[200]	[240]		< 8 351
<b>Other Analytes Detected</b>										
<b>As</b>	< 31	[104]	[84]			< 235	< 239	< 219		< 41 [79]
<b>Nd</b>	< 12	< 13	< 13			< 94	< 96	< 87		< 16 [29]
<b>P</b>	< 12	353	293	19		< 94	[360]	[410]		< 16 501
<b>Sr</b>	< 2	< 2	< 2			< 14	[24]	[24]		< 2 [17]
(1) Overall error for reported results is estimated to be within ±15%; however, results in brackets "[ ]" are less than the estimated quantitation level (i.e., 10-times MDL listed in Table 5.1) and error is anticipated to be greater than ±15%. (2) Solids acid digestions results normalized to KOH-KNO <sub>3</sub> fusion sodium results. See narrative 4.1. (3) RPD only calculated when both sample and duplicate exceed estimated quantitation level.										

**Table 3.2 AN-107 Diluted Feed --- ICP Results**

<i>Tank Material</i>	AN 107 Diluted Feed <sup>(1)</sup>											
<i>Matrix</i>	Supernatant				Centrifuged Wet Solids							
<i>Dissolution</i>	Acid Digest				KOH-KNO <sub>3</sub> Fusion				Acid Digest <sup>(2)</sup>			
<i>Lab ID</i>	99-0644-pb	99-0645	99-0645-d	<sup>(3)</sup>	99-0646-pb	99-0647	99-0647-d	<sup>(3)</sup>	99-0646-pb	99-0647	99-0647-d	<sup>(3)</sup>
<i>Sample ID</i>	ProcBlank	Sample	Duplicate	RPD	ProcBlank	Sample	Duplicate	RPD	ProcBlank	Sample	Duplicate	RPD
<i>Units</i>	µg/mL	µg/mL	µg/mL	(%)	µg/g	µg/g	µg/g	(%)	µg/g	µg/g	µg/g	(%)
<b>BNFL List</b>												
Ag	< 3	< 3	< 3		< 24	< 23	< 25		< 4	< 3	< 3	
Al	< 7	4,040	3,820	6	[91]	7,550	7,450	1	< 10	7,140	7,650	7
Ba	< 1	[4.1]	[4.0]		< 9	[44]	[44]		< 2	45	46	2
Ca	[52]	461	416	10	< 235	[780]	[520]		< 41	359	377	5
Cd	< 2	48	46	5	< 14	[37]	[36]		< 2	33	34	3
Co	< 6	< 4	< 4		< 47	< 46	< 51		< 8	< 6	< 7	
Cr	< 2	149	142	5	< 19	725	718	1	< 3	697	723	4
Cu	< 3	[22]	[20]		< 24	< 23	< 25		< 4	[19]	[20]	
Fe	[5.6]	1,170	1,110	5	[91]	9,960	8,670	14	< 4	8,260	8,690	5
K	< 234	[1,300]	[1,240]		n/a	n/a	n/a		< 326	[670]	[647]	
La	< 6	[23]	[22]		< 47	[65]	[60]		< 8	108	112	4
Mg	< 12	< 12	< 12		< 94	< 93	< 102		< 16	[30]	[30]	
Mn	< 6	108	106	2	[56]	4,910	5,130	4	< 8	4,920	4,989	1
Mo	< 6	< 6	< 6		< 47	< 46	< 51		< 8	< 6	< 7	
Na	[34]	176,000	171,000	3	[1,300]	134,000	139,000	4	[140]	134,000	139,000	4
Ni	< 4	402	382	5	n/a	n/a	n/a		< 5	269	285	6
Pb	< 12	263	249	5	< 94	[580]	[640]		< 16	755	784	4
Si	< 59	< 45	< 44		< 470	< 463	< 509		[230]	[264]	[419]	
Ti	< 3	< 3	< 3		< 24	< 23	< 25		< 4	[4.5]	[4.8]	
U	< 234	< 244	< 241		< 1,882	< 1,851	< 2,036		< 326	< 231	< 279	
Zn	[11]	[22]	[16]		< 47	< 46	< 51		< 8	64	[67]	
Zr	< 6	[42]	[44]		< 47	[110]	[92]		< 8	197	206	4
<b>Other Analytes Detected</b>												
As	< 29	[98]	[93]		< 235	< 231	< 254		< 41	[77]	[83]	
Ce	< 23	[27]	[26]		< 188	[190]	< 204		< 33	[212]	[219]	
Nd	< 12	[73]	[68]		< 94	[210]	[190]		< 16	311	326	5
P	< 12	505	488	3	< 94	[500]	[520]		< 16	418	436	4
Sr	< 2	[2.7]	[2.5]		< 14	< 14	< 15		< 2	[6.2]	[6.3]	
Y	< 6	[11]	[11]		< 47	< 46	< 51		< 8	[31]	[32]	
<p>(1) Overall error for reported results is estimated to be within ±15%; however results in brackets “[ ]” are less than the estimated quantitation level (i.e., 10-times MDL listed in Table 5.1) and error is anticipated to be greater than ±15%..</p> <p>(2) Solids acid digestion results normalized to KOH-KNO<sub>3</sub> fusion sodium results. See narrative 4.1.</p> <p>(3) RPD only calculated when both sample and duplicate exceed estimated quantitation level.</p>												

**Table 3.3 AW-101 & AN-107 Diluted Feed --- Radiochemical Results**

Tank Material Matrix/Dissolution Lab ID Sample ID Units (%Error ±1σ)	AW-101 Diluted Feed													
	Supernatant – Acid Digest							Centrifuged Wet Solids -- KOH-KNO <sub>3</sub> Fusion <sup>(1)</sup>						
	99-0648-pb		99-0644		99-0644-d		<sup>(2)</sup> RPD (%)	99-0646-pb		99-0646		99-0646-d		<sup>(2)</sup> RPD (%)
	ProcBlnk	Sample	Sample	Duplicate	ProcBlnk	Sample		Duplicate						
μCi/mL	%Err	μCi/mL	%Err	μCi/mL	%Err	μCi/g	%Err	μCi/g	%Err	μCi/g	%Err			
Co-60 (GEA) <sup>(3)</sup>	< 3.E-4		< 1.E-2		< 1.E-2			< 5.E-2		< 7.E-2		< 7.E-2		
Sr-90	1.69E-2	21	< 5.E-1		< 5.E-1			1.60E-2	12	1.41E+2	4	1.60E+2	4	13
Cs-134 (GEA) <sup>(3)</sup>	< 3.E-4		5.60E-2	15	5.64E-2	12		< 5.E-2		< 8.E-2		< 6.E-2		
Cs-137 (GEA)	8.67E-4	13	2.50E+2	2	2.10E+2	2	18	2.25E-1	12	1.96E+2	2	1.87E+2	2	5
Eu-154 (GEA)	< 7.E-4		< 4.E-2		< 4.E-2			< 2.E-1		< 2.E-1		< 2.E-1		
Eu-155 (GEA)	< 7.E-4		< 4.E-1		< 4.E-1			< 2.E-1		< 5.E-1		< 5.E-1		
Pu-238 <sup>(3)</sup>	7.08E-6	15	< 3.E-5		< 5.E-5			6.36E-5	30	3.43E-2	9	4.61E-2	7	29
Pu-239+Pu-240 <sup>(3)</sup>	2.49E-6	29	1.65E-4	15	1.37E-4	13		7.42E-5	19	2.48E-1	4	2.56E-1	4	3
Am-241 (GEA)	< 7.E-4		< 4.E-1		< 4.E-1			< 2.E-1		< 5.E-1		< 5.E-1		
Am-241 (AEA)	9.12E-6	19	1.16E-4	13	8.94E-5	14		< 6.E-7		2.53E-1	5	2.43E-1	5	4
Cm-242 <sup>(3)</sup>	< 1.E-6		< 5.E-6		< 4.E-6			< 5.E-8		< 6.E-4		4.84E-4	45	
Cm-243+Cm-244	9.96E-6	18	2.41E-5	31	< 9.E-6			4.93E-7	23	8.45E-3	14	9.49E-3	12	
Total Beta	4.48E-2	3	2.75E+2	3	2.25E+2	3	20	5.03E-2	7	4.80E+2	4	4.78E+2	4	0
Total Alpha	< 3.E-4		< 1.E-2		< 1.E-2			<2.E-3		4.56E-1	9	5.66E-1	7	22
Alpha Sum <sup>(4)</sup>	2.17E-5	10	3.04E-4	10	2.27E-4	10	29	1.38E-4	17	5.44E-1	3	5.55E-1	3	2
	μg/mL	%Err	μg/mL	%Err	μg/mL	%Err		μg/g	%Err	μg/g	%Err	μg/g	%Err	
Total Cs <sup>(3)</sup>	--	--	1.17E+1	2	9.80E+0	2	18	--	--	9.17E+0	2	--	--	
Total U	2.20E-2	2	3.32E+0	2	3.12E+0	2	6	2.86E-1	2	5.42E+3	4	5.46E+3	4	1

Tank Material Matrix/Dissolution Lab ID Sample ID Units (%Error ±1σ)	AN-107 Diluted Feed													
	Supernatant – Acid Digest							Centrifuged Wet Solids -- KOH-KNO <sub>3</sub> Fusion <sup>(1)</sup>						
	99-0644-pb		99-0645		99-0645-d		<sup>(2)</sup> RPD (%)	99-0646-pb		99-0647		99-0647-d		<sup>(2)</sup> RPD (%)
	ProcBlnk	Sample	Sample	Duplicate	ProcBlnk	Sample		Duplicate						
μCi/mL	%Err	μCi/mL	%Err	μCi/mL	%Err	μCi/g	%Err	μCi/g	%Err	μCi/g	%Err			
Co-60 (GEA) <sup>(3)</sup>	< 3.E-4		1.11E-1	7	1.15E-1	7	4	< 5.E-2		< 9.E-2		< 9.E-2		
Sr-90	< 4.E-3		7.72E+1	5	7.46E+1	5	4	1.60E-2	12	1.90E+2	4	1.93E+2	4	2
Cs-134 (GEA) <sup>(3)</sup>	< 3.E-4		< 3.E-2		< 3.E-2			< 5.E-2		< 8.E-2		< 9.E-2		
Cs-137 (GEA)	4.71E-4	27	2.61E+2	2	2.50E+2	2	4	2.25E-1	12	1.65E+2	2	1.65E+2	2	0
Eu-154 (GEA)	< 5.E-4		6.20E-1	4	6.03E-1	4	3	< 2.E-1		1.44E+0	5	1.17E+0	7	21
Eu-155 (GEA)	< 7.E-4		4.50E-1	16	2.61E-1	25		< 2.E-1		9.87E-1	14	6.49E-1	21	
Pu-238 <sup>(3)</sup>	7.57E-6	21	7.02E-3	15	8.36E-3	9		6.36E-5	30	5.01E-2	7	3.75E-2	9	29
Pu-239+Pu-240 <sup>(3)</sup>	4.06E-6	31	3.08E-2	7	3.20E-2	5	4	7.42E-5	19	1.68E-1	5	1.33E-1	5	23
Am-241 (GEA)	< 5.E-4		5.66E-1	23	2.30E-1	50		< 2.E-1		2.49E+0	12	1.68E+0	18	
Am-241 (AEA)	6.61E-6	18	3.93E-1	5	3.64E-1	5	8	< 6.E-7		1.67E+0	5	1.27E+0	5	4
Cm-242 <sup>(3)</sup>	< 4.E-7		1.60E-3	21	1.28E-3	28		< 5.E-8		4.18E-3	16	4.24E-3	11	
Cm-243+Cm-244	3.43E-6	25	1.19E-2	9	1.26E-2	10	6	4.93E-7	23	3.67E-2	7	2.52E-2	23	
Total Beta	1.40E-2	3	4.66E+2	3	4.34E+2	3	7	5.03E-2	7	5.20E+2	4	5.09E+2	4	2
Total Alpha <sup>(4)</sup>	< 1.E-4		4.43E-1	3	4.50E-1	3	2	<2.E-3		2.14E+0	4	1.52E+0	5	34
Alpha Sum	1.58E-5	12	4.45E-1	4	4.19E-1	4	6	1.38E-4	17	1.93E+0	4	1.47E+0	4	27
	μg/mL	%Err	μg/mL	%Err	μg/mL	%Err		μg/g	%Err	μg/g	%Err	μg/g	%Err	
Total Cs <sup>(3)</sup>	--	--	1.23E+1	2	1.17E+1	2	4	--	--	7.72E+0	2%	7.63E+0	2	1
Total U	9.84E-3	2	7.44E+1	2	7.18E+1	2	4	2.86E-1	2	1.03E+2	2%	1.03E+2	2	0

(1) Total cesium performed by TIMS from water leach of solids, not from KOH-KNO<sub>3</sub> fusion.

(2) RPD only calculated when both sample and duplicate have error uncertainties <10%.

(3) Not an analyte of interest specified in Test Plan BNFL-29953-6; included for information only.

(4) Alpha Sum equals the  $\mu\text{Ci/mL}$  or  $\mu\text{Ci/g}$  summation of Pu-238, Pu-239+240, Am-241, Cm-242, and Cm-243+244.

**Table 3.4 AW-101 & AN-107 Diluted Feed --Tc-99, TOC/TIC, IC, OH, and pH Results**

Tank Material  Matrix  Lab ID  Sample ID  Units	AW-101 Diluted Feed									
	Supernatant					Centrifuged Wet Solids				
	Type of Prep	99-0648-pb	99-0644	99-0644-d	(1)	Type of Prep	99-0646-pb	99-0646	99-0646-d	(1)
		ProcBlnk	Sample	Duplicate	RPD		ProcBlnk	Sample	Duplicate	RPD
		µg/mL (2)	µg/mL (2)	µg/mL (2)	(%)		µg/g (2)	µg/g (2)	µg/g (2)	(%)
Tc-99 (ICP/MS)	Acid Digest	<0.02 (<3E-4)	5.88 (1.0E-1)	5.12 (8.7E-2)	14	Fusion	0.1 (1.7E-3)	20.9 (3.5E-1)	20.9 (3.5E-1)	0
Tc-99 (ICP/MS)	Direct/Dilution	n/a	5.20 (8.8E-2)	5.24 (8.9E-2)	1	n/a	n/a	n/a	n/a	
TIC	Hot Persulfate	73	2,190	2,120	3	Hot Persulfate	n/a	27,500	n/m	
TOC	Hot Persulfate	<85	1,460	1,660		Hot Persulfate	n/a	20,100	n/m	
TC (sum)		73	3,650	3,780	4		n/a	47,600		
Fluoride	Direct/Dilution	<21	1000	660	40	Water Leach	<120	1,600	n/m	
Chloride	Direct/Dilution	<21	3,300	3,300	1	Water Leach	<120	2,700	n/m	
Nitrite (3)	Direct/Dilution	<42	63,500	62,000	2	Water Leach	<240	41,500	n/m	
Bromide (3)	Direct/Dilution	<21	<400	<380		Water Leach	<120	<1200	n/m	
Nitrate	Direct/Dilution	<42	125,000	121,000	3	Water Leach	<240	80,900	n/m	
Phosphate	Direct/Dilution	<42	2,000	1,900	3	Water Leach	<240	<2300	n/m	
Sulfate	Direct/Dilution	<42	1,900	1,800	4	Water Leach	<240	<2300	n/m	
Oxalate (3)	Direct/Dilution	<41	<800	<760		Water Leach	<240	42,000	n/m	
		mmole/mL	mmole/mL	mmole/mL			mmole/mL	mmole/m	mmole/m	
Hydroxide	Direct/Dilution	(4)	3.02	3.09	2	n/m	n/m	n/m	n/m	
		pH	pH	pH			pH	pH	pH	
pH	Direct	n/m	13.58	13.62	0	n/m	n/m	n/m	n/m	
Tank Material  Matrix  Lab ID  Sample ID  Units	AN-107 Diluted Feed									
	Supernatant					Centrifuged Wet Solids				
	Type of Prep	99-0644-pb	99-0645	99-0645-d	(1)	Type of Prep	99-0646-pb	99-0647	99-0647-d	(1)
		ProcBlnk	Sample	Duplicate	RPD		ProcBlnk	Sample	Duplicate	RPD
		µg/mL (2)	µg/mL (2)	µg/mL (2)	(%)		µg/g (2)	µg/g (2)	µg/g (2)	(%)
Tc-99 (ICP/MS)	Acid Digest	<0.02 (<3E-4)	4.40 (7.5E-2)	4.23 (7.2E-2)	4	Fusion	0.1 (1.7E-3)	3.62 (6.2E-2)	3.92 (6.7E-2)	8
Tc-99 (ICP/MS)	Direct/Dilution	<0.05 (<9E-4)	4.09 (7.0E-2)	3.98 (6.8E-2)	3	n/a	n/a	n/a	n/a	
TIC	Direct/Dilution	76	16,400	16,200	1	Direct	n/a	18,200	17,500	4
TOC	Direct/Dilution	<85	30,000	29,800	0	Direct	n/a	31,100	32,900	1
TC (sum)	Direct/Dilution	76	46,400	46,000	1	Direct	n/a	51,200	50,400	2
Fluoride	Direct/Dilution	<17	6,300	6,400	2	Water Leach	<120	4,500	4,300	3
Chloride	Direct/Dilution	<17	1,400	1,400	2	Water Leach	<120	<1200	<1200	
Nitrite (3)	Direct/Dilution	<35	51,100	51,600	1	Water Leach	<240	30,900	31,200	1
Bromide (3)	Direct/Dilution	<17	<490	<480		Water Leach	<120	<1200	<1200	
Nitrate	Direct/Dilution	<35	161,000	161,000	0	Water Leach	<240	111,000	111,000	0
Phosphate	Direct/Dilution	<35	3,000	3,000	2	Water Leach	<240	<2400	<2400	
Sulfate	Direct/Dilution	<35	7,900	7,400	6	Water Leach	<240	7,000	7,000	1
Oxalate (3)	Direct/Dilution	<34	1,300	1,300	1	Water Leach	<240	32,200	32,000	1
		mmole/mL	mmole/mL	mmole/mL			mmole/mL	mmole/m	mmole/m	
Hydroxide	Direct/Dilution	(4)	0.722	0.712	1	n/m	n/m	n/m	n/m	
		pH	pH	pH			pH	pH	pH	
pH	Direct	n/m	13.33	13.31	0	n/m	n/m	n/m	n/m	

(1) RPD only calculated when sample and duplicate results above threshold for method's RPD calculation. (Calculated prior to rounding)

(2) Value in parentheses for Tc-99 are in units of µCi/mL for supernatants and µCi/g for solids.

(3) Not an analyte of interest specified in Test Plan BNFL-29953-6; included for information only.

(4) No titration inflection point detected; no hydroxide calculated.

n/a = not applicable to method; n/m = not measured due to applicability of method OR availability of sample material



## 4.0 Quality Control and Data Evaluation

General Comment: Due to a mislabeling error (reported via Quality Problem Report 99BNFL-02), the AW-101 diluted feed and AN-107 as received supernatants were processed together, and AW-101 as received and AN-107 diluted feed supernatants were processed together. This mislabeling error applied to the acid digestion, dilutions, and direct sub-sampling of each of the supernatants. The error was detected and corrected prior to the analysis of diluted feed supernatants. Due to this error there are two batch process blanks reported: 99-0648-pb for AW-101 supernatant and 99-0644-pb for AN-107 supernatant. This causes minor confusion since the diluted feed laboratory numbers (i.e., 99-0644 through 99-0647) do not include 99-0648 which is the laboratory number for the AW-101 as received supernatant. Based on the batch processing of the samples, process blanks labeled 99-0648-pb were processed with AW-101 supernatant samples 99-0644 and process blanks labeled 99-0644-pb were processed with AN-107 supernatant samples 99-0645.

### 4.1 Metals by Inductively Coupled Plasma Spectrometry – Tables 3.1 & 3.2

Due to the high radiological dose from the acid digestion and KOH-KNO<sub>3</sub> fusion preparations, aliquots were diluted in the SAL to reduce the radiological dose prior to transferring the samples to the ICP workstation. The acid dissolution of the AW-101 and AN-107 supernatants and the KOH-KNO<sub>3</sub> fusion dissolution and acid digestion of the AW-101 and AN-107 solids were analyzed by ICP in four analytical batches following procedure PNL-ALO-211.

Quality control for the ICP analysis consists of duplicates, process blanks, serial dilution, matrix spikes, laboratory control standards or blank spikes, post spikes, verification check standards, and high calibration standards. All quality control (QC) samples are within the acceptance criteria established by the governing QA Plan, MCS-033 except the following:

Duplicates: Due to lack of material, no acid digestion duplicate was prepared for the AW-101 solids sample.

Matrix Spikes: As a result of the dilutions for ALARA (as low as reasonably achievable) radiation concerns, the matrix spike samples were diluted such that the spike concentration was below the estimated quantitation level (EQL). Since matrix spikes these concentrations are meaningless, post spikes are used to evaluate matrix effects.

Blank Spikes: For the AW-101 supernatant, the blank spike was subjected to the same ALARA dilution as the matrix spike, resulting in diluting the blank spike concentration to below the EQL. The blank spike prepared with the AN-107 supernatant was not diluted and produced recoveries within acceptance criteria of 80% to 120% recovery.

Post Spikes: For the acid digestions of the AW-101 and AN-107 supernatants tin failed to meet the acceptance criteria of 75% to 125%. The tin post spike concentration falls below the elevated tin detection limit, resulting in meaningless recovery results. Also at 129% recovery, the silicon post spike recovery from the acid digestion of the AW-101 solids is slightly above the acceptance criteria. The silicon post spike recoveries for all other diluted feed samples are acceptable.

Although the relative percent differences (RPD) for AW-101 supernatant were within the acceptance criteria of 20%, the analytes of interest (with concentrations above 10-times the method detection limit) demonstrated RPDs ranging from 18% to 20%. This poor precision between the sample and duplicate for the acid digestion of the AW-101 supernatant is exhibited in all analyses using the acid digestion solutions (e.g., ICP, radiochemistry, and ICP/MS Tc-99). This suggests that there was an error in preparing either the sample or the duplicate; however, there is no documented evidence to suggest which may be in error. Since the RPDs met the acceptance criteria, no effort was made to re-prepare the acid digestions for the AW-101 supernatant sample. The average sodium concentration (i.e., 148,500  $\mu\text{g/mL}$  – 6.46 molar) is very close to the target sodium concentration for the AW-101 supernatant (i.e., 6.5 molar). In comparison, the average sodium concentration of the AN-107 supernatant (i.e., 173,500  $\mu\text{g/mL}$  – 7.55 molar) is slightly lower than the target sodium concentration (i.e., 7.7 molar).

The KOH-KNO<sub>3</sub> fusions for the AW-101 and AN-107 solids were performed soon after the phase separation of the samples, and it is anticipated that very little drying of the solids occurred prior to sub-sampling the solids for the fusion preparations. However, the acid digestions for the AW-101 and AN-107 solids were performed more than two weeks following the phase separation. There were very few solids remaining following phase separation and extraction of sub-samples for KOH-KNO<sub>3</sub> fusion preparation, and the remaining solids used for acid digestion preparation appeared dry and were difficult to extract from the sample jars. Since the samples taken for acid digestion appear to be drier than those taken for the KOH-KNO<sub>3</sub> fusion preparation, analyte concentration in  $\mu\text{g/g}$  was anticipated to be significantly higher. This is exactly what was observed.

The reason for performing acid digestion on the diluted feed samples was to obtain potassium and nickel results, since these analytes of interest could not be measured on the KOH-KNO<sub>3</sub> fusion (in nickel crucibles) preparations. In order to correlate the acid digestion results with the KOH-KNO<sub>3</sub> fusion results, considering the differences in the acid digestion and KOH-KNO<sub>3</sub> fusion “wet” fractions, the acid digestion results have been normalized to the KOH-KNO<sub>3</sub> fusion results using the sodium results. For identical solids samples (i.e., solids with exactly the same liquid and solids fractions), the KOH-KNO<sub>3</sub> fusion and acid digestion should produce the same sodium results. The normalized acid digestion results for both diluted feed solids are nearly identical to those results produced from the KOH-KNO<sub>3</sub> fusion, and the reported acid digestion potassium and nickel results should be accurate for the centrifuged wet solids.

## 4.2 Radiochemical Analysis – Table 3.3

### Gamma Emitters by Gamma Energy Analysis (GEA)

The sample preparations from the SAL were diluted further in a laboratory, then packaged for gamma counting following procedure PNL-ALO-450. Most of the gamma emission from the samples is from Cs-137. Other detected gamma emitters are Co-60, Cs-134, Eu-154, Eu-155, and Am-241. All of these gamma emitters are at much lower concentration than the Cs-137, and not all were detected in every sample.

Two of the three SAL process blanks had detectable quantities of Cs-137, but at insignificant levels when compared to the Cs-137 levels in the samples. No other gamma emitters were detected in the blanks.

All of the sample and duplicate results agree within the expected uncertainties, except for the AW-101 supernatant Cs-137 results and the AN-107 solids Eu-154 results. The RPD of 18% for the AW-101 supernatant Cs-137 results is significantly higher than expected from the counting uncertainties (i.e., 2%). This difference is also evident in other analyses (e.g., ICP and total beta activity) and is probably due to a sample preparation error. The counting uncertainties for the AN-107 solids Eu-154 results are reasonably good, at 5% and 7% for the sample and duplicate. The RPD of 21% for the Eu-154 is most likely due to sample heterogeneity.

Since the Am-241 activity in both AW-101 and AN-107 is reasonably low, the results from the alpha energy analysis (AEA) should provide better Am-241 results than GEA. Americium-241 was not detected by GEA in the AW-101 samples, and the counting uncertainties ranged from 12% to 50% for the AN-107 samples. Although Am-241, along with Pu-239+240, makes up most of the alpha activity for the AW-101 and AN-107 samples, the gamma activities are too low to measure accurately by GEA.

Since gamma energy analyses do not involve chemical separations, no sample spiking is performed.

#### Total Alpha and Total Beta

For total alpha and total beta activity measurements, the SAL preparations were further diluted, then small aliquots were evaporated on planchets for counting following procedures PNL-ALO-420, 421, 430, and 431.

The AW-101 supernatant sample had no detectable alpha activity by this method since the sample had high dissolved solids, which caused high mass loading on the counting planchet. Due to the high dissolved solids, sample volumes were reduced to minimize the self-absorption effect from the solids/salts. The other samples had high dissolved solids, but also had more alpha activity, so that alpha activity was detectable by this method. In some cases, a better estimate of the total alpha activity can be obtained by summing the individual alpha emitters measured by AEA (i.e., Pu-238, Pu-239+240, Am-241, Cm-242, and Cm-243+244). The "Alpha Sum" in Table 3.3 provides the sum of the individual alpha emitters. This sum agrees fairly well with the total alpha results, even for those samples containing high dissolved solids. The poor RPDs for the solids samples are attributed to sample heterogeneity and high solids loading on the counting planchets.

The total beta activity results are considerably less affected by mass loading than the total alpha results, and the much higher beta activity in these samples allows a smaller aliquot than alpha counting requires. The duplicate beta results agree within expected uncertainty for all samples except AW-101 supernatant (as with all the analytes from the acid digestion, as noted previously). The SAL process blanks have beta activity four orders of magnitude less than the samples. The total beta activities show good agreement with the sum of the beta emitters (i.e., mainly Cs-137 plus 2 times Sr-90) for all samples. All of the total alpha and total beta matrix and blank spikes were recovered within the acceptance criteria.

#### Plutonium, Americium, and Curium

Plutonium, americium, and curium were separated from the SAL preparations using Eichrom TRU resin according to procedure PNL-ALO-417. The separated fractions were mounted for AEA by co-precipitation on a neodymium fluoride (NdF<sub>3</sub>) carrier (procedure PNL-ALO-496). Absolute

activity of the alpha emitters was calculated using Pu-242 and Am-243 tracers added to the sample aliquots at the start of the chemistry in the radioanalytical laboratory. Plutonium-239+240 and Am-241 make up most of the alpha activity of these samples. The AN-107 samples have about 10 times as much Am-241 as Pu-239+240.

The SAL process blanks indicated detectable plutonium, but the activities were 50 times lower than the lowest sample and five orders of magnitude less than the highest sample. Two SAL process blanks and both laboratory reagent blanks have slightly detectable Am-241, far less than any sample except AW-101 supernatant, which also has very little plutonium, americium and curium. The highest SAL process blank is about 10% of the activity of the AW-101 supernatant.

The RPDs for the Pu-238 results for AW-101 solids and AN-107 solids are outside those expected from the counting uncertainties and inexplicably out of line with the close agreement of the Pu-239 and Am-241 results. Many of the RPDs for sample AN-107 solids exceed 20% (e.g., total alpha activity, Eu-154, and Pu). However, there is excellent agreement for total beta activity, Cs-137, Sr-90, and uranium. Contamination from the SAL hot cells does not explain this discrepancy. All of the Pu-239 and Am-241 matrix spikes had acceptable recoveries. No matrix spike was prepared for curium.

#### Uranium

Uranium was measured directly from dilutions of the SAL fusion preparations by kinetic phosphorescence following procedure PNL-ALO-4014. The SAL process blanks have detectable uranium, but considerably less than any of the samples. The duplicates agree well in all cases. No uranium was detectable in any instrument or reagent blanks. All eight instrument check standards demonstrated recoveries between 98% and 102%. The uranium result from kinetic phosphorescence compare very well with the ICP results where the uranium concentration is above the ICP MDL.

#### Strontium-90

The Sr-90 analyses were conducted according to procedure PNL-ALO-476, which utilizes Sr-Spec resin that contains a crown-ether for the selective extraction of strontium from the radioactive and inactive matrix. After thorough washing, the strontium is back-extracted from the resin with water. The water is dried onto 2-inch planchets and counted with a gas-flow proportional counter according to procedure PNL-ALO-484. Radiochemical yields were determined with a Sr-85 tracer counted by GEA according to procedure PNL-ALO-450. The beta count rate is corrected for the interference from the Sr-85 tracer and Y-90 ingrowth.

The samples were analyzed in two batches; the supernatants were analyzed in one batch and the solids material analyzed in another batch. No analytical problems or anomalies were noted during the course of analysis. The RPDs between the samples and duplicates were equal to or less than 13%, well within the acceptance criteria of 20%. Contamination apparent in the process blanks was nominally four orders of magnitude less than the Sr-90 detectable in the samples. Thus contamination from the SAL hot cells has no effect on the reported results. Sample matrix spikes and blank spikes were prepared in the radioanalytical laboratory and were processed with the sample batches. The blank spike recoveries were excellent at 100% and 97%. Two matrix spikes resulted in recoveries of 107% and 96%.

The AW-101 supernatant samples have no detectable Sr-90 by this method. Aliquots for Sr-90 analysis were chosen by estimating Sr-90 activity from the total beta activity counts; however, the beta from these samples is essentially all from Cs-137. The 0.5  $\mu\text{Ci/mL}$  detection limit obtained is within a factor of three of the 0.15  $\mu\text{Ci/mL}$  MRQ requested. Due to the cost impact for reanalyzing additional aliquots and the minimal usefulness of lowering the Sr-90 reported values, no additional Sr-90 analyses were performed.

### Cesium Isotopic Analysis

Analytical samples for cesium isotopic analysis were prepared by acid digestion of the supernatants and water leaching of the solids. The cesium was separated from these sample preparations by cation exchange chromatography, then analyzed for mass ratios by TIMS following procedure PNL-ALO-452. All samples had essentially the same cesium isotopic ratio; i.e., Cs-133 : Cs-135 : Cs-137 ratio of approximately 59% : 16% : 25%.

For determining the total cesium concentration, the GEA Cs-137 results are converted to units of  $\mu\text{g/mL}$  for supernatants and  $\mu\text{g/g}$  for solids using the specific activity of Cs-137 (i.e., 86.84  $\mu\text{Ci}$  Cs-137 per  $\mu\text{g}$  Cs-137). The atom percent of Cs-137 from the TIMS is used to convert to total cesium.

Blank spikes and matrix spikes are not used for these measurements since absolute values are calculated by comparison of the mass ratios to the Cs-137 gamma energy analysis results. Since natural cesium is mono-isotopic, cesium isotopic standards are not commercially available.

### **4.3 Anion Analysis by Ion Chromatography – Table 3.4**

The AW-101 and AN-107 diluted feed supernatants were diluted 5-fold to 15-fold during the preparation of the samples in the SAL, and were diluted an additional 100-fold to 1000-fold at the ion chromatography (IC) workstation to ensure that all anions of interest were within the calibration range. Solid samples were leached using procedure PNL-ALO-103 resulting in a SAL dilution factor of approximately 50 for each sample. The leaches were diluted an additional 100-fold prior to analysis. The supernatants and leach solutions from the solids were analyzed by IC for inorganic anions per procedure PNL-ALO-212. Bromide, nitrite, and oxalate are not analytes of interest for the diluted feed material, and are reported for information only.

Matrix spikes were prepared at the IC workstation immediately following the dilution and leaching in the SAL. Except for the fluoride recovery for AN-107 supernatant (99-0645), all matrix spikes and blank spikes demonstrated recoveries between 78% and 100%. The fluoride recovery for 99-0646 was 52%, significantly below the acceptance criteria of 75% to 125%. This poor recovery is largely due to the inability to deconvolute the fluoride peak from interfering peaks. Interferences from suspected organic anions are prevalent in nearly all samples. Based on the inability to deconvolute interference peaks and the demonstrated poor matrix spike recovery, the reported fluoride values for all samples should be considered the “upper” bounds for the fluoride concentration.

All samples except AW-101 solids (99-0646) were analyzed in duplicate. There was only enough material available for a single leaching of sample 99-0646. Where both the sample and duplicate

results are above the EQL (i.e., for IC the lowest calibration standard adjusted for processing and analytical dilutions factors), the RPD is 10% or less for all samples and for all anions.

In comparing the phosphorus results between the ICP (as P) and IC (as  $\text{PO}_4^{3-}$ ), the IC results are consistently double the results from the ICP. However, the IC results are obtained from very high dilutions, resulting in phosphate “measured” valued only slightly higher than the instrument detection limit. The high dilutions were required to control column overloading due to the high nitrate and nitrite concentrations. Column overload results in retention time shifts and peak distortion, impacting the accurate quantitation of the detected anions. Near the instrument detection limit the phosphate results have a very high uncertainty (e.g., factor of 2); therefore the IC results should be considered only as an indication of the magnitude of the phosphorus/phosphate concentration.

As required by the governing QA Plan, mid-range verification standards were analyzed at the beginning of the analysis, after every 10 injections, and at the end of the analysis. For all reported results except chloride, all analytes of interest were recovered within the acceptance criteria of 90% to 110% for the verification standard. All chloride verification standards recoveries were within 88% to 90%. Unfortunately, this low recovery was not recognized until after the completion of all the analyses. The low recovery is suspected to be due to an unknown error associated with preparation of the mid-range verification standard. Following the analyses, fresh mid-range verification standard solution was prepared and analyzed, resulting in recoveries in excess of 95% for chloride. Since the availability of additional sample was limited and the verification failure could be traced to an inaccurate verification standard, the results have been reported as analyzed. Since the low chloride recoveries demonstrated on the mid-range verification standard are suspected to be from a preparation error, no bias is suspected in the reported chloride results for the samples.

#### **4.4 TOC/TIC Analysis by Hot Persulfate/Coulometry – Table 3.4**

The analyses of the AW-101 and AN-107 diluted feed samples were done by the hot persulfate wet oxidation method, PNL-ALO-381. Although an alternate furnace method was available, the limited sample quantity and the governing test plan restricted measurement to one method. Based on analytical information from both the diluted feed (i.e., oxalate by IC) and the as received material (i.e., oxalate and formate by IC reported in PNWD-2461) the major carbon components appear to be oxalate and formate. Both oxalate and formate demonstrate reasonable recoveries (e.g., >90%) when analyzed by the hot persulfate method. Although the furnace method typically provides a better total carbon results on difficult to decompose organic salts, the hot persulfate results are considered accurate within the acceptance criteria of the governing QA plan.

The hot persulfate method uses acid decomposition for total inorganic carbon (TIC) and acidic potassium persulfate oxidation at 92-95 °C for total organic carbon (TOC), all on the same weighed sample, with total carbon (TC) being the sum of the TIC and TOC. Per the analytical method, sample results are bias corrected for average percent recovery of system calibration check standards and are also corrected for contribution from the system blank. The TOC/TIC results are the only results subjected to this bias correction calculation.

The QC for the methods involves system calibration blanks, system calibration standards, sample duplicates, and matrix spikes. The QC system calibration standards were all within acceptance

criteria, with the average recovery being 97% for TIC and 100% for TOC for the supernatant analysis and 96% TIC and 98% TOC for the solids analysis.

Due to the limited quantity of diluted feed sample available, the solids fraction from AW-101 was not analyzed in duplicate and no spiking was performed on either the AW-101 or AN-107 diluted feed samples. The TIC and TOC RPDs for the AN-107 solids were well within the acceptance criteria of 20%. For the AW-101 and AN-107 supernatants the TIC and TOC RPDs were less than 7% when the sample and duplicate exceed five times the MDL.

The AW-101 and AN-107 diluted feed supernatants were analyzed in an analytical batch with AW-101 and AN-107 as received supernatants. One of the “as received” samples was chosen for the batch matrix spike and demonstrated a recovery of 103% for TIC and 99% for TOC. No matrix spikes were performed on the diluted feed supernatants.

#### **4.5 Technetium-99 Analysis by Inductively Coupled Plasma/Mass Spectrometry – Table 3.4**

The Tc-99 analyses were performed by ICP/MS per procedure PNL-ALO-281. For the supernatants, the Tc-99 was analyzed on both the acid digestions and water dilutions of the supernatants. For the solids, the samples were prepared by KOH-KNO<sub>3</sub> fusion prior to analysis.

The RPDs from both AW-101 and AN-107 supernatants and solids were less than 15%; well within the acceptance criteria of 20%. No Tc-99 matrix spikes were prepared; however, post spikes were prepared and analyzed at the ICP/MS workstation. The post spike recoveries were slightly on the high side, ranging from 106% to 115%, but well within the acceptance criteria of 75% to 125%.

The reported Tc-99 results assume that the ruthenium present is exclusively fission-product ruthenium, and therefore does not have an isotope at mass 99. The calculated results assume that everything observed at the mass 99 is due to technetium. The observed ruthenium mass spectra are not typical of natural ruthenium and are consistent with spectra observed in previous tank waste analyses. Therefore, the assumption that observed mass 99 is primarily technetium should be valid.

The Tc-99 supernatant results from the acid digestion appear to be slightly higher on average than the Tc-99 results from water dilution of the supernatants; however, additional sampling is required to verify if the difference is statistically valid.

#### **4.6 Free Hydroxide and pH Analysis – Table 3.4**

Analysis of free hydroxide was performed following analytical dilution of the supernatants in the SAL. The AW-101 and AN-107 diluted feed supernatant samples were analyzed according to procedure PNL-ALO-228. The samples were titrated with NIST-traceable hydrochloric acid. Quality control check standards were prepared from NIST-traceable sodium hydroxide. The accuracy of the check standards measured within 2.4% of the true hydroxide concentration.

The free hydroxide is calculated from the first equivalence point on the titration curve. To verify that the hydroxide equivalence point was the first equivalence point, AW-101 supernatant was spiked with sodium hydroxide standard; the first equivalence point was identical to that of the

sample (i.e., pH = 10.27). Recovery of the matrix spike was 100.2%. The reported RPDs for the free hydroxide results for the AW-101 and AN-107 supernatants are less than 4%.

The pH measurements were performed in duplicate on the AW-101 and AN-107 supernatants per procedure PNL-ALO-225.



## 5.0 Method Detection Limits & Minimum Reportable Quantities

The MDLs for specific analytes of interest vary significantly based on the procedures used for preparing the samples for analysis (e.g., acid digestion, fusion), the sample size taken for the analysis, required dilutions for ALARA safety considerations, and the magnitude of interfering analytes. For the work presented in this report, efforts were made to optimize the sample preparation parameters (e.g., minimal dilutions). Table 5.1 provides a direct comparison of each analyte MDL to the target minimum reportable quantity (MRQ) provided by BNFL. The MDLs are nominal values based on average sample sizes used for analysis of the AW-101 and AN-107 diluted feed samples. The MDLs are presented for both liquids and solids. Where solids are prepared by both acid digestion and fusion, both the acid digestion MDL and fusion MDL are provided for comparison. The MDLs that are shaded and boxed with double lines exceed the BNFL requested MRQs.

As is evident from the Table 5.1, some analytes of interest have not been measured at the target MRQ. As would be expected due to high preparative dilution factors, fusion preparations have the largest quantity of MDLs not meeting the target MRQ. For AW-101 and AN-107, this is not a significant problem, since the acid digestion of the solids provides an apparent 100% dissolution.

Many of the high MDLs from the fusion preparation are within a factor of five of the target MRQ; specifically, calcium, cadmium, copper, iron, uranium (by ICP), Co-60, Eu-154, Eu-155, and total alpha. With further optimization of sample size and analytical dilutions, these fusion MDLs may improve sufficiently to meet the target MRQs. However, the fusion MDLs for cobalt, molybdenum, and zinc are from 8 to 15 times higher than the target MRQs, and it is unlikely that fusion preparation can be optimized to this extent. The samples for GEA required dilution due to the high activity from the Cs-137; therefore, the other radionuclides measured by GEA (i.e., Co-60, Eu-154, Eu-155, and Am-241) did not meet the target MDLs.

The solids acid digestion MDLs for cobalt, molybdenum, and zinc are within a factor of three of the target MRQs, and with additional optimization of the digestion preparation these MDLs may be able to be reduced. Also, the MDLs for TIC and TOC for solids are about a factor of two to three higher than the target MRQs. The TIC and TOC MDLs can be reduced by increasing the solids sample size although, ALARA considerations make this approach questionable.

For supernatant analysis, only potassium and chloride MDLs are above the target MRQs. The liquid acid digestion MDL for potassium is about a factor of three higher than the target MRQ, and additional optimization may be able to improve the MDL. As for chloride, it is unlikely that the MRQ of 3 µg/mL can be achieved consistently on tank waste supernatants by using IC as the analysis method. The presence of other anions (particularly very high nitrate) requires significant dilution of the samples prior to analysis to prevent IC column overloading. This required dilution, and the often presence of interfering organic anions, significantly limit the chloride MDL.

**Table 5.1 Comparison of Measurement MDLs to Target MRQs**

(1) Analyte	Liquid		Solids			(1) Radionuclide	Liquid		Solids	
	MDL	BNFL	MDL		BNFL		MDL	BNFL	MDL	BNFL
	(2)	MRQ	(2)	(Fusion)	MRQ		(2)	MRQ	(Fusion)	MRQ
	µg/mL	µg/mL	µg/g	µg/g	µg/g		µCi/mL	µCi/mL	µCi/g	µCi/g
Ag	3.09E+0	1.75E+1	4.07E+0	2.35E+1	9.00E+2	Co-60 (GEA)	3.00E-4	2.10E-3	5.00E-2	1.20E-2
Al	7.42E+0	7.50E+1	9.77E+0	5.65E+1	3.30E+2	Sr-90	4.00E-3	1.50E-1	4.00E-2	7.01E+1
Ba	1.24E+0	7.80E+1	1.63E+0	9.41E+0	6.00E+2	Cs-137 (GEA)	2.00E-4	9.00E+0	5.00E-2	6.00E-2
Ca	3.09E+1	1.50E+2	4.07E+1	2.35E+2	1.80E+2	Eu-154 (GEA)	6.00E-4	2.00E-3	2.00E-1	6.00E-2
Cd	1.85E+0	7.50E+0	2.44E+0	1.41E+1	1.10E+1	Eu-155 (GEA)	7.00E-4	9.00E-2	2.00E-1	6.00E-2
Co	6.18E+0	3.00E+1	8.14E+0	4.70E+1	3.00E+0	Am-241(GEA)	5.00E-4	7.20E-4	2.00E-1	1.20E-3
Cr	2.47E+0	1.50E+1	3.26E+0	1.88E+1	1.20E+2	Am-241 (AEA)	1.00E-6	7.20E-4	1.00E-5	1.20E-3
Cu	3.09E+0	1.70E+1	4.07E+0	2.35E+1	1.80E+1	Cm-243+Cm-244	5.00E-7	1.50E-1	5.00E-6	6.00E-5
Fe	3.09E+0	1.50E+2	4.07E+0	2.35E+1	1.40E+2	Total Beta	2.00E-4		4.00E-3	
K	2.47E+2	7.50E+1	3.26E+2		1.50E+3	Total Alpha	2.00E-4	2.30E-1	2.00E-3	1.00E-3
La	6.18E+0	3.50E+1	8.14E+0	4.70E+1	6.00E+1		µCi/mL	µCi/mL	µg/g	µg/g
Mg	1.24E+1	1.50E+2	1.63E+1	9.41E+1	5.40E+2	Tc-99 (ICP/MS)	3.00E-4	1.50E-3	1.00E-1	6.00E+0
Mn	6.18E+0	1.50E+2	8.14E+0	4.70E+1	3.00E+2	Note: MDLs shaded and boxed exceed the target MRQs requested by BNFL				
Mo	6.18E+0	9.00E+1	8.14E+0	4.70E+1	6.00E+0					
Na	1.85E+1	7.50E+1	2.44E+1	1.41E+2	1.50E+2					
Ni	3.71E+0	3.00E+1	4.88E+0		1.60E+2					
Pb	1.24E+1	3.00E+2	1.63E+1	9.41E+1	6.00E+2					
Si	5.86E+1	1.70E+2	8.14E+1	4.70E+2	3.00E+3					
Ti	3.09E+0	1.70E+1	4.07E+0	2.35E+1	1.50E+2					
U	2.47E+2	6.00E+2	3.26E+2	1.88E+3	6.00E+2					
Total U <sup>(4)</sup>	1.00E-4	6.00E+2		1.00E-4	6.00E+2					
Zn	6.18E+0	1.65E+1	8.14E+0	4.70E+1	6.00E+0					
Zr	6.18E+0		8.14E+0	4.70E+1	6.00E+2					
Cl	1.70E+1	3.00E+0	1.20E+2		2.30E+2					
F	1.70E+1	1.50E+2	1.20E+2		7.50E+3					
NO3	3.50E+1	3.00E+3	2.40E+2		4.50E+2					
PO4	3.50E+1	2.50E+3	7.80E+1		6.00E+2					
SO4	3.50E+1	2.30E+3	8.00E+1		1.20E+3					
OH (total)	(3)	1.70E+2								
OH (free)	1.70E+2	1.70E+2								
TIC	1.40E+1	1.50E+2	7.35E+1		3.00E+1					
TOC	2.55E+1	1.50E+3	1.20E+2		6.00E+1					

(1) Analyte and Radionuclide List per Test Plan BNFL-29953-6

(2) Acid Digestion or Water Leach, or Direct Analysis, as applicable

(3) Method detection limit for total hydroxide measurement not established

(4) Total U by kinetic phosphorescence

(1) Analyte and Radionuclide List per Test Plan BNFL-29953-6

(2) Acid Digestion or Water Leach, or Direct Analysis, as applicable

(3) Method detection limit for total hydroxide measurement not established

(4) Total U by kinetic phosphorescence