PNWD-3174
WTP-RPT-022

Chemical Analysis and Physical Property Testing of Diluted 241-AP-101 Tank Waste

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Prepared for Bechtel National, Inc.
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LEGAL NOTICE

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Battelle, Pacific Northwest Division
Richland, Washington, 99352

Completeness of Testing

This report describes the results of work and testing specified by test specification TSP-W375-00-0003, Rev. 1 and test instruction TI-PNNL-WTP-032. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Instruction. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test instruction results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager WTP R&T Support Project	Date

Approved for RPP-WTP Project Use:

G. Todd Wright, Manager Research and Technology	Date

Summary

Battelle - Pacific Northwest National Laboratory (PNWD) is conducting integrated, process verification, and waste-form qualification tests on Hanford waste from underground storage Tank 241-AP-101 (AP-101) in support of the River Protection Project - Waste Treatment Plant (RPP-WTP). This report presents the results of sample compositing, dilution, homogenization, and characterization as specified in test instruction (TI) TI-PNNL-WTP-032 (Appendix A) and analytical service request (ASR) 6031 (Appendix B). The TI and ASR implement the requirements of Test Specification (TS) TSP-W375-00-00003 Revision 1 (Appendix A), which is further defined in Test Scoping Statement B-3a (work breakdown structure 1.01.2.02).

The objectives defined by the TS were to:

- Prepare a composite sample from multiple bottles of AP-101 waste samples
- Verify the homogeneity of the composite sample
- Prepare a diluted feed by adjusting the composite sample sodium concentration to 4.7 M
- Analyze the AP-101 diluted feed waste sample
- Compare analytical results with the low-activity waste (LAW) feed specifications for the WTP

Thirteen bottles containing AP-101 waste (retrieved from tank AP-101 in February of 2000) were provided to the PNWD in November and January of 2001. All bottles were similar in appearance, containing clear and colorless liquid. Neither an organic layer nor a precipitate could be discerned in these bottles.

The contents of the 13 bottles were mixed together into a single composite and homogenized by stirring. Following stirring, the composite was sub-sampled and the sub-samples measured for density to evaluate the homogeneity of the composite. Based on the sodium concentrations of the contents of the 13 bottles, the composite was then diluted with water to a target sodium concentration of 4.7 M.

This diluted AP-101 composite (diluted feed) was sub-sampled and characterized for physical properties and inorganic, radiochemical, and selected organic analytes. The characterization of the homogenized AP-101 diluted feed included:

- inductively coupled plasma (ICP-AES) spectrometry
- radiochemical analyses, including $^{99}Tc^{+7}$
- inductively coupled plasma mass spectrometry (ICP-MS)
- kinetic phosphorescence (KPA) analysis for total uranium
- ion chromatography (IC) analysis
- titration for hydroxide
- ion specific electrode (ISE) analysis for ammonia
- cold vapor atomic absorption (CVAA) analysis for mercury
- density
- weight percent total dissolved solids (TDS)
- total inorganic carbon (TIC) and total organic carbon (TOC)
- heat capacity
- viscosity (shear stress versus shear rate)

- particle size

Table S.1 presents the physical properties measurements and Tables S.2 and S.3 presents the chemical and radioisotope characterization results. The AP-101 diluted feed composite met all contract limits (i.e., molar ratio of analyte to sodium or becquerels of analyte to moles of sodium) defined in Specification 7 Envelope A. Table S.4 summarizes the Envelope A analytes relative to the specification. As shown, sulfate is at the limit and potassium is at approximately 80% of the limit, with many other analytes being above 20% of the specification. Uranium, lanthanum, phosphate, barium, lead, TIC by furnace, ^{154}Eu, mercury, and cadmium were not detected above the method detection limit (MDL). Using the MDL as the measured 'less than' value, only uranium and lanthanum were above 10% of the specification (at <19%, and <12%, respectively).

Table S.1. AP-101 Diluted Feed Composite –Physical Properties

	Average	**Std Dev**
Undiluted Composite; Homogenization Test		
Density (g/mL)	1.294	0.005
Diluted Feed Composite; Homogenization Test		
Density (g/mL)	1.256	0
Diluted Feed Composite; Characterization Sub-Sample		
Density (g/mL)	1.258	0
TDS (wt%)	31.6	0.7
Heat Capacity (J/g-K)	3.43	0.022 (a)
Viscosity (cP)		
Average @ 25°C	4.5	0.5
Average @ 35°C	4.4	(b)
Average @ 50°C	2.7	0.3
Average @ 80°C	3.0	(b)
Particle Size		
Volume Distribution – 53% Peak 1 (µm)	5.44	2.10 (c)
Volume Distribution – 47% Peak 2 (µm)	1.47	1.08 (c)
Number Distribution – 1% Peak 1 (µm)	5.18	1.72 (c)
Number Distribution – 66% Peak 2 (µm)	1.12	0.55 (c)
Number Distribution – 33% Peak 3 (µm)	0.60	0.52 (c)

(a) Standard deviation about the mean for 16 measurements.
(b) Not applicable, only one result obtained at this temperature.
(c) Peak/mode width

Table S.2. AP-101 Diluted Feed Composite – Analyte Summary

Analyte	Measure Method	MRQ µg/mL	MDL/EQL[a] µg/mL	01-520 Average µg/mL	Data Flag	Mole Analyte per Mole Na	Mole Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit
Al	ICP-AES	7.5E+01	8E+00	6.98E+03	X	5.2E-02	2.5E-01	21
B	ICP-AES		*7E+00*	*5.50E+01*	*JB*			
Ba	ICP-AES	2.3E+00	1E+00	1E+00	U	< 2.0E-06	1.0E-04	< 2.0
Ca	ICP-AES	1.5E+02	3E+01	2.10E+02	JB	1.1E-03	4.0E-02	2.8
Cd	ICP-AES	7.5E+00	2E+00	2E+00	U	< 3.7E-03	4.0E-03	< 0.09
Cl	IC	3.0E+02	5E+02	1.45E+03		8.4E-03	3.7E-02	23
Cr	ICP-AES	1.5E+01	3E+00	1.52E+02		5.9E-04	6.9E-03	8.6
Cs	ICP-MS	1.6E-02	7E-02	2.96E+00				
F [b]	IC	1.5E+02	5E+02	2.30E+03		2.4E-02	9.1E-02	26
Fe	ICP-AES	1.5E+02	3E+00	3.60E+00	JB	1.3E-05	1.0E-02	0.1
Hg	CVAA	1.5E+00	7E-02	7E-02	UX	< 7.0E-08	1.4E-05	< 0.5
K	ICP-AES	7.5E+01	3E+02	2.98E+04	X	1.5E-01	1.8E-01	83
La	ICP-AES	3.5E+01	7E+00	7E+00	U	< 9.9E-06	8.3E-05	< 12
Mg	ICP-AES	3.0E+02	1E+01	1E+01	U			
Mo	ICP-AES		*7E+00*	*1.40E+01*	*J*			
Na	ICP-AES	7.5E+01	2E+01	1.14E+05	X			
NH_3	ISE	1.4E+02	1E+01	2.60E+01				
Ni	ICP-AES	3.0E+01	4E+00	4.25E+00	JB	1.5E-05	3.0E-03	0.5
NO_2	IC	3.0E+03	1E+03	3.25E+04		1.4E-01	3.8E-01	37
NO_3	IC	3.0E+03	2E+03	1.04E+05		3.4E-01	8.0E-01	43
OH	Titrate	7.5E+04	2E+02	3.29E+04				
P	ICP-AES	6.0E+02	1E+01	3.85E+02		2.5E-03	3.8E-02 [c]	6.6
Pb	ICP-AES	3.0E+02	1E+01	1E+01	U	< 1.3E-05	6.8E-04	< 1.9
PO_4	IC	2.5E+03	1E+03	1E+03	U	< 2.0E-03	3.8E-02	< 5.3
Rb	ICP-MS	1.0E+00	7E-02	3.90E+00				
S	ICP-AES			n/m				
Si	ICP-AES		*7E+01*	*3.60E+02*	*JBX*			
SO_4	IC	2.3E+03	2E+03	4.65E+03		9.8E-03	1.0E-02	98
TIC	Hot Pers.	1.5E+02	1E+01	5.35E+03		9.0E-02	3.0E-01	30
TIC [d]	Furn.Ox.	1.5E+02	2E+02	2E+02	U	< 2.9E-03	3.0E-01	< 1.0
TOC	Hot Pers.	1.5E+03	4E+01	1.64E+03		2.8E-02	5.0E-01	5.6
TOC	Furn.Ox.	1.5E+03	2E+02	7.90E+03		1.4E-01	5.0E-01	28
U	ICP-AES	6.0E+02	3E+02	3E+02	U	< 1.7E-03	1.2E-03	< 141
U	KPA	7.8E+02	6E-03	4.07E+01		< 2.3E-04	1.2E-03	< 19
Zn	ICP-AES		*7E+00*	*8.00E+00*	*JB*			

Table S.2. (Cont'd)

Analyte	Measure Method	MRQ µg/mL	MDL/EQL(a) µg/mL	01-520 Average µg/mL	Data Flag	Mole Analyte per Mole Na	Mole Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit

Results in italics represent analytes measured that were not listed in TS and are provided for information only.
MDL = method detection limit
n/m = not measured; ICP-AES used for this work does not have a S channel.

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, and Hg results are only reported above the EQL; the value in this column therefore represents the EQL. For all other analytes the value represents the MDL.

(b) The fluoride results should be considered the upper bound concentration for the fluoride. Significant peak distortion of the fluoride peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(c) Specification 7 Envelope C limit for phosphate.

(d) TIC by difference (TIC = TC-TOC).

Flags: U = not detected above the MDL
J = estimated value; detected above the MDL but not above the EQL
B = blank >EQL or >5% of sample concentration
X = QC deficiency (See Section 6.1)

Table S.3. AP-101 Diluted Feed Composite – Radioisotope Summary

Analyte	Measure Method	MRQ µCi/mL	MDA/ MDL(a) µCi/mL	01-520 Average µCi/mL	Data Flag	Bq Analyte per Mole Na	Bq Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit
^{60}Co	GEA	1.0E-02	2E-04	2.52E-03		1.9E+04	6.1E+04	31.1
^{90}Sr	RadChem	1.5E-01	4E-03	7.14E-02	B	5.3E+05	4.4E+07	1.2
^{99}Tc	ICP-MS	1.5E-03	2E-03	3.92E-02		2.9E+05	7.1E+06	4.1
^{99}Tc^{+7}	RadChem	1.5E-03	5E-06	3.46E-02	X			
^{137}Cs	GEA	9.0E+00	6E-03	1.26E+02		9.4E+08	4.3E+09	21.9
^{154}Eu	GEA	2.0E-03	1E-03	1E-03	U	< 7.5E+03	1.2E+06	< 0.6
^{155}Eu	GEA	9.0E-02	1E-02	1E-02	U			
^{237}Np	ICP-MS	2.7E-02	4E-06	4E-06	U			
^{238}Pu	RadChem	1.0E-02	6E-07	1.40E-05				
$^{239/240}$Pu	RadChem	3.0E-02	6E-07	1.10E-04				
^{239}Pu	ICP-MS	3.0E-02	8E-04	8E-04	U			
^{240}Pu	ICP-MS	1.0E-02	7E-04	7E-04	UX			
^{241}Am	RadChem	3.0E-02	6E-07	1.38E-04				
^{241}Am	GEA		1E-02	1E-02	U			
^{241}Am (b)	ICP-MS	5.1E-02	8E-03	8E-03	U			

Table S.3. (Cont'd)

Analyte	Measure Method	MRQ µCi/mL	MDA/ MDL(a) µCi/mL	01-520 Average µCi/mL	Data Flag	Bq Analyte per Mole Na	Bq Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit
^{242}Cm	RadChem	1.5E-01	4E-07	4E-07	U			
$^{243/244}$Cm	RadChem	1.5E-02	5E-07	2.12E-06	J			
Alpha	RadChem	2.3E-01	9E-05	2.17E-04	J			
Sum of Alpha (TRU)			3E-06	2.64E-04		1.97E+03	4.80E+05	0.4

(a) MDL used for ICP-MS, MDA used for all radiochemistry analyses.

(b) Based on AMU-241 response; ^{241}Am used for calibration.

Flags: U = not detected above the MDL
J = estimated value; detected above the MDL but not above the EQL
B = blank >EQL or >5% of sample concentration
X = QC deficiency (See Section 6.1)

MDA = minimum detectable activity

MDL = method detection limit

Decay correction reference dates nominally May 2001.

Table S.4. AP-101 Specification 7 Envelope A Summary

Analytes Measured above MDL		Analytes not Detected above MDL	
Results % of Limit	**Analyte**	**Results % of Limit based on MDL**	**Analyte**
98	SO_4	< 19	U
83	K	< 12	La
43	NO_3	< 10 or less(a)	PO_4, Ba, Pb, TIC-F (b), ^{154}Eu, Hg, Cd
37	NO_2		
31	^{60}Co		
30	TIC-P (b)		
28	TOC-F (b)		
26	F		
23	Cl		
22	^{137}Cs		
21	Al		
10 or less(a)	Cr, Fe, Ca, Ni, TOC-P(b), ^{99}Tc, ^{90}Sr, TRU (c), PO_4(d)		

(a) Analytes are presented from 10% in descending order.

(b) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC).

(c) TRU = alpha emitting radionuclides with atomic number greater than 92 and half-life greater than ten years; Alpha summation of ^{238}Pu, $^{239+240}$Pu, ^{241}Am, and $^{243+244}$Cm.

(d) Phosphate based on ICP-AES average total P result of 385 µg/mL.

Terms and Abbreviations

AMU	atomic mass unit
ASR	Analytical Service Request
BNI	Bechtel National Inc.
BS	blank spike
COC	chain of custody
CVAA	code vapor atomic absorption
DI	deionized
EQL	estimated quantitation limit
GEA	gamma energy analysis
HASQARD	Hanford Analytical Services Quality Assurance Requirements Documents
HLRF	High Level Radiation Facility
HPIC	high-performance ion chromatography
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
IDL	instrument detection limit
ISE	ion specific electrode
KPA	kinetic phosphorescence
LAW	low-activity waste
LCS	laboratory control standard
MDA	minimum detectable activity
MDL	method detection limit
MRQ	minimum reportable quantity
MS	matrix spike
MSD	matrix spike duplicate
n/a	not applicable
NIST	National Institute of Standards and Technology
n/m	not measured
n/r	not recovered
%D	percent difference
PB	process blank
PNWD	Battelle - Pacific Northwest National Laboratory
QA	quality assurance
QC	quality control
RPD	relative percent difference
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
RSD	relative standard deviation
SAL	Shielded Analytical Laboratory

SRM	Standard Reference Material
TC	total carbon
TDS	total dissolved solids
TI	test instruction
TIC	total inorganic carbon
TOC	total organic carbon
TP	test plan
TRU	transuranic
TS	test specification
UPA	Ultrafine Particle Analyzer (MicroTrac™)
WTP	Waste Treatment Plant

Units

Bq	Becquerel
cP	centipoise
°C	degree Centigrade
g	gram
J	Joule
K	Kelvin
μCi	microcurie
μg	microgram
μm	micrometer
mL	milliliter
M	molarity
N	normality
nm	nanometer
wt%	weight percent

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Tables

1.0 Introduction

Battelle – Pacific Northwest Division is conducting physical property testing and inorganic, and radiochemical waste characterization of diluted waste from underground storage tank number 241-AP-101 (AP-101) for Bechtel National, Inc. (BNI). This effort supports the operation of the River Protection Project-Waste Treatment Plant (RPP-WTP).

Waste from tank AP-101 was sampled February 2000 from Riser 002 at depths of 10, 100, 190, 290, and 400 inches from the bottom of the tank.[1] Each sampling bottle collected nominally 125 mL per sample. Five of the bottles collected were transported directly to the PNWD, with the remaining bottles being delivered to the 222-S Laboratory. The contents of five 125-mL bottles were composited, homogenized, sub-sampled, and characterized (Fiskum 2000). The analyses of this composite sample determined PCBs were not present at or above the detection limit of 1.4 µg/L. These results confirmed that waste contained in tank AP-101 meets the criteria of low activity waste (LAW) envelope A feed, as defined in Specification 7.

To conduct the work in this report, an additional 1.2 liters of tank AP-101 waste was received on November 2000 and January 2001 from the 222-S Laboratory in 13 bottles. These bottles consisted of full bottles, bottles containing residual AP-101 left over from processing at the 222-S Laboratory, and bottles that contained diluted AP-101 material. The objectives of this work were:

- Prepare a composite sample from 13 bottles of AP-101 waste material
- Verify the homogeneity of the composite sample
- Dilute the composite sample to 4.7 M sodium
- Analyze the AP-101 diluted feed composite
- Compare analytical results with LAW feed Specification 7

The PNWD Quality Assurance Program Plan “Conducting Analytical Work in Support of Regulatory Programs” was used in support of all analytical operations and is compliant with the Hanford Analytical Services Quality Assurance Requirements Documents (HASQARD) DOE/RL-96-68. The sample compositing, homogeneity, analysis, and dilution test specification (TS), TSP-W375-00-00003 (Appendix A), was provided by CH2Mhill Hanford Group. The quality requirements for the characterization of the AP-101 liquid (as well as solid, if present) were included in the TS and transmitted to the laboratory staff via the Analytical Service Request (ASR) 6031.

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[1] Wood, R.F., Letter Report, CH2M Hill, Hanford Group, Inc., to J.J. Short, DOE-ORP, “Sample Management Document Package for Grab Samples from Tank 241-AP-101,” Letter No. CHG-0000767 dated February 15, 2000.

2.0 Sample Receiving

Thirteen 500-mL bottles containing samples obtained from Hanford waste tank 241-AP-101 (AP-101) in November 2000 and January 2001 were received from the 222S Lab under chain of custody (COC). The COC records are included in Appendix A. The 13 sample bottles had been archived at the 222-S laboratory from an earlier sampling event (February 2000). Five of the 13 sample bottles had not been previously opened at the 222-S facility. Six of the sample bottles had been opened and some of the material had been removed for characterization; however, the bottles contained unaltered AP-101 liquid. The remaining two bottles contained AP-101 liquid had been diluted at 222-S Laboratory with deionized (DI) water.

Upon receipt at the High Level Radiation Facility (HLRF), each bottle containing the AP-101 samples was visually inspected, and the inspection was documented through TI number TI-PNNL-WTP-032 (Appendix A). All bottles and lids were in good condition. All samples were similar in appearance, containing clear and colorless liquid (see footnote Table 2.1). Neither an organic layer nor a precipitate could be discerned in these samples. No crystalline phases were apparent. The results of the inspection are provided in Table 2.1.

Prior to compositing or other sub-sampling activities, three 3-mL sub-samples from sample S00T002190 were removed while stirring, and relevant information is shown in Table 2.2. These samples represented as-received AP-101 tank waste material and were sub-sampled to provide additional analytical and quality control results for the characterization of the AP-101 as received material (Fiskum 2000).

Table 2.1. Received AP-101 Samples

Tank Sample Bottle Label	222-S Laboratory ID	Net Mass Received, g	[a] Visual Appearance	Na Concentration (M) [b]	Description
Received at the PNWD in November 2000					
1AP-00-2	S00T000450	171	Clear	5.62	AP-101 Tank Waste
1AP-00-5	S00T000452	174	Clear	5.62	AP-101 Tank Waste
1AP-00-8	S00T000454	175	Clear	5.62	AP-101 Tank Waste
1AP-00-11	S00T000456	173	Clear	5.62	AP-101 Tank Waste
1AP-00-14	S00T000458	177	Clear	5.62	AP-101 Tank Waste
Received at the PNWD in January 2001					
1AP-00-3	S00T000451	32.4	Clear	5.62	AP-101 Tank Waste
1AP-00-6	S00T000453	31.4	Clear	5.62	AP-101 Tank Waste
1AP-00-9	S00T000455	30.9	Clear	5.62	AP-101 Tank Waste

Table 2.1. (Cont'd)

Tank Sample Bottle Label	222-S Laboratory ID	Net Mass Received, g	[a] Visual Appearance	Na Concentration (M) [b]	Description
1AP-00-12	S00T000457	34.5	Clear	5.62	AP-101 Tank Waste
1AP-00-15	S00T000459	32.8	Clear	5.62	AP-101 Tank Waste
None	S00T002190	152 [c]	Clear	5.62	AP-101 Tank Waste
None	S00T002194	241	Clear	5.13	AP-101 Tank Waste diluted 10% with water
None	S00T002195	176	Clear	4.69	AP-101 Tank Waste diluted 20% with water
Total Mass Received		1601 g			

(a) The samples appeared to be colorless when viewed through the hot cell window; however, when sub-samples were removed from the hot cells and could be viewed directly (i.e., not though the hot cell windows), they were a very pale yellow in color.

(b) Na molarity provided by 222-S Laboratory

(c) Net mass following sub-sampling of 12 g for as-received characterization analysis

Table 2.2. Sub-Samples Removed Prior to Compositing and Mixing

Sub-Sample ID	Net Weight (g)	RPL ID #	Analysis[a]
AP-101-AR-1R	3.8996	01-0521	ICP-AES, ICP/MS, U (KPA) Analysis
AP-101-AR-2R	3.9928	01-0521DUP	
AP-101-AR-3R	4.0085	01-0521TRIP	

(a) Results for these analyses are reported in to be published revision of Fiskum 2000.

3.0 Compositing and Sub-Sampling

The objective of compositing the AP-101 samples was to provide homogeneous material for characterization, as well as to provide homogeneous diluted feed for process testing. The homogenization and sub-sampling activity was performed in accordance with TSP-W375-00-00003, which was implemented through TI number TI-PNNL-WTP-032 (Appendix A). The overall sample compositing and sub-sampling activity is summarized in Figure 3.1.

Following the removal of the 3 sub-samples identified in Table 2.2, the contents of the 13 sample bottles (Table 2.1) were combined in a large polypropylene mixing vessel with a motorized impeller. The composite was mixed for about 5 minutes at 26°C on January 26, 2001, and three sub-samples (AP-101 A, AP-101 B, and AP-101 C) were transferred to 10-mL volumetric flasks for density determination. Based on the densities presented in Table 3.1, the composite was considered homogenized.

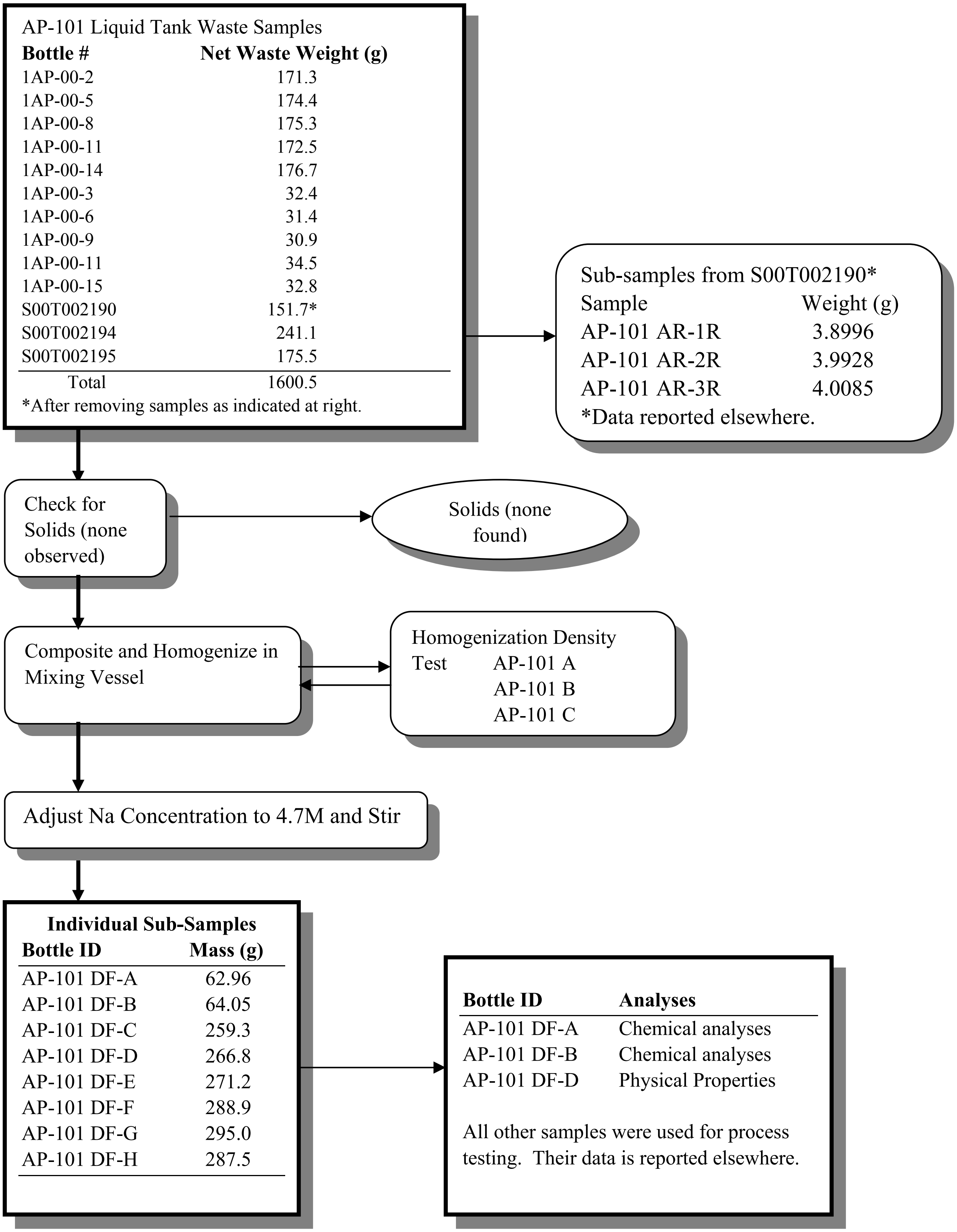
Table 3.1. AP-101 Composite Sample Density

AP-101 A Density g/mL	AP-101 B Density g/mL	AP-101 C Density g/mL	Average Density g/mL	RSD (%)
1.289	1.298	1.294	1.294	0.3%

RSD = relative standard deviation

Following the density determination, these 10-mL sub-samples were returned to the mixing vessel. The total volume of composite sample (1237 mL) was calculated from the mass (1601 g) and density (1.294 g/mL).

Based on the Na concentrations and volumes of the contents of the 13 bottles received (Table 2.1), the Na concentration for the composite was calculated to be 5.44 M. Per the TS, the AP-101 material was to be diluted to 4.7 M Na. To achieve this Na dilution, 196 mL of water was added to the 1237 mL of 5.44 M Na composite and homogenized by stirring for five minutes. Calculation of the average composite Na molarity and water dilution volume needed to dilute the composite to 4.7 M Na is included as attachment A to Test Instruction TI-PNNL-WTP-032 (Appendix A). Following mixing, eight sub-samples were collected. Table 3.2 provides the detailed information on the eight AP-101 dilute feed sub-samples, labeled AP-101 DF A through H.



AP-101 Liquid Tank Waste Samples

Bottle #	**Net Waste Weight (g)**
1AP-00-2	171.3
1AP-00-5	174.4
1AP-00-8	175.3
1AP-00-11	172.5
1AP-00-14	176.7
1AP-00-3	32.4
1AP-00-6	31.4
1AP-00-9	30.9
1AP-00-11	34.5
1AP-00-15	32.8
S00T002190	151.7*
S00T002194	241.1
S00T002195	175.5
Total	1600.5

*After removing samples as indicated at right.

Sub-samples from S00T002190*

Sample	Weight (g)
AP-101 AR-1R	3.8996
AP-101 AR-2R	3.9928
AP-101 AR-3R	4.0085

*Data reported elsewhere.

Individual Sub-Samples

Bottle ID	**Mass (g)**
AP-101 DF-A	62.96
AP-101 DF-B	64.05
AP-101 DF-C	259.3
AP-101 DF-D	266.8
AP-101 DF-E	271.2
AP-101 DF-F	288.9
AP-101 DF-G	295.0
AP-101 DF-H	287.5

Bottle ID	**Analyses**
AP-101 DF-A	Chemical analyses
AP-101 DF-B	Chemical analyses
AP-101 DF-D	Physical Properties

All other samples were used for process testing. Their data is reported elsewhere.

Figure 3.1. Flow Diagram of the AP-101 Sample Receiving, Homogenizing, and Sub-Sampling

Table 3.2. AP-101 Diluted Feed Sub-Samples

Sub-Sample ID	Net Weight (g)	Sample Use	Analysis Performed	RPL ID#
AP-101 DF A	63.0	Chemical analysis	(a)	01-00520
AP-101 DF B	64.1	Chemical analysis	(a)	01-00520 DUP
AP-101 DF C	259.3	Process Testing		None
AP-101 DF D	266.8	Physical Properties	(b)	None
AP-101 DF E	271.2	Process Testing		None
AP-101 DF F	288.9	Process Testing		None
AP-101 DF G	295.0	Process Testing		None
AP-101-DF H	287.5	Process Testing		None
Total Weight (g)	1795.8 (c)			

a) Density, total dissolved solids, ICP-AES, ICP-MS, ammonia, mercury, OH^-, ion chromatography, radiochemistry, and TOC/TIC

b) Heat capacity, particle size, and shear stress versus shear rate

c) Approximately 1 gram of loss (i.e., 1600.5 g AP-101 + 196 g water = 1796.5 g)

4.0 Physical Measurements

The composite material from bottle AP-101 DF-D was selected for physical properties: 1) heat capacity, 2) particle size, and 3) viscosity (shear stress versus shear rate). As part of the compositing and sub-sampling activities defined by TI-PNNL-WTP-032 (Appendix A), density measurements were performed on sub-samples AP-101 DF C and AP-101 DF H, the last bottles collected. These density measurement were obtained to provide initial starting density information for process testing not included in this report. However, the densities are reported here for comparison with the density measurement performed as part of the AP-101 diluted feed characterization (see Section 5.1).

4.1 Density

The density of the AP-101 diluted feed material was determined on the contents of bottles AP-101 DF-C and AP-101 DF-H. The density results are presented in Table 4.1. The measured density of the diluted feed is consistent with the starting density (1.294 g/mL) and the volumes of the AP-101 composite (1237 mL) and water (196 mL) mixed together to produce the AP-101 diluted feed (i.e., [(1.294 g/ml * 1237 mL) + (1.00 g/mL * 196 mL) / (1237 mL + 196 mL)] = 1.254 g/mL).

Table 4.1. AP-101 Diluted Feed Composite Density

	AP-101 DF C	AP-101 DF H	Average	RPD (%)
Density (g/mL)	1.256	1.256	1.256	0

4.2 Heat Capacity

4.2.1 Background

A differential scanning calorimeter (DSC) was used to measure the heat capacity, which is the amount of heat required to raise a material 1°C. The DSC measures enthalpy (heat) changes either 1) as the temperature is increased at a known and constant rate or 2) at constant temperature by measuring differences in heat requirements between a sample and a reference located in a second sample holder. The heat capacity was measured on AP-101 diluted feed using a nominal sample size being 10 mg.

4.2.2 Sample Testing Parameters and Model

For the heat capacity measurement, a three-step approach is generally used. First the empty sample pan is heated to the starting temperature, held for 10 minutes, then heated over the temperature range of interest at a controlled rate, and then held at the final temperature for 10 minutes. Second, the sample pan is filled with roughly the same amount of reference material as will be used for the sample and the same temperature program repeated. The reference material is removed and replaced with the sample and the same temperature program repeated. The sample's heat capacity is calculated based on differences between the reference and the baseline and differences between the sample and the baseline taking into account differences in reference and sample masses. Typically, the reference material is similar in state and mass to the samples to be analyzed; e.g., typically water is used for aqueous samples and sapphire is used for solids sample.

The AP-101 diluted feed sample material from bottle AP-101 DF D was an aqueous sample, which presented a particular challenge because of the temperature range of interest (room temperature to above 100°C) and the volatility of water in that range. To prevent water evaporation and eliminate associated heat losses, which would mask measurement of the heat capacity, a 10 mg DI water reference and 10 mg AP-101 diluted feed samples were placed in hermetically sealed gold pans with a sealed volume of approximately 15 µL. The DI water reference was encapsulated in its own gold pan; the DI water reference was reused for each analysis and weighed between analyses to ensure no water loss. A linear least squares regression of water's heat capacity from 300 K (30°C) to 473 K (100°C) (Weast 1984) was used to model the DI water reference standard's heat capacity at constant pressure (C_p); e.g. $C_p = 0.000562*T+3.9998$ J/(g K). This model was used to extrapolate above the boiling point of water based on the assumption that the bulk of the water remained as liquid until the sealed pan ruptures; a rupture would be observed as a major endotherm by the DSC. The model was used to calculate the reference C_p at each data point temperature; data points were taken by the instrument every 0.4°C. Each AP-101 diluted feed sample analyzed was encapsulated in the same pan used for its baseline (i.e., empty pan) determination, and it was assumed that the behavior for these pans is equivalent to the behavior of the pan used for the DI water reference.

4.2.3 Sample Heat Capacity Results

The temperature program used for the triplicate analysis of the AP-101 diluted feed was to 1) heat to 30°C, 2) hold at 30°C for 10 minutes, 3) heat to 120°C at 5°C/min, and 4) hold at 120°C for 10 min. High purity water, which is recommended by the equipment manufacturer as the reference for aqueous samples, was used as a reference for the AP-101 diluted feed analysis. The results are presented in Table 4.2 and Figure 4.1 and provide the average measured heat capacity of the AP-101 diluted feed sample, 3.43 J/(g K). Figure 4.1 also provides a linear regression of the average heat capacity as a function of temperature. The linear least squares regression of data from the three analyses yields Equation 4.1 with a 95% confidence interval of ±0.34 J/(g K).

$$C_p = (-0.00012 * T) + 3.48 \qquad \text{(Equation 4.1)}$$

Where, C_p = heat capacity at constant pressure , J/(g K)
T = temperature in degrees Kelvin.

As shown in Table 4.2, the heat capacity of AP-101 dilute feed is lower than the heat capacity of water for the same temperature range. This is likely due to dissolved components in the AP-101 diluted feed, which typically have much lower heat capacities than water. For example, sodium nitrate at 300 K has a heat capacity of 1.10 J/(g K) compared to 4.18 J/(g K) for liquid water. The slight negative slope is unexpected. Rough calculations indicate that changes in the distribution of gaseous and liquid water (i.e., evaporation into the 5 µL container headspace) is not responsible for the negative slope; gaseous water at 300 K has a C_p of 1.88 J/(g K) or about half that of liquid water.

Table 4.2. Measured Heat Capacity of AP-101 Diluted Feed

Temperature (K)	Analysis 1 Cp J/(g K)	Analysis 2 Cp J/(g K)	Analysis 3 Cp J/(g K)	Average Cp J/(g K)	Water Cp J/(g K)
310	3.21	3.41	3.63	3.42	4.17
315	3.27	3.41	3.62	3.43	4.18
320	3.27	3.44	3.65	3.45	4.18
325	3.22	3.40	3.64	3.42	4.18
330	3.20	3.39	3.65	3.41	4.19
335	3.29	3.45	3.61	3.45	4.19
340	3.20	3.41	3.70	3.44	4.19
345	3.32	3.47	3.63	3.48	4.19
350	3.21	3.42	3.62	3.42	4.20
355	3.19	3.36	3.67	3.41	4.20
360	3.16	3.40	3.69	3.42	4.20
365	3.25	3.40	3.64	3.43	4.21
370	3.23	3.47	3.68	3.46	4.21
375	3.29	3.32	3.68	3.43	4.21
380	3.18	3.38	3.70	3.42	4.21
385	3.18	3.33	3.68	3.39	4.22
			Average Heat Capacity	**3.43**	

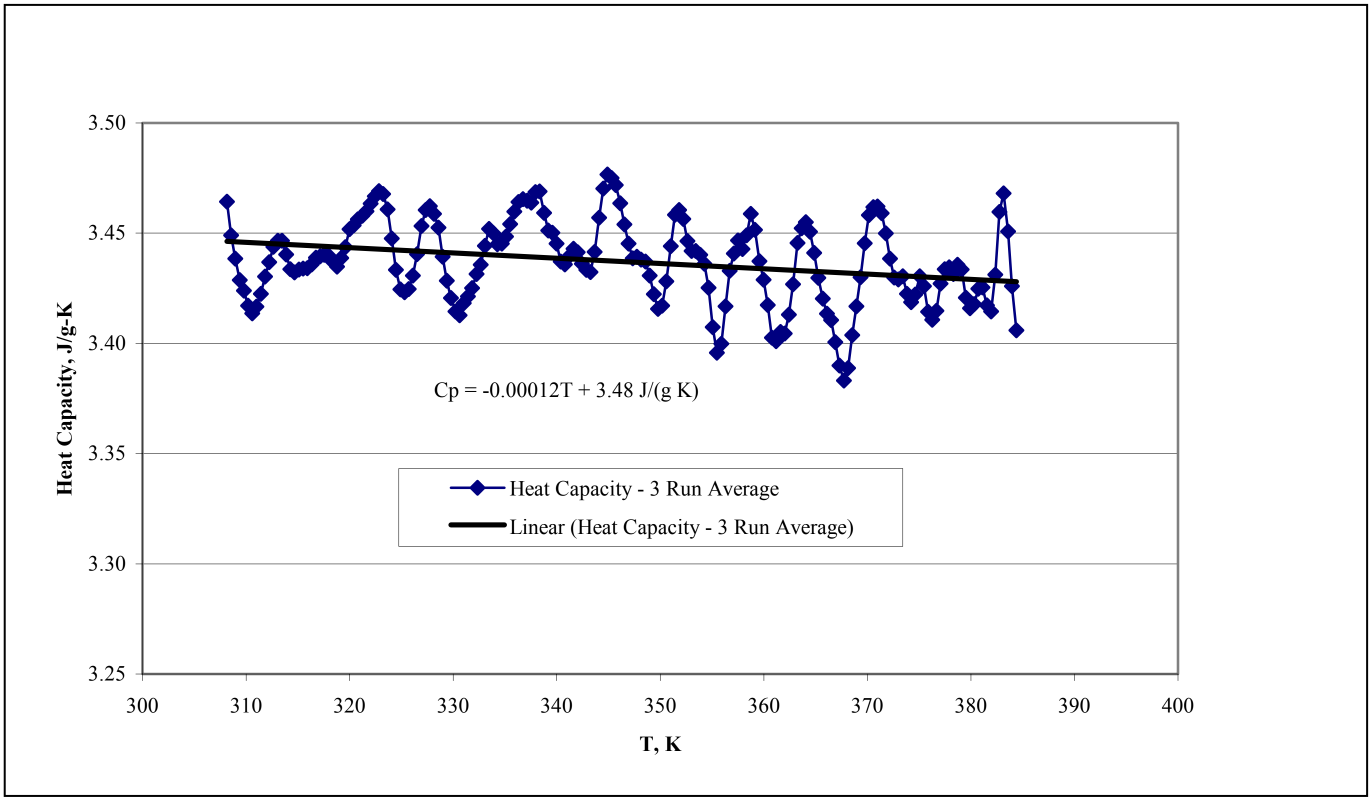


Figure 4.1. Plotted Heat Capacity of AP-101 Diluted Feed

4.3 Shear Stress Versus Shear Rate

Rheology testing of AP-101 slurry was performed with the Bohlin® CS10 modified for glovebox operations. The primary tests were standard shear stress vs. shear rate curves at 25°C, 35°C and 80°C.

4.3.1 Background

Viscosity is the internal resistance to flow of a fluid against external forces. Viscosity is mathematically defined as the shear stress divided by the shear rate. For a Newtonian fluid this ratio is constant. For non-Newtonian fluids this ratio can change based on flow conditions and shear history. High-molecular-weight liquids, slurries, and suspensions are often non-Newtonian, in that the viscosity is a function of shear rate. The rheological data most often requested and provided is a rheogram. Rheograms provide flow data over a range of shear stresses or shear rates. From a rheogram viscosity data, yield stress data and flow curve information are obtained. Viscosity is usually reported in centipoises (cP). One cP is equal to a millipascal second. There are several types of flow curves that have been well studied and have defined mathematical curve fits assigned to them. These curve fits are usually used to describe and predict flow behaviors of fluids. Some materials have a yield point, or minimal external force that must be applied before any flow is obtained. The AP-101 data did not always intercept the y-axis at zero, but the values were small enough to be neglected and therefore no yield stress is likely associated with this material. Therefore, the two curve fits used to evaluate the AP-101 are as follows:

1) Newtonian Equation ………………………… $\tau = \eta * \gamma$
2) Ostwald Equation
   (Pseudo-plastic or Power Law Fluid): ……… $\tau = \eta_p * \gamma$

Where: τ = Shear Stress (Pascal, Pa)
γ = Shear Rate (per second, $^1/_s$)
η = Viscosity (Pascal-seconds, Pa-s; reported in cP)
η_p = coefficient related to flow resistance, similar to apparent viscosity.
    $\eta_p = \eta$ for Newtonian fluid
n = power law factor
    n = 1 for Newtonian fluid
    n > 1 for dilatant fluid
    n < 1 for pseudo-plastic fluid

Classic examples of Newtonian fluids are water and honey. The viscosity is a constant over all shear conditions. A pseudo-plastic, or power law fluid, has a viscosity that varies with stress in a non-linear fashion.

4.3.2 Equipment Capabilities and Sensor Selection

The Bohlin® system used is a controlled stress device with a cone and plate measuring system. The sensor has a known geometry with a specified gap and is used to apply a stress on a fluid. The resulting fluid resistance to the flow causes measurable defection on an electronic transducer. This signal is read and combined with the applied stress data to determine shear rate data. The advantages of the Bohlin® CS10 system are that it uses very small sample (~6 ml) compared to the Haake® M5 system (~40 mL) and is more sensitive for low viscosity materials than the Haake® M5 system. The disadvantage of the Bohlin® CS10 system is that due to applying specific stresses instead of rates, sometimes the data is taken in a more random order. This makes it difficult to determine shear history effects on the material. However, hysterisis is generally not an issue for liquid samples, such as the AP-101 diluted feed. Also, the Bohlin® CS10 system limits the number of points gathered for any specific run. A 9.8 cP standard oil is used to validate the calibration of the system.

4.3.3 Sample Testing Parameters

The AP-101 slurry samples were tested at four temperatures: 25°C, 35°C, 50°C and 80°C. They were tested at multiple shear stresses. Replicate sample runs were performed at each temperature, but not all the runs provided usable data. In general, sample evaporation became a problem at higher temperatures resulting in poor reproducibility and higher than expected rheological behavior.

4.3.4 Rheology Curve Fits and Results

The viscosity data points obtained by this system are limited in number and contain large amounts of scatter. The large observed variation is probably the result of the low viscosity of the sample. Therefore, the best way to quantify the viscosity and flow behavior of this material is though reliance on curve fit data. All the utilized runs produce data that is predominantly Newtonian in nature.

The measured viscosity for the AP-101 diluted feed is 4 cP to 5 cP within the 25°C to 35°C temperature range. The viscosity decreased to between 2.5 cP to 3 cP when the temperature was raised to greater than 50°C.

As can be seen in Table 4.3, the best curve fits based on a least squares fit of the data to the models were found to be Newtonian for all AP-101 diluted feed runs reported. The Ostwald n and R^2 are included for a reference when the R^2 values for an Ostwald fit are close to the Newtonian R^2. The ‘n’ factor is a measure of the degree of pseudo-plasticity or deviation from Newtonian the fluid exhibits. The closer the n factor is to 1.0 the more Newtonian the fluid. Any intercepts or yield factors are most likely an artifact of the system at very low shear stresses due to the mechanical drag forces and have been neglected.

Table 4.3. Viscosity Model Fit Parameters

Sample	Newtonian		Ostwald		
	η (cP)	R^2	η_p	n	R^2
Standard	10.8	0.973	n/a		
AP-101 25 C 1-1	4.3	1.00	n/a		
AP-101 25 C 2-1	4.2	.980	n/a	0.607	.957
AP-101 25 C 2-2	4.1	.972	n/a	0.543	.937
AP-101 25 C 2-3	5.2	.989	n/a	0.490	.888
AP-101 35 C 1-1	4.4	.852	n/a	0.399	.851
AP-101 50 C 1-1	2.5	.965	n/a		
AP-101 50 C 1-2	2.9	.985	n/a		
AP-101 80 C 1-2	3.0	.902	n/a	0.442	.872
n/a – not applicable since the Newtonian fit was superior					

4.4 Particle Size

4.4.1 Background

The particle size distribution of the AP-101 diluted feed is described in this section. A Microtrac™ Ultrafine Particle Analyzer (UPA) was used to measure the particle size distribution of the tank samples. The Microtrac™ UPA measures particle diameter by Doppler shifted scattered light. This method is limited to particles with diameters between 3 nm and 6.5 µm. When the PNWD received the AP-101 sample, the sample was observed to be a clear yellow liquid with no visible solids. However, prior to the particle size measurements the sample was observed to be a translucent (i.e., cloudy) pale yellow liquid. A thin layer of white particulates appeared to be present on the bottom of the sample vial. The change in physical appearance is most likely due to solids that had precipitated in the sample during storage. This precipitation was most likely the result of temperature change, or minor evaporation since preparing the diluted feed composite. The presence of these precipitates indicates that the AP-101 diluted feed has a chemical composition that is close to a solubility product constant for at least one compound. Based on these observations, the reported particle size data reported may not be representative of the diluted feed composite. However, it provides insight into the particles that could form in the waste treatment plant during recovery and storage operations.

The Microtrac™ X-100 particle size analyzer, with a particle size range of 0.12 µm and 700 µm, could not be used for analysis. The Microtrac™ X-100 requires approximately 300 mL of liquid sample for analysis. When sufficient sample is unavailable, this large sample size requirement is typically overcome by diluting the sample with a large fraction of liquid phase simulant. Unfortunately, the use of a liquid simulant could change the liquid composition such that misrepresentative particle size data are obtained (e.g., dissolution or precipitation of solids). The UPA only requires a small volume of slurry, so no liquid simulant was needed. The particle size data reported here was conducted directly on the AP-101 diluted feed.

4.4.2 Standards

The UPA instrument performance was checked against a set of standards from Duke Scientific Corporation traceable to the National Institute of Standards and Technology (NIST). These standards are polymer microspheres dispersed in a 1 mM potassium chloride solution. These standards were run prior to and after analysis of the AP-101 dilute feed samples. Results from these standard tests are presented in Table 4.4. The percentile data shown in the table represent the given percent of the volume (or weight if the specific gravity for all particles is the same) or given percent of the number of particles that is smaller than the indicated particle size. The mean diameter of the distribution represents the centroid of the distribution. The difference between the volume and number basis calculations can be explained by recognizing for a given number of particles at a specific size, that as particle size increases the volume contribution of these particles increases cubically. This weights the volume distribution more heavily towards larger particles (i.e. a few larger particles will greatly affect the volume basis but will have no significant effect on the number basis).

Table 4.4. UPA Calibration Standards

	UPA (Measurement Prior to Analyses)			
	Size on a Volume Basis (nm)	**Size on a Number Basis (nm)**	**Size on a Volume Basis (nm)**	**Size on a Number Basis (nm)**
Standard Mean Size	96	96	895	895
Measured Mean Size	114	98	907	825
10% < Size	88	87	712	624
50% < Size	100	97	901	816
90% < Size	116	111	1110	1018
	UPA (Measurement After Analyses)			
	Size on a Volume Basis (nm)	**Size on a Number Basis (nm)**	**Size on a Volume Basis (nm)**	**Size on a Number Basis (nm)**
Standard Mean Size	96	96	895	895
Measured Mean Size	101	91	978	890
10% < Size	78	73	763	683
50% < Size	98	88	970	874
90% < Size	128	112	1201	1100

4.4.3 Sample Particle Size Results

Table 4.5 and Table 4.6 contain a summary of the particle size analysis from the UPA instrument on a volumetric and numeric basis, respectively. The data in these tables represent the separation of the particle size data into one or more peaks or modes (first column). The peak/mode particle size (second column) represents the value where 50% of the particles in this peak/mode are smaller than the given value. The peak/mode width (third column) provides a measure of the size variability within the peak/mode. The fourth column represents the percent contribution of each peak/mode to the entire distribution.

The data presented in Table 4.5 indicate a large volume of particles in the 0.5 μm to 2.5 μm range. The peak value is at about 1.5 μm. There is a large increase in the volume of particles in the 2.5 μm to 6 μm range. From these results there appears to be a significant volume of particles larger than 6 μm. Table 4.6 presents the same data on a particle number basis. From these data, the number of particles in the 0.3 μm to 3 μm range account for nearly all of the particles in the sample.

Table 4.5. Particle Size Distribution (Volume) of AP-101 Diluted Feed

Sample Conditions	Peak/Mode Number	Peak/ Mode Particle Size (μm)	Peak/Mode Width (μm)	Approximate Volume Percent of Particles in Peak/Mode
UPA Run #1	1	5.30	2.39	66%
	2	1.15	1.09	34%
UPA Run #2	1	5.50	1.88	54%
	2	1.89	1.27	46%
UPA Run #3	1	5.51	2.03	40%
	2	1.38	0.89	60%
UPA Average	1	5.44	2.10	53%
	2	1.47	1.08	47%

Table 4.6. Particle Size Distribution (Number) of AP-101 Diluted Feed

Sample Conditions	Peak/Mode Number	Peak/ Mode Particle Size (μm)	Peak/Mode Width (μm)	Approximate Number Percent of Particles in Peak/Mode
UPA Run #1	1	0.60	0.52	100%
UPA Run #2	1	5.18	1.72	3%
	2	1.45	0.88	80%
	3	0.90	0.10	17%
UPA Run #3	1	1.02	0.66	100%
UPA Average	1	5.18	1.72	1%
	2	1.12	0.55	66%
	3	0.60	0.52	33%

The particle size distributions on a volume basis are presented graphically in Figure 4.2 and Figure 4.3. Figure 4.2 presents the volume percent of particles in a small, discrete range. Figure 4.3 presents the sum of these data from small particles to large particles and is referred to as the cumulative volume percent. These data represent the volume percent of particles smaller than a given particle size. The volume distribution data indicate that most of the particles are larger than 0.3 μm. From the shape of the curves in Figure 4.3, there appears to be a significant volume of particles larger than 6 μm.

The particle size distributions on a number basis are presented graphically in Figure 4.4 and Figure 4.5. Because the number basis distribution weighs small particles more heavily, nearly all of the particles in the sample are accounted for in the 0.3 μm to 3 μm range.

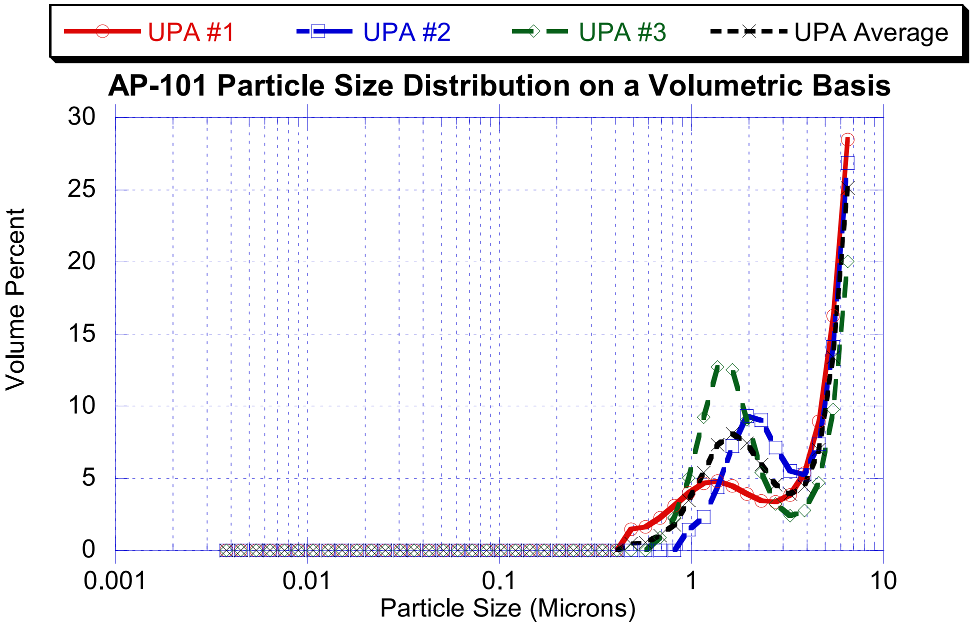


Figure 4.2. AP-101 Diluted Feed Particle Size (Volume Basis)

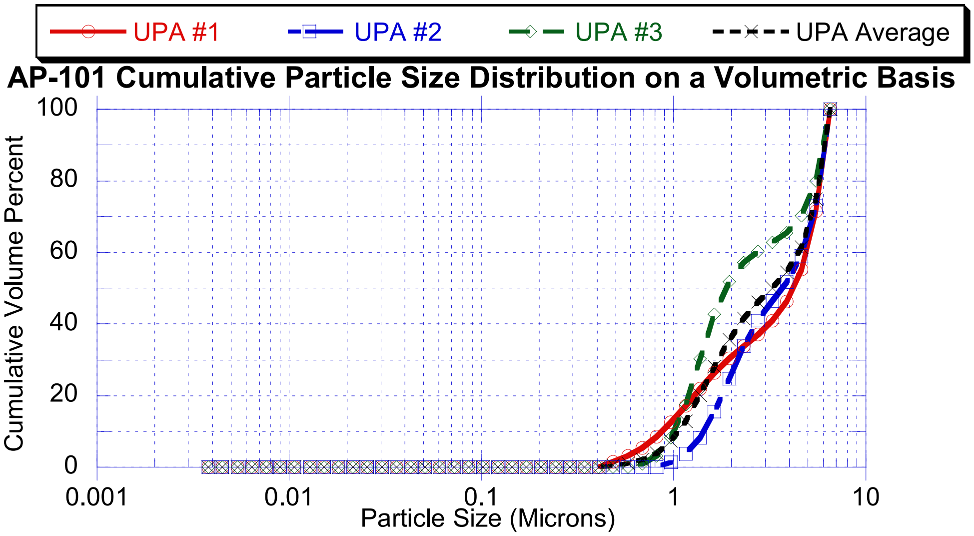


Figure 4.3. AP-101 Diluted Feed Particle Size AP-101 (Cumulative Volume Basis)

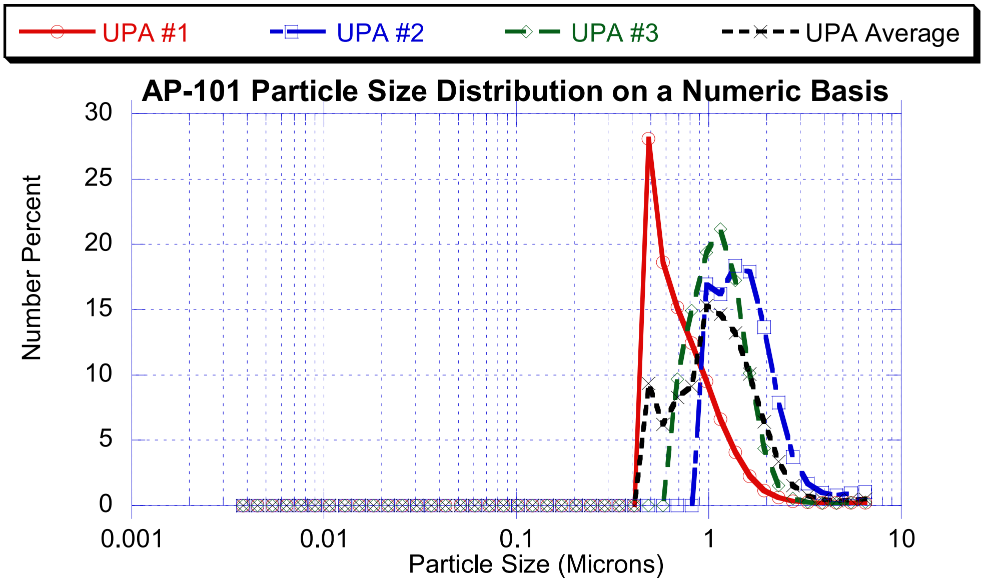


Figure 4.4. AP-101 Diluted Feed Particle Size (Number Basis)

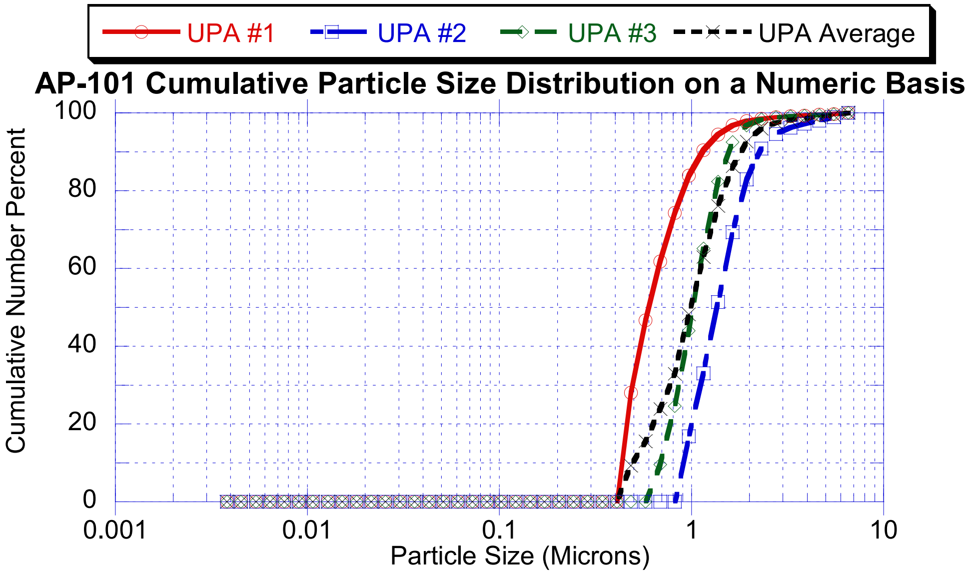


Figure 4.5. AP-101 Diluted Feed Particle Size (Cumulative Number Basis)

5.0 Analytical Sample Processing

The analytical processing of the AP-101 diluted feed composite and distribution of the unprocessed and processed sample aliquots are detailed in Figure 5.1. The contents of the three bottles of AP-101 diluted feed composite were analyzed for the physical properties and chemical and radioisotope analytes defined in the TS. Analytical Service Request 6031 initiated the analytical operations as defined in the TS, and per the ASR the AP-101 diluted feed was assigned RPL Number 01-00520.

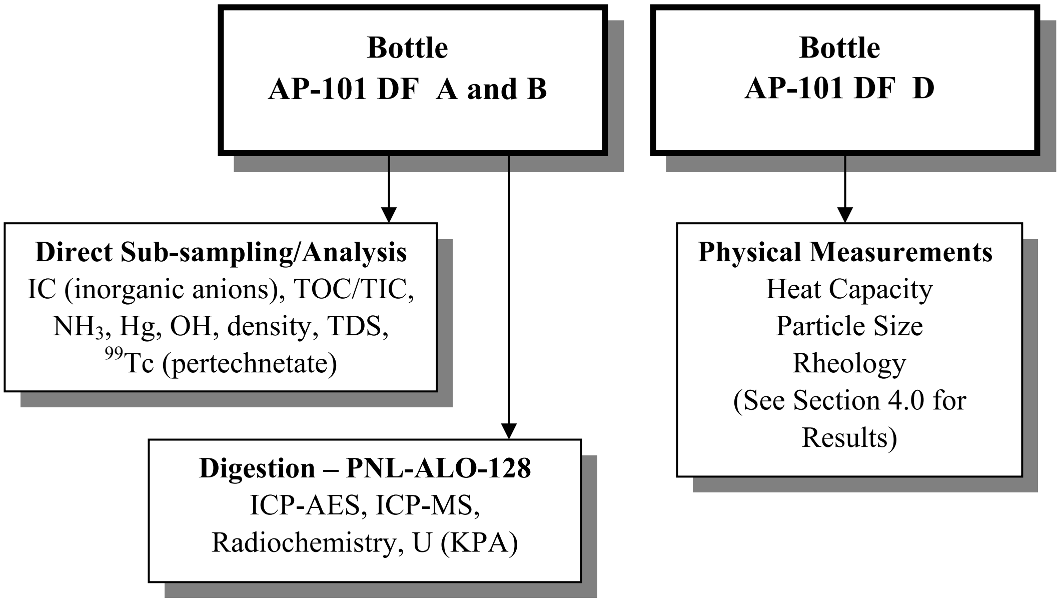


Figure 5.1. Flow Diagram for Analytical Processing of AP-101 Sub-samples

5.1 Density and Total Dissolved Solids

The contents of bottles AP-101 DF A and AP-101 DF B were measured for density for comparison to the density results obtained on the AP-101 diluted feed composite prior to sub-sampling. The contents were also measured for weight percent total dissolved solids (TDS) by drying aliquots at 105°C to a constant weight. The density and TDS analyses were performed per PNL-ALO-501, *Laboratory Procedure for Measurement of Physical and Rheological Properties of Solutions, Slurries, and Sludges*. The results of the density and TDS are presented in Table 5.1.

Table 5.1. AP-101 Diluted Feed Density and TDS

	AP-101 DF A	AP-101 DF B	Average	RPD (%)
Density (g/mL)	1.258	1.258	1.258	0
TDS (Wt%)	31.1	32.1	31.6	3

5.2 Direct Sub-sampling/Analysis

The AP-101 diluted feed samples AP-101 DF A and AP-101 DF B were sub-sampled in the Shielded Analytical Laboratory (SAL) hot cells and then delivered to the RPL analytical workstations for various measurements including inorganic anions, hydroxide, ammonia, mercury, total organic and inorganic carbon (TOC/TIC), and ^{99}Tc (pertechnetate). For these sub-samples, the analytical workstation is responsible for ensuring that the appropriate batch and analytical QC samples are analyzed, as well as providing any additional processing to the sub-samples that might be required (e.g., digestions for mercury analysis).

5.3 Acid Digestion

Portions of the AP-101 diluted sample were acid digested according to procedure PNL-ALO-128, *HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*, in the SAL hot cells. Aliquots of the digested solutions were delivered to the 329 Facility for inductively coupled plasma-mass spectrometry (ICP-MS) and to various RPL analytical workstations for inductively coupled plasma-atomic emission spectroscopy (ICP-AES), total U by kinetic phosphorescence analysis (KPA), and the following radiochemical analyses: total alpha, gamma emitters by gamma energy analysis (GEA), $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, $^{243+244}$Cm, and ^{90}Sr.

The SAL processed 1-mL aliquots of the supernatant in duplicate. The acid extracted solutions were brought to a nominal 25-mL volume, and absolute volumes were determined based on final solution weights and densities. Along with a sample and duplicate, the SAL processed duplicate digestion process blanks (PB), two blank spikes (BS) (one for ICP-AES and one for ICP-MS), and two matrix spikes (MS) (one for ICP-AES and one for ICP-MS). Aliquots of the BS, MS, and the PBs were sent with aliquots of the duplicate samples for ICP-AES or ICP-MS analyses. For radiochemical analyses, only the two PBs were sent with aliquots of the duplicate samples for analysis. Post digestion BS and MS samples were prepared at the time of radiochemical separation except for GEA, which does not require any additional sample preparation.

6.0 Analytical Results

6.1 Introduction

Tables 6.1 through 6.4 provide inorganic, and radioisotopic analytical results for the AP-101 diluted feed samples. Results are reported in µg/mL or µCi/mL, as appropriate. For many analyses the nominal propagated uncertainties are also provided as 1-σ, unless otherwise noted.

Besides the sample and duplicate results, the results obtained on the PBs are also reported, as applicable. Generally, analyte concentrations in the PBs were either insignificant relative to the sample analyte concentration or at or near the MDL. This indicates that in most cases, the processing steps did not result in significant sample contamination. Where the blank contribution exceeds the acceptance criteria established by the governing Quality Assurance (QA) Program's plan *Conducting Analytical Work in Support of Regulatory Programs* (Sections 4 and 5), the sample and duplicate results are flagged with a 'B', as described below.

The Analytical Results Tables 6.1 through 6.4 and the QC Tables 7.1 through 7.4 include a Data Flag column (i.e., a "Data Qualifier Code") and the analyte concentrations or averages are flagged, as appropriate. The codes utilized were taken from the QA Plan and are defined below, as they relate to this report:

U	Undetected. Analyte was analyzed, but not detected (e.g., no measurable instrument response) or response was less than the MDL. (Note: For some analyses, no results are reported below the lowest calibration standard, and any results less than the lowest calibration standard are reported as less than values and flagged with a U. Footnotes in the tables identify which analyses use the lowest calibration standard as the reporting level.)
J	Estimated value. The value reported is below the estimated quantitation limit (EQL) and above the MDL. For radiochemical data, the J flag identifies results that have a propagated error of >10%, indicating that the results are typically within 10 times the MDA.
B	Analyte found in associated laboratory processing blank above the QA plan acceptance criteria (i.e., the blank is greater than the EQL or the blank exceeds 5% of sample concentration).
X	A QC deficiency was associated with the reported result. For this report the X flag is used for the following: a) batch laboratory control sample (LCS) fails or was not analyzed, b) both the MS <u>and</u> the post spike fail, c) serial dilution test (if required) fails for analytes with concentration greater than 0.1%.

The term MDL used in this report is an 'estimated' MDL. That is, the MDLs have not been determined on the tank waste matrix per SW-846[2] protocol; however, a few MDLs have been

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[2] U.S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, Third Edition including Updates I, II, IIA, IIB, III, and IIIA, Office of Solid Waste and Emergency Response. Washington. D.C.

determined for reagent water per the SW-846 protocol (e.g., cyanide and mercury). For most methods, the 'estimated' MDLs are based on an instrument detection limit (IDL) estimated from using reagents and/or low concentration high-purity standards as samples and evaluating instrument response near background levels. The estimated quantitation limit (EQL) is typically set at 10 times the estimated MDL adjusted for dilution factors resulting from digestion or leaching processing. For a few methods (e.g., IC and ammonia), no 'estimated' MDL is determined and the EQL is based on the lowest calibration standard; no results are reported below the EQL for these methods. For radiochemical methods, the minimum detectable activity (MDA) is calculated per the QA Plan and is based on the background counting statistics.

Specific quality control and quality assurance discussions are given in Section 7.0.

6.2 Analyte List Modifications

The AP-101 diluted feed analyte list is defined by the TS. A few modifications to the analyte list or procedures defined by the TS had to be incorporated, and are detailed below:

- Pertechnetate ($^{99}TcO_4^-$) as opposed to total ^{99}Tc was to be determined using separations and beta counting techniques. The ^{99}Tc procedure was modified slightly to exclude the sample oxidation step so that the non-pertechnetate fraction was not oxidized. Also, instead of measuring the ^{99}Tc by liquid scintillation, sample preparations were counted with gas-flow proportional counters.
- Analyte concentrations in addition to those required by the TS are provided. These additional analytes were measured as part of the method and are provided for additional information only.
- Sulfur by ICP-AES could not be performed, since the ICP-AES used for this work does not have a sulfur channel. An alternate method was not available for sulfur determination; therefore, no sulfur results are reported.

6.3 Data Limitations

- The fluoride results have significant technical deficiencies. The reported fluoride results may represent the summation of fluoride, acetate, and formate concentrations, as these are not readily resolved on the anion analysis IC system. Based on the formate and acetate results reported on the AP-101 as-received waste (Fiskum 2000), the fluoride results are most likely an overestimate of the actual fluoride present in the AP-101 waste.
- Although the pertechnetate ($^{99}Tc^{+7}$) and total ^{99}Tc agree reasonably well, the pertechnetate MS contributed about 12% to the measured pertechnetate concentration resulting in a very poor MS recovery. Based solely on the MS recovery, the results have been flagged as having a QC deficiency.
- Total Cs concentration is calculated based on the ICP-MS ^{133}Cs result in the AP-101 diluted feed and the Cs atomic mass ratios determined by ICP-MS following ion exchange to separate the Cs.

6.4 General Observations

- The total ^{99}Tc measured by ICP-MS agrees reasonably well with the pertechnetate analysis (^{99}Tc^{+7}) measured by separations and beta counting. This suggests that most of the ^{99}Tc is in the pertechnetate state.
- The total alpha measurement results (i.e., 2.17e-04 μCi/mL) agreed well with the sum of alpha emitting radioisotopes (^{238}Pu, $^{239/240}$Pu, ^{241}Am, $^{243/244}$Cm, and ^{242}Cm) measured (i.e., 2.64e-04 μCi/mL).

6.5 AP-101 Diluted Feed Results

The analytical results for the AP-101 diluted feed samples are presented in Tables 6.1 through 6.4. Comparison of the diluted feed samples to Specification 7 is presented in Section 6.6.

Table 6.1. AP-101 Diluted Feed- ICP Metals Results

	Process Blank 1			**Process Blank 2**			**Sample**			**Duplicate**		
	MDL	**01-520 PB1**	**Data**	**MDL**	**01-520 PB2**	**Data**	**MDL**	**01-520**	**Data**	**MDL**	**01-520 D**	**Data**
Analyte	**µg/mL**		**Flag**	**µg/mL**		**Flag**	**µg/mL**		**Flag**	**µg/mL**		**Flag**
ICP-AES Test Specification Analytes (a)												
Al	1.6	4.7	J	1.6	4.7	J	8.2	6,930	X	8.1	7,030	X
Ba	0.27	0.27	U	0.27	0.27	U	1.4	1.4	U	1.4	1.4	U
Ca	6.7	6.7	U	6.8	47	J	34.2	210	JB	33.9	210	JB
Cd	0.4	0.4	U	0.4	0.4	U	2.1	2.1	U	2.0	2.0	U
Cr	0.54	0.54	U	0.55	0.55	U	2.7	151		2.7	153	
Fe	0.67	1.2	J	0.68	0.73	J	3.4	3.8	JB	3.4	3.4	UB
K	54	54	U	55	55	U	274	29,800	X	271	29,700	X
La	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U
Mg	2.7	2.7	U	2.7	2.7	U	14	14	U	14	14	U
Na	4	76.5		4.1	61.2		21	113,000	X	20	115,000	X
Ni	0.81	2.2	J	0.82	1.7	J	4.1	4.4	JB	4.1	4.1	UB
P	2.7	2.7	U	2.7	2.7	U	14	381		14	389	
Pb	2.7	2.7	U	2.7	2.7	U	14	14	U	14	14	U
U	54	54	U	55	55	U	270	270	U	270	270	U
Other Analytes Measured												
Ag	0.67	0.67	U	0.68	0.68	U	3.4	3.4	UX	3.4	3.4	UX
As	6.7	6.7	U	6.8	6.8	U	34	34	U	34	34	U
B	1.3	47		1.4	43		6.8	54	JB	6.8	56	JB
Be	0.27	0.27	U	0.27	0.27	U	1.4	1.4	U	1.4	1.4	U
Bi	2.7	2.7	U	2.7	2.7	U	14	14	U	14	14	U
Ce	5.4	5.4	U	5.5	5.5	U	27	27	U	27	27	U
Co	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U
Cu	0.67	0.67	U	0.68	0.68	U	3.4	3.4	U	3.4	3.4	U
Dy	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U
Eu	2.7	2.7	U	2.7	2.7	U	14	14	U	14	14	U

Table 6.1. (Cont'd)

Analyte	Process Blank 1			Process Blank 2			Sample			Duplicate		
	MDL	01-520 PB1	Data Flag	MDL	01-520 PB2	Data Flag	MDL	01-520	Data Flag	MDL	01-520 D	Data Flag
	µg/mL			µg/mL			µg/mL			µg/mL		
Li	0.81	0.81	U	0.82	0.82	U	4.1	4.1	U	4.1	4.1	U
Mn	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U
Mo	1.3	1.3	U	1.4	1.4	U	6.8	14	J	6.8	14	J
Nd	2.7	2.7	U	2.7	2.7	U	14	14	U	14	14	U
Pd	20	20	U	20	20	U	103	103	U	102	102	U
Rh	8.1	8.1	U	8.2	8.2	U	41	41	U	41	41	U
Ru	30	30	U	30	30	U	150	150	U	150	150	U
Sb	14	14	U	14	14	U	68	68	U	68	68	U
Se	6.7	6.7	U	6.8	6.8	U	34	34	U	34	34	U
Si	14	120	J	14	130	J	68	420	JBX	68	300	JBX
Sn	41	41	U	41	41	U	210	210	U	200	200	U
Sr	0.4	0.4	U	0.41	0.41	U	2.1	2.1	U	2	2	U
Te	41	41	U	41	41	U	210	210	U	200	200	U
Th	27	27	U	27	27	U	140	140	U	140	140	U
Ti	0.67	0.67	U	0.68	0.68	U	3.4	3.4	U	3.4	3.4	U
Tl	14	14	U	14	14	U	68	68	U	68	68	U
V	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U
W	54	54	U	55	55	U	270	270	U	270	270	U
Y	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U
Zn	1.3	1.3	U	1.4	2.7	J	6.8	7.6	JB	6.8	8.4	JB
Zr	1.3	1.3	U	1.4	1.4	U	6.8	6.8	U	6.8	6.8	U

(a) All ICP-AES analytes reported except sulfur. (See Section 6.2)

Table 6.2. AP-101 Diluted Feed – ICP-MS Results

	Process Blank 1				Process Blank 2				Sample				Duplicate			
	MDL	01-520-PB1	± 1SD	Data Flag	MDL	01-520-PB2	± 1SD	Data Flag	MDL	01-520	± 1SD	Data Flag	MDL	01-520 D	± 1SD	Data Flag
Analytes	µg/mL				µg/mL				µg/mL				µg/mL			
U(KPA)(a)	6E-03	3.41E-01	2%		6E-03	1.92E-01	2%		6E-03	4.11E+01	4%		6E-03	4.02E+01	4%	
^{133}Cs	8.2E-02	8.2E-02		U	7.5E-02	7.5E-02		U	5.7E-02	2.99E+00	1.47E-02		5.7E-02	2.92E+00	3.61E-02	
^{135}Cs(c)	8.2E-02	2.1E-02		U	7.5E-02	1.9E-02		U	5.7E-02	7.62E-01	6.70E-03		5.7E-02	7.49E-01	1.07E-02	
^{137}Cs(c)	8.2E-02	3.3E-02		U	7.5E-02	3.0E-02		U	5.7E-02	1.19E+00	1.22E-02		5.7E-02	1.17E+00	1.57E-02	
Total Cs(c)	8.2E-02	1.4E-01		U	7.5E-02	1.2E-01		U	5.7E-02	4.95E+00	n/a		5.7E-02	4.83E+00	n/a	
Rb	1.1E-01	1.1E-01		U	9.7E-02	9.7E-02		U	7.4E-02	3.99E+00	3.83E-02		7.3E-02	3.88E+00	6.23E-02	
AMU-241(b)	1.3E-03	1.3E-03		U	1.3E-03	1.3E-03		U	2.3E-03	2.3E-03		U	2.6E-03	2.6E-03		U
	µCi/mL				µCi/mL				µCi/mL				µCi/mL			
AMU-241(b)	4.2E-03	4.2E-03		U	4.2E-03	4.2E-03		U	7.4E-03	7.4E-03		U	8.4E-03	8.4E-03		U
^{99}Tc	2.3E-03	2.3E-03		U	2.1E-03	2.1E-03	1.09e-03		1.6E-03	4.00E-02	9.62E-04		1.6E-03	3.83E-02	1.14E-03	
^{237}Np	1.3E-06	1.3E-06		U	1.3E-06	1.3E-06		U	3.7E-06	3.7E-06		U	3.9E-06	3.9E-06		U
^{239}Pu	3.2E-04	3.2E-04		U	3.1E-04	3.1E-04		U	7.3E-04	7.3E-04		U	7.7E-04	7.7E-04		U
^{240}Pu	2.3E-04	2.3E-04		U	2.3E-04	2.3E-04		U	6.7E-04	6.7E-04		UX	7.0E-04	7.0E-04		UX

n/a = not applicable.

(a) Uranium results by KPA; standard deviation reported in percent.

(b) AMU-241 is either ^{241}Am or ^{241}Pu or a combination thereof. The µg/mL results are calculated based on the calibration of the AMU-241 as ^{241}Am and the µCi/mL results are calculated using the specific activity of ^{241}Am (3.23 Ci/g).

(c) Total Cs, ^{135}Cs, and ^{137}Cs calculated from the ^{133}Cs results and independent Cs atomic mass ratios determined by ICP-MS. MDL set to MDL for ^{133}Cs.

Decay correction reference date is nominally May 2001.

Table 6.3. AP-101 Diluted Feed – Radioisotope Results

	Process Blank 1				**Process Blank 2**				**Sample**				**Duplicate**			
	MDA	**01-520-PB1**	**Err**	**Data**	**MDA**	**01-520-PB2**	**Err**	**Data**	**MDA**	**01-520 Sample**	**Err**	**Data**	**MDA**	**01-520 Dup**	**Err**	**Data**
Analyte	**µCi/mL**		**% $^{(a)}$**	**Flag**	**µCi/mL**		**% $^{(a)}$**	**Flag**	**µCi/mL**		**% $^{(a)}$**	**Flag**	**µCi/mL**		**% $^{(a)}$**	**Flag**
Total Alpha	2E-04	2E-04		U		n/m			9E-05	2.03E-04	17%	J	9E-05	2.31E-04	16%	J
^{238}Pu	6E-07	6E-07		U		n/m			4E-07	1.51E-05	5%		8E-07	1.29E-05	6%	
$^{239/240}$Pu	6E-07	6E-07		U		n/m			5E-07	1.10E-04	2%		7E-07	1.10E-04	3%	
^{241}Am	7E-07	9.91E-07	28%	J		n/m			6E-07	1.37E-04	2%		5E-07	1.39E-04	3%	
^{241}Am (GEA)	1E-03	1E-03		U	1E-03	1E-03		U	1E-02	1E-02		U	1E-02	1E-02		U
$^{243/244}$Cm	6E-07	6E-07		U		n/m			4E-07	2.89E-06	13%	J	5E-07	1.34E-06	22%	J
^{242}Cm	4E-07	4E-07		U		n/m			4E-07	4E-07		U	4E-07	4E-07		U
Sum of Alpha	3E-06	9.91E-07	4%			n/m			2E-06	2.65E-04	4%		3E-06	2.63E-04	4%	
^{90}Sr	4e-04	1.05E-02	5%			n/m			3E-03	6.79E-02	4%	B	4E-03	7.49E-02	4%	B
^{99}Tc^{+7}	2E-06	4.46E-06	15%	J		n/m			4E-06	3.24E-02	4%	X	5E-06	3.67E-02	4%	X
^{134}Cs	*3e-04*	*3E-04*		*U*	*3E-04*	*3E-04*		*U*	*1E-03*	*2.96E-02*	*2%*		*1E-03*	*2.77E-02*	*2%*	
^{137}Cs	3E-04	8.49E-03	4%		3E-04	1.00E-02	3%		6E-03	1.27E+02	2%		6E-03	1.25E+02	2%	
^{60}Co	6E-04	6E-04		U	6E-04	6E-04		U	2E-04	2.50E-03	5%		2E-04	2.53E-03	5%	
^{154}Eu	1E-03	1E-03		U	9E-04	9E-04		U	1E-03	1E-03		U	1E-03	1E-03		U
^{155}Eu	8E-04	8E-04		U	8E-04	8E-04		U	1E-02	1E-02		U	1E-02	1E-02		U

(a) The % error represents the uncertainty at 1-σ.

n/m = not measured; actinides and ^{90}Sr results from 2nd digestion processing which produced only a single PB. See Section 7.4.
Results in italics indicate analytes not specified in the test specification and are for information only.

Decay correction reference date is nominally May 2001

Table 6.4. AP-101 Diluted Feed – Other Analytes Results

	Process Blank			Sample			Duplicate		
	EQL/ MDL (a)	01-520-PB	Data	EQL/ MDL (a)	01-520	Data	EQL/ MDL (a)	01-520 D	Data
Analyte	µg/mL		Flag	µg/mL		Flag	µg/mL		Flag
Test Specification Analytes									
F (b)	0.28	0.28	U	480	2,300		480	2,300	
Cl	0.28	0.28	U	480	1,400		480	1,500	
NO_2	0.55	0.55	U	950	31,200		950	33,800	
NO_3	0.55	0.55	U	1900	103,000		1900	105,000	
PO_4	0.55	0.55	U	950	950	U	950	950	U
SO_4	0.55	0.55	U	1900	4,700		1900	4,600	
OH	170	170 (d)	U	170	32,400		170	33,400	
NH_3	10	10 (e)	U	10	26		10	26	
Hg	0.07	0.07	U	0.07	0.07	UX	0.07	0.07	UX
TOC-F(c)	n/a	n/a		220	7,900		220	8,000	
TIC-F(c)	n/a	n/a		170	170	U	170	170	U
TOC-P(c)	n/a	n/a		36	1,650		36	1,620	
TIC-P(c)	n/a	n/a		13	5,360		13	5,350	
Other Analytes Measured									
Br	0.28	0.28	U	480	480	U	480	480	U
Oxalate	0.55	0.55	U	950	950	U	950	950	U

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, oxalate, and NH_3 are reported only results above the EQL; therefore, the EQL is presented in this column. For all other analytes, the MDL is presented.

(b) Fluoride results should be considered the upper bound concentration for the fluoride. Significant peak distortion of the fluoride peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(c) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC); System blanks are subtracted from all sample results per procedure and are not applicable (i.e., n/a).

(d) For OH blank, no inflection point was detected.

(e) Ammonia detected in the blank at 0.5 µg/mL, well below the linear calibration range and the EQL.

6.6 Comparison of AP-101 Diluted Feed Results to Specification 7

Specification 7 for Envelope A defines limits for several analytes relative to sodium concentration (moles analyte per mole Na or Bq analyte per mole Na). Table 6.5 and Table 6.6 present the ratio limits and the measured ratios. For all analytes, the mole or Bq analyte to moles Na ratio did not exceed the limits defined in Specification 7 for Envelope A.

Table 6.5. AP-101 Diluted Feed – Mole Analyte per Mole Na Ratio

Analytes	MRQ µg/mL	MDL/EQL (a) µg/mL	01-520 Average µg/mL	Data Flag	Measured Mole Analyte per Mole Na Ratio	Spec 7 Envelope A Limits Mole Analyte per Mole Na Ratio	% of Limit	Meets Spec 7?
Al	75	8.2	6,980		5.2E-02	2.5E-01	21	Yes
Ba	2.3	1.4	1.4	U	< 2.0E-06	1.0E-04	< 2.0	Yes
Ca	150	34	210	JB	1.1E-03	4.0E-02	2.8	Yes
Cd	7.5	2.1	2.1	U	< 3.7E-06	4.0E-03	< 0.09	Yes
Cl	300	480	1,450		8.4E-03	3.7E-02	23	Yes
Cr	15	2.7	152		5.9E-04	6.9E-03	8.6	Yes
F	150	480	2,300		2.4E-02	9.1E-02	26	Yes
Fe	150	3.4	3.6	JB	1.3E-05	1.0E-02	0.1	Yes
Hg	1.5	0.070	0.070	U	< 7.0E-08	1.4E-05	< 0.5	Yes
K	75	272	29,800	X	1.5E-01	1.8E-01	83	Yes
La	35	6.8	6.8	U	< 9.9E-06	8.3E-05	< 12	Yes
Na	75	20	114,000			n/a		
Ni	30	4.1	4.4	JB	1.6E-05	3.0E-03	0.5	Yes
NO_2	3000	950	32,500		1.4E-01	3.8E-01	37	Yes
NO_3	3000	1,900	104,000		3.4E-01	8.0E-01	43	Yes
Pb	300	14	14	U	< 1.3E-05	6.8E-04	< 1.9	Yes
PO_4 (b)	2500	n/a	1180		2.5E-03	3.8E-02	6.6	Yes
PO_4	2500	950	950	U	< 2.0E-03	3.8E-02	< 5.3	Yes
SO_4	2300	1,900	4,650		9.8E-03	1.0E-02	98	Yes
TIC-F (c)	150	170	170	U	< 2.9E-03	3.0E-01	< 1.0	Yes
TOC-F (c)	1500	220	8,000		1.4E-01	5.0E-01	28	Yes
TIC-P (c)	150	13	5,350		9.0E-02	3.0E-01	30	Yes
TOC-P (c)	1500	36	1,640		2.8E-02	5.0E-01	5.6	Yes
U	600	272	272	U	< 2.3E-04	1.2E-03	< 19	Yes

n/a = not applicable; all analytes ratioed to sodium.

(a) F, Cl, NO_2, NO_3, PO_4, and SO_4 report only results above the EQL; therefore, the EQL is presented in this column. For all other analytes, the MDL is presented.

(b) Phosphate based on ICP-AES average total P result of 385 µg/mL.

(c) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC).

Table 6.6. AP-101 Diluted Feed – Bq Radioisotope per Mole Na Ratio

[a] Radioisotopes	MRQ µCi/mL	MDA/ MDL [b] µCi/mL	01-520 Average µCi/mL	Data Flag	Measured Bq Analyte per Mole Na Ratio	Spec 7 Envelope A Limits Bq Analyte per Mole Na Ratio	% of Limit	Meets Spec?
TRU [c]	2.3E-01 [d]	n/a	2.6E-04	n/a	2.0E+03	4.8E+05	0.4	Yes
^{137}Cs	9.0E+00	6E-03	1.3E+02		9.4E+08	4.3E+09	22	Yes
^{90}Sr	1.5E-01	3E-03	7.1E-02	B	5.3E+05	4.4E+07	1.2	Yes
^{99}Tc	1.5E-03	1.6E-06	3.9E-02		2.9E+05	7.1E+06	4.1	Yes
^{60}Co	1.0E-02	2E-04	2.5E-03		1.9E+04	6.1E+04	31	Yes
^{154}Eu	2.0E-03	1E-03	1E-03	U	< 7.5E+03	1.2E+06	<0.6	Yes

(a) Radioisotopes measurement performed by radiochemistry methods except ^{99}Tc is by ICP-MS.
(b) Values represent MDA for all analytes except ^{99}Tc.
(c) TRU = alpha emitting radionuclides with atomic number greater than 92 and half-life greater than ten years; Alpha summation of ^{238}Pu, $^{239+240}$Pu, ^{241}Am, and $^{243+244}$Cm.
(d) MRQ for total alpha used as TRU MRQ.

Decay correction reference dates nominally May 2001.

7.0 Procedures, Quality Control and Data Evaluation

A discussion of procedures, data quality, and quality control is provided below for each analytical method. Analytical instrument calibration and calibration verification were performed in accordance with the QA Program's plan *Conducting Analytical Work in Support of Regulatory Programs*, which is in compliance with HASQARD. Raw data including bench sheets, instrument printouts, data reduction, and calibration files are maintained or cross-referenced in the Project 42365 file. The sample average, MRQ, data flags, QC parameters and QC acceptance criteria are summarized in Table 7.1 through 7.4. In some cases, one sample value was reported as less than the MDL/MDA (i.e., U flagged) and the duplicate reported with a value (i.e., either J flagged or a value measured above the EQL). The reported average is conservatively estimated as the single reported value above the MDL/MDA.

The QC and results evaluations provided in the following sections are limited to the analytes of interest defined by the TS. Analytes other than those specified by the TS are included in some tables and are provided for additional information. Some of these other analytes were measured per the requirements stated in the governing QA Plan; however, the data has not been fully evaluated against the acceptance criteria.

7.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy

Tables 6.1 and 7.1

The AP-101 diluted feed acid digested samples required 5-fold dilutions in order to quantify all analytes of interest according to PNL-ALO-211, *Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry*. The detected analytes at or above the EQL (equivalent to ten times the MDL) were reported with an uncertainty of ±15% (2-σ). As the MDL was approached, uncertainty increased to 100%.

Quality control for the ICP-AES analysis consisted of sample duplicates, PBs, MSs, LCS (or BS), post spikes, calibration verification check standards, interference check standards, and linear range check standards. Matrix spike recovery, LCS (or BS) recovery and precision (based on duplicate analyses) QC acceptance criteria are defined by the TS. These QC criteria were evaluated in detail and are summarized below.

Analytes of interest, other than Na, with concentrations greater than the EQL have Relative Percent Differences (RPD) within the acceptance criteria of <15%. The RPD for the duplicate Na analysis is within the acceptance criteria of <3.5%.

No analytes of interest were measured in the two PBs above the acceptance criteria (i.e., < EQL or <5% of sample concentration). Three analytes of interest (Ca, Fe, and Ni) with low concentrations have been flagged with a 'B' since the blank contribution exceeded 5% of the sample; however, the PB concentration for these analytes is < EQL.

For the LCS/BS, all analytes of interest were recovered within acceptance criteria of 80% to 120%. All matrix-spiked analytes of interest (spiked at greater than 20% of the sample concentration) were recovered within acceptance criteria of 75% to 125%. The spikes for Al, K, and Na could not be recovered since the spikes were less than 20% of the analyte concentration. Post spikes for Al and Na could not be recovered and the post spike for K failed the acceptance criteria. Since the MS and PS could not be recovered for Al and Na, serial dilution was required to evaluate matrix interference effects. The sodium in the supernatant was so high that sufficient successive serial dilutions were not obtained during the analysis of the diluted feed to calculate the percent difference (%D). Since the supernatant sodium and aluminum concentrations are too high for matrix spiking and the data for serial dilution was not obtained, the sodium and aluminum results have been flagged with and "X", indicating a QC deficiency. However, the other analytical QC for aluminum and sodium (i.e., LCS/BS and calibration checks) indicates that the reported aluminum and sodium results are most likely valid, with uncertainties of <10%.

Only Al, Ca, Cr, K, and Na were detected above their MRQs. The estimated MDLs exceeded the MRQs only for K. However, the measured K concentration is approximately 400 times the specified MRQ. The EQL exceeds the MRQ for nearly all analytes, with the exceptions being Fe, Mg, P, and Pb.

7.2 Inductively Coupled Plasma/Mass Spectrometry

Tables 6.2 and 7.2

The AP-101 diluted feed acid digested samples were analyzed by ICP-MS analysis according to procedure PNL-ALO-280, *Inductively Coupled Plasma-Mass Spectrometer Analysis*. Except for the MS and LCS, the acid digested samples were from the same processed solutions as were delivered for ICP-AES analysis.

Quality control for the ICP-MS analysis consisted of sample duplicates, PBs, MS, LCS or BS, post spikes, and calibration verification check standards and blanks. Matrix spike recoveries, LCS recovery, and precision (based on duplicate analyses) QC criteria are defined by the TS.

All QC meet the acceptance criteria defined in the TS except the LCS for ^{240}Pu. The LCS for ^{240}Pu recovered at 79%, slightly below the lower threshold of 80%. Based on the fact that no ^{240}Pu was detected above the MDL and the MDL was two orders of magnitude lower than the specified MRQ, this failure does not impact the reported results.

The duplicate analyses met the QC criterion of <20% RPD for the Cs, Rb, and Tc analysis. RPDs for the actinides were not calculated since their concentrations are <MDL. No MS was prepared during the acid digestion for the actinides; however, actinide post spikes were performed and recoveries meet the MS criteria. No analytes of interest were detected in the two PB above the MDL.

Only Cs, Rb, and ^{99}Tc were detected above the MRQ. The estimated MDL exceeds the MRQ for Cs and ^{99}Tc. However, both Cs and ^{99}Tc were detected at concentrations at least 25 times greater than the specified MRQ. The EQL exceeds the MRQ for Cs, ^{99}Tc, and ^{241}Am (AMU-241).

The Cs isotopic distribution (^{133}Cs, ^{135}Cs, and ^{137}Cs) was determined according to PNL-SC-01, *Inductively Coupled Plasma Mass Spectrometric (ICP-MS) Analysis*. The Cs was separated from isobaric interferences using high-performance ion chromatography (HPIC) and the eluant was fed directly to the ICP-MS. The ^{133}Cs atomic abundance (0.604 and 0.604), ^{135}Cs atomic abundance (0.154 and 0.155), and

^{137}Cs atomic abundance (0.241 and 0.241) were used with the AP-101 diluted feed ICP-MS ^{133}Cs result for determining the total Cs.

7.3 U Analysis by KPA

Tables 6.2 and 7.2

Aliquots from the acid digestion (PNL-ALO-128) of the AP-101 diluted feed were further processed for uranium analysis. The aliquots were treated with concentrated nitric acid, evaporated to dryness, then re-dissolved in dilute nitric acid for uranium analysis. Total uranium was measured according to procedure RPG-CMC-4014, *Uranium by Kinetic Phosphorescence Analysis*. No uranium separation was performed. The uranium concentration (41 µg/mL) was well below the MRQ value of 780 µg/mL. The repeatability of duplicate samples was excellent with a RPD value of 2%. Uranium was detected in the SAL hot cell blanks, but at a concentration less than 1% of the sample uranium concentration. The LCS (i.e., a mid-range standard) recovered at 98% and within the 80% to 120% acceptance criteria. No MS sample was analyzed.

7.4 Radiochemical Analyses

Tables 6.2, 6.3, 7.2 and 7.3

The acid digested (PNL-ALO-128) AP-101 diluted feed samples were analyzed for gamma emitters, ^{90}Sr, total alpha, $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, and $^{243+244}$Cm. An aliquot of the AP-101 diluted feed was provided directly from the SAL hot cells (i.e., not subjected to the acid digestion procedure) for subsequent analysis of the pertechnetate form of ^{99}Tc.

The initial SAL hot cell acid digestion PBs (two) showed significant alpha contamination and ^{90}Sr contamination. These PBs and associated samples from the initial acid digestion batch could only be used for GEA. Additional samples and a PB were prepared for re-analysis of total alpha, the actinides, and ^{90}Sr. The re-analyses showed some contamination for ^{90}Sr; however, no alpha contamination was detected. The actinides and ^{90}Sr results are reported only for the sample prepared from the second acid digestion processing.

For all radiochemical analyses the MDAs are lower than the MRQ. Although ^{154}Eu and ^{155}Eu (by GEA) were not detected in the samples, the MDAs for ^{154}Eu and ^{155}Eu are within a factor of 10 of the MRQ.

7.4.1 Gamma Spectrometry

Digested sample aliquots were directly counted for gamma emitters according to procedure PNL-ALO-450, *Gamma Energy Analysis and Low-Energy Photon Spectrometry*. Laboratory blanks and spikes were not prepared, nor required, for this analyses since the measurement is a direct reading of the gamma energy and is not subject to matrix interferences. Initially, the samples were diluted prior to GEA. However, in order to meet the requested MRQs, direct aliquots of the SAL hot cell preparations were counted for periods of 4 to 14 hours. All of the samples showed the presence of significant ^{137}Cs activity, with ^{60}Co being the only other gamma emitter detected. The MDAs for extended counting time GEA met the MRQ requirements in all cases. All of the SAL hot cell blanks showed the presence of ^{137}Cs, but the activities in the blanks were negligible with respect to the samples. For those radioisotopes determined at concentrations greater than 10 times the MDA, the sample duplicates showed excellent repeatability with RPD values <15%.

7.4.2 Total Alpha

The total alpha activity was determined by direct-plating small aliquots of the acid-digested samples onto planchets according to RPG-CMC-4001, *Source Requirements for Gross Alpha and Gross Beta Analysis.* The samples were then counted on Ludlum detectors according to RPG-CMC-408, *Low Background Alpha and Beta Counting - Proportional*. The initial SAL hot cell PBs were significantly contaminated with alpha activity. Therefore, all samples were re-digested and re-analyzed. The second acid digestion batch contained one PB, and no alpha contamination was detected in this PB. The ^{239}Pu LCS and MS recoveries were 112% and 79%, respectively. No RPD was calculated since the total alpha result was less than 10 times the MDA. The sums of the individual alpha emitters, as discussed below, are in very good agreement with the total alpha data indicating minimal losses due to alpha self-absorption.

7.4.3 Plutonium, Americium, and Curium

The Pu and Am/Cm separations were performed according to PNL-ALO-417, *Separation of Am and Pu and Actinide Screen by Extraction Chromatography*. The separated fractions were precipitation plated according to PNL-ALO-496, *Precipitation Plating of Actinides for High Resolution Alpha Spectrometry*, and counted by alpha spectrometry according to RPG-CMC-422, *Solution Analysis: Alpha Spectrometry*. Plutonium recovery was traced with ^{242}Pu. The curium is known to follow the americium and both these isotopes were traced with ^{243}Am. The initial SAL hot cell PBs were significantly contaminated with alpha activity. Therefore, all samples were re-digested and re-analyzed. The second acid digestion batch contained one PB, with no Pu, Am, or Cm contamination detected. Only the results generated from the reanalysis is reported. Neither Pu, Am, nor Cm were detected in the laboratory workstation reagent blank.

The LCS recoveries for ^{241}Am and $^{239/240}$Pu were 98% and 112%, respectively, and the MS recoveries for ^{241}Am and $^{239/240}$Pu were 99% and 113%, respectively; all well within the acceptance criteria. For those radioisotopes determined at concentrations greater than 10 times the MDA, the RPD values were within the acceptance criteria of <15% except for ^{238}Pu (RPD = 16%).

7.4.4 Strontium-90

The Sr separation was performed according to PNL-ALO-476, *Strontium Determination using Sr-SPEC*, and radiochemical yields were traced with ^{85}Sr. The separated fractions were then beta counted according to RPG-CMC-408, *Low Background Alpha and Beta Counting – Proportional* (for ^{90}Sr determination). Following the beta counting, the samples were gamma counted according to PNL-ALO-450, *Gamma Energy Analysis and Low-Energy Photon Spectrometry* (for ^{137}Cs impurity assessment). Two of the separated fractions contained a small amount of ^{137}Cs and a correction to the beta count rate was applied for these samples. However, this correction was negligible with respect to the activity in the samples. The initial SAL hot cell PBs were significantly contaminated with ^{90}Sr beta activity. Therefore, all samples were re-digested and re-analyzed. The second acid digestion batch contained one PB, which still exhibited a slight ^{90}Sr contamination (approximately 4 times the MDA, but about 20% of the sample concentration). No ^{90}Sr was detected in the laboratory workstation reagent blank.

The ^{90}Sr concentration in the AP-101 diluted feed sample (i.e., 0.07 μCi/ml) is about 20 times the MDA and approximately half the requested MRQ value of 0.15 μCi/ml. The reported ^{90}Sr results may be slightly bias high by about 20%, since the ^{90}Sr contamination was detected in the PB. However, the RPD value was 4%, indicating good sample reproducibility. The LCS and MS recoveries were 95% and 105%, respectively; however, per the TS, the MS was not required and the acceptance criterion was not defined.

7.4.5 Technetium-99 (Pertechnetate)

The radiochemical ^{99}Tc determination was requested to measure only Tc in the +7 oxidation state (pertechnetate). To this end, all sample manipulations had to be non-oxidizing so as not to alter the original Tc oxidation state. A small aliquot from the diluted feed sample (no digestion) was taken for analysis according to procedure PNL-ALO-432, *Separation of Technetium by Cation Exchange and Solution Extraction Prior to Measurement by Beta Counting*. This procedure normally requires the use of a sodium dichromate addition to oxidize the Tc to the +7 oxidation state. The sodium dichromate addition was omitted and the procedure was otherwise performed as written. The separated fraction was then counted according to RPG-CMC-408, *Low Background Alpha and Beta Counting – Proportional*. The sample was also counted by liquid scintillation counting according to RPG-CMC-474, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*, to confirm that the beta energy spectra matched that of ^{99}Tc and that no other beta emitters were present.

The LCS (or BS) recovery of a ^{99}Tc standard was 92%. However, the MS gave a recovery of 248%, which was outside of the 70% to 130% acceptance criteria. The process batch MS was prepared from a sample of AN-102 as-received material and analyzed in the same batch as the AP-101 diluted feed samples. The quantity of pertechnetate added for preparing the MS contributed only about 12% to the measured pertechnetate. The MS preparation benchsheets provide no indication that an error was made in either the preparation of the MS solution or the addition of the MS to the diluted feed sample. Since the poor MS recovery is most likely due to insufficient MS addition and the AP-101 diluted feed results compare favorably with AP-101 as-received results (Fiskum 2000) adjusted for feed dilution, the reported results are considered good. However, due to the batch MS failure, the results have been flagged as having a QC deficiency.

The ^{99}Tc activities in the SAL hot cell processing blank and a laboratory reagent blank were negligible or non-detectable and well below the requested MRQ value of 0.0015 μCi/mL, and the duplicates (from bottles AP-101 DF-A and AP-101 DF-B) demonstrated good agreement with an RPD of 12%.

7.5 Inorganic Anions

Tables 6.4, and 7.4

Inorganic anion analysis was conducted according to method PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*. The IC method was used to evaluate the anions of interest on unprocessed sub-samples of the diluted feed. The samples were prepared for IC anion analysis by dilution at 1900-fold and 3800-fold in order to ensure that the anions were measured within the calibration range. Column overloading prohibited analysis of the sample as dilutions less than 1900-fold.

Quality control for the anion analysis consisted of sample duplicates, PBs, MSs, BSs, and calibration verification check standards and blanks. The MS recovery, BS recovery, and precision (based on duplicate analyses) QC acceptance criteria are defined by the TS. These QC criteria were evaluated in detail and are summarized below.

The duplicate analyses met the specified QC criteria of <15% RPD for all anions detected above the MDL. A MS for the AP-101 diluted feed was prepared at the IC workstation, with all anions meeting the acceptance criteria of 75% to 125% recovery. Based on the precision demonstrated on the duplicates and the MS recoveries, the AP-101 diluted feed results have uncertainties of <10% (except in those cases where interferences bias the reported results).

A BS and PB (i.e., water used in SAL for dilutions and handled/transferred like the samples) were prepared at the IC workstation and analyzed at the same time as the samples and MS. The BS demonstrated recoveries within the acceptance criteria of 80% to 120%, and no anions were detected in the SAL PB.

Only those anions detected above the lowest calibration standard concentration (i.e., EQL) are reported by the IC system. The EQL is less than the required MRQ for all anions with the exception of fluoride and chloride. For fluoride the EQL is about 3 times the MRQ, and for chloride the EQL is about 1.5 times the MRQ. It was necessary to dilute the AP-101 dilute feed composite for IC analysis due to the high nitrate and nitrite concentrations; resulting in fluoride and chloride EQLs that exceed the MRQs. The IC analysis is limited by the quantity of anions that can be loaded on the IC column; quantities of anion exceeding this limit result in peak distortion and shifts in retention time, severely affecting the quantitation of all anions. Since most IC methods are limited by the quantity of anions loaded on the column and require large dilutions for samples with high anion concentrations (e.g., >10%), an alternate method should be evaluated for both fluoride and chloride.

7.6 TOC/TIC by Hot Persulfate and Furnace

Tables 6.4 and 7.4

The AN-102 diluted supernatant was analyzed for total organic and inorganic carbon by two different procedures: Procedure PNL-ALO-381, *Direct Determination of TC, TOC, and TIC in Radioactive Sludges and Liquids by Hot Persulfate Method*, and PNL-ALO-380, *Determination of Carbon in Solids Using the Coulometric Carbon Dioxide Coulometer*.

7.6.1 Hot Persulfate Method (PNL-ALO-381)

The hot persulfate wet oxidation method uses acid decomposition for the measurement of TIC and acidic potassium persulfate oxidation at 92-95°C for measurement of TOC, with both the TIC and TOC being obtained from the same sample. The TC is defined as the sum of the TIC and TOC. All sample results were corrected for average percent recovery of system calibration standards and were also corrected for contribution from the system blanks, as per procedure PNL-ALO-381 calculations. The QC for the method involves sample duplicates, LCS (or BS), and a MS.

All QC sample results for hot persulfate TIC/TOC analysis method met the acceptance criteria defined by the TS. The RPD for duplicate analysis was <15%. The LCS (or BS) recoveries ranged from 102% to 105%, well within the acceptance criteria of 80% to 120%. The performance of the MS was similar with recoveries ranging from 92% to 97%, well within the acceptance criteria of 75% to 125%.

7.6.2 Furnace Oxidation Method (PNL-ALO-380)

The furnace method that determines the TOC is performed by combusting an aliquot of the sample (solids or liquid) in oxygen at 750°C for 30 minutes. The total carbon (TC) is determined on another aliquot of the sample by combusting at 1000°C for 30 minutes, and the TIC is obtained by difference between the TC and TOC. All sample results were corrected for average percent recovery of system calibration standards and were also corrected for contribution from the system blanks, as per procedure PNL-ALO-380 calculations. The QC for the method involves sample duplicates, LCS (or BS), and a MS.

Calibration blanks were analyzed at the beginning, middle, and end of the three analysis runs (three different days). The TOC determination produced an average blank of 15 µg C (run 2) and the TC determinations produced average blanks of 4 (run 1) and 54 µg C (run 3). Although the 54 µg C is somewhat higher than usual for the method, the blank was quite reproducible (i.e., 49 to 59 µg C).

All QC sample results for the furnace TC and TOC analysis method met the acceptance criteria defined by the TS. The RPD result for the duplicate analyses was <15%. The LCS (or BS) recoveries ranged form 99 % to 102%, well within the acceptance criteria of 80% to 120%. The performance of the MS was similar with recoveries ranging from 96% to 101%, well within the acceptance criteria of 75% to 125%.

7.6.3 Comparison of TIC/TOC by Hot Persulfate and Furnace Oxidation Methods

Table 7.4 presents the TOC and TIC results obtained from the hot persulfate method and the furnace oxidation method for the AP-101 diluted feed. The TIC results from the furnace method are obtained by difference (TC – TOC), with the analysis being performed on two independent sample aliquots. The TC for the hot persulfate method is the summation of the TIC and TOC, with the analyses being performed on the same aliquot under different oxidation conditions.

The average TC result from the hot persulfate method (7,000 µg C/mL) is similar to the average TC result from the furnace method (7,900 µg C/mL). However, there are significant differences between the TOC and TIC results between the methods. The furnace method essentially obtains the same carbon result for the TOC and TC analyses, indicating that there is little, if any, TIC; however, the hot persulfate measures a significantly higher TIC than TOC. It is unlikely that there is no TIC in that samples based on the OH titration (Section 7.8) which produced inflection points typical of carbonate. Although these inflection points are not unique to carbonate in complex tank matrices (i.e., aluminate contributes significantly to the first inflection point) and have not been verified in the OH titration, the estimated carbon (as carbonate) from the OH titration equate to about 12,000 µg C/mL (or twice that determined by the hot persulfate method).

Based on previous organic analyses of AP-101 waste material (Fiskum 2000), the results from the hot persulfate most likely provides the best TIC result and the furnace method the best TC result.

Therefore, the TOC result reported from the hot persulfate methods may be low by approximately 1000 µg C/mL.

7.7 Mercury Analysis
Table 6.4, and 7.4

The AP-101 diluted feed samples and associated batch QC samples were digested for mercury analysis per procedure RPG-CMC 131, *Mercury Digestion*, and analyzed by RPG-CMC-201, *Mercury Analysis*. Quality control for the mercury analysis consisted of sample duplicates, PB, MS, LCS (or BS), and calibration verification check standards and blanks. The MS spike recovery, LCS/BS recovery, and precision (based on duplicate analyses) quality control criteria were defined by the TS.

The lowest calibration standard concentration adjusted for the sample dilution is used to calculate the EQL for the reported results. Concentrations of mercury in the sample and duplicate were below the EQL, which is 20 times less than the MRQ. Since the concentration of mercury in the sample was below the EQL, no RPD was calculated.

The mercury LCS/BS recovered at 97%, well within the acceptance criteria of 80% to 120%. However, the MS recovery (i.e., 27%) did not meet the acceptance criteria of 75% to 125%. Based on the excellent precision and recoveries from the other QC samples, the failure of the MS is considered to be from an unknown matrix effect. Further study is needed to understand the reason for these poor MS recovery on the AP-101 diluted feed matrix, since the MS for the AP-101 as-received sample recovered well (Fiskum 2000). However, adjusting the sample mercury concentration (i.e., <0.07 µg/mL) for the low MS recovery, the resulting estimated concentration (i.e., 0.3 µg/mL) is still five times below the MRQ.

7.8 Hydroxide Titration
Tables 6.4 and 7.4

The AP-101 diluted feed were analyzed in duplicate for the hydroxide content following procedure PNL-ALO-228, *Determination of Hydroxyl and Alkalinity of Aqueous Solutions, Leachates & Supernates*. Direct sample aliquots were analyzed using a Brinkman® 636 Auto-Titrator. A 0.1186 N NaOH solution was prepared for use as a verification standard and the matrix spiking solution and a 0.2040 M HCl solution was prepared as the titrant. The analysis produced an average hydroxide molarity of 1.94 (or 32,900 µg/mL hydroxide) with an RPD of 1%. The measured hydroxide concentration is about half of the required MRQ (i.e., 75,000 µg/mL). The hydroxide verification standard recovery averaged 93% and the MS recovered at 97%. No hydroxide was detected in the cell blanks or a reagent blank.

For information only – The second and third inflection points were detected in the samples at an average of 0.79 molar with a 4% RPD and 0.56 molar with a 7% RPD, respectively. The second inflection point is primarily from both carbonate and aluminate and the third inflection point from carbonate (i.e., second equivalent point). Weak acids such as acetate, oxalate, formate, citrate, etc. also contribute to these inflection points, but are too low in concentration relative to the carbonate and aluminate to be detected separately.

7.9 Ammonia Analysis

Tables 6.4 and 7.4

Duplicate aliquots of the AP-101 diluted feed and a SAL hot cell blank (i.e., PB) were transferred from the SAL to the laboratory workstation for ammonia analysis. The samples were not diluted or preserved with acid in the SAL and no LCS or MS was transferred with the samples from the SAL hot cells.

The sample was analyzed for ammonia by ion selective electrode, procedure RPG-CMC-226, *Measurement of Ammonia in Aqueous Samples*. Quality control for the ammonia analysis consisted of sample duplicates, PB, MS, LCS (or BS), and calibration verification check standards and blanks. The MS spike recovery, LCS/BS recovery, and precision (based on duplicate analyses) quality control criteria were defined by the TS. Because of the high sample dose rate, approximately 0.1 mL of sample was diluted to 5 mL with water for analysis.

The ammonia probe slope and linearity were initially measured with ammonium chloride standards ranging from 0.00085 µg/mL (5e-07 M) to 8,500 µg/mL (1e-01 M). The probe was linear from about 0.25 µg/mL to 8,500 µg/mL. Probe slope checks were evaluated routinely during the analysis of the samples using at least three standards within the linear range. The ammonia probe slope was reproducible to within about 1% on the day the AP-101 samples were analyzed. Although the linearity of the ammonia probe is established by the measuring standards over the linear range, all sample measurements are performed by the method of standard addition if the measured concentration is within the linear range.

Ammonia is reported for those analyses that have measured ammonia concentrations within the linear calibration range of the ammonia probe, with the lowest reported concentration being 0.25 µg/mL. Based on this measurement value and the 50-fold sample dilution, the ammonia EQL is approximately 10 µg/mL. The AP-101 diluted feed ammonia concentration (i.e., 26 µg/mL) is about twice the EQL and 14 times less than the MRQ defined by the TS. The RPD result for the duplicate analyses was <15%. A mid-range BS recovered at 103% and the MS prepared at the time of sample analysis recovered at 87%.

For sample ammonia concentrations below the EQL (i.e., below the linear range of the ammonia probe), the calibration curve is used to estimate the ammonia concentration. This approach was used to estimate the ammonia concentration of the SAL hot cell blank (PB). The SAL PB had a detectable level of ammonia estimated to be 0.5 µg/mL.

Table 7.1. AP-101 Diluted Feed – ICP-AES QC Results

Analyte	MRQ µg/mL	MDL µg/mL	01-520 Average µg/mL	Data Flag	RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Acceptance Criteria							*80% - 120%*	*75% - 125%*	*75% - 125%*	*75% - 125%*	*< ±10%*
Test Specification Analytes											
Al	75	8.2	6,980	X	1	<15	101	n/r	n/r		**n/m**
Ba	2.3	1.4	1.4	U	(a)	<15	96	98	100		
Ca	150	34	210	JB	(a)	<15	98	12	105		
Cd	7.5	2.0	2.0	U	(a)	<15	97	111	107		
Cr	15	2.7	152		1	<15	96	98	107		
Fe	150	3.4	3.6	JB	(a)	<15	100	103	107		
K	75	272	29,800	X	0	<15	86	n/r	**57**		
La	35	6.8	6.8	U	(a)	<15	94	98		101	
Mg	300	14	14	U	(a)	<15	100	107	109		
Na	75	20	114,000	X	2	<3.5	108	n/r	n/r		**n/m**
Ni	30	4.1	4.4	JB	(a)	<15	97	99	106		
P	600	14	385		2	<15	97	104	107		
Pb	300	14	14	U	(a)	<15	100	114	113		
S			n/m								
U	600	270	270	U	(a)	<15	94	100		100	
Other Analytes											
Ag		3.4	3.4	UX	(a)		22	23	96		
As		34	34	U	(a)				105		
B		6.8	55	JB	(a)				106		
Be		1.4	1.4	U	(a)				109		
Bi		14	14	U	(a)		93	97	99		
Ce		27	27	U	(a)					103	
Co		6.8	6.8	U	(a)				107		
Cu		3.4	3.4	U	(a)		100	123	103		
Dy		6.8	6.8	U	(a)					103	
Eu		14	14	U	(a)					111	
Li		4.1	4.1	U	(a)				95		
Mn		6.8	6.8	U	(a)		101	105	109		
Mo		6.8	14	J	(a)				105		
Nd		14	14	U	(a)		94	98		101	
Pd		102	102	U	(a)		90	99		110	

Table 7.1. (Cont'd)

Analyte	MRQ µg/mL	MDL µg/mL	01-520 Average µg/mL	Data Flag	RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Rh		41	41	U	(a)		95	102		103	
Ru		150	150	U	(a)		93				
Sb		68	68	U	(a)				104		
Se		34	34	U	(a)				108		
Si		68	360	JBX	(a)		113	63	134		
Sn		204	205	U	(a)						
Sr		2.0	2.0	U	(a)		96	100	102		
Te		204	205	U	(a)						
Th		140	140	U	(a)					105	
Ti		3.4	3.4	U	(a)		94	96	99		
Tl		68	68	U	(a)				97		
V		6.8	6.8	U	(a)				97		
W		270	270	U	(a)						
Y		6.8	6.8	U	(a)				98		
Zn		6.8	8.0	JB	(a)		98	102	107		
Zr		6.8	6.8	U	(a)		97	102	106		

Blank areas indicate QC not required for specified analyte

Outlined/bolded results highlight non-compliances with BNI acceptance criteria, see report for discussion.

n/r = not recovered (spike concentration <20% of sample concentration); n/m = not measured (See Section 7.1).

(a) RPD only calculated when both the sample and duplicate results are greater than the EQL.

Table 7.2. AP-101 Diluted Feed – ICP-MS QC Results

Analyte	MRQ µg/mL	MDL µg/mL	01-520 Average µg/mL	Data Flag	RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) % Rec.	Post Matrix Spike (PS) % Rec.
Acceptance Criteria							*80% - 120%*	*70% - 130%*	*70% - 130%*
Test Specification Analytes									
U(KPA) (a)	7.8E+02	6E-03	4.07E+01		2	<15	98(b)	(b)	(b)
Cs	1.6E-02	5.7E-02	4.89E+00		2	none	92	96	86
Rb	1.0E+00	7.4E-02	3.94E+00		3	<15	103	123	103
AMU-241	1.6E-02	2.3E-03	2.3E-03	U	(c)	<15	89(d)	(f)	97
	µCi/mL	**µCi/mL**	**µCi/mL**						
AMU-241	5.1E-02	7.9E-03	7.9E-03	U	(c)	<15	89(d)	(f)	97
^{99}Tc	1.5E-03	1.6E-03	3.92E-02		4	<15	94(d)	(f)	81
^{237}Np	2.7E-02	3.8E-06	3.8E-06	U	(c)	<15	97(d,e)	(f)	97(e)
^{239}Pu	3.0E-02	7.5E-04	7.5E-04	U	(c)	<15	93(d)	(f)	122
^{240}Pu	1.0E-02	6.9E-04	6.9E-04	UX	(c)	<15	**79**(d)	(f)	114

Blank areas indicate QC not required for specified analyte.

Outlined/bolded results highlight non-compliances with BNI acceptance criteria, see report for discussion.

(a) Uranium result by KPA; unprocessed mid-range standard used as the LCS.

(b) No acceptance criteria for BS, MS, or PS samples in TS.

(c) RPD only calculated when both the sample and duplicate results are greater than the EQL.

(d) The post-spiked blank sample is used as the LCS.

(e) A BS acceptance criterion is 90% - 110%, MS and PS acceptance criteria are 75% - 125%.

(f) Post spiking of radioisotope performed following digestion.

Table 7.3. AP-101 Diluted Feed - Radioisotope QC Results

Analyte	MRQ µCi/mL	MDA µCi/mL	01-520 Average µCi/mL	Err % (a)	Data Flag	RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) % Rec.
Acceptance Criteria								*(c)*	*(c)*
Alpha	2.3Ee-01	9E-05	2.17E-04	17	J	(b)	<15	112	79
^{238}Pu	1.0E-02	6E-07	1.40E-05	6		**16**	<15		
$^{239/240}$Pu	3.0E-02	6E-07	1.10E-04	3		0	<15	112	113
^{241}Am	3.0E-02	6E-07	1.38E-04	3		(b)	<15	98	99
^{241}Am by GEA		1E-02	1E-02		U	(b)			
$^{243/244}$Cm	1.5E02	5E-07	2.12E-06	18	J	(b)	<15		
^{242}Cm	1.5E-01	4E-07	4E-07		U	(b)	<15		
Sum of Alpha		3E-06	2.64E-04	4		1			
^{90}Sr	1.5E-01	4E-03	7.14E-02	4	B	10	<15	95	105
^{99}Tc^{+7}	1.5E-03	5E-06	3.46E-02	4	X	12	<15	92	**248**(d)
^{137}Cs	9.0E+00	6E-03	1.26E+02	2		2	<15		
^{60}Co	1.0E-02	2E-04	2.52E-03	5		1	<15		
^{154}Eu	2.0E-03	1E-03	1E-03		U	(b)	<15		
^{155}Eu	9.0E-02	1E-02	1E-02		U	(b)	<15		

Blank areas indicate QC not required for specified analyte.

Outlined/bolded results highlight non-compliances with BNI acceptance criteria, see report for discussion.

(a) The Err % represents the uncertainty at 1-σ.

(b) RPD only calculated when both the sample and duplicate results are greater than 10 times the MDA.

(c) Acceptance criteria listed for total alpha (LCS 70% - 130%, MS 70% - 130%), ^{90}Sr (LCS 75% - 125%) and ^{99}Tc (LCS 80% - 120%, MS 70% - 130%).

(d) The batch MS was prepared from sample AN-102 as-received material (RPL # 01-0429). The spike concentration is at <20% (i.e., 12%) of the sample concentration making recovery of the MS difficult.

Table 7.4. AP-101 Diluted Feed – Other Analysis QC Results

Analyte	MRQ µg/mL	EQL/ MDL (e) µg/mL	01-520 Average µg/mL	Data Flag	RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) % Rec.
Acceptance Criteria							*80% - 120%*	*75% - 125%*
Test Specification Analytes								
F (b)	150	480	2,300		0	<15	107	97
Cl	300	480	1,450		5	<15	105	93
NO_2	3,000	950	32,500		6	<15	105	102
NO_3	3,000	1,900	104,000		1	<15	101	102
PO_4	2,500	950	950	U	(a)	<15	104	97
SO_4	2,500	1,900	4,650		1	<15	102	91
OH	75,000	170	32,900		1	<15	93	97
NH_3	140	10	26		2	<15	103	87
Hg	1.5	0.069	0.069	UX	(a)	<15	96	**27**
TOC-F (c)	1,500	220	8,000		3	<15	99	96
TIC-F (c)	150	170	170	U	(a)	<15	102 (d)	101 (d)
TOC-P (c)	1,500	36	1,640		1	<15	104	92
TIC-P (c)	150	13	5,350		2	<15	103	97
Other Analytes								
Br		480	480	U	(a)		106	97
Oxalate		950	950	U	(a)		107	105

Blank areas indicate QC not required for specified analyte.

Outlined/bolded results highlight non-compliances with BNI acceptance criteria; see report for discussion.

(a) RPD only calculated when both the sample and duplicate results are greater than the EQL.

(b) The fluoride results should be considered the upper bound concentration for the fluoride. Significant peak distortion of the fluoride peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(c) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC).

(d) TIC from furnace is measure by difference from TC and TOC determinations. The LCS and MS recovery represents the recovery for the TC analysis.

(e) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, oxalate and ammonia are reported only above the EQL; therefore, the EQL is presented in this column. For all other analytes, the MDL is presented.

8.0 References

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Appendix A

- Memorandum “Shipment of AP-101 to Pacific Northwest National Laboratory”
- Chain of Custody Records – November 2000 and January 2001 Shipments
- Test Specification: TSP-W375-00-0003, Rev. 1
- Test Instruction: TI-PNNL-WTP-032, “AP-101 Sample Compositing for Process Testing”

Appendix B

- ASR 6031 (+ASR 6031 Addendum)
- ICP-AES Results
- ICP-MS Results (+ICP-MS Cs isotopic)
- Radiochemical Results and U KPA Results
- IC Results
- Mercury Results
- Ammonia Results
- Hydroxide Results
- TOC/TIC/TC Results – Hot Persulfate Method
- TOC/TIC/TC Results – Furnace Method
- Heat Capacity Results
- Particle Size Results
- Rheology Results

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