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WTP-RPT-069, Rev. 0

Chemical Analysis and Physical Property Testing of 241-AP-104 Tank Waste

D. L. Baldwin
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S. K. Fiskum
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C. Z. Soderquist
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M. P. Thomas
M. W. Urie
J. J. Wagner

September 2003

Prepared for Bechtel National, Inc.
under Contract No. 24590-101-TSA-W000-00004

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Test specification: 24590-WTP-TSP-RT-01-011, Rev 0
Test plan: TP-RPP-WTP-138, Rev 0
Test exceptions: 24590-WTP-TEF-RT-02-092
R&T focus area: Pretreatment
Test Scoping Statement(s): B-05a

Battelle – Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by 24590-WTP-TSP-RT-01-011 Rev. 0 and TP-RPP-WTP-138 Rev 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan 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 *Date*
WTP R&T Support Project

Summary

Battelle – Pacific Northwest Division (PNWD) is conducting integrated process verification and waste-form qualification tests on Hanford waste from underground storage Tank 241-AP-104 (AP-104) in support of the River Protection Project-Waste Treatment Plant (RPP-WTP). Testing includes sample compositing, homogenization, and characterization, which are described in this report. A follow-up effort including pretreatment process testing and vitrification of the resulting low-activity waste (LAW) stream will be reported later. Characterization of the AP-104 waste provides an opportunity to underpin the pretreatment facility design basis. Additionally, it provides data to the WTP to validate assumptions in the flowsheet and to support process verification testing and safety related activities.

Primary Objectives

- Receive, composite, homogenize, and sub-sample AP-104 waste
- Measure physical properties of a composite sub-sample as defined in test specification Table 1
- Perform chemical and radiochemical analysis of a composite sub-sample as defined in test specification Tables 2 and 3
- Determine compliance to Contract Specification 7 (Envelope A) of DE-AC27-01RV14136
- Report analysis results in accordance with Standard Electronic Format Specification for Tank Waste Characterization Data Loader

Conduct of Testing

The homogenization and characterization activities were conducted per test plan TP-RPP-WTP-138 rev. 0, *Tank 241-AP-104 Sample Compositing, Homogenization and Analyses* (Appendix C). This test plan implemented the requirements set forth in test specification 24590-WTP-TSP-RT-01-011 rev. 0, *Tank 241-AP-104 Sample Compositing, Homogenization and Analyses* (Appendix A), which was initially defined in test scoping statement B-05a. This report summarizes sample receipt, compositing, homogenization, and initial characterization activities of the AP-104 tank waste. The results for all analytes of interest specified by the test specification are reported with the exception of bis-(2-ethylhexyl) phosphate (D2EHP), particle size distribution, and particle shape. No reliable method was available for D2EHP, and due to the limited quantity of solids in the supernatant composite, Bechtel National, Inc. (BNI) directed PNWD not to perform the particle size and particle shape measurements.

To support the characterization and testing activities, 10 of the 21 grab samples retrieved from Tank AP-104 in January 2001 were provided to the PNWD from the 222-S Laboratory in December 2001. The 10 grab samples received from 222-S contained small quantities of white precipitated solids settled on the bottom of the bottles. Efforts to dissolve these solids by heating were unsuccessful, and based on directions from BNI, the liquid phase was decanted from the solids and the solids archived. Later direction from BNI (i.e., test exception 24590-WTP-TEF-RT-02-092) resulted in these solids being analyzed for a selected set of analytes; the results of the solids analyses are presented in Section 8.0. Only the decanted liquid phase from each bottle was combined and homogenized into a single composite and separated into 10 sub-samples for characterization and process testing. Following sub-sampling, trace quantities of dark solids were observed in the samples; these solids were included as part of the AP-104 sample for all further characterization and process testing. One sub-sample was used to test for physical properties, including density, percent solids, rheology, and heat capacity. In addition, one sub-

sample was selected for inorganic, radiochemical, and selected organic analyses; the analyses were performed in triplicate. The characterization of the representative AP-104 composite sub-samples included but was not limited to:

- inductively coupled plasma plasma-atomic emission spectrometry (ICP-AES)
- radiochemical analyses, including $^{99}Tc^{+7}$
- inductively coupled plasma-mass spectrometry (ICP-MS)
- total uranium by kinetic phosphorescence analysis (KPA)
- ion chromatography (IC, inorganic and organic anions)
- titration for hydroxide
- total inorganic carbon (TIC) and total organic carbon (TOC)
- other inorganic analyses (e.g., mercury, cyanide, and ammonia)
- other organic analytes (e.g., chelators)
- selected physical properties: density, weight percent solids, heat capacity, and rheology

Results And Performance Against Objectives

Table S.1 summarizes the physical property results measured on the AP-104 composite supernatant and Table S.2 and Table S.3 summarize the results of the radiochemical and chemical analysis of the composite supernatant. Table S.2 and Table S.3 also contain the performance against the Contract Specification 7 Envelope A limits for those analytes or radionuclides included in the specification. The Contract Specification 7 limits were not exceeded for any analyte or radionuclide. Although ^{60}Co is at the limit (i.e., 98%) and has a relatively high uncertainty (i.e., actual activity may exceed the limit), ^{60}Co is expected to decay too well below the specification limit by the time of actual waste processing.

Table S.1. AP-104 Supernatant Composite – Physical Properties

Matrix	Physical Property Measurement	Average	RSD
Bulk Composite *(with trace quantity dark solids)*	Density (g/mL)	1.26	1.4%
	Total solids (wt%)	31.2	5.9%
	Heat capacity (J/g-K) at 25°C	3.10	5.0%
	Heat capacity (J/g-K) at 40 °C	3.11	4.8%
	Newtonian viscosity (cP) at 25 °C	3.47	5.3%
	Newtonian viscosity (cP) at 40 °C	2.36	0.5%
Supernatant Only *(with dark solids removed)*	Density (g/mL)	1.30	0.1%
	Total dissolved solids (wt%)	32.0	3.0%
RSD: relative standard deviation.			

Table S.2. AP-104 Supernatant Composite – Radionuclide Summary (mCi/L)

Method(a)	Radionuclide	MRQ mCi/L	MDL/ MDA mCi/L	Sample Average mCi/L	DF	%RSD	Bq per Mole Na, Sample	Bq per Mole Na, Spec 7 Envelope A Limit	% of Limit
H-3	^{3}H	2.1E-2	2.0E-5	1.98E-3		1	--	--	--
GEA	^{60}Co	2.1E-3	2.0E-3	9.36E-3		8	5.98E+4	6.1E+4	98
Se-79	^{79}Se	9.0E-5	2.5E-5	8.93E-4	B	8	--	--	--
Sr-90	^{90}Sr	1.5E-1	2.0E-1	1.95E+0		10	1.25E+7	4.4E+7	28
ICP-MS	^{99}Tc	1.5E-3	2.0E-4	1.44E-1		3	9.20E+5	7.1E+6	13
Tc-99	^{99}Tc^{+7}	1.5E-3	2.0E-4	5.03E-2		2	--	--	--
GEA	^{125}Sb	4.0E-4	2.0E-1	2.0E-1	U	--	--	--	--
GEA	^{126}Sn	6.0E-3	9.3E-2	9.3E-2	U	--	--	--	--
ICP-MS	^{129}I	2.7E-4	1.4E-5	2.57E-4		5	--	--	--
ICP-MS	^{135}Cs(b)	1.8E-3	2.7E-5	2.07E-3		3	--	--	--
GEA	^{137}Cs	9.0E+0	4.0E-2	1.90E+2		1	1.22E+9	4.3E+9	28
ICP-MS	^{137}Cs(b)	1.5E+0	2.0E+0	1.67E+2		3	--	--	--
C-14	^{14}C	7.2E-4	4.0E-5	7.17E-4		3	--	--	--
GEA	^{154}Eu	2.0E-3	7.0E-3	7.0E-3	U	--	<4.7E+4	1.2E+6	<4
GEA	^{155}Eu	9.0E-2	1.7E-1	1.7E-1	U	--	--	--	--
GEA	^{231}Pa	7.9E-5	2.0E+0	2.0E+0	U	--	--	--	--
ICP-MS	^{233}U	4.1E-4	1.9E-6	5.6E-6	J	15	--	--	--
ICP-MS	^{234}U	1.2E-4	3.2E-7	4.46E-6	B	6	--	--	--
ICP-MS	^{235}U	6.2E-8	7.5E-10	1.80E-7		0.2	--	--	--
ICP-MS	^{236}U	1.4E-6	6.4E-9	3.19E-7	e	3	--	--	--
ICP-MS	^{237}Np	1.9E-5	3.0E-7	3.90E-6	B	5	--	--	--
AEA	^{238}Pu	1.0E-2	1.2E-5	5.5E-5	J	5	--	--	--
ICP-MS	^{238}U	7.5E-9	1.8E-8	3.13E-6	a	0.03	--	--	--
AEA	$^{239/240}$Pu	3.0E-2	8.3E-6	4.17E-4		1	--	--	--
ICP-MS	^{239}Pu	3.0E-2	2.6E-5	1.05E-3	Bd	20	--	--	--
ICP-MS	^{240}Pu	1.0E-2	1.1E-5	1.51E-4	B	12	--	--	--
AEA	^{241}Am	3.0E-2	1.3E-5	5.79E-3		1	--	--	--
ICP-MS	^{241}Pu / ^{241}Am(c)	3.0E-1	2.1E-4	5.85E-3	B	4	--	--	--
AEA	^{242}Cm	1.5E-1	5.0E-6	1.1E-5	J	30	--	--	--
AEA	$^{243/244}$Cm	1.5E-2	8.7E-6	9.22E-4	d	19	--	--	--
Alpha	Total Alpha	2.3E-1	5.7E-2	5.7E-2	U	--	--	--	--
Beta	Total Beta	--	4.7E-1	2.06E+2		3	--	--	--
--	TRU	--	--	7.21E-3(d)		--	4.61E+4	4.8E+5	10

MDL: method detection limit (with all processing factors applied).

MDA: minimum detectable activity (with all processing factors applied). (--) indicates no MDA available.

DF: Data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide measured above EQL and no data qualifiers apply.

Table S.2. AP-104 Supernatant Composite – Radionuclide Summary (mCi/L) (cont.)

MRQ: minimum reportable quantity (defined by test specification). (--) indicates no MRQ defined by test specification.

RSD: relative standard deviation. (--) indicates one or more triplicate results <MDL and RSD not calculated.

TRU: Z>92, alpha emitter, half-life >10yr (^{237}Np, $^{239/240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm); Pu, Am, and Cm from AEA and Np from ICP-MS.

(a) ICP-MS radionuclide results provided in mCi/L for comparison to radiochemical results and evaluation against the Contract Specification 7 Envelope A limits. Test specification required ICP-MS radionuclide results to be reported in mg/L.

(b) ^{135}Cs and ^{137}Cs results calculated from ^{133}Cs results and Cs isotopic results obtained from HPIC/ICP-MS analysis.

(c) AMU-241 (^{241}Pu/^{241}Am) calibrated using ^{241}Am. Results in mCi/L calculated using ^{241}Am specific activity.

(d) TRU = 7.21E-3 mCi/L = AEA sum at 7.204E-3 mCi/L + ^{237}Np at 0.00390E-3 mCi/L.

Table S.3. AP-104 Supernatant Composite – Radionuclide/Analyte Summary (mg/L)

Method(l)	Radionuclide/ Analyte	MRQ mg/L	MDL mg/L	Sample Average mg/L	DF	%RSD	Mole Analyte per Mole Na, Sample	Mole Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit
ICP-MS	^{99}Tc	8.8E-2	1.2E-2	8.46E+0		3	--	--	--
ICP-MS	^{127}I	1.0E-1	2.3E-1	5.67E+0	B	3	--	--	--
ICP-MS	^{129}I	1.5E+0	7.8E-2	1.43E+0		5	--	--	--
ICP-MS	^{133}Cs	1.5E+0	2.5E-3	5.58E+0		3	--	--	--
ICP-MS	^{135}Cs(j)	1.5E+0	2.3E-2	1.73E+0		3	--	--	--
ICP-MS	^{137}Cs(j)	1.7E-2	2.3E-2	1.92E+0		3	--	--	--
ICP-MS	^{233}U	4.2E-2	1.9E-4	5.7E-4	J	15	--	--	--
ICP-MS	^{234}U	2.0E-2	5.1E-5	7.19E-4	B	6	--	--	--
ICP-MS	^{235}U	2.8E-2	3.4E-4	8.20E-2		0.2	--	--	--
ICP-MS	^{236}U	2.2E-2	9.8E-5	4.92E-3	e	3	--	--	--
ICP-MS	^{237}Np	2.7E-2	4.3E-4	5.49E-3	B	5	--	--	--
ICP-MS	^{238}U	2.2E-2	5.4E-2	9.19E+0	a	0.03	--	--	--
ICP-MS	^{239}Pu	4.8E-1	4.2E-4	1.69E-2	Bd	20	--	--	--
ICP-MS	^{240}Pu	4.4E-2	4.7E-5	6.58E-4	B	12	--	--	--
ICP-MS	^{241}Pu/^{241}Am(i)	8.7E-2	6.3E-5	1.72E-3	B	4	--	--	--
IC-Org	Acetate	--	110	870	J	7	--	--	--
ICP-AES	Al	75	1.7	12,800		1	8.20E-2	2.5E-1	33
ISE	Ammonia	140	8.0	402		14	--	--	--
ICP-AES	B	2.3	1.3	40.2		4	--	--	--
ICP-MS	B	2.3	4.9	39	JBab	1	--	--	--
ICP-AES	Ba	2.3	0.28	0.28	U	--	< 3.5E-7	1.0E-4	< 0.4
ICP-MS	Ba	2.3	0.052	1.7	Bd	30	--	--	--
IC-Inorg	Br(b)	300	130	130	U	--	--	--	--
C (Furn)	C as TC	--	14	8,130		1	--	--	--
C (HP)	C as TC	--	--(h)	8,450		1	--	--	--
C (Furn)	C as TIC	150	--(h)	5,160		8	7.45E-2	3.0E-1	25
C (HP)	C as TIC	150	30	4,210		2	6.06E-2	3.0E-1	20

Table S.3. AP-104 Supernatant Composite – Radionuclide/Analyte Summary (mg/L) (cont.)

Method(l)	Radionuclide/ Analyte	MRQ mg/L	MDL mg/L	Sample Average mg/L	DF	%RSD	Mole Analyte per Mole Na, Sample	Mole Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit
C (Furn)	C as TOC	1,500	400	2,970	J	13	4.32E-2	5.0E-1	9
C (HP)	C as TOC	1,500	70	4,240		1	6.11E-2	5.0E-1	12
ICP-AES	Ca	150	6.9	72		3	3.12E-4	4.0E-2	0.8
ICP-AES	Cd	7.5	0.41	1.8	J	0	2.77E-6	4.0E-3	0.07
ICP-AES	Ce	2.3	5.5	5.5	U	--	--	--	--
ICP-MS	Ce	2.3	0.099	0.14	J	(g)	--	--	--
IC-Org	Citrate	1,500	460	860	J	5	--	--	--
GC/FID	Citric acid	--	5.8	420		14	--	--	--
IC-Inorg	Cl(b)	300	130	5,440		2	2.65E-2	3.7E-2	72
Colorimetry	CN	3.0	0.24	45.6		1	--	--	--
ICP-AES	Cr	15	0.55	475		1	1.58E-3	6.9E-3	23
GC/FID	D2EHP	1,500	--	(c)		--	--	--	--
GC/FID	ED3A	1,500	4.9	310		15	--	--	--
GC/FID	EDTA	1,500	4.9	570	b	14	--	--	--
IC-F	F(a)	150	2	162		2	1.47E-3	9.1E-2	2
ICP-AES	Fe	150	0.65	9.0	B	11	2.78E-5	1.0E-2	0.3
IC-Org	Formate	1,500	180	3,730		4	--	--	--
IC-Org	Gluconate(d)	1,500	320	4,000		--	--	--	--
IC-Org	Glycolate(d)	1,500	130	1,630		4	--	--	--
GC/FID	HEDTA	1,500	8.8	8.8	Uab	--	--	--	--
CVAA	Hg	1.5	0.00007	0.0013	B	9	1.11E-9	1.4E-5	0.01
ICP-AES	K	75	52	1,870		3	8.27E-3	1.8E-1	5
ICP-AES	La	35	1.4	1.4	U	--	< 1.7E-6	8.3E-5	< 2
ICP-AES	Li	2.3	0.83	0.83	U	--	--	--	--
ICP-MS	Li	2.3	0.085	0.085	U	--	--	--	--
ICP-AES	Mg	300	2.8	2.8	U	--	--	--	--
ICP-AES	Na	75	21	133,000		2	--	--	--
ICP-AES	Ni	30	0.83	40.5		1	1.19E-4	3.0E-3	4
GC/FID	NIDA/IDA	1,500	11	883	b	2	--	--	--
IC-Inorg	NO_2(b)	500	1,300	69,200		1	2.60E-1	3.8E-1	68
IC-Inorg	NO_3(b)	500	1,300	111,000		1	3.09E-1	8.0E-1	39
GC/FID	NTA	1,500	5.6	247		8	--	--	--
Titration	OH	3,500	170	22,300		3	--	--	--
IC-Inorg	Oxalate(b)	1,500	100	900	J	13	--	--	--
IC-Org	Oxalate	1,500	230	730	J	2	--	--	--
ICP-AES	P	600	2.8	1,590		1	--	--	--
ICP-AES	Pb	300	2.8	8.3	J	10	6.92E-6	6.8E-4	1
IC-Inorg	PO_4(b,e)	1,500	100	5,520		1	1.00E-2	3.8E-2	26
ICP-MS	Rb	1.0	0.036	5.56		3	--	--	--

Table S.3. AP-104 Supernatant Composite – Radionuclide/Analyte Summary (mg/L) (cont.)

Method(l)	Radionuclide/ Analyte	MRQ mg/L	MDL mg/L	Sample Average mg/L	DF	%RSD	Mole Analyte per Mole Na, Sample	Mole Analyte per Mole Na, Spec 7 Envelope A Limit	% of Limit
IC-Inorg	SO_4(b,f)	1,500	100	3,100		1	5.58E-3	1.0E-2	56
GC/FID	Succinic acid	1,500	6.1	91	B	1	--	--	--
ICP-AES	Th	2.3	28	28	U	--	--	--	--
ICP-MS	Th	2.3	0.36	0.62	J	5	--	--	--
ICP-AES	U	600	55	55	U	--	< 4.0E-5	1.2E-3	< 3
ICP-MS	U(k)	--	--	9.28		0.03	6.74E-6	1.2E-3	0.6
KPA	U	780	0.60	10.9		2	7.92E-6	1.2E-3	0.7
ICP-AES	V	2.3	1.4	1.4	U	--	--	--	--
ICP-MS	V	2.3	0.28	2.8	Jd	16	--	--	--
ICP-AES	W	2.3	55	83	J	1	--	--	--
ICP-MS	W	2.3	0.23	93.6	be	6	--	--	--

MRQ: minimum reportable quantity (established by test specification). (--) indicates no MRQ defined by test specification.

MDL: method detection limit (with all processing factors applied). (--) indicates no MDL available for radionuclide/analyte.

DF: Data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide/analyte measured above EQL and no data qualifiers apply.

RSD: relative standard deviation. (--) indicates one or more of the triplicate results <MDL and RSD not calculated.

D2EHP: bis-(2-ethylhexyl) phosphoric acid; CAS 298-07-7.

EDTA: ethylenediaminetetraacetic acid; CAS 60-00-4.

ED3A: ethylenediaminetriacetic acid; CAS – none available.

HEDTA: N-(2-hydroxyelthyl) ethylenediaminetriacetic acid; CAS 150-39-0.

NIDA/IDA: nitrosoiminodiacetic acid/iminodiacetic acid; CAS 142-73-4 (IDA).

NTA: nitrilotriacetic acid; CAS 139-73-4.

(a) Fluoride analyzed by two methods; initial IC method exhibited significant interference and produced a maximum bounding fluoride concentration of about 2,100 µg/mL.

(b) IC MDLs are based on the lowest calibration standard adjusted for sample dilution; equivalent to SW-846 EQL definition.

(c) D2EHP was not measured due to lack of reliable method.

(d) Glycolate and gluconate results should be considered the upper bound concentration, since glycolate and gluconate are not resolved by the IC measurement method used for the analysis. IC system calibrated using glycolate; gluconate estimate based on gluconate-to-glycolate response factor. Each result assumes 100% of response due to each analyte.

(e) MRQ for PO_4 defined in test specification as 500 (as P) but reported here as PO_4 (500 x 3.066).

(f) MRQ for SO_4 defined in test specification as 500 (as S) but reported here as SO_4 (500 x 2.996).

(g) Reported average calculated from 1 or 2 results; RSD only calculated when all results exceed the MDL.

(h) C (Furn) TIC by difference, C (HP) TC by sum; no MDLs determined.

(i) AMU-241 calibrated using ^{241}Am.

(j) ^{135}Cs and ^{137}Cs calculated from ^{133}Cs results and Cs HPIC/ICP-MS isotopic analysis.

(k) ICP-MS U is sum of all U isotopes measured by ICP-MS.

(l) ICP-MS Analyses: See Section 6.4. Unless separated prior to analysis, analytes reported as elements may be biased due to altered isotopic distribution. Only Cs, U, and Pu separated prior to analysis.

Quality Requirements

PNWD implements the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements are implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs.* A matrix that cross-references the NQA-1 and 2a requirements with the PNWD's procedures for this work is given in TP-RPP-WTP-138, Attachment 3. It includes justification for those requirements not implemented. The applicable quality control (QC) parameters for chemical analysis are delineted in TP-RPP-WTP-138, Attachment 1.

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System" assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results. As specified in Test Specification, 24590-WTP-TSP-RT-01-011, rev. 0, *Tank 241-AP-104 Sample Compositing, Homogenization and Analyses*, BNI's QAPjP, PL-24590-QA00001, is not applicable since the work was not performed in support of environmental/regulatory testing, and the data will not be used as such.

PNWD addresses internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

Issues

There were no major technical issues. All QC acceptance criteria were met for all methods and analytes except as outlined and discussed in the following three sections:

6.2 General Comments of Methods
6.4 Data Limitations
7.0 Procedures, Quality Control, and Data Evaluation

Below are listed several minor issues, as discussed and described in various places in the report, including Sections 6.2 and 6.4:

- There are differences in target minimum reportable quantities (MRQs) specified in the test specification for some analytes and radionuclides depending on the method used to report the results (i.e., Radiochemistry, ICP-MS, ICP-AES, or KPA).
- Element (analyte) concentrations reported by ICP-MS are determined by comparison of a selected isotope mass response for a given element to the calibration curve generated for that element. The concentration versus response calibration curve assumes natural isotopic abundance. Elements

subjected to or generated from nuclear processes may have significantly altered isotopic abundances. If the isotopic abundance of the mass used to calibrate the ICP-MS is altered in the sample matrix, the concentration reported by ICP-MS will be biased. For the most accurate analysis of elements with altered isotopic abundances, chemical separation of the element is required so that individual isotope concentrations can be quantified and summed. Except for the Cs, U, and Pu, no chemical separations were performed prior to the ICP-MS analysis of the AP-104 supernatant. For those elements not chemically separated, the isotopes used for calibration are ^{7}Li, ^{11}B, ^{51}V, ^{85}Rb, ^{138}Ba, ^{140}Ce, ^{182}W, and ^{232}Th. However, the ICP-MS results for Li, B, V, W, and Th are considered reliable (barring any QC failures) since the impact from any nuclear process on isotopic abundance is considered small (i.e., <10% and within the error of the analysis). High fission yields will have a moderate effect on the ^{85}Rb and ^{138}Ba; i.e., reported results may be biased low by 10% to 20%. The largest potential impact is on cerium, where the reported value could be biased low by 50% to 60%. Unfortunately, the extent to which the ^{85}Rb, ^{138}Ba, and ^{140}Ce abundance may be altered in the AP-104 supernatant is unknown, as is the actual uncertainty of the reported ICP-MS results for these elements.

- One required analytes requested in the test specification, D2EHP, could not be analyzed due to the lack of a reliable analysis method. Therefore, no results are reported in this report. Methods development is required.
- Glycolate results should be considered the upper bound concentration for glycolate, since glycolate and gluconate cannot be resolved using the IC measurement method used for the analysis. This is due to the required choice of IC analytical column that coelutes glycolate and gluconate at the same retention time; therefore it cannot resolve the two compounds. The reported average glycolate concentration is 1,600 mg/L; if the entire response is due to gluconate, the gluconate concentration would be about 4,000 mg/L. No alternate method is available for independent measurement of gluconate and glycolate. Methods development is necessary if both gluconate and glycolate are required.
- Boron was identified as both an ICP-AES and ICP-MS analyte. Since significant ICP-MS QC failures are noted for boron, the ICP-AES results should be used for boron.

Terms and Abbreviations

AEA	alpha energy analysis
AMU	atomic mass unit
ASR	Analytical Service Request
BNI	Bechtel National Inc.
BS	blank spike
COC	chain-of-custody
CVAA	cold vapor atomic absorption
DSC	differential scanning calorimeter
DIW	deionized water
DQO	data quality objective
EQL	estimated quantitation limit
GC/FID	gas chromatography with a flame ionization detector
GEA	gamma energy analysis
HASQARD	Hanford Analytical Services Quality Assurance Requirements Documents
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
LSC	liquid scintillation counting
MDA	minimum detectable activity
MDL	method detection limit
MRQ	minimum reportable quantity
MS	matrix spike
MSD	matrix spike duplicate
NA	not applicable
NM	not measured
%D	percent difference
PB	process blank
PNWD	Battelle - Pacific Northwest National Laboratory
QA	quality assurance
QC	quality control
RIDS	Records Inventory and Disposition Schedule

RPD	relative percent difference
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
RSD	relative standard deviation
SAL	Shielded Analytical Laboratory
TC	total carbon
TDS	total dissolved solids
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
TWINS	Tank Waste Information System
WTP	Waste Treatment Plant

Units

Bq	Becquerel
cP	centipoise
°C	degree Centigrade
ºF	degree Fahrenheit
g	gram
J	Joule
K	Kelvin
kg	kilogram
L	liter
µCi	microcurie
mCi	millicurie
µg	microgram
mg	milligram
mL	milliliter
mPa	millipascal
M	molarity
Pa	Pascal
s	second
vol%	volume percent
wt%	weight percent

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1.0 Introduction

1.1 Objective

Battelle – Pacific Northwest Division (PNWD) is conducting physical property testing and inorganic, radiochemical, and selected organics characterization of waste from underground storage tank number 241-AP-104 (hereafter designated as AP-104) for Bechtel National, Inc. (BNI). This effort supports the planning and design of the River Protection Project – Waste Treatment Plant (RPP-WTP). Tank wastes are compared to analyte and radionuclide compositions described for Envelope A in Contract Specification 7. The results of the characterization of the AP-104 tank wastes are used to define pretreatment and separations processes prior to final stabilization (vitrification) of the waste.

Grab samples were taken from tank AP-104 in January 2001(1). Four samples each were collected from five different waste depths from riser 001 using 500-mL bottles. Approximately half of the grab samples were transferred to PNWD to satisfy requirements of ICD-23(2) for process testing. Table 1.1 provides identification and mass information for the grab samples collected.

Table 1.1. Grab Samples from Tank AP-104

Core Number	Date Sampled	Date Received at 222-S	Use for Material	Estimated Sample Mass (g)	222-S Laboratory ID
4AP-00-01	9-Jan-01	11-Jan-01	Characterization at 222-S	592	S01T000201
4AP-00-02	9-Jan-01	11-Jan-01	Retained by 222-S	573	S01T000202
4AP-00-03	9-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	585	S01T000203
4AP-00-04	9-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	593	S01T000204
4AP-00-05	9-Jan-01	11-Jan-01	Characterization at 222-S	575	S01T000205
4AP-00-06	9-Jan-01	11-Jan-01	Retained by 222-S	595	S01T000206
4AP-00-07	9-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	585	S01T000207
4AP-00-08	9-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	585	S01T000208
4AP-00-09	9-Jan-01	11-Jan-01	Characterization at 222-S	583	S01T000209
4AP-00-10	9-Jan-01	11-Jan-01	Retained by 222-S	588	S01T000210
4AP-00-11	9-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	591	S01T000211
4AP-00-12	11-Jan-01	12-Jan-01	Shipped to PNNL (ICD-23)	585	S01T000213
4AP-00-13	11-Jan-01	12-Jan-01	Characterization at 222-S	580	S01T000214
4AP-00-14	11-Jan-01	12-Jan-01	Retained by 222-S	577	S01T000215
4AP-00-15	11-Jan-01	12-Jan-01	Shipped to PNNL (ICD-23)	570	S01T000216
4AP-00-16	11-Jan-01	12-Jan-01	Shipped to PNNL (ICD-23)	584	S01T000217
4AP-00-17	11-Jan-01	11-Jan-01	Characterization at 222-S	583	S01T000221
4AP-00-18	11-Jan-01	11-Jan-01	Retained by 222-S	583	S01T000222
4AP-00-19	11-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	577	S01T000223
4AP-00-20	11-Jan-01	11-Jan-01	Shipped to PNNL (ICD-23)	583	S01T000224
4AP-00-21	11-Jan-01	11-Jan-01	Retained by 222-S	584	S01T000225
4AP-00-FB	9-Jan-01	12-Jan-01	Characterization at 222-S	--	--

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1 RPP-7266, rev. 2, *Tank 241-AP-104 Grab Sampling and Analysis Plan*, March 2001.

2 24590-WTP-ICD-MG-01-023 Rev A, *Interface Control Document for Waste Treatability Samples*, July 2001.

Approximately 5.8 kg (4.7 L) of AP-104 waste, which was retrieved from the tank in January 2001 and shipped to PNWD December 2001, was used as starting material for this characterization task. Test specification 24590-WTP-TSP-RT-01-011 rev. 0, *Tank 241-AP-104 Sample Compositing, Homogenization and Analyses* (Appendix A), defined the work scope. Test plan TP-RPP-WTP-138, Rev 0, *Tank 241-AP-104 Compositing, Homogenization, and Analysis* (Appendix C), was prepared by the PNWD to conduct the work scope defined in the test specification. The objectives of this work as defined in the test specification include:

- Receive sample bottles that contain AP-104 waste
- Dissolve precipitated solids into solution by heating (if possible)
- Combine contents of all bottles into a single composite and thoroughly mix
- Observe sample for the presence of foaming or any visual changes during mixing
- Provide sub-samples from the homogeneous composite (for characterization and process testing)
- Measure physical properties of a composite sub-sample as defined in test specification Table 1
- Perform chemical and radiochemical analysis of a composite sub-sample as defined in test specification Tables 2 and 3
- Determine compliance to Contract Specification 7 (Envelope A) of DE-AC27-01RV14136
- Report analysis results in accordance with Standard Electronic Format Specification for Tank Waste Characterization Data Loader
- Provide a comprehensive technical report.

The inorganic, radionuclide, and organic analytes tested were identified in the test plan. The analysis and quality control (QC) requirements for the analyses were included in the test plan and transmitted to PNWD laboratory staff via the Analytical Service Requests (ASR) 6378, 6378.01, 6378.02, and 6378.03 for the AP-104 supernatant composite and ASRs 6670, 6670.01, and 6670.02 for the white precipitated solids removed prior to compositing.

Initial analytical sample processing is discussed in Section 5.0, Analytical Sample Processing. The characterization results, data limitations, method modifications, and general observations are discussed in Section 6.0, Analytical Results. Methods, average sample results, QC results, and method detection limits (MDLs) are presented in Section 7.0: Procedures, Quality Control, and Data Evaluation.

1.2 Quality Assurance Requirements

1.2.1 Application of RPP-WTP Quality Assurance Requirements

PNWD implements the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements are implemented through PNWD’s *Conducting Analytical Work in Support of Regulatory Programs.* The PNWD Quality Assurance (QA) Plan, *Conducting Analytical Work in Support of Regulatory Program*, which is compliant with the *Hanford Analytical Service Quality Assurance Requirements Documents* (HASQARD)(3).

A matrix that cross-references the NQA-1 and 2a requirements with the PNWD's procedures for this work is given in TP-RPP-WTP-138, Attachment 3 (Appendix C). It includes justification for those requirements not implemented.

1.2.2 Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 *Scientific Investigations* and QA-RPP-WTP-1201 *Calibration Control System* assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in Test Specification, 24590-WTP-TSP-RT-01-011, rev. 0, *Tank 241-AP-104 Sample Compositing, Homogenization and Analyses*, BNI's QAPjP, PL-24590-QA00001, is not applicable since the work was not performed in support of environmental/regulatory testing, and the data will not be used as such.

The applicable QC parameters for chemical analysis are delineated in TP-RPP-WTP-138, Attachment 1 (Appendix C).

1.2.3 Internal Data Verification and Validation

PNWD addresses internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual.*

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3 Hanford Analytical Services Quality Assurance Requirements Document; Volume 4: Laboratory Technical Requirements. DOE/RL-96-68, Rev 2, September 1998.

2.0 Sample Inspection

The AP-104 waste samples were received at PNWD's Radiochemical Processing Laboratory (RPL) from the Hanford 222-S Laboratory under chain-of-custody (COC) (Appendix B). Upon receipt, the AP-104 waste samples were visually inspected. The inspection was documented through test instruction TI-RPP-WTP-144, *AP-104 Sample Inspection*. The sample lids (phenolic type) were in poor condition and were immediately replaced with new radiation resistant I-CHEM lids. The 222-S Laboratory only recorded the average tare mass of a "batch" of 10 bottles with the manufacturer's lid (phenolic). Bottle masses without lids were not recorded. For this reason, a mass shipping-receiving balance of the samples can only be estimated. Correcting for the lid change involved weighing 10 lids of each type (phenolic and I-CHEM), and estimating the mass loss due to evaporation during storage and transportation. These calculations are shown in Table 2.1. Only 0.10% of the sample was unaccounted for, which is within the error associated with the estimation.

Table 2.1. AP-104 As-Received Samples from 222-S Laboratory

Bottle ID	Gross Mass with Phenolic Lids (g)	Average Tare Mass of 10 Bottles with I-CHEM Lids (g)	Calculated Sample Mass in RPL (g)	Approximate Mass Loss Due to Change of Lids[(a)] (g)	Calculated Sample Mass in RPL Based on I-CHEM Lids (g)	Net Sample Mass as recorded in 222-S with I-CHEM Lids (g)	Difference in Mass from 222-S & RPL Based on Consistent Lids (g)	Mass Percent Lost During Transfer Based on Consistent Lids (%)
4AP-00-03	889.35	296.3	593.05	9.42	583.63	585	-1.37	-0.23
4AP-00-04	898.38	296.3	602.08	9.42	592.66	593	-0.34	-0.06
4AP-00-07	889.92	296.3	593.62	9.42	584.20	585	-0.80	-0.14
4AP-00-08	887.91	296.3	591.61	9.42	582.19	585	-2.81	-0.48
4AP-00-11	897.19	296.3	600.89	9.42	591.47	591	0.47	0.08
4AP-00-12	889.92	296.3	593.62	9.42	584.20	585	-0.80	-0.14
4AP-00-15	876.35	296.3	580.05	9.42	570.63	570	0.63	0.11
4AP-00-16	889.03	296.3	592.73	9.42	583.31	584	-0.69	-0.12
4AP-00-19	882.83	296.3	586.53	9.42	577.11	577	0.11	0.02
4AP-00-20	888.21	296.3	591.91	9.42	582.49	583	-0.51	-0.09
Total	8889.09	2963.0	5926.09	94.21	5831.88	5838	-6.12	-0.10

(a) The 9.42 g mass loss is the difference between average weight of 10 I-Chem lids (9.39 g) and 10 phenolic lids (18.81 g).

Following the lid replacements, the samples were visually inspected. Photographs of the samples were taken and are shown in Figure 2.1. The samples were observed to have a small quantity of white precipitated solids settled on the bottom of the sample bottles. These solids were not anticipated during the work planning process, since the COCs indicated 'no solids' were observed.

a) 4AP-00-3, 4AP-00-4, 4AP-00-7
b) 4AP-00-4, 4AP-00-7, 4AP-00-8, 4AP-00-11
c) 4AP-00-4, 4AP-00-7, 4AP-00-8, 4AP-00-11
d) 4AP-00-8, 4AP-00-11, 4AP-00-12, 4AP-00-15
e) 4AP-00-15, 4AP-00-16, 4AP-00-19, 4AP-00-20
f) 4AP-00-16, 4AP-00-19, 4AP-00-20

Figure 2.1. As-Received AP-104 Samples

3.0 Homogenization and Sub-Sampling

The objective of compositing the AP-104 samples was to provide homogeneous feed to tasks within the project. The homogenized feed was used to support the characterization task as well as process testing. The homogenization and sub-sampling activity was performed according to the test instruction TI-RPP-WTP-139, *AP-104 Sample Homogenization*. Figure 3.1 provides a flowchart, which describes the compositing and sub-sampling activities.

As prescribed by the test plan TP-RPP-WTP-138, PNWD heated three of the samples to approximately 150ºF (65ºC)(4) while stirring in an attempt to redissolve the solids prior to analysis. Little to no solids dissolution was visually observed. Following direction from BNI, the as-received samples were decanted to separate the white precipitated solids and the supernatant. The decanted supernatant was transferred into the clean bottles that were eventually used for the homogenized sub-samples. These bottles were labeled **AP104ARA** to **AP104ARJ**. The bottle containing the precipitated solids was labeled **AP104K**. The final mass of material in **AP-104K** was about 65 g, which included the separated white solids and a significant fraction of tank supernatant. These solids appeared to possess high yield stress, since a significant amount of force was required to suspend the solids from their settled state for transfer into the **AP104K** bottle. Per test exception 24590-WTP-TEF-RT-02-092, analyses were performed on the solids; results of these analyses are presented in Section 8.0. Images of the decanted supernatant can be seen in Figure 3.2. (bottles AP104ARA and AP104ARB are not pictured).

The next step in the homogenization process was to consolidate the decanted supernatant samples into a mixing vessel, homogenize by stirring, and draw sub-samples. The mixing vessel was thoroughly cleaned with water and sodium lauryl sulfate and rinsed with deionized water. In alphabetical sequence from **AP104ARA** to **AP104ARJ**, the samples were placed into the mixing vessel. Only the decanted supernatant was used to prepare the AP-104 composite feed material; i.e., the precipitated white solids collected in bottle **AP104K** were not added to the mixing vessel. A lid was placed on the vessel to prevent any cross-contamination. The agitator was started and mixing proceeded for one hour. A slight degree of foaming was observed during the homogenization process. Sub-samples were then drawn from the homogenization vessel in alphabetical sequence from **AP104ARA** to **AP104ARJ** through the ball valve located on the bottom of the vessel. A small quantity of dark precipitate was observed in each of the bottles after sub-sampling. Since the mixing vessel was thoroughly cleaned prior to introducing the AP-104 samples, the source of the dark solids is unknown. Images of the homogenized AP-104 material can be seen in Figure 3.3. Due to dead-zones at the bottom of the mixing vessel, a decreasing amount of the dark solids was observed as sub-sampling proceeded. Based on a visual estimation, the first bottle (**AP104ARA**) contained approximately 2.5% volume dark solids. Subsequent bottles (**AP104ARB** through **AP104ARI**) contained approximately 0.5% volume dark solids. The final sample drawn (**AP104ARJ**) was approximately half full and only contained a trace amount of dark solids. The precipitated dark solids in each bottle are considered part of the AP-104 composite feed material and are included in all physical properties measurements, characterization analyses, and process testing activities.

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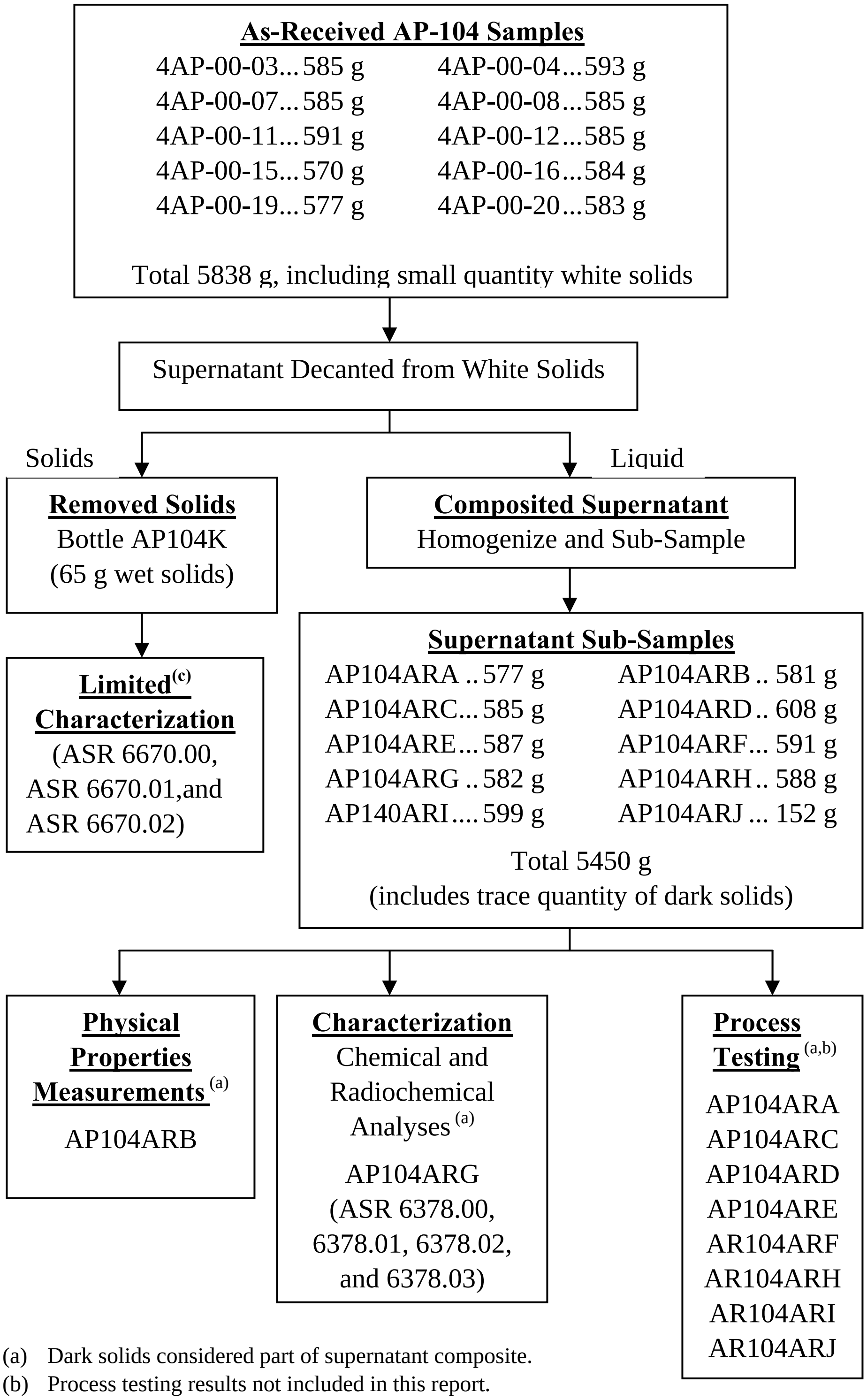
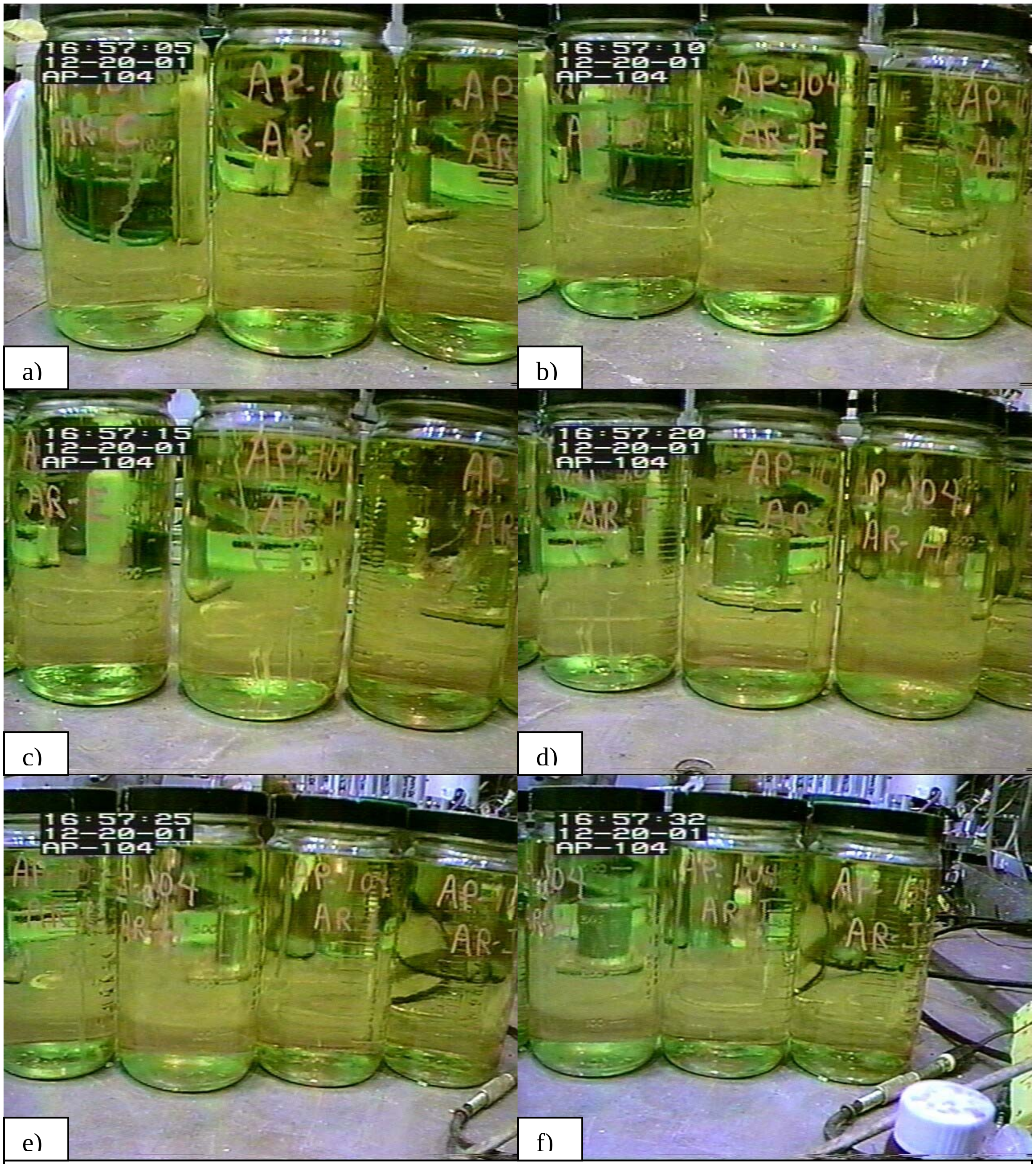
4 Due to thermocouple malfunction during heating temperature, dissolution temperature could not be accurately quantified. However, with a similar hotplate at the same temperature settings, a temperature of 150ºF was measured on a water surrogate sample. Although this temperature is above the 100°F required by the test specification, recovery was not possible. BNI approved use of the contents of the three containers heated above 100°F for compositing..



(a) Dark solids considered part of supernatant composite.
(b) Process testing results not included in this report.
(c) Limited: ICP-AES, IC, GEA, total alpha, total beta, XRD.

Figure 3.1. AP-104 Compositing and Sub-Sampling Flowchart



a) AP104ARC, AP104ARD, AP104ARE
b) AP104ARD, AP104ARE, AP104ARF
c) AP104ARE, AP104ARF, AP104ARG
d) AP104ARF, AP104ARG, AP104ARH
e) AP104ARG, AP104ARH, AP104ARI, AP104ARJ
f) AP104ARH, AP104ARI, AP104ARJ

Figure 3.2. AP-104 As-Received Samples After Decanting

a) AP104ARA, AP104ARB, AP104ARC, AP104ARD
b) AP104ARB, AP104ARC, AP104ARD, AP104ARE, AP104ARF,
c) AP104ARE, AP104ARF, AP104ARG, AP104ARH
d) AP104ARF, AP104ARG, AP104ARH
e) AP104ARI
f) AP104ARJ

Figure 3.3. AP-104 Samples After Homogenization and Sub-Sampling

Each bottle was weighed, and the mass of each sub-sample was calculated by subtracting the tare; results are presented in Table 3.1. The as-received bottles were also weighed and a mass balance was performed to estimate the amount of material lost during the homogenization and sub-sampling process; results are presented in Table 3.2. Approximately 3% of the sample was lost due to residual material in the mixing vessel and evaporative losses. This value is consistent with previous homogenization and sub-sampling efforts (Urie et al. 2002).

Table 3.1. AP-104 Homogenized Composite Sub-Samples

Bottle ID	Mass of Bottle and Lid (g)	Mass of Bottle without Lid (g)	Mass of Bottle, Lid, and Sample (g)	Sample Mass (g)
AP104ARA	320.56	296.25	898.00	577.44
AP104ARB	320.19	295.70	901.68	581.49
AP104ARC	318.05	293.38	902.87	584.82
AP104ARD	319.13	294.25	927.40	608.27
AP104ARE	320.94	296.38	907.81	586.87
AP104ARF	317.95	293.52	908.76	590.81
AP104ARG	319.29	295.05	901.43	582.14
AP104ARH	318.21	293.68	906.21	588.00
AP104ARI	319.26	294.73	917.98	598.72
AP104ARJ	319.01	295.50	470.99	151.99
AP104K(a)	217.77	202.13	267.12	64.99
Total	3410.34	3150.56	8910.25	5515.54

(a) White solids collected prior to compositing and sub-sampling.

Table 3.2. Amount of Sample Lost During Homogenization and Sub-Sampling

As-Received Sample Mass (g)	Mass of Samples after Homogenization and Sub-Sampling (g)	Mass of Sample Remaining in As-Received Bottles (g)	Total Mass Accounted For (g)	Mass Loss During Homogenization and Sub-Sampling (g)	Mass Percent Lost During Homogenization and Sub-Sampling
5831.88	5515.54	138.75	5654.30	177.58	3.05%

To evaluate the stability of the supernatant composite, sample **AP104ARB** was agitated with a stir bar and approximately 10 mL was drawn and placed in a centrifuge cone labeled **AP104B**. This centrifuge cone was moved to the Shielded Analytical Laboratory (SAL) hot cells where the ambient temperature is approximately 25°C. The sample was observed for a two-week period for further precipitation. No further precipitation was observed.

4.0 Physical Properties

Physical properties were measured on material taken from bottle **AP104ARB**, which was sub-sampled from the homogenized supernatant composite (see Section 3.0). Physical properties measurements were obtained using PNWD operating procedure, which implement BNI standard methodology.(5)

4.1 Selected Physical Properties

The physical properties listed in Table 4.1 were measured on the content from bottle **AP104ARB**, which contained a visible trace (i.e., about 0.5% by volume) of dark precipitate material.

Table 4.1. List of Required Physical Property Analyses

Physical Property
Slurry Density
Liquid Density
Vol% Centrifuged solids
Wt% Centrifuged solids
Wt% Total Dried solids
Wt% Dissolved solids
Wt% Undissolved solids

The sample was stirred using a magnetic stir bar while 5 to 10-mL sub-samples were transferred into three pre-weighed volume-graduated centrifuge cones. The mass and volume of material in each cone was recorded. The cones were centrifuged for one hour at ~1000 x G. The total sample volume and volume of centrifuged solids were recorded. The standing supernatant layer was decanted into the graduated cylinder of known mass. The mass and volume of supernatant in the cylinders was recorded, as was the mass of centrifuged solids left in the centrifuge cones. The supernatant was transferred to a pre-weighed vial and reweighed. The vials (containing primarily liquid) and cones (containing primarily solids with interstitial liquid) were transferred to an oven at 105°C and dried for at least 24 hours. The centrifuge cones and vials were reweighed periodically until a stable mass was reached (e.g., a change in mass of less than 0.1% in 24 hours). The volumes and masses obtained through this process allow for the calculation of the physical properties listed in Table 4.2. Insufficient solid precipitate was present to calculate many of the physical property parameters; therefore, only slurry density, liquid density, wt% total dried solids, and wt% dissolved solids were measured.

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5 *Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements*. 24590-WTP-GPG-RTD-001 Revision 1. BNI. 2002.

Table 4.2. Physical Properties of AP-104 Supernatant Composite

Physical Property [(a)]	Aliquot-1	Aliquot-2	Aliquot-3	Average	RSD
Density – bulk slurry (g/mL)	1.27	1.27	1.24	1.26	1.4%
Density – centrifuged supernatant (g/mL)	1.30	1.30	1.30	1.30	0.1%
Wt% total dried solids[(b)]	32.1	32.5	29.1	31.2	5.9%
Wt% dissolved solids	32.2	32.8	30.9	32.0	3.0%

(a) Solid-liquid separations were performed at 25°C.
(b) Trace quantity of dark solids included in measurement.

4.2 Rheology

4.2.1 Background

Viscosity is the internal resistance to flow of a fluid against external forces. Mathematically, viscosity is defined as the ratio of shear stress to shear rate. For a Newtonian fluid, this value is constant. For non-Newtonian fluids, this ratio can change based on flow conditions and shear history. The rheological data is most often presented as a rheogram. Rheograms provide flow data over a range of shear rates rather than at one shear rate. A rheometer changes the shear rate to a chosen value while measuring and recording the resulting shear stress. This is the primary difference between a rheometer and a viscometer. Viscosity data, yield stress data, and flow curve information are obtained from a rheogram. Viscosity is usually reported in units of centipoise (cP). One cP is equal to a millipascal second (mPas). 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 stress, a minimal external force that must be applied before any flow is obtained. The four curve fits that best describe most slurries and consequently tank waste are as follows:

1. Newtonian:

$$\tau = \eta\dot{\gamma}$$

Where, τ is the shear stress
η is the Newtonian viscosity
$\dot{\gamma}$ is the shear rate

2. Ostwald (or Power Law)

$$\tau = m\dot{\gamma}^{n}$$

Where, τ is the shear stress
m is the consistency coefficient
n is the power law exponent
$\dot{\gamma}$ is the shear rate

If $n<1$, the material is referred to as pseudoplastic (shear thinning). If $n>1$, the material is referred to as dilatant (shear thickening). Since dilatant flow behavior is rare, dilatant behavior is an indication of possible Taylor Vortices or other measurement errors.

3. Bingham Plastic

$$\tau = \tau_O^B + \eta_P \dot{\gamma}$$

Where, τ is the shear stress

τ_O^B is the Bingham yield stress

η_P is the plastic viscosity

$\dot{\gamma}$ is the shear rate

4. Herschel-Bulkley

$$\tau = \tau_O^H + k\dot{\gamma}^b$$

Where, τ is the shear stress

τ_O^H is the yield stress

k is the Herschel-Bulkley consistency coefficient

b is the Hershel-Bulkley power law exponent

$\dot{\gamma}$ is the shear rate

For Newtonian fluids, the viscosity is constant over all shear conditions. A pseudoplastic, or power law fluid, has a viscosity that varies with stress in a non-linear fashion and is modeled by the Ostwald equation. A Bingham plastic is a fluid that contains a yield stress, but once enough force has been applied to exceed the yield stress, the material behaves in a Newtonian fashion over the rest of the shear rate range. A yield pseudoplastic is a power law fluid with a yield stress and is modeled with the Herschel-Bulkley equation.

4.2.2 Equipment Details

A Haake RS300 rheometer was used for the work described in this section. The RS300 system has been configured as a concentric cylinder rotational system. The sensor system consists of an inner cylinder that is placed inside an outer cylinder with a known annulus. When the inner cylinder rotates, the resulting fluid resistance to the flow is measured electronically. When this signal is combined with the rotational rate, it can be mathematically transformed into shear stress and shear rate data. For the AP-104 samples analyzed, a Haake DG41 sensor system was utilized. The DG41 sensor has a large available surface area to increase the instrument sensitivity for relatively low viscosity samples.

The testing was conducted as follows. The samples were loaded into the sample container, and the shear rate was increased linearly from 0/s to 1000/s over 5 minutes. The sample was held at a shear rate of 1000/s for 1 minute. Lastly, the shear rate was decreased linearly from 1000/s to 0/s over 5 minutes. The test was then immediately repeated with the same sample. If the subsequent data were in close agreement with previous runs, the testing for that sample was considered complete. If there was noticeable variation in the data, the sample was ramped through this cycle again until two consecutive similar data sets were obtained. The purpose of this repetition was to determine if rheological changes are made to the material while under the influence of shear. Shear history is often an important part of determining expected rheological behaviors. Once the previous sample was tested to the point of obtaining consistent data, it was removed and a new sample loaded for the next run.

The purpose of this set of testing parameters was to identify the rheological behavior and shear sensitivity of the materials. The first ramp cycle shows newly loaded or fresh sample behavior including breakdown of sample structure through hysteresis, if present. Hysteresis is when the ramp down curve is different from the ramp up curve. An immediate repeat allows little or no time for the sample to recover. The complete cycle repeat with the used sample shows the effects of a shear history with a short time of recovery for the sample.

A 9.8 cP (at 25°C) viscosity standard oil was used to validate the calibration of the machine. A value of 10.1 cP was measured at 25°C, which is within the acceptance criterion of ±10%. This plot is shown in Figure 4.1

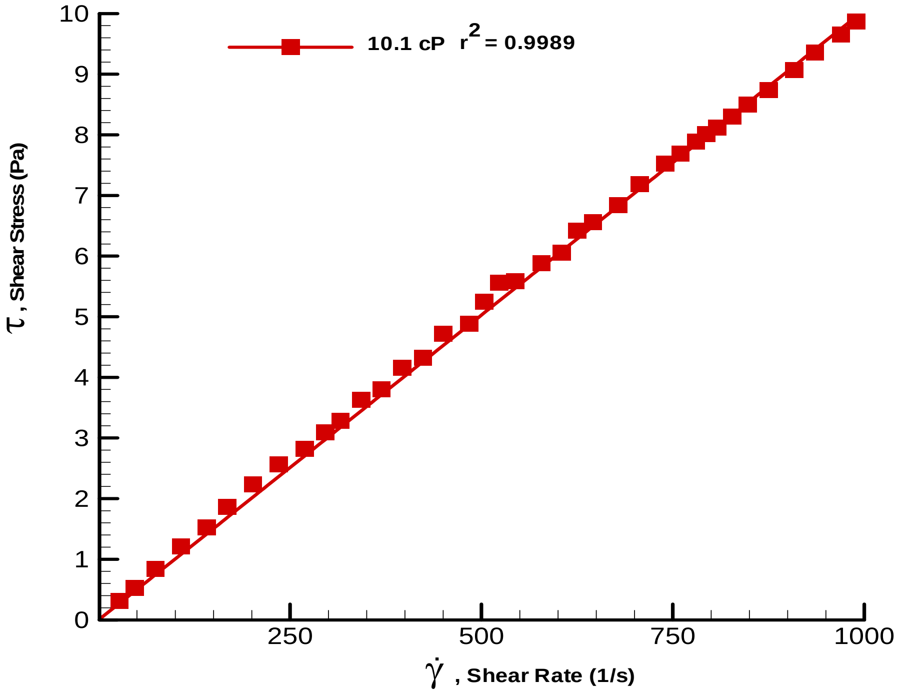

Figure 4.1. Haake RS300 Viscosity Standard Calibration Check at 25°C

4.2.3 Rheology Results

Rheograms from AP-104 supernatant composite at two temperatures are shown in Figure 4.2 and Figure 4.3. Rheological model fit parameters are shown in Table 4.3 and Table 4.4, respectively. Since the AP-104 supernatant demonstrated nearly Newtonian behavior, the results from each of the rheological models are similar. However, the Ostwald or Power-Law model appears to provide the best fit. As expected, the AP-104 supernatant does not exhibit a yield stress, and as the temperature increases, the Ostwald power law exponent increases approaching unity (i.e., approaching Newtowian behavior). Therefore, at all temperatures, a Newtonian model can adequately describe the behavior of the AP-104 supernatant fluid. The Newtonian results are shown in Table 4.5. At 25°C the viscosity of the fluid was measured at 3.5 cP. The viscosity dropped to 2.4 cP when the measurement temperature was increased to 40°C.

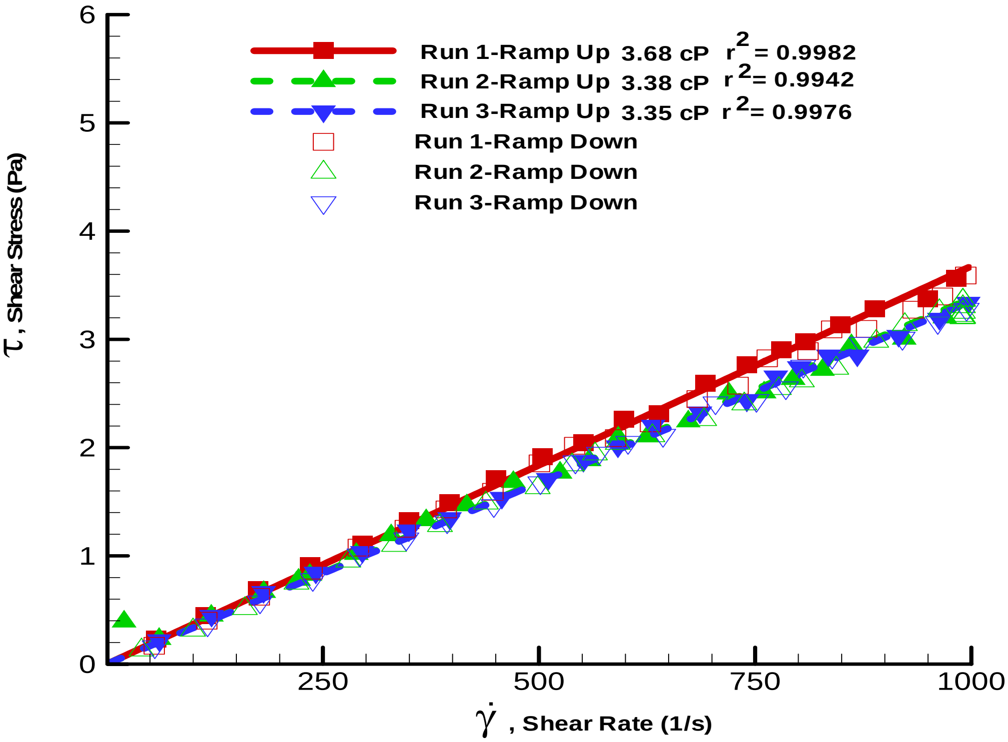

Figure 4.2. Rheograms of AP-104 Supernatant Composite at 25°C

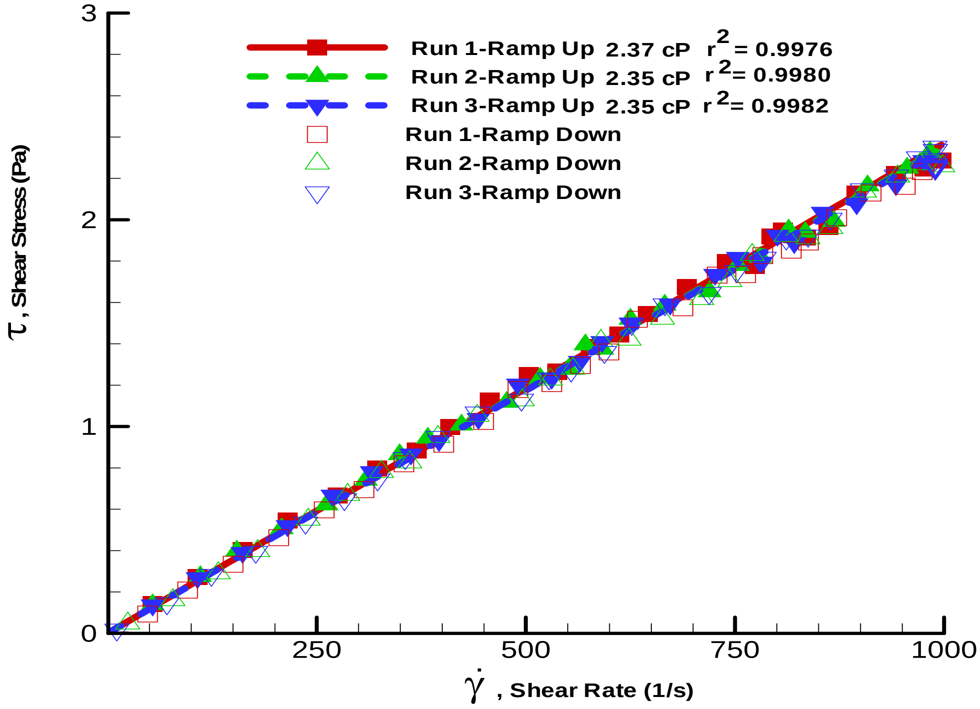

Figure 4.3. Rheograms of AP-104 Supernatant Composite at 40°C

Table 4.3. AP-104 Supernatant Composite – Rheology Data at 25°C

Model / Model Parameter	Run #1[(a)]	Run #2[(a)]	Run #3[(a)]
Shear Strength (by Vane Method):			
τ_O - Shear Strength (Pa)	[(b)]	[(b)]	[(b)]
Newtonian:			
η - Newtonian viscosity (cP)	3.68	3.38	3.35
r^2 - correlation coefficient	0.9982	0.9942	0.9976
Ostwald (or Power Law):			
m - the consistency coefficient (cP)	4.80	5.47	4.63
n - the power law exponent	0.959	0.927	0.951
r^2 - correlation coefficient	0.9990	0.9970	0.9988
Bingham Plastic:			
τ_O^B - the Bingham yield stress (Pa)	0.049	0.095	0.054
η_p - the plastic viscosity (cP)	3.60	3.24	3.27
r^2 - linear correlation coefficient	0.9988	0.9968	0.9984
Herschel-Bulkley:			
τ_O^H - the yield stress (Pa)	0	0.04312	0
k - the Herschel-Bulkely consistency coefficient (cP)	4.80	4.49	4.63
b - the Hershel-Bulkely power law exponent	0.959	0.954	0.951
r^2 - correlation coefficient	0.9990	0.9970	0.9988

(a) Run #1, #2, and #3 data from rheogram file 053002c, 053002d, and 05002e, respectively.

(b) Not applicable to matrix; required to be reported by BNI guidance document 24590-WTP-GPG-RTD-001.

Table 4.4. AP-104 Supernatant Composite – Rheology Data at 40°C

Model / Model Parameter	**Run #1(a)**	**Run #2(a)**	**Run #3(a)**
Shear Strength (by Vane Method):			
τ_O - Shear Strength (Pa)	(b)	(b)	(b)
Newtonian:			
η - Newtonian viscosity (cP)	2.37	2.35	2.35
r^2 - correlation coefficient	0.9976	0.9980	0.9982
Ostwald (or Power Law):			
m - the consistency coefficient (cP)	3.24	2.99	2.97
n - the power law exponent	0.9525	0.9635	0.9642
r^2 - correlation coefficient	0.9988	0.9986	0.9988
Bingham Plastic:			
τ_O^B - the Bingham yield stress (Pa)	0.03798	0.02835	0.02596
η_p - the plastic viscosity (cP)	2.31	2.31	2.31
r^2 - linear correlation coefficient	0.9984	0.9986	0.9986
Herschel-Bulkley:			
τ_O^H - the yield stress (Pa)	0.0002143	0	0
k - the Herschel-Bulkley consistency coefficient (cP)	3.23	2.99	2.97
b - the Hershel-Bulkley power law exponent	0.9527	0.9635	0.9642
r^2 - correlation coefficient	0.9988	0.9986	0.9988

(a) Run #1, #2, and #3 data from rheogram file 053002f, 053002g, and 05002h, respectively.
(b) Not applicable to matrix; required to be reported by BNI guidance document 24590-WTP-GPG-RTD-001.

Table 4.5. Newtonian Viscosity of the AP-104 Supernatant Composite

Run	**Newtonian Fit at 25°C (cP)**	**Correlation Coefficient (r^2)**	**Newtonian Fit at 40°C (cP)**	**Correlation Coefficient (r^2)**
1	3.68	0.9982	2.37	0.9976
2	3.38	0.9942	2.35	0.9980
3	3.35	0.9976	2.35	0.9982
Average	3.47	--	2.36	--
RSD	5.3%	--	0.5%	--

RSD: relative standard deviation
cP: centipoise

4.3 Heat Capacity

4.3.1 Background

For heat capacity measurement using a differential scanning calorimeter (DSC), the instrument manufacturer prescribes a three-step approach. First the empty sample pan is heated or cooled 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 to be used for the sample and the same temperature program repeated. Then, the reference material is removed and replaced with the sample, and the same temperature program repeated.

The heat capacity of the sample is calculated using Equation 4.1, which employs the difference between the reference and the baseline and the difference between the sample and the baseline taking into account the reference and sample masses. The reference standard, having a known heat capacity, is selected to be similar in state and mass to the samples to be analyzed; e.g., the DSC manufacturer suggests water for aqueous samples and sapphire or alumina for solid samples.

$$C_p^S = \frac{Y_S}{Y_R} \times \frac{M_R}{M_S} \times C_p^R \qquad \text{Equation 4.1}$$

Where,

C_P^S is the heat capacity at constant pressure of the sample material (J/g-K)
C_P^R is the known heat capacity at constant pressure of the reference material (J/g-K)
Y_S is the curve difference between the sample and the empty container (K)
Y_R is the curve difference between the reference and the empty container (K)
M_S is the sample mass (g)
M_R is the reference mass (g)

To prevent heat of vaporization of water from masking the heat absorption due to an increase in temperature, hermetically sealed 15-µL gold pans were used for the single 10-mg deionized water (DIW) reference and each of the 10-mg aqueous AP-104 samples. Even though the sealed pans provide a constant volume, the DSC manufacturer's approach provides heat capacity at constant pressure (C_P), rather than a heat capacity at constant volume (C_v), for the sample, since the reference material has a known C_P.

Since the reference standard used is similar in state and mass to the sample, the heat capacity ratio (γ, where $\gamma = C_V/C_P$) of the sample and reference standard should be approximately equal. The DSC manufacturer's recommended method assumes that the DSC responds proportionally for both the sample and the reference material. In general, γ is more important for gases, but since a constant volume system is being used, γ is required to calculate C_p.

With this assumption, C_P can be calculated as shown by Equations 4.2 and 4.3.

$$\gamma^S \cong \gamma^R$$

$$\frac{C_P^S}{C_V^S} = \frac{C_P^R}{C_V^R} \qquad \text{Equation 4.2}$$

$$C_P^S = \left(\frac{C_V^S}{C_V^R}\right) \cdot C_P^R$$

$$C_P^S = \left(\frac{\Delta U^S}{\Delta U^R}\right) \cdot C_P^R \qquad \text{Equation 4.3}$$

Where,

γ^S is the heat capacity ratio of the sample material (dimensionless)
γ^R is the heat capacity ratio of the reference material (dimensionless)
C_V^S is the heat capacity at constant volume of the sample material (J/g-K)
C_V^R is the heat capacity at constant volume of the reference material (J/g-K)
ΔU^S is the change in internal energy of the sample material (J)
ΔU^R is the change in internal energy of the reference material (J)

Equation 4.4 can then be derived from Equations 4.1 and Equation 4.3:

$$\frac{\Delta U^S}{\Delta U^R} = \frac{Y_S}{Y_R} \times \frac{M_R}{M_S} \qquad \text{Equation 4.4}$$

The use of hermetically sealed pans prevented reusing the same pan for both the reference standard and sample as recommended by the DSC manufacturer. To overcome this complication, a single sample of high purity DIW was encapsulated in its own individual gold pan and used as the reference standard for each sample aliquot analysis. Each AP-104 sample aliquot was encapsulated in the same pan as used for its baseline (i.e., empty pan) determination. It is assumed that the pan used for the sample aliquot analysis was equivalent to the pan used for the DIW reference. After each analysis, the water reference and AP-104 aliquot masses were checked to ensure that no water escaped thus compromising the analysis. For C_P^R in Equation 4.3, the heat capacities for water (Weast 1984) of 4.180 J/g-K at 298 K (25°C) and 4.179 J/g-K at 313 K (40°C) were used to calculate the heat capacity of the AP-104 samples.

4.3.2 Heat Capacity Results

Before withdrawing aliquots for analysis, the entire 100-mg sub-sample of AP-104 supernatant provided for the heat capacity analysis was mixed by stirring with a pipette tip and then repeatedly drawing the sample into a pipette and discharging it back into the container down the side of the container. No solids were visible in the 100-mg sample during this mixing. Following the mixing, a nominal 10-mg aliquot of sample was withdrawn with a micropipette and transferred to a DSC gold sample pan. Three aliquots of the AP-104 supernatant composite were prepared for the heat capacity measurements in this manner, with each of the three aliquots being measured at least twice.

The temperature program used for the triplicate analyses of the AP-104 sample was to 1) cool to 10°C, 2) hold at 10°C for 10 minutes, 3) heat to 70°C at 2.5°C/min, and 4) hold at 70°C for 10 min. As recommended by the DSC manufacturer, DIW was used as the reference standard for aqueous AP-104 samples. The requested heat capacities at 298 K (25°C) and 313 K (40°C) and their 95% confidence intervals are provided in Table 4.6.

Table 4.6. Measured Heat Capacity of AP-104 Supernatant Composite

Temperature K (°C)	Aliquot 1 C_p (J/g-K)	Aliquot 2 C_p (J/g-K)	Aliquot 3 C_p (J/g –K)	Average C_p (J/g-K)	RSD
298 (25)	3.25 ±0.06	2.94 ±0.06	3.10 ±0.04	3.10 ±0.65	5.0%
313 (40)	3.25 ±0.06	2.95 ±0.06	3.12 ±0.04	3.11 ±0.64	4.8%

RSD: relative standard deviation
The ± values represent a 95% confidence interval.

The 95% confidence interval reported for each aliquot is based on a pooled variance calculated per Snedecor and Cochran (1980) across all of the repeated aliquot analyses. The overall AP-104 mean heat capacity was calculated by averaging the heat capacities from each aliquot. The 95% confidence interval for the overall mean is based on variance across the three aliquots with 2 degrees of freedom for the Student's *t*-value.

4.3.3 Evaluation of the Heat Capacity Results

Table 4.6 shows a small to negligible temperature effect consistent with the small temperature effect between these two temperatures for water. The heat capacity of water (C_p) at 298 K is 4.180 J/g-K and at 313 K is 4.179 J/g-K; i.e., there is no change in the second decimal compared to the heat capacity of water at the two temperatures.

Comparison of the AP-104 heat capacity results with those of water at 298 K and 313 K finds the heat capacity of the sample to be less than that of water. This lower heat capacity relative to pure water is consistent with expectations since the AP-104 supernatant is 68-wt% water and 32-wt% dissolved solids, which have a much lower heat capacity than water. For example, at 298 K sodium nitrate has a C_p of 1.10 J/g-K as compared to 4.18 J/g-K for water (Barin 1989).

The heat capacities show some variability between the different sample aliquots. The variability is most likely due to slight inhomogeneity compounded by the necessity of using very small (i.e., 10-mg) aliquots for analysis.

5.0 Analytical Sample Processing

The chemical and radiochemical characterization of the AP-104 supernatant composite was performed on the contents from bottle **AP104ARG**. The very small quantity of dark precipitate in the bottle was considered part of the sample. Thorough mixing of the contents of the bottle was performed prior to withdrawing sub-samples for analysis; i.e., solids are included in analyses, except for those analyses that require filtering prior to processing/analysis (e.g., IC). ASRs 6378, 6378.01, 6378.02 and 6378.03 provided instructions to the laboratory staff to successfully complete the analytical and QC requirements defined in the test plan.

5.1 Direct Sub-Sampling

The AP-104 supernatant was sub-sampled in the SAL hot cells and then delivered to analytical workstations for various measurements including inorganic anion, hydroxide, ammonia, cyanide, mercury, total organic and inorganic carbon (TOC/TIC), ^{127}I, ^{129}I, ^{3}H, ^{14}C, and ^{99}Tc (pertechnetate). For these sub-samples, the QC samples were prepared and analyzed at the analytical workstation, as was any required sub-sample processing (e.g., digestions for mercury analysis or distillations for cyanide analysis).

5.2 Direct Sub-Sampling Followed by Ion Exchange for Dose Reduction

The AP-104 supernatant was sub-sampled and subjected to an ion exchange procedure (i.e., procedure TPR-RPP-WTP-049, *Ion Exchange for Activity Reduction*) in the SAL to reduce the sample dose levels. The resulting effluents from the ion exchange procedure were delivered to the 329 Facility analytical workstations for measurements of organic acids and chelators. Besides a process blank (PB) and laboratory control sample/blank spike (LCS/BS), additional AP-104 sample was processed through the ion exchange procedure to provide the analytical workstation with separate samples for the matrix spike (MS) and matrix spike duplicate (MSD). The appropriate batch and analytical QC samples were prepared and analyzed at the analytical workstation, as was any required sub-sample processing (e.g., derivatization for the chelators).

5.3 Acid Digestion

The AP-104 supernatant was acid digested in the SAL according to procedure PNL-ALO-128, *HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*. Aliquots of the digested sub-samples 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 spectrometry (ICP-AES), total U by kinetic phosphorescence (KPA) and the following radiochemical analyses: total alpha/beta, gamma emitters by gamma energy analysis (GEA), ^{79}Se, ^{90}Sr, ^{238}Pu, $^{239/240}$Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm.

The SAL processed 1-mL aliquots of the supernatant in triplicate. The acid digestion solutions were brought to a nominal 25-mL volume, and absolute volumes were determined based on final solution weights and densities. Along with the triplicate samples, the SAL processed a digestion PB, two LCS/BSs (one for ICP-AES and one for ICP-MS), and two MSs (one for ICP-AES and one for ICP-MS). Aliquots of the LCS/BSs, MSs, and the PB were sent with aliquots of the triplicate samples for ICP-AES or ICP-MS analyses. For radiochemical analyses, only the PB was sent with aliquots of the triplicate samples for analysis. For the radiochemical analyses (except GEA) and radionuclides by ICP-MS, post-digestion LCS/BS and MS samples were prepared in the laboratory just prior to analysis. Most radiochemical analyses required additional sample preparation (e.g., distillation, chemical separation) prior to counting; these preparations are described in Section 7.0.

5.4 Solvent Extraction for Organic Phosphates

The AP-104 supernatant was sampled and extracted in the SAL for analysis of D2EHP according to the test plan TP-RPP-WTP-047, *Identification and Quantification of D2EHP in Tank Waste*. Sub-samples consisted of triplicate aliquot samples of the supernatant (surrogate spike only) and duplicate MS samples (surrogate and D2EHP spike) adjusted to pH <2. A PB consisting of DIW (surrogate spike only) and a LCS/BS consisting of DIW spiked with D2EHP and surrogate were processed with the sample batch.

Five-mL aliquots of the samples were first extracted three times with 25-mL portions of methylene chloride and then were extracted three times with 25-mL portions of butanol. The extracts were transferred to the 329 Facility analysis workstation, where the methylene chloride extracts were concentrated to a volume <1 mL, derivatized with diazomethane/ether solution, and concentrated to a final volume of 1 mL for analysis. The analysis was performed per test plan TP-RPP-WTP-047 using gas chromatography with a flame ionization detector (GC/FID).

6.0 Analytical Results

6.1 Introduction

The inorganic, radiochemical, and organic analytical results for the AP-104 supernatant composite are provided in Tables 6.1 through 6.5. Results are reported in mCi/L or mg/L, as appropriate. For the radiochemical analyses, the nominal propagated uncertainties are provided as 1-σ, unless otherwise noted. For the inorganic and organic analyses, no uncertainties are included in the tables; the estimated uncertainty is 10-15% for results above the estimated quantitation limit (EQL) (See 6.4 Data Limitations for analyses that exceed this estimated uncertainty). Besides the triplicate sample results, the results obtained on the PBs are also reported, as appropriate.

The analyte concentrations reported in Table 6.2 and Table 6.3 include a data flag column (i.e., a data qualifier code). The data flags are consistent with the Tank Waste Information System (TWINS) and are defined below:

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 an EQL established by the lowest calibration standard adjusted for sample and analytical dilutions. In these cases, results less than the EQL are 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 EQL and above the MDL. For radiochemical data, the J flag identifies results that have a propagated error of >10%, indicating that the radionuclide result is typically within 10 times the minimum detectable activity (MDA).
B	Analyte found in associated PB above the QA Plan acceptance criteria (i.e., the analyte concentration in the blank is greater than the EQL or exceeds 5% of sample concentration).
a	The LCS percent recovery is outside the acceptance criterion. The failure of the LCS may indicate that the method is not applicable to analyte measured.
b	The MS, MSD, or post spike percent recovery is outside acceptance criteria and the spike is at a concentration greater than 25% of the analyte concentration or radionuclide activity in the sample. Failure to recover spikes typically indicates a severe sample matrix-related problem.
d	% RSD is outside the acceptance criteria and the analyte concentration is greater than the EQL or the radionuclide activity is greater than 10 times the MDA. A poor %RSD is generally associated with difficulty in subsampling and/or sample heterogeneity.
e	The serial dilution % Difference is outside the acceptance criterion. This failure generally indicates a concentration-limiting and/or sample matrix-related problem.

The term MDL used in this report is an estimated MDL. That is, the MDLs have not been determined on the AP-104 waste matrix per SW-846(6) protocol. For most inorganic and organic methods, the estimated MDLs are based on an instrument detection limit (IDL) established using reagents and/or low concentration high-purity standards as samples and evaluating instrument response near background levels. For mercury and cyanide, the MDLs are based on the MDLs established from the Regulatory Data Quality Objective (DQO) work (Patello et al. 2001) using samples from Tanks 241-AN-102 (supernatant). For radiochemical methods, the MDA is calculated per the QA Plan and is based on the background counting statistics.

The EQL is typically set at 10 times the estimated MDL, which is adjusted for dilution factors resulting from digestion or other 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, no EQL is established; however, results are flagged with a "J" when uncertainty exceeds 10%. Specific QC and QA discussions are given in Section 7.0.

6.2 General Comments on Methods

- Results for analytes not specified by the test specification are included in this report for information only, and are footnote in each table. These additional analytes are measured as part of a specific method and may or may not have adequate QC performance to validate the results.
- Total Cs concentration is calculated based on the ICP-MS ^{133}Cs result and the Cs atomic mass ratios determined by ICP-MS following high-performance ion chromatography (HPIC) to separate the Cs.
- No alpha activity was detected above the MDA from the Total Alpha analysis, which counts the total alpha activity from small sample aliquots evaporated on planchets. An estimate of the total alpha activity is made by summing the activity of the alpha emitters measured by AEA (i.e., $^{239/240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm) and is presented in Table 6.2 as "Alpha Sum".
- The tritium procedure was slightly modified to include a cation exchange and a second distillation to ensure the removal of relatively high levels of ^{90}Sr and ^{137}Cs from the samples. This procedural modification produced a clean tritium beta spectra (i.e., no detectable beta contamination).
- Fluoride was measured by two different IC methods. The fluoride results from method PNL-ALO-212 exhibited significant co-elution interferences from some organic anions (e.g., acetate and formate) and provided only a bounding upper concentration estimate (i.e., 2,100 µg/mL). Only the fluoride results from method TP-RPP-WTP-212 are included in the tables in this report (see Sections 7.5.1 and 7.5.2 for more discussion).
- There are differences in target MRQs specified in the test specification for some analytes and radionuclides depending on the method used to report the results (i.e., Radiochemistry, ICP-MS, ICP-AES, or KPA).

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6 U.S. Environmental Protection Agency (EPA). . *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, latest issue, 1998, Office of Solid Waste and Emergency Response. Washington, D.C.

6.3 Comparison of Selected Results Between Methods

- Total U results measured by KPA and ICP-MS are in agreement with a relative percent difference (RPD) of 16% for an average value of 10.1 mg/L, even with an order of magnitude difference in MDLs. The less-sensitive (by 100x) ICP-AES method gives an undetected value at the much higher MDL of 55 mg/L but is consistent with the KPA and ICP-MS results.
- ^{99}Tc^{+7} (measured by direct counting of the pertechnetate form) may be compared with the total ^{99}Tc measured by ICP-MS. When compared in units of mCi/L, the ^{99}Tc result by ICP-MS is 2.9 times higher than the +7 form. This indicates that only about 1/3 of the existing ^{99}Tc exists in the +7 oxidation state.
- Phosphate (PO_4) by IC and PO_4 as P by ICP-AES may be compared. Converting P by ICP-AES to PO_4 gives the value of 4,900 mg/L. This is in agreement with the IC value of 5,500 mg/L, resulting in an RPD of 11% with an average of 5,200 mg/L as PO_4.
- Elements measured by both ICP-MS and ICP-AES may be compared. These elements and their respective results are shown in Table 6.1. Of the eight elements measured, only B and W were measured above the ICP-AES MDL. At 3% and 12% RPD, respectively, these elements showed agreement between the two methods.

Table 6.1. Elements Measured by Both ICP-MS and ICP-AES

Element	ICP-MS Result mg/L	DF	ICP-AES Result mg/L	DF	Average mg/L	%RPD	Reasonable Agreement?
Li	0.085	U	0.83	U	NA	NA	NA
B	39	JBab	40.2		40	3	Yes
V	2.8	JY	1.4	U	NA	NA	NA
Ba	1.7	Bd	0.28	U	NA	NA	NA
Ce	0.16	J	5.5	U	NA	NA	NA
W	93.6	be	83	J	88	12	Yes
Th	0.62	J	28	U	NA	NA	NA
U	9.28		55	U	NA	NA	NA

DF: data flag. See Section 6.1 for data flag definitions. No entry in DF indicates element measured above EQL and no data qualifiers apply.
RPD: relative percent difference.
NA: not applicable

- The ^{137}Cs results may be compared between the ICP-MS method and the GEA method. Converting the GEA ^{137}Cs mCi/L to units of mg/L, gives the result of 2.18 mg/L. This value is in agreement with the ICP-MS value of 1.92 mg/L, with a %RPD of 13% and an average value of 2.05 mg/L. The two methods have comparable MDLs.
- The ICP-MS ^{239}Pu and ^{240}Pu results may be added together and compared to the AEA $^{239/240}$Pu result. The ICP-MS result, when added and the units converted, is 1.20E-3 mCi/L compared to 4.17E-4 mCi/L by AEA. The ICP-MS result is higher by ~3x. This is likely due to the fact that both ICP-MS

results have significantly high contribution from the PB, whereas the AEA PB exhibited no contamination from alpha-emitters. Therefore the AEA result should be considered more reliable.

- There is agreement in total carbon (TC) between the hot persulfate and furnace oxidation methods; i.e., results vary by less than 5%, which is within the uncertainty of the methods. For TIC, the agreement is not as good but near the acceptable range, ranging from 11%-25% RPD for the three pairs of replicate samples. For TOC the agreements are poor, but are typical for tank waste supernatants. The low TOC results for the furnace method suggests the presence of organics that may be hard to oxidize at 700°C, such as formate or oxalate. Based on the organic acid results, AP-104 supernatant contains a relatively high concentration of formate (3,700 mg/L), as well as relatively high glycolate. In addition, the very high NO_3 concentration of 111,000 mg/L may also impact the furnace results.
- TIC may be compared with the OH second inflection point. The second inflection point is primarily due to carbonate (though aluminate may also contribute), while the third inflection point is primarily due to bicarbonate. The upper bound for TIC based on these inflections is about 9,400 mg/L compared to the hot persulfate method result of about 4,200 mg/L, indicating a significant contribution from non-carbonate species. The high level of Al (12,800 mg/L) may possibly be contributing to the upper bound for TIC, while other possible contributors like weak organic acids, such as formate (3,700 mg/L), may affect the accurate determination of the inflection points.
- The ^{241}Am by AEA may be compared with ^{241}Pu/^{241}Am by ICP-MS. When converted into like units, there is agreement between the two methods, with %RPD of 1% and a mean of 5.82E-3 mCi/L. This agreement indicates that the ^{241}Pu concentration is negligible compared to the ^{241}Am concentration.
- Oxalate by IC-Inorg method (PNL-ALO-212) may be compared with oxalate by IC-Org method (TP-RPP-WTP-046); the two IC methods use different IC columns for anion determination. Though both results are flagged with a J, the two methods compare reasonably well, with RPD of 21% for a mean of 815 mg/L.
- The total beta activity may be compared with the sum of the major beta radionuclides. Total beta activity is in agreement with the sum of the ^{137}Cs activity plus twice the ^{90}Sr activity (to allow for the ^{90}Y daughter). The summed value is 94% of the total beta activity, indicating that these two isotopes account for most of the beta activity in AP-104 supernatant. Alternatively, the RPD between the two values is 6% with an average of 200 mCi/L.

6.4 Data Limitations

- Element (analyte) concentrations reported by ICP-MS are determined by comparison of a selected isotope mass response for a given element to the calibration curve generated for that element. The concentration versus response calibration curve assumes natural isotopic abundance. Elements subjected to or generated from nuclear processes may have significantly altered isotopic abundances. If the isotopic abundance of the mass used to calibrate the ICP-MS is altered in the sample matrix, the concentration reported by ICP-MS will be biased. For the most accurate analysis of elements with altered isotopic abundances, chemical separation of the element is required so that individual isotope concentrations can be quantified and summed. Except for the Cs, U, and Pu, no chemical separations were required or performed prior to the ICP-MS analysis of the AP-104 supernatant. For those elements not chemically separated, the isotopes used for calibration are ^{7}Li, ^{11}B, ^{51}V, ^{85}Rb, ^{138}Ba, ^{140}Ce, ^{182}W, and ^{232}Th. However, the ICP-MS results for Li, B, V, W, and Th are considered reliable (barring any QC failures) since the impact from any nuclear process on isotopic abundance is considered small (i.e., <10% and within the error of the analysis). High fission yields will have a moderate effect on the ^{85}Rb and ^{138}Ba; i.e., reported results may be biased low by 10% to 20%. The largest potential impact is on cerium, where the reported value could be biased low by 50% to 60%. Unfortunately, the extent to which the ^{85}Rb, ^{138}Ba, and ^{140}Ce abundance may be altered in the AP-104 supernatant is unknown, as is the actual uncertainty of the reported ICP-MS results for these elements.

- One required analytes requested in the test specification, D2EHP, could not be analyzed due to the lack of a reliable analysis method. Therefore, no results are reported in this report. Methods development is required.
- Glycolate results should be considered the upper bound concentration for glycolate, since glycolate and gluconate cannot be resolved using the IC measurement method used for the analysis. This is due to the required choice of IC analytical column that coelutes glycolate and gluconate at the same retention time; therefore it cannot resolve the two compounds. The reported average glycolate concentration is 1,600 mg/L; if the entire response is due to gluconate, the gluconate concentration would be about 4,000 mg/L. No alternate method is available for independent measurement of gluconate and glycolate. Methods development is necessary if both gluconate and glycolate are required.
- Boron was identified as both an ICP-AES and ICP-MS analyte. Since significant ICP-MS QC failures are noted for boron, the ICP-AES results should be used for boron. The ICP-MS boron recovery was poor for both the BS and MS. Also, the instrument continuing calibration verification failed. Boron continues to be problematic for the ICP-MS instrumentation used for the analysis due to drifting backgrounds and memory effects.
- For ICP-MS analysis of ^{99}Tc the uncertainty is estimated at ±30%, versus the typical 10-15% for ICP-MS analyses. Six months following the ^{99}Tc analysis, the calibration and verification standards used for the analysis were analyzed by liquid scintillation counting (LSC) and although the standards measured within acceptance criteria, the measured values for both standards were biased slightly high from the assigned standard value. To ensure that the ^{99}Tc results are bounded properly, the uncertainty has been increased to include the measured-to-assigned value differences.

6.5 AP-104 Supernatant Composite Results

Much of the sample preparation work was performed by aliquoting samples by weight and calculating the volume of the sample using the sample density. Density of the AP-104 supernatant composite was determined as part of the physical properties measurements (See Section 4.0). The analytical results for the AP-104 supernatant are presented in Table 6.2 and Table 6.3. The comparison of the supernatant results to Contract Specification 7 Envelope A is presented in Table 6.4.

Table 6.2. AP-104 Supernatant Composite – Radionuclide Results (mCi/L)

			Process Blank 1				Process Blank 2				Sample (02-1832)				Duplicate (02-1832D)				Triplicate (02-1832T)			
Analysis Method$^{(h)}$	**Prep Method**	**Radio-nuclide**	**MDA/ MDL$^{(c)}$ mCi/L**	**Result mCi/L**	**1-σ$^{(g)}$ mCi/L**	**DF**	**MDA/ MDL$^{(c)}$ mCi/L**	**Result mCi/L**	**1-σ$^{(g)}$ mCi/L**	**DF**	**MDA/ MDL$^{(c)}$ mCi/L**	**Result mCi/L**	**1-σ$^{(g)}$ mCi/L**	**DF**	**MDA/ MDL$^{(c)}$ mCi/L**	**Result mCi/L**	**1-σ$^{(g)}$ mCi/L**	**DF**	**MDA/ MDL$^{(c)}$ mCi/L**	**Result mCi/L**	**1-σ$^{(g)}$ mCi/L**	**DF**
H-3	Direct	^{3}H	2.0E-5	2.0E-5	4.6E-6	J	--	--	--	--	2.0E-5	1.98E-3	7.92E-5		2.0E-5	1.97E-3	7.88E-5		2.0E-5	2.00E-3	8.00E-5	
C-14	Direct	^{14}C	2.0E-5	2.0E-5	--	U	--	--	--	--	4.0E-5	7.40E-4	4.44E-5		4.0E-5	6.92E-4	4.15E-5		4.0E-5	7.19E-4	4.31E-5	
GEA	Acid-128	^{60}Co	2.0E-4	2.0E-4	--	U	2.0E-4	2.0E-4	--	U	2.0E-3	9.07E-3	8.16E-4		2.0E-3	8.80E-3	7.92E-4		2.0E-3	1.02E-2	8.16E-4	
Se-79	Acid-128	^{79}Se	2.5E-5	2.5E-5	--	U	2.5E-5	4.67E-5	9.26E-6		2.5E-5	9.51E-4	3.48E-5		2.5E-5	9.20E-4	3.52E-5	B	2.5E-5	8.09E-4	3.22E-5	B
Sr-90	Acid-128	^{90}Sr	2.0E-4	1.37E-3	9.59E-5		2.0E-4	1.94E-3	9.70E-5		2.0E-1	2.10E+0	1.05E-1		2.0E-1	1.73E+0	1.04E-1		2.0E-1	2.03E+0	1.02E-1	
ICP-MS	Acid-128	^{99}Tc$^{(a,i)}$	3.9E-5	6.39E-4	--		3.9E-5	4.5E-4	--		2.0E-4	1.41E-1	--		2.0E-4	1.48E-1	--		2.0E-4	1.42E-1	--	
Tc-99	Direct	^{99}Tc^{+7}	5.0E-5	8.97E-4	4.49E-5		5.0E-5	5.0E-5	--	U	2.0E-4	5.14E-2	1.54E-3		2.0E-4	4.99E-2	1.50E-3		2.0E-4	4.97E-2	1.49E-3	
GEA	Acid-128	^{125}Sb	4.0E-4	4.0E-4	--	U	4.0E-4	4.0E-4	--	U	2.0E-1	2.0E-1	--	U	2.0E-1	2.0E-1	--	U	2.0E-1	2.0E-1	--	U
GEA	Acid-128	^{126}Sn	2.0E-4	2.0E-4	--	U	2.0E-4	2.0E-4	--	U	1.0E-1	1.0E-1	--	U	9.0E-2	9.0E-2	--	U	9.0E-2	9.0E-2	--	U
ICP-MS	Direct	^{129}I$^{(a)}$	1.4E-5	1.4E-5		U	--	--	--	--	1.5E-5	2.52E-4	--		1.5E-5	2.72E-4	--		1.2E-5	2.48E-4	--	
ICP-MS	Acid-128	^{135}Cs$^{(d)}$	9.8E-7	9.8E-7	--	U	9.8E-7	9.8E-7	--	U	2.9E-5	2.00E-3	--		2.7E-5	2.13E-3	--		2.5E-5	2.09E-3	--	
GEA	Acid-128	^{137}Cs	2.0E-4	5.2E-4	7.3E-5	J	2.0E-4	1.06E-3	8.48E-5		4.0E-2	1.92E+2	5.76E+0		4.0E-2	1.89E+2	5.67E+0		4.0E-2	1.90E+2	5.70E+0	
ICP-MS	Acid-128	^{137}Cs$^{(d)}$	7.1E-2	7.1E-2	--	U	7.1E-2	7.1E-2	--	U	2.1E+0	1.62E+2	--		2.0E+0	1.72E+2	--		1.8E+0	1.68E+2	--	
GEA	Acid-128	^{154}Eu	4.0E-4	4.0E-4	--	U	4.0E-4	4.0E-4	--	U	7.0E-3	7.0E-3	--	U	8.0E-3	8.0E-3	--	U	7.0E-3	7.0E-3	--	U
GEA	Acid-128	^{155}Eu	4.0E-4	4.0E-4	--	U	4.0E-4	4.0E-4	--	U	2.0E-1	2.0E-1	--	U	2.0E-1	2.0E-1	--	U	1.0E-1	1.0E-1	--	U
GEA	Acid-128	^{231}Pa	5.0E-3	5.0E-3	--	U	5.0E-3	5.0E-3	--	U	2.0E+0	2.0E+0	--	U	2.0E+0	2.0E+0	--	U	2.0E+0	2.0E+0	--	U
ICP-MS	Acid-128	^{233}U	1.9E-6	1.9E-6	--	U	1.9E-6	1.9E-6	--	U	2.0E-6	5.3E-6	--	J	1.9E-6	4.9E-6	--	J	1.7E-6	6.5E-6	--	J
ICP-MS	Acid-128	^{234}U	3.2E-7	3.6E-7	--	J	3.2E-7	3.2E-7	--	U	3.5E-7	4.7E-6	--	B	3.2E-7	4.2E-6	--	B	2.9E-7	4.5E-6	--	B
ICP-MS	Acid-128	^{235}U	7.5E-10	7.5E-10	--	U	7.5E-10	7.5E-10	--	U	8.1E-10	1.80E-7	--		7.5E-10	1.81E-7	--		6.9E-10	1.81E-7	--	
AEA	Acid-128	^{236}Pu	1.0E-6	1.0E-6	--	U	6.0E-7	6.0E-7	--	U	8.0E-6	8.0E-6	--	U	1.0E-5	1.0E-5	--	U	8.0E-6	8.0E-6	--	U
ICP-MS	Acid-128	^{236}U	6.4E-9	6.4E-9	--	U	6.4E-9	6.4E-9	--	U	6.9E-9	3.08E-7	--		6.3E-9	3.25E-7	--		5.9E-9	3.25E-7	--	
ICP-MS	Acid-128	^{237}Np$^{(j)}$	3.0E-7	1.2E-6	--	J	3.0E-7	1.7E-6	--	J	3.3E-7	4.00E-6	--	B	3.0E-7	4.01E-6	--	B	2.8E-7	3.68E-6	--	B
AEA	Acid-128	^{238}Pu	2.0E-6	2.0E-6	--	U	2.0E-6	2.5E-6	5.8E-7	J	8.0E-6	5.7E-5	7.4E-6	J	9.0E-6	5.3E-5	7.4E-6	J	2.0E-5	5.7E-5	7.3E-6	J
ICP-MS	Acid-128	^{238}U	1.8E-8	1.8E-8	--	U	1.8E-8	1.8E-8	--	U	2.0E-8	3.13E-6	--		1.8E-8	3.13E-6	--		1.7E-08	3.13E-6	--	
AEA	Acid-128	$^{239/240}$Pu	1.0E-6	1.8E-6	4.6E-7	J	8.0E-7	2.5E-6	5.0E-7	J	8.0E-6	4.18E-4	2.09E-5		9.0E-6	4.14E-4	2.07E-5		8.0E-6	4.20E-4	2.10E-5	
ICP-MS	Acid-128	^{239}Pu$^{(j)}$	2.6E-5	1.55E-3	--		2.6E-5	1.13E-3	--		2.8E-5	1.27E-3	--	B	2.6E-5	1.03E-3	--	B	2.4E-5	8.39E-4	--	B

Table 6.2. AP-104 Supernatant Composite – Radionuclide Results (mCi/L) (cont.)

			Process Blank 1				Process Blank 2				Sample (02-1832)				Duplicate (02-1832D)				Triplicate (02-1832T)			
Analysis Method(h)	Prep Method	Radio-nuclide	MDA/ MDL(c) mCi/L	Result mCi/L	1-σ(g) mCi/L	DF	MDA/ MDL(c) mCi/L	Result mCi/L	1-σ(g) mCi/L	DF	MDA/ MDL(c) mCi/L	Result mCi/L	1-σ(g) mCi/L	DF	MDA/ MDL(c) mCi/L	Result mCi/L	1-σ(g) mCi/L	DF	MDA/ MDL(c) mCi/L	Result mCi/L	1-σ(g) mCi/L	DF
ICP-MS	Acid-128	^{240}Pu(j)	1.1E-5	1.26E-4	--		1.1E-05	8.9E-5	--	J	1.2E-5	1.69E-4	--	B	1.1E-5	1.51E-4	--	B	1.0E-5	1.34E-4	--	B
AEA	Acid-128	^{241}Am	9.0E-7	8.91E-6	8.02E-7		9.0E-7	1.57E-5	9.42E-7		8.0E-6	5.84E-3	1.17E-4		2.0E-5	5.79E-3	1.16E-4		1.0E-5	5.74E-3	1.15E-4	
ICP-MS	Acid-128	^{241}Pu/^{241}Am(e)	2.1E-4	3.3E-4	--	J	2.1E-4	4.6E-4	--	J	2.3E-4	5.76E-3	--	B	2.1E-4	5.65E-3	--	B	2.0E-4	6.13E-3	--	B
AEA	Acid-128	^{242}Cm	4.0E-7	4.0E-7	--	U	4.0E-7	4.0E-7	--	U	5.0E-6	1.3E-5	3.1E-6	J	5.0E-6	1.2E-5	2.8E-6	J	5.0E-6	7.1E-6	2.3E-6	J
ICP-MS	Acid-128	^{242}Pu(b)	2.6E-7	2.6E-7	--	U	2.6E-7	2.6E-7	--	U	2.8E-7	2.8E-7	--	U	2.5E-7	2.5E-7	--	U	2.4E-7	2.4E-7	--	U
AEA	Acid-128	$^{243/244}$Cm	7.0E-7	5.9E-6	6.5E-7	J	7.0E-7	1.07E-5	8.56E-7		7.0E-6	9.63E-4	2.89E-5	d	1.0E-5	1.07E-3	3.21E-5	d	9.0E-6	7.34E-4	2.20E-5	d
--	--	Alpha Sum(f)	--	2.00E-5	1.40E-6	--	--	3.24E-5	1.10E-8	--	--	7.30E-3	1.21E-6	--	--	7.35E-3	1.20E-6	--	--	6.97E-3	1.17E-6	--
Alpha	Acid-128	Total Alpha	6.0E-5	6.0E-5	--	U	5.0E-5	5.0E-5	--	U	5.0E-2	5.0E-2	--	U	6.0E-2	6.0E-2	--	U	6.0E-2	6.0E-2	--	U
Beta	Acid-128	Total Beta	2.0E-4	2.01E-2	6.03E-4		2.0E-4	1.10E-2	4.40E-4		5.0E-1	2.07E+2	6.21E+0		4.0E-1	2.11E+2	6.33E+0		5.0E-1	1.99E+2	5.97E+0	

MDL: method detection limit (with all processing factors applied).

MDA: minimum detectable activity (used with all radiochemical analysis results).

DF: data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide measured above EQL and no data qualifiers apply.

--: not applicable

(a) Results from a re-preparation and analysis of the samples; all other results from initial preparation and analysis. Reanalysis required due to QC/standards failures.

(b) Opportunistic analyte; analyte not included in test specification.

(c) MDL used for all ICP-MS results; MDA used for all radiochemistry results.

(d) ^{135}Cs and ^{137}Cs results calculated from ^{133}Cs results and Cs isotopic results obtained from HPIC/ICP-MS analysis.

(e) Specific activity for ^{241}Am used for converting ICP-MS ^{241}Pu/^{241}Am results from mg/L to mCi/L.

(f) Alpha Sum: Summation of AEA results only ($^{239/240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm).

(g) 1-sigma: Nominal propagated uncertainty calculated for radiochemistry results includes preparation and counting error.

(h) ICP-MS mCi/L results calculated from mg/L results using specific activity. See Table 6.3 for ICP-MS mg/L results.

(i) Uncertainty estimated at ±30%; see Section 6.4 for further details.

(j) Same certified source standard used to prepare calibration and verification standards for ICP-MS. Calibration and verification standards prepared approximately 1 year apart; prepared standards verified by independent analysis (i.e., LSC, AEA, or GEA).

Nominal decay correction dates:
GEA (March 14, 2002); AEA – Pu, Am, Cm (year 2002); ^{90}Sr (March 20, 2002); ^{99}Tc (January 23, 2002); ^{79}Se (March 20, 2002); ^{3}H (April 01, 2002); and ^{14}C (June 19, 2002).
ICP-MS: ^{99}Tc (December 17, 2002); Cs isotopes (October 14, 2002); U isotopes, Pu isotopes, and ^{237}Np (year 2002); ^{129}I (year 2003).

Table 6.3. AP-104 Supernatant Composite – Radionuclide/Analyte Results (mg/L)

Analysis Method(j,m)	Prep Method	Radionuclide/ Analyte(l)	Process Blank 1			Process Blank 2			Sample (02-1832)			Duplicate (02-1832D)			Triplicate (02-1832T)		
			MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF
ICP-MS	Acid-128	^{99}Tc(a,n)	2.3E-3	3.76E-2		2.3E-3	2.64E-2		1.2E-2	8.31E+0		1.2E-2	8.72E+0		1.2E-2	8.37E+0	
ICP-MS	Direct	^{127}I(a)	2.2E-1	3.3E-1	J	--	--	--	2.4E-1	5.66E+0	B	2.4E-1	5.85E+0	B	2.0E-1	5.51E+0	B
ICP-MS	Direct	^{129}I(a)	7.7E-2	7.7E-2	U	--	--	--	8.3E-2	1.40E+0		8.4E-2	1.51E+0		6.7E-2	1.38E+0	
ICP-MS	Acid-128	^{133}Cs(a)	2.4E-3	1.6E-2	J	2.4E-3	2.1E-2	J	2.5E-3	5.38E+0		2.5E-3	5.73E+0		2.5E-3	5.63E+0	
ICP-MS	Acid-128	^{135}Cs(i)	8.2E-4	8.2E-4	U	8.2E-4	8.2E-4	U	2.5E-2	1.67E+0		2.3E-2	1.78E+0		2.1E-2	1.74E+0	
ICP-MS	Acid-128	^{137}Cs(i)	8.2E-4	8.2E-4	U	8.2E-4	8.2E-4	U	2.5E-2	1.87E+0		2.3E-2	1.98E+0		2.1E-2	1.93E+0	
ICP-MS	Acid-128	^{233}U	1.9E-4	1.9E-4	U	1.9E-4	1.9E-4	U	2.1E-4	5.4E-4	J	1.9E-4	5.1E-4	J	1.8E-4	6.7E-4	J
ICP-MS	Acid-128	^{234}U	5.1E-5	5.8E-5	J	5.1E-5	5.1E-5	U	5.6E-5	7.58E-4	B	5.1E-5	6.71E-4	B	4.8E-5	7.28E-4	B
ICP-MS	Acid-128	^{235}U	3.4E-4	3.4E-4	U	3.4E-4	3.4E-4	U	3.7E-4	8.18E-2		3.4E-4	8.20E-2		3.2E-4	8.22E-2	
ICP-MS	Acid-128	^{236}U	9.8E-5	9.8E-5	U	9.8E-5	9.8E-5	U	1.1E-4	4.75E-3	e	9.8E-5	5.01E-3	e	9.1E-5	4.99E-3	e
ICP-MS	Acid-128	^{237}Np(o)	4.3E-4	1.7E-3	J	4.3E-4	2.4E-3	J	4.6E-4	5.64E-3	B	4.3E-4	5.65E-3	B	4.0E-4	5.19E-3	B
ICP-MS	Acid-128	^{238}U	5.4E-2	5.4E-2	U	5.4E-2	5.4E-2	U	5.9E-2	9.20E+0	a	5.4E-2	9.19E+0	a	5.0E-2	9.19E+0	a
ICP-MS	Acid-128	^{239}Pu(o)	4.2E-4	2.50E-2		4.2E-4	1.83E-2		4.6E-4	2.04E-2	Bd	4.2E-4	1.67E-2	Bd	3.9E-4	1.35E-2	Bd
ICP-MS	Acid-128	^{240}Pu(o)	4.7E-5	5.49E-4		4.7E-5	3.9E-4	J	5.1E-5	7.36E-4	B	4.7E-5	6.55E-4	B	4.3E-5	5.83E-4	B
ICP-MS	Acid-128	^{241}Pu/^{241}Am	6.3E-5	9.8E-5	J	6.3E-5	1.4E-4	J	6.8E-5	1.69E-3	B	6.3E-5	1.66E-3	B	5.8E-5	1.80E-3	B
ICP-MS	Acid-128	^{242}Pu(b)	6.5E-5	6.5E-5	U	6.5E-5	6.5E-5	U	7.1E-5	7.1E-5	U	6.5E-5	6.5E-5	U	6.0E-5	6.0E-5	U
IC-Org	Direct	Acetate	110	110	U	--	--	--	110	900	J	110	900	J	110	800	J
ISE	Direct	Ammonia(d)	20	20	U	--	--	--	8.0	361		8.0	376		8.0	468	
ICP-AES	Acid-128	Ag(b)	0.63	0.63	U	0.65	0.65	U	0.75	0.75	U	0.69	0.69	U	0.64	0.64	U
ICP-AES	Acid-128	Al	1.5	5.4	J	1.6	6.4	J	1.8	12,600		1.6	12,900		1.5	12,800	
ICP-AES	Acid-128	As(b)	6.3	6.3	U	6.5	6.5	U	7.5	7.5	U	6.9	6.9	U	6.4	6.4	U
ICP-AES	Acid-128	B(a)	1.3	1.3	U	1.3	1.3	U	1.3	38.6		1.3	41.6		1.3	40.4	
ICP-MS	Acid-128	B(a)	4.7	10	J	4.8	11	J	5	39	JBab	4.9	40	JBab	4.8	39	JBab
ICP-AES	Acid-128	Ba	0.25	0.25	U	0.26	0.26	U	0.30	0.30	U	0.27	0.27	U	0.26	0.26	U
ICP-MS	Acid-128	Ba(a)	0.051	1.94		0.051	8.40		0.053	1.16	Bd	0.052	1.90	Bd	0.052	2.17	Bd
ICP-AES	Acid-128	Be(b)	0.25	0.25	U	0.26	0.26	U	0.30	0.30	U	0.27	0.27	U	0.26	0.26	U
ICP-AES	Acid-128	Bi(b)	2.5	2.5	U	2.6	2.6	U	3.0	3.0	U	2.7	2.7	U	2.6	2.6	U
IC-Inorg	Direct	Br(d)	0.13	0.13	U	--	--	--	130	130	U	130	130	U	130	130	U

Table 6.3. AP-104 Supernatant Composite – Radionuclide/Analyte Results (mg/L) (cont.)

			Process Blank 1			Process Blank 2			Sample (02-1832)			Duplicate (02-1832D)			Triplicate (02-1832T)		
Analysis Method[j,m]	Prep Method	Radionuclide/ Analyte[l]	MDL mg/L	Result[k] mg/L	DF	MDL mg/L	Result[k] mg/L	DF	MDL mg/L	Result[k] mg/L	DF	MDL mg/L	Result[k] mg/L	DF	MDL mg/L	Result[k] mg/L	DF
C (Furn)	Direct	C as TC	--	--	--	--	--	--	14	8,100		14	8,200		14	8,100	
C (HP)	Direct	C as TC	--	--	--	--	--	--	--	8,470		--	8,540		--	8,340	
C (Furn)	Direct	C as TIC	--	--	--	--	--	--	--	5,400		--	5,400		--	4,700	
C (HP)	Direct	C as TIC	--	--	--	--	--	--	30	4,190		30	4,300		30	4,150	
C (Furn)	Direct	C as TOC	--	--	--	--	--	--	400	2,700	J	400	2,800	J	400	3,400	J
C (HP)	Direct	C as TOC	--	--	--	--	--	--	70	4,280		70	4,240		70	4,190	
ICP-AES	Acid-128	Ca	6.3	6.3	U	6.5	6.5	U	7.5	72	J	6.9	74.3		6.4	70.7	
ICP-AES	Acid-128	Cd	0.38	0.38	U	0.39	0.39	U	0.45	1.8	J	0.41	1.8	J	0.38	1.8	J
ICP-AES	Acid-128	Ce	5.1	5.1	U	5.2	5.2	U	6.0	6.0	U	5.5	5.5	U	5.1	5.1	U
ICP-MS	Acid-128	Ce	0.0036	0.0036	U	0.0036	0.0036	U	0.11	0.11	U	0.099	0.16	J	0.092	0.15	J
IC-Org	Direct	Citrate	460	460	U	--	--	--	460	820	J	460	860	J	460	900	J
GC/FID[g]	Derivatize	Citric acid	5.8	5.8	U	--	--	--	5.8	460		5.8	450		5.8	350	
IC-Inorg	Direct	Cl[d]	0.13	0.13	U	--	--	--	130	5,500		130	5,490		130	5,340	
Colorimetry	Distill-287	CN	0.24	0.24	U	--	--	--	0.24	45.1		0.24	45.5		0.24	46.3	
ICP-AES	Acid-128	Co[b]	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U
ICP-AES	Acid-128	Cr	0.51	0.51	U	0.52	0.52	U	0.60	472		0.55	478		0.51	475	
ICP-AES	Acid-128	Cu[b]	0.63	0.63	U	0.65	0.65	U	0.75	0.75	U	0.69	0.69	U	0.64	0.64	U
GC/FID	Derivatize	D2EHP[e]	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ICP-AES	Acid-128	Dy[b]	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U
GC/FID[g]	Derivatize	ED3A	4.9	4.9	U	--	--	--	4.9	300		4.9	360		4.9	270	
GC/FID[g]	Derivatize	EDTA	4.9	4.9	U	--	--	--	4.9	500	b	4.9	550	b	4.9	660	b
ICP-AES	Acid-128	Eu[b]	2.5	2.5	U	2.6	2.6	U	3.0	3.0	U	2.7	2.7	U	2.6	2.6	U
IC-F	Direct	F[c]	2.0	2.0	U	--	--	--	2.0	164		2.0	161		2.0	161	
ICP-AES	Acid-128	Fe[a]	0.65	0.76	J	0.65	0.65	U	0.66	10.1	B	0.65	8.75	B	0.65	8.12	B
IC-Org	Direct	Formate	180	180	U	--	--	--	180	3,900		180	3,600		180	3,700	
IC-Org	Direct	Gluconate[f]	320	320	U	--	--	--	320	4,000		320	4,300		320	4,000	
IC-Org	Direct	Glycolate[f]	130	130	U	--	--	--	130	1,600		130	1,700		130	1,600	
GC/FID[g]	Derivatize	HEDTA	8.8	8.8	U	--	--	--	8.8	8.8	Uab	8.8	8.8	Uab	8.8	8.8	Uab

Table 6.3. AP-104 Supernatant Composite – Radionuclide/Analyte Results (mg/L) (cont.)

			Process Blank 1			Process Blank 2			Sample (02-1832)			Duplicate (02-1832D)			Triplicate (02-1832T)		
Analysis Method(j,m)	Prep Method	Radionuclide/ Analyte(l)	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF	MDL mg/L	Result(k) mg/L	DF
CVAA	Acid-131	Hg	0.00007	0.00055	J	--	--	--	0.00007	0.00138	B	0.00007	0.00132	B	0.00007	0.00116	B
ICP-AES	Acid-128	K(a)	52	52	U	52	52	U	53	1,800		52	1,930		52	1,870	
ICP-AES	Acid-128	La	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U
ICP-AES	Acid-128	Li	0.76	0.76	U	0.78	0.78	U	0.90	0.90	U	0.82	0.82	U	0.77	0.77	U
ICP-MS	Acid-128	Li	0.0031	0.0031	U	0.0031	0.0031	U	0.092	0.092	U	0.085	0.085	U	0.079	0.079	U
ICP-AES	Acid-128	Mg	2.5	2.5	U	2.6	2.6	U	3.0	3.0	U	2.7	2.7	U	2.6	2.6	U
ICP-AES	Acid-128	Mn(b)	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U
ICP-AES	Acid-128	Mo(b)	1.3	1.3	U	1.3	1.3	U	1.5	57.4		1.4	58.2		1.3	58.2	
ICP-AES	Acid-128	Na	3.8	67.8		3.9	67.2		22	131,000		21	132,000		19	136,000	
ICP-AES	Acid-128	Nd(b)	2.5	2.5	U	2.6	2.6	U	3.0	3.0	U	2.7	2.7	U	2.6	2.6	U
ICP-AES	Acid-128	Ni	0.76	0.76	U	0.78	0.78	U	0.9	41.1		0.82	40.1		0.77	40.2	
GC/FID(g)	Derivatize	NIDA/IDA	11	11	U	--	--	--	11	880	b	11	900	b	11	870	b
IC-Inorg	Direct	NO_2(d)	0.25	0.25	U	--	--	--	1,300	69,600		1,300	69,400		1,300	68,700	
IC-Inorg	Direct	NO_3(d)	0.25	0.25	U	--	--	--	1,300	111,000		1,300	111,000		1,300	110,000	
GC/FID(g)	Derivatize	NTA	5.6	5.6	U	--	--	--	5.6	230		5.6	240		5.6	270	
Titration	Direct	OH	170	170	U	--	--	--	170	23,100		170	21,600		170	22,200	
IC-Inorg	Direct	Oxalate(d)	0.25	0.25	U	--	--	--	100	1,040		100	820	J	100	850	J
IC-Org	Direct	Oxalate	230	230	U	--	--	--	230	740	J	230	710	J	230	740	J
ICP-AES	Acid-128	P	2.5	2.5	U	2.6	2.6	U	3.0	1,570		2.7	1,600		2.6	1,600	
ICP-AES	Acid-128	Pb	2.5	2.5	U	2.6	2.6	U	3.0	9.2	J	2.7	7.5	J	2.6	8.3	J
ICP-AES	Acid-128	Pd(b)	19	19	U	20	20	U	22	22	U	21	21	U	19	19	U
IC-Inorg	Direct	PO_4(d)	0.25	0.25	U	--	--	--	100	5,520		100	5,550		100	5,480	
ICP-MS	Acid-128	Rb(a)	0.035	0.050	J	0.035	0.053	J	0.037	5.35		0.036	5.69		0.036	5.65	
ICP-AES	Acid-128	Rh(b)	7.6	7.6	U	7.8	7.8	U	9.0	9.0	U	8.2	8.2	U	7.7	7.7	U
ICP-AES	Acid-128	Ru(b)	28	28	U	29	29	U	33	33	U	30	30	U	28	28	U
ICP-AES	Acid-128	Sb(b)	13	13	U	13	13	U	15	15	U	14	14	U	13	13	U
ICP-AES	Acid-128	Se(b)	6.3	6.3	U	6.5	6.5	U	7.5	7.5	U	6.9	6.9	U	6.4	6.4	U
ICP-AES	Acid-128	Si(a,b)	13	13	U	13	13	U	13	147		13	131		13	120	J

Table 6.3. AP-104 Supernatant Composite – Radionuclide/Analyte Results (mg/L) (cont.)

			Process Blank 1			Process Blank 2			Sample (02-1832)			Duplicate (02-1832D)			Triplicate (02-1832T)		
Analysis Method(j,m)	**Prep Method**	**Radionuclide/ Analyte(l)**	**MDL mg/L**	**Result(k) mg/L**	**DF**	**MDL mg/L**	**Result(k) mg/L**	**DF**	**MDL mg/L**	**Result(k) mg/L**	**DF**	**MDL mg/L**	**Result(k) mg/L**	**DF**	**MDL mg/L**	**Result(k) mg/L**	**DF**
ICP-AES	Acid-128	Sn(b)	38	38	U	39	39	U	45	45	U	41	41	U	38	38	U
IC-Inorg	Direct	SO_4(d)	0.25	0.25	U	--	--	--	100	3,130		100	3,110		100	3,070	
ICP-AES	Acid-128	Sr(b)	0.38	0.38	U	0.39	0.39	U	0.45	0.45	U	0.41	0.41	U	0.38	0.38	U
GC/FID(g)	Derivatize	Succinic acid	6.1	18	J	--	--	--	6.1	91.0	B	6.1	92	B	6.1	90	B
ICP-AES	Acid-128	Te(b)	38	38	U	39	39	U	45	45	U	41	41	U	38	38	U
ICP-AES	Acid-128	Th	25	25	U	26	26	U	30	30	U	27	27	U	26	26	U
ICP-MS	Acid-128	Th	0.013	0.020	J	0.013	0.023	J	0.39	0.61	J	0.36	0.65	J	0.33	0.60	J
ICP-AES	Acid-128	Ti(b)	0.63	0.63	U	0.65	0.65	U	0.75	0.75	U	0.69	0.69	U	0.64	0.64	U
ICP-AES	Acid-128	Tl(b)	13	13	U	13	13	U	15	15	U	14	14	U	13	13	U
ICP-AES	Acid-128	U	51	51	U	52	52	U	60	60	U	55	55	U	51	51	U
ICP-MS	Acid-128	U(h)	--	--	--	--	--	--	--	9.28	--	--	9.28	--	--	9.28	--
KPA	Acid-128	U	0.0060	0.021	J	0.0060	0.031	J	0.60	10.9		0.60	11.0		0.60	10.7	
ICP-AES	Acid-128	V	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U
ICP-MS	Acid-128	V	0.010	0.072	J	0.010	0.082	J	0.31	3.33	d	0.28	2.6	Jd	0.26	2.5	Jd
ICP-AES	Acid-128	W	51	51	U	52	52	U	60	82	J	55	84	J	51	83	J
ICP-MS	Acid-128	W	0.0084	0.021	J	0.0084	0.011	J	0.25	93.3	be	0.23	99.5	be	0.21	88.0	be
ICP-AES	Acid-128	Y(b)	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U
ICP-AES	Acid-128	Zn(b)	1.3	1.3	U	1.3	1.4	J	1.5	1.5	U	1.4	1.4	U	1.3	1.4	JB
ICP-AES	Acid-128	Zr(b)	1.3	1.3	U	1.3	1.3	U	1.5	1.5	U	1.4	1.4	U	1.3	1.3	U

MDL: method detection limit (with all processing factors applied).

DF: data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide/analyte measured above EQL and no data qualifiers apply.

--: not applicable.

D2EHP: bis-(2-ethylhexyl) phosphoric acid; CAS 298-07-7.

EDTA: ethylenediaminetetraacetic acid; CAS 60-00-4.

ED3A: ethylenediaminetriacetic acid; CAS – none available.

HEDTA: N-(2-hydroxyelthyl) ethylenediaminetriacetic acid; CAS 150-39-0.

NIDA/IDA: nitrosoiminodiacetic acid/iminodiacetic acid; CAS 142-73-4 (IDA).

NTA: nitrilotriacetic acid; CAS 139-73-4.

Table 6.3. AP-104 Supernatant Composite – Radionuclide/Analyte Results (mg/L) (cont.)

(a) Results from a re-preparation and analysis of the samples; all other results from initial preparation and analysis. Reanalysis required due to QC/standards failures.

(b) Opportunistic analyte; analyte not included in test specification.

(c) Fluoride analyzed by two methods; initial IC method exhibited significant interference and produced a maximum bounding fluoride concentration of 2,100 µg/mL.

(d) IC and ammonia MDLs are based on the lowest calibration standard adjusted for sample dilution; equivalent to SW-846 EQL definition.

(e) D2EHP was not measured due to lack of reliable method.

(f) Glycolate and gluconate results should be considered the upper bound concentration, since glycolate and gluconate are not resolved by the IC measurement method used for the analysis. IC system calibrated using glycolate; gluconate estimate based on gluconate-to-glycolate response factor. Each result assumes 100% of response due to each analyte. Methods development required if both analytes are required.

(g) Adipic acid used as surrogate: Surrogate recovery for PB, Sample, Duplicate, and Triplicate were 73%, 98%, 100%, and 98%, respectively.

(h) U calculated from sum of all U isotopes measured by ICP-MS.

(i) ^{135}Cs and ^{137}Cs results calculated from ^{133}Cs results and Cs isotopic results obtained from HPIC/ICP-MS analysis.

(j) ICP-MS radionuclide results also provided in mCi/L based on specific activity (See Table 6.2).

(k) Typical analysis precision/accuracy better than ±15% for results >10xMDL (i.e., for results without a U or J flag and free of blank contamination).

(l) Radionuclide data presented in scientific notation due to wide range of results.

(m) ICP-MS Analyses: See Section 6.4. Unless separated prior to analysis, analytes reported as elements may be biased due to altered isotopic distribution. Only Cs, U, and Pu separated prior to analysis.

(n) Uncertainty estimated at ±30%; see Section 6.4 for further details.

(o) Same certified source standard used to prepare calibration and verification standards for ICP-MS. Calibration and verification standards prepared approximately 1 year apart; prepared standards verified by independent analysis (i.e., LSC, AEA, or GEA).

6.6 Comparison of Results to Specification 7 Envelope A Criteria

Contract Specification 7 Envelope A defines limits for several analytes relative to sodium concentration (moles analyte per mole Na or Bq analyte per mole Na). Table 6.4 presents the Contract Specification 7 ratio limits and compares them to the measured AP-104 supernatant ratios. For all analytes, the mole or Bq analyte to moles Na ratio did not exceed the limits defined in the specification. However, ^{60}Co is at 98% of the limit. At an average of 9.36E-3 mCi/L, the measured ^{60}Co activity is only about five times the MDA (2.0E-3 mCi/L) and has a high uncertainty (8% RSD). At 98% of the limit and an RSD of 8%, the true ^{60}Co activity may exceed the Contract Specification 7 limit. However, with only about a 5-year half-life, ^{60}Co is expected to decay too well below the specification limit prior to actual waste processing.

Table 6.4. AP-104 Supernatant Composite Compared to Specification 7 Envelope A

Method	Prep	Analyte	MRQ mg/L	MDL mg/L	Average mg/L	DF	Average Moles	Average M/M Na	Table TS-7.1 M/M Na	% of Limit	Meet Spec7
ICP-AES	Acid-128	Al	75	1.7	12,800		4.74E-1	8.20E-2	2.5E-1	33	Yes
ICP-AES	Acid-128	Ba	2.3	0.28	0.28	U	< 2.0E-6	< 3.5E-7	1.0E-4	< 0.4	Yes
ICP-AES	Acid-128	Ca	150	6.9	72		1.80E-3	3.12E-4	4.0E-2	0.8	Yes
ICP-AES	Acid-128	Cd	75	0.41	1.8	J	1.60E-5	2.77E-6	4.0E-3	0.07	Yes
ICP-AES	Acid-128	Cr	15	0.55	475		9.14E-3	1.58E-3	6.9E-3	23	Yes
ICP-AES	Acid-128	Fe(a)	150	0.70	8.99	B	1.61E-4	2.78E-5	1.0E-2	0.3	Yes
ICP-AES	Acid-128	K(a)	75	52	1,870		4.78E-2	8.27E-3	1.8E-1	5	Yes
ICP-AES	Acid-128	La	35	1.4	1.4	U	< 1.0E-5	< 1.7E-6	8.3E-5	< 2	Yes
ICP-AES	Acid-128	Na	*75*	*19*	*133,000*		*5.79E+0*	*1.00E+0*	--	--	--
ICP-AES	Acid-128	Ni	30	0.83	41		6.90E-4	1.19E-4	3.0E-3	4	Yes
ICP-AES	Acid-128	Pb	300	2.8	8.3	J	4.01E-5	6.92E-6	6.8E-4	1	Yes
ICP-AES*	Acid-128	U	600	55	55	U	< 2.3E-4	< 4.0E-5	1.2E-3	< 3	Yes
KPA	Acid-128	U	780	0.60	10.9		4.58E-5	7.92E-6	1.2E-3	0.7	Yes
ICP-MS	Acid-128	U	--	0.054	9.28		3.90E-5	6.74E-6	1.2E-3	0.6	Yes
IC-F	Direct	F(b)	150	2.0	162		8.53E-3	1.47E-3	9.1E-2	2	Yes
IC-Inorg	Direct	Cl	300	130	5,440		1.53E-1	2.65E-2	3.7E-2	72	Yes
IC-Inorg	Direct	NO_2	500	1,300	69,200		1.50E+0	2.60E-1	3.8E-1	68	Yes
IC-Inorg	Direct	NO_3	500	1,300	111,000		1.79E+0	3.09E-1	8.0E-1	39	Yes
IC-Inorg	Direct	PO_4	1,500(c)	100	5,520		5.81E-2	1.00E-2	3.8E-2	26	Yes
ICP-AES	Acid-128	P as PO_4	1,500(c)	8.6(e)	4,910(e)		5.17E-2	8.94E-3	3.8E-2	24	Yes
IC-Inorg	Direct	SO_4	1,500(d)	100	3,100		3.23E-2	5.58E-3	1.0E-2	56	Yes
CVAA	Acid-131	Hg	1.5	0.00007	0.00129	B	6.43E-9	1.11E-9	1.4E-5	0.01	Yes
C (Furn)	Direct	C as TIC	150	(f)	5,170		4.31E-1	7.45E-2	3.0E-1	25	Yes
C (HP)	Direct	C as TIC	150	70	4,210		3.51E-1	6.06E-2	3.0E-1	20	Yes
C (Furn)	Direct	C as TOC	1,500	400	3,000	J	2.50E-1	4.32E-2	5.0E-1	9	Yes
C (HP)	Direct	C as TOC	1,500	70	4,240		3.53E-1	6.11E-2	5.0E-1	12	Yes

Table 6.4. AP-104 Supernatant Composite Compared to Specification 7 Envelope A (cont.)

Method	Prep	Radio-nuclide	MRQ mCi/L	MDA mCi/L	Average mCi/L	DF	Average Bq/L	Average Bq/M Na	Table TS-7.2 Bq/M Na	% of Limit	Meet Spec7
GEA	Acid-128	^{60}Co	2.1E-3	2.0E-3	9.36E-3		3.46E+5	5.98E+4	6.1E+4	98	Yes
Sr-90	Acid-128	^{90}Sr	1.5E-1	2.0E-1	1.95E+0		7.23E+7	1.25E+7	4.4E+7	28	Yes
ICP-MS	Acid-128	^{99}Tc(a)	1.5E-3	2.0E-4	1.44E-1		5.32E+6	9.20E+5	7.1E+6	13	Yes
GEA	Acid-128	^{137}Cs	9.0E+0	4.0E-2	1.90E+2		7.04E+9	1.22E+9	4.3E+9	28	Yes
GEA	Acid-128	^{154}Eu	2.0E-3	7.0E-3	7.0E-3	U	<2.7E+5	<4.7E+4	1.2E+6	<4	Yes
--	--	TRU(g)	--	--	7.21E-3	--	2.67E+5	4.61E+4	4.8E+5	10	Yes

MDA: minimum detectable activity (with all processing factors applied).

MDL: method detection limit (with all processing factors applied).

DF: data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide/analyte measured above EQL and no data qualifiers apply.

MRQ: minimum reportable quantity (defined in test specification).

--: not applicable.

(a) Results from a re-preparation and analysis; all other results from initial preparation and analysis. Reanalysis required due to QC failures.

(b) Fluoride analyzed by two methods; initial IC method exhibited significant interference and produced a maximum bounding fluoride concentration of about 2,100 µg/mL (or 21% of limit).

(c) MRQ for PO_4 defined in test specification as 500 (as P) but reported here as PO_4 (500 x 3.066).

(d) MRQ for SO_4 defined in test specification as 500 (as S) but reported here as SO_4 (500 x 2.996).

(e) Phosphate based on ICP-AES phosphorus results: MDL = 2.8 mg/L, Sample average = 1,600 mg/L.

(f) TIC from furnace combustion calculated from difference between TC and TOC; no MDL established.

(g) TRU: Z>92, alpha emitter, half-life >10yr (^{237}Np, $^{239/240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm); Pu, Am, and Cm from AEA and Np from ICP-MS (i.e., 7.21E-3 mCi/L = AEA sum at 7.204E-3 mCi/L + ^{237}Np at 0.00390E-3 mCi/L).

7.0 Procedures, Quality Control, and Data Evaluation

A discussion of procedures, data quality, and QC is provided below for each analytical method. Analytical instrument calibration and calibration verification were performed in accordance with the QA Plan. Raw data including bench sheets, instrument printouts, data reduction, and calibration files are maintained or cross-referenced in the Project 42365 Records Inventory and Disposition Schedule (RIDS) file. Table 7.1 provides a summary of the preparation and analysis methods performed.

Table 7.1. Summary of Analytical Preparative and Analysis Methods

Analysis	Preparative Method(s)	Analysis Method(s)
Density	Direct	PNL-ALO-501
Wt% Total Solids / TDS	Direct	PNL-ALO-501
ICP-AES (metals)	PNL-ALO-128	PNL-ALO-211
ICP-MS (except iodine)	PNL-ALO-128	PNL-OP-SC-01
ICP-MS (iodine)	Direct/Dilution	PNL-OP-SC-01
KPA (uranium)	PNL-ALO-128	RPG-CMC-4014
IC-Inorg (inorganic anions)	Direct/Dilution	PNL-ALO-212
IC-F (F only)	Direct/Dilution	TP-RPP-WTP-212
IC-Org (organic acids/anions)	TP-RPP-WTP-049	TP-RPP-WTP-046
TOC/TIC – furnace	Direct	PNL-ALO-380
TOC/TIC - hot persulfate	Direct	PNL-ALO-381
CN	PNL-ALO-287	PNL-ALO-289
Hg	RPG-CMC-131	RPG-CMC-201
OH	Direct	PNL-ALO-228
ISE (ammonia)	Direct/Dilution	RPG-CMC-226
GC/FID (chelators)	TP-RPP-WTP-049	TP-RPP-WTP-048
GC/FID (D2EHP)	TP-RPP-WPT-047	TP-RPP-WPT-047
GEA	PNL-ALO-128	PNL-ALO-450
Total alpha	PNL-ALO-128	RPG-CMC-4001, RPG-CMC-408
Total beta	PNL-ALO-128	RPG-CMC-4001, RPG-CMC-408
^{90}Sr	PNL-ALO-128, PNL-ALO-476	RPG-CMC-408, PNL-ALO-450
^{99}Tc^{+7}	PNL-ALO-432 (without sodium dichromate added)	RPG-CMC-474, RPG-CMC-408
^{3}H	PNL-ALO-418	RPG-CMC-474
^{14}C	PNL-ALO-482	RPG-CMC-474
^{79}Se	PNL-ALO-128, PNL-ALO-440	RPG-CMC-474
Pu, Am, Cm	PNL-ALO-128, PNL-ALO-417, PNL-ALO-496	RPG-CMC-422

The sample averages, MDLs, minimum reportable quantities (MRQs), data flags, and QC results (including QC acceptance criteria) are presented in Table 7.2 through Table 7.3. The QC acceptance criteria are defined in the test specification (i.e., Table 3, *QC Parameters for Liquid Analyses*). Where the

Table 7.2. AP-104 Supernatant Composite– Radionuclide QC Results

							QC Acceptance Criteria →	<15%	80%-120%	75%-125%
Method	**Prep**	**Radionuclide**	**MRQ mCi/L**	**MDA mCi/L**	**MRQ > 3xMDA?**	**Average mCi/L**	**DF**	**RSD %**	**LCS/BS %Rec**	**MS %Rec**
H-3	Direct	^{3}H	2.1E-2	2.0E-5	Yes	1.98E-3		1	91(j)	92(b)
C-14	Direct	^{14}C	7.2E-4	4.0E-5	Yes	7.17E-4		3	101	95
GEA	Acid-128	^{60}Co	2.1E-3	2.0E-3	No(h)	9.36E-3		8	--	--
Se-79	Acid-128	^{79}Se	9.0E-5	2.5E-5	Yes	8.93E-4	B	8	--	--
Sr-90	Acid-128	^{90}Sr	1.5E-1	2.0E-1	No(h)	1.95E+0		10	104(c)	93(b)
Tc-99	Direct	^{99}Tc^{+7}	1.5E-3	2.0E-4	Yes	5.03E-2		2	94	89(d)
GEA	Acid-128	^{125}Sb	4.0E-4	2.0E-1	No(h,i)	2.0E-1	U	---	--	--
GEA	Acid-128	^{126}Sn	6.0E-3	9.3E-2	No(h)	9.3E-2	U	---	--	--
GEA	Acid-128	^{137}Cs	9.0E+0	4.0E-2	Yes	1.90E+2		1	--	--
GEA	Acid-128	^{154}Eu	2.0E-3	7.0E-3	No(h)	7.0E-3	U	---	--	--
GEA	Acid-128	^{155}Eu	9.0E-2	1.7E-1	No(h)	1.7E-1	U	---	--	--
GEA	Acid-128	^{231}Pa	7.9E-5	2.0E+0	No(h)	2.0E+0	U	---	--	--
AEA	Acid-128	^{236}Pu	--	8.7E-6	--	8.7E-6	U	---	(f)	(f)
AEA	Acid-128	^{238}Pu	1.0E-2	1.2E-5	Yes	5.5E-5	J	5	(f)	(f)
AEA	Acid-128	$^{239/240}$Pu	3.0E-2	8.3E-6	Yes	4.17E-4		1	112	113(b)
AEA	Acid-128	^{241}Am	3.0E-2	1.3E-5	Yes	5.79E-3		1	88	99(b)
AEA	Acid-128	^{242}Cm	1.5E-1	5.0E-6	Yes	1.1E-5	J	30	(g)	(g)
AEA	Acid-128	$^{243/244}$Cm	1.5E-2	8.7E-6	Yes	9.22E-4	d	**19**	(g)	(g)
--	--	Alpha Sum(a)	--	--	--	7.20E-3		3	--	--
Alpha	Acid-128	Total Alpha	2.3E-1	5.7E-2	Yes	5.7E-2	U	---	114(d)	115(d)
Beta	Acid-128	Total Beta(e)	--	4.7E-1	--	2.06E+2		3	113	117

Outlined and bolded results exceed QC acceptance criteria.

MRQ: minimum reportable quantity (defined in test specification).

MDA: minimum detectable activity (used with all radiochemical analysis results).

DF: data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide measured above EQL and no data qualifiers apply.

RSD: relative standard deviation. (---) indicates one or more triplicate results <MDL and RSD not calculated.

--: not applicable.

(a) Alpha Sum: Summation of AEA results only (i.e., $^{239/240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm).

(b) MS not required by test specification.

(c) QC acceptance criterion 75% to 125%.

(d) QC acceptance criterion 70% to 130%.

(e) No QC acceptance criteria specified in test specification; QC acceptance criteria for Total Alpha were used for performance evaluation.

(f) QC performance established by $^{239/240}$Pu QC results.

(g) QC performance established by ^{241}Am QC results.

(h) MDAs adjusted for process and analysis dilution factors. An “achievable” MDA can be estimated from the PB MDA. If the PB MDA is compared against the MRQ, the MDA meets the acceptance criterion of “MRQ > 3xMDA” except for ^{125}Sb. (PB MDA for ^{60}Co, ^{90}Sr, and ^{126}Sn = 2.0E-4 mCi/L, for ^{125}Sb, ^{154}Eu, and ^{155}Eu = 4.0E-4 mCi/L, and for ^{231}Pa = 5.0E-3 mCi/L)

(i) At the extended counting times used for GEA, the PB MDA for ^{125}Sb is equal to the MRQ (i.e., 4.0E-4 mCi/L).

(j) A trip BS from the SAL recovered at only 50%, suggesting results are biased low.

Nominal decay correction dates: GEA (March 14, 2002); AEA – Pu, Am, Cm (year 2002); ^{90}Sr (March 20, 2002); ^{99}Tc (January 23, 2002); ^{79}Se (March 30, 2002); ^{3}H (April 01, 2002); and ^{14}C (June 19, 2002).

Table 7.3. AP-104 Supernatant Composite – Radionuclide/Analyte QC Results

QC Acceptance Criteria →								<15%(v)	80%-120%(v)	75%-125%(v)	75%-125%(v)	75%-125%(v)	<±10%
Method(y)	**Prep**	**Radionuclide/ Analyte**	**MRQ mg/L**	**MDL mg/L**	**MRQ > 3xMDL?**	**Average mg/L**	**DF**	**RSD %**	**LCS/BS %Rec**	**MS %Rec**	**MSD %Rec**	**PS %Rec**	**Serial Dil.(n) %D**
ICP-MS	Acid-128	^{99}Tc(a,o)	8.8E-2	1.2E-2	Yes	8.46E+0		3	98	94	--	--	1
ICP-MS	Acid-128	^{127}I(a)	1.0E-1	2.3E-1	No	5.67E+0	B	3	(p)	(p)	--	--	1
ICP-MS	Acid-128	^{129}I(a)	1.5E+0	7.8E-2	Yes	1.43E+0		5	108	107	--	118	4
ICP-MS	Acid-128	^{133}Cs(a)	1.5E+0	2.5E-3	Yes	5.58E+0		3	99	95	--	93	1
ICP-MS	Acid-128	^{135}Cs	1.5E+0	2.3E-2	Yes	1.73E+0		3	(s)	(s)	--	(s)	--
ICP-MS	Acid-128	^{137}Cs	1.7E-2	2.3E-2	No	1.92E+0		3	(s)	(s)	--	(s)	--
ICP-MS	Acid-128	^{233}U	4.2E-2	1.9E-4	Yes	5.7E-4	J	15	(r)	(r)	--	(r)	--
ICP-MS	Acid-128	^{234}U	2.0E-2	5.1E-5	Yes	7.19E-4	B	6	(r)	(r)	--	(r)	--
ICP-MS	Acid-128	^{235}U	2.8E-2	3.4E-4	Yes	8.20E-2		0.2	(r)	(r)	--	(r)	-9
ICP-MS	Acid-128	^{236}U	2.2E-2	9.8E-5	Yes	4.92E-3	e	3	(r)	(r)	--	(r)	$\boxed{\mathbf{-17}}$
ICP-MS	Acid-128	^{237}Np(o)	2.7E-2	4.3E-4	Yes	5.49E-3	B	5	96	98	--	--	--
ICP-MS	Acid-128	^{238}U(o)	2.2E-2	5.4E-2	No	9.19E+0	a	0.03	$\boxed{\mathbf{131}}$/100(u)	91	--	100	-8
ICP-MS	Acid-128	^{239}Pu(o)	4.8E-1	4.2E-4	Yes	1.69E-2	Bd	$\boxed{\mathbf{20}}$	94	98	--	--	--
ICP-MS	Acid-128	^{240}Pu(o)	4.4E-2	4.7E-5	Yes	6.58E-4	B	12	94	98	--	--	--
ICP-MS	Acid-128	^{241}Pu /^{241}Am(o,t)	8.7E-2	6.3E-5	Yes	1.72E-3	B	4	95	99	--	--	--
ICP-MS	Acid-128	^{242}Pu(b)	--	6.5E-5	Yes	6.5E-5	U	---	(q)	(q)	--	--	--
IC-Org	Direct	Acetate	--	110	No	870	J	7	103	93	102	--	--
ISE	Direct	Ammonia(d)	140	8.0	Yes	402		14	104	(j)	--	--	--
ICP-AES	Acid-128	Ag(b)	--	0.69	--	0.69	U	---	--	--	--	99	--
ICP-AES	Acid-128	Al	75	1.7	Yes	12,800		1	95	(j)	--	(j)	2
ICP-AES	Acid-128	As(b)	--	6.9	--	6.9	U	---	--	--	--	103	--
ICP-AES	Acid-128	B(a)	2.3	1.3	No	40.2		4	100	103	--	99	--

Table 7.3. AP-104 Supernatant Composite – Radionuclide/Analyte QC Results (cont.)

QC Acceptance Criteria →								<15%(v)	80%-120%(v)	75%-125%(v)	75%-125%(v)	75%-125%(v)	<±10%
Method(y)	**Prep**	**Radionuclide/ Analyte**	**MRQ mg/L**	**MDL mg/L**	**MRQ > 3xMDL?**	**Average mg/L**	**DF**	**RSD %**	**LCS/BS %Rec**	**MS %Rec**	**MSD %Rec**	**PS %Rec**	**Serial Dil.(n) %D**
ICP-MS	Acid-128	B(a)	2.3	4.9	No	39	JBab	1	$\boxed{56}$	$\boxed{37}$	--	94	--
ICP-AES	Acid-128	Ba	2.3	0.28	Yes	0.28	U	---	94	86	--	98	--
ICP-MS	Acid-128	Ba(a)	2.3	0.052	Yes	1.74	Bd	$\boxed{30}$	102	82	--	92	--
ICP-AES	Acid-128	Be(b)	--	0.28	--	0.28	U	---	92	91	--	100	--
ICP-AES	Acid-128	Bi(b)	--	2.8	--	2.8	U	---	98	--	--	102	--
IC-Inorg	Direct	Br(d,m)	300	130	No	130	U	---	98	103	85	--	--
C (Furn)	Direct	C as TC	--	14	Yes	8,130		1	102	94	--	--	--
C (HP)	Direct	C as TC	--	(w)	--	8,450		1	(w)	(w)	--	--	--
C (Furn)	Direct	C as TIC	150	(w)	---	5,160		8	(w)	(w)	--	--	--
C (HP)	Direct	C as TIC	150	30	Yes	4,210		2	94	103	--	--	--
C (Furn)	Direct	C as TOC	1,500	400	Yes	2,970	J	13	104	81/95(k)	--	--	--
C (HP)	Direct	C as TOC	1,500	70	Yes	4,240		1	95	103	--	--	--
ICP-AES	Acid-128	Ca	150	6.9	Yes	72		3	96	90	--	102	--
ICP-AES	Acid-128	Cd	7.5	0.41	Yes	1.8	J	0	96	91	--	105	--
ICP-AES	Acid-128	Ce	2.3	5.5	No	5.5	U	---	94	87	--	96	--
ICP-MS	Acid-128	Ce	2.3	0.099	Yes	0.14(i)	J	---	117	108	--	107	--
IC-Org	Direct	Citrate	1,500	460	Yes	860	J	5	99	91	88	--	--
GC/FID(l)	Derivatize	Citric acid	--	5.8	--	420		14	88	91	88	--	--
IC-Inorg	Direct	Cl(d,m)	300	130	No	5,440		2	97	95	97	--	--
Color	Distill-287	CN	3.0	0.24	Yes	45.6		1	100	(j)	--	--	--
ICP-AES	Acid-128	Co(b)	--	1.4	--	1.4	U	---	--	--	--	103	--
ICP-AES	Acid-128	Cr	15	0.55	Yes	475		1	96	(j)	--	107	5
ICP-AES	Acid-128	Cu(b)	--	0.69	--	0.69	U	---	98	81	--	99	--

Table 7.3. AP-104 Supernatant Composite – Radionuclide/Analyte QC Results (cont.)

								QC Acceptance Criteria →	<15%(v)	80%-120%(v)	75%-125%(v)	75%-125%(v)	75%-125%(v)	<±10%
Method(y)	**Prep**	**Radionuclide/ Analyte**	**MRQ mg/L**	**MDL mg/L**	**MRQ > 3xMDL?**	**Average mg/L**		**DF**	**RSD %**	**LCS/BS %Rec**	**MS %Rec**	**MSD %Rec**	**PS %Rec**	**Serial Dil.(n) %D**
GC/FID(l)	Derivatize	D2EHP(e)	1,500	--	--	--		--	--	--	--	--	--	--
ICP-AES	Acid-128	Dy(b)	--	1.4	--	1.4		U	---	--	--	--	102	--
GC/FID(l)	Derivatize	ED3A	1,500	4.9	Yes	310			15	--	--	--	--	--
GC/FID(l)	Derivatize	EDTA	1,500	4.9	Yes	570		b	14	103	$\boxed{\textbf{61}}$	85	--	--
ICP-AES	Acid-128	Eu(b)	--	2.8	--	2.8		U	---	--	--	--	102	--
IC-F	Direct	F(c)	150	2.0	Yes	162			1	113	115	115	--	--
ICP-AES	Acid-128	Fe(a)	150	0.65	Yes	9.0		B	11	102	97	--	102	--
IC-Org	Direct	Formate	1,500	180	Yes	3,730			4	95	111	99	--	--
IC-Org	Direct	Gluconate(f)	1,500	320	Yes	4,000			--	--	--	--	--	--
IC-Org	Direct	Glycolate(f)	1,500	130	Yes	1,630			4	98	102	104	--	--
GC/FID(l)	Derivatize	HEDTA	1,500	8.8	Yes	8.8		Uab	---	$\boxed{\textbf{170}}$	$\boxed{\textbf{70}}$	103	--	--
CVAA	Acid-131	Hg	1.5	0.00007	Yes	0.0013		B	9	97	102	106	--	--
ICP-AES	Acid-128	K(a)	75	52	No	1,870			3	96	99	--	97	--
ICP-AES	Acid-128	La	35	1.4	Yes	1.4		U	---	97	93	--	100	--
ICP-AES	Acid-128	Li	2.3	0.83	No	0.83		U	---	97	89	--	100	--
ICP-MS	Acid-128	Li	2.3	0.085	Yes	0.085		U	---	102	102	--	102	--
ICP-AES	Acid-128	Mg	300	2.8	Yes	2.8		U	---	95	90	--	106	--
ICP-AES	Acid-128	Mn(b)	--	1.4	--	1.4		U	---	98	91	--	104	--
ICP-AES	Acid-128	Mo(b)	--	1.4	--	57.9			1	97	90	--	101	--
ICP-AES	Acid-128	Na	75	21	Yes	133,000			2	110	(j)	--	(j)	6
ICP-AES	Acid-128	Nd(b)	--	2.8	--	2.8		U	---	98	93	--	100	--
ICP-AES	Acid-128	Ni	30	0.83	Yes	40.5			1	97	88	--	101	--
GC/FID(l)	Derivatize	NIDA/IDA	1,500	11	Yes	883		b	2	--	121	$\boxed{\textbf{131}}$	--	--

Table 7.3. AP-104 Supernatant Composite – Radionuclide/Analyte QC Results (cont.)

QC Acceptance Criteria →								<15%(v)	80%-120%(v)	75%-125%(v)	75%-125%(v)	75%-125%(v)	<±10%
Method(y)	**Prep**	**Radionuclide/ Analyte**	**MRQ mg/L**	**MDL mg/L**	**MRQ > 3xMDL?**	**Average mg/L**	**DF**	**RSD %**	**LCS/BS %Rec**	**MS %Rec**	**MSD %Rec**	**PS %Rec**	**Serial Dil.(n) %D**
IC-Inorg	Direct	NO_2(d)	500	1300	No	69,200		1	102	104(m)	(m)	--	--
IC-Inorg	Direct	NO_3(d)	500	1300	No	111,000		1	94	96(m)	(m)	--	--
GC/FID(l)	Derivatize	NTA	1,500	5.6	Yes	247		8	111	78	81	--	--
Titration	Direct	OH	3,500	170	Yes	22,300		3	104	98	--	--	--
IC-Org	Direct	Oxalate	1,500	230	Yes	730	J	2	108	108	100	--	--
IC-Inorg	Direct	Oxalate(d,m)	1,500	100	Yes	900	J	13	107	106	104	--	--
ICP-AES	Acid-128	P	600	2.8	Yes	1,590		1	98	(j)	--	104	1
ICP-AES	Acid-128	Pb	300	2.8	Yes	8.3	J	10	101	95	--	109	--
ICP-AES	Acid-128	Pd(b)	--	21	--	21	U	---	--	--	--	(z)	--
IC-Inorg	Direct	PO_4(d,m)	1,500(g)	100	Yes	5,520		1	103	103	98	--	--
ICP-MS	Acid-128	Rb(a)	1.0	0.036	Yes	5.56		3	100	96	--	94	--
ICP-AES	Acid-128	Rh(b)	--	8.3	--	8.3	U	---	--	--	--	97	--
ICP-AES	Acid-128	Ru(b)	--	30	--	30	U	---	--	--	--	(z)	--
ICP-AES	Acid-128	Sb(b)	--	14	--	14	U	---	--	--	--	100	--
ICP-AES	Acid-128	Se(b)	--	6.9	--	6.9	U	---	--	--	--	104	--
ICP-AES	Acid-128	Si(a,b)	--	13	--	133		10	102	106	--	105	--
ICP-AES	Acid-128	Sn(b)	--	41	--	41	U	---	--	--	--	89	--
IC-Inorg	Direct	SO_4(d,m)	1,500(h)	100	Yes	3,100		1	102	102	100	--	--
ICP-AES	Acid-128	Sr(b)	--	0.41	--	0.41	U	---	95	94	--	100	--
GC/FID(l)	Derivatize	Succinic acid	1,500	6.1	Yes	91	B	1	97	90	91	--	--
ICP-AES	Acid-128	Te(b)	--	41	--	41	U	---	--	--	--	100	--
ICP-AES	Acid-128	Th	2.3	28	No	28	U	---	96	92	--	101	--
ICP-MS	Acid-128	Th	2.3	0.36	Yes	0.62	J	5	99	76	--	96	--

Table 7.3. AP-104 Supernatant Composite – Radionuclide/Analyte QC Results (cont.)

QC Acceptance Criteria →								<15%(v)	80%-120%(v)	75%-125%(v)	75%-125%(v)	75%-125%(v)	<±10%
Method(y)	**Prep**	**Radionuclide/ Analyte**	**MRQ mg/L**	**MDL mg/L**	**MRQ > 3xMDL?**	**Average mg/L**	**DF**	**RSD %**	**LCS/BS %Rec**	**MS %Rec**	**MSD %Rec**	**PS %Rec**	**Serial Dil.(n) %D**
ICP-AES	Acid-128	Ti(b)	--	0.69	--	0.69	U	---	94	87	--	96	--
ICP-AES	Acid-128	Tl(b)	--	14	--	14	U	---	--	--	--	101	--
ICP-AES	Acid-128	U	600	55	Yes	55	U	---	99	91	--	101	--
KPA	Acid-128	U	780	0.60	Yes	10.9		2	102	99	--	--	--
ICP-MS	Acid-128	U(x)	---	--	--	9.28		0.03	--	--	--	--	--
ICP-AES	Acid-128	V	2.3	1.4	No	1.4	U	---	91	85	--	97	--
ICP-MS	Acid-128	V	2.3	0.28	Yes	2.8	Jd	**16**	99	96	--	97	--
ICP-AES	Acid-128	W	2.3	55	No	83	J	1	97	86	--	(z)	--
ICP-MS	Acid-128	W	2.3	0.23	Yes	93.6	be	6	112	**60**	--	104	**-13**
ICP-AES	Acid-128	Y(b)	--	1.4	--	1.4	U	---	--	--	--	100	--
ICP-AES	Acid-128	Zn(b)	--	1.4	--	1.4(i)	JB	---	98	94	--	106	--
ICP-AES	Acid-128	Zr(b)	--	1.4	--	1.4	U	---	96	83	--	100	--

Outlined and bolded results exceed QC acceptance criteria.

--: not applicable or not required.

MRQ: minimum reportable quantity (defined in test specification).

MDL: method detection limit (with all processing factors applied).

DF data flag. See Section 6.1 for data flag definitions. No entry in DF indicates radionuclide/analyte measured above EQL and no data qualifiers apply.

RSD: relative standard deviation. (---) indicates one or more triplicate results <MDL and RSD not calculated.

D2EHP: bis-(2-ethylhexyl) phosphoric acid; CAS 298-07-7.

EDTA: ethylenediaminetetraacetic acid; CAS 60-00-4.

ED3A: ethylenediaminetriacetic acid; CAS – none available.

HEDTA: N-(2-hydroxyelthyl) ethylenediaminetriacetic acid; CAS 150-39-0.

NIDA/IDA: nitrosoiminodiacetic acid/iminodiacetic acid; CAS 142-73-4 (IDA).

NTA: nitrilotriacetic acid; CAS 139-73-4.

Table 7.3. AP-104 Supernatant Composite – Radionuclide/Analyte QC Results (cont.)

(a) Results from a re-preparation and analysis of the samples; all other results from initial preparation and analysis. Reanalysis required due to QC/standards failures.

(b) Opportunistic analyte; analyte not included in test specification.

(c) Fluoride analyzed by two methods; initial IC method exhibited significant interference and produced a maximum bounding fluoride concentration of about 2,100 µg/mL with acceptable QC.

(d) IC and ammonia MDLs are based on the lowest calibration standard adjusted for sample dilution; equivalent to SW-846 EQL definition.

(e) D2EHP was not measured due to lack of reliable method.

(f) Glycolate and gluconate results should be considered the upper bound concentration, since glycolate and gluconate are not resolved by the IC measurement method used for the analysis. IC system calibrated using glycolate; gluconate estimate based on gluconate-to-glycolate response factor. Each result assume 100% of response due to each analyte. LCS/BS and MS contain no gluconate.

(g) MRQ for PO_4 defined in test specification as 500 (as P) but reported here as PO_4 (500 x 3.066).

(h) MRQ for SO_4 defined in test specification as 500 (as S) but reported here as SO_4 (500 x 2.996).

(i) Reported average calculated from 1 or 2 results; RSD only calculated when all results exceed the MDL.

(j) Not recovered; spike concentration less than 20% of sample concentration.

(k) TOC MS measured at two different combustion times, 10 minutes (81%) and 20 minutes (95%); results reported from 10 minute combustion time.

(l) Adipic acid used as surrogate: Surrogate recovery for LCS, MS, and MSD were 62%, 99%, and 106%, respectively.

(m) The IC MS prepared from a sample diluted 10,000x. MSD prepared from a sample diluted 2,000x; NO_2 and NO_3 over range and recovery not calculated.

(n) Serial dilution only calculates when sample result exceeds 50xMDL.

(o) Per QA Plan protocol for radionuclides, LCS, and MS prepared following digestion. LCS/BS prepared by post-spiking process blank; MS prepared by post-spiking sample.

(p) Iodine QC performance established by ^{129}I.

(q) ^{242}Pu QC performance established by ^{239}Pu.

(r) U isotope QC performance established by ^{238}U.

(s) ^{135}Cs and ^{137}Cs calculated from ^{133}Cs results and Cs HPIC/ICP-MS isotopic analysis; QC performance established by ^{133}Cs.

(t) ^{241}Am used to establish QC performance for AMU-241 (^{241}Pu/^{241}Am). AMU-241 calibrated using ^{241}Am.

(u) LCS/BS recovery: The first result is for a blank spike. The second result is for a post-spiked process blank (as per the QA Plan protocol for preparation of a radionuclide LCS/BS). Reason for over-recovery is unknown but suspected to be contamination from hot cell preparation.

(v) General QC Acceptance Criteria listed. Exceptions are ICP-MS for MS, MSD, and PS (70% to 130%) and ICP-AES (sodium only) for LCS/BS, MS, MS, and PS (90% to 110%) and RSD (<3.5%).

(w) Not applicable. Furnace TIC by difference; see C (Furn) for QC performance. HP TC by sum; see C (HP) TIC and TOC for QC performance.

(x) U is the sum of all measured isotopes of U by ICP-MS; see U isotopes for QC performance.

(y) ICP-MS Analyses: See Section 6.4. Unless separated prior to analysis, analytes reported as elements may be bias due to altered isotopic distribution. Only Cs, U, and Pu separated prior to analysis.

(z) ICP-AES: Pd and Ru opportunistic analytes; not included in post spiking solutions. W not required to be post-spiked since MS within acceptance criterion.

result for one (or two) of the triplicate analysis is reported at <MDL (i.e., flagged with a U) and remaining sample result(s) is(are) >MDL (i.e., either not flagged or flagged with a J), the average is based only on the result(s) >MDL.

The QC and results evaluations provided in the following sections are limited to the analytes of interest defined by the test plan. Analytes other than those specified by the test plan are considered "opportunistic" and are provided for information only. Some of these opportunistic analytes have been measured per the requirements stated in the governing QA Plan or test plan; however, the data may not have been fully evaluated against the QC acceptance criteria.

7.1 Inductively Coupled Plasma - Atomic Emission Spectroscopy

Tables 6.3 and 7.3; Appendix D3

The AP-104 supernatant sample was prepared by acid digestion per procedure PNL-ALO-128. All samples were then analyzed 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 increases to 100%.

Quality control for the ICP-AES analysis consisted of triplicate samples, PBs, MS, LCS/BS, PS, serial dilution, calibration verification check standards and blanks, interference check standards, and linear range check standards. Analytes of interest were specified in the test specification and included Al, B, Ba, Ca, Cd, Ce, Cr, Fe, K, La, Li, Mg, Na, Ni, P, Pb, Th, U, V, and W. For the reported analytes of interest, all LCS/BS recoveries were within the QC acceptance criterion. A few analytes (i.e., Al, Cr, Na, and P) failed to meet the MS recovery criterion due to the spike being less than 20% of the sample concentration. Post spiking for these elements was performed, with Cr and P meeting the PS recovery criterion. Aluminum and Na concentrations were so high that neither the MS nor PS could be recovered. However, the percent difference (%D) for the serial dilution for these analytes is well within the serial dilution QC acceptance criterion, indicating the absence of any serious matrix interference. It should be noted that the target MRQ values were met for only about half of the analytes of interest; B, Ce, K, Li, Th, V and W failed to meet the target MRQ.

7.2 Inductively Coupled Plasma - Mass Spectrometry

Tables 6.2, 6.3, 7.2 and 7.3; Appendix D12

The PNL-ALO-128 acid digested samples of the AP-104 supernatant were submitted for ICP-MS analysis and analyzed according to procedure PNL-OP-SC-01, *Inductively Coupled Plasma Mass Spectrometric (ICP-MS) Analysis*. Except for the MS and LCS, the acid digest solutions were the same as those analyzed by ICP-AES.

Quality control for the ICP-MS analysis consisted of sample triplicates, PB, LCS/BS, MS, PS, calibration verification check standards and blanks, and interference check standards. Except for ^{238}U and ^{129}I, radionuclides were not spiked into the LCS/BS or the MS samples during sample preparation (i.e., dilution or digestion) processing. The quantities of isotopes required would be extremely large given the large dilutions necessary to perform the analysis. Therefore, radionuclides are post-spiked into samples following dissolution.

Analytes of interest included both elements and isotopes and were specified in the test specification; elements included B, Ba, Ce, Cs (total, $^{133+135+137}$Cs), Li, Rb, Th, V, and W and isotopes included ^{99}Tc, ^{127}I, ^{129}I, ^{133}Cs, ^{135}Cs, ^{137}Cs, ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Pu/^{241}Am. For the reported analytes of interest, all LCS/BS recoveries were within the QC acceptance criterion except for B (56%) and ^{238}U (131%). Matrix spike failures were limited to B (37%) and W (60%), relative standard deviation (RSD) failures to ^{239}Pu (20%) and Ba (30%), and serial dilutions failures (required by QA Plan) to ^{236}U (-17%) and W (-13%). Post spikes for B and W produced good recoveries, indicating a potential matrix-related problem for these analytes; the poor percent difference (%D) from serial dilution for W also suggests a matrix or processing issue. The reason for the poor %D for ^{236}U is unknown; however, other U isotopes showed the same high tendency with %Ds near the ±10% limit. The RSD failure for ^{239}Pu is most likely due to a variable blank level; the process blank concentration is very high relative to the measured sample concentration. The RSD failure for Ba is due to each of the triplicate sample results being only estimated values within 10x the MDL (flagged “J”).

Two LCS failures are noted in the ICP-MS results; boron and ^{238}U. The boron failure is due to an ICP-MS instrument memory effect. Based on these and other data, boron is not considered a good candidate for ICP-MS analysis at the concentrations measured and the ICP-AES results should be used. The ^{238}U LCS failure is considered to have no effect on the reported results, since the total uranium by KPA is slightly higher than that measured by ICP-MS (i.e., 10.9 mg/L for KPA to 9.3 mg/L for ICP-MS).

Due to the high sensitivity of the ICP-MS, a few of radionuclides (i.e., ^{127}I, ^{234}U, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Pu/^{241}Am) and analytes (i.e., B and Ba) exhibited PB concentrations that exceed the PB acceptance criteria. The ^{127}I PB (i.e., dilution) contamination is from natural iodine impurity in the matrix modifier solution (p-cyano-phenol) used for the analysis. The analytes present in the acid digestion PB are typically from the glassware, plasticware, and chemicals used for processing, whereas the radionuclides are from the SAL environment in which the samples were processed.

7.3 U Analysis by KPA

Tables 6.3 and 7.3; Appendix D11

Total uranium was measured on the AP-104 supernatant according to procedure RPG-CMC-4014, *Uranium by Kinetic Phosphorescence Analysis (KPA)*. For the total uranium analysis by KPA the supernatant sample was prepared in the SAL per procedure PNL-ALO-128. The acid-digested samples were taken to dryness and redissolved in 0.5 M HNO_3 prior to KPA analysis to eliminate potential interferences. The samples were analyzed in triplicate with excellent reproducibility (RSD = 2%) and all QC samples produced results well within acceptance criteria. The KPA average uranium result (10.9 mg/L) compares favorably to the average result from ICP-MS (9.3 mg/L). The uranium concentration is well below the requested MRQ value of 780 mg/L.

7.4 Radiochemical Analyses

Tables 6.2 and 7.2; Appendix D11

The AP-104 supernatant samples were prepared per procedure PNL-ALO-128 and analyzed for gamma emitters (^{60}Co, ^{125}Sb, ^{126}Sn, ^{137}Cs, ^{154}Eu, ^{155}Eu, and ^{231}Pa), total alpha, total beta, ^{79}Se, ^{90}Sr, ^{238}Pu, $^{239/240}$Pu, ^{241}Am, ^{242}Cm, and $^{243/244}$Cm. The analysis of ^{3}H, ^{14}C, and ^{99}Tc (as pertechnetate) were performed using unprocessed supernatant (i.e., not digested per PNL-ALO-128). For all radiochemical analyses, the

LCS/BSs and MSs were prepared at the analytical workstation. The reported errors (1-σ) represent the total propagated error including counting, dilution, yield, and calibration errors, as appropriate.

The MDAs for the samples are included in the Table 7.2 and are compared against the target MRQ values. However, these MDAs reflect the sample sizes used for the analysis, the dilutions necessary for optimum counting, and the counting times used for the sample analysis. Many times the sample MDAs exceeded the MRQ requirement due to high activity. In these cases, it is better to use the MDAs from the PBs to assess whether the target MRQ can be measured (see Table 7.2, footnote 'h').

7.4.1 Gamma Spectrometry

Aliquots of the sample digestion solutions were directly counted for gamma emitters (^{60}Co, ^{125}Sb, ^{126}Sn, ^{137}Cs, ^{154}Eu, ^{155}Eu, and ^{231}Pa) according to procedure PNL-ALO-450, *Gamma Energy Analysis and Low-Energy Photon Spectrometry*. No LCS/BSs or MSs are required for this analysis; the measurement is a direct reading of the gamma energy and is not subject to matrix interferences; laboratory counter control standards analyses and background counts were performed. The samples were counted for up to 3 hours to give extended-time MDAs. Samples are normally counted for 14 hours when extended count time is required to meet low MRQ values. However, an evaluation of the 3-hour counts showed that counting for 14 hours would reduces the MDA values by only a factor of about 2 (i.e., $\sqrt{14/3}$). Of the five radionuclides reported at below the MDA, only ^{155}Eu (and possibly ^{154}Eu) might benefit from counting times of 14 hours or greater. However, even at a 14-hour count, the ^{155}Eu MDA only equals the MRQ. The ^{137}Cs activity in AP-104 is so high that it is improbable that the MRQ values for ^{125}Sb, ^{126}Sn, and ^{231}Pa can be met, regardless of the count time, without the removal of Cs. Due to the very high concentration of ^{137}Cs in the supernatant, no other gamma emitting isotopes except ^{60}Co were detected. Even with the extended counting time, ^{137}Cs was the only gamma emitter with an MDA to meet the test specification MRQ requirement. The decay correction reference date for radionuclides reported by GEA is March 14, 2002.

7.4.2 Total Beta

The total beta activity was determined by evaporating small aliquots of the sample digestion solutions onto planchets according to procedure RPG-CMC-4001, *Source Requirements for Gross Alpha and Gross Beta Analysis*. The planchets were counted on a gas proportional counter according to procedure RPG-CMC-408, *Low Background Alpha and Beta Counting - Proportional*. The triplicate results were in good agreement with an RSD of 3%. The beta activity in the PBs was negligible with respect to the samples. The test specification defines no QC acceptance criteria for the total beta analysis and no MRQ is defined. The LCS/BS and MS recoveries were somewhat high at 113% and 117%, respectively.

The total beta activity is in good agreement with the sum of the ^{137}Cs activity plus twice the ^{90}Sr activity (to allow for the ^{90}Y daughter) indicating that these two isotopes account for most of the beta activity in AP-104 supernatant.

7.4.3 Total Alpha

The total alpha activity was determined by evaporating small aliquots of the sample digestion solutions onto planchets according to procedure RPG-CMC-4001, *Source Requirements for Gross Alpha and Gross Beta Analysis*. The samples were counted on Ludlum detectors according to procedure RPG-

CMC-408, *Low Background Alpha and Beta Counting - Proportional*. No alpha activity was detected in the samples or the PBs, and the MDAs for the PBs are well below the requested MRQ value of 0.23 mCi/L. Since the total alpha activity is below the MDA, the best estimate of the total alpha activity is given by the sum of the alpha emitters, as discussed in Section 7.4.4. Although within the acceptance criteria, the LCS/BS and MS gave somewhat high recoveries at 114% and 115%, respectively.

7.4.4 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. Since curium is known to follow the americium chemistry, both curium and americium were traced with ^{243}Am.

When detected, the alpha activities in the PBs were negligible with respect to the sample activities, and all MDAs are below the target MRQ requirements. The ^{239}Pu and ^{241}Am LCS/BS and MS recoveries are well within the QC acceptance criteria. For the radionuclides with low counting uncertainties (i.e., <10% and no “J” flag), only $^{243/244}$Cm with an RSD of 19% failed to meet the RSD acceptance criteria. The reason for the failure is unknown. The decay correction reference date for the plutonium, americium, and curium isotopes is year 2002. The total of individual alpha emitters determined by alpha spectrometry (i.e., ‘Alpha Sum’) combined with the alpha activity from ^{237}Np by ICP-MS is considered the best estimate of the total alpha activity.

7.4.5 Strontium-90

The strontium separation was performed on aliquots of the AP-104 supernatant digestion solutions according to PNL-ALO-476, *Strontium Determination using Sr-SPEC*, and radiochemical yields were traced with ^{85}Sr. The separated fractions were beta counted according to RPG-CMC-408, *Low Background Alpha and Beta Counting – Proportional* (for ^{90}Sr determination). Following beta counting, the samples were gamma counted according to PNL-ALO-450, *Gamma Energy Analysis and Low-Energy Photon Spectrometry* (for ^{85}Sr yield determination and ^{137}Cs impurity assessment).

All QC analyses were within acceptance criteria. Although ^{90}Sr was detected in the PBs, the activity was negligible compared to that of the samples, and the MDAs for the PBs were well below the requested MRQ value of 0.15 mCi/L. One of the triplicate samples exhibited a slight ^{137}Cs contamination, and a suitable small correction to the beta counting results was necessary. The decay correction reference date for ^{90}Sr is March 20, 2002.

7.4.6 Technetium-99 (Pertechnetate)

The radiochemical ^{99}Tc determination was requested to measure only technetium in the +7 oxidation state (as pertechnetate); therefore, all sample processing was conducted so as not to alter the original technetium oxidation state. Small aliquots of the supernatant (no digestion) were 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 technetium to the +7 oxidation state. The sodium dichromate addition was omitted; otherwise the procedure was performed as written. The separated technetium fraction was 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.

The beta energy spectra matched that of ^{99}Tc and showed no measurable contamination from other beta emitters. All QC analyses were within acceptance criteria, and the sample MDA meets the target MRQ requirement. The decay correction reference date for ^{99}Tc by this method is January 23, 2002.

7.4.7 Tritium

Tritium was distilled directly from diluted aliquots of the supernatant according to procedure PNL-ALO-418, *Tritium Determination in Soil and Water Using a Lachat Micro-Dist™ System,* and measured by liquid scintillation counting according to procedure RPG-CMC-474, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*. The procedure was modified to include a cation exchange and a second distillation to ensure the removal of relatively high levels of ^{90}Sr and ^{137}Cs from the samples. This procedural modification produced a clean tritium beta spectra (i.e., no detectable beta contamination) and is fully documented in the Project 42365 RIDS file. All QC analyses were within acceptance criteria and the sample MDA meets the target MRQ requirement. The decay correction reference date for tritium is April 01, 2002.

Although not required, a SAL trip BS was processed and analyzed to assess the SAL environment and sample handling. The SAL trip BS was a tritium standard that was diluted and handled in the SAL identically to the samples prior to the distillation performed in the laboratory. The recovery for the trip BS was only 50%. The reason for the low recovery is unknown and requires additional investigation, but suggests that the reported results may be biased low.

7.4.8 Carbon-14

The supernatant composite was sub-sampled in the SAL and prepared in triplicate for ^{14}C analysis according to procedure PNL-ALO-482, *Determination of Carbon-14 in Radioactive Liquids, Soils, and Sludges, Method A (Furnace)*. The samples were combusted in oxygen at 1000°C along with a calcium carbonate carrier and the $^{14}CO_2$ collected in a basic trap solution. The trap solution was measured by LSC according to procedure RPG-CMC-474, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*. Beside the triplicate samples, an LCS/BS, MS, and PB were analyzed. Per PNL-ALO-482 (and like the TIC and TOC results measured by PNL-ALO-381), the samples, duplicate, LCS, PB, and MSs were corrected for the recovery obtained on calibration check standards that were processed and analyzed with the samples. All QC analyses were within acceptance criteria, and the sample MDA meets the target MRQ requirement. The decay correction reference date for ^{14}C is June 19, 2002.

7.4.9 Selenium-79

The selenium separation was performed on 2-mL aliquots of the sample digestion solutions according to procedure PNL-ALO-440, *Selenium-79 by Ion Exchange and Distillation Separation prior to Measurement by Liquid Scintillation Counting*. This procedure involves an anion/cation exchange to remove most radiochemical interferences followed by a selenium bromide distillation and reduction of selenium to elemental form.

Since radioactive ^{79}Se is not available as a standard, a non-radioactive selenium carrier was used in the analysis for establishing the yield and ^{14}C was used to establish the liquid scintillation detector efficiency since it has a very similar beta maximum energy (156 keV for ^{14}C versus 149 keV for ^{79}Se). The selenium gravimetric recoveries for the PB and triplicate samples ranged from 55% to 75%. The ^{79}Se activities were measured by LSC according to procedure PNL-ALO-474, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*. Peaks were observed in the ^{79}Se region of interest in the beta energy spectra, and no other higher energy beta contaminants were observed.

One of the PB results was marginally above the MDA (i.e., two times). However, this PB activity exceeds 5% of the ^{79}Se activity found in two of the samples, requiring that the ^{79}Se results be flagged with a "B" indicating a significant blank contribution. The ^{79}Se results meet the only QC criteria established by the test specification (i.e., RSD <15%), and the sample MDA meets the target MRQ requirement. The decay correction reference date for ^{79}Se is March 30, 2002.

7.5 Inorganic Anions

Tables 6.3 and 7.3: Appendices D4

Due to the low molecular weight organic anions present in the AP-104 waste, two IC methods were required in order to measure the seven inorganic anions of interest (Br, Cl, F, NO_2, NO_3, PO_4, and SO_4).

7.5.1 IC for Br, Cl, NO_2, NO_3, PO_4, and SO_4 (PNL-ALO-212)

The AP-104 supernatant composite was sub-sampled in the SAL and provided to the IC workstation for triplicate analysis for Cl, Br, NO_2, NO_3, PO_4, and SO_4 (F and C_2O_4 are considered opportunistic analyte by this method, although F exhibited significant interferences). The anion analysis was conducted according to method PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*. Prior to analysis, the supernatant samples were matrix matched to the standards by adding an appropriate quantity of IC mobile phase solution (eluent) to minimize the 'water dip' associated with aqueous samples. The supernatant samples required from 400x to 5,000x dilutions to ensure that each of the anions was measured within the calibration range; column overloading prohibited analysis at dilutions less than 400x.

Quality control for the anions analysis consisted of sample triplicates, PBs, MSs, LCS/BSs, and calibration verification check standards and blanks. All QC analyses produced results that were within acceptance criteria. Due to the dilutions required to prevent column overloading, the MDLs for Cl, Br, NO_2, and NO_3 did not meet the test plan target MRQ requirement; although the halides were very close (i.e., within 1.5x).

7.5.2 IC for F (TP-RPP-WTP-212)

The AP-104 supernatant composite was sub-sampled in the SAL and provided to the 329 Facility IC workstation for triplicate analysis for fluoride. The fluoride analysis was conducted according to method TP-RPP-WTP-212, *Analysis and Quantification of Fluoride and other Inorganic and Organic Anions in Hanford Tank Waste by Ion Chromatography*. The supernatant samples required from 50x to 250x dilutions to ensure that each of the anions was measured within the calibration range; column overloading prohibited analysis at dilutions less than 50x.

Quality control for the fluoride analysis consisted of sample triplicates, PB, MSs, LCS/BS, and calibration verification check standards and blanks. All QC analyses produced results that were within acceptance criteria.

7.6 TOC/TIC by Hot Persulfate and Furnace

Tables 6.3 and 7.3; Appendix D5

The AP-104 supernatant composite was analyzed in triplicate for TOC and TIC 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 used acid decomposition for TIC and acidic potassium persulfate oxidation at 92 to 95°C for TOC, both on the same sample, with TC being the sum of the TIC and TOC. All sample results were corrected for average percent recovery of system calibration check standards and are also corrected for contribution from the system blanks (i.e., PB), as per calculations defined in procedure PNL-ALO-381.

For the analysis, pure chemical solid compounds were used for system calibration check standards, as well as for the LCSs and MSs. The TIC analysis used two calcium carbonate compounds, and the TOC analysis used two α-glucose compounds. The QC for the method involved sample triplicates, LCS, and MS. All QC analyses were within acceptance criteria, and the sample MDL meets the target MRQ requirement for both TIC and TOC.

7.6.2 Furnace Oxidation Method (PNL-ALO-380)

The furnace oxidation method determined TOC by oxidizing organic carbon in oxygen at a temperature of 700°C and TC by oxidizing all carbon species at 1000°C. By the furnace oxidation method, TIC was determined by difference. All sample results were corrected for average percent recovery of system calibration standards and also corrected for contribution from the system blank (i.e., PB), as per calculations defined in procedure PNL-ALO-380. It should be noted that the samples were not acidified and purged of TIC prior to performing the TOC determination.

For the supernatant analyses, pure chemical solid compounds were used for system calibration check standards as well as for the LCSs and MSs. The TC analysis (1000°C) used two calcium carbonate compounds, and the TOC analysis (700°C) used two α-glucose compounds. The QC for the method involved sample triplicates, LCS, and MS. All QC analyses were within acceptance criteria and the sample MDL meets the target MRQ requirement for both TIC and TOC.

7.6.3 Comparison of Hot Persulfate and Furnace Oxidation Method Results

Table 7.4 presents the TOC and TIC results obtained from the hot persulfate method and the furnace oxidation method for the AP-104 supernatant. The TIC results from the furnace method were obtained by difference (TC – TOC), with the analysis being performed on two independent sample aliquots. The TC for the hot persulfate method was the summation of the TIC and TOC, which were performed on the same aliquot under different oxidation conditions.

There is excellent TC agreement between the methods; i.e., results vary by less than 5%, which is within the uncertainty of the methods. For TOC and TIC, the agreements are not nearly as good but are typical for tank waste supernatants. Typically the furnace method produces the most accurate TC results (i.e., results from single measurements and not a summation of two measurements) and the hot persulfate method produces the most accurate TIC results; thus the best estimate for TOC is the difference between the TC from the furnace method and the TIC from the hot persulfate method (shown in the last column of Table 7.4). The low TOC results for the furnace method suggests the presence of organics that may be hard to oxidize at 700°C, such as formate or oxalate.

Table 7.4. Comparison Summary of Carbon Results by Two Methods

Sample ID	TIC/F[(a)] Results mgC/L	TIC/HP Results mgC/L	TOC/F Results mgC/L	TOC/HP Results mgC/L	TC/F Results mgC/L	TC/HP[(b)] Results mgC/L	Est. TOC Results[(c)] mgC/L
Sample (02-1832)	5,400	4,200	2,700	4,300	8,100	8,500	3,900
Duplicate (02-1832D)	5,400	4,300	2,800	4,200	8,200	8,500	3,900
Triplicate (02-1832T)	4,700	4,200	3,400	4,200	8,100	8,300	3,900

HP= Hot Persulfate Combustion Method.

F= Furnace Combustion Method.

(a) TIC/F is determined by difference (TC/F minus TOC/F).

(b) TC/HP is determined by sum (TIC/HP plus TOC/HP).

(c) Best estimate of TOC concentration (TC/F minus TIC/HP).

7.7 Cyanide

Tables 6.3 and 7.3; Appendix D6

Aliquots of AP-104 supernatant were distilled at the cyanide analysis workstation and analyzed in triplicate. The aliquots were micro-distilled according to PNL-ALO-287, *Midi and Micro Distillation of Cyanide in Liquid and Solid Samples*, with the addition of sulfamic acid to minimize interference from high nitrates present in the sample. The distillates were analyzed by automated spectrophotometry according to PNL-ALO-289, *Total Cyanide Determination with Spectrophotometry (Manual or Automated) or Argentometric Titration*. Quality control for the cyanide analysis consisted of sample triplicates, PBs, MSs, LCS/BS, and calibration verification check standards and blanks.

Except for the MS, all QC analyses were within acceptance criteria, and the sample MDL meets the target MRQ requirement. The MS was prepared and distilled with the samples; however, due to the high CN concentration in the samples, the spiking level was insufficient (i.e., <20% of sample concentration) to accurately assess recovery. Since all other preparative and analysis QC results were acceptable, no reanalysis of the samples was undertaken.

7.8 Mercury Analysis

Tables 6.3 and 7.3; Appendix D7

The AP-104 supernatant samples and associated batch QC samples were digested at the mercury analysis workstation per procedure RPG-CMC-131, *Mercury Digestion*, and analyzed by cold vapor atomic absorption (CVAA) spectroscopy for inorganic mercury according to procedure RPG-CMC-201, *Mercury Analysis*. Quality control for the mercury analysis consisted of sample triplicates, PB, MSs, LCS/BS, and calibration verification check standards and blanks.

All QC analyses were within acceptance criteria, and the sample MDL meets the target MRQ requirement. The measured mercury concentration was 1,000 times less than the MRQ. All Hg results are flagged with a "B" indicating a significant blank contribution; PB is approximately 40-50% of the sample concentration. The Hg concentration measured in the samples was only about 1 μg/L (or 1 part per billion), and at this level blank contamination can come from many sources.

7.9 Hydroxide Titration

Tables 6.3and 7.3; Appendix D9

The AP-104 supernatant was analyzed for free 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 0.0103 M sodium hydroxide solution was prepared for use as a standard and spiking solution. The titrant was 0.02030 M hydrochloric acid standardized solution.

The triplicate sample showed a significant downward trend at the first inflection point volume. The results from the initial triplicate analysis were discarded and another triplicate prepared. The resulting average OH molarity was 1.30 with a RSD of 4%. This OH molarity result is equivalent to 22,100 mg/L, well above the required MRQ value of 3,500 mg/L. All QC analyses were within acceptance criteria, and the sample MDL meets the target MRQ requirement. No hydroxide was detected in a PB.

The second and third inflection points were detected in the samples at an average of 0.90 molar (6% RSD) and 0.31 molar (17% RSD), respectively. The second inflection point is primarily from both carbonate and aluminate and the third inflection point from bicarbonate (i.e., second equivalent point). Weak acids such as acetate, oxalate, formate, citrate, etc. also affect the accurate determination of these inflection points. Based on these inflection points, the upper bound for TIC (i.e., inflection points due solely to carbonate) is approximately 9,400 mg/L; the hot persulfate carbon method produced an average TIC result of approximately 4,200 mg/L.

7.10 Ammonia Analysis

Tables 6.3 and 7.3; Appendix D8

Triplicate samples of the AP-104 supernatant, a PB, MS, and LCS/BS (i.e., diluted ammonium chloride standard) were preserved in the SAL by acidifying with sulfuric acid prior to transferring to the ammonia analytical workstation. The samples were analyzed for ammonia by ion selective electrode (ISE) procedure RPG-CMC-226, *Measurement of Ammonia in Aqueous Solutions*. As part of the preservation process and to reduce the sample dose, the AP-104 samples were diluted 6x in the SAL; the samples were diluted an additional 5x during analysis.

Except for the MS, all QC analyses were within acceptance criteria, and the sample MDL meets the target MRQ requirement. A MS was prepared with the samples; however, due to the high ammonia concentration in the samples, the spiking level was insufficient (i.e., <20% of sample concentration) to accurately assess recovery. Since the ISE ammonia analysis is performed by the method of standard addition, no PS results are available. Since all other preparative and analysis QC results were acceptable, no reanalysis of the samples was undertaken.

7.11 Organic Acids

Tables 6.3 and 7.3; Appendix D4

Triplicate samples of the AP-104 supernatant were sub-sampled in the SAL and subjected to an ion exchange procedure (using Bio-Rad AG 50W-X8, 50-100 mesh, Na form) to reduce the sample dose, such that the resulting samples could be analyzed at the 329 Facility organic IC workstation. Following the ion exchange, the samples were analyzed for glycolate/gluconate, formate, oxalate, and citrate (with acetate being an opportunistic analyte) by IC procedure TP-RPP-WTP-046, *Method for the Analysis and Quantification of Organic Acids in Simulated and Actual Hanford Tank Waste by Ion Chromatography*. A PB, LCS/BS, and MSs were also prepared for analysis. The LCS/BS was subjected to the ion exchange process to provide assurances that the ion exchange processing did not impact the analytes of interest. The MSs were prepared following the ion exchange processing.

The IC analysis was performed using two analytical columns that have different loading characteristics. The samples were analyzed at dilutions such that the separation capacity for the columns was not exceeded. Gluconate and glycolate coelute at the same retention time on the column used; no method was found for the independent determination of gluconate and glycolate. The calibration was performed using glycolate; therefore, the response at the glycolate/gluconate retention time is reported as glycolate. Independent analysis established the signal response of gluconate to be approximately 40% that of glycolate. The reported average glycolate concentration is 1,600 mg/L; if the entire response is due to gluconate, then the gluconate concentration would be 4,000 mg/L. Methods development is necessary if both gluconate and glycolate are required.

All QC analyses were within acceptance criteria, and the sample MDLs meet the target MRQ requirement for all organic acids measured.

7.12 Chelator Analysis and Degradation Products

Tables 6.3 and 7.3; Appendix D10

The analysis of the AP-104 supernatant samples for chelators and chelator-degradation products was performed on a best-effort basis, since the method is still considered under development. The chelators, ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), ethylenediaminetriacetic acid (ED3A), iminodiacetic acid (IDA) [measured as nitrosoiminodiacetic acid (NIDA)], succinic acid, and nitrilotriacetic acid (NTA) have low volatility and high polarity precluding direct analysis by GC/FID. Derivatizing the chelators with a boron trifluoride/methanol mixture produces a methyl ester that is amenable to GC/FID separation and analysis. The derivatization process and analysis are still considered under development; i.e., the method has not been fully qualified for complex matrices such as Hanford tank waste. Additional work is required to provide a reliable, robust technique for the analysis of chelators in tank waste.

The 5-gram (nominal) sub-samples of AP-104 supernatant were diluted with 5 mL of DIW and subjected to an ion exchange procedure, TP-RPP-WTP-049, *Ion Exchange for Activity Reduction*, to reduce the sample dose. Following the ion exchange, the samples were transferred from the SAL to the 329 Facility organic laboratory where they were subjected to a derivatization process and analyzed per procedure TP-RPP-WTP-048 *Derivatization GC/FID Analysis of Chelators and Degradation Products*. Adipic acid was added to each sub-sample (prior to ion exchange and derivatization) as a surrogate and derivatization monitor. NIDA and IDA are not distinguishable, since IDA is completely converted to NIDA in the presence of nitrite. No standard for ED3A was available; the reported results for ED3A are based on the EDTA calibration. Citric acid was analyzed by derivatization GC/FID as an opportunistic analyte for comparison with the results generated by IC.

Per the test specification, the QC criteria established for the chelator analyses are target values only, since insufficient method data is available to set the QC parameters. The LCS/BS contained HEDTA, EDTA, NTA, succinic acid, and citric acid, and the MSs contained all analytes of interest except ED3A. For the AP-104 supernatant analysis, four QC failures were observed. The most notable was the failure of the LCS/BS for HEDTA; the LCS/BS produced very high recovery (170%). The MS for EDTA (61%) and HEDTA (70%) and the MSD for IDA/NIDA (131%) also failed. Due to these failures, another LCS/BS, MS, and MSD were prepared and the samples reanalyzed. The reanalysis showed similar trends. Only the results from the initial analysis are presented in Table 6.3 and Table 7.3. Table 7.5 compares the LCS/BS, MS, and MSD results from the initial analysis and the re-analysis. Although HETDA was not detected in any sample, based on the HEDTA QC results, the HEDTA results have been flagged with an “X” to indicate a severe QC performance issue.

Table 7.5. Chelator LCS/BS and MS QC Performance Summary

	LCS/BS		MS		MSD	
Compound	**Initial %Rec**	**Re-prep %Rec**	**Initial %Rec**	**Re-prep %Rec**	**Initial %Rec**	**Re-prep %Rec**
EDTA	103	111	**61**	**65**	85	**74**
HEDTA	**170**	**221**	**70**	**135**	103	**155**
ED3A	(a)	(a)	(a)	(a)	(a)	(a)
NTA	111	118	78	80	81	89
IDA/NIDA	(b)	(b)	121	110	**131**	111
Citric Acid(c)	88	93	91	82	88	83
Succinic Acid	97	104	90	94	91	96
AA (surrogate)	62	118	99	107	106	110

Outlined and bold results exceed target QC acceptance criteria.

(a) ED3A not included in LCS/BS or MSs; no standards available.
(b) IDA not added to LCS/BS; no nitrate present to convert to NIDA.
(c) Opportunistic analyte by this method.

7.13 Organic Phosphates Analysis

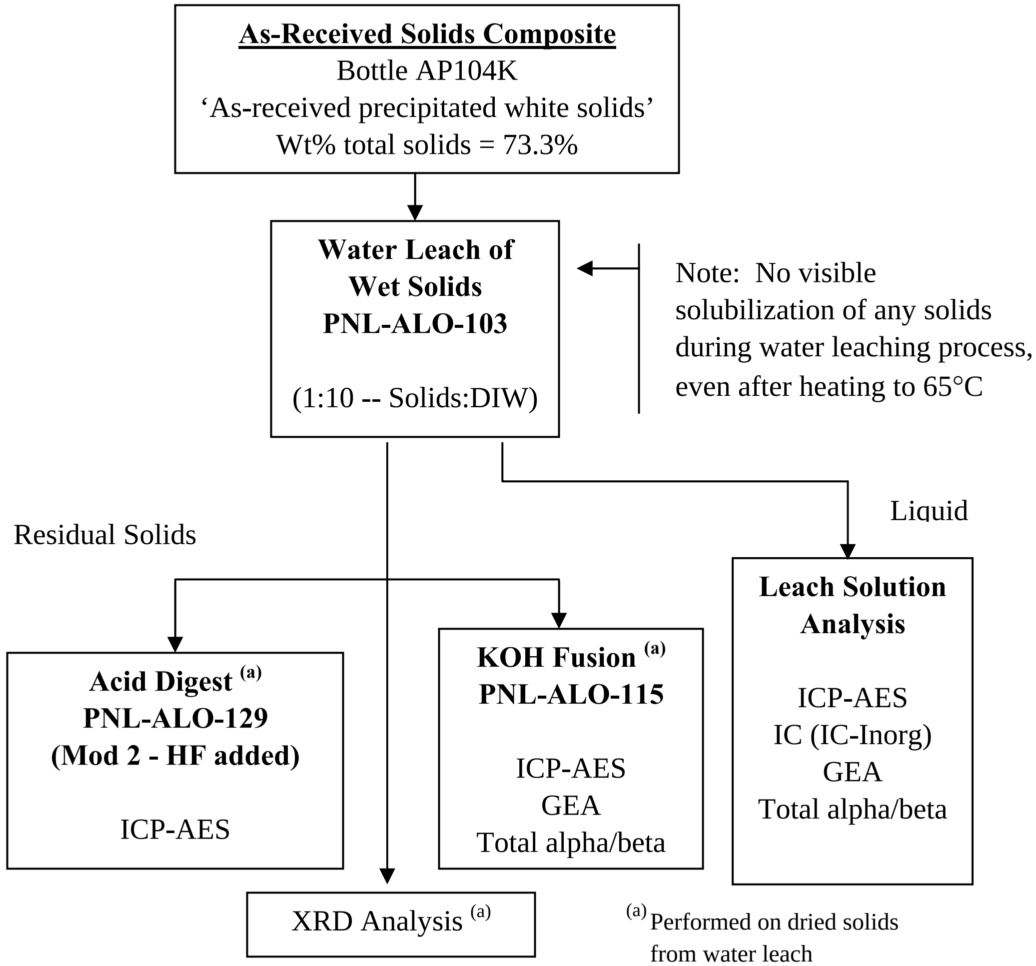
Tables: none – no results reported

Following extraction of the AP-104 supernatant in the SAL with both methylene chloride and butanol for the organic phosphate analysis, the resulting extracts were transferred to the Building 329 Facility for analysis. A five-point calibration curve was constructed for both diphenylphosphate (surrogate compound) and D2EHP. The supernatant samples and QC samples were analyzed per test plan TP-RPP-WTP-047, *Identification and Quantification of D2EHP in Tank Wastes*. This method describes a derivatization technique using diazomethane, followed by measurement using GC/FID.

The sample and QC data obtained from this method were unacceptable and no results are reported. Similar unacceptable results were obtained for supernatant samples from Tank 241-AZ-101 (Urie et al. 2002). The problems encountered are potentially due to critical pH adjustment, poor extraction, and/or incomplete and variable derivatization, and they are compounded by the necessity of performing the pH adjustment and extraction operations in a remote handling facility (i.e., SAL). The analysis method therefore proved to be unreliable for the analysis of D2EHP, and no further work was undertaken to evaluate the failure. If this analyte is required, it will be necessary to undertake method development or modification activities, followed by method validation for tank waste materials.

8.0 As-Received Solids

Following the characterization of the AP-104 supernatant composite, BNI requested that PNWD perform investigative analyses to determine the composition of the as-received solids; i.e., the solids retained following decanting of the as-received supernatant for characterization and process testing (See Figure 3.1). These investigative analyses were authorized by Test Exception 24590-WTP-TEF-RT-02-092. The scope of solids characterization was only to provide enough information to determine what the precipitated solids were. Only major quality control issues are discussed below, the full and complete QC information is included in the Appendices. Figure 8.1 provides a flowchart, which identifies how the as-received solids were processed and analyzed. The intent of the investigation was to identify the white precipitated material observed in the sample bottle received from the 222-S Laboratory, since no sampling or COC documentation indicated the presence of any solids. The investigative analytical work was conducted per ASRs 6670.00, 6670.01, and 6670.02 (Laboratory Sample ID 03-0472, AP104K Solids).



[a] Performed on dried solids from water leach

Figure 8.1. Sampling and Analysis Flowchart for As-received Solids

The as-received solids were water leached per PNL-ALO-103, *Water Leach of Sludges, Soils, and other Solid Samples*, but produced no visible dissolution of the solids. The water leach solution was decanted from the water-insoluble residual solids (hereafter referred to as residual solids) and analyzed for metals by ICP-AES, gamma emitters by GEA, total alpha, and total beta. The residual solids were acid digested per PNL-ALO-129, *HNO_3-HCl Acid Extraction of Solids Using a Dry-block Heater*. The residual solids did not exhibit any visible solubility during a nitric acid and hydrochloric acid digestion process (equivalent of 1 mL of HNO_3 and 1 mL of HCl used per 0.5 g of solids). Solubility was only accomplished after the addition of hydrofluoric acid (1 mL), followed by heating to 95°C (i.e., PNL-ALO-129 Mod 2 processing). The residual solids were also prepared by fusion procedure PNL-ALO-115, *Solubilization of Metals from Solids Using KOH-HNO_3 Fusion*.

Table 8.1 provides a summary of the chemical and radionuclide analyses of the AP-104 as-received solids. Since the limited analyses were to primarily identify the solids composition, only those analytes detected above the EQL in one of the sample measurements (i.e., supernatant, water-leached as-received solids, or residual solids) are presented. Total alpha was measured but not detected in either the as-received solids or the residual solids as a MDL of 1E+0 μCi/g. The results for the XRD analysis of the residual solids are present in Figure 8.2 and Figure 8.3; the 'stick figure' at the bottom of the sample diffraction pattern is from International Centre for Diffraction Data card 33-18 [$Al(OH)_3$ gibbsite]. All analysis results for the as-received solids results are consistent with $Al(OH)_3$, with numerous trace analytes and radionuclides. The analytical summary reports for the as-received solids are included in Appendix E.

Using the TDS and density from the AP-104 supernatant and wt% solids from the AP-104 as-received solids, the interstitial liquid composition has been mathematically stripped from the wet as-received solids in order to better estimate the insoluble as-received solids composition and trace element content. The stripping of the interstitial liquids was performed as detailed in Section 8.6 of Urie, et al. (2002). Also, an estimate of the concentration of the AP-104 'slurry' (i.e., as-received solids + supernatant) is provided in Table 8.1 based on the calculated total as-received insoluble solids mass (i.e., 37.9 g) and the calculated total liquid mass (i.e., 5477 g supernatant plus interstitial liquid.). The as-received insoluble solids contributed about 0.7 wt% to the total received from 222-S Laboratory (not counting losses due to transferring from bottles).

Most notable from Table 8.1 is the fact that many analytes appear to be only in the as-received solids (e.g., Ba, Be, Cu, Mn, Sr, and Zr). Although some analytes appear to have reasonably high concentrations in the insoluble solids, this may be an artifact of the supernatant stripping calculation (i.e., high uncertainty in subtracting values of similar magnitude). If the as-received solids are added to the as-received supernatant results to estimate a 'slurry' concentration, the concentration of Al, Ca, Fe, Pb, and Si are significantly increased, with Al contributing by far the greatest mass.

QC Issues: Of the limited analyses performed on the AP-104 as-received solids, only one QC issue was identified, resulting in two QC failures; one of two fusion PBs prepared with the residual solids exceeded the QC acceptance criteria for the GEA ^{137}Cs and total beta analysis. The PB contamination appeared to be from ^{137}Cs with the PB being about 12% of the ^{137}Cs and 6% of the total beta result. The other fusion PB showed negligible contamination. One of the PB exhibited high contamination levels; however, the sample results for ^{137}Cs (RSD=8%) and total beta (RSD=4%) were reasonably reproducible. Both these QC failures had the same cause, namely the high ^{137}Cs in the one fusion PB. PNWD and BNI concluded the impact of this QC failure is negligible. The contaminated PB was discarded and not included in any calculation (e.g., calculating the AP-104 ‘slurry’ concentration). To confirm the ^{137}Cs results and validate the decision to discard the high PB, GEA was performed on two PBs and one of the residual solids samples dissolved by acid digestion. The acid-digest sample (3.4E+1 μCi/g) compared well with the fusion sample (3. 6E+1 μCi/g). Both acid-digested PBs were free of contamination.

Table 8.1. Summary of AP-104 As-Received Solids Results

	Water Leached As-received & Residual Solids Analysis							Wet As-Received Solids(f)	As-received Supernatant		As-received Insoluble Solids(h)	AP-104 Slurry(i)	Diff(j)
	Water Leach		Residual Solids			Sample Inventory							
	Results(a)		Results(b)			Water Leach(d)	Residual Solids(e)		Results(g)				
Analyte	µg/g	DF	µg/g	A/F(c)	DF	Total µg	Total µg	µg/g	µg/g	DF	µg/g	µg/g	%
Al	5,370		313,000	A		17,300	526,000	169,000	10,100		282,000	11,900	19
B	26		--	F	U	82	ND	26	32		21	32	-0.2
Ba	0.16	J	5.2	A		0.52	8.7	2.9	ND	U	4.9	0.034	♦
Ca	83		810	A		270	1,360	510	57		830	62	9
Cd	0.82	J	11	A		2.7	18	6.3	1.4	J	10	1.5	4
Cr	230		420	A		740	710	450	370		500	370	0.2
Fe	1.5	J	170	A		4.8	290	92	6.5		150	7.5	16
K	1,290		1,730	A	J	4,140	2,900	2,190	1,470		2,700	1,480	0.6
Na	75,300		18,600	A		242,000	31,200	85,000	105,000		71,000	104,000	-0.2
Ni	22		230	A		70	380	140	31		220	33	4
P	910		360	A		2,920	600	1,100	1,260		980	1,260	-0.2
Pb	10	J	740	F	J	33	1,240	400	6.5	J	670	11	70
W	49		51	A		160	85	75	65	J	83	65	0.2
Be	0.013	J	1.5	A		0.042	2.6	0.81	ND	U	1.4	0.010	♦
Cu	1.8	J	590	F		5.7	980	310	ND	U	530	3.6	♦
Mn	0.14		7.5	A		0.43	13	4.0	ND	U	6.9	0.047	♦
Mo	36	J	15	A	J	120	24	43	46		42	45	-0.1
Si	39		2,090	A		120	3,500	1,130	105		1,860	120	12
Sr	0.23	J	8.6	A		0.74	14	4.7	ND	U	8.1	0.056	♦
Zr	0.52	J	16	A		1.7	27	9.0	ND	U	15	0.11	♦
Cl	3,180		NM			10,200	NM	3,180	4,280		2,390	4,260	-0.3
NO_2	38,700		NM			124,000	NM	38,700	54,400		27,400	54,200	-0.3
NO_3	63,300		NM			204,000	NM	63,300	87,300		46,200	87,000	-0.3
PO_4	2,500		NM			8,050	NM	2,500	4,320		1,200	4,300	-0.5
SO_4	1,640		NM			5,260	NM	1,640	2,440		1,070	2,430	-0.4
C_2O_4	900		NM			2,880	NM	900	710	J	1,030	710	0.3
	µCi/g		µCi/g			Total µCi	Total µCi	µCi/g			µCi/g	µCi/g	
^{60}Co	6.0E-3		ND	F	U	1.9E-2	ND	6.0E-3	7.4E-3		5.0E-3	7.3E-3	-0.2
^{137}Cs	1.1E+2		3.6E+1	F		3.4E+2	6.0E+1	1.2E+2	1.5E+2		1.1E+2	1.5E+2	-0.2
Beta	9.8E+1		1.0E+2	F		3.1E+2	1.7E+2	1.5E+2	1.6E+2		1.4E+2	1.6E+2	-0.1

NM = Analyte not measured; ND = Analyte not detected above MDL.

DF = data flag. See Section 6.1 for data flag definitions. No entry in DF indicates analyte measured above EQL and no data qualifiers apply.

♦ = Concentration entirely from as-received solids

(a) PB corrected result from water leach of as-received solids on a per g of wet as-received solids.

(b) PB corrected results for residual solids on a per g of dried water-leached residual solids.

(c) A/F; Either acid digest (A) or KOH fusion (F) result used for water-leach residual solids.

(d) Total µg or µCi from water leach solution = (water leach results/10.84) times average 32.9 mL leach volume. 10.84 = factor to convert from per g of wet as-received solids to per mL of leach solution.

(e) Total µg or µCi from residual solids = residuals solids results times average 1.68 g of dried solids.

(f) Results of wet as-received solids = sum of total µg or µCi from water leach and residual solids divided by average 3.22 g wet as-received mass subjected to the water leach.

(g) PB corrected average supernatant results from Tables 7.2 and 7.3 divided by average supernatant density 1.272 g/mL.

(h) Insoluble solids results; supernatant stripped from wet as-received solids per PNWD 3215 Section 8.6 (Urie et al. 2002).

(i) Calculated 'Slurry' concentration based on insoluble solids and supernatant composition. Assumes 5477 g liquid (supernatant and interstitial liquid) and 37.9 g insoluble solids; total mass process = 5515 g.

(j) Difference between supernatant and ‘slurry’ concentration prior to rounding; 1 digit used for <10%, 2 digits for ≥10%.

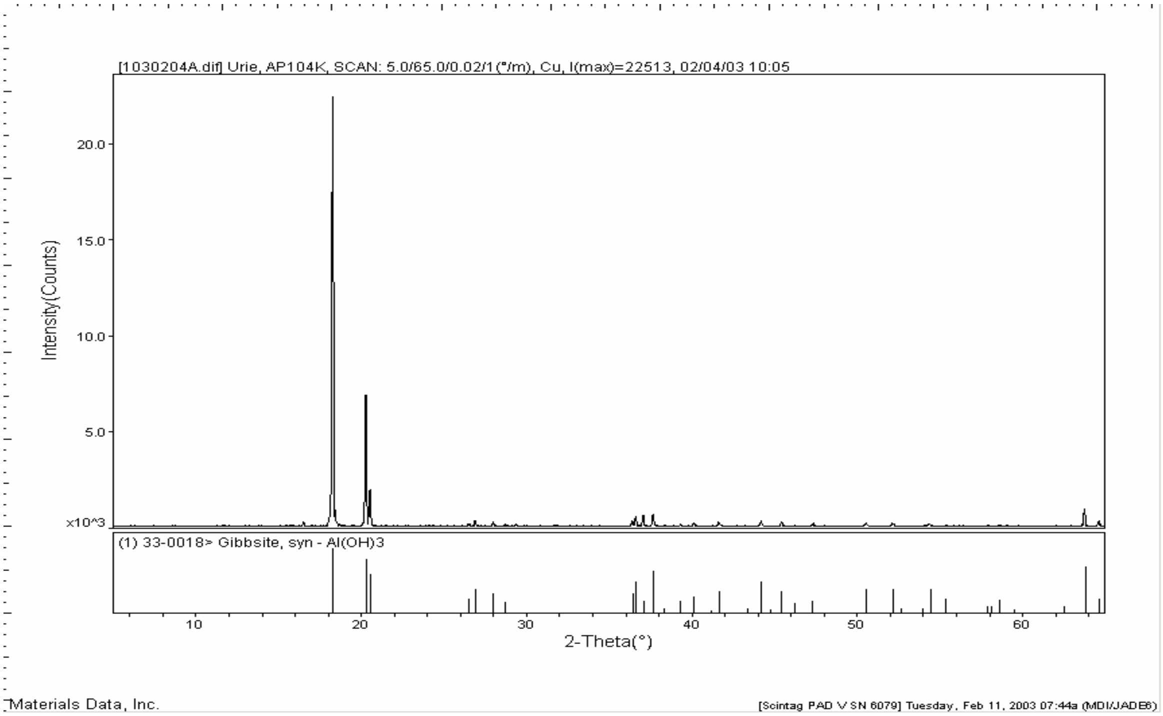


Figure 8.2. AP-104 Water-Leached Residual Solids XRD Results

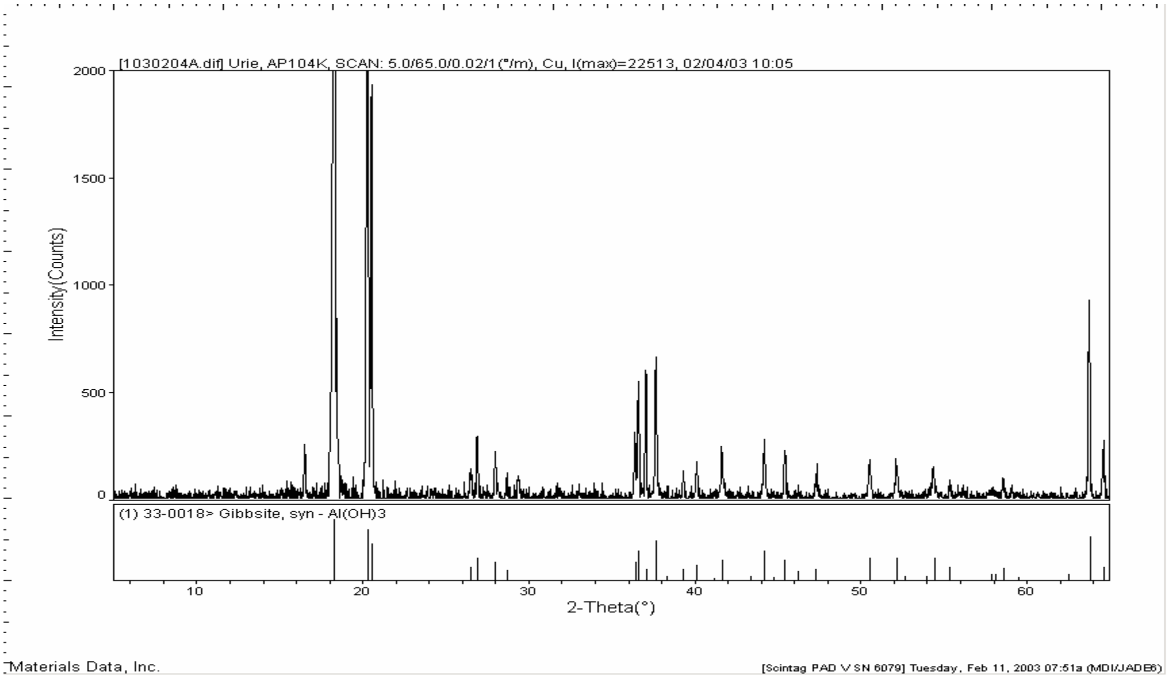


Figure 8.3. AP-104 Water-Leached Residual Solids XRD Results – Expanded Intensities

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