PNWD-2464
BNFL-RPT-005 Rev. 0

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

LETTER REPORT

AN-107 Entrained Solids – Solubility Versus Temperature

Gregg J. Lumetta
Ralph C. Lettau

August 1999

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

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Contents

1.0 Introduction

BNFL, Inc. (BNFL) is under contract with the U.S. Department of Energy, River Protection Project (DOE-RPP) to design, construct, and operate facilities for the treatment of wastes stored in the single-shell and double-shell tanks at the Hanford Site, Richland Washington. BNFL has contracted with Battelle Pacific Northwest Division to conduct tests to verify and validate the BNFL waste treatment process. The DOE-RPP has provided samples from tanks 241-AW-101, 241-AN-107, 241-C-104, and 241-C-106 to BNFL for this purpose.

This report describes the results of a test conducted by Battelle to assess the solubility of the solids entrained in the diluted AN-107 low-activity waste (LAW) sample. BNFL requested Battelle to dilute the AN-107 sample using sodium hydroxide and de-ionized water to mimic expected plant operating conditions. BNFL further requested Battelle to assess the solubility of the solids present in the diluted AN-107 sample versus temperature conditions of 30, 40, and 50°C. BNFL requested these tests to assess the composition of the LAW supernatant and solids versus expected plant-operating conditions. The work was conducted according to test plan BNFL-TP-29953-7, Rev. 0, *Determination of the Solubility of LAW Entrained Solids*. Some deviations from the test plan were required due to the nature of the AN-107 material. These deviations will be discussed in the Experimental Section.

2.0 Personnel

The Battelle personnel and their responsibilities in performing this test are given below.

Staff Member	Responsibilities
G.J. Lumetta	Cognizant scientist. Prepared test plan and designed experiment. Supervised performance of the test. Prepared analytical service request. Interpreted data and reported results.
R.C. Lettau	Hot cell technician. Performed test.
M.W. Urie	Managed chemical and radiochemical analytical work.
B.M. Rapko	Technical reviewer.
K.P. Brooks	Task Leader.

3.0 Experimental

Sample Description. The sample used in this test was labeled as AN-107 ST. The homogenization, dilution, caustic adjustment, and sub-sampling of the as-received AN-107 sample were described by Urie 1999. The total volume of sample AN-107 ST was 24 mL.

Because the material was very dark, it was not possible to accurately determine the volume of settled solids in the sample.

Apparatus. The apparatus used consisted of an aluminum heating block placed on a hot plate/stirrer. The hot plate/stirrer was modified so that separate power could be applied to the heating and stirring functions. This allowed for continuous stirring, while the hot plate was powered by a temperature controller. The temperature controller used was a J-KEM Model 270 (J-KEM Electronics, Inc., St. Louis, MO). This temperature controller consists of two separate circuits. One is the temperature control circuit, while the other serves as an over-temperature device, which shuts down the system if a preset temperature is exceeded. The set point for the over-temperature circuit was set at 60°C for this test. A dual K-type thermocouple (model number CASS-116G-12-DUAL, Omega Engineering, Stamford, CT) was used to provide inputs to the temperature controller and over-temperature circuits. Both the J-KEM Model 270 and the dual thermocouple were calibrated before use. The aluminum heating block contained two wells. A vial containing water was placed in one of the wells, with the thermocouple wedged between this vial and the aluminum block. The vial containing the sample was placed in the other well.

Procedure.[a] The sample in AN-107 ST was mixed by swirling. The homogenized slurry was then transferred to a 30-mL high-density polyethylene (HDPE) vial (this vial also contained a Teflon®-coated magnetic stir bar). There were several large (2 to 3 mm) particles that did not transfer readily. A spatula was used to transfer these larger particles into the HDPE vial. The sample was heated and stirred at 30 ± 2 °C for 4 h. An attempt was made to filter a 2-mL aliquot of the slurry through a 0.45-μm nylon syringe filter. The filter immediately plugged. The experiment was suspended for several days; during this hiatus, the sample stood at ambient temperature (~25°C).

After consultation with BNFL, the 0.45-μm nylon filters were replaced with 1.2-μm nylon filters. The sample was heated and stirred at 30 ± 2 °C for 23 h.[b] Two aliquots (2-mL each) were taken for analysis. Each aliquot was filtered through a 1.2-μm nylon syringe filter that had been preheated by immersion in a boiling water bath. The filter was preheated to avoid precipitation during the filtration step. The filtration was still quite difficult and took 10 to 15 minutes to achieve (the filter probably cooled to ambient temperature during this time). After plugging of the filter membrane, additional solution could be filtered by pulling back on the syringe filter which appeared to pull some solid back off the membrane, which in turn allowed more solution to pass. (The mixture was also difficult to filter at both 40 and 50°C.)

The temperature was increased to 40 ± 2 °C and the sample was stirred for 25 h. The mixture was sampled in the same manner as described above with the 1.2-μm filters. The temperature was increased to 50 ± 2 °C and the sample was stirred for 4 h. Again, the mixture was sampled in the same manner as described above. Because of the small volume of samples available (< 2

(a) The test plan and the associated procedural notes are included as Appendix A to this report.

(b) The test plan required the AN-107 sample to be maintained at temperature for at least 1 hour before sampling. For convenience, the sample was maintained at 30 and 40°C overnight, whereas the equilibration at 50°C was conducted within one work day. It should be noted that this test was not designed to address the kinetics of dissolution. Kinetics could potentially be important regarding the phenomena investigated here, but separate testing would be required to address this issue.

mL), only the following analytical procedures were performed: acid digestion, ICP/AES, and total alpha. Furthermore, there had been apparent evaporation of one of the aliquots taken at 40°C and one of the ones taken at 50°C before the samples were removed from the shielded analytical facility. These two aliquots were not processed. Further evaporation was evident for some of the other aliquots prior to acid digestion. Because of this, the analyses were reported on a per gram basis for each aliquot. These data were then normalized to the Na content as discussed below.

4.0 Results

Tables 1, 2, and 3 present the concentrations of various waste components at 30, 40, and 50°C, respectively. As mentioned above, it was suspected that some of the samples partially evaporated prior to analysis. This evaporation was indicated by significant formation of solids in the sample coupled with relatively small liquid volumes. Because of this, it was impossible to directly compare the measured concentration values. So that the concentrations could be compared, they were normalized to the Na content. For example at 40°C, the Al concentration was 3,100 µg/g and that for Na was 136,000 µg/mL. Thus, there were (1,000,000 µg/g x 3,100 µg Al/g ÷136,000 µg Na/mL) = 22,794 µg Al/g Na in the solution at 40°C. Note that this treatment of the data assumes that the Na concentration does not change with increasing temperature.[a]

Table 4 shows the changes in the concentrations relative to those at 30°C. Concentrations for most of the analyzed metals showed slight concentration increases (5 to 8%) when the temperature was changed from 30 to 40°C. But further concentration increases generally did not occur when the temperature was raised to 50°C. Iron is perhaps an exception to this in that further dissolution of Fe occurred between 40 and 50°C. Barium, La, Si, Ti, and Zn also indicted slight increases between 40 and 50°C, but the concentrations of these components are low and are thus subject to greater experimental uncertainty.

Because duplicate analyses were not done on the 40 and 50°C samples, a rigorous analysis of the statistical meaning of the data was not performed. But based on the standard deviations given in Table 1 (and assuming analogous uncertainties for the values in Tables 2 and 3), most of the increases (e.g., Al, Cr, Fe, and P) can be viewed as meaningful.

The total alpha analyses (Table 1 through 3) indicated that the AN-107 waste is a transuranic (TRU) waste with TRU concentrations of ~0.3 µCi/g which is well over the 0.1 µCi/g NRC Class C LLW limit for TRU. The TRU concentration appeared to drop when the temperature was raised from 30 to 40°C, but increased to about the original 30°C value when the temperature was increased to 50°C. It is doubtful that these changes are statistically significant.

---

[a] This assumption is perhaps not strictly true. In the case of the AW-101 LAW sample, a 1.7% increase in the Na concentration was observed when the temperature was increased from 30 to 50°C (Lumetta, Lettau, and Piepel 1999). Clearly, this assumption introduces another uncertainty into the interpretation of the results. Because of this, the results reported in Table 4 should be viewed as qualitative.

5.0 Conclusions

The AN-107 sample was very difficult to filter through 0.45-μm nylon membranes. Improved filtration was achieved with 1.2-μm membranes, but the filtration was still very difficult. Because filtration took several minutes, it is likely that significant temperature changes occurred during the course of the filtration. The impact of this on the results is unknown. Furthermore, several of the aliquots taken for analysis underwent evaporation prior to beginning the analytical procedures. Because of this, the analytical data was reported in terms of units per gram of sample and these values were normalized to the Na content in the sample. This introduced an additional uncertainty in the results because this treatment of the data requires the assumption that the Na concentration does not change with increasing temperature.

Concentrations for most of the analyzed metals showed slight concentration increases (5 to 8%) when the temperature was changed from 30 to 40°C. But further concentration increases generally did not occur when the temperature was raised to 50°C. The AN-107 waste is a transuranic (TRU) waste with soluble TRU concentrations of ~0.3 μCi/g. The TRU concentration did not appear to change significantly with increasing temperature.

6.0 References

Lumetta, G.J., R.C. Lettau, and G.F. Piepel. 1999. *AW-101 Entrained Solids – Solubility Versus Temperature*, PNWD-2466, Battelle Pacific Northwest Division, Richland, Washington.

Urie, M.W. et al. 1999. *Inorganic and Radiochemical Analysis of AW-10 and AN-107 "Diluted Feed" Materials*, PNWD-2463, Battelle Pacific Northwest Division, Richland, Washington.

Table 1. AN-107 Component Concentrations in Solution at 30°C.

	µg or µCi/g sample[a]		µg or µCi/g Na[b]			
Analyte	AN107-SOL-30-1	AN107-SOL-30-2	AN107-SOL-30-1	AN107-SOL-30-2	Mean	Std. Dev.
Total Alpha	0.289	0.321	2.17	2.24	2.21	0.05
Ag	< 0.29	< 0.30	< 2	< 2	< 2	--
Al	2900	3000	21805	20979	21392	584
Ba	2.33	2.47	17.5	17.3	17.4	0.2
Ca	330	341	2481	2385	2433	68
Cd	35.8	36.9	269	258	264	8
Co	(2.6)	(2.7)	19.5	18.9	19.2	0.5
Cr	106	110	797	769	783	20
Cu	15.4	16.0	116	112	114	3
Fe	709	752	5331	5259	5295	51
K	894	931	6722	6510	6616	149
La	14.3	15.0	108	105	106	2
Mg	< 2.0	< 2.0	< 15	< 14	< 14	--
Mn	55.7	58.7	419	410	415	6
Mo	< 0.6	< 0.6	< 4	< 4	< 4	--
Na	133000	143000	--	--	--	
Ni	289	298	2173	2084	2128	63
P	375	389	2820	2720	2770	70
Pb	181	189	1361	1322	1341	28
Si[c]	55.3	40.2	416	281	348	95
Ti	(0.47)	(0.49)	3.5	3.4	3.5	0.1
U	(77)	(83)	579	580	580	1
Zn	11.0	11.4	82.7	79.7	81.2	2.1
Zr	32.3	33.7	243	236	239	5

(a) Concentrations in the sample on a per gram basis. For radionuclides, the concentration units are µCi/g sample; all other components are in units of µg/g sample. Values in parentheses are near the analytical detection limit.
(b) Concentrations values normalized to the amount of Na in the sample. For radionuclides, the concentration units are µCi/g Na; all other components are in units of µg/g Na. Values in parentheses are near the analytical detection limit.
(c) The process blank had a relatively high Si content of 44.8 µg/g sample.

Table 2. AN-107 Component Concentrations in Solution at 40°C.

	AN107-SOL-40-1	
Analyte	µg or µCi/g sample[a]	µg or µCi/g Na[b]
Total Alpha	0.28	2.06
Ag	< 0.35	< 3
Al	3100	22794
Ba	2.44	18
Ca	351	2581
Cd	38.0	279
Co	(2.8)	(21)
Cr	113	831
Cu	16.6	122
Fe	739	5434
K	963	7081
La	15.1	111
Mg	< 2.3	< 17
Mn	57.9	426
Mo	< 0.7	< 5
Na	136000	--
Ni	307	2257
P	396	2912
Pb	192	1412
Si[c]	56.6	416
Ti	(0.51)	(4)
U	(85)	(625)
Zn	11.6	85
Zr	33.3	245

(a) Concentrations in the sample on a per gram basis. For radionuclides, the concentration units are µCi/g sample; all other components are in units of µg/g sample. Values in parentheses are within 10 times the analytical detection limit.

(b) Concentrations values normalized to the amount of Na in the sample. For radionuclides, the concentration units are µCi/g Na; all other components are in units of µg/g Na.

(c) The process blank had a relatively high Si content of 44.8 µg/g sample.

Table 3. AN-107 Component Concentrations in Solution at 50°C.

	AN107-SOL-50-2	
Analyte	µg or µCi/g sample[a]	µg or µCi/g Na[b]
Total Alpha	0.327	2.22
Ag	< 0.47	< 3
Al	3320	22585
Ba	(2.8)	(19)
Ca	376	2558
Cd	40.5	276
Co	(3.0)	(20)
Cr	123	837
Cu	17.8	121
Fe	833	5667
K	1030	7007
La	16.6	113
Mg	< 3.1	< 21
Mn	63.3	431
Mo	< 0.9	< 6
Na	147000	--
Ni	328	2231
P	420	2857
Pb	207	1408
Si[c]	79.9	544
Ti	(0.58)	(4)
U	(90)	(612)
Zn	13.7	93
Zr	36.0	245

(a) Concentrations in the sample on a per gram basis. For radionuclides, the concentration units are µCi/g sample; all other components are in units of µg/g sample. Values in parentheses are within 10 times the analytical detection limit.
(b) Concentrations values normalized to the amount of Na in the sample. For radionuclides, the concentration units are µCi/g Na; all other components are in units of µg/g Na.
(c) The process blank had a relatively high Si content of 44.8 µg/g sample.

Table 4. Concentration Changes Relative to 30°C[a]

	Change, %[b]	
Analyte	40°C	50°C
Total Alpha	-6.8	0.7
Ag	(c)	(c)
Al	6.6	5.6
Ba	3.1	9.5
Ca	6.1	5.1
Cd	6.0	4.5
Co	7.1	6.2
Cr	6.1	6.8
Cu	7.2	6.4
Fe	2.6	7.0
K	7.0	5.9
La	4.5	6.3
Mg	(c)	(c)
Mn	2.7	3.9
Mo	(c)	(c)
Na	(c)	(c)
Ni	6.1	4.8
P	5.1	3.1
Pb	5.3	5.0
Si[d]	19.4	56.0
Ti	7.8	13.4
U	7.8	5.6
Zn	5.0	14.8
Zr	2.3	2.4

(a) Values in parentheses are near the analytical detection limit.

(b) The percent change is given by: %Change = $100*(C_T - C_{30})/C_{30}$, where C_T is the concentration at temperature T (40 or 50°C) and C_{30} is the concentration at 30°C.

(c) Analyte not detected.

(d) The values for Si should be veiwed with caution because of the high process blank.

Appendix A. Test Plan

Work place Copy

PNNL Test Plan

Document No.: BNFL-TP-29953-7
Rev. No.: 0

Title: Determination of the Solubility of LAW Entrained Solids

Work Location: RPL/SAL

Author: GJ Lumetta

Effective Date: December 14, 1998
Supersedes Date: New

Use Category Identification: Mandatory

Identified Hazards:
__ Radiological
__ Hazardous Materials
__ Physical Hazards
__ Hazardous Environment
__ Other:

Required Reviewers:
X Technical Reviewer
__ Building Manager
__ Radiological Control
__ ES&H
X Quality Engineer
X Other: Client
X Other: Project Manager
X Other: RPL Manager

Are One-Time Modifications Allowed to this Procedure?
x Yes __ No

NOTE: If Yes, then modifications are not anticipated to impact safety. For documentation requirements of a modification see SBMS or the controlling Project QA Plan as appropriate.

On-The Job Training Required? ____ Yes or _x_ No

FOR REVISIONS:

Is retraining to this procedure required? ___ Yes ___ No
Does the OJT package associated with this procedure require revision to reflect procedure changes? __ Yes__ No__ N/A

Approval:

	Signature	Date
Author	Gregg J. Lumetta	1/5/99
Technical Reviewer	Brian Lyska	1-11-99
RPL Manager	[signature]	1-12-99
Project Manager	[signature]	1/11/99
RPG QE	[signature]	1/12/99
BNFL	[signature]	1/19/99

Applicability

This test plan is to be used to determine the effect of temperature on the solubility of entrained solids in the BNFL LAW samples. The work will be conducted in the SAL hot cells. The work will be conducted by Radiochemical Processing Group staff. This work is being done as part of the Technical Support to BNFL for Phase 1B project.

Test Objectives

Justification: This activity supports confirmation of the process sequence, equipment performance and design basis for the LAW entrained solids removal process. BNFL must complete research and testing activities conducted to confirm system design bases before March 1999.

Objective: Determine the components in solution at 30, 40, and 50°C and their concentrations. Infer from the solution composition the components dissolved in going from 30 to 40°C and from 40 to 50°C.

Definitions

BNFL	British Nuclear Fuels Ltd.
HDPE	High-density polyethylene
RPL	Radiochemical Processing Laboratory

Emergency Response

In the event of building audible alarms (e.g., fire or criticality) personnel should proceed in accordance with the RPL Building Emergency Procedure. If time permits, ensure that test materials are secured from spilling prior to exiting the area.

Quality Control

Quality assurance for work conducted under this Test Plan is governed by the Standards-Based Management System (SBMS). The quality control for each analysis will be established per Quality Assurance Plan MCS-033. MCS-033 specifies the minimum calibration and verification requirements for analytical systems, as well as batch processing quality control samples to monitor preparations (i.e., blanks, duplicates, matrix spikes, and laboratory control standards).

A work place copy of this document shall be present at the work location. Specific information regarding each test (e.g., sample numbers) will be recorded on the work place copy and kept as project records.

Hand written changes or corrections made to the work place copy will be made by means of a single line-out. Such changes or corrections shall be initialed and dated by the staff member making the change and by the cognizant scientist.

Equipment Description

A standard laboratory hot plate/magnetic stirrer will be used for this test. An aluminum heating block will be placed on the hot plate/stirrer to heat the sample. The apparatus will be equipped

with two thermocouples. One of the thermocouples will be connected to a temperature controller, while the other will be connected to an over-temperature shut-off device. The latter will be used to ensure the sample is not over heated, which could result in loss of sample.

Prerequisites

Staff performing the work must read and understand the entire test plan prior to beginning work.

The following are items that should be staged prior to start of the test.

30-mL HDPE bottle
20-mL HDPE vial (6)
Hot plate/stirrer
Aluminum heating block
Temperature controller with temperature read-out
Over-temperature shut-off device
0.45-µm nylon syringe filters (6)
5-mL syringes (6)
Adjustable 5-mL pipette
Boiling water bath
Small plastic bag

The temperature controller shall be calibrated by maintenance services. Record the following information regarding the temperature controller used.

Calibration ID: 02093
Calibration Date: 1-12-99
Expiration Date: 1-2000

Work Instructions

Note
Where practical, catch pans should be used when working with the tank waste samples, so that they can be recovered if spilled.

1. Prepare the sample vials according to the following table. All vials should be HDPE.

Sample ID[a]
AW 107 -SOL-30-1
AW107 -SOL-30-2
AW 107 -SOL-40-1
AW107 -SOL-40-2
AW 107 -SOL-50-1
AW107 -SOL-50-2

(a) The prefix to the sample IDs should be the tank number; e.g. "AW101."

this ~~insert~~ seemed to pull some solids back off the filter which allowed more liquid to go through.

(a) Per agreement with BNFL, we attempted to filter through a 1.2-μm nuclepore membrane (i.e., steps 8–10). We were able to filter ~1.5 mL through before the filter plugged. With further work we were able to filter nearly all the 2-mL slurry. It seemed to help if the syringe filter was periodically shaken.

2. Label a 30-mL HDPE bottle as "AN107-SOL-TEST" (_____ = tank number) and place a magnetic stir bar in this bottle.

   Place 25 mL of deionized water in the bottle and mark the liquid level. Empty the water from the bottle.

3. Mix the stock LAW sample to give a homogeneous slurry → AN-107 ST

4. Transfer approximately 25 mL of the homogenized LAW slurry to AN107-SOL-TEST; use the 25-mL mark established in step 2 as a guide

   Transferred entire AN-107 ST sample into AN107-SOL-TEST. There were some chunky pieces of solid that did not readily pour out of AN-107 ST these solids were scraped out of AN-107 ST with a pipet + transferred to AN107-SOL-TEST. Just quite up to the 25-mL mark. Probably more like 22 or 23 mL.

5. Place AN107-SOL-TEST into an aluminum heating block thermostatted at 30°C

6. Stir the contents of AN107-SOL-TEST

7. Once the temperature has equilibrated at 30°C, stir the sample for at least 1 h

   for attempt through 1.2-μm filter.

   3/1/99 ~9:30
   3/2/99 8:45

   Start date/time: 2/24/99 10:20
   Stop date/time: 2/24/99 14:35

8. Preheat two syringe/filter assemblies by placing them in a plastic bag and submersing the plastic bag with the syringe/filters into a boiling water bath

9. Withdraw a 2-mL aliquot of the slurry and filter into vial AN107-SOL-30-1

   The filter immediately plugged. Only a couple of drops went through. Poured material in syringe back into AN107-SOL-TEST.

10. Withdraw a second 2-mL aliquot of the slurry and filter into vial AN107-SOL-30-2

    Continued to stir at 30°C. 2/24/99 14:45 → Turned off shortly thereafter. (See (a))

11. Adjust the temperature of aluminum heating block assembly to 40°C

12. Once the temperature has equilibrated at 40°C, stir the sample for at least 1 h

    Start date/time: 3/2/99 9:15
    Stop date/time: 3/3/99 10:40

13. Preheat two 1.2-μm syringe/filter assemblies by placing them in a plastic bag and submersing the plastic bag with the syringe/filters into a boiling water bath

    → After 0.5–1.0 mL had filtered it looked like material was leaking through the seal in the filter assembly. Pulled solution back into syringe & put back in AN107-SOL-TEST.

14. Withdraw a 2-mL aliquot of the slurry and filter into vial AN107-SOL-40-1

15. Withdraw a second 2-mL aliquot of the slurry and filter into vial AN107-SOL-40-2

    → Same thing happened with the second filter. Used two more syringes to get more material filtered into -40-1 & -40-2.

16. Adjust the temperature of aluminum heating block assembly to 50°C

17. Once the temperature has equilibrated at 50°C, stir the sample for at least 1 h

    Start date/time: 3/3/99 ~11:30
    Stop date/time: 3/3/99 15:20

18. Preheat two 1.2-μm syringe/filter assemblies by placing them in a plastic bag and submersing the plastic bag with the syringe/filters into a boiling water bath

MJ.2. 3/3/99

Same deal with plugging of the filters.

19. Withdraw a 2-mL aliquot of the slurry and filter into vial AN107 -SOL-50-1

20. Withdraw a second 2-mL aliquot of the slurry and filter into vial AN107 -SOL-50-2

21. The samples collected during the test are to be submitted for the following analyses: IC(anions), TOC/TIC, acid digestion, ICP/AES, ICP-MS(Tc-99), Sr-90, total alpha, total uranium, and GEA. The cognizant scientist will prepare the required ASR.

Note

With a small amount (~1 mL) of residual AN107 sample. => Tried to filter through a 5.0-μm filter. Difficult to filter, even though this membrane.

S.A.C.
3/3/99

Appendix B. Raw Data

Analytical Chemistry Laboratory (ACL) Analytical Services Request (ASR)

(Cover Page ... information applicable to all samples in series)

Requested By: Gregg J. Lumetta (Print Name) | Gregg J. Lumetta 3/5/99 (Signature/Date) | 376-6911 (Phone) | P7-25 (MSIN)

Requester - Please Complete All Fields In This Section, Unless Specified "Optional" or ASR is a Revision

Request ID (optional): _____

PNL Project Number (if known): 29953

Work Order/Pkg.: W48482

Cost Estimate ($): _____

Protocol Requirement: X None __RCRA __CERCLA, or

Other (specify): _____

Hold Time Requirement: X None __RCRA __CERCLA, or

Other (specify): _____

TPA Support: X No, or

Milestone No.: _____

QA Plan: X MCS-033, or

Other ACL QA Plan (specify): _____

Additional QA Requirements: X No, or

Reference Doc.: _____

ACL COC Req'd (PNL-ALO-010): X No __Yes

Sample Storage Requirements: X No __Refrigerate, or

Other (specify): _____

Date Sampled (optional): _____

Time Sampled (optional): _____

Matrix: __Samples vary (specify on Request Page), or

Liquid: X Aqueous __Organic __Multi-phasic

Solid: __Soil __Sludge __Sediment __Glass

__Filter __Smear __Metal __Organic __Other Solids

Solid/Liquid Mixture: __ Gas: __

Biological: __Tissue __Urine __Feces

Process Knowledge: X Sample Information Check List, or

Reference Doc.: _____

PCBs Present: X No __Yes

Sample Disposition ...

Untreated Sample(s): __Return X Dispose __Store, or

Reference Doc.: _____

Prep'd Sample(s): X Dispose __Return __Store, or

Reference Doc.: _____

Additional Instructions: X No, or

Reference Doc.: _____

Date Report Req'd: 4/9/99

Send Report to: G.J. Lumetta

_____

MSIN: P7-25 Phone: _____

Fax (optional): _____

For ACL Use Only ... Do Not Complete This Section

Date Delivered: _____

Time Delivered (optional): _____

Deliv. By (if known): _____

Received By: _____

Resp. ACL Mgr.: _____

Signature/Date: _____

Job Group (optional): _____

Sample Group (optional): _____

PNL Impact Level: __1 __2 __3

DQ Review Req'd: __No __Yes ACL Waste: __No __Yes

ASR Number: _____ Revision: __Yes

ACL Numbers: _____

Analytical Chemistry Laboratory (ACL) Analytical Services Request (ASR)
(Request Page ... information specific to individual samples).

ACL Number (for ACL use only)	Client Sample Number (list each sample separately)	Sample Description	Analyses Requested	Test Name (for ACL use only)	Library (for ACL use only)
	AN107-SOL-30-1	Tank AN107 Liquid	Acid digestion, ICP/AES, Total α		
	-30-2				
	-40-1				
	-40-2				
	-50-1				
	-50-2				

ASR Number (for ACL use only): _____

Page ___ of ___

glass / plastic dry -1

Battelle Pacific Northwest Laboratories
Analytical Chemistry Laboratory

EXHIBIT I
PAGE 1 of 1

PNL-ALO-128 : Nitric and Hydrochloric Acid Extraction of Liquids Using a Dry-Block Heater W48481

Client name: Hugo Lumetta
Work Auth. Doc (WAD): ASE-5294 + 5319
Tank/Core/Project:
Special Instructions:

Work package number: W48482
Project number: 29953
PNL QA plan: MCS-053
PNL Impact level:
Prop. lab (SAL/SRPL/other): SRPL
Preparation batch number:

	ACL Sample ID	ACL order number or Client sample ID	Vial Identifier	Sample Volume (ml)	Spike added Volume (ml)	Spike added Weight (g)	Final solution Volume (ml)	Process Factor (1)	Vial wt before and after
1	99-1295	AN107-SOL-30-1	1			2.5559	25 mls		19.8414 / 17.2855
2	-1296	30-2	2			2.5439			19.7046 / 17.1607
3	-1297	40-1	3			2.1580			19.4613 / 17.3033
4	-1300	50-2	4			1.5949			18.8645 / 17.2896
5	-1454	AN107-AQ- 30	5	5 mls	(5.4146g.)				
6	-1455	50	6	5 mls	(5.0527g.)				
7	-1456	70	7	4.5 mls	(4.5423g.)				
8	-1457	90	8	5 mls	(5.0268g.)				
9	Blank,	DDI - H_2O	9	20 mls					
10									
11									
12									
13									
14									

4-15-99
A0573
TOPAES

Analyst's sample preparation comments: Sample # 99-1300 contained solids that dissolved upon the addition of water for transfer. Samples 1–4 showed some effervescence with the addition of the 1ml of HNO_3. All samples were diluted to 20mls with DDI-H_2O and digested using 1ml of TMG HNO_3 + 1ml TMG-HCl, covered with a watchglass and diluted to 25mls upon completion + cooling. No dupe's or matrix spikes were done due to ISV.

Spike source:
PNL spike ID number:
Anal. balance M&TE: 360-06-01-037
Sample filtered (yes/no):

(1) Process factor = Final volume (ml) / Sample volume (ml)

Other sample preparation workshoots may be substituted at the discretion of the Cognizant Scientist. Use one workshoot per client.

Analyst/Date: Lori P. Darnell 4-13-99
Reviewer/Date:

Rev. 2.0 7-28-95 JMR

Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...
ICPAES Data Report

Project: 29953
Client: G. J. Lumetta

ACL Number(s): 99-1295 through 99-1297, 99-1300 and 99-1454 through 99-1457

Client ID: "AN107-SOL-30-1" through "AN107-SOL-40-1", "AN107-SOL-50-2" and "AN107-AQ-30" through "AN107-AQ-90"

ASR Number: 5294 & 5319

Total Samples: 8

Procedure: PNL-ALO-211, "Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry" (ICP-AES).

Analyst: J. J. Wagner

Analysis Date (Filename): 4-15-99 (A0523)

See system file: "ICP-325-405-1" for traceability to Calibration, Quality Control, Verification, and Raw Data.

M&TE Number: ICPAES instrument -- WB73520
Mettler AT400 Balance -- Ser.No. 360-06-01-029

Terry J. Wagner 4-20-99
Reviewed by

M W Thun 4/21/99
Concur

Four radioactive liquid samples, AN107-SOL-30-1 through AN107-SOL-50-2, were analyzed by ICPAES after preparation by the Sample Receiving and Preparation Laboratory (SRPL) using PNNL-ALO-128 Acid Digestion procedure. The liquid content of each sample vial was transferred to a digestion vessel prior to treatment using a plastic transfer pipette and distilled deionized water. Individual sample weights were obtained by subtracting the empty, dry sample vial weight from the weight of the vial containing the original liquid sample. Approximately 1.6 to 2.6 grams of aqueous sample (AN107-SOL-30-1 through AN107-SOL-50-2) was digested and diluted to a final volume of 25 ml. Sample AN107-SOL-50-2 contained a small amount of solids and liquid. The solids dissolved on contact with water during sample transfer. Additional dilution, up to 30 fold, was performed during ICPAES analysis. All measurement results reported have been corrected for preparation and analytical dilution. Analytical results are reported as µg/g as agreed to by the client. Analytes of interest (ASR 5294) include Al, Cr, Fe, Mn, Na, Ni, P, and Si.

Sample AN107-AQ-30 through AN107-AQ-90 was also prepared by SRPL using PNNL-ALO-128 Acid Digestion procedure. Approximately 4.5 or 5ml aliquots of aqueous sample was pipetted (and weighed), digested and diluted to a final volume of 25 ml. Additional dilution up to 10 fold was performed during ICPAES analysis. Analytes of interest for ASR 5319 include Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, U, Zn, and Zr. All measurement results reported have been corrected for preparation and analytical dilutions and reported as µg/ml.

All quality control checks met MCS-033 QC tolerance requirements for analytes of interest except as noted below. Following is a list of quality control check measurement results relative to ICPAES analysis requirements under MCS-033.

Five fold serial dilution:

(Solid samples)	--
(Aqueous samples)	All results are within tolerance limit of ≤ 10% after correcting for dilution except sample 99-1296 @10 and 99-1296 @2 dilution (AN107-SOL-30-2). The following analyte concentration was recovered within 11% after dilution correction: Chromium, Iron, Manganese, and Nickel.

Duplicate RPD (Relative Percent Difference):

(Solid samples) --

(Aqueous samples) Duplicate samples were within MCS-033 tolerance limit of ≤ 20% RPD (Relative Percent Difference) except Silicon (32% RPD) in sample AN107-SOL-30-1. Silicon concentration in all samples was low and similar to the concentration found in the process blank. The source of Si is probably from labware used to digest samples.

Post-Spiked Samples (Group A):

(Solid samples) --

(Aqueous samples) All analytes of interest were recovered within MCS-033 tolerance of 75 to 125%.

Post-Spiked Samples (Group B):

(Solid samples) --

(Aqueous samples) All analytes of interest were recovered within MCS-033 tolerance of 75 to 125%.

Blank Spike:

(Solid samples) --

(Aqueous samples) A blank spike was not prepared.

Matrix Spiked Sample:

(Solid samples) --

(Aqueous samples) A matrix spike was not prepared.

Quality Control Check Standards:

Concentration of all analytes of interest, with one exception, was recovered within MCS-033 tolerance of ± 10% accuracy in the standards: QC_MCVA, QC_MCVB, and QC_SSTMCV. Calibration Blank (ICP98.0) concentration was less than two times IDL. The one exception was Silicon which was slightly high (about 11%) in QC_SSTMCV. All Si concentrations found in samples were about the same as that found in the preparation blank

High Calibration Standard Check:

Verification of the high-end calibration concentration for all analytes of interest was within MCS-033 tolerance of ± 5% accuracy.

Process Blank:

(Solid samples) --

(Aqueous samples) All analytes of interest were within MCS-033 tolerance limit of ≤ EQL or < 5% of sample concentration except Silicon. The concentration of Silicon in all samples was about the same as that found in the process blank. Silicon contamination is low in concentration and probably due to labware (glass) used in preparing samples.

Laboratory Control Standard:

(Solid samples) --

(Aqueous samples) LCS not supplied.

Analytes other than those requested by the client are for information only. Please note bracketed values listed in the data report are within ten times instrument detection limit and have a potential uncertainty much greater than 15%.

Comments:

1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis unless specifically noted.

2) Detection limits (DL) shown are for acidified water. Detection limits for other matrices may be determined if requested.

3) Routine precision and bias is typically ± 15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations greater than ten times detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight).

4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.

5) The maximum number of significant figures for all ICP measurements is 2.

Battelle PNNL/RPG/Inorganic Analysis ... ICPAES Data Report

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	10.0 PROCESS BLANK (99-1295 & -1454 batch) 4/15/99 ug/g	19.6 99-1295 @2 AN107-SOL-30-1 4/15/99 ug/g	19.7 99-1296 @2 AN107-SOL-30-2 4/15/99 ug/g	23.2 99-1297 @2 AN107-SOL-40-1 4/15/99 ug/g	31.3 99-1300 @2 AN107-SOL-50-2 4/15/99 ug/g
0.015	Ag	--	--	--	--	--
0.060	Al	[2.5]	2,900	3,000	3,100	3,320
0.080	As	--	[5.0]	[5.3]	[5.0]	[4.9]
0.050	B	26.8	41.5	38.4	47.2	63.2
0.010	Ba	--	2.33	2.47	2.44	[2.8]
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	[3.2]	330	341	351	376
0.015	Cd	--	35.8	36.9	38.0	40.5
0.100	Ce	--	[19]	20.5	[20]	[22]
0.025	Co	--	[2.6]	[2.7]	[2.8]	[3.0]
0.020	Cr	--	106	110	113	123
0.015	Cu	--	15.4	16.0	16.6	17.8
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	--	709	752	739	833
2.000	K	--	894	931	963	1,030
0.025	La	--	14.3	15.0	15.1	16.6
0.005	Li	--	[0.39]	[0.39]	[0.44]	[0.47]
0.100	Mg	--	--	--	--	--
0.005	Mn	--	55.7	58.7	57.9	63.3
0.030	Mo	--	--	--	--	--
0.100	Na	30.6	133,000	143,000	136,000	147,000
0.100	Nd	--	48.4	50.5	50.0	53.7
0.030	Ni	--	289	298	307	328
0.100	P	--	375	389	396	420
0.060	Pb	--	181	189	192	207
0.300	Pd	--	[27]	[28]	[28]	[30]
0.300	Rh	--	[6.8]	[7.3]	[7.6]	--
0.075	Ru	--	21.1	21.8	22.4	24.0
0.050	Sb	--	[1.8]	[1.7]	[1.8]	[2.2]
0.050	Se	--	[2.4]	[2.6]	[2.7]	[2.9]
0.100	Si	44.8	55.3	40.2	56.6	79.9
1.000	Sn	--	--	--	--	--
0.005	Sr	--	1.81	1.87	1.92	2.09
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Tl	--	[0.47]	[0.49]	[0.51]	[0.58]
0.250	Tl	--	--	--	--	--
2.000	U	--	[77]	[83]	[85]	[90]
0.015	V	--	[0.40]	[0.42]	[0.45]	[0.48]
0.500	W	--	[96]	99.5	[100]	[110]
0.010	Y	--	7.90	8.23	8.30	8.73
0.020	Zn	--	11.0	11.4	11.6	13.7
0.025	Zr	--	32.3	33.7	33.3	36.0

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.

2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.

3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Data (1) from `A0523 G.Lumetta ALO-128 BNFL AN107-SOL&AQ ASR5294 & 5319 ICP98 low.xls 4/19/99 @ 9:06 AM

Battelle PNNL/RPG/Inorganic Analysis ... ICPAES Data Report

Det. Limit (ug/mL)	Multiplier= / Run Date= (Analyte)	5.0 PROCESS BLANK (99-1295 & -1454 batch) 4/15/99 (ug/mL)	5.0 99-1454 AN107-AQ-30 4/15/99 (ug/mL)	5.0 99-1455 AN107-AQ-50 4/15/99 (ug/mL)	5.6 99-1456 AN107-AQ-70 4/15/99 (ug/mL)	5.0 99-1457 AN107-AQ-90 4/15/99 (ug/mL)
	ALO#=					
	Client ID=					
0.015	Ag	--	--	--	--	--
0.060	Al	[1.2]	1,140	83.4	44.6	28.2
0.080	As	--	[1.3]	--	--	--
0.050	B	13.4	18.0	16.4	16.9	11.8
0.010	Ba	--	--	--	--	--
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	[1.6]	70.0	[1.3]	--	[0.62]
0.015	Cd	--	7.26	[0.29]	--	--
0.100	Ce	--	--	--	--	--
0.025	Co	--	[0.55]	--	--	--
0.020	Cr	--	59.8	17.1	10.2	5.94
0.015	Cu	--	3.76	[0.27]	[0.11]	--
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	--	3.06	[0.62]	4.86	9.02
2.000	K	--	183	--	--	--
0.025	La	--	[0.48]	--	--	--
0.005	Li	--	[0.072]	--	--	--
0.100	Mg	--	--	--	--	--
0.005	Mn	--	0.978	[0.15]	0.833	1.57
0.030	Mo	--	--	--	--	--
0.100	Na	15.3	32,900	1,500	354	243
0.100	Nd	--	[1.1]	--	--	--
0.030	Ni	--	58.6	2.14	[0.18]	--
0.100	P	--	73.9	[3.0]	[2.8]	[1.7]
0.060	Pb	--	46.0	[1.9]	--	[0.43]
0.300	Pd	--	--	--	--	--
0.300	Rh	--	--	--	--	--
0.075	Ru	--	4.07	--	--	--
0.050	Sb	--	[0.44]	--	--	--
0.050	Se	--	[0.57]	--	--	--
0.100	Si	22.4	17.3	24.9	23.9	16.6
1.000	Sn	--	--	--	--	--
0.005	Sr	--	[0.25]	--	--	--
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	--	[0.029]	--	--	--
0.250	Tl	--	--	--	--	--
2.000	U	--	[16]	--	--	--
0.015	V	--	--	--	--	--
0.500	W	--	[24]	--	--	--
0.010	Y	--	0.530	--	--	--
0.020	Zn	--	2.36	[0.26]	--	[0.14]
0.025	Zr	--	--	--	--	[0.18]

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.

2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.

3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Radioanalytical Applications Team

99-1295
4/29/99

Client : GJ Lumetta

Cognizant Scientist: _____ Date : _____

Concur : _____ Date : _____

Measured Activities (uCi/g)

ALO ID Client ID	Alpha Error %
99-1295 AN107-SOL-30-1	2.89E-1 3%
99-1296 AN107-SOL-30-2	3.21E-1 2%
99-1297 AN107-SOL-40-1	2.80E-1 3%
99-1300 AN107-SOL-50-2	3.27E-1 3%
Matrix Spike	110%
Blank Spike	106%
Blank	<3.E-6

Appendix C. Calculations

Battelle
Pacific Northwest Laboratories

ENGINEERING WORKSHEET

Prepared By: M.J. Steele | Date: 4/29/99 | Project: 29953

Title/Subject: AW 107 LAW Entrained Solids Solubility Versus Temperature

Data work up for the AW107 test was similar to that for the AW 101 test. Major differences were: 1) only the 30°C solution was analyzed in duplicate and 2) the concentration values needed to be normalized to the Na concentration (because of evaporation of the samples).

Example: Aluminum

At 30°C: AW107-SOL-30-1 → 2900 mg Al/g sample
→ 133000 mg Na/g sample

$$\frac{1000000\ \text{mg Na}}{\text{g Na}} \cdot \frac{2900\ \text{mg Al/g sample}}{133000\ \text{mg Na/g sample}} = 21805\ \frac{\text{mg Al}}{\text{g Na}}$$

AW107-SOL-30-2 → 3000 mg Al/g
→ 143000 mg Na/g

$$\frac{1000000\ \text{mg Na}}{\text{g Na}} \cdot \frac{3000\ \text{mg Al/g}}{143000\ \text{mg Na/g}} = 20979\ \text{mg Al/g Na}$$

Mean Value: $\frac{21805 + 20979}{2} = 21392$ mg Al/g Na

$$\sigma = \sqrt{\frac{2(21805^2 + 20979^2) - (21805 + 20979)^2}{2}} = 584$$

At 40°C: AW107-SOL-40-1 → 1000000 (3100 mg Al/g)/(136000 mg Na/g) = 22794 mg Al/g Na

% Change = 100 (22794 − 21392)/21392 = 6.6 %

At 50°C: AW107-SOL-50-2 → 1000000 (3320 mg Al/g)/(147000 mg Na/g) = 22585 mg Al/g

% Change = 100 (22585 − 21392)/21392 = 5.6 %

* See attached Excel printouts for the results of the calculations.

Tables 1-4