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Inorganic, Radioisotopic, and Organic Analysis of 241-AP-101 Tank Waste

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Summary

Battelle received five samples from Hanford waste tank 241-AP-101, taken at five different depths within the tank. No visible solids or organic layer were observed in the individual samples. Individual sample densities were measured, then the five samples were mixed together to provide a single composite. The composite was homogenized and representative sub-samples taken for inorganic, radioisotopic, and organic analysis. All analyses were performed on triplicate sub-samples of the composite material.[1] The sample composite did not contain visible solids or an organic layer. A subsample held at 10°C for seven days formed no visible solids.

The characterization of the 241-AP-101 composite samples included:

- Inductively-coupled plasma spectrometry for Ag, Al, Ba, Bi, Ca, Cd, Cr, Cu, Fe, K, La, Mg, Mn, Na, Nd, Ni, P, Pb, Pd, Ru, Rh, Si, Sr, Ti, U, Zn, and Zr (Note: Although not specified in the test plan, As, B, Be, Co, Li, Mo, Sb, Se, Sn, Tl, V, W, and Y were also measured and reported for information only)
- Radioisotopic analyses for total alpha and total beta activities, ^{3}H, ^{14}C, ^{60}Co, ^{79}Se, ^{90}Sr, ^{99}Tc as pertechnetate, ^{106}Ru/Rh, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{242}Cm, and $^{243+244}$Cm
- Inductively-coupled plasma mass spectrometry for ^{237}Np, ^{239}Pu, ^{240}Pu, ^{99}Tc, ^{126}Sn, ^{129}I, ^{231}Pa, ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{241}AMU, ^{242}AMU, ^{243}AMU, As, B, Be, Ce, Co, Cs, Eu, I, Li, Mo, Pr, Rb, Sb, Se, Ta, Te, Th, Tl, V, and W
- Total U by kinetic phosphorescence analysis
- Ion chromatography for Cl, F, NO_2, NO_3, PO_4, SO_4, acetate, formate, oxalate, and citrate
- Density, inorganic carbon and organic carbon by two different methods, mercury, free hydroxide, ammonia, and cyanide
- Polychlorinated biphenyls

The 241-AP-101 composite met all contract limits (molar ratio of analyte to sodium or ratio of becquerels of analyte to moles of sodium) defined in Specification 7 for Envelope A.[2] Except for a few cases, the characterization results met or surpassed the quality control requirements established by the governing quality assurance plan and met or surpassed the minimum reportable quantity requirements specified by BNFL.

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[1] Specific inorganic, radiochemical, and organic analytes of interest and reporting requirements were defined in CCN: 01260 Letter to Eugene Morrey and translated to the laboratory personnel via ASR 5778, test instructions BNFL-TP-29953-81 and -83.

[2] As provided by Tank Waste Remediation System Privatization Contract DE-AC27-96-RL13308, Mod 14 (4/18/00) Table TS-7.1 LAW Chemical Composition, Soluble Fraction Only and Table TS-7.2 LAW Radionuclide Content, Soluble Fraction Only.

Terms and Abbreviations

AEA	alpha energy analysis
ASR	analytical services request
AMU	atomic mass units
BNFL	BNFL, Inc; subsidiary of British Nuclear Fuels, Ltd.
CCV	continuing calibration verification
COC	chain of custody
CVAA	cold vapor atomic absorption
EQL	estimated quantitation level
GEA	gamma energy analysis
HASQARD	Hanford analytical services quality assurance requirements document
IC	ion chromatography
ICP	inductively coupled plasma/atomic emission spectrometry
ICP/MS	inductively coupled plasma/mass spectrometry
IDL	instrument detection limit
ISE	ion specific electrode
KPA	kinetic phosphorescence analyzer
LCS	laboratory control standard
MDL	method detection limit
MRQ	minimum reportable quantity
MSA	method of standard addition
NA	not applicable
NIST	National Institute of Standards and Technology
NP	not performed
PCB	polychlorinated biphenyl
QA	quality assurance
QC	quality control
RPD	relative percent difference
RSD	relative standard deviation
SAL	Shielded Analytical Laboratory
SBMS	standards based management system
SRM	Standard Reference Material
TC	total carbon
TCLP	toxicity characteristic leaching procedure
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic

Units

°C - °F	degrees Centigrade / degrees Fahrenheit
Bq	becquerel (disintegrations per second)
g	gram
g/mL	gram per milliliter
µg/mL	microgram per milliliter
µCi/mL	microcurie per milliliter
mL	milliliter
mmole/mL	millimole per milliliter
M	molarity, moles per liter

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1.0 Introduction

This report presents the inorganic, organic and radioisotopic analytical results for a composite sample obtained from tank 241-AP-101 (AP-101). This work was conducted in response to a request by BNFL.[3] The results of the analyses are used to assess the waste composition relative to the contract limits defined in Specification 7 for envelope A.

Hanford waste tank 241-AP-101 was sampled on February 8, 2000 from Riser 002 at depths of 10, 100, 190, 290, and 400 inches from the tank bottom, collecting nominally 130 mL per sample.[4] These samples were received under chain-of-custody by the Radiochemical Processing Laboratory Shielded Analytical Laboratory. All samples were clear yellow with no visible settled or suspended solids. The AP-101 grab samples were mixed to form one large composite sample according to Test Plan BNFL-TP-29953-083. Sub-samples from this homogenized AP-101 composite sample were then delivered to various laboratories for specific analyses as defined in the analytical service request (ASR) 5778. The sample was given an internal tracking number of 00-1701. All analyses were run in triplicate.

The PNNL standards based management system (SBMS) quality assurance plan was used in support of all analytical operations and is in compliance with HASQARD. The inorganic, radioisotopic, and organic analytes of interest, recommended methods, detection limits, and quality assurance parameters were defined by BNFL. The quality requirements were included in ASR 5778. Analyte determinations were performed according to project-approved procedures.

This report presents the physical observations from AP-101 and individual density measurements from the various tank depths sampled. Precipitate production was evaluated at 10°C for seven days on a composite subsample. Also presented are the inorganic, radioisotopic, and organic analytical results for the triplicate AP-101 composite samples. Analyte results are compared to Specification 7 Envelope A limits, where applicable. Data limitations are also described. Quality control, detection limits, and other quality control indicators are discussed relevant to the reporting method.

Revision 1 includes addition of PCB results as well as minor editorial corrections.

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[3] Statement of Work for 241-AP-101 Samples. Transmitted via letter: ME Johnson to EV Morrey, Contract No. DE-AC06-96RL13308-W375-Request for Proposal to Conduct Revised Analysis of Tank 241-AP-101 Samples, CCN: 012160.

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

2.0 Initial Sample Processing

2.1 Sample Density and Homogenization

The samples from the five different sampling depths were confirmed to be clear and yellow with no suspended or settled solids, as indicated on the chain-of-custody form. Each sample density was taken by determining the net sample mass in a 25-mL glass volumetric flask.[5] The individual densities, given in Table 2.1, show a slight decrease with increasing sampling elevation.

Table 2.1. 241-AP-101 Sample Densities and Volumes

Sample ID	1AP-00-1	1AP-00-4	1AP-00-7	1AP-00-10	1AP-00-13
*Elevation (inches)**	400	290	190	100	10
Density (g/mL)	1.290	1.291	1.291	1.320	1.328
Mass received (g)	174.3	170.2	169.7	173.6	172.2
Volume received (mL)	135.2	131.8	131.5	131.6	129.7

*Elevation is the distance from the tank bottom to the mouth of the sample bottle.

The entire contents of each sample container were transferred to a 1-L jar; the net mass transferred was calculated by difference from the full and empty container masses.[6] The 860-g (659.8-mL) AP-101 composite was sealed and stirred for 54 minutes using a magnetic stir bar. A 101-mL sub-sample was transferred to a glass bottle and sealed for subsequent precipitation/crystallization testing at reduced temperature. Portions of the remaining composite material were used for subsequent analyses. The composite sample did not show signs of phase separation or precipitation. The overall sample processing and associated dates are summarized in Figure 2.1.

2.2 Sample Digestion for Analysis

After sample homogenization, the AP-101 composite sub-samples were delivered directly to the laboratories for various measurements including mercury, cyanide, hydroxide, tritium, total organic carbon, total inorganic carbon, ammonia, ion chromatography (inorganic and organic ions), ^{14}C, pertechnetate, ^{79}Se, and gamma spectrometry. The AP-101 composite density (see Table 3.5) was determined in the Shielded Analytical Laboratory (SAL).

The SAL processed 5-mL aliquots in triplicate according to PNL-ALO-128, HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater, for subsequent ICP and ICP/MS analyses. The acid extracted solutions were brought to a nominal 25-mL volume and absolute volumes determined based on final solution weights and densities. This acid digestion resulted in a solution with a small amount of white floating particulates. The floating particulates were removed by filtration. The filtrates were analyzed by ICP and ICP/MS. Along with the samples, the SAL processed a reagent blank, a toxicity characteristic leach protocol (TCLP)-metals spiked blank, and TCLP-metals spiked sample. The TCLP metals spike included Ag, As, Ba, Cd, Cr, Ni, Pb, Se, Tl, and Zn.

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[5] PNNL Test Instruction Number 29953-81, Rev. 0, "Density Measurements on As-Received AP-101 Samples," by Paul Bredt, 2/10/00

[6] PNNL Test Instruction Number BNFL-TP-29953-83, Rev. 0, "AP-101 Homogenization and Subsampling," by Paul Bredt, 3/31/00

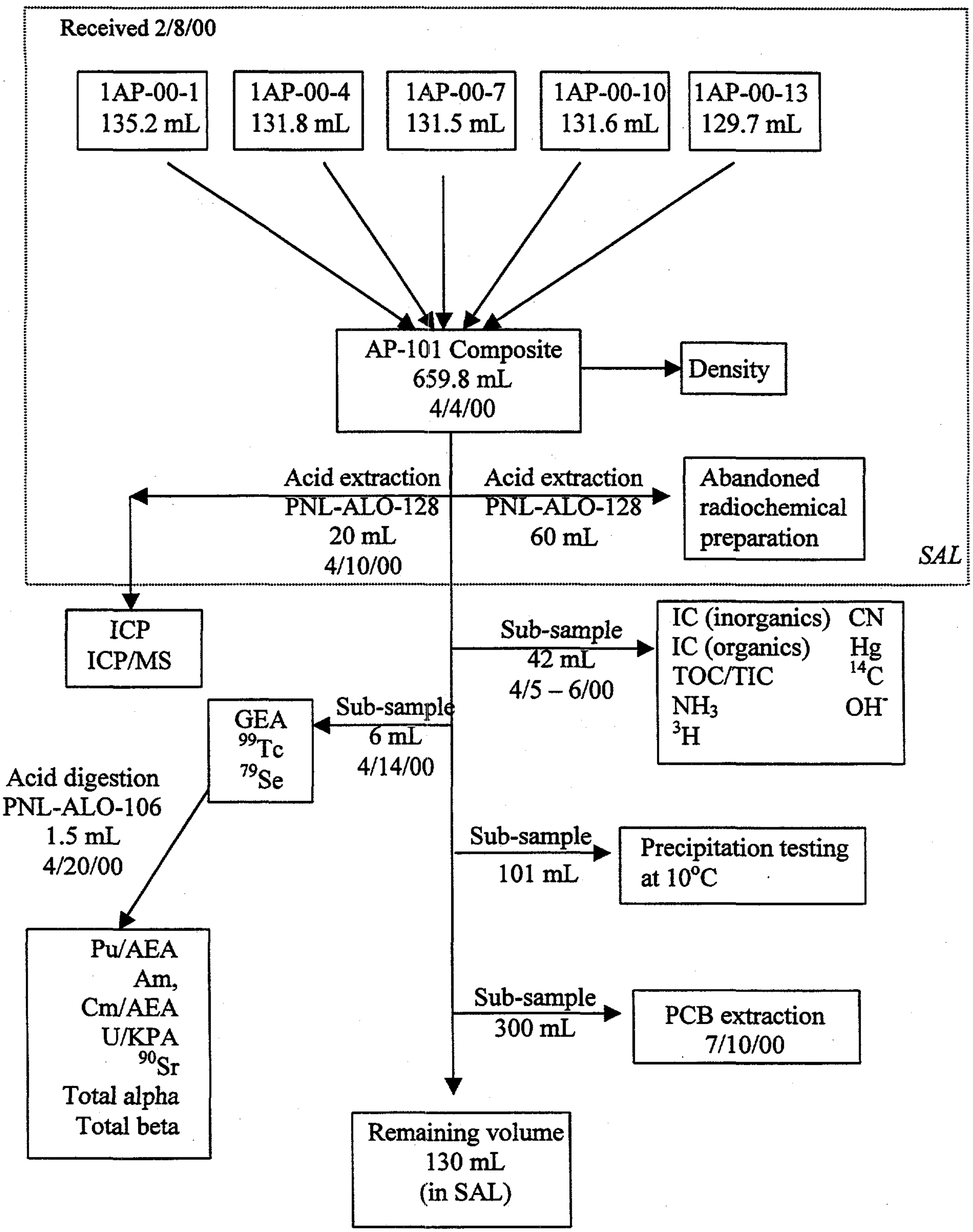

Figure 2.1. 241-AP-101 Sample Processing

The SAL also processed 20-mL AP-101 composite aliquots in triplicate according to PNL-ALO-128. The acid extraction was insufficient to neutralize the 20-mL sample and it resulted in a small amount of solid residue formation (settled on the vial bottom as opposed to floating particulates). Additional 8M HNO_3 was added to one aliquot to dissolve the residual solids. This resulted in severe foaming as well as visible NOx production. Continued 8M HNO_3 addition resulted in mixed-phases consisting of whitish floating material (estimated volume of between 0.1 and 0.5 cubic centimeters) on top of a near colorless solution. Acid digestion/neutralization of the three 20-mL aliquots of AP-101 composite was abandoned in favor of performing a nitric acid digestion on 0.5-mL aliquots according to PNL-ALO-106, Acid Digestion for Preparation of Samples for Radiochemical Analysis. Nitric acid additions and heating continued until all organic/nitric reactions had visibly ceased. The samples were then brought to volume in 10-mL volumetric flasks with 2M HNO_3. If insoluble material formed, it was too small to discern. A reagent blank was run with the samples. These digestions were used for the subsequent analyses of total alpha, total beta, $^{239+240}Pu$, ^{238}Pu, ^{241}Am, ^{242}Cm, $^{243+244}Cm$, total U by kinetic phosphorescence analysis (KPA), and ^{90}Sr. A laboratory control sample (LCS) was not available for radiochemical analyses. Post digestion blank spikes and matrix spikes were prepared at the time of radiochemical separation.

2.3 Sample Precipitation at Reduced Temperature

A 101-mL aliquot of the AP-101 composite was visually inspected using a video camera installed in the HLRF hot cell. The sample contained a very a small amount of particulate material. This was removed by filtering through a 0.45-µm nylon membrane. The clarified liquid was transferred to a clean glass jar and was then placed in a cooling bath at 10°C. The sample was inspected daily (excluding weekends) for a period for seven days. No solids formed after seven days. Thus, the AP-101 solution appears to be stable towards precipitation at 10°C.

2.4 Polychlorinated Biphenyl Extraction

The AP-101 composite was sampled and extracted for polychlorinated biphenyl (PCB) analysis according to special instructions in ASR 5778 and test plan BNFL-TP-29953-089. Sub-samples consisted of duplicate 100-mL aliquots (surrogate spike only) and duplicate 50-mL aliquots (surrogate and Aroclor spike); a blank consisting of water (surrogate spike only) was processed with the sample set. All samples were extracted three times with 25-mL methylene chloride. The extracts were combined and transferred from the SAL to the PCB workstation under COC. The methylene chloride extracts were dried over anhydrous sodium sulfate and concentrated to a 2-mL volume. Additional extract cleanup was performed following exchange into hexane. The hexane residues were then analyzed for PCBs according to BNFL-TP-29953-027 by gas chromatography.

2.5 Remaining AP-101 Composite Material

The combined total volume sampled for the various analyses was 529-mL. The amount remaining after all sampling events were completed is nominally 130-mL or 171-g.

3.0 Analytical Results

Tables 3.1 through 3.5 provide inorganic, radioisotopic, and organic analytical results for the triplicate AP-101 composite samples. The average of the triplicate values and the relative standard deviation (RSD) are also given. Results are reported in µg/mL or µCi/mL. The reference date for radioisotope activities is the analysis date. The nominal propagated uncertainties are also provided as 1-σ unless otherwise noted.

Preparation blank results are also reported, as appropriate. Several analytes were measured directly, requiring no preparation blank (e.g., GEA, IC, and hydroxide). In these instances, the preparation blank field is empty. Generally, analyte concentrations in the preparation blanks were either insignificant relative to the sample analyte concentration or at or near the method detection limit. This indicates processing steps did not result in significant sample contamination (except in the case of B, see discussion in section 3.2).

Specification 7 for Envelope A defines limits for several analytes relative to sodium concentration (moles analyte per mole Na or Bq analyte per mole Na). These ratio limits are provided in conjunction with as-measured ratios. In all cases the mole or Bq analyte to moles Na ratio did not exceed the limits defined in Specification 7 for Envelope A. It should be noted the K concentration is also relatively high (0.8M) and may also affect other process steps including Cs ion exchange, Tc ion exchange, and vitrification.

Specific quality control and quality assurance discussions are given in Section 4.0.

3.1 Analyte List Modifications

The analyte list provided by the client was extracted from Contract Specification 7. Several modifications to this analyte list had to be incorporated as follows:

- The Pu separation and subsequent analysis by AEA requires ^{239}Pu and ^{240}Pu be measured together as a sum, not as separate isotopes. The alpha energy peaks from these isotopes are non-resolvable. The lower of the two MRQs for these analytes was used for compliance purposes.

- The radiochemistry laboratory was directed to determine pertechnetate ($^{99}TcO_4^{+7}$) using separations and beta counting techniques, as opposed to total ^{99}Tc. The procedure was modified slightly to exclude the sample oxidation step so that the nonpertechnetate fraction was not oxidized. Also, instead of measuring the ^{99}Tc by liquid scintillation, sample preparations were counted with gas-flow proportional counters. The ^{99}Tc determination by ICP/MS was not effected where total ^{99}Tc was determined.

- Analysis for ^{135}Cs was not performed as requested by gamma spectrometry. There are no gamma-emissions associated with this isotope.

- Analyte concentrations, in addition to the required and opportunistic analytes, are provided in Tables 3.1 and 3.4. These additional analytes were measured as part of the method and are provided for additional information.

- Total carbon was measured using the furnace oxidation method as opposed to individual measurements of TOC and TIC. This method is considered reliable for only total carbon.

3.2 Data Limitations

- The reported fluoride results, average 2900 µg/mL, represent the summation of fluoride, acetate, and formate concentrations, as these are not resolvable on the inorganic anion analysis IC system. The acetate and formate were quantified on the organic anion IC system. The sum of these two analytes is 2840 µg/mL. This indicates very little fluoride is present in AP-101.

- The reported acetate results represent the summation of glycolate and acetate, as these are not resolvable on the organic IC system.

- ICP-MS analytes at AMU-241, 242, and 243, were measured relative to a ^{239}Pu standard and the reported results are considered semi-quantitative. They are listed in the stable element data Table 3.3. with concentration units of µg/mL. Although these elements are unstable, an activity concentration cannot be applied without knowing the specific activity, and thus the analyte identity. For example, if ^{241}AMU is assigned to Am, then the activity becomes <0.038 µCi/mL; if ^{241}AMU is assigned to Pu, then the activity becomes <1.2 µCi/mL.

- The ^{126}Sn and ^{231}Pa ICP-MS analytes were determined relative to related isotopes and the reported results are considered semi-quantitative.

- Boron was present in the preparation blank at 40% of the sample concentration indicating the sample boron concentration could be biased high by the digestion method.

- Arsenic was present in the preparation blank at 10% of the sample concentration indicating the sample arsenic concentration could be biased high by the digestion method.

- The alpha summation is a better representation of the total alpha activity than the total alpha determination for this matrix. Solids loading on the total alpha mount resulted in some alpha attenuation.

- The acid digestion preparations for ICP and ICP-MS were filtered to remove a small amount of floating particulates. This leaves open the possibility that one or more analyses could be biased low.

- PCBs have low solubilities and tend to plate out on vessel walls. Typically sample vessels are rinsed with a PCB solvent (methylene chloride) to remove potentially plated PCBs. No vessel rinsing was performed during the sampling, homogenization, or sub-sampling steps. This could cause a low bias for the PCB results.

- The reported total PCB MDL represents the MDL summation of seven Aroclors, where each Aroclor MDL is 0.2 µg/L.

3.3 General Observations

- The total ^{99}Tc measured by ICP-MS agreed well with the pertechnetate analysis (separations and beta counting), indicating the ^{99}Tc in AP-101 is present in the pertechnetate form.
- The U concentrations determined by KPA and ICP-MS agreed within the 2-σ uncertainty.
- The total beta activity is equivalent to the ^{137}Cs activity indicating ^{137}Cs is the primary β^-emitting isotope in this waste.
- The phosphorous concentration is virtually identical to the phosphate concentration indicating the phosphorous is primarily present as phosphate.
- Generally the analyte concentrations measured by both ICP-MS and ICP were consistent.

Table 3.1. 241-AP-101 Composite, ICP Metals Results

Lab ID	PB-1701	00-1701	00-1701D	00-1701T				Measured Mole analyte per mole Na Ratio	Specification 7 Envelope A Limits Mole analyte per mole Na Ratio
Sample ID	prep blank	sample	duplicate	triplicate					
Run date	4/11/00	4/11/00	4/11/00	4/11/00	Average	RSD	Average		
Units	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	%	M		
Analyte$^{(1)}$									
Ag	<0.12	<0.63	<0.63	<0.62	<0.63				
Al	4.5	7,380	6,680	6,760	6,940	5.5	2.6E-1	4.6E-2	2.5E-1
Ba	<0.05	[0.32]	[0.34]	[0.33]	[0.33]	3.0	[2.4E-6]	[4.3E-7]	1.0E-4
Bi	<0.48	<2.5	<2.5	<2.5	<2.5				
Ca	[1.4]	[7.8]	[7.5]	[7.7]	[7.7]	2.0	[1.9E-4]	[3.4E-5]	4.0E-2
Cd	<0.07	[2.0]	[1.9]	[2.0]	[2.0]	2.9	[1.7E-5]	[3.1E-6]	4.0E-3
Cr	<0.1	158	137	135	143	8.9	2.8E-3	4.9E-4	6.9E-3
Cu	[0.18]	[1.7]	[1.5]	[1.5]	[1.6]	7.4			
Fe	[0.38]	[2.9]	[2.4]	[2.2]	[2.5]	14	[4.5E-5]	[8.0E-6]	1.0E-2
K	<9.7	31,700	30,500	31,500	31,200	2.1	8.0E-1	1.4E-1	1.8E-1
La	<0.24	<1.3	<1.3	<1.2	<1.3		<9.4E-6	<1.7E-6	8.3E-5
Mg	<0.48	<2.5	<2.5	<2.5	<2.5				
Mn	<0.24	<1.3	<1.3	<1.2	<1.3				
Na	14	132,000	125,000	131,000	129,300	2.9	5.62E+0		
Nd	<0.48	<2.5	<2.5	<2.5	<2.5				
Ni	1.6	8.6	7.7	7.5	7.9	7.6	1.4E-4	2.4E-5	3.0E-3
P	<0.48	371	290	281	314	16	1.0E-2	1.8E-3	3.8E-2
Pb	<0.48	[15]	[15]	[15]	[15]	0	[7.2E-5]	[1.3E-5]	6.8E-4
Pd	<3.6	<19	<19	<19	<19				
Rh	<1.5	<7.6	<7.6	<7.5	<7.6				
Ru	<5.3	<28	<28	<27	<28				
Si	[24]	143	132	137	137	4.0			
Sr	<0.07	<0.38	<0.38	<0.37	<0.38				
Ti	<0.12	<0.63	<0.63	<0.62	<0.63				
U	<9.7	[68]	[62]	[56]	[62]	9.7	[2.6E-4]	[4.6E-5]	1.2E-3
U(KPA)$^{(2)}$	0.0054	51.7	51.2	50.3	51.1	1.4	2.1E-4	3.8E-5	1.2E-3
U(ICP-MS)$^{(3)}$	<0.14	58.9	52.9	54.1	55.3	5.7	2.3E-4	4.1E-5	1.2E-3
Zn	[0.91]	[5.8]	[5.5]	[5.4]	[5.6]	3.7			
Zr	<0.24	[1.4]	[1.4]	[1.3]	[1.4]	4.2			
Additional analyte information									
As$^{(4)}$	<1.21	<6.3	<6.3	<6.2	<6.3				
B$^{(4)}$	6.62	15	14	15	15	2.6			
Be$^{(4)}$	<0.05	[1.1]	[1.0]	[1.0]	[1.0]	5.6			
Co$^{(4)}$	<0.24	<1.3	<1.3	<1.2	<1.3				
Li$^{(4)}$	<0.15	<0.76	<0.76	<0.75	<0.76				
Mo$^{(4)}$	<0.24	[12]	[10]	[9.8]	[11]	11			
Se$^{(4)}$	<1.2	<6.3	<6.3	<6.2	<6.3				
Sn	<7.3	[60]	<38	<37	<38				
Tl$^{(4)}$	<2.4	<13	<13	<12	<13				
V$^{(4)}$	<0.24	<1.3	<1.3	<1.2	<1.3				
W$^{(4)}$	<9.7	<51	<51	<50	<51				
Y	<0.24	<1.3	<1.3	<1.2	<1.3				

(1) Overall error for reported results is estimated to be within +/-15%, 2-σ; however results in brackets "[ ]" are less than the estimated quantitation level (i.e., 10-times MDL) and error is anticipated to exceed +/-15%.

(2) U (KPA) indicates U determination by kinetic phosphorescence on 4/26/00 with an uncertainty of 3%, 1-σ.

(3) U (ICP-MS) indicates opportunistic U determination by ICP-MS on 4/18/00, with an uncertainty of 3.5%, based on one standard deviation triplicate sample summing all U isotopes.

(4) Analytes on ICP-MS Specification 7 list.

Table 3.2. 241-AP-101 Composite, Radionuclide Results

Lab ID	PB-1701	00-1701	00-1701D	00-1701T	Propagated				Measured	Specification Envelope A Limits
Sample ID	prep blank(1)	sample	duplicate	triplicate	1-σ	Average	RSD	Analysis	Bq analyte per mole Na	Bq analyte per mole Na
Units	µCi/mL	µCi/mL	µCi/mL	µCi/mL	% Error(3)	µCi/mL	%	Date	Ratio	Ratio
Analyte										
^{3}H	<2E-4	5.05E-3	4.84E-3	4.60E-3	3	4.83E-3	4.7	4/16-21/00		
^{14}C	<4E-5	2.56E-4	2.55E-4	2.77E-4	8	2.63E-4	4.7	5/11/00		
^{60}Co (GEA)		3.22E-3	3.40E-3	3.24E-3	7	3.29E-3	3.0	4/28-30/00	2.2E+4	6.1E+4
^{79}Se	<3E-6	5.56E-5	6.97E-5	4.93E-5	5-11	5.82E-5	18	5/18/00		
^{90}Sr	<2E-4	8.71E-2	8.77E-2	8.75E-2	3	8.74E-2	0.3	5/1/00	5.8E+5	4.4E+7
^{99}Tc (+7)	<2E-5	4.71E-2	4.34E-2	5.10E-2	4	4.72E-2	8.1	4/24-25/00	3.1E+5	7.1E+6
^{106}Ru/Rh (GEA)		<9E-2	<9E-2	<9E-2		<9E-2		4/28-30/00		
^{125}Sb (GEA)		<6E-2	<6E-2	<6E-2		<6E-2		4/28-30/00		
^{134}Cs (GEA)		4.77E-2	4.81E-2	4.62E-2	3	4.73E-2	2.1	4/28-30/00		
^{137}Cs (GEA)		1.44E+2	1.44E+2	1.45E+2	2	1.44E+2	0.4	4/28-30/00	9.5E+8	4.3E+9
^{152}Eu (GEA)		<2E-3	<3E-3	<2E-3		<2E-3		4/28-30/00		
^{154}Eu (GEA)		<2E-3	<2E-3	<2E-3		<2E-3		4/28-30/00	<3E+5(4)	1.2E+6(4)
^{155}Eu (GEA)		<4E-2	<4E-2	<4E-2		<4E-2		4/28-30/00		
^{238}Pu	<2E-7	1.39E-5	1.49E-5	1.54E-5	6	1.47E-5	5.2	4/25-26/00		
^{239}Pu + ^{240}Pu	<2E-7	1.24E-4	1.28E-4	1.27E-4	4	1.26E-4	1.6	4/25-26/00		
^{241}Am (GEA)		<4E-2	<4E-2	<4E-2		<4E-2		4/28-30/00		
^{241}Am	<5E-7	1.73E-4	1.65E-4	1.70E-4	5	1.69E-4	2.4	4/25-26/00		
^{242}Cm	<8E-8	<1E-7	<9E-8	<2E-7		<2E-7		4/25-26/00		
$^{243+244}$Cm	<8E-8	1.34E-6	7.40E-7	1.02E-6	21	1.03E-6	29.1	4/25-26/00		
Total alpha	<7E-5	2.55E-4	2.22E-4	2.65E-4	14	2.47E-4	9.1	4/24/00		
Alpha sum(2)		3.12E-4	3.09E-4	3.13E-4		3.11E-4	0.7	4/25-26/00	2.0E+3	4.8E+5
Total beta	8.57E-5	1.46E+2	1.40E+2	1.54E+2	4	1.47E+2	4.8	4/20-24/00		
ICP-MS Analytes										
^{99}Tc (total)	<2.5E-4	5.14E-2	4.76E-2	4.80E-2	1-4	4.90E-2	4.3	4/13/00	3.2E+5	7.1E+6
^{126}Sn	<1.3E-3	<8.6E-4	<8.6E-4	<8.2E-4		<8.6E-4		4/19/00		
^{129}I	<2.5E-6	7.72E-5	7.73E-5	8.71E-5	3-7	8.05E-5	7.1	4/17/00		
^{231}Pa	<1.0E-4	<1.0E-4	<1.1E-4	<1.1E-4		<1.1E-4		4/19/00		
^{233}U	<8.8E-6	5.50E-5	5.60E-5	4.80E-5	7-11	5.30E-5	8.2	4/13/00		
^{234}U	<5.7E-6	2.70E-5	2.40E-5	2.10E-5	12-21	2.40E-5	12.5	4/13/00		
^{235}U	<6.8E-9	1.06E-6	9.94E-7	9.82E-7	0.3	1.01E-6	4.2	4/13/00		
^{236}U	<5.9E-8	2.23E-6	2.07E-6	2.08E-6	2-6	2.13E-6	4.2	4/13/00		
^{238}U	<4.7E-8	1.95E-5	1.76E-5	1.80E-5	0.5	1.84E-5	5.5	4/13/00		
^{237}Np	<5.3E-6	<5.4E-6	<5.4E-6	<5.5E-6		<5.5E-6		4/19/00		
^{239}Pu	<1.2E-3	<1.2E-3	<1.2E-3	<1.2E-3		<1.2E-3		4/19/00		
^{240}Pu	<2.4E-3	<2.4E-3	<2.4E-3	<2.4E-3		<2.4E-3		4/19/00		

(1) Samples run directly by GEA and did not require a preparation blank.

(2) Alpha sum refers to the summation of ^{238}Pu, $^{239+240}$Pu, ^{241}Am, and $^{243+244}$Cm alpha activities.

(3) The error represents the error of each reported sample concentration. In some cases, the error was identical and a single error value is given. In other cases, the reported values had varying errors and the error range is given.

(4) Based on the summation of ^{154}Eu and ^{155}Eu.

Table 3.3. 241-AP-101 Composite, ICP-MS Stable Element Results

Lab ID	PB-1701	00-1701	00-1701D	00-1701T			
Sample ID	prep blank	sample	duplicate	triplicate	Propagated	Average	RSD
Run date	4/13-19/00	4/13-19/00	4/13-19/00	4/13-19/00	1-σ		
Units	μg/mL	μg/mL	μg/mL	μg/mL	% Error(1)	μg/mL	%
Analyte							
As	0.13	1.46	1.15	1.18	2-4	1.26	14
B	6.42	15.5	15.3	17.2	1	16.0	6.5
Be	0.012	1.32	1.28	1.35	1-2	1.32	2.7
Ce	<0.079	<0.077	<0.075	<0.072		<0.077	
Co	0.014	0.356	0.331	0.369	1-3	0.352	5.5
^{133}Cs	0.014	4.96	4.90	5.40	1	5.09	5.4
Eu	<0.017	<0.016	<0.016	<0.015		<0.016	
^{127}I	<0.013	2.42	2.49	2.73	2-5	2.55	6.4
Li	< 0.064	0.323	0.329	0.367	1	0.340	7.0
Mo	<0.013	15.9	13.4	14.1	1-2	14.5	8.9
Pr	<0.018	<0.018	<0.017	<0.017		<0.018	
Rb	0.017	3.92	3.78	4.22	1	3.97	5.7
Sb	0.029	0.045	0.041	0.040	4-10	0.042	7.2
Se	<2.3	<2.3	<2.3	<2.3		<2.3	
Ta	<0.087	<0.087	<0.089	<0.089		<0.089	
Te	<0.17	<0.17	<0.16	<0.16		<0.17	
Th	<0.011	<0.011	<0.011	<0.011		<0.011	
Tl	<0.0055	0.0192	0.0168	0.0165	3-8	0.018	8.5
U	<0.14	58.9	52.9	54.1	3.5	55.3	5.7
V	<0.79	<0.77	<0.75	<0.72		<0.77	
W	<0.089	28.5	28.4	28.9	2-5	28.6	0.9
^{241}AMU	<0.011	<0.011	<0.011	<0.011		<0.011	
^{242}AMU	<0.010	<0.010	<0.010	<0.010		<0.010	
^{243}AMU	<0.0069	<0.0071	<0.0072	<0.0072		<0.0072	

Note: the last 3 listed elements, AMU-241, 242, and 243, were listed in this table with a concentration of μg/mL as opposed to the radionuclide table in units of μCi/mL. In order to determine the concentration in μCi/mL, the mass would have to be assigned to a radioisotope and multiplied by the specific activity. Thus if AMU-241 is assigned to Am, then the activity becomes <0.038 μCi/mL; if AMU-241 is assigned to Pu, then the activity becomes <1.2 μCi/mL. The same concept is applicable to the other two masses.

(1) The error represents the error of each reported sample concentration. In some cases, the error was identical and a single error value is given. In other cases, the reported values had varying errors and the error range is given.

Table 3.4. 241-AP-101 Composite, IC Results

Lab ID	00-1701	00-1701D	00-1701T				Measured Mole analyte	Specification 7 Envelope A Limits Mole analyte
Sample ID	sample	duplicate	triplicate	Average	RSD	Average	per mole Na	per mole Na
Units	µg/mL	µg/mL	µg/mL	µg/mL	%	M	Ratio	Ratio
Inorganic Anions(1), run date 4/23-24/00								
Fluoride(2)	2,880	2,880	2,940	2,900	1.2	1.5E-1	2.7E-2	9.1E-2
Chloride	2,000	1,920	2,010	1,980	2.5	5.6E-2	9.9E-3	3.7E-2
Nitrite	42,200	41,000	42,400	41,900	1.8	9.1E-1	1.6E-1	3.8E-1
Nitrate	133,000	130,000	133,000	132,000	1.3	2.1E+0	3.8E-1	8.0E-1
Phosphate	1,040	1,000	1,020	1,020	2.0	1.1E-2	1.9E-3	3.8E-2
Sulfate	4,070	3,940	4,080	4,030	1.9	4.2E-2	7.5E-3	1.0E-2
Organic Anions(3), run date 5/11-13/00								
Acetate(4)	1,540	1,790	1,600	1,640	8.0			
Formate	1,130	1,260	1,200	1,200	5.4			
Oxalate	1,800	1,780	1,820	1,800	1.1			
Citrate	<890	<890	<890					
Additional analyte information from Inorganic Anion analysis								
Bromide	<500	<500	<500					

(1) Overall error for reported results is estimated to be within +/-15%, 2-σ.

(2) The fluoride results represents the summation of fluoride, acetate, and formate.

(3) Overall error for the reported results is estimated to be within +/-30%, 2-σ.

(4) The acetate value represents the summation of acetate and glycolate.

Table 3.5. 241-AP-101 Composite, Miscellaneous Analyte Results

Lab ID	PB-1701	00-1701	00-1701D	00-1701T					Measured	Specification 7 Envelope A Limits
Sample ID	prep blank	sample	duplicate	triplicate	Average	RSD	Average		Mole analyte per mole Na	Mole analyte per mole Na
Units	µg/mL	µg/mL	µg/mL	µg/mL	µg/mL	%	M	Run Date	Ratio	Ratio
Analyte[(1)]										
Persulfate Method[(2)]										
TIC		6,550	6,400	6,430	6,460	1.2	5.4E-1	4/13-14/00	9.58E-2	3.0E-1
TOC		1,860	1,980	2,030	1,960	4.5	1.6E-1	4/13-14/00	2.91E-2	5.0E-1
TC[(3)]		8,410	8,390	8,460	8,420	0.4		4/13-14/00		
TC, Furnace Method[(2)]		8,530	8,670	8,620	8,610	0.8		4/13-14/00		
Mercury	0.026	<0.025	<0.025	0.032			<2E-7	5/11/00	<3E-8	1.4E-5
Cyanide		5.81	5.56	5.73	5.70	2.2		5/11/00		
Ammonia[(4)]		1.83	1.70	1.61	1.71	6.5		4/11/00		
Total hydroxide		42,300	41,100	40,500	41,300	2.2	2.4E+0	5/11/00		
Units	µg/L	µg/L	µg/L							
Total PCB	<1.4	<1.4	<1.4					8/14/00		
Units		g/mL	g/mL	g/mL	g/mL	%				
Density		1.307	1.309	1.308	1.308	0.076		4/5/00		

(1) Overall error for the reported results (except for ammonia) is estimated to be within +/-15%, 2-σ.

(2) Reporting units are µg C/mL solution.

(3) Total carbon is the sum of the TIC and TOC of the persulfate oxidation method.

(4) Error is estimated to be +/-20%, 2-σ.

4.0 Procedures, Quality Control, and Data Evaluation

A discussion of procedures, data quality, and quality control is provided below for each analytical method. The PNL-ALO-128 preparative blank spike and matrix spike recoveries are relevant to ICP and specifically included TCLP metals. However, two of the TCLP metals (As and Se) are included in the ICP-MS analysis. Other analytical methods, as well as ICP, generally relied on post digestion blank spikes and post digestion matrix spikes for use in data quality assessments. Analytical instrument calibration and calibration verification was performed in accordance with the SBMS Quality Assurance Program. This QA program is in compliance with HASQARD. Raw data including bench sheets, instrument printouts, data reduction, and calibration files are maintained or cross-referenced in the project files.

Tables 4.1, 4.3, 4.4, and 4.5 include a "Data Qualifier Code" section. The codes utilized were taken from the SBMS Quality Assurance Program exhibit "Conducting Analytical Work in Support of Regulatory Programs" and are defined below:

U	Analyte was analyzed but not detected
J	Estimated quantity used for detection below the EQL but above the IDL, or for tentatively identified compounds
B	Analyte found in associated laboratory blank above the QA plan acceptance criteria
X	A significant quality assurance deficiency was associated with the reported result
Y	A potential low bias is associated with the reported result.

4.1 Metals Analysis by ICP—Tables 3.1 and 4.1

The PNL-ALO-128 acid extracted samples required 5, 10 and 50-fold dilutions in order to quantify all analytes of interest according to PNL-ALO-211. The detected analytes at or above the estimated quantitation level (EQL) are reported with an uncertainty of ±15% (2-σ), and is equivalent to ten times the MDL. Values in brackets "[ ]" are less than the EQL, and have uncertainties greater than ±15%. Non-detected analytes are reported as less than the MDL. As the MDL is approached, uncertainty increases to 100%.

Quality control for the ICP analysis consists of sample duplicates, process blanks, serial dilution, matrix spikes, laboratory control standards (LCS) or blank spikes, post spikes, verification check standards, and high calibration standards. Matrix spike and LCS recovery and precision quality control parameters were also defined by BNFL. These quality control parameters were evaluated in detail and are summarized below.

Replicates: All analytes of interest were recovered within the precision tolerance limit of ≤15% relative standard deviation (RSD) except for P where the RSD was 16%.

Preparation blanks: All preparation blank analytes of interest were within tolerance limit of ≤ EQL or < 5% of sample concentration in the prepared samples.

Serial dilution: Results from serial dilution were within tolerance limit of ≤ 10% for all analytes tested after correcting for dilution.

Matrix spikes: All matrix-spiked analytes of interest were recovered within tolerance limits of 75% to 125% recoveries except silver, barium and lead. Silver recovery (about 35%), barium recovery (about 30%) and lead recovery (about 65%) were low. Barium and Pb may have precipitated as carbonates or sulfates from the carbonate and sulfate present in the sample matrix. Low silver recovery is probably due to the small amount of hydrochloric acid used during sample processing resulting in some silver chloride precipitation.

LCS: All LCS aliquots had a small amount of precipitate remaining after processing that required filtration. All analytes of interest were recovered within tolerance limit of 80% to 120% recoveries except silver. Low recovery of silver in the blank spike (about 69%) was probably due to the small amount of hydrochloric acid used during sample preparation resulting in some silver chloride precipitating from solution. The LCS for silver recovery was 69%, below QC Acceptance Criteria of 80%-120%.

Post-spiked samples: All analytes of interest were recovered within tolerance of 75% to 125% except silicon and palladium. Silicon recovery (147%) and palladium recovery (53%) exceeded the tolerance limit. All other analytes of interest above the EQL were within tolerance. Palladium was found low in the group B spike. Single element palladium at 2.0 µg/ml measured at the beginning, middle and end of the run, were well within the tolerance limit. Palladium was not detected in the sample aliquots.

Verification check standards: Concentrations of all analytes were within the tolerance limit of ± 10% accuracy in standards (except palladium). The calibration blank concentration was acceptable, less than two times the IDL. The palladium in the QC check standard was low (about 42% to 48%), however, a single element standard of palladium at 2.0 µg/ml measured at the beginning, middle and end of the ICP run was well within tolerance limit indicating acceptable palladium accuracy.

High calibration standard check: Verification of the high-end calibration for all analytes measured was within tolerance limits of ± 5% accuracy.

Detection limits: The reported MDLs for all analytes were less than the BNFL MRQs and in most cases, the EQLs were less than the MRQs (Ba, La, Rh, Ru, and Si EQLs were higher than the associated MRQs).

4.2 Total Uranium (KPA) Tables 3.1 and 4.1

Triplicate PNL-ALO-106 acid digested samples were measured for total uranium according to procedure PNNL-ALO-4014 using Kinetic Phosphorescence Analysis (KPA). The triplicate results showed excellent agreement with a RSD of 1%. A small amount of uranium was detected in the acid digestion process blank; however, the level was a factor of 10,000 lower than the uranium measured in the samples. A blank prepared at the time of the analysis did not detect any uranium. Uranium continuing calibration verification (CCV) standards analyzed before and after the samples agreed within 3% of the known values. A specific blank spike and a matrix spike were not run. The U(KPA) analysis results agreed well with the U(ICP-MS) analysis results.

4.3 Radioisotopic Analyses, Tables 3.2 and 4.2

Gamma energy analysis (GEA), pertechnetate, tritium, ^{14}C, and ^{79}Se analyses were performed on as-received samples, i.e., acid digestion of sub-samples was not performed. Other radioisotopic analyses were performed using the PNL-ALO-106 acid digested samples. Because a radioisotopic LCS is not available, post digestion spikes, tracers, and/or carriers were used, as appropriate, for monitoring process control.

Gamma Spectrometry
Triplicate 100-µL aliquots of the AP-101 original material were prepared into 2-mL geometries with deionized water (no acid digestion was applied). The small aliquot size was necessary to reduce the detector dead time attributed to the high ^{137}Cs activity. The samples were counted and analyzed directly by GEA according to procedure PNL-ALO-450. Because no sample manipulation was performed other than simple aliquoting and diluting, no preparation blank was prepared. In order to meet the required detection limits, the samples were counted for 14 hours each. Despite the longer counting time, the ^{241}Am MRQ was not met; this isotope however was quantified using radiochemical separations. Only ^{137}Cs, ^{134}Cs, and ^{60}Co could be identified in the gamma spectra. The triplicate concentrations of ^{137}Cs, ^{134}Cs, and ^{60}Co agreed to within ±3%, well within the <15% RSD acceptance criteria. The other requested analyte concentrations were below the minimum reportable quantities. Analysis for ^{135}Cs by GEA was not possible because this isotope has no γ-emissions.

Pertechnetate
The radiochemical ^{99}Tc determination was requested to measure only Tc in the +7 oxidation state (pertechnetate). To this end, all sample manipulations had to be non-oxidizing so as not to alter the original Tc oxidation state. Small aliquots from the as-received material (no digestion) were taken for analysis according to procedure PNL-ALO-432. A blank was prepared and run in parallel with the samples. This procedure normally requires the use of a sodium dichromate addition to oxidize the Tc to the +7 oxidation state. The sodium dichromate addition was omitted and the procedure was otherwise performed as written. The separated fractions were then counted according to RPG-CMC-408. One sample was also counted by gamma spectrometry (according to PNL-ALO-450) to verify the absence of ^{137}Cs. Pertechnetate was added to the blank spike and matrix spike and their recoveries were 99% and 84%, respectively, well within project requirements. The sample activity propagated 1-σ uncertainty was 4%. The RSD of the triplicate samples was 8%, again well within the project-required <15% RSD. The blank contained no measurable ^{99}Tc with a detection limit well below the MRQ.

Comparison of the pertechnetate values to the ICP-MS generated values show excellent agreement. This indicates the ^{99}Tc present in AP-101 is primarily in the +7 oxidation state.

Total Alpha
The total alpha activity was determined by direct-plating small aliquots of the acid-digested samples onto planchets according to RPG-CMC-4001. The samples were then counted on Ludlum detectors according to RPG-CMC-408. The sample activities resulted in a 9% RSD, well within the <15% RSD acceptance criteria. Alpha activity was not found in the preparation blank. The blank spike ^{239}Pu recovery was 99% and the matrix spike ^{239}Pu recovery was only 55%. The low matrix spike recovery is attributed to the solids loading on the planchet from the sample matrix salts that attenuate/absorb the alpha emissions. This is a physical problem with the sample as it is presented to the detector and does not indicate the analysis is out of control. What this does indicate is that the analytical method (which does not correct for solids loading) is probably biased low by as much as 45% for this matrix. A better indication of the total alpha activity is given by the summation of the

alpha emitters ($^{239+240}$Pu, ^{238}Pu, ^{241}Am, $^{243+244}$Cm and ^{242}Cm), where matrix effects have been eliminated through radiochemical separations. These alpha-emitter summations range from 18% to 39% higher than the total alpha activity found by direct plating. The RSD for the summation method is ±1%.

Total Beta

The total beta activity was determined by directly plating small aliquots of the acid-digested samples onto planchets according to RPG-CMC-4001. The samples were then counted on a low-background alpha/beta gas-flow proportional counter according to RPG-CMC-408. The detectors were calibrated for beta activity relative to ^{90}Sr/^{90}Y. The beta energy of ^{137}Cs is similar to that of ^{90}Sr and will have a counting efficiency similar to that of pure ^{90}Sr. The total beta analyses compared to the ^{137}Cs determinations shows that virtually all of the beta activity is due to ^{137}Cs as the two activity concentrations are in excellent agreement. The 5% RSD is within the experimental error. The blank spike and matrix spike showed excellent ^{90}Sr/^{90}Y recoveries at 100% and 103%, respectively.

Plutonium, Americium, and Curium

Analyses of Pu, Am, and Cm were conducted on the acid-digested samples. The Pu and Am/Cm separations were performed according to PNL-ALO-417; the separated fractions were precipitation plated according to PNL-ALO-496; and the samples were counted by alpha spectrometry according to PNL-ALO-422. Plutonium recovery was traced with ^{242}Pu. The curium chemistry is known to follow the americium and both these isotopes were traced with ^{243}Am. Plutonium radiochemical yields were excellent at >90%. Radiochemical yields for Am ranged from 70% to 86%. In both cases, ample counts were obtained to define analyte and tracer activities. Neither Pu, Am nor Cm were detected in the preparation blank. The blank spike and matrix spike for Pu resulted in 98% and 101% yield-corrected recovery. This indicates the chemistry and analyses were not biased. The blank spike and matrix spike for the Am (and Cm) fractions resulted in 94% and 91% yield-corrected recovery. The $^{239+240}$Pu RSD was 2% and the ^{238}Pu RSD was 5%. The ^{241}Am RSD was 2% and the $^{243+244}$Cm RSD was 29%. This latter high RSD reflects the much higher uncertainty associated with the analytical results, which were approximately 5 orders of magnitude less than the requested MRQ.

Strontium-90

The Sr separation was performed on the acid-digested samples according to PNL-ALO-476 and radiochemical yields were traced with ^{85}Sr. The separated fractions were then beta-counted according to RPG-CMC-408 and gamma counted according to PNL-ALO-450 (for ^{85}Sr determination and ^{137}Cs impurity assessment). Two of the separated fractions contained a small amount of ^{137}Cs and a correction to the beta count rate was applied for these samples. Strontium-90 was not found in the preparation blank. The RSD was 0.3%, indicative of excellent precision. The LCS and matrix spike recoveries were 92% and 99%, respectively, indicating good accuracy.

Tritium

Aliquots of AP-101 composite were diluted in water and distilled for ^{3}H determination according to procedure PNL-ALO-418. Two serial distillations were required to isolate tritium from ^{137}Cs. Tritium was then measured using liquid scintillation counting according to procedure PNL-ALO-474. The first distillation showed the presence of higher-energy beta activity, most likely due to ^{137}Cs. A second distillation succeeded in removing most of this contamination; however, two of the triplicate samples required subtraction of weak beta contamination using the ratio of the counts in the tritium energy region to the counts at higher energies, as determined from the first counting results. The triplicate results showed good agreement with a RSD of 5%. A blank spike showed good recovery at 96%. No tritium was detected in a blank processed with the samples.

Selenium-79

Direct AP-101 composite sub-samples were analyzed in triplicate for ^{79}Se following procedure PNL-ALO-440. Each sample was spiked with 20 mg Se carrier in solution for yield correction. The samples were passed through mixed-bed anion and cation exchange resins that removed most radiochemical interferences. Selenium was distilled as selenium bromide and then reduced to elemental form. The chemical yield was determined gravimetrically by weighing the recovered elemental selenium. The selenium was then dissolved and the ^{79}Se activity was determined by liquid scintillation counting according to procedure PNL-ALO-474. The liquid scintillation spectra did not show clear evidence for a ^{79}Se peak and there appeared to be some weak beta contamination evident in the higher energy region of the beta spectrum. Hence, the results probably have a slight high bias. The measured ^{79}Se activity (averaging 5.8E-5 µCi/ml) was below the requested MRQ of 9.0E-5 µCi/ml and only slightly above the nominal MDL of 2.E-5 µCi/ml. The sample RSD of 18% exceeded the RSD acceptance criterion of <15%; however, measurement uncertainties were as high as 11% (1-σ) and the sample activities were only a factor of three higher than the MDL. A ^{79}Se standard was not available, thus ^{14}C (similar beta endpoint energy as ^{79}Se) was used to calibrate the liquid scintillation detector. For the same reason a blank spike and a sample spike could not be run. The sample carrier recoveries were generally low at 27% to 63% and the blank recovery was 68%. All sample activities were corrected for radiochemical yield. The process blank did not show any evidence of contamination.

Carbon-14

Direct samples of the AP-101 composite were analyzed in triplicate for ^{14}C following procedure PNL-ALO-482. The samples were combusted in a Coulometrics Carbon Analyzer Furnace causing oxidation of all carbon species present to CO_2. A natural carbon compound was added as a carrier and all of the CO_2 released was collected in a sodium hydroxide trap. An aliquot of the trap solution was then counted by liquid scintillation counting according to procedure PNL-ALO-474. The triplicate results showed good agreement with a RSD of 5%. The blank spike and sample spike showed good recoveries at 97% and 96%, respectively. Carbon-14 was not detected in the blank.

4.4 Inductively-Coupled Plasma—Mass Spectrometry, Tables 3.2, 3.3, 4.2, and 4.3

Splits from the acid extraction (PNL-ALO-128) were submitted for ICP-MS analysis according to procedure PNL-ALO-280, Rev. 1. The sample splits were from the same processed solutions as were delivered for ICP analysis. A preparative blank and TCLP-spiked blank and sample were also submitted for ICP-MS analysis (As and Se were the relevant spiked analytes).

Values for the following isotopes were obtained using responses from related isotopes: ^{126}Sn (obtained from ^{118}Sn), ^{231}Pa (obtained from ^{232}Th), and ^{240}Pu, ^{241}AMU, ^{242}AMU, ^{243}AMU (obtained from ^{239}Pu). Because the concentrations of these isotopes were determined indirectly, ^{126}Sn, ^{231}Pa, ^{240}Pu, ^{241}AMU, ^{242}AMU, and ^{243}AMU results should be considered semi-quantitative.

In general, the results for the quality control samples (i.e., calibration verification standards, duplicates, blank spike, sample spike, and post digestion sample spikes) were well within acceptance criteria. One of the CCV results for tellurium and tantalum and the spike recovery for thallium, were outside the acceptance window (<20% for the CCV and <30% for the Spike). Tellurium and tantalum did have another CCV result that was acceptable. The CCV results for thallium were acceptable. The RSDs for all detected analytes were <15%. The MDL for ^{231}Pa was slightly above the MRQ. The preparation blank for As and B represented 10% and 40% of the measured sample concentrations, higher than the 5% acceptance criteria defined in the QA plan.

The ^{99}Tc values reported assume that the Ru present is exclusively fission-product Ru, and therefore does not have an isotope at mass to charge ratio (m/z) 99; i.e., everything observed at m/z 99 is due to ^{99}Tc. From the appearance of the Ru isotopic abundance, this appears to be a reasonable assumption; the isotopic fingerprint exhibited is not natural. Good agreement between the total ^{99}Tc and the pertechnetate (radiochemical determination) values were obtained.

4.5 Anion Analysis, Tables 3.4 and 4.4

Anion analysis was conducted according to two different methods in an effort to achieve the desired specificity. One method, PNL-ALO-212, Determination of Inorganic Anions by Ion Chromatography, is optimized for determination of inorganic anions. The other method, AOAM-1, Method for the Analysis and Quantification of Organic Acids in Simulated and Actual Hanford Tank Wastes by Ion Chromatography, is optimized for the determination of organic acids. Both methods were used to evaluate the anionic analytes of interest on unprocessed AP-101 composite sub-samples. Oxalate concentration was determined by the inorganic anion method, however the reliability of the organic anion method is considered to provide superior oxalate results.

Inorganic Anions

The AP-101 composite sub-samples were diluted 2000 to 5000 fold at the IC workstation to ensure that all anions reported were measured within the calibration range. All client-defined MRQs were met at the dilutions analyzed. From recoveries demonstrated on some of the verification standards, the AP-101 sample matrix had an adverse effect on the IC column and some reported results may be 10% to 20% low. By further diluting the sample, this effect could be minimized, but at the expense of meeting the MRQs (particularly phosphate and sulfate).

For the IC column and parameters used, the IC system cannot separate fluoride, acetate, and formate; the IC system quantifies and reports all as fluoride. Acetate (and/or glycolate) and formate were quantified in the organic anion analysis, the sum of these nearly equaling the "fluoride" concentration. An upper bound to the fluoride concentration can be calculated by subtracting the acetate and formate sum from the reported fluoride concentration providing 50+/- 960µg F/mL or <1000 µg F/mL.

Duplicates: The RSD was <3% for all anions, well within the <15% RSD acceptance criterion.

Matrix Spike: The matrix spike recoveries for all anions, except nitrate, were within the spiking acceptance criteria of 75% to 125%. The high nitrate concentration of the sample relative to the nitrate spiking level (i.e., sample concentration was 10 times greater than the spike concentration) significantly impacts the ability to measure the nitrate spike. No attempt was made to spike the samples at an additional spiking level. A 10,000x dilution provided a result of 130,000µg/mL nitrate, in good agreement with the 2000x dilution. This indicates the matrix effects on nitrate determination are negligible.

Blank Spike: The blank spike recoveries for all anions, except nitrate, were within the Laboratory Control Samples (LCS) acceptance criteria of 80% to 120%. The nitrate recovery was slightly low at 78%. It should be noted that the blank spike nitrate recovery was not consistent with other control standards analyzed during the analysis run (e.g., Verification Check Standards).

System Blank/Processing Blanks: A dozen system blanks were processed during the analysis of the samples. No anions were detected in the system blanks above the method detection limit.

Quality Control Calibration Verification Check Standards: Over twenty mid-range verification standards were analyzed throughout the analysis runs. Numerous verification standards analyzed just after the analysis of some of the AP-101 samples demonstrated low recoveries (i.e., recoveries ranging from 80% to 90%). Failure of the verification standard was only observed in those standards analyzed just after the AP-101 samples that were prepared with the least dilution. Numerous reruns were performed alternating the AP-101 (at various dilutions) and the verification standard to obtain valid data.

Organic Anions
Sample AP-101 was diluted 2000-fold to give acceptable total ion loading on the column. The reported acetate concentration represents the summation of acetate and glycolate, since both ions co-elute under the sample analysis conditions. From tank waste and solubility studies, the acetate and glycolate concentrations are tank waste type dependent. That is, for one tank waste the component may be entirely acetate; for another tank with a different fill history, the component may be primarily glycolate, or a combination of both analytes (Sharma et al. 1998, Camaioni et al. 1998, Barney 1996, Ashby et al. 1994).

The RSD of the triplicate values were well within the <15% acceptance criteria. The method detection limits are given in Table 4.4. The oxalate MDL was below the client-directed MRQ; other analyte MRQs were undefined.

Matrix spiking was done in triplicate at a level approximately 1.5 times the level of analyte in the final diluted samples. This level of spiking is at a challenging level for accurate quantitation; the reported levels are near the lowest calibration point for each analyte. The acetate matrix spike recoveries were 175%, 91%, and 105%, averaging 124%. The formate matrix spike recoveries were 71%, 104% and 79%, averaging 84%. The oxalate matrix spike recoveries were 122%, 92%, and 129%, averaging 114%. The value for acetate in the matrix spike sample should be considered suspect, as the peak quantitation had to be done by estimation (since the peak size was so small). The other data represent quantitation that was extracted directly from electronic integration data. Overall, the average data for MS and MSD were within acceptable limits. The LCS consisted of a mixture of formate and oxalate and resulted in 89.3 and 103.8% recoveries, respectively.

4.6 Miscellaneous Analytes, Tables 3.5 and 4.5

Inorganic and Organic Carbon
The AP-101 composite analysis was performed by the hot persulfate wet oxidation method according to PNL-ALO-381 and by the furnace oxidation method according to PNL-ALO-380. The hot persulfate method uses acid decomposition for TIC and acidic potassium persulfate oxidation at 92-95°C for TOC, all on the same sample, with TC being the sum of the TIC and TOC. The furnace oxidation method determines TC by oxidizing all forms of carbon (i.e., inorganic and organic) in oxygen at 1000 °C. Although the ASR requested TOC and TIC by the furnace method, the method is considered reliable only for TC. For the sample matrix analyzed, the furnace method and hot persulfate method should provide equivalent TC results; this was confirmed, with the average hot persulfate TC being 8420 μg/ml and the furnace TC being 8610 μg/ml, an RPD of about 2%.

Per procedures, all sample results were corrected for average percent recovery of system calibration standards and were also corrected for contribution from the blank. Precision and bias were estimated to be ±15% (2-σ).

The TIC standard is calcium carbonate and TOC/TC standard is α-Glucose. The standard materials were used in solid form for system calibration check standards as well as matrix spikes. The QC for the methods involves calibration blanks, system calibration standards, sample duplicates, and one matrix spike per matrix type.

Calibration Standards: The QC system calibration check standards were all within acceptance criteria of 90% to 110%, with the average recovery being about 99% for TIC and 99% for TOC over the two days that the hot persulfate analyses were performed and about 100% for TC for the furnace analyses.

Calibration Blanks: The calibration blanks run at the beginning, middle, and end of the analysis run were acceptable and the standard deviations for the TIC and TOC blanks were near the historical pooled standard deviation used to establish the method detection limits. On the May 12th run, the TOC blanks were about 2 to 3 times higher than normal, but were quite consistent. Because the blank results were subtracted from the sample results, the high blanks should have no effect on the reported data within the reported uncertainty.

Replicates: All RSDs were less than 5%, indicating good precision between all measurements. The RSDs met the acceptance criterion of <15%.

Matrix Spike: The accuracy of the carbon measurements can be estimated by the recovery results from the matrix spike. The matrix spike for both the hot persulfate and furnace method demonstrated recoveries of about 96% to 99% for TIC, TOC, and TC; well within the acceptance criteria of 75% to 125% recovery.

Laboratory Control Sample: No LCS was included in the carbon analysis procedure.

Mercury

The samples were analyzed by cold vapor atomic absorption spectrophotometry for inorganic mercury according to PNNL-ALO-201. Four aliquots of 0.2 ml including one for matrix spike, was processed and diluted to a final volume of 25 ml per procedure PNNL-ALO-131; no additional dilution was performed. Concentration of all sample aliquots measured were near instrument detection limit and several times lower than MRQ (1.5 μg/ml). The low calibration standard was defined as the instrument detection limit (DL) for the reported results and assumes non-complex aqueous matrices. Routine precision and bias is typically ± 15% (2-σ) or better for non-complex aqueous samples that are free of interference.

Following are results of quality control checks performed during Hg analyses. In general, quality control checks met the requirements of the governing QA Plan.

Working Blank Spike/Process Blank Spike: The process blank spike recovery was 100%, well within the acceptance criteria of 80% to 120%.

Matrix Spiked Sample: A matrix spike was prepared for the samples submitted under this ASR. Recovery of the matrix spike was 97%, well within the acceptance criteria of 75% to 125%.

Duplicate/replicates: The RSD was not calculated since all replicate results were less than 5 x IDL.

Laboratory Control Sample (liquid): Sample recovery of mercury in SRM-1641d (certified by NIST to contain 1.60 ± 0.018 μg/ml) was recovered within acceptance criteria of 75% to 125%.

System Blank/Processing Blanks: A system blank was processed during the analysis of the sample. The concentration measured was within about two times detection limit or less. Samples were about the same concentration as the process blank.

Quality Control Calibration Verification Check Standards: Six mid-range verification standards were analyzed throughout the analysis run. All were within the acceptance criteria of 80% to 120% recovery for the verification standard.

Cyanide

The AP-101 composite samples were distilled according to PNL-ALO-287 with the addition of sulfamic acid to minimize interference from high nitrates present in the sample. The distillates were analyzed for CN concentration according to PNL-ALO-289. The reporting limits were estimated to be approximately 0.25 µg CN/ml based on the sample quantity distilled. No quality control or other measurement problems were encountered.

An independent mid-range calibration check solution run at the beginning, middle, and end of the analysis batch gave an average recovery of 100%. These calibration check standards ranged from 99% recovery to 100% recovery, which is within the 85% to 115% acceptance criteria of the governing QA plan.

The AP-101 composite was analyzed in triplicate. The RPD between the sample and duplicate was 4.4% and the RSD for the triplicates was 3.1%. The measurement precision met the quality control criterion of <15% RSD. The LCS (a distilled blank spike) recovery was 101%, well within the quality control acceptance criteria. The spike recovery for the spiked AP-101 composite was 95%, well within the acceptance criteria of 75% to 125%.

Ammonia

Ammonia was measured in triplicate sample aliquots of AP-101 composite using an ion selective electrode according to procedure PNL-ALO-226. The ammonia probe was calibrated using five standards spanning ammonia concentrations from 1.0E-2 to 1.0E-6 M. The method of standard additions was used to determine the ammonia concentrations by first taking a direct reading and then adding a known standard to each sample. The triplicate concentrations were in good agreement with a RSD of 6%. The method detection limit was estimated at 0.2 µg/ml, well below the requested MRQ value of 140 µg/ml.

Hydroxide

A sample of the AP-101 composite was analyzed in triplicate for the free hydroxide content following procedure PNL-ALO-228. Direct sample aliquots were analyzed using a Brinkman 636 Auto-Titrator. A 0.1186 N NaOH solution was prepared for use as a standard and sample spike and the titrant was a 0.2040 M HCl prepared solution. Triplicate determinations resulted in ±3% RSD. The standard recoveries averaged 100% and the sample spike recovery was 88%. Hydroxide was not detected in the reagent blank, demonstrating an MDL of 0.02M OH or 340 µg OH/mL.

PCB

Sample handling processes were inconsistent with a procedure that would be employed for low concentration PCB analysis in that sample vessels were not rinsed with a PCB miscible solvent following sample transfer. The rinse is employed to remove adsorbed PCBs from container walls, ensuring complete analyte transfer. However, the client-requested MRQ of 3300 µg/kg (4300 µg/L) is much greater than a concentration of PCBs where adsorption issues would be of concern such as nanogram per milliliter quantities. Thus any potential loss of analyte would be of little consequence. However, if PCBs were present in the sample, the actual detection limit may have been affected and is potentially higher than reported. Despite the potential bias, the actual method detection limit would be substantially below the MRQ, particularly since there is more than three orders of magnitude between the reported detection limit and MRQ.

Because limited sample was available, the quantity of sample used for spiking was approximately half of that used for unspiked sample analysis. The LCS consisted of a spiked blank at a volume similar to that used for the samples (100 mL). The LCS recovery (71.8%) is less than the 80-120% recommended by USEPA SW-846 method 8082. However, the spiking level employed is considerably lower than the levels used in the SW-846 method by as much as 25 times. The lower spiking level used is more consistent with up-to-date regulatory expectations. The recovery does meet the general acceptance criteria of 70-130% referred to in USEPA method 8000, which would be applied since the spiking level used falls outside of the range applied in USEPA method 8082.

While no specific surrogate acceptance criteria have been developed for tank matrices, the recoveries are all within SW-846 recommended initial criteria of 20-150%, and meet USEPA CLP SOW OLM01.8 advisory criteria of 60-150% for water.

Density

The density of the AP-101 composite was calculated using the net sample mass in a 10-mL volumetric flask at ambient temperature. The RSD of the measurements was 0.08%.

Table 4.1. 241-AP-101 Composite, ICP Metals QC Results

Units	00-1701 Average µg/mL	Data Qualifier Code	RSD %	MDL µg/mL	BNFL MRQ µg/mL	LCS % Recovery	Matrix Spike % Recovery	Post Matrix Spike (A) % Recovery	Post Matrix Spike (B) % Recovery
Acceptance Criteria			<15%[3]			80%-125%	75%-125%		
Analyte[1]									
Ag	<0.63	U, X		0.63	17	69	35	96	
Al	6,940		5.5	1.5	75			113	
Ba	[0.33]	J, X	3.0	0.25	2.3	87	30	96	
Bi	<2.5	U		2.5	170			95	
Ca	[7.7]	J, B	2.0	6.3	150			97	
Cd	[2.0]	J	2.9	0.38	7.5	92	87	97	
Cr	143		8.9	0.51	15	93	94	103	
Cu	[1.6]	J, B	7.4	0.63	17			97	
Fe	[2.5]	J, B	14	0.63	75			97	
K	31,200		2.1	51	750			115	
La	<1.3	U		1.3	2.3				100
Mg	<2.5	U		2.5	170			102	
Mn	<1.3	U		1.3	17			99	
Na	129,000		2.9	3.8	170				
Nd	<2.5	U		2.5	170				101
Ni	7.9	B	7.6	0.76	30	88	85	99	
P	314	X	16	2.5	330			98	
Pb	[15]	J, X	0.0	2.5	300	101	65	107	
Pd	<19	U, X		19	390				53
Rh	<7.6	U		7.6	18				95
Ru	<28	U		28	36				96
Si	137	B	4.0	13	90			147	
Sr	<0.38	U		0.38	17			97	
Ti	<0.63	U		0.63	17			95	
U	[62]	J	9.7	51	780				104
U(KPA)[2]	51.1		1.4	0.0002	780				
U(ICP-MS)[2]	55.3		5.7	0.02	NP			115	
Zn	[5.6]	J, B	3.7	1.3	17	89	92	96	
Zr	[1.4]	J	4.2	1.3	17			100	
Additional analyte information									
As[4]	<6.3	U				95	[97]	107	
B[4]	15	B	2.6					97	
Be[4]	[1.0]	J	5.6					97	
Co[4]	<1.3	U						97	
Li[4]	<0.76	U						95	
Mo[4]	[11]	J	11					97	
Se[4]	<6.3	U				95	[80]	104	
Sn	<38	U							93
Tl[4]	<13	U				92	[91]	97	
V[4]	<1.3	U						97	
W[4]	<51	U							95
Y	<1.3	U						99	

Shaded areas highlight non-compliances with BNFL acceptance criteria, see report for discussion.

(1) Overall error for reported results is estimated to be within +/-15% 2-σ; however results in brackets "[ ]" are less than the estimated quantitation level (i.e., 10-times MDL) and error is anticipated to exceed +/-15%.

(2) U (KPA) indicates U determination by kinetic phosphorescence; U (ICP-MS) indicates U determination by ICP-MS. QC parameters for these techniques were not specified.

(3) RSD acceptance criteria for Na concentration is <3.5%.

(4) Analytes on ICP-MS Specification 7 list.

U = not detected
J = estimated value EQL>sample result >IDL
X = quality assurance deficiency, see text
B = analyte found in associated lab blank above QA acceptance criteria

Table 4.2. 241-AP-101 Composite, Radionuclide QC Results

Units	00-1701 Average µCi/mL	% Err 1-σ	RSD(3) %	MDL µCi/mL	BNFL MRQ µCi/mL	Blank Spike % Recovery	Blank spike Acceptance Criteria % Recovery	Matrix Spike % Recovery	MS Acceptance Criteria % Recovery
Radiochemical Analytes									
^{3}H	4.83E-3	3	4.7	2.0E-4	2.1E-2	96	80-120		N/A(5)
^{14}C	2.63E-4	8	4.7	4.0E-5	7.2E-4	97	80-120	96	75-125
^{60}Co (GEA)(1)	3.29E-3	7	3.0		2.1E-3		NP(4)		N/A
^{79}Se	5.82E-5	5	18	3.0E-6	9.0E-5		NP		N/A
^{90}Sr	8.74E-2	3	0.3	2.0E-4	3.0E-2	92	75-125	99	N/A
^{99}Tc (+7)	4.72E-2	4	8.1	2.0E-5	1.5E-3	99	80-120	84	70-130
^{106}Ru/Rh (GEA)(1)	<9E-2			9.0E-2			NP		N/A
^{125}Sb (GEA)(1)	<6E-2			6.0E-2	1.7E+0		to be obtained		N/A
^{134}Cs (GEA)(1)	4.73E-2	3	2.1		3.9E-2		NP		N/A
^{137}Cs (GEA)(1)	1.44E+2	2	0.4		3.9E-1		NP		N/A
^{152}Eu (GEA)(1)	<2E-3			2.0E-3			NP		N/A
^{154}Eu (GEA)(1)	<2E-3			2.0E-3	2.0E-2		NP		N/A
^{155}Eu (GEA)(1)	<4E-2			4.0E-2	9.0E-2		NP		N/A
^{238}Pu	1.47E-5	6	5.2	2.0E-7	1.0E-2		NP		N/A
$^{239+240}$Pu	1.26E-4	4	1.6	2.0E-7	1.0E-2	98	NP	101	N/A
^{241}Am (GEA)(1)	<4E-2			4.0E-2	1.0E-2		NP		N/A
^{241}Am	1.69E-4	5	2.4	5.0E-7	3.0E-2	94	NP	91	N/A
^{242}Cm	<2E-7			2.0E-7	1.5E-1		NP		N/A
$^{243+244}$Cm	1.03E-6	21	29	8.0E-8	1.5E-1		NP		N/A
Total alpha	2.47E-4	14	9.1	7.0E-5	2.3E-1	99	70-130	55	70-130
Alpha sum(2)	3.11E-4		0.7						
Total beta	1.47E+2	4	4.8	2.0E-1		100	70-130	103	70-130
ICP-MS Analytes									
^{99}Tc (total)	4.90E-2	1-4	4.3	2.6E-4	1.5E-3		80-120	101	70-130
^{126}Sn	<9E-4			9.0E-4	6.0E-3		80-120		70-130
^{129}I	8.05E-5	3-7	7.1	6.7E-6	1.8E-5		NP	99	N/A
^{231}Pa	<1E-4			1.1E-4	7.9E-5		developed by lab		developed by lab
^{233}U	5.30E-5	7-11	8.2	8.8E-6	4.2E-4		90-110		75-125
^{234}U	2.40E-5	12-21	12.5	5.7E-6	1.2E-4		90-110		75-125
^{235}U	1.01E-6	0.3	4.2	6.8E-9	4.5E-8		90-110		75-125
^{236}U	2.13E-6	2-6	4.2	5.8E-8	1.4E-6		90-110		75-125
^{238}U	1.84E-5	0.5	5.5	4.7E-8	7.2E-8		80-120		70-130
^{237}Np	<6E-6			5.4E-6	3.9E-5		90-110	119	75-125
^{239}Pu	<2E-3			1.2E-3	3.0E-2		not provided	110	not provided
^{240}Pu	<3E-3			2.4E-3	3.0E-2		not provided		not provided

Shaded areas highlight non-compliances with BNFL acceptance criteria, see report for discussion.

(1) Samples were run directly by GEA and did not require a preparation blank

(2) Alpha sum refers to the summation of ^{238}Pu, $^{239+240}$Pu, ^{241}Am, and $^{243+244}$Cm alpha activities

(3) In all cases the QC acceptance criteria for the RSD is <15%

(4) NP: not performed, as stated in Quality Control Parameters for Liquid Analysis

(5) N/A: not applicable, as stated in Quality Control Parameters for Liquid Analysis

Table 4.3. 241-AP-101 Composite, ICP-MS Stable Element QC Results

Units	00-1701 Average µg/mL	Data Qualifier Code	RSD %	MDL µg/mL	BNFL MRQ µg/mL	LCS % recovered	MS % recovered	Post Matrix Spike % recovered
Acceptance Criteria			<15%			80%-120%	70%-130%	70%-130%
Analyte								
As	1.26	B	14	0.063	2.3	117	120	109
B	16.0	B	6.5	0.16	2.3			105
Be	1.32		2.7	0.004	2.3			105
Ce	<0.077	U		0.077	2.3			117
Co	0.352		5.5	0.012	2.3			108
^{133}Cs$^{(1)}$	5.09		5.4	0.004	1.5			108
Eu$^{(1)}$	<0.016	U		0.016	60			115
^{127}I$^{(1)}$	2.55		6.4	0.037	TBD$^{(2)}$			94
Li	0.34		7.0	0.063	2.3			123
Mo	14.5		8.9	0.013	2.3			105
Pr	<0.018	U		0.018	2.3			118
Rb	3.97		5.7	0.011	2.3			106
Sb	0.042	B	7.2	0.014	2.3			94
Se	<2.3	U		2.3	2.3	102	118	
Ta	<0.089	U		0.089	2.3			89
Te	<0.17	U		0.17	2.3			73
Th	<0.011	U		0.011	2.3			122
Tl	0.0180		8.5	0.011	2.3			139
V	<0.77	U		0.77	2.3			110
W	28.6		0.9	0.23	2.3			124
^{241}AMU$^{(1)}$	<0.011	U		0.011				
^{242}AMU$^{(1)}$	<0.010	U		0.010				
^{243}AMU$^{(1)}$	<0.0072	U		0.0072				

Shaded area highlights non-compliance with BNFL acceptance criteria, see report for discussion.

(1) QC acceptance criteria for LCS and matrix spike recoveries and precision were not specified.

(2) To be determined by method

U = not detected

B = analyte found in preparation blank above QA acceptance criteria

Table 4.4. 241-AP-101 Composite, IC QC Results

Units	00-1701 Average µg/mL	Data Qualifier Code	RSD %	MDL µg/mL	BNFL MRQ µg/mL	LCS % recov.	Matrix Spike % recov.
Acceptance Criteria			<15%			80%-120%	75%-125%
Inorganic Anions(1)							
Fluoride(2)	2,900	J(2)	1.2	130	150	110	114
Chloride	1,980		2.5	130	300	107	111
Nitrite	41,900		1.8	250	2300	105	119
Nitrate	132,000	X	1.3	250	3000	78	128
Phosphate	1,020		2.0	250	2300	104	119
Sulfate	4,030		1.9	250	2300	106	108
Organic Anions(3)							
Acetate(4)	1,640		8.0	550	TBD(5)		124(6)
Formate	1,200		5.2	450	TBD(5)	89.3	84(6)
Oxalate	1,800		1.0	890	1800	103.8	114(6)
Citrate	<890	U		890	TBD(5)		
Additional analyte information							
Bromide	<500	U				108	108

Shaded areas highlight non-compliances with BNFL acceptance criteria, see report for discussion.

(1) Overall error for reported results is estimated to be within +/-15%, 2-σ

(2) The fluoride results represents the summation of fluoride, acetate, and formate concentrations as these cannot be resolved on the IC column

(3) Overall error for reported results is estimated to be within +/-30% at 2-σ

(4) Acetate concentration represents the summation of acetate and glycolate concentrations

(5) To be determined by the method

(6) Based on the average of 3 matrix spike recoveries

U = not detected
J = tentatively identified compound, see text
X = quality assurance deficiency, see text

Table 4.5. 241-AP-101 Composite, Miscellaneous Analyte QC Results

Units	00-1701 Average µg/mL	Data Qualifier Code	RSD %	MDL µg/mL	BNFL MRQ µg/mL	Blank Spike % Recovery	Matrix Spike % Recovery
Acceptance Criteria			<15			80-120	75-125
Analyte							
Persulfate Method(1)							
TIC	6,460		1.2	40	150		98.5
TOC	1,960		4.5	80	1500		96.3
TC	8,420		0.4	80			97.5
TC, Furnace Method	8,610		0.8	170			97.5
Mercury(2)	0.032	B		0.025	1.5	100	97
Cyanide	5.70		2.2	0.25	4.5	101	95
Ammonia	1.71		6.5	0.20	140		
Total hydroxide	41,300		4.2	340	75,000	100	88
Units	µg/L		%	µg/L	µg/L(4)	%	%
Total PCB	<1.4	Y, U		1.4	4300	71.8	101(5)
Units	g/mL		%	g/mL	g/mL		
Density(3)	1.308		0.076		0.9		

(1) Reporting units are µgC/mL solution.
(2) Two results were reported as <0.025 µg/mL, one result was reported at 0.032µg/mL. The worst-case value is reported in this table.
(3) Acceptance criteria for precision was not specified.
(4) MRQ of 3300µg/kg corrected for density.
(5) Average of MS (106%) and MSD (96.9%) recoveries.

B = analyte found in preparation blank above the QA acceptance criteria
U = not detected
Y = potential low bias, see text

5.0 References

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APPENDIX A

Appendix A: Tank 241-AP-101 Grab Samples

CH2M HILL
Hanford Group, Inc.
P.O. Box 1500
Richland, WA 99352

CH2MHILL
Hanford Group, Inc.

February 15, 2000

CHG-0000767

Mr. J. J. Short, Contracting Officer
Office of Procurement Services
U.S. Department of Energy
Office of River Protection
Post Office Box 450
Richland, Washington 99352-0450

Dear Mr. Short:

CONTRACT NUMBER DE-AC06-99RL14047; SAMPLE MANAGEMENT DOCUMENT PACKAGE FOR GRAB SAMPLES FROM TANK 241-AP-101

Reference: Letter, J. J. Short II, ORP, to M. P. DeLozier, CHG, "Contract No. DE-AC06-99RL14047 – Direction to Provide Sample From Tank 241-AP-101 to BNFL Inc. (BNFL) and to Archive Sample at 222-S Laboratory," 00-OPD-0017/0000166, dated January 14, 2000.

As requested in the Reference (1), this letter transmits to the U.S. Department of Energy, Office of River Protection, three copies of a "sample management document package" for grab samples from tank 241-AP-101 on February 8, 2000. In accordance with Reference (1), five grab samples were delivered to the 325 Laboratory and five grab samples are archived at the 222-S Laboratory for use by BNFL Inc. Five samples were also archived at the 222-S Laboratory for use by the Waste Feed Delivery program. The attached sample management document package includes the following information regarding tank 241-AP-101 and the samples obtained: recent waste transfer history for tank 241-AP-101, past sampling and analysis of tank 241-AP-101 wastes, sample location selection, sampling information and chain-of-custody forms for the current sampling event.

If you have any questions, please contact Ms. C. DeFigh-Price, at 373-9596.

Very truly yours,

J. M. Bateman for
R. F. Wood, Manager
Contracts Administration
CH2M HILL Hanford Group, Inc.

ldf

Attachment

SECTION V: Sampling Information

Waste in tank 241-AP-101 has been identified as potentially a suitable candidate LAW Envelope A feed. On February 8, 2000, ten 120-mL grab samples were obtained from this tank and provided to BNFL Inc. (BNFL) for analysis and testing to evaluate the waste composition and ability to process the waste. An additional five samples were obtained for the Waste Feed Delivery Program.

Table 1 lists the fifteen grab samples and their locations. All samples were obtained on February 8, 2000 from riser 002. At the time of sampling, all samples were clear, yellow liquids with no solids. Five samples were shipped to the Pacific Northwest National Laboratory (PNNL) 325 Laboratory on February 8, 2000, and ten samples were shipped to the Fluor Hanford (FH) 222-S Laboratory on February 9 and 10, 2000. Chain-of-custody forms for the fifteen samples are provided in Section VI.

Table 1. Tank 241-AP-101 Sampling Information

Sample Number	Actual Sample Elevation (inches)[1]	Receiving Laboratory	Organization
1AP-00-1	400	325	BNFL
1AP-00-2	400	222-S	BNFL
1AP-00-3	400	222-S	WFD
1AP-00-4	290	325	BNFL
1AP-00-5	290	222-S	BNFL
1AP-00-6	290	222-S	WFD
1AP-00-7	190	325	BNFL
1AP-00-8	190	222-S	BNFL
1AP-00-9	190	222-S	WFD
1AP-00-10	100	325	BNFL
1AP-00-11	100	222-S	BNFL
1AP-00-12	100	222-S	WFD
1AP-00-13	10	325	BNFL
1AP-00-14	10	222-S	BNFL
1AP-00-15	10	222-S	WFD

Note:
[1] Sample elevation is the distance from the tank bottom to the mouth of the sample bottle. All samples were obtained at the requested sample elevations.

BNFL = BNFL Inc.
WFD = Waste Feed Delivery

CHAIN-OF-CUSTODY RECORD FOR CPO

(1) Sample Number: IAP-001

(2) Supervisor/Sampler: Robert J Prazniki

(3) Tank: AP-101

(4) Riser: 02

(5) Cask/Pig Serial No.: A00460-16

(6) Shipment Description:

A. Work Package Number ES-00-00045/0

B. Cask/Pig Seal Number 12627

C. Date Sample Collected 2-8-00

D. Time Sample Collected 1143 hrs.

(7) Sampling Data

	Y	N
- Lithium Bromide	☐	☐
Amount		
Concentration		
- X-Ray	☐	☐
- Partial Sample	☐	☐
- Retrieved Partial Sample Stroke Length		

B 2-7-00

(8) Field Comments:

-TO BE SHIPPED TO 325 BLDG. B 2-7-00

-Clear yellow, NO SOLIDS B 2-8-00

(9) Seal Intact Upon Release? ☒ Yes ☐ No

(10) Seal Intact Upon Receipt? ☐ Yes ☐ No

(11) Seal Number AND Cask/Pig SERIAL Number consistent with this record? (Block 5 & 6b) ☐ Yes ☐ No

(12) Laboratory Comments:

(13) Relinquished By (Sign and PRINT) Robert J Prazniki	(14) Received By (Sign and PRINT) M Dunnington	(15) Date/Time 2/8/00 1430	(16) Receiver Comments
(17) Relinquished By (Sign and PRINT) M Dunnington	(18) Received By (Sign and PRINT) F Ullorpes	(19) Date/Time 2/8/00 2011	(20) Receiver Comments
(21) Relinquished By (Sign and PRINT)	(22) Received By (Sign and PRINT)	(23) Date/Time	(24) Receiver Comments
(25) Relinquished By (Sign and PRINT)	(26) Received By (Sign and PRINT)	(27) Date/Time	(28) Receiver Comments

DISTRIBUTION: Original - Laboratory Copy - Sampling Operations

CHAIN-OF-CUSTODY RECORD FOR CPO

(1) Sample Number: 1AP-00-1

(2) Supervisor/Sampler: Robert J. Praznik

(3) Tank: AP-101

(4) Riser: 02

(5) Cask/Pig Serial No.: A00460-1

(6) Shipment Description:

A. Work Package Number: ES-00-00045/0

B. Cask/Pig Seal Number: 12630

C. Date Sample Collected: 2-8-00

D. Time Sample Collected: 1159 hrs.

(7) Sampling Data — Y N

- Lithium Bromide ☐ ☐
  - Amount ______
  - Concentration ______
- X-Ray ☐ ☐
- Partial Sample ☐ ☐
- Retrieved Partial Sample Stroke Length ______

NA 2.7.00

(8) Field Comments:

- TO BE DELIVERED TO 325 BLDG. 2-7-00
- Clear yellow, No solids 2-8-00

(9) Seal Intact Upon Release? ☑ Yes ☐ No

(10) Seal Intact Upon Receipt? ☐ Yes ☐ No

(11) Seal Number AND Cask/Pig SERIAL Number consistent with this record? (Block 5 & 6b) ☐ Yes ☐ No

(12) Laboratory Comments:

(13) Relinquished By (Sign and PRINT) Robert J. Praznik	(14) Received By (Sign and PRINT) S. M. Dunnington	(15) Date/Time 2/8/00 1630	(16) Receiver Comments
(17) Relinquished By (Sign and PRINT) S. M. Dunnington	(18) Received By (Sign and PRINT) Fullhayes	(19) Date/Time 2/8/00 2011	(20) Receiver Comments
(21) Relinquished By (Sign and PRINT)	(22) Received By (Sign and PRINT)	(23) Date/Time	(24) Receiver Comments
(25) Relinquished By (Sign and PRINT)	(26) Received By (Sign and PRINT)	(27) Date/Time	(28) Receiver Comments

DISTRIBUTION: Original - Laboratory Copy - Sampling Operations

CHAIN-OF-CUSTODY RECORD FOR CPO

(1) Sample Number: 1AP-00-7

(2) Supervisor/Sampler: Robert J. Fraznik

(3) Tank: AP-101

(4) Riser: 02

(5) Cask/Pig Serial No: A00460-10

(6) Shipment Description:

A. Work Package Number: ES-00-00045/10

B. Cask/Pig Seal Number: 12633

C. Date Sample Collected: 2-8-00

D. Time Sample Collected: 1211 hr

(7) Sampling Data — Y N

- ~~Lithium Bromide ☐ ☐~~
- ~~Amount ____~~
- ~~Concentration ____~~
- ~~X-Ray ☐ ☐~~
- ~~Partial Sample ☐ ☐~~
- ~~Retrieved Partial Sample Stroke Length ____~~

NA JJJ 2.7.00

(8) Field Comments:

-TO BE DELIVERED TO 325 BLDG. 2-7-00

-yellow clear, No solids 2-8-00

(9) Seal Intact Upon Release? ☑ Yes ☐ No

(10) Seal Intact Upon Receipt? ☐ Yes ☐ No

(11) Seal Number AND Cask/Pig SERIAL Number consistent with this record? (Block 5 & 6b) ☐ Yes ☐ No

(12) Laboratory Comments:

(13) Relinquished By (Sign and PRINT) Robert J Pluznik	(14) Received By (Sign and PRINT) V. Matthews V. Matthews	(15) Date/Time 1615 2-8-00	(16) Receiver Comments
(17) Relinquished By (Sign and PRINT) V. Matthews V. Matthews	(18) Received By (Sign and PRINT)	(19) Date/Time 1940 2-8-00	(20) Receiver Comments
(21) Relinquished By (Sign and PRINT)	(22) Received By (Sign and PRINT)	(23) Date/Time	(24) Receiver Comments
(25) Relinquished By (Sign and PRINT)	(26) Received By (Sign and PRINT)	(27) Date/Time	(28) Receiver Comments

DISTRIBUTION: Original - Laboratory Copy - Sampling Operations

CHAIN-OF-CUSTODY RECORD FOR CPO

(1) Sample Number: 1AP-00-10

(2) Supervisor/Sampler: Robert J. Plaznik

(3) Tank: AP-101

(4) Riser: 02

(5) Cask/Pig Serial No.: A004601-7

(6) Shipment Description:

A. Work Package Number: ES-00-00045/0

B. Cask/Pig Seal Number: 12636

C. Date Sample Collected: 2-8-00

D. Time Sample Collected: 1222hrs

(7) Sampling Data

	Y	N
- Lithium Bromide	☐	☐
Amount		
Concentration		
- X-Ray	☐	☐
- Partial Sample	☐	☐
- Retrieved Partial Sample Stroke Length		

NA JGJ 2.7.00

(8) Field Comments:

- Deliver to 325 Lab @ 300 Area JGJ 2.7.00
- yellow clear, NO solids 2-8-00

(9) Seal Intact Upon Release? ☑ Yes ☐ No

(10) Seal Intact Upon Receipt? ☐ Yes ☐ No

(11) Seal Number AND Cask/Pig SERIAL Number consistent with this record? (Block 5 & 6b) ☐ Yes ☐ No

(12) Laboratory Comments:

(13) Relinquished By (Sign and PRINT) Robert J Plaznik	(14) Received By (Sign and PRINT) V. Matthews V. Matthews	(15) Date/Time 16.15 2-8-00	(16) Receiver Comments
(17) Relinquished By (Sign and PRINT) V. Matthews V. Matthews	(18) Received By (Sign and PRINT)	(19) Date/Time 1940 2-8-00	(20) Receiver Comments
(21) Relinquished By (Sign and PRINT)	(22) Received By (Sign and PRINT)	(23) Date/Time	(24) Receiver Comments
(25) Relinquished By (Sign and PRINT)	(26) Received By (Sign and PRINT)	(27) Date/Time	(28) Receiver Comments

DISTRIBUTION: Original - Laboratory Copy - Sampling Operations

CHAIN-OF-CUSTODY RECORD FOR CPO

(1) Sample Number: 1AP-00-13

(2) Supervisor/Sampler: Robert J. Pruznik

(3) Tank: AP101

(4) Riser: 02

(5) Cask/Pig Serial No.: A00460-15

(6) Shipment Description:

A. Work Package Number ES-00-00045/0

B. Cask/Pig Seal Number 12639

C. Date Sample Collected 2-8-00

D. Time Sample Collected 1235h

(7) Sampling Data

	Y	N
- Lithium Bromide	☐	☐
Amount		
Concentration		
- X-Ray	☐	☐
- Partial Sample	☐	☐
- Retrieved Partial Sample Stroke Length		

NA JAJ 2.7.00

(8) Field Comments:

- Deliver to 325 LAB @ 300 AREA JAJ 2.7.00

- Clear yellow, No solids. RJP 2-8-00

(9) Seal Intact Upon Release? ☑ Yes ☐ No

(10) Seal Intact Upon Receipt? ☐ Yes ☐ No

(11) Seal Number AND Cask/Pig SERIAL Number consistent with this record? (Block 5 & 6b) ☐ Yes ☐ No

(12) Laboratory Comments:

(13) Relinquished By (Sign and PRINT) Robert J Pruznik	(14) Received By (Sign and PRINT) V. P. Matthews V.P. Matthews	(15) Date/Time 2050 2-8-00	(16) Receiver Comments
(17) Relinquished By (Sign and PRINT) V. Matthews V.P. Matthews	(18) Received By (Sign and PRINT) F.L. Hoopes	(19) Date/Time 2130 2-8-00	(20) Receiver Comments
(21) Relinquished By (Sign and PRINT)	(22) Received By (Sign and PRINT)	(23) Date/Time	(24) Receiver Comments
(25) Relinquished By (Sign and PRINT)	(26) Received By (Sign and PRINT)	(27) Date/Time	(28) Receiver Comments

DISTRIBUTION: Original - Laboratory Copy - Sampling Operations

BC-6001-326 (02/98)

APPENDIX B

Appendix B: Test Instructions

~~[illegible]~~

PNNL Test Instruction

Document No.: 29953-81
Rev. No.: 0
Document Control: Only the original signed copy is controlled

Title: Density Measurements on As-Received AP-101 Samples

Work Location: Radiochemical Processing Laboratory

Page 1 of 3

Author: Paul Bredt

Use Category Identification: Reference

Effective Date: Upon Final Approval
Supersedes Date: New

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

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

PRB
2/10/00

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 X No

Does the OJT package associated with this procedure require revision to reflect procedure changes?
_____Yes _____No X N/A

Approval	**Signature**	**Date**
Author	Paul Br	2/10/00
Technical Reviewer	D E Kurath	2/10/00

Density Measurements on As-Received AP-101 Samples

Scope

This test plan defines density measurements on samples of tank 241-AP-101 supernatant received from the Hanford tank farms on 2/8/00. These test instructions provides specific details to RPG staff regarding the implementation of Technical Procedure 29953-010, "Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges".

Justification of Use Category

This test instruction is reference use. Reference use was selected as the use category since this analysis is not a complex process and there are no safety impacts to the order of events. In addition, we may wish to modify the order of analyses or eliminate some analyses depending on the needs at the time of the operation.

Applicability

This test plan applies to RPL staff performing work on BNFL Privatization samples under Project 29953.

Work with actual samples is to be performed in the SAL hot cells by staff under the direction of a cognizant scientist.

Prerequisites

1) Keep the sample in a sealed glass container as much as possible to prevent it from drying and reduce the potential for organic contamination.
2) Cross-contamination between samples and contamination of samples from outside sources must be minimized at each step. Use new tools and bottles for each sample as much as possible. Those tools which are reused should be washed and rinsed prior to reuse.
3) Secondary containment is to be used whenever practical to minimize sample loss in the event of a spilled sample or broken sample bottle.

Quality Control

Quality control has been implemented in Technical Procedure 29953-010, "Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges". This work is to be conducted under the quality requirements of the Standards-Based Management System (SBMS).

M&TE List

✓ Balance 1: Calib ID 360-06-01-016 Calib Exp Date 2/01 Location Cell 2/SAL

Masses of 4 similar Jars to 1AP Samp → from Julie Johnston of LMHC, payroll #55327

1) 125.7 g
2) 124.9 g
3) 125.8 g
4) 124.5 g

$\bar{x} = 125.22$ g

PR Bredt
02/10/00

1) Weight five new clean volumetric flasks (between 5 and 25 ml) labeled as indicated below.

1AP-00-1	1AP-00-4	1AP-00-7
Tare 19.2593 g	Tare 19.2709 g	Tare 19.3125 g
1AP-00-10	**1AP-00-13**	
Tare 19.3396 g	Tare 19.4298 g	

2) Weigh samples 1AP-00-1, 1AP-00-4, 1AP-00-7, 1AP-00-10, and 1AP-00-13. Record the masses.

1AP-00-1	1AP-00-4	1AP-00-7
Mass ______ g	Mass ______ g	Mass ______ g
1AP-00-10	**1AP-00-13**	
Mass ______ g	Mass ______ g	

High end balance is broken PRB 2/11/00

3) Fill the volumetrics with supernatant for the respective jars. Record the new mass of the full volumetrics. used new glass transfer pipet for each sample

	1AP-00-1	1AP-00-4	1AP-00-7
Total	51.4983 g	51.5504 g	51.5914 g
Tare	19.2593 g	19.2709 g	19.3125 g
Slurry	32.2390 g	32.2795 g	32.2789 g
Volume	25.00 ml	25.00 ml	25.00 ml
	ρ = 1.2896 g/ml	ρ = 1.2912 g/ml	ρ = 1.2912 g/ml

	1AP-00-10	1AP-00-13
Total	52.3296 g	52.6236 g
Tare	19.3396 g	19.4298 g
Slurry	32.9900 g	33.1938 g
Volume	25.00 ml	25.00 ml
	ρ = 1.3196 g/ml	ρ = 1.3278 g/ml

4) Return the supernatant to the respective jars.

5) Weigh samples 1AP-00-1, 1AP-00-4, 1AP-00-7, 1AP-00-10, and 1AP-00-13. Record the masses.

1AP-00-1	1AP-00-4	1AP-00-7
Mass ______ g	Mass ______ g	Mass ______ g
1AP-00-10	**1AP-00-13**	
Mass ______ g	Mass ______ g	

High end Balance is Broken PRB 2/11/00

Work done on 2/11/00
PB

PNNL Test Instruction

Document No.: BNFL-TP-29953-83
Rev. No.: 0
Document Control: Only the original signed copy is controlled

Title: AP-101 Homogenization and Subsampling

Work Location: Shielded Analytical Laboratory/Radiochemical Processing Laboratory

Page 1 of 5

Author: Paul Bredt

Use Category Identification: Reference

Effective Date: Upon Final Approval
Supersedes Date: New

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

Required Reviewers:
X Technical Reviewer
~~X Building Manager~~
___ Radiological Control
___ ES&H
~~X Quality Engineer~~
X Project Manager
X RPL Manager
___ SFO Manager

not required JRB 4/4/00

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 X No

Does the OJT package associated with this procedure require revision to reflect procedure changes?
_____ Yes _____ No X N/A

Approval	**Signature**	**Date**
Author	Paul B	3/31/00
Technical Reviewer	D E Kurath	3/31/00
Project Manager	D E Kurath	3/31/00
SFO Manager	Rich T. Steele for RE Thornhill	4/3/00

AP-101 Homogenization and Subsampling

Scope

This test plan defines work to be conducted on five AP-101 liquid samples delivered to Battelle from the Hanford tank farms on 2/8/00. Under this Test Plan, the five samples will be combined into a single jar, stirred and then subsampled for other tasks.

Applicability

This test plan applies to RPL staff performing work on BNFL Privatization samples under Project 29953.

Work will be performed in the Shielded Analytical Laboratory (SAL) of the Radiochemical Processing Laboratory (RPL) by staff under the direction of a cognizant scientist.

Prerequisites

1) Keep the sample in a sealed glass container as much as possible to prevent it from drying and reduce the potential for organic contamination.
2) Cross-contamination between samples and contamination of samples from outside sources must be minimized at each step. Use new tools and bottles for each sample as much as possible. Those tools which are reused should be washed and rinsed prior to reuse.
3) Secondary containment is to be used whenever practical to minimize sample loss in the event of a spilled sample or broken sample bottle.
4) Since organic analyses will be performed on some of this material, staff are to avoid contacting the samples with plastics. The exception to this is Teflon which is already a sealing material already present in the sample lids.
5) This material may contain regulated levels of PCBs. Handle the samples and segregate all wastes accordingly.
6) If a balance is not available for this testing, skip the weighing steps.

Quality Control:

This work is to be conducted under the quality requirements of the Standards-Based Management System (SBMS).

M&TE List:

_____ Balance 1:

Calib ID 360-06-01-040 Calib Exp Date 2/01

Location 201

If a Category 1 balance is not available, conduct a performance check on an available balance. If needed, user calibrate an available balance and record calibration data below. Data from a user calibrated balance will be limited to information only use.

In Cell Balance is a sartorius max 424g
property # WA 82993

4/4/00 used 100.003g check weight, reading was 100.004g

Work Instructions:

Note:

This is a very high visibility task within DOE-RL. Secondary containment should be used whenever and wherever possible to prevent inadvertent sample loss and/or hot cell contamination. Great care should be taken during sample transfers.

1) Weigh a clean ~1L jar labeled "**AP-101 COMP**".

AP-101 COMP

Tare 535 g ← Balance 360-06-01-043 ex 8/2000

2) Weigh a clean Teflon stir bar.

Stir bar

Tare 7.0498 g ← using Balance 360-06-01-040

3) Add the Teflon stir bar to "**AP-101 COMP**".

4) Weigh the sample jars listed below. Transfer all material from the jars to "**AP-101 COMP**". Reweigh the empty jars and record the masses in the space provided.

Sample Label	Mass (Full)	Mass (Empty)	Mass Transferred
1AP-00-1	300.308	125.973	
1AP-00-4	296.724	126.494	
1AP-00-7	294.544	124.805	
1AP-00-10	299.031	125.430	
1AP-00-13	298.009	125.777	

all samples were clear yellow with no observable solids or separable organics layers. PRB 5/23/00

5) Set up secondary containment such that if the primary sample jar (**AP-101 COMP**) breaks during stirring then the sample material can be easily and cleanly recovered. It is preferred that this be done by placing "**AP-101 COMP**" in a secondary container that will still allow for proper operation of the stir bar. If this is not possible, then the magnetic stir plate can be placed in secondary containment.

6) Securely replace the lid on "**AP-101 COMP**" and stir the material in "**AP-101 COMP**" for a minimum of 30 minutes using the magnetic stirrer. Consult with the cognizant scientist on the appropriate stir rate. started stirring @ 9:31 am 4/4/00 stopped @ 10:25 am

7) Weigh a volume graduated 120 ml glass jar labeled "**AP-101 GL**".

AP-101 GL

Tare ~~133.7723~~ g using 3600[illegible]06-01-040
133.9021 PRB 4/4/00

8) Transfer 100 ml (±10ml) of supernatant from "**AP-101 COMP**" to "**AP-101 GL**". Securely replace the lid on "**AP-101 COMP**", and "**AP-101 GL**". Record the mass and volume of material in "**AP-101 GL**".

AP-101 GL

Total 263.164 g
Tare 133.9021 g
Liquid 129.243 g
Volume 101 ml

very approximate due to unknown error of both volume
~ρ = 1.2796

9) Store both "**AP-101 COMP**", and "**AP-101 GL**" in secondary containment in a location where they are unlikely to be disturbed.

all work completed during morning of 4/4/00

Paul Bredt
4/4/00

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature D E Kurath 4/4/00
Print Name DEAN E KURATH
Phone 376-6752 MSIN P7-28

PNNL Project #: 29953
Charge Code: W 54906
Date Required: 5-12-00

Matrix Type Information

- **Liquids:** ✓ Aqueous ___ Organic ___ Multi-phase
- **Solids:** ___ Soil ___ Sludge ___ Sediment
  ___ Glass ___ Filter ___ Metal
  ___ Smear ___ Organic ___ Other
- **Other:** ___ Solid/Liquid Mixture, Slurry
  ___ Gas ___ Biological Specimen

If sample matrices vary, specify on Request Page

Disposal Information

- **Disposition of Virgin Samples:**
  Virgin samples are returned to requestor unless archiving provisions are made with receiving group!
  If archiving, provide:
  Archiving Reference Doc # ___
- **Disposition of Treated Samples:**
  Dispose ✓ after 60 days Return ___

QA/Special Requirements

- **QA Plan:**
  SBMS ___
  HASQARD (CAWSRP) ✓
- **Additional QA Requirements?** No ___
  or Reference Doc # SEE TABLE 4 ATTACHMENT 1 2
- **Field COC?** INDIVIDUAL RPLS ~~No~~ ___ Yes ✓
- **Lab COC Required?** No ✓ Yes ___
- **Hold Time:** None ✓
  or RCRA ___ CERCLA ___
  Other, Specify ___
  & Date Sampled ___
  Time Sampled ___
- **Special Storage Requirements:**
  None ✓ Refrigerate (4°C) ___
  or Other, specify ___
- **Data Quality Review Required?** No ✓ Yes ___

Waste Designation Information

- **Sample Information Check List Attached?** Yes ✓
  or Reference Doc # ___
  or Previous ASR # ___
  or Previous RPL ID # ___

Does the Waste Designation Documentation Indicate Presence of PCBs?
No ___ Yes ✓ SEE ATTACHMENT TO SICL

Additional or Special Instructions SEE ATTACHMENT 1 & 2

Send Report To D. E. KURATH **Phone** 376-6752
Phone ___

Preliminary results requested, as available? No ___ Yes ✓ (requesting preliminary results may increase cost)

Receiving and Login Information (*to be completed by laboratory staff*)

Date Delivered: RESIDENT IN SAL
Delivered By (optional) ___
Time Delivered (optional) ___
Group ID (optional) ___
CMC Waste Sample? No ✓ Yes ___
Cost Estimate, if requested: $ ___

Received By: ___

ASR Number: 00-01701
RPL Numbers: 5778

RPG/CMC Work Accepted By: MW Urie **Signature/Date:** MW Urie 4/3/00

Analytical Service Request (ASR)

(REQUEST PAGE ----- Information Specific to Individual Samples)

Lab Staff Use Only				Lab Staff Use Only	
RPL ID #	Client Sample ID	Sample Description (& Matrix, If Varies)	Analysis Requested (1)	Test	Library
00-01701	AP-101 Comp	WASTE TANK AP-101	SEE AttAchment	SEE	
		COMPOSITE		AttAchment 1	
		DATE REQUIRED IS	MANDATORY		
		AP-101 TAKE PRIORITY	OVER		
		ANY OTHER BNFL	SAMPLE.		
		NOTE SUSPECTED	PRESENCE		
		OF PCB. ALL LABS	PERFORMING		
		ANALYSES MUST BE	APPROPRIATELY		
		POSTED.			

(1) See "Analysis Requested" Instructions: Provide analytes of interest and required detection levels. [Information provided: Above ____ ; On Attachment ___]

ASR # 5778

Page 1 of 1

Attachment 1
Page 1of 2

ASR 5778

AP101 DKJ 6/6/00

00-01701 ~~C-104~~ Supernatant Composite

Digestion-128	**SAL**	**-- Use W54906**
ICP-211-CMC	**LAB**	**-- Use CMC WP Number**
ICP/MS	**ADV INORG**	**-- Use W54906**
GEA-381/474-CMC	**RAD**	**-- Use CMC WP Number**
Alpha/Gross-4001/408-CMC	**RAD**	**-- Use CMC WP Number**
Beta/Gross-4001/408-CMC	**RAD**	**-- Use CMC WP Number**
Am,Cm/AEA-417/422-CMC	**RAD**	**-- Use CMC WP Number**
Pu/AEA-417/422-CMC	**RAD**	**-- Use CMC WP Number**
U/KPA-4014-CMC	**RAD**	**-- Use CMC WP Number**
Sr-90-476/408-CMC	**RAD**	**-- Use CMC WP Number**
Se79-440/474-CMC	**RAD**	**-- Use CMC WP Number**
Tc99-432/408-CMC	**RAD**	**-- Use CMC WP Number**
Direct Sub-Sample		
Density/Solution	**SAL**	**-- Use W54906**
IC-212-CMC	**LAB**	**-- Use CMC WP Number**
TOC/TIC-381-CMC	**LAB**	**-- Use CMC WP Number**
TOC/TIC-380-CMC	**LAB**	**-- Use CMC WP Number**
NH3-ISE	**LAB**	**-- Use W54906**
CN/Total	**LAB**	**-- Use W54906**
H3-418/474-CMC	**RAD**	**-- Use CMC WP Number**
C14-381/474-CMC	**RAD**	**-- Use CMC WP Number**
Hg-131/201-CMC	**LAB**	**-- Use CMC WP Number**
OH-/Titration-228-CMC	**LAB**	**-- Use CMS WP Number**
IC-Organic	**ORG**	**-- Use W54906**
Ext-Solvent (PCB/Prep)	**SAL**	**-- Hold (Use W54906)**
PCB/Pesticide (PCB only)	**ORG**	**-- Hold (Use W54906)**

Special Instructions

See Attached Table 2, Table 3 and Table 4 for analyte list, MRQs, and QC Parameters

All analyses are to be done in **Triplicate**.
Results are to be reported in ug/ml or uCi/ml, as applicable
QC is to include process blank, matrix spike, and LCS (or blank spike)
Method detection limit is to be reported for all analytes.

Digestion:
Prepare one set of triplicate digestions using the sample quantity defined by the procedure (i.e., total of 60 ml). This set of digestions (without further dilutions) will be distributed for all radiochemistry. Additional dilutions may be required due to dose. No MS prepared, where required by method the radionuclides are to be post-spiked.

Prepare a second set of triplicate digestions using 5 ml sample sizes and additional MS (i.e., total 20 ml). This set of digestions will be distributed for ICP (10 ml each) and ICP/MS (15 ml each) analyses. Additional dilutions may be required due to dose. The MS is to include only TCLP metals, all other analytes are to be post-spiked.

Estimated Subsample quanities: (Total ml. including MS) May need to be diluted due to dose

Density/Solution (perform in volumetrics and reuse sample for other analyses)
IC-212-CMC (5 ml)
TOC/TIC-381-CMC (3 ml)
NH3-ISE (4 ml) – No subsample for MS required
H3-418/474-CMC (5 ml)
Hg-131/201-CMC (1 ml)
IC-Organic (5 ml)
TOC/TIC-380-CMC (3 ml)
CN/Total (8 ml)
C14-381/474-CMC (3 ml)
OH-/Titration-228-CMC (5 ml)

Attachment 1
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PCB Extraction/Analysis: Hold until authorization to proceed has been obtained from D.E. Kurath.

Hot Cell Instructions for Preparation of PCB Organic Samples

1) Transfer 100-ml aliquot (40-ml aliquot for MS and MSD) of the AP-101 Comp into a separatory funnel. (Note: if 300 mls are available after all other subsamples have been taken, then use 50-ml aliquots for MS and MS duplicate)

2) Add the surrogate spiking solution to all samples (including blank) and the target compound spiking solution to the MS and MSD. Use the entire contents of the vial(s) provided for spiking. After transferring the contents of the spiking vial to the sample, add approximately 0.2 mL of methylene chloride to the vial(s) and transfer this rinsate to the sample. (Note: surrogate and spiking solutions are to be supplied by E. W. Hoppe)

3) Perform three sequential separatory funnel shakeout extractions of the supernatant using ~~50~~ 25 MWL 1/4/00 -mL portions of methylene chloride. Collect and combine the three extracts in a 250-mL amber bottle labeled AP-101-PCB-X

   Where X = S for sample, D for duplicate, MS for matrix spike and MSD for matrix spike duplicate.

4) Dry extracts with anhydrous sodium sulfate. Volume reduction will be performed outside the hot cells.

For further guidance and questions, contact Eric W. Hoppe, (509) 376-2126.

HDK 0113
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Table 2
Supernate Analyses Required by Contract Specification 7
and Opportunistic Analytes

Analyte	Minimum Reportable Quantity	Analysis Method
	µg/ml	
Al	7.5E+01	ICP-AES
Ba	2.3E+00	
Ca	1.5E+02	
Cd	7.5E+00	
Cr	1.5E+01	
Fe	7.5E+01	
K	7.5E+02	
La	2.3E+00	
Na	1.7E+02	
Ni	3.0E+01	
Pb	3.0E+02	
U	7.8E+02	
U	7.8E+02	Kin. Phosphorescence
Ag	1.7E+01	ICP-AES (Opportunistic)
Bi	1.7E+02	
Cu	1.7E+01	
Mg	1.7E+02	
Mn	1.7E+01	
Nd	1.7E+02	
P	3.3E+02	
Pd	3.9E+02	
Rh	1.8E+01	
Ru	3.6E+01	
Si	9.0E+01	
Sr	1.7E+01	
Ti	1.7E+01	
Zn	1.7E+01	
Zr	1.7E+01	
TIC	1.5E+02	Furnace Oxidation
TOC	1.5E+03	
TOC	1.5E+03	Silver catalyze persulfate and furnace oxidation method
TIC	1.5E+02	Silver catalyze persulfate and furnace oxidation method
Hg	1.5E+00	Cold Vapor AA
Cl	3.0E+02	IC
F	1.5E+02	
NO_2	2.3E+03	
NO_3	3.0E+03	
PO_4	2.3E+03	
SO_4	2.3E+03	
Formate	To be determined by method	IC (Opportunistic)
Oxalate	1.8E+03	
Acetate	To be determined by method	
Citrate	To be determined by method	

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Table 2
Supernate Analyses Required by Contract Specification 7
and Opportunistic Analytes

Analyte	Minimum Reportable Quantity	Analysis Method
	µCi/ml	
^{237}Np	3.9E-05	ICP-MS
^{239}Pu	3.0E-02	
^{240}Pu	3.0E-02	
^{99}Tc	1.5E-03	
	µg/ml	ICP-MS (Opportunistic)
As	2.3E+00	
B	2.3E+00	
Be	2.3E+00	
Ce	2.3E+00	
Co	2.3E+00	
Cs (total)	1.5E+00	
Eu (total)	6.0E+01	
I (natural ^{127}I)	To be determined by method	
Li	2.3E+00	
Mo	2.3E+00	
Pr	2.3E+00	
Rb	2.3E+00	
Sb	2.3E+00	
Se	2.3E+00	
Ta	2.3E+00	
Te	2.3E+00	
Th	2.3E+00	
Tl	2.3E+00	
V	2.3E+00	
W	2.3E+00	
	µCi/ml	
^{241}AMU	To be determined by method	
^{242}AMU	To be determined by method	
^{243}AMU	To be determined by method	
^{231}Pa	7.9E-05	
^{233}U	4.2E-04	
^{234}U	1.2E-04	
^{235}U	4.5E-08	
^{236}U	1.4E-06	
^{238}U	7.2E-08	
^{126}Sn	6.0E-03	
^{129}I (or GEA method)	1.8E-05	
^{90}Sr	3.0E-02	Separations / Liquid Scintillation
^{99}Tc	1.5E-03	Separations / Liquid Scintillation (Opportunistic)
^{238}Pu	1.0E-02	Separations / AEA
^{239}Pu	1.0E-02	
^{240}Pu	5.1E-02	
^{241}Am	3.0E-02	
^{242}Cm	1.5E-01	
$^{243/244}$Cm	1.5E-01	

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Table 2
Supernate Analyses Required by Contract Specification 7 and Opportunistic Analytes

Analyte	Minimum Reportable Quantity	Analysis Method
	µCi/ml	
^{154}Eu	2.0E-02	Extended Counting Time GEA
^{155}Eu	9.0E-02	
^{60}Co	2.1E-03	
^{137}Cs	3.9E-01	
	µCi/ml	
^{106}Ru/Rh	To be determined by method	Extended Counting Time GEA (Opportunistic)
^{125}Sb	1.7E+00	
^{134}Cs	3.9E-02	
^{135}Cs	3.9E-02	
^{152}Eu	To be determined by method	
^{241}Am	1.0E-02	
total and free OH	7.5E+04 µg/ml	Titration
~~Wt% Centrifuged Solids~~	~~0.5 wt%~~	~~Gravimetry~~
~~Wt% Oven Dried Solids~~	~~0.25 wt%~~	~~Gravimetry~~
Separate Organic Phase	N/A	Visual Observation
Density	0.9 gm/ml	

Table 3
Additional Supernate Analyses Required by Waste Feed Staging DQO and LAW / HLW Feed Processing DQO (PNNL-12163)

Analyte	Minimum Reportable Quantity	Analysis Method
	µg/ml	
NH_3/NH_4	1.4E+02	ISE
CN	4.5E+00	Distillation / Colorimetric
Total Alpha	2.3E-01 µCi/ml	Alpha Counting
^{3}H	2.1E-02 µg/ml	Separations / Liquid Scintillation
^{14}C	7.2E-04 µCi/ml	Separations / Liquid Scintillation
^{79}Se	9.0E-05 µCi/ml	Separations / Liquid Scintillation
Total Beta	To be determined (µCi/ml)	Beta Counting
Sum of Alpha	To be determined (µCi/ml)	Summation of Pu-238, Pu239 + 240, Am-241, Cm-242, Cm-243 + 244

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Table 4. Quality Control Parameters for Liquid Analysis

Liquid Fraction(a)	Analytical Technique	QC Acceptance Criteria		
		LCS %Recovery(b)	Spike %Recovery(c)	Duplicate RSD(d)
Ag, Al, Bi, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Nd, Ni, P, Pb, Pd, Rh, Ru, S, Sr, Si, Ti, U, Zn, Zr	ICP/AES	80 - 120%	75 - 125%	<15%
Na	ICP/AES	80 - 120%	75 - 125%	<3.5%
As, B, Ba, Be, Ce, Co, La, Li, Mo, Pr, Rb, Sb, Se, Ta, Te, Th, Tl, V, W, mass unit 90(e)	ICP/MS	80 - 120%	70 - 130%	<15%
Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{-3}(f), SO_4^{-2}(f),	IC	80 - 120%	75 - 125%	<15%
CN^-	Distillation colorimetric	80 - 120%	75 - 125%	<15%
Cs(g), Eu(g)	ICP/MS	N/A	N/A	N/A
Hg	CVAA	80 - 120%	75 - 125%	<15%
NH_3/NH_4^+	ISE, standard additions	80 - 120%	75 - 125%	<15%
OH-	Potentiometric titration	80 - 120%	N/A	<15%
TIC/$CO_3^{=}$	Persulfate and combustion furnace	80 - 120%	75 - 125%	<15%
TOC(h)	Silver catalyzed persulfate and combustion furnace	80 - 120%	75 - 125%	<15%
Y	Derived from calculation	N/A	N/A	N/A
^{3}H	Separation/liq. Scintillation	80 - 120%	N/A(i)	<15%
^{14}C	Separation/liq. Scintillation	80 - 120%	75 - 125%	<15%
^{60}Co(j)	GEA	NP	N/A(k)	<15%
^{79}Se(i)	Liq. scintillation	NP	N/A(i)	<15%
^{90}Sr	Isotopic specific separation/beta count	75 - 125%	N/A(i)	<15%
^{99}Tc	ICP/MS	80 - 120%	70 - 130%	<15%
^{99}Tc (pertechnetate)(j)	Separation/beta count	80 - 120%	70 - 130%	<15%
^{125}Sb	GEA	to be obtained		
^{126}Sn	ICP/MS	80 - 120%	70 - 130%	<15%
^{129}I	ICP/MS or Separation/GEA	NP	N/A(k)	<15%
^{137}Cs	GEA	NP	N/A(k)	<15%
^{152}Eu(i)	GEA	NP	N/A(k)	<15%

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Table 4. Quality Control Parameters for Liquid Analysis (contd)

		QC Acceptance Criteria		
Liquid Fraction(a)	Analytical Technique	LCS %Recovery(b)	Spike %Recovery(c)	Duplicate RSD(d)
^{154}Eu(i)	GEA	NP	N/A(k)	<15%
^{155}Eu(i)	GEA	NP	N/A(k)	<15%
^{231}Pa (f)	ICP/MS	Developed by Laboratory		
^{233}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{234}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{235}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{236}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{238}U	ICP/MS	80 - 120%	70 - 130%	<15%
^{237}Np(f)	ICP/MS	90 - 110%	75 - 125%	<15%
Total Pu	Sum of Isotopes	N/A	N/A	N/A
^{238}Pu, ^{239}Pu, ^{240}Pu(l), (m)	Separation/AEA	NP	N/A(i)	<15%
^{241}Pu/Am, ^{242}Pu(m)	ICP/MS	80 - 120%	70 - 130%	<15%
^{241}Am(m)	Separation/AEA	NP	N/A(i)	<15%
^{242}Cm(m)	Separation/AEA	NP	N/A(i)	<15%
^{243}Am/Cm(m)	ICP/MS	90 - 110%	75 - 125%	<15%
$^{243+244}$Cm(m)	Separation/AEA	NP	N/A(i)	<15%
Total Alpha(l)	Proportional counter	70 - 130%	70 - 130%	<15%
Total Beta	Beta counting	70 - 130%	70 - 130%	<15%
Total Gamma	GEA-Sum of isotopes	N/A	N/A	N/A
Density		N/A	N/A	N/A
Wt% dissolved solids(a)	Gravimetric	80 - 120%	N/A	<21%

Acronyms:

AEA	– Alpha Energy Analysis
CVAA	– Cold Vapor Atomic Absorption
GEA	– Gamma Energy Analysis
IC	– Ion Chromatography
ICP/AES	– Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP/MS	– Inductively Coupled Plasma Mass Spectroscopy
LSC	– Laboratory Control Standard
N/A	– Not applicable
NP	– Not performed
RSD	– Relative Standard Deviation
Wt%	– Weight percent

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Table 4. Quality Control Parameters for Liquid Analysis (cont'd)

Liquids footnotes

(a) Analytes for the Solubility Screening Test are a subset of this analyte list. Refer to Section 7.6.3.

(b) LCS = Laboratory Control Standard. This standard is carried through the entire method. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS is a matrix with known concentration of analytes processed with each preparation and analyses batch. It is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

(c) For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. It is expressed as percent recovery; i.e., the amount measured less the amount in the sample, divided by the spike added, times 100. One matrix spike is performed per analytical batch. Samples are batched with similar matrices.

For other analytes, the accuracy is determined based on use of serial dilutions as described in Section 7.7.2.2.

(d) RSD = Relative Standard Deviation between the samples. Sample precision is estimated by analyzing replicates taken separately through preparation and analysis. Acceptable sample precision is usually <15% RSD if the sample result is at least 10 times the instrument detection limit.

RSD = (standard deviation of the mean/mean) x 100

(e) ICP-MS mass unit 90 includes ^{90}Sr, ^{90}Y, and ^{90}Zr.

(f) Analysis required for only liquid fraction.

(g) Total Cs and Eu are sums of all isotopes, therefore spiking and LCS does not apply.

(h) Analysis for oxalate may be required as described in Section 7.5.

(i) Matrix spike analyses are not required for this method because a tracer is used to correct for analyte loss during sample preparation and analysis. The result generated using the tracer accounts for any inaccuracy of the method on the matrix. The reported results reflect this correction.

(j) An extended counting time in the presence of high ^{137}Cs activity may be required to achieve the minimum reportable quantity for ^{60}Co and ^{154}Eu, ^{155}Eu.

(k) The measurement is a direct reading of the energy and the analysis is not affected by the sample matrix; therefore, a matrix spike is not required.

(l) The sum of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Am activities will be used as a measurement of alpha-emitting TRU when total alpha measurement in the liquid fraction is equal to or exceeds 6.0E-05Ci/L for Envelopes A and B and 4.0E-04 Ci/L for Envelope C. The selected trigger values correspond to 70% of the LAW envelope limits for TRU. The selected isotopes account for greater than 95% of the alpha-emitting TRU activity based on previous analysis of Phase I candidate tank waste (Esch 1997a, 1997b, 1997c). Additional isotopes which are defined as alpha-emitting TRU (e.g., ^{237}Np, ^{242}Pu, ^{242}Cm, ^{243}Am, and $^{243+244}$Cm) are not used to calculate total TRU activity because *the MDAs for these isotopes* are large in comparison with the envelope limits and it is expected that their concentrations are well below the MDA. Note that ^{241}Pu is a beta-emitting TRU whose analysis, along with ^{242}Cm, is required specifically for class C waste determination.

(m) Analysis for these analytes is required only if the total alpha measurement is equal to or exceeds 6.0E-05Ci/L for Envelope A and B feed and 4.0E-04 Ci/L for Envelope C. These values correspond to 70% of the envelope limit for TRU. Based on the previous analysis results for Phase I tanks, at total alpha values less than specified, the values for these analytes are less than the MDA. Therefore, if the total alpha values are less than specified, the MDA for the individual analyte will be used to fulfill the data needs for this DQO.

(n) Weight percent dissolved solids method is described in Section 7.3.4.

RPL Sample Information Checklist

(Please have client or sample owner complete to the best of their knowledge or provide the information obtained from the client.)

CLIENT

Name: D. E KURATH

Phone: 376-6752

Employer: BATTELLE

CHECKLIST PREPARED BY:

Print Name: M. W. URIE

Signature: MW Urie

Date: 4/3/00

(To be complete by Battelle research or laboratory staff)

Client Sample Number(s)	Description (Use page 2 if more than 4 samples)	RPL Unique Identifier(s)
AP-101 COMP	AP-101 TANK WASTE COMPOSITE	00-01701

1. Is the sample from a commercial chemical product, manufacturing chemical intermediate, or off-specification commercial chemical product (i.e., P or U Listed)? (See 40 CFR 261.33) ☐ Yes ☒ No
   If yes, what chemicals or waste codes? ________

2. Is the sample from an F or K listed source? (See 40 CFR 261.31 and 261.32). ☑ Yes ☐ No
   If yes, what is the source and waste code? HANFORD TANK WASTE

3. Mark any of the following physical and chemical characteristics or constituents (and associated waste code) you suspect to be present:

☐ Explosive (D003)
☐ Oxidizer (D001)
☐ Sulfides (D003)
☐ Water Reactive (D003)
☑ Corrosive (D002); pH = 12.5 or less

☐ Pyrophoric (D003)
☐ Asbestos
☐ Cyanides (D003)
☐ Air Reactive (D003)

☐ Shock Sensitive (D003)
☐ Peroxide Former (D003)
☐ Corrosive Solids(WSC2)
☐ Corrosive to Steel (D002)
☐ Ignitable (D001); Flashpoint = ______ °F or ______ °C

☐ Generates Toxic Gases in Water (D003)
☐ Halogenated Hydrocarbons (WP01 or WP02)
☐ Polycyclic Aromatic Hydrocarbons (WP03)

4. Mark any of the following constituents (and associated waste code) you suspect to be present (40 CFR 261.24):

☐ Arsenic (D004)
☐ Barium (D005)
☐ Cadmium (D006)
☑ Chromium D007)
☑ Lead (D008)
☐ Mercury (D009)
☐ Selenium (D010)
☐ Silver (D011)

☐ Benzene (D018)
☐ Carbon tetrachloride (D019)
☐ Chlordane (D020)
☐ Chlorobenzene (D021)
☐ Chloroform (D022)
☐ Cresol, o-, m-, or p- (D023-D025)
☐ 2,4,D (D016)
☐ 1,4-Dichlorobenzene (D027)
☐ 1,2-Dichloroethane (D028)
☐ 1,1-Dichloroethylene (D029)

☐ 2,4-Dinitrotoluene (D030)
☐ Endrin (D012)
☐ Heptachlor (& its epoxide)(D031)
☐ Hexachlorobenzene (D032)
☐ Hexachlorobutadiene(D033)
☐ Hexachloroethane (D034)
☐ Lindane (D013)
☐ Methoxychlor (D014)
☐ Methyl ethyl ketone (D035)

☐ Nitrobenzene (D036)
☐ Pentachlorophenol (D037)
☐ Pyridine (D038)
☐ Tetrachloroethylene (D039)
☐ Toxaphene (D015)
☐ Trichloroethylene (D040)
☐ 2,4,5-Trichlorophenol (D041)
☐ 2,4,6-Trichlorophenol (D042)
☐ 2,4,5-TP (Silvex) (D017)
☐ Vinyl chloride (D043)

5. List any known RCRA Underlying Hazardous Constituents: None Known

6. Are there any state hazardous waste codes associated with the sample? ☐ Yes ☒ No
   If yes, please list: ________

7. Is the sample known to contain >2 ppm PCBs? ☐ Yes ☐ No
   If yes, is the sample concentration: ☐ <50 ppm ☐ >50 ppm?
   If <50 ppm, what is the source of PCBs (if known)?
   PCB CONCENTRATION UNKNOWN. HOWEVER. CONSIDER SAMPLE AS HAVING PCBs from Source >50ppm: SEE attached letter

8. Is the sample radioactive? ☒ Yes ☐ No If yes, list any known isotopes, activities, or dose rates associated with the sample:
   See Attachment for best estimate of RADIONUCLIDE Concentrations

(To be completed by Battelle research or laboratory staff)

Battelle Project #: 29953

Charge Code #: W54906

Signature: ________ Date: ________

Receiving Inspection	
No Anomalies Found	☐
Anomalies Found, RPL POC Notified	☐

Best TWINS estimate of contents of AP-101 for use with SICL

Analyte	Units	AP-101
Al	g/L	9.66E+00
Bi	g/L	0.00E+00
Ca	g/L	3.87E-02
Cl	g/L	1.32E+00
TIC as CO3	g/L	1.40E+01
Cr	g/L	1.08E-01
F	g/L	2.29E+00
Fe	g/L	3.87E-03
Hg	g/L	0.00E+00
K	g/L	1.79E+01
La	g/L	0.00E+00
Mn	g/L	0.00E+00
Na	g/L	1.46E+02
Ni	g/L	6.30E-03
NO2	g/L	4.03E+01
NO3	g/L	1.31E+02
OHTOTAL	g/L	6.95E+01
Pb	g/L	3.13E-03
PO4	g/L	9.94E-01
Si	g/L	8.39E-02
SO4	g/L	3.43E+00
Sr	g/L	3.29E-06
TOC	g/L	3.15E+00
UTOTAL	g/L	2.53E-02
Zr	g/L	1.74E-02

Analyte	Units	AP-101
3H	mCi./L	1.38E-02
14C	mCi./L	1.77E-04
59Ni	mCi./L	3.29E-04
60Co	mCi./L	3.29E-03
63Ni	mCi./L	3.29E-02
79Se	mCi./L	3.87E-04
90Sr	mCi./L	1.35E-01
90Y	mCi./L	1.35E-01
93Zr	mCi./L	2.90E-03
93mNb	mCi./L	2.10E-03
99Tc	mCi./L	5.12E-02
106Ru	mCi./L	7.92E-06
113mCd	mCi./L	1.52E-02
125Sb	mCi./L	2.55E-02
126Sn	mCi./L	1.25E-02
129I	mCi./L	5.56E-05
134Cs	mCi./L	2.55E-03
137Cs	mCi./L	1.73E+02
137mBa	mCi./L	1.64E+02
151Sm	mCi./L	2.08E+00
152Eu	mCi./L	7.74E-04
154Eu	mCi./L	7.32E-02
155Eu	mCi./L	4.05E-02
226Ra	mCi./L	7.60E-08
227Ac	mCi./L	1.48E-07
228Ra	mCi./L	4.42E-05
229Th	mCi./L	1.04E-06
231Pa	mCi./L	6.65E-07
232Th	mCi./L	6.00E-06
232U	mCi./L	3.64E-06
233U	mCi./L	1.40E-05
234U	mCi./L	1.15E-05
235U	mCi./L	4.42E-07
236U	mCi./L	8.27E-07
237Np	mCi./L	1.82E-04
238Pu	mCi./L	1.07E-05
238U	mCi./L	8.39E-06
239Pu	mCi./L	1.44E-04
240Pu	mCi./L	3.43E-05
241Am	mCi./L	1.95E-04
241Pu	mCi./L	9.96E-04
242Cm	mCi./L	3.20E-07
242Pu	mCi./L	4.15E-09
243Am	mCi./L	1.80E-08
243Cm	mCi./L	1.62E-05
244Cm	mCi./L	3.54E-04

BNFL
Inc.

River Protection Project
Waste Treatment Plant
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Kathleen Whelan
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Direct tel: 509-375-4312
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CCN#: 012259

March 17, 2000

Dear Kathy:

Contract No. DE-AC06-96RL13308 – W375-SC-98-4168 – REQUEST FORPROPOSAL TO CONDUCT PCB ANALYSIS OF TANK 241-AP-101 SAMPLE

References: 1. CCN 012160, Letter M. E. Johnson, BNFL Inc., to Eugene Morrey, Battelle, "Request for Proposal to Conduct Revised Analysis of Tank 241-AP-101 Samples", dated March 15, 2000.

BNFL Inc. received verbal notification on March 15, 2000 from Dr. N. R. Brown, U.S. Department of Energy Office of River Protection (DOE-ORP), the tank 241-AP-101 sample currently at Battelle facilities may have in part originated from a waste source that contained greater than 50ppm polychlorinated biphenyl (PCB) compounds. Battelle personnel should conduct appropriate handling practices for this waste sample, consistent with Battelle procedures.

BNFL Inc. is requesting Battelle to prepare a proposal for conducting analysis of the tank 241-AP-101 sample to determine the concentration of PCB compounds following EPA *Test Methods for Evaluation of Solid Waste Physical / Chemical Methods*, SW-846. The requested PCB analysis of the tank 241-AP-101 sample is to be conducted in addition to the analyses already requested by BNFL Inc. in correspondence number 012160 (ref.).

RECEIVED
CONTRACT SERVICES
MAR 20 2000

Please indicate in your proposal the volume of additional tank 241-AP-101 sample (if necessary) for conducting the PCB analyses. Please submit your proposal to Ms. Anne Thompson by March 24, 2000. Please contact Michael Johnson, if you have technical inquiries relating to this request for proposal

Sincerely,

James O. Knight
Systems Acquisition Manager

ANT/vle

cc:

D. Blumenkranz	BNFL Inc.	ETC-1/P-122
J. R. Cook	BNFL Inc.	ETC-1/P113
M. E. Johnson	BNFL Inc.	B-267
Contracts File	BNFL Inc.	
Contracts Correspondence File	BNFL Inc.	
PDC	BNFL Inc.	
Neil R. Brown	DOE-O	H6-60
Karyn Wiemers	DOE-O	H6-60

Test Instruction

Unique Numerical Designation: TI-29953-086
Revision number: 0
Effective Date: April 17, 2000
Controlling Procedure No: N/A

Author Approval: 4/17/00
Technical Reviewer: D E Kurath 4/17/00
BNFL Reviewer: N/A

TITLE: AP-101 Precipitation/Crystallization Versus Temperature

1. Set bath temperature to 10°C

2. Inspect the AP-101 sample (sample ID: **AP-101 GL**) for precipitates

6/6/00

Notes: Appears to be some solids floating around in the AP-101 GL sample. Will filter, then transfer filtrate to clean glass bottle → "AP-101 GL Filter"

3. If the sample has solids, filter through a 0.45-µm nylon membrane. If there are no solids, proceed directly to step 4.

4. Place the sample in the cooling bath at 10°C PLACED 1040 6/8/00 mRZ

5. Inspect the sample for solids each day (excluding weekends) for a period of seven days; note observations below

Date	Time	Observations	TEMP.	g WT.
6-9-00	1040	NO VISIBILITY CHANGES	9°C	mRZ
6-12-00	1230	NO VISIBLE CHANGES	9°C	mRZ
6-13-00	1530	No visibility changes	10°C	mRZ
6-14-00	–	NOT TAKEN	–	mRZ
6-15-00	0930	NO visible changes	9°C	mRZ (END OF TEST)

tare Wt = 133.5504
Balance Cal. info
384-06-01-004
Due 8/2000

Note
If no solids have formed after seven days, proceed to step 17.

6. Label a 120-mL glass jar as **AP101-10°-Liquid**

7. Weigh vial **AP101-10°-Liquid**

Wt. **AP101-10°-Liquid** = __________ g (7a)

Note balance calibration information:

Calibration ID: ____________________

Calibration Date: ____________________

Due Date: ____________________

Note
During steps 8 through 11, keep **AP-101 GL** in the 10°C water bath to the extent possible to avoid warming the sample

8. Using a pipette transfer the liquid from **AP-101 GL** to **AP101-10°-Liquid**; take care not to transfer any solids during this process

9. Weigh vial **AP101-10°-Liquid**

Wt. **AP101-10°-Liquid** = __________ g (9a)

Wt. liquid = 9a – 7a = __________ g (9b)

10. Place a piece of filter paper into **AP-101 GL** and tip the jar so that the excess liquid wicks up the filter paper; take care not to remove any solids during this process

11. Remove the filter paper

12. Weigh vial **AP-101 GL** with the damp solids

Wt. **AP-101 GL** = __________ g (12a)

13. Calculate the weight of the damp solids

Wt. wet solids = 12a – 133.9021 = __________ g (13a)

Note: The tare weight of **AP-101 GL** is 133.9021 g

14. Dry the solids in **AP-101 GL** to a constant weight at 105°C

Notes:

15. Weigh vial **AP-101 GL** with the dry solids

Wt. **AP-101 GL** = __________ g (15a)

16. Calculate the weight of the dry solids

Wt. solids = 15a – 133.9021 = __________ g (16a)

17. End of Test

PNNL Test Plan

Document No.: BNFL-TP-29953-027
Rev. No.: 0

Title: Analysis for Pesticides and PCBs by Gas Chromatography Dual Electron Capture Detection

Work Location: 329 bld.

Page 1 of 7

Author: Eric Hoppe

Effective Date: February 8, 1999

Use Category Identification: Information use

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

Required Reviewers:
_X_ Technical Reviewer
___ Building Manager
_X_ Radiological Control
___ ES&H
___ Quality Engineer
_X_ Project Manager
___ RPL Manager
___ SFO Manager
___ Other

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 _X_ No

Does the OJT package associated with this procedure require revision to reflect procedure changes?
_____ Yes _____ No _X_ N/A

Approval	**Signature**	**Date**
Author	E Hoppe	2-9-99
Technical Reviewer	J.A. Campbell	2-11-99
Project Manager	Michael W Thi for EV Morrey	3-5-99
Radiological Control	Forrest Bronson	3/8/99

Applicability

The PNNL approach to analysis of radioactive samples for pesticides and PCBs is based upon existing procedures PNL-ALO-346, 347, and USEPA methodologies. Modifications of the methods are primarily due to the limited sample available and consequently the procedure is scaled down. The modifications reduce the initial sample size and proportionately lower the amount of surrogate or spike compounds that are added. Surrogates and spikes are approximately the same concentrations in the reduced sample size to those used in the PNNL and USEPA procedures. The final volume is reduced as well to allow for similar analysis conditions. Additionally, specific method performance criteria have been included.

Equipment Description

This method employs a variety of materials and glassware that is described below. Analysis is performed using a gas chromatograph (GC) equipped with two columns of dissimilar stationary phases and dual electron capture detectors. This laboratory uses a Hewlett Packard 5890 GC and 30 meter x 0.32 mm columns. The stationary phases are DB-1701 and a DB-17.

Work Instructions

Extraction of Liquid/Water Samples:

USEPA Contract Laboratory Program and SW-846 Method 3510 procedures typically begin with a nominal 1 liter sample added to a separatory funnel or continuous liquid-liquid extractor. This is followed by the addition of surrogates tetrachloro-m-xylene (TCX) and decachlorobiphenyl (DCB). Spike compounds are also added if the sample is designated for quality control. The surrogates are added to achieve a concentration in the sample of 0.2 to 5.0 ug/L for analysis by gas chromatograph/ electron capture detection (GC/ECD). Following sample extraction, the residue is exchanged into hexane and reduced to 10.0 mL final volume.

In most cases, a full liter of radioactive sample is not available or should not be used due to ALARA concerns. Typically, a nominal 100 mL of liquid or water sample is available. The procedure can be proportionately scaled down. For example, a nominal 100 mL of sample will be added to a separatory funnel and one-tenth the quantity of surrogate or spike compounds which would be added to a liter sample is used. Typically, 0.04 ug of each of the surrogates are added resulting in a 0.4 ug/L concentration in the 100 mL sample for GC/ECD analysis. For samples designated, 0.2 ug of Aroclor 1254 spike is typically added resulting in a concentration of 2.0 ug/L. An Aroclor spike at this level is below the current concentration of regulatory concern which is 3.0 ug/L. Spiking near the regulatory decision level provides additional confidence in the data when proposing a waste designation. The amount of sample and the surrogate/spiking levels may be varied by the cognizant scientist based on matrix, analytical instrumentation to be used for the analysis, and other factors. For example, if analysis is performed for individual PCB congeners, then the spiking levels for each congener will be approximately the same as the surrogate additions. If analysis is performed using electron impact ionization low resolution mass spectrometric detection (GC/MS), the surrogate and spike levels will need to be about 1000 times greater than for GC/ECD.

As with the USEPA methods, methylene chloride is used as the partitioning solvent for three extractions. The methylene chloride extracts are combined, concentrated, and exchanged into hexane. The final volume of the residue is reduced from 10 mL, as specified in the USEPA procedures, to 1-2 mL for most samples. This results in approximately the same concentration factor as the USEPA procedures. Residues may be placed in storage for up to 40 days at 4°C. Residues chilled in storage must be allowed to completely warm to room temperature before use.

Continuous liquid-liquid extraction is not recommended for samples less than 1 liter as the required dilution to make the proper volume is contrary to waste reduction practices.

Extraction of Solid/Sludge Samples:

Sample heterogeneity is generally the greatest source of variability in analytical results. Although dependent on particle size and the distribution of analyte, extractions performed on less than approximately 0.5 to 1 gram samples, are generally subject to substantially increasing variations of the results. If, because of limited sample availability or ALARA concerns, sample size can not be increased to compensate for these effects, then homogenization of the sample prior to extraction is critical. To provide samples which are as homogenous as possible, samples should be well mixed as a slurry rather than centrifuged solids. This provides better mixing of the samples prior to obtaining discrete sample aliquots. Dewatering methods such as centrifugation and subsequent addition of drying agents, for example sodium sulfate, are then performed. Extractions should be accomplished in radiological fume hoods to the extent possible to reduce the complications associated with performing these procedures in a glove box or remote handling facilities. Extracts obtained from remote handling can usually undergo further treatment and concentration in a radiological fume hood.

Ultrasonic extraction is recommended as the method for performing sludge sample extractions. It is known that very non-polar species, such as PCBs, can be difficult to extract from materials with a great deal of surface area, particularly when they are comprised of insoluble organic materials. While most tank materials do not contain an appreciable quantity of insoluble organic material, they do contain small particle sizes and offer substantial surface area. To minimize this potential problem, the sample is solvent contacted and sonicated three times rather than once as is done in the USEPA CLP or SW-846 3550 medium level methods. The samples are extracted employing as much sample material as possible, although this is usually 5 grams or less.

An alternate to sonication extraction is to employ Soxhlet extraction. The Soxhlet method is time consuming and is not conducive to work in remote handling facilities. If sample radiation doses allow, Soxhlet extraction can be performed in a radiological fume hood. Historically, sample dose levels have been prohibitively high and in these cases Soxhlet extractions are not recommended.

Sample aliquoting is often performed using remote handling. Free water is removed and sodium sulfate is added to the sample aliquot as a drying agent followed by the addition of approximately 0.04 ug of each of the surrogate compounds TCX and DCB. Samples designated for spiking should have 0.2 ug of Aroclor 1254 added. The amount of sample and the surrogate/spiking levels may be varied by the cognizant scientist based on matrix, analytical instrumentation to be used for the analysis, and other factors. For example, if analysis is performed for individual PCB congeners, then the spiking levels for each congener will be approximately the same as the surrogate additions.

The samples can be extracted using methylene chloride/acetone (1:1) or hexane/acetone (1:1) solvent mixtures. The methylene chloride mixture is recommended to reduce the amount of flammable solvent usage when working with radioactive materials. The samples are subjected to high intensity sonication for approximately 1 minute using a 400 watt transducer at 50% power. The solvent is removed and the extraction process repeated twice more. The resulting extracts are combined and concentrated. They are then exchanged into hexane and reduced to a final volume of 1-2 mL. Residues may be placed in storage for up to 40 days at 4°C. Residues chilled in storage must be allowed to completely warm to room temperature before use.

Alternately, if GC/MS analysis is required for PCB confirmation or other organic constituents from the same sample, the combined extracts may be concentrated to 10 mL. From the 10 mL extract, 2 mL can be removed and exchanged into hexane. This will be used for GC/ECD analysis. The remaining 8 mL of solvent can be refrigerated and later reduced to 0.8 mL for confirmation by GC/MS if constituent levels permit. If analysis is only to be performed using electron impact ionization mass spectrometric detection (GC/MS), the surrogate and spike levels will need to be about 1000 times greater than for GC/ECD.

In cases where the same sample is to be used for SVOA and pesticide/PCB analysis, some special considerations must be made prior to performing extraction. As mentioned previously, the amount of the extract residue that will be split for GC/MS and GC/ECD must be considered. The surrogate and spike levels should be adjusted accordingly so that a sufficient amount of the compounds remain for GC/ECD analysis. The adjusted levels are specified by the cognizant scientist after a split between various analytical needs has been considered.

Sample Residue Cleanup:

When residues to be analyzed by this method are splits from semivolatile extractions or sample are suspected of containing substantial interference's, then additional cleanup should be performed. These are typically columns employing silica gel or Florisil. Whenever silica gel or Florisil (SW-846 Method 3630 or 3620) cleanups are used, the analyst must demonstrate that the fractionation scheme is reproducible. Batch to batch variation in the composition of the silica gel or Florisil or overloading the column may cause a change in the distribution patterns of the organochlorine pesticides. When compounds are found in two fractions, add the concentrations found in the fractions, and correct for any additional dilution.

Typically, Florisil cleanup is preferred because of the ease of use. Each lot number of cartridges should be evaluated for recovery of pesticides and PCBs and removal of unwanted polar materials before processing sample. The procedure for this cleanup is as follows:

Using 1-g Florisil cartridges, pre-condition the cartridges with 5 mL of hexane. Just before the column goes dry, transfer the 1 mL (or other appropriate volume) of the extract to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute. When the entire extract has passed through the cartridge, but before the cartridge becomes dry, rinse the sample vial with an additional 0.5 mL of hexane, and add the rinse to the cartridge to complete the quantitative transfer. Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never goes dry. Place a 10-mL vial or flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial. If there is no need to separate the organochlorine pesticides from the PCBs, then add 9 mL of acetone/hexane (10/90, v/v) to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial. Concentrate the resulting cleaned residue to the appropriate volume.

To evaluate cartridge performance, use approximately 0.5 mL of a combined Florisil check standard of 2,4,5-trichlorophenol and pesticide solution. Condition the cartridge as described previously and then perform the cartridge cleanup. Elute the cartridge with 9 mL of acetone/hexane (10/90, v/v) only. Reduce the volume to 1.0 mL and analyze. The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 120 %, if the recovery of trichlorophenol is less than 5 %, and if no peaks interfering with the target analytes are detected.

Analysis:

As with the USEPA methods, analysis using electron capture detectors will be performed using a dual capillary gas chromatograph. This allows for simultaneous analysis and confirmation of constituents found in the sample residue. For the individual pesticides or PCB congeners, identification is made by matching the retention time of a chromatographic peak on each column to those obtained for the standards. For multicomponent pesticides and Aroclors (PCB mixtures), the method identifies the pattern of the mixtures present by direct comparison to authentic reference standards. Analysis by GC/MS is less reliant on pattern recognition to identify Aroclors. However, the GC/MS instrument is calibrated in much the same manner as the GC/ECD for pesticides, Aroclors, or individual PCB congeners when conformational quantitation is performed and the analyte concentration is sufficient. In all cases, quantitation is performed following calibration of the instrument using authentic materials of known concentration.

Initial Calibration:

Before obtaining data to construct a calibration curve, and before analysis of samples in an analytical batch, breakdown of DDT and Endrin must be evaluated. DDT and Endrin are easily degraded in the injection port and the front end of the column. Breakdown occurs when the injection port liner is contaminated with high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard which contains 4,4'-DDT and Endrin but none of the degradation components. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding with calibration.

$$\text{\% breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} * 100$$

$$\text{\% breakdown of Endrin} = \frac{\text{sum of degradation peak areas (aldehyde + ketone)}}{\text{sum of all peak areas (Endrin + aldehyde + ketone)}} * 100$$

Prior to analysis, a minimum 3 point initial calibration for each target pesticide, a representative Aroclor, typically 1254, or a congener representing each level of chlorination to be quantitated, will be performed over a concentration range of at least one order of magnitude. The lowest concentration should be at or near the quantitation limit to be reported as the component is present in the sample residue. A standard level standard representing each multicomponent analyte must also be analyzed. However, this single point calibration for multicomponent analytes, at approximately the mid-point concentration of the representative Aroclor, is primarily for identification. Calibration for multicomponent quantitation is described below.

The response factors obtained for the quantitation column will not exceed 20% RSD over the range of the initial calibration. The RSD for the surrogates may be as high as 30%. If the RSD for each analyte is less than 20%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantitate sample results. If the RSD is greater than 20%, then linearity through the origin cannot be assumed. The analyst must use a calibration curve or a non-linear calibration model (e.g., a polynomial equation) for quantitation. The retention time for a given analyte can not vary by more than ±0.10 minutes.

After an initial analysis it may be determined by comparison to the single level standard that multicomponent analytes are present. In this case, a three point initial calibration will be performed for any additional multicomponent analyte or PCB congeners which are to be quantitated. The three point calibration should be performed over the same concentration range as the initial calibration and the same acceptance criteria applied. For example, if Aroclor 1254 was used in the initial calibration and all other Aroclors were found in the samples, three point calibrations of Aroclors 1016 combined with 1260, 1221 combined with 1268, 1232, 1242, 1248, and 1262 are obtained. It is not necessary to combine the Aroclors but this will save calibration time. When calibrating for Aroclors, responses for five chromatographic peaks, each of which presumably represent an individual PCB congener, should be used. In the case of Aroclor 1221, four peaks may be used. Care should be taken to select peaks which are as indicative to a particular Aroclor as possible. This may be achieved by selecting congener peaks which have distinct retention times or exhibit minimal response by other Aroclors. Aroclors 1016 and 1242, however, will likely use the same chromatographic peaks due to their similarities.

An instrument blank will be run immediately following the highest standard to assess potential carry over contamination. Carry over will not exceed 1.0%.

Continuing Calibration:

Immediately following the initial calibration, and at least every ten samples thereafter, a continuing calibration standard will be analyzed. The continuing calibration verification (CCV) standards which are chosen should alternate between a pesticide mix, a multicomponent analyte, and the performance evaluation mix discussed previously to evaluate DDT and Endrin breakdown. The Aroclor or PCB congeners used for the continuing calibration verification (CCV) will be the same as those used in the initial 5 point calibration. The CCV should be at about the mid-range of concentration used in the initial calibration. Quantitation of samples using the initial calibration factors will continue as long as the relative percent difference (RPD) for the continuing calibration does not exceed ±25%. The retention times may not vary by more than ±0.10 minutes from the initial calibration or the updated retention times obtained by a CCV following system maintenance. Another initial calibration will be performed when, following system maintenance, the continuing calibration fails. A set of sample analysis will always be preceded and completed using a passing continuing calibration standard and an instrument blank.

Sample Quantitation:

Single components analytes are identified by matching the appropriate retention times obtained from each column. The amount present is then quantified using the calibration curves obtained from the initial calibration. Chromatograms obtained for each of the multicomponent analytes from the initial calibration are used to identify patterns present in the sample. Once the Aroclor pattern(s) has been identified, the quantity is determined of each component peak in the sample chromatogram only if a multi-point calibration was obtained for that Aroclor. If it has not, a minimum three point calibration shall be obtained for the identified Aroclor followed by sample reanalysis. Proper peak integration by the data system should be reviewed for all samples. Lower concentrations of material present in the sample will increase the amount of analyst review and manual integration required. The amount of Aroclor is calculated using the individual calibration factor for each of the characteristic congener peaks chosen. The quantitative result for those peaks are averaged to determine the concentration of Aroclor present.

In cases where a quantitation congener peak chosen for an Aroclor exhibits substantial interference, >±50% deviation from the mean calculated concentration, quantitation should be recalculated without the affected congener peak. If two congeners fail the ±50% test, the Aroclor identification should be reviewed carefully. If a clearly distinct Aroclor pattern is verified to exist, then quantitation may be performed and the congener observation noted in the narrative. If compound identification or quantitation is precluded due to interference, such as broad, rounded, or severely co-eluted peaks, then further cleanup of the sample residue may be required. The cognizant scientist will be responsible for making decisions for cleanup or analytical system maintenance. In some instances, the confirmation column may not exhibit the same level of interference observed on the quantitation column. Quantitation may be performed using the confirmation column provided it has met all of the calibration criteria.

In addition to the GC/ECD analysis, GC/MS confirmation may be performed using a properly tuned instrument. Refer to other procedures such as PNL-ALO-345 or USEPA CLP for the proper GC/MS parameters. GC/MS confirmation can only be employed if target components are detected in sufficient concentration by the GC/ECD. If confirmation is performed using electron impact ionization GC/MS, each Aroclor usually must be present at >10 ng/uL in the final extract to perform quantitation. If the GC/MS is used for quantitation, a multi-point calibration of the GC/MS will be performed for the Aroclor(s) present as described previously. Since GC/MS is less susceptible to interference's, it is anticipated to provide results which are more accurate than those produced from the GC/ECD instrument.

Quality Control

In addition to the parameters previously discussed, there are method application and performance criteria. Analysis of a method blank, matrix spike, and a matrix spike duplicate should be performed with every analytical batch or every twenty samples, which ever is most frequent, when analyzing unknown samples. While the surrogate compounds may differ from those referred to previously, they must be added to every sample. Advisory surrogate and spike compound recovery acceptance criteria have been established for these particular matrices. However, these limits are only advisory and are based on a limited data set. These limits are complete indicators for re-extraction or re-analysis decisions.

References:

USEPA Contract Laboratory Program, Statement of Work of Organic Analysis, Multi-Media, Multi-Concentration, 1988.

USEPA Contract Laboratory Program, Statement of Work of Organic Analysis, Multi-Media, Multi-Concentration, OLM01.8, August 1991.

SW-846, Test Methods for Evaluating Solid Waste, Physical and Chemical Methods, Method 8082, Polychlorinated Biphenyls (PCBs) by Capillary Column Gas Chromatography, rev 0, January 1995.

Battelle, Analytical Chemistry (ACL) Procedure Compendium, Methods PNL-ALO-120, 345, 346, 347. Analytical method for extraction and analysis of Pesticides/PCBs and Semivolatile compounds.

Controlled Copy 08/24/2000

PNNL Test Plan

Document No.: BNFL-TP-29953-089
Rev. No.: 0

Title: Organic Extraction of AP-101 for PCBs

Work Location: 325/SFO, 329/general labs

Page 1 of 4

Author: Eric Hoppe

Effective Date: Upon Final Signature
Supersedes Date: n/a

Use Category Identification: Mandatory

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

Required Reviewers:
_x_ Technical Reviewer
__ Building Manager
__ Radiological Control ES&H
_x_ Quality Engineer
_x_ Task Manager
_x_ RPL Manager
_x_ SFO Manager
__ Other

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 _x_ No

Does the OJT package associated with this procedure require revision to reflect procedure changes?
____ Yes ____ No _x_ N/A

Approval	Signature	Date
Author	E C Hoppe	6-6-00
Technical Reviewer	J. A. Campbell	6/7/00
Task Manager	D E Kurath	6/8/00
RPL Manager	S M Barnes for DE Knudson	6-8-00
Quality Engineer	T L Almeida	6/8/00
SFO Manager	Rick J. Steele	6/7/00
AO&M Technical Group Manager	Steven C. Johnson	6/7/00

Applicability

This Organic Extraction Test Plan describes work to be performed in the Shielded Analytical Laboratory (SAL) to extract AP-101 tank waste liquid for Polychlorinated Biphenyl (PCB) analysis. The volume reduction of the extracts and the PCB analysis is to be performed in the 329 building organic laboratories. Based on the history of the samples, exceptions are being taken to the preservation, temperature control, sample size, and hold time requirements specified by SW-846 protocols. The choice of spiking solutions and extraction solvents is based upon SW-846 method 8082 guidelines, where applicable.

Hazards Assessment and Mitigation

The radioactive work conducted under this Test Plan is comprised of analytical organic analysis preparative operations that have been conducted routinely in the RPL and 329 Facilities. The organic extractions with small quantities of methylene chloride have been performed in the Shielded Analytical Laboratory (SAL) many times and are included as a standard preparative activity on the RPL Analytical Service Request. The organic solvent extraction operations are included in the SAL work authorization. Since all of the analytical preparative operations fall within current work authorizations, no further assessment of the hazards is detailed in this Test Plan.

Quality Control

The PCB extractions and analysis are governed by PNNL's web-based Quality Assurance Planning Subject Area, "Conducting Analytical Work in Support of Regulatory Programs". The PCB analyses will be performed in duplicate and matrix spikes will be analyzed. Surrogate spike compounds will be added to the sample, sample duplicate, and blank, and surrogate spike compounds and target compounds will be added to the matrix spikes in order to provide information on analyte recoveries. Separate laboratory control samples (LCS) will be prepared outside the SAL.

Integrity of the sub-samples and processed extracts distributed throughout the laboratory will be maintained by chain-of-custody documentation. The Task Manager shall approve changes to this Test Plan (initialed markups are allowed).

Work Instructions

1.0 General Comments:

Since there is approximately 300 mL of AP-101 available for analysis, 100-mL aliquots will be used for the sample and duplicate and 50-mL aliquots used for the matrix spike and matrix spike duplicate.

Teflon separatory funnels, with FEP caps, are used for the liquid-liquid extraction processing.

The three extracts from each sample (duplicate, MS, MSD, and blank) are combined and transferred from the SAL to the 329 building organic laboratory. Volume reduction and any other pre-analysis processing are performed in the 329 building.

The Method Detection Limit (MDL) for total PCBs is approximately 1 µg/L, using a 100-mL sample.

Surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to each sample, matrix spike, blank, and LCS at 0.04 µg prior to extraction.

Target compound, Aroclor 1254, at 0.2 µg is added to each matrix spike and the LCS prior to extraction.

2.0 Extraction Instructions

The extractions of the AP-101 liquid samples will be performed in the SAL within the 325 Facility. An extraction scheme for the PCB extraction is provided in Figure 1.

1) Transfer aliquot of sample into a separatory funnel.

   Note: 100-mL aliquots of AP-101 are to be used for the sample and duplicate, 50-mL aliquots of AP-101 are to be used for the matrix spike and matrix spike duplicate, and 100-mL aliquot of organic-free water are to be used for the blank.

2) Add the surrogate spiking solution to all samples (including blank) and the target compound spiking solution to the MS and MSD.

   Note: Use the entire contents of the vial(s) provided for spiking. After transferring the contents of the spiking vial to the sample, add approximately 0.2 mL of methylene chloride to the vial(s) and transfer this rinsate to the sample.

3) Perform three sequential separatory funnel shakeout extractions of the supernatant using 25-mL portions of methylene chloride. Collect and combine the three extracts in a 125-mL amber bottle labeled as:

   AP101-P-x

   Where,
   x = B for blank, S for sample, D for sample duplicate, MS for matrix spike,
   MSD for matrix spike duplicate

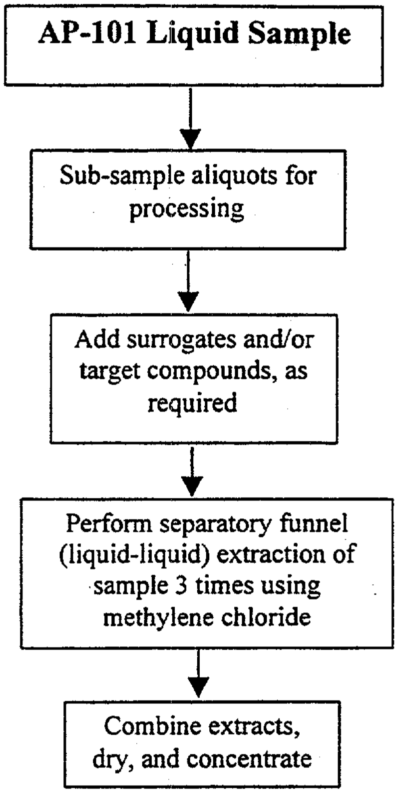
4) Remove samples from SAL and transfer under COC to 329 building organic laboratory for further processing.

For further guidance and questions regarding execution of these steps for PCB extraction, contact Eric W. Hoppe, 376-2126.

3.0 Preparation of Laboratory Control Sample

A separate LCS will be prepared for the PCB analysis outside the SAL using the same reagents as used for the extraction of the AP-101 samples. The LCS matrix will consist of 100 mL of distilled water. The LCS will be extracted using liquid-liquid extraction. The LCS will be spiked with the same surrogate and target compounds as the AP-101 matrix spikes.

Figure 1: PCB Extraction Process Diagram



APPENDIX C

Appendix C: Analytical Reports

1.0 Polychlorinated Biphenyls/Pesticides Analysis

1.1 Introduction

Analysis of 241-AP-101 liquid composite samples for Polychlorinated Biphenyls (PCBs) was performed by the AOAM group at PNNL. 100 mL sample aliquots were prepared using liquid-liquid extractions in the SAL. This procedure is outlined in the test instructions found in appendix B, of the technical report PNWD-3046 *Inorganic, Radioisotopic, and Organic Analysis of 241-AP-101 Tank Waste*, June 2000. The resulting methylene chloride residues were transferred under COC to the laboratory for concentration, cleanup, and analysis for PCBs. The analysis was performed using gas chromatography/electron capture detection (GC/ECD) and confirmation by mass spectrometry if necessary. The PCB analysis was not included in the previously referenced report pending authorization to proceed and is presented separately as this addendum.

1.2 Sample Preparation

300 mL of composite 241-AP-101 sample material was available for PCB analysis. Prior sample handling indicated the composite samples were combined from a number of containers. For ascertaining low concentrations of PCBs, each of the original sample containers and those used to perform the composite, should be rinsed with a PCB miscible solvent such as methylene chloride to obtain an accurate sample representation. The rinsing process is performed because the solubilities of PCBs are quite low in aqueous samples and are subject to "plating out" on the surfaces of sample containers. This is particularly important for high salt solutions, such as the tank materials here, where the solubility of PCBs is even lower. However, this procedure was not performed for this analysis.

Extractions for PCBs were performed according to the test plan, BNFL-TP-29953-089, *Organic Extraction of AP-101 for PCBs.* Duplicate 100 mL and 50 mL aliquots of the liquid samples were obtained for extraction. For the sample and sample duplicate preparations, 100 mL each was used. For the spike and spike duplicate samples, 50 mL aliquots were used for each preparation. 0.04 ug (0.4-0.8 ug/L) of each surrogate compound was added to all samples. 0.20 ug (4.0 ug/L) of Aroclor 1254 was added to the spike samples. Each of the samples were liquid-liquid extracted in a separatory funnel three times using 25 mL methylene chloride. The resulting residues were removed from the SAL, and concentrated in a radiological fume hood to 2 mL.

Additional cleanup of the extract residue was performed following exchange into hexane. The residues were cleaned by washing with concentrated sulfuric acid. The remaining hexane residues were then analyzed for PCBs.

1.3 Instrumentation

Analysis was performed according to the test plan BNFL-TP-29953-027, *Analysis for Pesticides and PCBs by Gas Chromatography Dual Electron Capture Detection.* The instrumentation used for the analysis of PCBs consists of a gas chromatograph equipped with two electron capture detectors (ECD). The analytical instrumentation is identified in Table 1.a. Both of the detectors were operated at 320° C. Injections were made on-column onto a 10 m fused silica retention gap, which was split between two analytical columns: a) 0.32 mm X 30 m CLP I (0.50 µm phase, Restek Corp.) and b) 0.32 mm X 30 m CLP II (0.25 µm film thickness, Restek Corp).

Table 1.a PCB/Pesticides Analysis Instrumentation

System/Instrument	Manufacturer	Model Number	M&TE (1) Number
Gas Chromatograph	Hewlett-Packard	5890	WD 11127

(1) Measuring and Test Equipment

If PCBs are detected at a sufficient concentration, confirmation is performed. The instrumentation used for confirmation is a gas chromatograph/ high-resolution mass spectrometer (GC/HRMS).

1.4 Analysis Results

PCB results are presented in Table 1.b. PCBs were not detected above the quantitation limit (MDL) for these samples.

Table 1.b PCB Results

	Tank Material	**AP-101 Supernatant**			
	Sample ID	**MDL**	**00-1701 Proc Blk**	**00-1701 Sample**	**00-1701 Duplicate**
CAS #	***Units***	µg/L	µg/L	µg/L	µg/L
12674-11-2 53469-21-9	Aroclor 1016/1242	0.2	U	U	U
11104-28-2	Aroclor 1221	0.2	U	U	U
11141-16-5	Aroclor 1232	0.2	U	U	U
12672-29-6	Aroclor 1248	0.2	U	U	U
11097-69-1	Aroclor 1254	0.2	U	U	U
11096-82-5 37324-23-5	Aroclor 1260/1262	0.2	U	U	U
11100-14-4	Aroclor 1268	0.2	U	U	U
	Total PCB	1.4	1.4	1.4	1.4
			% Rec	**% Rec**	**% Rec**
	TCX (surrogate)		67.8	86.7	90.2
	DCB (surrogate)		100	80.9	113

U flag = Not detected; results less than MDL

As seen in Table 1.c, the BNFL target MRQs have been met for supernatants (after adjusting for density).

Table 1.c Target PCB/Pesticides Minimum Reportable Quantities

CAS #	Compound	Solids Target MRQ[1] µg/Kg	Supernatant Target MRQ (Density = 1.31 g/mL) µg/L
All	Polychlorinated Biphenyls	3300	4300

[1] MRQ = Minimum Reportable Quantity as provided by BNFL

1.5 QC Evaluation

The sample homogenization process used was not consistent with a procedure that would be employed for low concentration PCB analysis. However, the client requested MRQ of milligram quantities is much greater than a concentration of PCBs where adsorption issues would be of concern such as microgram or lower quantities. In this case, any potential loss of analyte would be of little consequence with regard to the MRQ. However, this means that if PCBs were present in the sample, the actual detection limit may have been affected and could be higher than found in Table 1.b. Regardless, the actual detection limit would be substantially below the MRQ, particularly since there is more than three orders of magnitude between the current detection limit and MRQ..

Because limited sample was available, the quantity of sample used for spiking was approximately half of that used for unspiked sample analysis. The laboratory control sample (LCS) consisted of a spiked blank water at a volume similar to that used for the samples (100 mL). The LCS recovery is less than the 80-120 % recommended by USEPA SW-846 method 8082. However, the spiking level employed here is considerably lower than the levels used in the SW-846 method by as much as 25 times. The lower spiking level used here is more consistent with up-to-date regulatory expectations. The recovery does meet the general acceptance criteria of 70-130% referred to in SW-846 method 8000, which would be applied since the spiking level used here falls well outside of the range applied in method 8082.

While no specific surrogate acceptance criteria have been developed for tank matrices, the recoveries are all within SW-846 recommended initial criteria of 20-150%, and meet USEPA CLP SOW OLM01.8 advisory criteria of 60-150% for water.

Table 1.d AP-101 – PCB Spike Recoveries

	Tank Material	**AP-101 Supernatant**		
	Sample ID	**00-1701**		**LCS**
		MS	**MSD**	
	Units	**%Rec (μg/L)**	**%Rec (μg/L)**	**%Rec (ug/L)**
CAS #	***MDL***	**0.2**	**0.2**	**0.2**
11097-69-1	Aroclor 1254	106 (4.3)	96.9 (3.9)	71.8 (1.4)
		% Rec	**% Rec**	**% Rec**
	TCX (surrogate)	90.2	94.4	76.1
	DCB (surrogate)	118	115	61.8

Data pertaining to the analysis of these samples is located in the project files. Supporting documentation is located in the files for samples 00-2321 (continuing calibration) and 00-1360 (initial calibration). All analytical QC criteria specified in the test plan BNFL-TP-29953-027, *Analysis for Pesticides and PCBs by Gas Chromatography Dual Electron Capture Detection* were met.

10-3-00

E.W. Hoppe
analyst/report author

J.A. Campbell 10/3/00

J.A. Campbell
techical reviewer

Radiochemical Processing Laboratory
Shielded Facility Operations Team

Shielded Analytical Laboratory
Bench Sheet

Client: MW URIE

WP Number: W54906

TI#/ASR: ASR 5778

Procedure: Bench Instruction

AP101 DENSITIES

SAMPLE IDENTIFICATION

LAB NUMBER	SAMPLE IDENT.	FLASK TARE WT (g)	FLASK GROSS WEIGHT (g)	FLASK SIZE (mL)	DENSITY (g/mL)
00-01701	AP-101 COMP	9.3824	22.4570	10	1.307
00-01701-DUP	AP-101 COMP	9.4763	22.5629	↓	1.309
00-01701-TRI	AP-101 COMP	9.5085	22.5902		1.308

$$\text{DENSITY} = \frac{\text{FLASK GROSS (g)} - \text{FLASK TARE (g)}}{\text{FLASK SIZE (mL)}}$$

M&TE: ☒ Cell 2 (360-06-01-016) Mettler AE160 Balance Other ______

☐ Cell 5 (360-06-01-019) Sartorius LP4200S Balance

☐ Bench (510-06-01-014) Mettler AT201 Balance

☐ Bench (360-06-01-040) Denver A160 Balance

Analyst:

Date: 4-5-00

Reviewer:

Date: 4/7/00

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

Project: 29953 / W54906
Client: D. Kurath

ACL Number(s): 00-01701

Client ID: "AP-101-COMP"

ASR Number: 5778

Total Sample: 1

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

Analyst: D.R. Sanders

Analysis Date (Filename): 04-11-00 (A0595) [ALO-128 SAL/vh]

See Chemical Measurement Center 98620: ICP-325-405-1 File for Calibration and Maintenance Records.

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

Jerry Wagner 5-17-00
Reviewed by

5-17-00
Concur

ASR-5778

Sample **AP-101-COMP** (RPL# 00-01701) was prepared in triplicate by the Shielded Analytic Lab (SAL) using ALO-128 acid digestion of liquids procedure. A process blank, blank-spike and matrix-spike were also prepared similarly at the same time as the samples. Approximately 6.6 grams of liquid (density 1.308 g/ml) or about 5ml, was processed and diluted to a final volume of about 25 ml (final solution volume was weighed and density corrected to a volume). Some insoluble precipitate remained after processing requiring filtration before analysis could be performed. Analytical dilution prior to ICPAES analysis required 5, 10 and 50-fold dilution in order to quantify all analytes of interest. Measurement results are reported in µg/ml corrected for sample density, processing and analytical dilution. Volumes and weights have been recorded on bench sheets and included with this report.

Quality control objectives were met for the majority of analytes of interest listed in ASR-5778 attachment 2: page 1 of 6 (Table 2 ...MRQ's) and page 4 of 6 (Table 4 ...QC Acceptance Criteria).

Objectives missed:

a) Sulfur is not available on the ICPAES instrument used for this work.
b) MRQ's required for "...Contract Specification 7..." for barium (2.3 µg/ml) and lanthanum (2.3 µg/ml) were below EQL (2.5 and 12.7 µg/ml respectively).
c) Also, MRQ's for "...Opportunistic Analytes" for rhodium (18), ruthenium (36), and silicon (90) were below EQL (76, 278, and 126 µg/ml respectively).
d) LCS for silver (69%R) was below "QC Acceptance Criteria" (80%-120%R).
e) Spike Recovery for silver (35%R), barium (30%R), and lead (65%R) was below "QC Acceptance Criteria" (75% - 125%R).
f) Duplicate %RPD (average) for phosphorous (15.8%RPD) was below "QC Acceptance Criteria" (<15%RPD).

See attachment 1 and 2 to this report.

Quality control check-standard results met tolerance requirements for all analytes except as noted below. Following is a list of quality control measurement results relative to ICPAES analysis tolerance requirements. Please note that MRQ is equivalent to EQL in this report.

Five fold serial dilution:

(liquid samples)	Results were within tolerance limit of ≤ 10% for all analytes tested after correcting for dilution.

Duplicate RPD (Relative Percent Difference):

(liquid samples) All analytes of interest were recovered within tolerance limit of ≤ 15%relative percent difference (RPD) except as follows. RPD for phosphorous in the three sample replicates ranged from about 15% to 28% RPD. Average RPD for phosphorous within the three replicates was 15.8%. Chromium in the three sample replicates ranged from about 1% RPD to about 16% RPD. Average RPD for chromium within the three replicates was about 8.9%.

Post-Spiked Samples (Group A):

(liquid samples) All analytes of interest were recovered within tolerance of 75% to 125% except silicon. Silicon recovery (147%) exceeded tolerance limit. All other analytes of interest above EQL were within tolerance.

Post-Spiked Samples (Group B):

(liquid samples) All analytes of interest were recovered within tolerance of 75% to 125% except palladium. Palladium recovery (53%) exceeded tolerance limit. All other analytes of interest above EQL were within tolerance. Palladium was found low in the group B spike. Single element palladium at 2 µg/ml measured at the beginning, middle and end of the run (2.00 ± 0.04 µg/ml) were well within tolerance limit. No palladium was detected in the sample.

Blank Spike:

(liquid samples) All analytes of interest were recovered within tolerance limit of 80% to 120% recoveries except silver. Low recovery of silver in the blank spike (about 69%) was probably due to the small amount of hydrochloric acid used during sample preparation resulting in some silver precipitating from solution.

Matrix Spiked Sample:

(liquid samples) All analytes of interest were recovered within tolerance limit of 75% to 125% recoveries except silver, barium and lead. Silver recovery (about 35%), barium recovery (about 30%) and lead recovery (about 65%) were all low and may be related to the presence of sulfate and/or carbonate present in the sample. Low silver recovery is probably, in part, due to the small amount of hydrochloric acid used during sample processing. All sample aliquots had a small amount of precipitate remaining after processing requiring filtration.

Quality Control Check Standards (solid and liquid samples):

Concentrations of all analytes were within tolerance limit of ± 10% accuracy in standards (except palladium): QC_MCVA, QC_MCVB, and QC_SSTMCV. Calibration Blank (ICP98.0) concentration is acceptable, less than two times IDL. Palladium in QC check standard MCVB was low (about 42% to 48%) however, a single element standard of palladium at 2.0 μg/ml measured at the beginning, middle and end of the ICP run was well within tolerance limit indicating acceptable palladium accuracy. No palladium was detected in the sample aliquots.

High Calibration Standard Check (solid and liquid samples):

Verification of the high-end calibration for all analytes measured is within tolerance limits of ± 5% accuracy.

Process Blank:
(liquid samples)

All analytes of interest were within tolerance limit of ≤ EQL or < 5% of sample concentration in the prepared samples.

Laboratory Control Standard (LCS):
(liquid samples)

The blank-spike and matrix-spike were prepared and measured as an LCS control (See results described above)

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

	Multiplier=	4.8	25.3	25.3	25.0
	RPL/LAB #=	00-1701-PB	00-1701 @5	00-1701-DUP @5	00-1701-TRI @5
	Client ID=	AP-101 Comp (Supernatant)	AP-101 Comp (Supernatant)	AP-101 Comp (Supernatant)	AP-101 Comp (Supernatant)
Det. Limit	Run Date=	4/11/00	4/11/00	4/11/00	4/11/00
(ug/mL)	(Analyte)	ug/mL	ug/mL	ug/mL	ug/mL
0.025	Ag	--	--	--	--
0.060	Al	4.52	7,380	6,680	6,760
0.250	As	--	--	--	--
0.050	B	6.62	15.0	14.4	15.1
0.010	Ba	--	[0.32]	[0.34]	[0.33]
0.010	Be	--	[1.1]	[1.0]	[1.0]
0.100	Bi	--	--	--	--
0.250	Ca	[1.4]	[7.8]	[7.5]	[7.7]
0.015	Cd	--	[2.0]	[1.9]	[2.0]
0.200	Ce	--	--	--	--
0.050	Co	--	--	--	--
0.020	Cr	--	158	137	135
0.025	Cu	[0.18]	[1.7]	[1.5]	[1.5]
0.050	Dy	--	--	--	--
0.100	Eu	--	--	--	--
0.025	Fe	[0.38]	[2.9]	[2.4]	[2.2]
2.000	K	--	31,700	30,500	31,500
0.050	La	--	--	--	--
0.030	Li	--	--	--	--
0.100	Mg	--	--	--	--
0.050	Mn	--	--	--	--
0.050	Mo	--	[12]	[10.0]	[9.8]
0.150	Na	14.3	132,000	125,000	131,000
0.100	Nd	--	--	--	--
0.030	Ni	1.63	8.62	7.68	7.50
0.100	P	--	371	290	281
0.100	Pb	--	[15]	[15]	[15]
0.750	Pd	--	--	--	--
0.300	Rh	--	--	--	--
1.100	Ru	--	--	--	--
0.500	Sb	--	--	--	--
0.250	Se	--	--	--	--
0.500	Si	[24]	143	132	137
1.500	Sn	--	[60]	--	--
0.015	Sr	--	--	--	--
1.500	Te	--	--	--	--
1.000	Th	--	--	--	--
0.025	Ti	--	--	--	--
0.500	Tl	--	--	--	--
2.000	U	--	[68]	[62]	[56]
0.050	V	--	--	--	--
2.000	W	--	--	--	--
0.050	Y	--	--	--	--
0.050	Zn	[0.91]	[5.8]	[5.5]	[5.4]
0.050	Zr	--	[1.4]	[1.4]	[1.3]

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 `A0595 D.Kurath ASR-5778 AP-101 Comp (ALO-128) Supernatant ICP98 hi.XLS 4/12/00 @ 1:02 PM

ASR-5778 "ICPAES Measurement Results -- Data"

A0595	*S.Vol(ml)=*	5.0539	5.0060	5.0650	5.0637
4-11-00/drs	*F.Vol(mL)=*	24.5000	25.3000	25.6000	25.3000
	(PF)	1.0000	1.0000	1.0000	1.0000
	(DF)	1.0000	1.0000	1.0000	1.0000
	(ADF)	1.0000	5.0000	5.0000	5.0000
	Multiplier=	4.8	25.3	25.3	25.0
	RPL/LAB #=	00-1701-PB	00-1701 @5	00-1701-DUP @5	00-1701-TRI @5
	Client ID=	*AP-101 Comp (Supernatant)*	*AP-101 Comp (Supernatant)*	*AP-101 Comp (Supernatant)*	*AP-101 Comp (Supernatant)*
Det. Limit	*Run Date=*	4/11/00	4/11/00	4/11/00	4/11/00
(ug/mL)	(Analyte)	ug/mL	ug/mL	ug/mL	ug/mL
0.025	Ag	--	--	--	--
0.060	Al	4.52	7,380	6,680	6,760
0.250	As	--	--	--	--
0.050	B	6.62	15.0	14.4	15.1
0.010	Ba	--	[0.32]	[0.34]	[0.33]
0.010	Be	--	[1.1]	[1.0]	[1.0]
0.100	Bi	--	--	--	--
0.250	Ca	[1.4]	[7.8]	[7.5]	[7.7]
0.015	Cd	--	[2.0]	[1.9]	[2.0]
0.200	Ce	--	--	--	--
0.050	Co	--	--	--	--
0.020	Cr	--	158	137	135
0.025	Cu	[0.18]	[1.7]	[1.5]	[1.5]
0.050	Dy	--	--	--	--
0.100	Eu	--	--	--	--
0.025	Fe	[0.38]	[2.9]	[2.4]	[2.2]
2.000	K	--	31,700	30,500	31,500
0.050	La	--	--	--	--
0.030	Li	--	--	--	--
0.100	Mg	--	--	--	--
0.050	Mn	--	--	--	--
0.050	Mo	--	[12]	[10.0]	[9.8]
0.150	Na	14.3	132,000	125,000	131,000
0.100	Nd	--	--	--	--
0.030	Ni	1.63	8.62	7.68	7.50
0.100	P	--	371	290	281
0.100	Pb	--	[15]	[15]	[15]
0.750	Pd	--	--	--	--
0.300	Rh	--	--	--	--
1.100	Ru	--	--	--	--
0.500	Sb	--	--	--	--
0.250	Se	--	--	--	--
0.500	Si	[24]	143	132	137
1.500	Sn	--	[60]	--	--
0.015	Sr	--	--	--	--
1.500	Te	--	--	--	--
1.000	Th	--	--	--	--
0.025	Ti	--	--	--	--
0.500	Tl	--	--	--	--
2.000	U	--	[68]	[62]	[56]
0.050	V	--	--	--	--
2.000	W	--	--	--	--
0.050	Y	--	--	--	--
0.050	Zn	[0.91]	[5.8]	[5.5]	[5.4]
0.050	Zr	--	[1.4]	[1.4]	[1.3]

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).

Attachment No. 1 of 2, ASR-5778 "ICPAES Measurement Results -- Statistical Summary"

	Multiplier=	4.8	25.3	25.3	25.0			
	RPL/LAB #=	00-1701-PB	00-1701 @5	00-1701-DUP @5	00-1701-TRI @5			
	Client ID=	*AP-101 Comp (Supernatant)*	*AP-101 Comp (Supernatant)*	*AP-101 Comp (Supernatant)*	*AP-101 Comp (Supernatant)*			
Det. Limit (ug/mL)	*Run Date=* (Analyte)	4/11/00 ug/mL	4/11/00 ug/mL	4/11/00 ug/mL	4/11/00 ug/mL	Ave (n=3)	StDev.	%RSD
0.025	Ag	–	–	–	–			
0.060	Al	4.52	7,380	6,680	6,760	6940	383	5.5
0.250	As	–	–	–	–			
0.050	B	6.62	15.0	14.4	15.1	14.83	0.38	2.6
0.010	Ba	–	[0.32]	[0.34]	[0.33]	[0.33]	0.010	3.0
0.010	Be	–	[1.1]	[1.0]	[1.0]	[1.03]	0.06	5.6
0.100	Bi	–	–	–	–			
0.250	Ca	[1.4]	[7.8]	[7.5]	[7.7]	[7.67]	0	2.0
0.015	Cd	–	[2.0]	[1.9]	[2.0]	[1.97]	0	2.9
0.200	Ce	–	–	–	–			
0.050	Co	–	–	–	–			
0.020	Cr	–	158	137	135	143.33	13	8.9
0.025	Cu	[0.18]	[1.7]	[1.5]	[1.5]	[1.57]	0.12	7.4
0.050	Dy	–	–	–	–			
0.100	Eu	–	–	–	–			
0.025	Fe	[0.38]	[2.9]	[2.4]	[2.2]	[2.50]	0.36	14.4
2.000	K	–	31,700	30,500	31,500	31233	643	2.1
0.050	La	–	–	–	–			
0.030	Li	–	–	–	–			
0.100	Mg	–	–	–	–			
0.050	Mn	–	–	–	–			
0.050	Mo	–	[12]	[10.0]	[9.8]	[10.60]	1.2	11.5
0.150	Na	14.3	132,000	125,000	131,000	129333	3786	2.9
0.100	Nd	–	–	–	–			
0.030	Ni	1.63	8.62	7.68	7.50	7.93	0.6	7.6
0.100	P	–	371	290	281	314.00	50	15.8
0.100	Pb	–	[15]	[15]	[15]	[15.00]	-	0.0
0.750	Pd	–	–	–	–			
0.300	Rh	–	–	–	–			
1.100	Pd	–	–	–	–			
0.500	Sb	–	–	–	–			
0.250	Se	–	–	–	–			
0.500	Si	[24]	143	132	137	137.33	5.5	4.0
1.500	Sn	–	[60]	–	–	[60]		
0.015	Sr	–	–	–	–			
1.500	Te	–	–	–	–			
1.000	Th	–	–	–	–			
0.025	Ti	–	–	–	–			
0.500	Tl	–	–	–	–			
2.000	U	–	[68]	[62]	[56]	[62]	6.0	9.7
0.050	V	–	–	–	–			
2.000	W	–	–	–	–			
0.050	Y	–	–	–	–			
0.050	Zn	[0.91]	[5.8]	[5.5]	[5.4]	[5.6]	0.21	3.7
0.050	Zr	–	[1.4]	[1.4]	[1.3]	[1.4]	0.06	4.2

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).

Attachment No. 2 of 2, ASR-5778 "ICPAES Measurement Results -- Quality Control Parameters"

ASR-5778 D. Kurath A0595 4/11/00 RPL#: 00-1701 *Client ID: "AP-101 COMP"*

PF= 25.3

	Analyte	MRQ (ug/ml)	IDL(ICPAES) (ug/ml)	EQL (ug/ml)	[80%-120%] LCS (%R)	[75%-125%] Spike Rec'y (%R)	[<15%] Dup %RSD (%RSD)
1	Ag	17	0.025	6.3	69 #	35 #	--
2	Al	75	0.06	15.2			5.5
3	Ba	2.3	0.01	2.5 #	87	30 #	[3]
4	Bi	170	0.1	25.3			--
5	Ca	150	0.25	63.3			[2]
6	Cd	7.5	0.015	3.8	92	87	[2.9]
7	Cr	15	0.02	5.1	93	94	8.9
8	Cu	17	0.025	6.3			[7.4]
9	Fe	75	0.025	6.3			[14]
10	K	750	2	506.0			2.1
11	La	2.3	0.05	12.7 #			--
12	Mg	170	0.1	25.3			--
13	Mn	17	0.05	12.7			--
14	Na	170	0.15	38.0			2.9
15	Nd	170	0.1	25.3			--
16	Ni	30	0.03	7.6	88	85	7.6
17	P	330	0.1	25.3			15.8 #
18	Pb	300	0.1	25.3	101	65 #	[0]
19	Pd	390	0.75	189.8			--
20	Rh	18	0.3	75.9 #			--
21	Ru	36	1.1	278.3 #			--
22	Si	90	0.5	126.5 #			4
23	Sr	17	0.015	3.8			--
24	Ti	17	0.025	6.3			--
25	U	780	2	506.0			[9.7]
26	Zn	17	0.05	12.7	89	92	[3.7]
27	Zr	17	0.05	12.7			[4.2]

Note: Gray areas indicate quality results outside of control limits of Table 2, "Supernate Analyses Required by Contract Specification 7 and Opportunistic Analytes" and Table 4, "Quality Control Parameters for Liquid Analysis" (reference: See ASR-5778 Attachment 2 page 1 of 6, and page 4 of 6)

Battelle PNNL/RPG/Inorganic Analysis --- IC Report

REVISION 1 (June 13, 2000)

Client:	D Kurath	**Charge Code/Project:**	W54906/29953
RPL Numbers:	00-1701 (triplicate)	**ASR Number:**	5778
Analyst:	MJ Steele	**Analysis Date:**	April 23-24, 2000

Procedure: PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography"
M&TE: IC system (WD25214); Balance (360-06-01-031) --- See Chemical Measurement Center 98620 RIDS IC File for Calibration, Standards Preparations, and Maintenance Records.

Final Results:

The AP-101 composite sample (00-1701) was analyzed in triplicate by ion chromatography (IC) for inorganic anions as specified in the governing ASR. The final results are presented in Table 1 below. All analytical samples were diluted 2000 to 5000 fold at the IC workstation to ensure that all anions reported were measured within the calibration range. Per the ASR the samples were analyzed in triplicate and the relative standard deviation between the measurements is reported. The minimum reportable quantity (MRQ) for each anion was defined by the ASR, and all MRQ were met at the dilutions analyzed. From recoveries demonstrated on some of the verifications standards analyzed, the AP-101 sample matrix has an adverse effect on the IC column and some reported results may be 10% to 20% low. By further diluting the sample, this effect could be minimized, but at the expense of meeting the MRQs (particularly phosphate, sulfate, and oxalate).

For IC column and parameters used, the IC system can not separate fluoride, acetate, and formate; the IC system quantifies and reports all as fluoride. It is unlikely that the levels of fluoride quantified are present in the tank waste, and since acetate and formate could be present in the AP-101 sample, the fluoride results should be used with reservation.

Table 1		F(*)	Cl	NO_2	Br	NO_3	PO_4	SO_4	C_2O_4
RPL Number	Sample ID	ug/ml	ug/ml	ug/ml	ug/ml	ug/ml	ug/ml	ug/ml	ug/ml
	Target MRQs	150	300	2,300	n/a	3,000	2,300	2,300	1,800
00-1701	AP-101 Composite	2,880	2,000	42,200	< 500	133,000	1,040	4,070	1,100
00-1701 Dup	AP-101 Composite Duplicate	2,880	1,920	41,000	< 500	130,000	1,000	3,940	1,060
00-1701 Trip	AP-101 Composite Triplicate	2,940	2,010	42,400	< 500	133,000	1,020	4,080	1,100
	Rel Std Dev (%)	1.2%	2.5%	1.8%	n/a	1.3%	2.0%	1.9%	2.1%
00-1701 MS	AP-101 Composite MS %Rec	114%	111%	119%	108%	128%	119%	108%	121%
	Blank Spike %Rec	110%	107%	105%	108%	78%	104%	106%	107%

Rel Std Dev (5) = Relative Standard Deviation – Sample, Duplicate, Triplicate
MS %Rec = Matrix Spike Standard % Recovery, BS %Rec = Blank Spike Standard % Recovery
(*) Use fluoride results with reservation; IC system can not resolve fluoride, acetate, and formate.

Battelle PNNL/RPG/Inorganic Analysis --- IC Report

Q.C. Comments

Duplicates/Replicates: The ASR requested that the analyses be performed in triplicate and therefore the relative standard deviation was calculated for the three analyses. The Quality Control parameters defined in Table 4 attached to the ASR states acceptance criteria of <15% relative percent difference (RSD). Table 1 presents the RSD based on comparison of the triplicate analysis. The RSD meets the acceptance criteria for all anion.

Matrix Spike: The matrix spike recoveries for all anions, except nitrate, were within the spiking acceptance criteria of 75% to 125% as established by ASR attachment Table 4. The high nitrate concentration of the sample relative to the nitrate spiking level (i.e., sample concentration was 10 times greater than the spike concentration) significantly impacts the ability to measure the nitrate spike. No attempt was made to spike the samples at additional spiking level.

Blank Spike: The blank spike recoveries for all anions, except nitrate, were within the Laboratory Control Samples (LCS) acceptance criteria of 80% to 120% as established by the ASR attachment Table 4. Nitrate recovered slightly low at 78%. It should be noted that the blanks spike nitrate recovery is not consistent with other control standards analyzed during the analysis run (e.g., Verification Check Standards).

System Blank/Processing Blanks: A dozen system blanks were process during the analysis of the slurry samples. No anions were detected in the system blanks above the method detection limit.

Quality Control Calibration Verification Check Standards: Over twenty mid-range verification standards were analyzed throughout the analysis runs. Numerous verification standards analyzed just after the analysis of some of the AP-101 samples demonstrated low recoveries (i.e., recoveries ranging from 80% to 90%). Failure of the verification standard was only observed in those standards analyzed just after the AP-101 samples that had were prepared with the least dilution. Numerous reruns were performed alternating the AP-101 (at various dilutions) and the verification standard to obtain valid data.

General Comments:

- The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
- The low calibration standards are defined as the estimated quantitation limit (EQL) for the reported results and assume non-complex aqueous matrices. Actual detection limits or quantitation limits for specific sample matrices may be determined, if requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference and have similar concentrations as the measured anions.

Approval: MW Urie　　**Date** 6-13-00

Archive Information:

Files: ASR 5778 Kurath Rev 1.doc　　ASR 5729 5764-68 5778.xls

IC Results for oxalate, formate, acetate, and citrate

G.M. Mong and J.A. Campbell

Gary Mong J.A. Campbell

Instrumentation

The analytical instrumentation utilized for the analysis of low-molecular weight organic acids consisted of an ion chromatography unit equipped with a conductivity detector. A Dionex AS-11 column and AG-11 guard column were used at ambient temperature with a 25-µL sample loop. An anion suppressor was used. The flow rate of the mobile phase was 2.0 mL/min. A description of the IC system is provided in Table 1.a.

Table 1.a Ion Chromatography Instrumentation

System/Instrument	Manufacturer	Model Number	M&TE (1) Number
Ion Chromatograph	Dionex	500 DX	WD 24293
Conductivity Detector	Dionex	CD20	WD 24295

(1) Measuring and Test Equipment

The IC gradient conditions were: (a) 0.0 min 0% 100 mM NaOH, 98.1% deionized water and 1.9% 5 mM NaOH, (b) 6.4 min 0% 100 mM NaOH, 0% deionized water and 100% 5 mM NaOH, and (c) 18.4 min 35% 100 mM NaOH, 0 % deionized water and 65% 5 mM NaOH. The mobile phase contained a gradient of deonized water and a weak solution of NaOH.

Analysis Results

Samples were analyzed using PNNL operating procedure AOAM-1 (Method for the Analysis and Quantification of Organic Acids in Simulated and Actual Hanford Tank Wastes by Ion Chromatography). Sample AP-101 was done in triplicate at a dilution found to give acceptable total ion loading to the column (Dionex AS-11 anion exchange media). This dilution was calculated to be a 2242 times the sample weight as delivered to the 325 shielded laboratory.

Although acetate is reported, acetate coelutes with glycolate and requires the use of an alternate column for separation from glycolate. Without additional separation, one can not unequivocally state that the acetate/glycolate peak contains only acetate, only glycolate, a combination of both analytes, or a possible contaminant. From tank waste and solubility studies, the results are tank waste type dependent. In other words, for one tank waste the component may be entirely acetate. For another tank with a different fill history, the analytical results may indicate the component may be primarily glycolate or a combination of both analytes (Sharma et al. 1998, Camaioni et al. 1998, Barney 199, Ashby et al. 1994).

The results are shown below for quantity (in micrograms) of acetate, formate, and oxalate found per milliliter of sample., based on a measured density of 1.308 g/mL. Citrate was below detectability in each sample using this dilution scheme.

Sample	µg acet/mL	µg form/mL	µg oxal/mL	µg citrate/mL
#1	1543	1131	1799	ND
#2	1793	1256	1781	ND
#3	1601	1196	1817	ND
Average	1645	1194	1800	ND

The detection limits for acetate, formate, oxalate, and citrate are estimated to be 550 µg/mL, 450 µg/mL, 890 µg/ml, and 890 µg/mL, respectively, based on the dilution factors.

QC Evaluation

Matrix spiking was done at a level approximately 1.5 times the level of analyte in the final diluted samples. This level of spiking is at a challenging level for accurate quantitation; the reported levels are near the lowest calibration point for each analyte. These results are summarized below:

MS spike		ms	msd-1	msd-2	average
recovery	Acetate	175%	105%	91%	124%
	Formate	71%	104%	79%	84%
	Oxalate	122%	92%	129%	114%

The value for acetate in the matrix spike sample should be considered suspect, as the peak quantitation had to be done by estimation (since the peak size was so small). The other data represent quantitation which was extracted directly from electronic integration data. Overall, the average data for MS and MSD is within acceptable limits. The LCS consisted of a mixture of formate and oxalate. The per cent recoveries obtained were 89.3 and 103.8%, respectively.

References

1. Sharma, A.K., S.A. Clauss, G.M. Mong, K.L. Wahl, J.A. Campbell. 1998. Analysis and quantification of organic acids in simulated Hanford tank waste and Hanford tank waste. J. of Chromatogr, 805, 101-107.

2. Camaioni, D.M., W.D. Samuels, J.C. Linehan, S.A. Clauss, A.K. Sharma, K.L. Wahl, J.A. Campbell. 1996. Organic Tanks Safety Program, FY 96 Waste Aging Studies, PNNL-11312, Pacific Northwest National Laboratory, Richland, Wa.

3. Ashby, E.C. et al. 1994. Synthetic Waste Chemical Mechanism Studies, WHC-EP-0823, Westinghouse Hanford Company, Richland, Wa.

4. Barney, GL. 1996. Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions-FY 1996 Progress Report, WHC-EP-0899, Westinghouse Hanford Company, Richland, Wa.

Battelle PNNL/RPG/Inorganic Analysis --- TOC/TIC Report

Client: D. Kurath
ACL Numbers: 00-1701
Analyst: MJ Steele

Charge Code/Project: W54906 / 29953
ASR Number: 5778
Analysis Date: May 12 and April 13-14, 2000

Procedure: PNL-ALO-381, "Direct Determination of TC, TOC, and TIC in Radioactive Sludges and Liquids by Hot Persulfate Method"
PNL-ALO-380, "Determination of Carbon in Solids Using the Coulometric Carbon Dioxide Coulometer"

M&TE: Carbon Analysis System (WA92040); Balance (360-06-01-023).

Final Results:

		HOT PERSULFATE METHOD						FURNACE METHOD	
RPL Number	Sample ID	TIC (μgC/ml)	TIC RPD	TOC (μgC/ml)	TOC RPD	TC (μgC/ml)	TC RPD	TC (μgC/ml)	TC RPD
00-01701	AP-101 COMPOSITE	6,550		1,860		8,410		8,530	
00-01701	AP-101 COMPOSITE	6,400	2%	1,980	6%	8,390	0%	8,670	2&
00-01701	AP-101 COMPOSITE	6,430		2,030		8,460		8,620	
	RSD	1.2%		4.5%		0.4%		0.8%	
00-01701 MS	MS Recovery	98.5%		96.3%		97.5%		97.5%	
	MDL	40		80		80		170	

RPD = Relative Percent Difference
RSD = Relative Standard Deviation

The analysis of the liquid sample submitted under ASR 5778 was performed by the hot persulfate wet oxidation method and by the furnace oxidation method. The hot persulfate method uses acid decomposition for TIC and acidic potassium persulfate oxidation at 92-95°C for TOC, all on the same sample, with TC being the sum of the TIC and TOC. The furnace oxidation method determines TC by oxidizing all forms of carbon (i.e., inorganic and organic) in oxygen at 1000 °C. Although the ASR requested TOC and TIC by the furnace method, the method is considered reliable only for TC. For the sample matrix analyzed the furnace method and hot persulfate method should provide equivalent TC results, and this was confirmed by the results, with the average hot persulfate TC being 8420 μg/ml and the furnace TC being 8610 μg/ml; an RPD of about 2%.

The table above shows the results, rounded to two to three significant figures. The raw data bench sheets and calculation work sheets showing all calculations are attached. All sample results are corrected for average percent recovery of system calibration standards and are also corrected for contribution from the blank.

Q.C. Comments:

The TIC standard is calcium carbonate and TOC/TC standard is α-Glucose (the certificates of purity are attached). The standard materials were used in solid form for system calibration check standards as well as matrix spikes. The QC for the methods involves calibration blanks, system calibration standards, sample duplicates, and one matrix spike per matrix type.

Calibration Standards: The QC system calibration check standards were all within acceptance criteria of 90% to 110%, with the average recovery being about 99% for TIC and 99% for TOC over the two days that the hot persulfate analyses were performed and about 100% for TC for the furnace analyses.

Calibration Blanks: The calibration blanks run at the beginning, middle, and end of the analysis run were acceptable and the standard deviations for the TIC and TOC blanks are near the historical pooled standard deviation used to establish the method detection limits. On the May 12th run, the TOC blanks were about 2 to 3 times higher than normal; however, the blanks were quite consistent and the high blanks should have no effect on the reported data.

Duplicates: No actual sample duplicates were identified on the ASR. However, the relative percent difference (RPD) between replicates (i.e., a sample and duplicate analysis) was less than 10% for TIC, TOC, and TC. Besides the RPD, the relative standard deviation (RSD) for the triplicate analyses was calculated, and all RSDs are less than 5%, indicate very good precision between for all measurements. The RSD met the ASR Table 4 RSD acceptance criterion of <15%.

Matrix Spike: The accuracy of the carbon measurements can be estimated by the recovery results from the matrix spike. The matrix spike for both the hot persulfate and furnace method demonstrated recoveries of about 96% to 99% for TIC, TOC, and TC; well within the acceptance criteria of 75% to 125% recovery.

Laboratory Control Sample: No LCS is included in the carbon analysis procedure.

General Comments:

- The reported "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
- Routine precision and bias are typically ±15% or better for non-complex samples that are free of interferences.
- The estimated quantitation limit (EQL) is defined as 5 times the MDL. Results less than 5 times the MDL have higher uncertainties, and RPDs are not calculated for any results less than 5 times the MDL.
- Some results may be reported as less than ("<") values. These less than values represent the sample MDL (method detection limit), which is the system MDL adjusted for the volume of sample used for the analysis. The system MDL is based on the attached pooled historical blank data. The evaluation and calculation of the system MDL is included in the data package.

Report Prepared by: ______________________ **Date** 5-18-00

Review/Approval by: ______________________ **Date** 5-22-00

Archive Information:

Files: ASR 5778 Kurath.doc ASR 5668R 5778 Kurath.xls

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Project No. 29953

Internal Distribution

File/LB

Date May 17, 2000

To K. E. Kurath

From S. K. Fiskum SK Fiskum

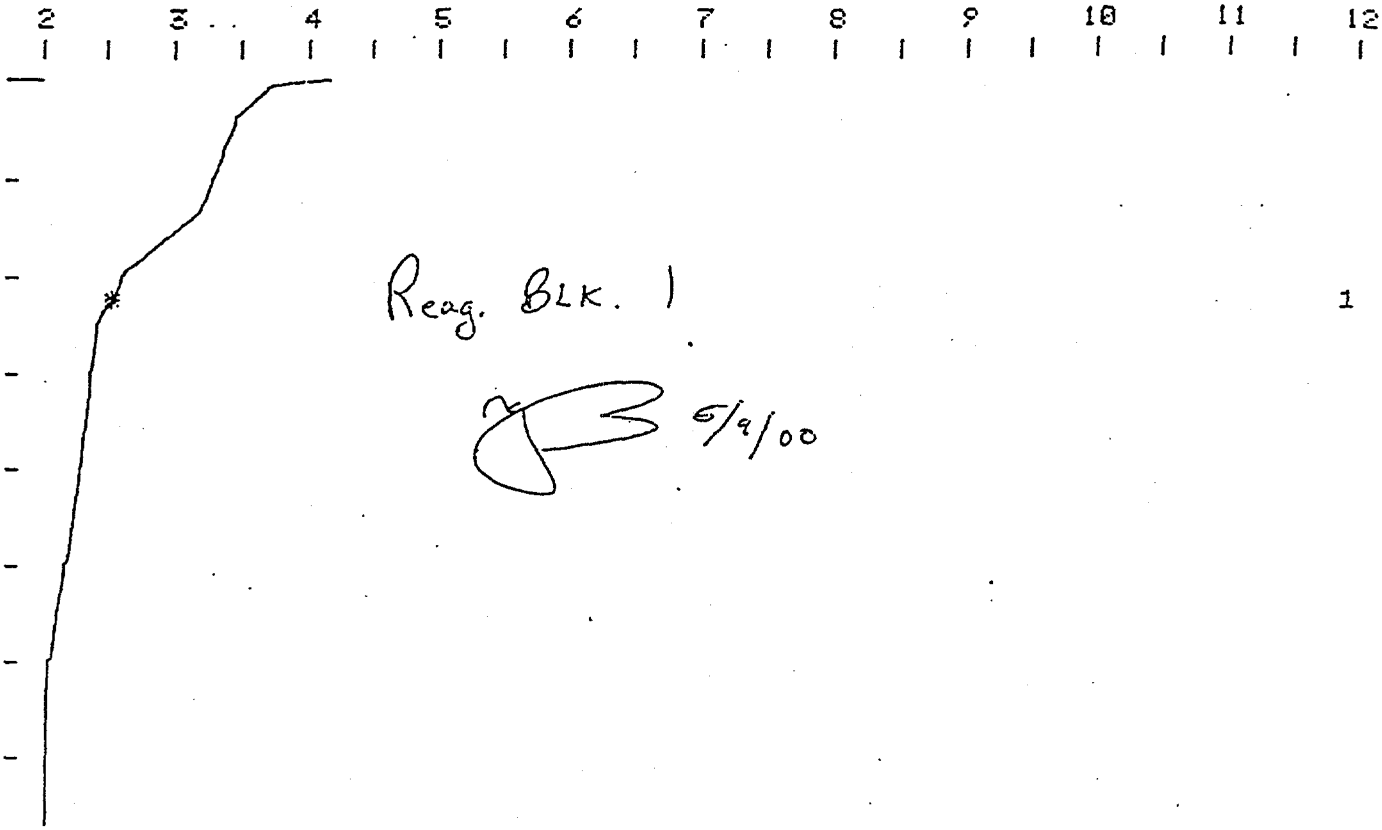
Subject Hydroxide Analyses for AP101 Composite ASR 5778, Rev. 1

A sample of the composite from tank AP101 (00-1701) was analyzed in triplicate for the hydroxide content following procedure PNL-ALO-228. Direct sample aliquots were analyzed using a Brinkman 636 Auto-Titrator. A 0.1186 N NaOH solution was prepared for use as a standard and sample spike and the titrant was a 0.2040 M HCl prepared solution. Triplicate results (2.49, 2.42, and 2.38 M OH) gave an average OH molarity of 2.43 with a relative standard deviation of ±3%. The standard recoveries averaged 100% and the sample spike recovered at 88%. Hydroxide was not detected in the reagent blank, demonstrating an MDC of 0.02M OH or 3.4E+2 µg OH/mL. A second titration inflection point was determined at an average pH of 7.5 and a third inflection point at an average pH of 4.9. The titration curves are attached.

Review: LRGreenwood 5/17/00

```
△ PH      0.012    0.012 -   0.024
TEMP/C     25.0    SLOPE     0.881   U(AS)/MV      29.3
```

```
0.25ML/DIV   V(START)/ML     0.000       PH
```



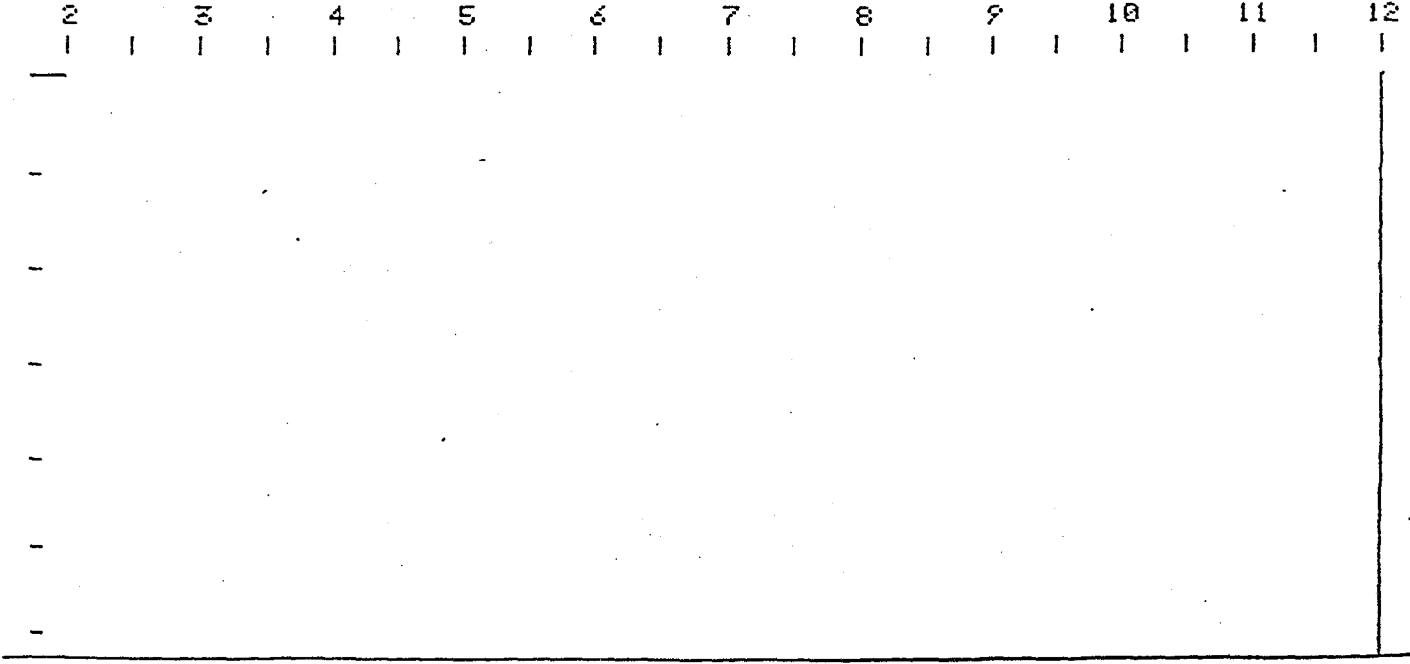
Reag. BLK. 1

6/9/00

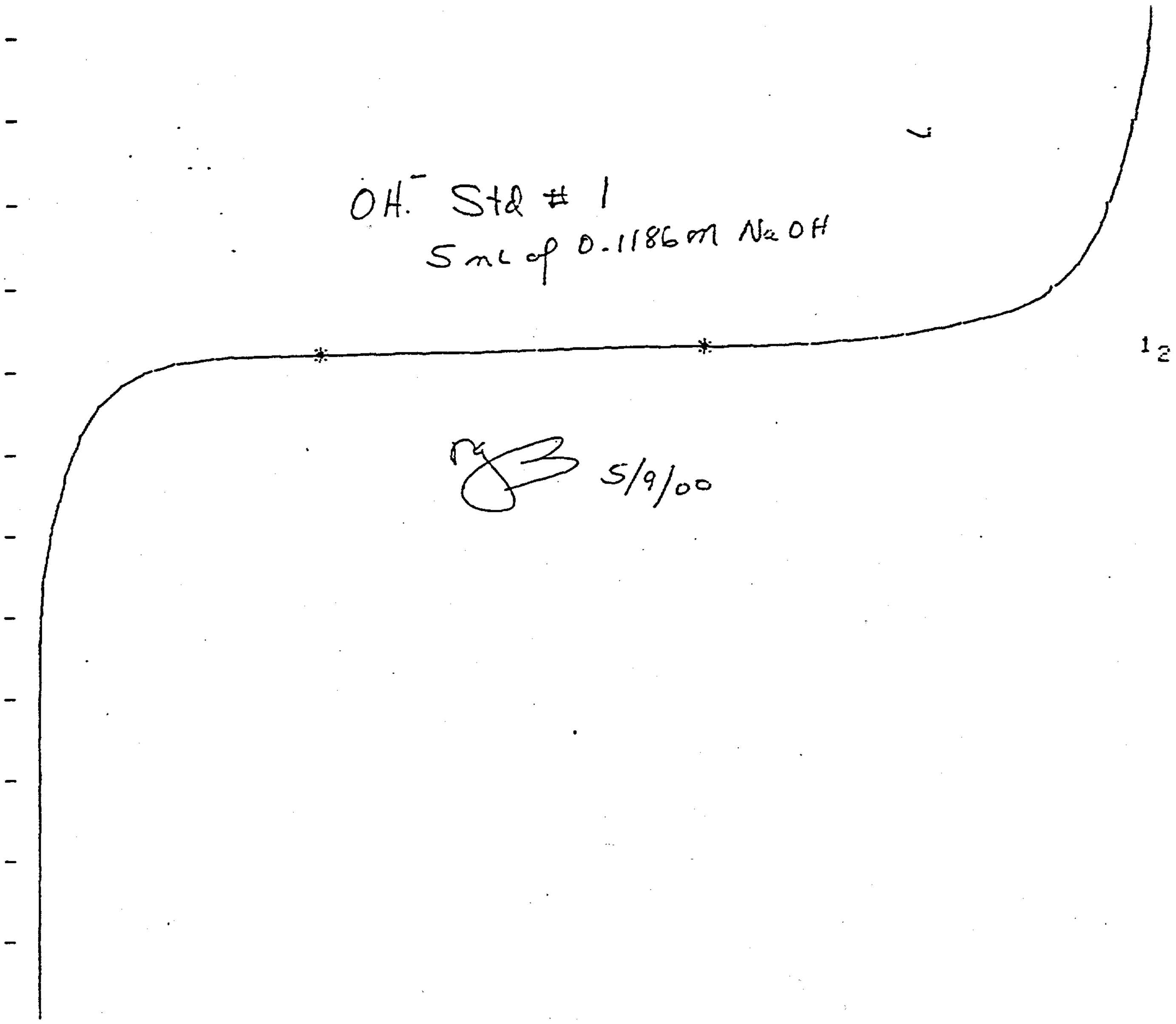
```
ROUTINE #     101
#       1    PH(INIT)    4.120    V(TE)/ML    2.149
1  V/ML    0.566  PH(M)    2.513
```

```
                                       DATE              NAME
```

```
0.25ML/DIV   V(START)/ML     0.000       PH
```



BRINKMANN CAT # 2025015-1



OH⁻ Std # 1
5 mL of 0.1186 M NaOH

5/9/00

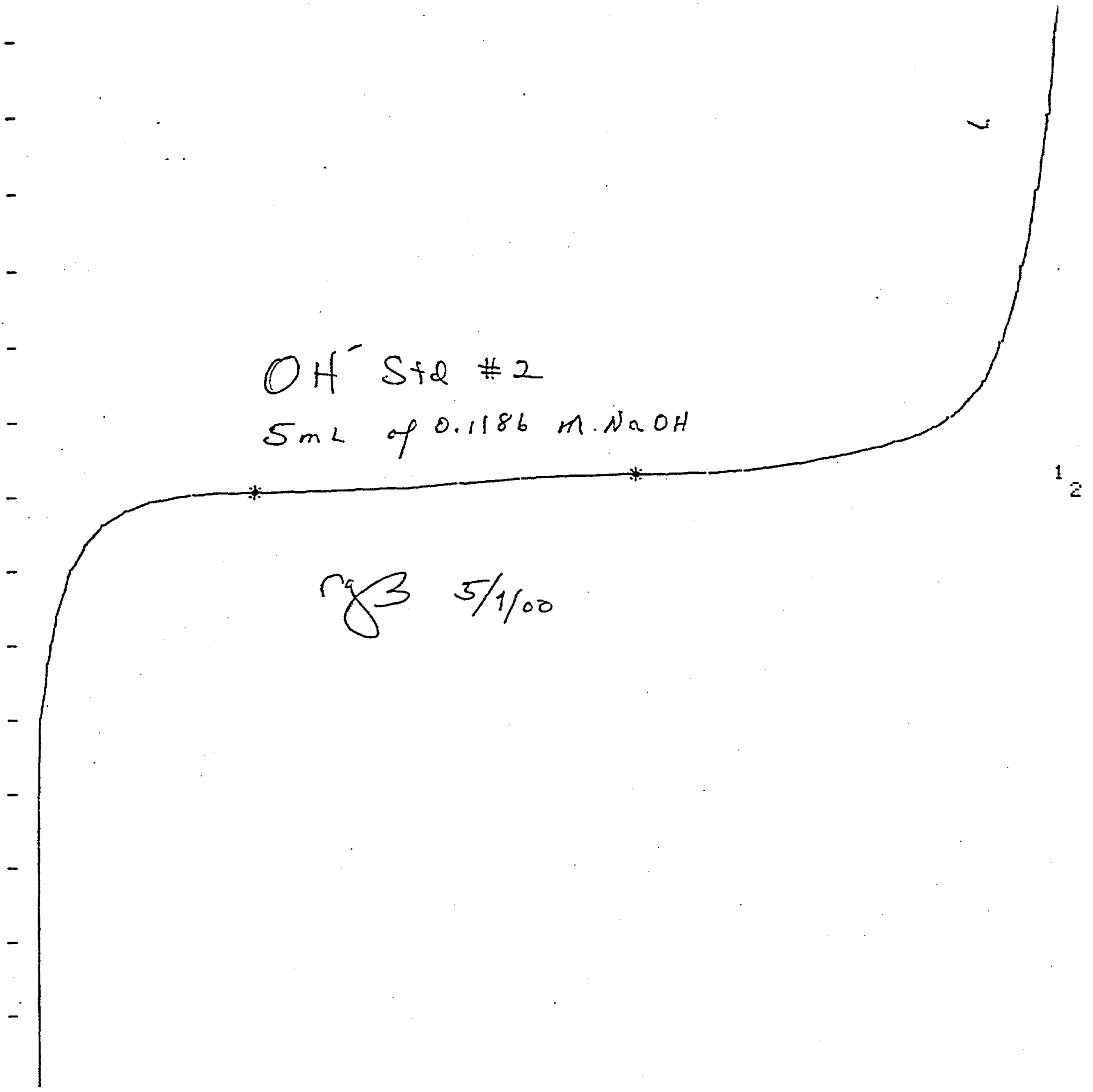
BRINKMANN CAT # 2025015-1

```
ROUTINE #     101
#       2   PH(INIT)  12.216   V(TE)/ML   5.000
1  V/ML    2.925  PH(M)    7.992
2  V/ML    2.954  PH(M)    4.511

                                DATE              NAME

     0.25ML/DIV   V(START)/ML     0.000      PH

2     3     4     5     6     7     8     9     10     11     12
```



OH⁻ Std #2
5mL of 0.1186 M NaOH

5/1/00

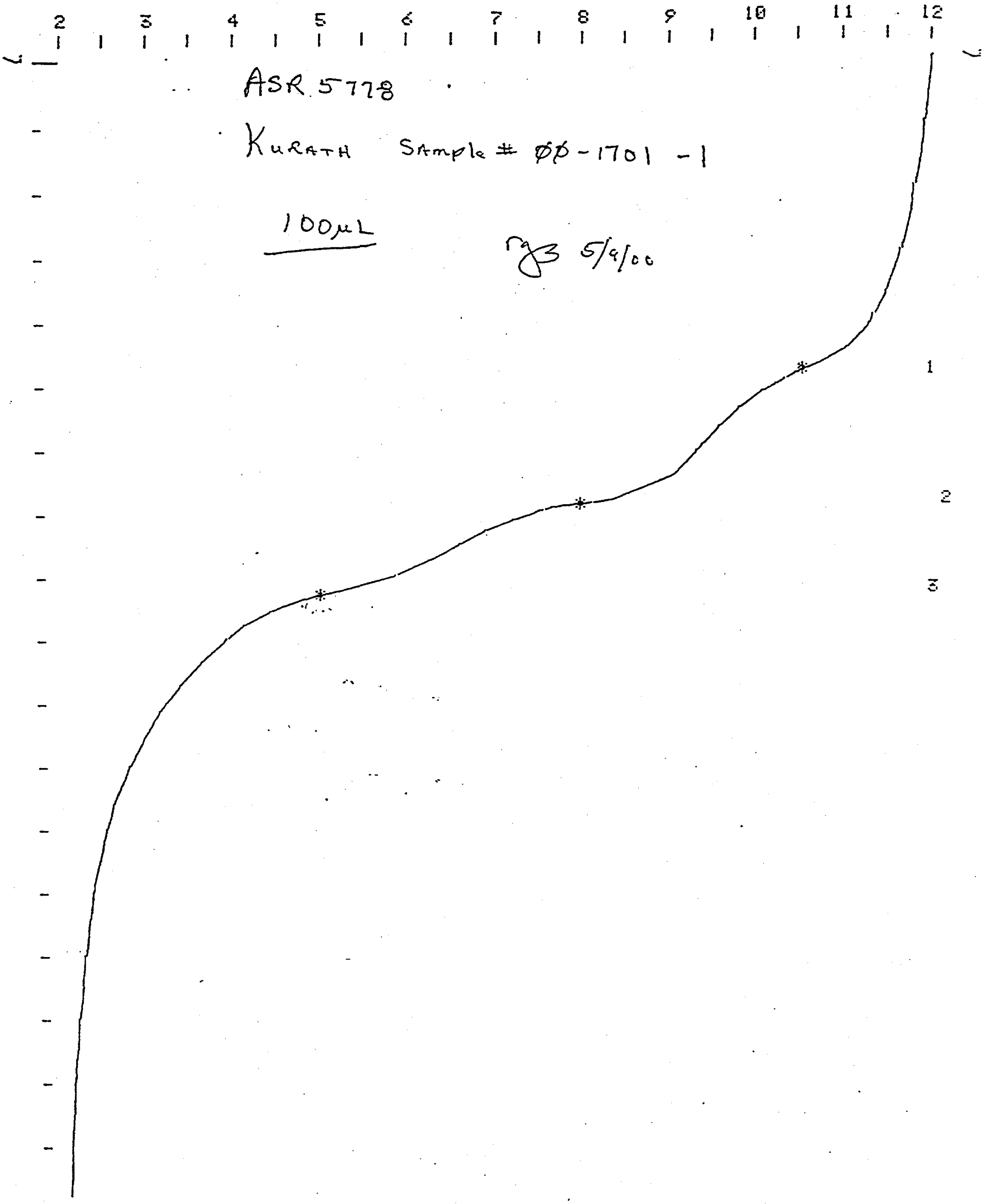
```
ROUTINE #     101
#      3   PH(INIT)  12.113   V(TE)/ML   5.000
1  V/ML    2.936  PH(M)    7.841
2  V/ML    2.993  PH(M) -  4.132

                                  DATE                NAME

    0.25ML/DIV  V(START)/ML    0.000      PH

2        3        4        5        6        7        8        9        10        11        12
```

```
0.25ML/DIV   V(START)/ML    0.000        PH
```



ASR 5778

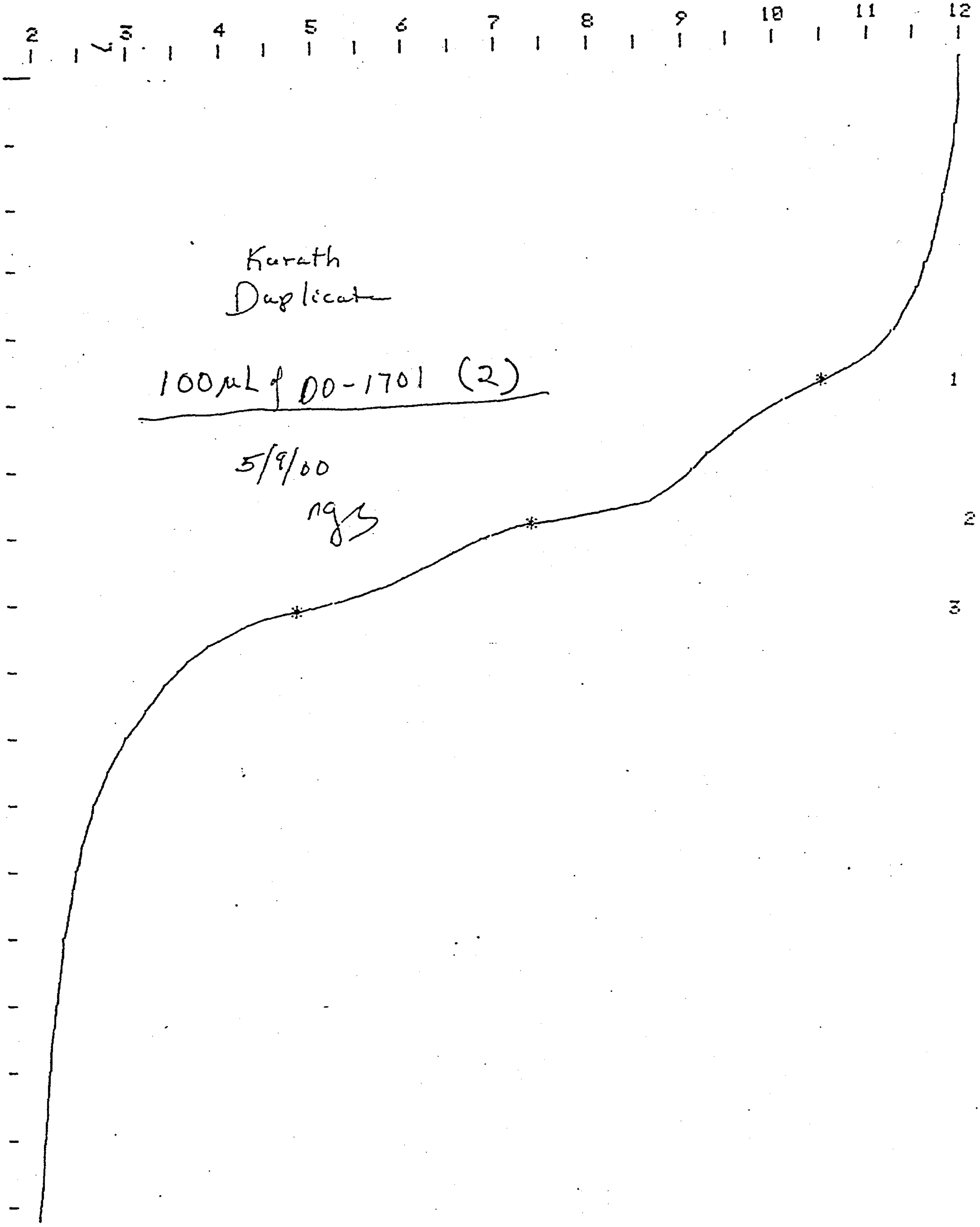
Kurath Sample # 00-1701 -1

100µL

5/9/00

```
ROUTINE #     101
#      7    PH(INIT)  12.074    V(TE)/ML    4.676
1   V/ML    1.219   PH(M)   10.523
2   V/ML    1.728   PH(M)    7.920
3   V/ML    2.081   PH(M)    4.951
```

0.25ML/DIV   V(START)/ML   0.000   PH



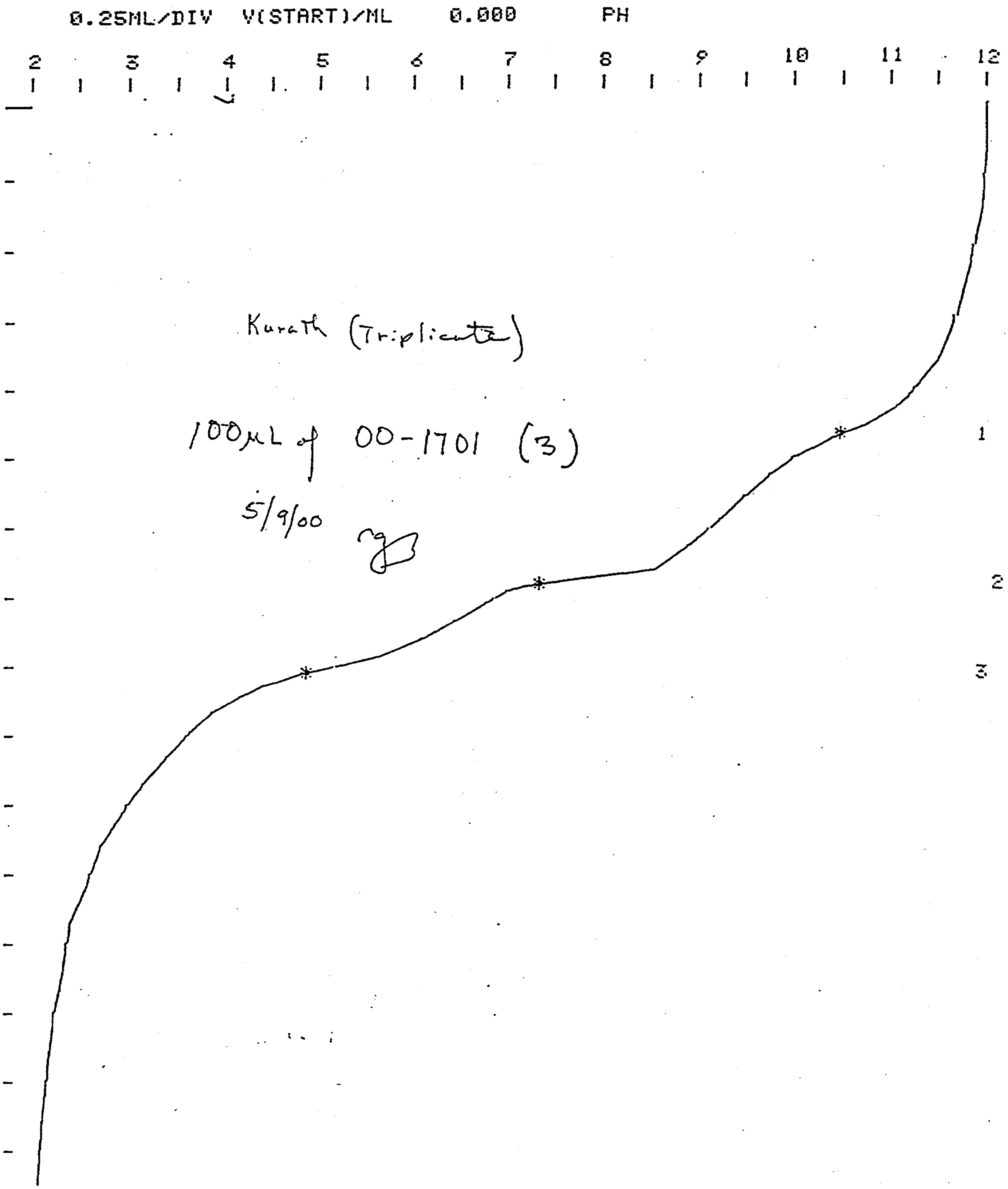
Karath
Duplicate

100µL of DO-1701 (2)

5/9/00

ngB

```
ROUTINE #     101
#        8   PH(INIT)  12.118   V(TE)/ML    4.533
1  V/ML    1.184  PH(M)  10.518
2  V/ML    1.703  PH(M)   7.402
3  V/ML    2.036  PH(M) ,  4.823
```



Kurath (Triplicate)

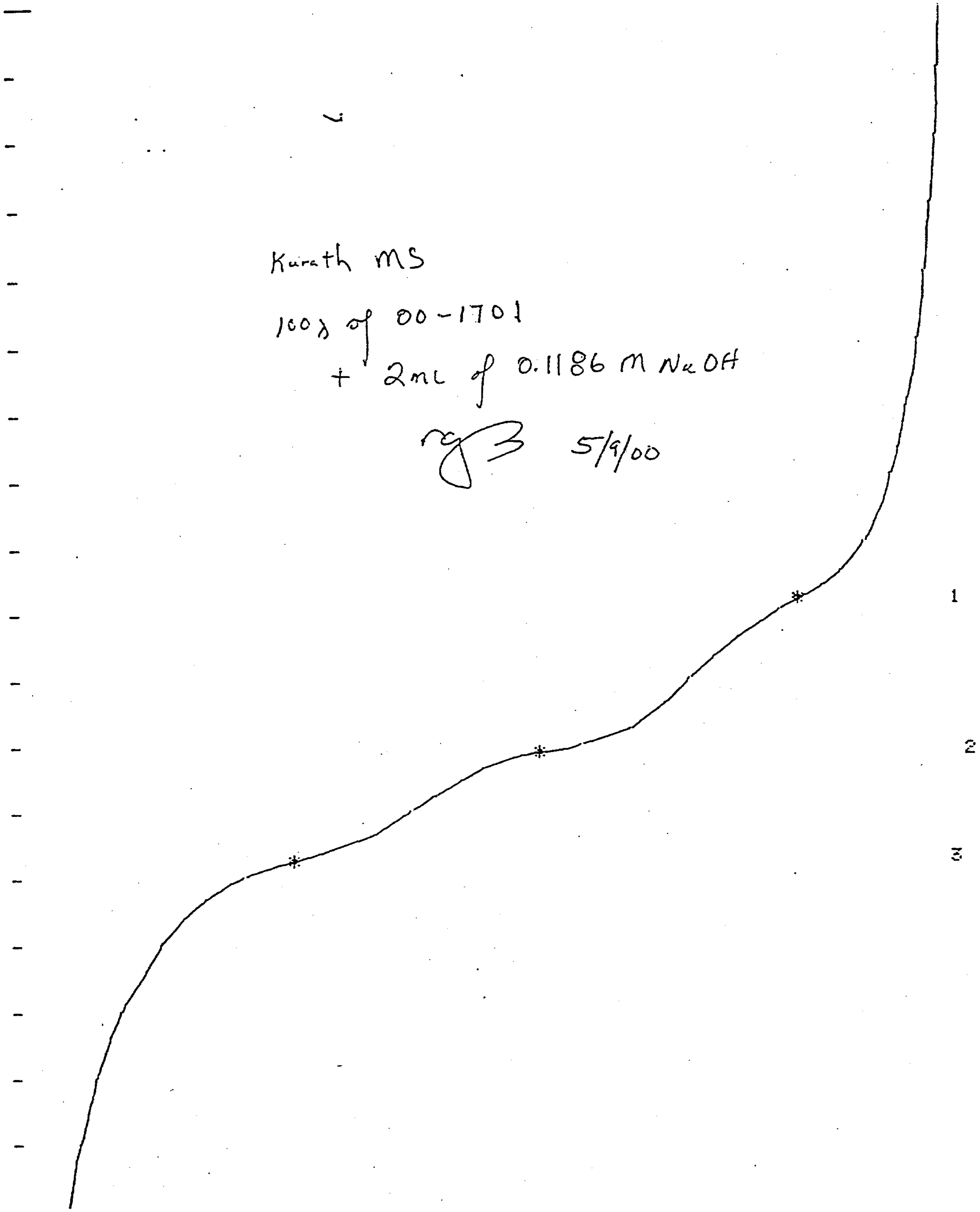
100µL of 00-1701 (3)

5/9/00

```
ROUTINE #     101
#       9   PH(INIT)  12.151   V(TE)/ML   4.098
1  V/ML    1.169  PH(M)  10.473
2  V/ML    1.700  PH(M)   7.313
3  V/ML    2.023  PH(M)   4.839
```

DATE NAME

0.000 PH



Kurath MS

100g of 00-1701
+ 2mL of 0.1186 M NaOH

5/9/00

```
ROUTINE #     101
#      10    PH(INIT)   11.810   V(TE)/ML    4.694
1  V/ML    2.214  PH(M)   10.251
2  V/ML    2.785  PH(M)    7.449
3  V/ML    3.194  PH(M)    4.740
```

DATE NAME

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Project No. 29953

Internal Distribution
File/LB

Date May 9, 2000

To D. E. Kurath

From S. K. Fiskum S.K. Fiskum

Subject Radiochemical Analyses for AP-101 Composite
ASR 5778

A sample of the composite from tank AP-101 (00-1701) was analyzed in triplicate for total alpha, total beta, gamma energy analysis, ^{3}H, uranium, ^{90}Sr, ^{99}Tc, Pu, and Am/Cm. The attached reports list measured analyte activities in the original AP101 material in units of uCi/ml except for uranium, which is reported in ug/ml. The reported errors (1-σ) represent the total propagated error including counting, dilution, yield, and calibration errors, as appropriate. Laboratory and process blank values given with each analysis are the best indicators of the method detection limits, taking into account the actual sample sizes and counting times used for each analysis.

Gamma Spectrometry

Triplicate 100-μL aliquots of AP101 original material were prepared into 2-mL geometries with deionized water (no acid digestion was applied). The small aliquot size was necessary to reduce the detector dead time attributed to the high ^{137}Cs activity. The samples were counted and analyzed directly by gamma energy analysis (GEA) according to procedure PNL-ALO-450. Because no sample manipulation was performed other than simple aliquoting and diluting, no preparation blank was prepared. In order to meet the required detection limits, the samples were counted for 14 hours each. Only ^{137}Cs, ^{134}Cs, and ^{60}Co could be identified in the gamma spectra. The triplicate concentrations of ^{137}Cs, ^{134}Cs, and ^{60}Co agreed to within $\pm$3%, well within the $<$15% RSD acceptance criteria. The other requested analyte concentrations were below the minimum reporting limits requested.

Pertechnetate ^{99}Tc

The radiochemical ^{99}Tc determination was requested to measure only Tc in the +7 oxidation state (pertechnetate). To this end, all sample manipulations had to be non-oxidizing so as not to alter the original Tc oxidation state. Small aliquots from the as-received material (no digestion) were taken for analysis according to procedure PNL-ALO-432. This procedure normally requires the use of sodium dichromate addition to oxidize the Tc to the +7 oxidation state. The sodium dichromate addition was omitted and the procedure otherwise was performed as written. The separated fractions were then counted according to RPG-CMC-408. One sample was also counted by gamma spectrometry (according to PNL-ALO-450) to verify the absence of ^{137}Cs. The LCS and matrix spike were spiked with pertechnetate and their recoveries were 99% and 84%, respectively, well within project requirements. The RSD of the triplicate samples was 8%, again well within the project-required < 15% RSD.

Acid Digestion

Triplicate 0.5-mL aliquots of AP101 were digested with nitric acid according to PNL-ALO-106. Heating and nitric acid additions continued until all organic/nitric reactions had visibly ceased. The samples were then brought to a 10-mL volume with 2M HNO_3. A preparation blank was run side by side with the samples. These digestions were used for the subsequent analyses of total alpha, total beta, $^{239+240}$Pu, ^{238}Pu, ^{241}Am, ^{242}Cm, $^{243+244}$Cm, total U, and ^{90}Sr. A laboratory control sample (LCS) was not available for radiochemical analyses. Specific reagent spikes or blank spikes were prepared subsequent to digestion and were used as LCSs.

Total Alpha

The total alpha activity was determined by direct-plating small aliquots of the acid-digested samples onto planchets according to RPG-CMC-4001. The samples were then counted on Ludlum detectors according to RPG-CMC-408. The sample activities resulted in a 9% RSD, well within the < 15% RSD acceptance criteria. Alpha activity was not found in the preparation blank. The LCS ^{239}Pu recovery was 99% and the matrix spike ^{239}Pu recovery was only 55%. The low matrix spike recovery is attributed to the solids loading on the planchet from the sample matrix salts that attenuate/absorb the alpha emissions. This is a physical problem with the sample as it is presented to the detector and does not indicate the analysis is out of control. What this does indicate is that the analytical method is probably biased low by as much as 45% for this matrix. A better indication of the total alpha activity is given by the summation of the alpha emitters ($^{239+240}$Pu, ^{238}Pu, ^{241}Am, $^{243+244}$Cm and ^{242}Cm), shown in the last column of the data report. These alpha-emitter summations range from 18% to 39% higher than the total alpha activity found by direct plating. The RSD for the summation method is 1%.

Total Beta

The total beta activity was determined by directly plating small aliquots of the acid-digested samples onto planchets according to RPG-CMC-4001. The samples were then counted on a low-background alpha/beta gas-flow proportional counter according to RPG-CMC-408. The detectors were calibrated for beta activity relative to ^{90}Sr/^{90}Y. The beta energy of ^{137}Cs is similar to that of ^{90}Sr and will have a counting efficiency similar to that of pure ^{90}Sr. The total beta analyses compared to the ^{137}Cs determinations shows that virtually all of the beta activity is due to ^{137}Cs and the two values are in excellent agreement. The precision, measured by the RSD, is 5%, within experimental error. The LCS and matrix spike showed excellent ^{90}Sr/^{90}Y recoveries at 100% and 103%, respectively.

Plutonium, Americium, and Curium

The Pu and Am/Cm separations were performed according to PNL-ALO-417; the separated fractions were precipitation plated according to PNL-ALO-496; and the samples were counted by alpha spectrometry according to PNL-ALO-422. Plutonium recovery was traced with ^{242}Pu. The curium is known to follow the americium and both these isotopes were traced with ^{243}Am.

Plutonium radiochemical yields were excellent at >90%. Radiochemical yields for Am ranged from 70% to 86%. In both cases, ample counts were obtained to define sample activities. Neither Pu, Am nor Cm were detected in the preparation blank. The LCS and matrix spike for Pu resulted in 98% and 101% yield-corrected recovery. This indicates the chemistry and analyses were not biased. The LCS and matrix spike for the Am (and Cm) fractions resulted in 94% and 91% yield-corrected recovery. The $^{239+240}$Pu analyses resulted in 2% RSD, for ^{238}Pu the RSD was 5%. The ^{241}Am resulted in 2% RSD, the $^{243+244}$Cm resulted in 29% RSD. This latter high RSD reflects the much higher uncertainty associated with the analytical results, which are approximately 5 orders of magnitude less than the requested detection limit.

Strontium-90

The Sr separation was performed according to PNL-ALO-476 and radiochemical yields were traced with ^{85}Sr. The separated fractions were then beta-counted according to RPG-CMC-408 and gamma counted according to PNL-ALO-450 (for ^{85}Sr determination and ^{137}Cs impurity assessment). Two of the separated fractions contained a small amount of ^{137}Cs and a correction to the beta count rate was applied for these samples. Strontium-90 was not found in the preparation blank. The RSD is 0.3%, indicative of excellent precision. The LCS and matrix spike recoveries were 92% and 99%, respectively, indicating good accuracy.

Total Uranium

Total uranium was measured in triplicate aliquots taken from the acid digestion according to procedure PNNL-ALO-4014 using Kinetic Phosphoresence Analysis (KPA). The triplicate results showed excellent agreement with a RSD of 1%. A small amount of uranium was detected in the acid digestion process blank; however, the level was a factor of 10,000 lower than the uranium seen in the samples. A blank prepared at the time of the analysis did not detect any uranium. Uranium standards analyzed before and after the samples agreed within 3% of the known values.

Tritium

Tritium was analyzed by distillation of direct sample material using procedure PNL-ALO-418 followed by liquid scintillation counting according to procedure PNL-ALO-474. The first distillation showed the presence of higher-energy beta activity, most likely due to ^{137}Cs. A second distillation succeeded in removing most of this contamination; however, two of the triplicate samples required subtraction of weak beta contamination using the ratio of the counts in the tritium energy region to the counts at higher energies, as determined from the first counting results. The triplicate results showed good agreement with a RSD of 5%. A blank spike showed good recovery at 96%. No tritium was detected in a blank prepared at the time of analysis in the laboratory.

Battelle / Pacific Northwest National Laboratory
Radiochemical Processing Laboratory / 325 Building
Radiochemical Processing Group

05/02/2000

Cognizant Scientist: Richard T. R Date: 5/2/00

Technical Reviewer: L R Greenwood Date: 5/2/00

Client: Kurath
MT&E Instrument: GEA Detector G
Reference Date: N.A.

Gamma Energy Analysis (Procedure PNL-ALO-450):

Measured Activity in µCi/ml

Sample ID ALO Number	Co-60 1σ Unc.	Ru/Rh-106 1σ Unc.	Sb-125 1σ Unc.	Cs-134 1σ Unc.	Cs-137 1σ Unc.	Eu-152 1σ Unc.	Eu-154 1σ Unc.	Eu-155 1σ Unc.	Am-241 1σ Unc.
AP-101 Composite 00-01701	3.22E-3 7%	<9E-2	<6E-2	4.77E-2 3%	1.44E+2 2%	<2E-3	<2E-3	<4E-2	<4E-2
AP-101 Composite Dup. 00-01701 Dup	3.40E-3 7%	<9E-2	<6E-2	4.81E-2 3%	1.44E+2 2%	<3E-3	<2E-3	<4E-2	<4E-2
AP-101 Composite Trip. 00-01701 Trip	3.24E-3 7%	<9E-2	<6E-2	4.62E-2 3%	1.45E+2 2%	<2E-3	<2E-3	<4E-2	<4E-2
RSD	**3.0%**			**2.1%**	**0.7%**				

Battelle Pacific Northwest Laboratory 00-1701
Radiochemical Processing Group-325 Building
Chemical Measurements Center 5/8/2000

Client : Kurath
Cognizant Scientist: S.K. Fiskum Date : 5/8/00
Concur : LR Greenwood Date : 5/8/00

Measured Activities (uCi/ml) with 1-sigma error

ALO ID Client ID	Total Alpha Error %	Pu-239+ Pu-240 Error %	Pu-238 Error %	Pu-236 Error %	Am-241 Error %	Cm-243+ Cm-244 Error %	Cm-242 Error %	Alpha* Sum
00-1701 PB AP-101 Comp	<7.E-5	<2.E-7	<2.E-7	<2.E-7	<5.E-7	<8.E-8	<8.E-8	
00-1701 AP-101 Comp	2.55E-4 14%	1.24E-4 4%	1.39E-5 6%	<9.E-8	1.73E-4 5%	1.34E-6 19%	<1.E-7	3.12E-4
00-1701Dup AP-101 Comp	2.22E-4 14%	1.28E-4 4%	1.49E-5 6%	<9.E-8	1.65E-4 5%	7.40E-7 24%	<9.E-8	3.09E-4
00-1701 T AP-101 Comp	2.65E-4 14%	1.27E-4 4%	1.54E-5 6%	<2.E-7	1.70E-4 5%	1.02E-6 21%	<2.E-7	3.13E-4
RSD	9%	2%	5%		2%	29%		1%
Matrix Spike	55%*	101%			91%			
Blank Spike	99%	98%			94%			
Blank	<8.E-5							

*The low matrix spike recovery is attributed to plated solids causing absorption/attenuation of alpha emissions. The ramifications of this are the sample activities are probably similarly affected. The sum of the alpha emitters in the last column is thus the best estimate of the total alpha activity.

The total alpha, total beta, Pu, Am, Sr, and U analyses were performed on sample aliquots prepared according to PNL-ALO-106. This is a digestion procedure using nitric acid and heating that destoys organic material.

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

00-1701
5/4/2000

Client : Kurath

Cognizant Scientist: L R Greenwood Date : 5/4/00

Concur : U. k Fiskum Date : 5/8/00

Measured Activities (uCi/ml) with 1-sigma error

ALO ID Client ID	Beta Error %	Tc-99 as pertechnetate Error %	Sr-90 Error %
00-1701 PB AP-101 Comp	8.57E-5 31%	<2.E-5	<2.E-4
00-1701 AP-101 Comp	1.46E+2 4%	4.71E-2 4%	8.71E-2 3%
00-1701Dup AP-101 Comp	1.40E+2 4%	4.34E-2 4%	8.77E-2 3%
00-1701 T AP-101 Comp	1.54E+2 4%	5.10E-2 4%	8.75E-2 3%
Matrix Spike	103%	84%	99%
Blank Spike	100%	99%	92%
Method detection limit	2.E-1**	6.E-5	<6.E-4

***Calculated with respect to specific sample-counting conditions, i.e., small sample size, short count time. A larger prepartion blank sample aliquot was taken and longer counting times applied, resulting in a lower detection limit for the preparation blank.*

The total alpha, total beta, Pu, Am, Sr, and U analyses were performed on sample aliquots prepared according to PNL-ALO-106. This is a digestion procedure using nitric acid and heating that destoys organic material.

Tc-99 determination was performed on an aliquot with no acid digestion, no sample oxidation. Thus, the Tc-99 represents the pertechnetate form.

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

00-1701

5/3/2000

Client : Kurath

Cognizant Scientist: Date : 5/3/00

Concur : Date : 5/3/00

ALO ID Client ID	Uranium ug/ml Error %	+/-%
00-1701 PB AP-101 Comp	5.41E-3	3%
00-1701 AP-101 Comp	5.17E+1	3%
00-1701Dup AP-101 Comp	5.12E+1	3%
00-1701 T AP-101 Comp	5.03E+1	3%
RSD	1%	
Blank	<1.E-5	

	Standard	Measured	Ratio
Prerun Standard 1	1.00E-2	9.92E-3	0.992
Prerun Standard 2	1.00E-1	1.02E-1	1.020
Prerun Standard 3	1.00E+0	1.09E+0	1.089
Post Standard 1	1.00E-2	9.71E-3	0.971
Post Standard 2	1.00E-3	1.01E-3	1.010

The total alpha, total beta, Pu, Am, Sr, and U analyses were performed on sample aliquots prepared according to PNL-ALO-106. This is a digestion procedure using nitric acid and heating that destoys organic material.

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

00-1701
5/9/2000

Client : Kurath

Cognizant Scientist: C-Soderqu

Date : 5-9-00

Concur :

Date : 5-9-00

Measured Activities (uCi/ml) with 1-sigma error

ALO ID Client ID	Tritium Error %
00-1701 AP-101 Comp	5.05E-3 4%
00-1701Dup AP-101 Comp	4.84E-3 3%
00-1701 T AP-101 Comp	4.60E-3 3%
RSD	5%
Blank Spike	96%
Blank	< 2.E-4

Note: Tritium was determined by liquid scintillation counting following two successive distillations of direct sample material. Weak contamination was observed in the beta spectra of the first two results reported above. This contamination was subtracted out of the tritium results reported above. (We used data from a previous attempt at this analysis to accurately calculate the amount of contamination to subtract.) The third result above did not show any significant contamination.

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Project No. 29953

Internal Distribution
File/LB

Date May 12, 2000

To D. E. Kurath

From L. R. Greenwood

Subject C-14 Analyses for AP-101 Composite ASR 5778

Direct samples of the composite from tank AP-101 (00-1701) were analyzed in triplicate for C-14 following procedure PNL-ALO-482. The samples are combusted in a Coulometrics Carbon Analyzer Furnace causing oxidation of all carbon species present to CO_2. A natural carbon compound is added as a carrier and all of the CO_2 released is collected in a sodium hydroxide trap. The trap solution is then counted by liquid scintillation counting according to procedure PNL-ALO-474. The triplicate results showed good agreement with a relative standard deviation of 5%. The blank and sample spikes showed good recovery at 97% and 96%, respectively. Due to the inadvertent spiking of a system blank prior to the analysis, some carryover was seen in the prior blanks. However, a system blank analyzed following the analyses did not show any contamination.

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

00-1701
5/12/2000

Client : Kurath

Cognizant Scientist: LRGreenwood Date : 5/12/00

Concur : Sandra K. Fisk Date : 5/12/00

Procedures PNL-ALO-482/474

Measured Activities (uCi/ml) with 1-sigma error

ALO ID Client ID	C-14 Error %
00-1701	2.56E-4
AP-101 Comp	8%
00-1701Dup	2.55E-4
AP-101 Comp	8%
00-1701 T	2.77E-4
AP-101 Comp	8%
RSD	5%
Blank	< 4.E-5
Sample Spike	96%
Standard	97%

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Project No. 29953

Internal Distribution
File/LB

Date May 18, 2000

To D. E. Kurath

From L. R. Greenwood LRG

Subject Se-79 Analyses for AP-101 Composite ASR 5778

Direct samples of the composite from tank AP-101 (00-1701) were analyzed in triplicate for Se-79 following procedure PNL-ALO-440. Each sample was spiked with 20 mg Se carrier in solution to be used for yield correction. Anion and cation exchange was used to remove most radiochemical interferences. Selenium was distilled as selenium bromide and then reduced to elemental form. The chemical yield was determined gravimetrically by weighing the recovered elemental selenium. The selenium is then dissolved and the Se-79 activity was determined by liquid scintillation counting according to procedure PNL-ALO-474. The liquid scintillation spectra did not show clear evidence for a Se-79 peak and there appears to be some weak beta contamination evident in the higher energy region of the beta spectrum. Hence, the results probably have a high bias. We did not rerun or attempt to further correct the data since the measured Se-79 activities are below the requested MRQ value of 9.0E-5 uCi/ml. The nominal MDL was 2.E-5 uCi/ml. The sample activity averaged 5.8E-5 uCi/ml with an RSD of 18%. The RSD acceptance criteria of < 15% was exceeded, although the measurement uncertainties were as high as 11% on one sample and the sample activity is only a factor of three higher than the MDL. Since Se-79 is not available as a standard, C-14 was used to calibrate the detector since C-14 has nearly the same beta energy as Se-79. Due to the lack of a Se-79 standard, blank and sample spikes are not possible. The sample carrier recoveries were low at 27% to 63% and the blank recovery was 68%. Sample activities were yield-corrected. A process blank did not show any evidence of contamination.

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Radiochemical Processing Group-325 Building
Chemical Measurements Center

00-1701
5/18/2000

Client : Kurath

Cognizant Scientist: Date : 5/18/00

Concur : S.K. Fiskum Date : 5/18/00

Procedures PNL-ALO-440/474

Measured Activities (uCi/ml) with 1-sigma error

ALO ID Client ID	Se-79 Error %
00-1701 AP-101 Comp	5.56E-5 8%
00-1701Dup AP-101 Comp	6.97E-5 5%
00-1701 T AP-101 Comp	4.93E-5 11%
RSD	18%
Blank	< 3.E-6
Blank Spike Recovery	68%

Note: The beta energy spectra did not show clear evidence for a Se-79 peak and there appears to be some beta contamination at higher beta energies. Hence, the results probably have a high bias. All measurements are below the requested MRQ value of 9.0E-5 uCi/ml.

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Pacific Northwest Laboratories

Project No. [illegible]

Internal Distribution

329 File
Mike Urie

Date May 10, 2000

To Dean Kurath

From Tom Farmer Orvill Thomas Farmer III

Subject ICPMS Analysis AP101 Samples
(ALO# 001701)

Pursuant to your request, the 6 samples that you submitted for analysis were analyzed on our radioactively-contained ICPMS for the selected analytes; semiquantitative analysis was necessary on certain isotopes for which a standard was not available (see below). The concentration results for the isotopes of interest are displayed on the attached spreadsheets.

Dilutions of Isotope Products standards for ^{129}I, ^{237}Np and ^{239}Pu, an Amersham ^{99}Tc standard, an NIST uranium standard (4321b), an ^{127}I standard, made from Fisher potassium iodide (LOT# 35260), and CPI single element standards for As, B, Be, Ce, Co, Cs, Eu, Li, Mo, Pr, Rb, Sb, Se, Ta, Te, Th, Tl, V, W and Sn, were used to generate the calibration curves. Independent standards of each analyte were used as the continuing calibration verification (CCV) standards. The 1% high-purity nitric acid solution used to dilute the standards and samples was used as a reagent blank. The results are reported in µg analyte /ml (ppm), or µCi analyte /ml of original sample material.

In general, the results for the quality control samples (i.e., calibration verification standards, duplicates, and matrix spikes) are well within acceptance criteria. One of the CCV results for tellurium and tantalum and the spike recovery for thallium, were outside the acceptance window (<20% for the CCV and <30% for the Spike). Tellurium and tantalum did have another CCV results that was acceptable. CCV results for Thallium were also acceptable. Also the the duplicate and triplicate for arsenic and the duplicate for molybdenum were outside the the acceptance window (<15%).

The ^{99}Tc values reported assume that the Ru present is exclusively fission-product Ru, and therefore does not have an isotope at m/z 99; i.e., everything observed at m/z 99 is due to ^{99}Tc. From the appearance of the Ru isotopic abundance, this appears to be a reasonable assumption; the fingerprint exhibited is obviously not natural.

Values for the following isotopes were obtained using responses from related isotopes: ^{126}Sn (obtained from ^{118}Sn),^{231}Pa (obtained from ^{232}Th), and ^{240}Pu, ^{241}AMU, ^{242}AMU, ^{243}AMU (obtained from ^{239}Pu). Because standards were not used and the concentrations of the isotopes were determined indirectly, these results should be considered semiquantitative.

If you have any questions regarding this analysis, please give me a call at 372-0700 or James Bramson at 376-0624.

5/17/00

Pg 1 of

AP101 Analysis

OTF

May 17, 2000

Sample ID	Client ID	MDL µg/ml	Lithium Analyzed µg/ml	±	1SD	MDL µg/ml	Beryllium Analyzed µg/ml	±	1SD	MDL µg/ml	Boron Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<2.3	< 0.064			<2.3	0.012	±	0.0024	<2.3	6.42	±	0.16
00-001701BS	BLANK SPIKE	<2.3	< 0.72			<2.3	0.12	±	0.016	<2.3	118	±	1.2
00-001701	AP-101-COMP	<2.3	0.323	±	0.004	<2.3	1.32	±	0.03	<2.3	15.5	±	0.1
00-001701D	AP-101-COMP	<2.3	0.329	±	0.002	<2.3	1.28	±	0.01	<2.3	15.3	±	0.1
00-001701T	AP-101-COMP	<2.3	0.367	±	0.003	<2.3	1.35	±	0.01	<2.3	17.2	±	0.1
00-001701+spike	AP-101-COMP	<2.3	1.95	±	0.01	<2.3	2.71	±	0.01	<2.3	17.6	±	0.1
Spike Recovery			123%				105%				105%		
00-001701MS	AP-101-COMP	<2.3	0.360	±	0.002	<2.3	1.39	±	0.01	<2.3	18.6	±	0.2
Blank and CCV results are reported in ng/ml (ppb)													
1%HNO3			< 0.27				< 0.018				< 0.71		
1%HNO3			< 0.28				0.139	±	0.012		1.0	±	0.6
1ppb Multi			0.837	±	0.018		0.977	±	0.018		0.81	±	0.08
10ppb Multi			11	±	2		11	±	2		11	±	2

V' 5/18/00

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AP101 Analysis OTF 18may00

May 17, 2000 (revised May 18, 2000)

Sample ID	Client ID	MDL µg/ml	Vanadium Analyzed µg/ml	±	1SD	MDL µg/ml	Cobalt Analyzed µg/ml	±	1SD	MDL µg/ml	Arsenic Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<2.3	< 0.79			<2.3	0.014	±	0.003	<2.3	0.13	±	0.004
00-001701BS	BLANK SPIKE	<2.3	< 8.8			<2.3	< 0.139			<2.3	373	±	1
Spike Recovery											117%		
00-001701	AP-101-COMP	<2.3	< 0.77			<2.3	0.356	±	0.005	<2.3	1.46	±	0.03
00-001701D	AP-101-COMP	<2.3	< 0.75			<2.3	0.331	±	0.007	<2.3	1.15	±	0.044
00-001701T	AP-101-COMP	<2.3	< 0.72			<2.3	0.369	±	0.001	<2.3	1.18	±	0.017
00-001701+spike	AP-101-COMP	<2.3	2.23	±	0.01	<2.3	1.75	±	0.01	<2.3	2.97	±	0.02
Spike Recovery			110%				108%				109%		
00-001701MS	AP-101-COMP	<2.3	< 0.66			<2.3	0.368	±	0.003	<2.3	29.7	±	0.05
Spike Recovery											120%		

Blank and CCV results are reported in ng/ml (ppb)

Sample ID	Client ID	MDL µg/ml	Vanadium Analyzed µg/ml	±	1SD	MDL µg/ml	Cobalt Analyzed µg/ml	±	1SD	MDL µg/ml	Arsenic Analyzed µg/ml	±	1SD
1%HNO3			< 3.3				< 0.053				< 0.27		
1%HNO3			< 3.4				0.132	±	0.009		< 0.28		
1ppb Multi			0.970	±	0.043		0.979	±	0.009		0.942	±	0.035
10ppb Multi			12	±	2		11	±	2		11	±	2

5/18/00

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AP101 Analysis

OTF 18may00

May 17, 2000 (revised May 18, 2000)

Sample ID	Client ID	MDL µg/ml	Selenium Analyzed µg/ml	± 1SD	MDL µg/ml	Rubidium Analyzed µg/ml	± 1SD	MDL µg/ml	Molybdenum Analyzed µg/ml	± 1SD
00-001701PB	PROCESS BLANK	<2.3	< 2.3		<2.3	0.017	± 0.004	<2.3	< 0.013	
00-001701BS	BLANK SPIKE	<2.3	65.1	± 0.14	<2.3	0.387	± 0.006	<2.3	2.76	± 0.32
Spike Recovery			102%							
00-001701	AP-101-COMP	<2.3	< 2.3		<2.3	3.92	± 0.01	<2.3	15.9	± 0.2
00-001701D	AP-101-COMP	<2.3	< 2.3		<2.3	3.78	± 0.02	<2.3	13.4	± 0.1
00-001701T	AP-101-COMP	<2.3	< 2.3		<2.3	4.22	± 0.03	<2.3	14.1	± 0.1
00-001701+spike	AP-101-COMP	<2.3	< 2.3		<2.3	5.46	± 0.02	<2.3	18.0	± 0.2
Spike Recovery						106%			105%	
00-001701MS	AP-101-COMP	<2.3	5.8	± 0.015	<2.3	4.13	± 0.01	<2.3	18.2	± 0.3
Spike Recovery			118%							
Blank and CCV results are reported in ng/ml (ppb)										
1%HNO3			< 0.45			< 0.050			< 0.057	
1%HNO3			< 0.45			0.136	± 0.004		0.288	± 0.063
1ppb Multi			< 2.3			1.02	± 0.02		0.920	± 0.015
10ppb Multi			12	± 3		11	± 2		11	± 2

5/17/00

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AP101 Analysis OTF

May 17, 2000

Sample ID	Client ID	MDL µCi/ml	Technetium 99 Analyzed µCi/ml	±	1SD	MDL µg/ml	Antimony Analyzed µg/ml	±	1SD	MDL µg/ml	Tellurium Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<1.5E-03	< 2.5E-04			<2.3	0.0289	±	0.0029	<2.3	< 0.17		
00-001701BS	BLANK SPIKE	<1.5E-03	< 3.1E-03			<2.3	0.301	±	0.040	<2.3	< 1.9		
00-001701	AP-101-COMP	<1.5E-03	5.14E-02	±	3.9E-04	<2.3	0.0454	±	0.0030	<2.3	< 0.17		
00-001701D	AP-101-COMP	<1.5E-03	4.76E-02	±	8.4E-04	<2.3	0.0410	±	0.0038	<2.3	< 0.16		
00-001701T	AP-101-COMP	<1.5E-03	4.80E-02	±	1.7E-02	<2.3	0.0396	±	0.0013	<2.3	< 0.16		
00-001701+spike	AP-101-COMP	<1.5E-03	6.91E-02	±	9.5E-04	<2.3	1.23	±	0.004	<2.3	1.04	±	0.029
Spike Recovery			101%				94%				73%		
00-001701MS	AP-101-COMP	<1.5E-03	4.96E-02	±	2.2E-03	<2.3	0.0420	±	0.0056	<2.3	0.196	±	0.064
Blank and CCV results are reported in ng/ml (ppb)													
1%HNO3			< 0.027				< 0.062				< 0.72		
1%HNO3			0.047	±	0.032		0.267	±	0.035		< 0.73		
1ppb Multi							1.06	±	0.05		1.36	±	0.10
10ppb Multi							11	±	2		11.3	±	1.2
5ppb Tc-99			4.92	±	0.09								
5ppb Tc-99			4.90	±	0.17								
20ppb Co			< 0.031										

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Sample ID	Client ID	MDL µCi/ml	*Tin 126 Analyzed µCi/ml	Iodine 127 Analyzed µg/ml	±	1SD	MDL µCi/ml	Iodine 129 Analyzed µCi/ml	±	1SD
00-001701PB	PROCESS BLANK	<6.0E-03	< 1.3E-03	<0.013			<1.8E-05	< 2.5E-06		
00-001701BS	BLANK SPIKE	<6.0E-03	< 1.0E-02	<0.18			<1.8E-05	< 3.4E-05		
00-001701	AP-101-COMP	<6.0E-03	< 8.6E-04	2.42	±	0.04	<1.8E-05	7.72E-05	±	5.2E-06
00-001701D	AP-101-COMP	<6.0E-03	< 8.6E-04	2.49	±	0.10	<1.8E-05	7.73E-05	±	3.9E-06
00-001701T	AP-101-COMP	<6.0E-03	< 8.2E-04	2.73	±	0.08	<1.8E-05	8.71E-05	±	2.7E-06
00-001701+spike Spike Recovery	AP-101-COMP	<6.0E-03	< 8.2E-04	3.48 94%	±	0.17	<1.8E-05	1.20E-04 99%	±	1.0E-05
00-001701MS	AP-101-COMP	<6.0E-03	< 7.4E-04	2.93	±	0.04	<1.8E-05	9.10E-05	±	2.3E-06
Blank and CCV results are reported in ng/ml (ppb)										
1%HNO3			< 0.13	0.423	±	0.013		< 0.061		
1%HNO3			< 0.13	0.160	±	0.012		< 0.120		
0.502ppb I-127				0.551	±	0.024				
5.02ppb I-127				5.04	±	0.28				
0.1ppb I-129								0.0981	±	0.0133
1ppb I-129								1.12	±	0.01

*Calculated from response of different isotope. Should be considered semiquantitative.

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Sample ID	Client ID	MDL µg/ml	Cesium Analyzed µg/ml	±	1SD	MDL µg/ml	Cerium Analyzed µg/ml	±	1SD	MDL µg/ml	Praseodymium Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<1.5	0.0136	±	0.0006	<2.3	< 0.079			<2.3	< 0.018		
00-001701BS	BLANK SPIKE	<1.5	0.50	±	0.04	<2.3	< 0.88			<2.3	< 0.203		
00-001701	AP-101-COMP	<1.5	4.96	±	0.02	<2.3	< 0.077			<2.3	< 0.018		
00-001701D	AP-101-COMP	<1.5	4.90	±	0.05	<2.3	< 0.075			<2.3	< 0.017		
00-001701T	AP-101-COMP	<1.5	5.40	±	0.04	<2.3	< 0.072			<2.3	< 0.017		
00-001701+spike	AP-101-COMP	<1.5	6.70	±	0.06	<2.3	1.57	±	0.01	<2.3	1.51	±	0.02
Spike Recovery			108%				117%				118%		
00-001701MS	AP-101-COMP	<1.5	5.32	±	0.06	<2.3	< 0.066			<2.3	< 0.015		
Blank and CCV results are reported in ng/ml (ppb)													
1%HNO3			< 0.018				< 0.33				< 0.077		
1%HNO3			0.138	±	0.002		< 0.34				0.139	±	0.011
1ppb Multi			1.10	±	0.03		0.928	±	0.031		0.963	±	0.032
10ppb Multi			11	±	2		11	±	2		11	±	2

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Sample ID	Client ID	MDL µg/ml	Europium Analyzed µg/ml	±	1SD	MDL µg/ml	Tanatalum Analyzed µg/ml	±	1SD	MDL µg/ml	Tungsten Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<60	< 0.017			<2.3	< 0.087			<2.3	< 0.089		
00-001701BS	BLANK SPIKE	<60	0.424	±	0.014	<2.3	< 1.12			<2.3	< 1.04		
00-001701	AP-101-COMP	<60	< 0.016			<2.3	< 0.087			<2.3	28.5	±	1.2
00-001701D	AP-101-COMP	<60	< 0.016			<2.3	< 0.089			<2.3	28.4	±	0.7
00-001701T	AP-101-COMP	<60	< 0.015			<2.3	< 0.089			<2.3	28.9	±	1.3
00-001701+spike	AP-101-COMP	<60	1.47	±	0.01	<2.3	0.190	±	0.002	<2.3	47.9	±	1.7
Spike Recovery			115%				89%				124%		
00-001701MS	AP-101-COMP	<60	0.015	±	0.003	<2.3	< 0.084			<2.3	26.0	±	0.2
Blank and CCV results are reported in ng/ml (ppb)													
1%HNO3			< 0.071				< 0.37				< 0.092		
1%HNO3			0.140	±	0.007		< 0.34				0.87	±	0.22
1ppb Multi			0.961	±	0.019								
10ppb Multi			11	±	2								
1ppb/0.5ppb Multi							1.1	±	0.2				
0.5ppb Multi							0.717	±	0.030				

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Sample ID	Client ID	MDL µg/ml	Thallium Analyzed µg/ml	±	1SD	MDL µCi/ml	*Protactinium 231 Analyzed µCi/ml	MDL µg/ml	Thorium Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<2.3	< 0.0055			<7.9E-05	< 1.0E-04	<2.3	< 0.0110		
00-001701BS	BLANK SPIKE	<2.3	310	±	8	<7.9E-05	< 1.3E-03	<2.3	< 0.14		
00-001701	AP-101-COMP	<2.3	0.0192	±	0.0010	<7.9E-05	< 1.0E-04	<2.3	< 0.011		
00-001701D	AP-101-COMP	<2.3	0.0168	±	0.0006	<7.9E-05	< 1.1E-04	<2.3	< 0.011		
00-001701T	AP-101-COMP	<2.3	0.0165	±	0.0013	<7.9E-05	< 1.1E-04	<2.3	< 0.011		
00-001701+spike	AP-101-COMP	<2.3	0.203	±	0.005	<7.9E-05	< 1.1E-04	<2.3	0.168	±	0.001
Spike Recovery			139%						122%		
00-001701MS	AP-101-COMP	<2.3	27.2	±	0.2	<7.9E-05	< 1.0E-04	<2.3	< 0.0107		
Blank and CCV results are reported in ng/ml (ppb)											
1%HNO3			< 0.023				< 0.0093		< 0.047		
1%HNO3			0.36	±	0.06		< 0.0087		< 0.043		
1ppb Multi											
10ppb Multi											
1ppb/0.5ppb Multi			0.493	±	0.008				0.558	±	0.032
0.5ppb Multi			0.500	±	0.036				0.497	±	0.013

*Calculated from response of different isotope. Should be considered semiquantitative.

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AP101 Analysis

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Sample ID	Client ID	Uranium 233 MDL µCi/ml	Uranium 233 Analyzed µCi/ml	± 1SD	Uranium 234 MDL µCi/ml	Uranium 234 Analyzed µCi/ml	± 1SD	Uranium 235 MDL µCi/ml	Uranium 235 Analyzed µCi/ml	± 1SD
00-001701PB	PROCESS BLANK	<4.2E-04	< 8.8E-06		<1.2E-4	< 5.7E-06		<4.5E-08	< 6.8E-09	
00-001701BS	BLANK SPIKE	<4.2E-04	< 8.8E-06		<1.2E-4	< 6.3E-05		<4.5E-08	< 4.6E-08	
00-001701	AP-101-COMP	<4.2E-04	5.5E-05	± 3.8E-06	<1.2E-4	2.7E-05	± 5.7E-06	<4.5E-08	1.06E-06	± 2.8E-09
00-001701D	AP-101-COMP	<4.2E-04	5.6E-05	± 3.8E-06	<1.2E-4	2.4E-05	± 4.1E-06	<4.5E-08	9.94E-07	± 2.8E-09
00-001701T	AP-101-COMP	<4.2E-04	4.8E-05	± 5.0E-06	<1.2E-4	2.1E-05	± 2.4E-06	<4.5E-08	9.82E-07	± 2.8E-09
00-001701+spike Spike Recovery	AP-101-COMP									
00-001701MS	AP-101-COMP	<4.2E-04	5.6E-05	± 2.5E-05	<1.2E-4	2.2E-05	± 8.2E-06	<4.5E-08	1.12E-06	± 4.5E-08
Blank and CCV results are reported in ng/ml (ppb)										
1%HNO3			< 0.0007			< 0.0007			< 0.0007	
1%HNO3										

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Sample ID	Client ID	MDL µCi/ml	Uranium 236 Analyzed µCi/ml	±	1SD	MDL µCi/ml	Uranium 238 Analyzed µCi/ml	±	1SD	Total Uranium Analyzed µg/ml	±	1SD
00-001701PB	PROCESS BLANK	<1.4E-06	< 5.9E-08			<7.2E-08	< 4.7E-08			< 0.14		
00-001701BS	BLANK SPIKE	<1.4E-06	< 8.1E-08			<7.2E-08	< 5.3E-07			< 1.6		
00-001701	AP-101-COMP	<1.4E-06	2.23E-06	±	1.1E-07	<7.2E-08	1.96E-05	±	8.8E-08	58.9	±	2.1
00-001701D	AP-101-COMP	<1.4E-06	2.07E-06	±	1.3E-07	<7.2E-08	1.76E-05	±	8.8E-08	52.9	±	1.8
00-001701T	AP-101-COMP	<1.4E-06	2.08E-06	±	4.2E-08	<7.2E-08	1.80E-05	±	8.8E-08	54.1	±	1.7
00-001701+spike	AP-101-COMP									91.3	±	3.6
Spike Recovery										115%		
00-001701MS	AP-101-COMP	<1.4E-06	2.39E-06	±	1.7E-07	<7.2E-08	2.08E-05	±	4.4E-08	62.3	±	0.8
Blank and CCV results are reported in ng/ml (ppb)												
1%HNO3			< 0.0007				< 0.0007			< 0.15		
1%HNO3										0.79	±	0.33
20ppb U										19.5	±	0.6
10/20ppb W/U										19.9	±	0.6

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AP101 Analysis OTF

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		Neptunium 237				Plutonium 239			
Sample ID	Client ID	MDL µCi/ml	Analyzed µCi/ml	±	1SD	MDL µCi/ml	Analyzed µCi/ml	±	1SD
00-001701PB	PROCESS BLANK	<3.9E-05	< 5.3E-06			<3.0E-02	< 1.2E-03		
00-001701BS	BLANK SPIKE	<3.9E-05	< 6.9E-05			<3.0E-02	< 1.6E-02		
00-001701	AP-101-COMP	<3.9E-05	< 5.4E-06			<3.0E-02	< 1.2E-03		
00-001701D	AP-101-COMP	<3.9E-05	< 5.4E-06			<3.0E-02	< 1.2E-03		
00-001701T	AP-101-COMP	<3.9E-05	< 5.5E-06			<3.0E-02	< 1.2E-03		
00-001701+spike	AP-101-COMP	<3.9E-05	1.12E-04	±	3.0E-06	<3.0E-02	9.98E-03	±	2.2E-04
Spike Recovery			119%				110%		
00-001701MS	AP-101-COMP	<3.9E-05	< 5.2E-06			<3.0E-02	< 1.2E-03		
Blank and CCV results are reported in ng/ml (ppb)									
1%HNO3			< 0.032				< 0.082		
1%HNO3			< 0.030				< 0.077		
1ppb/0.5ppb Multi			0.508	±	0.031		0.445	±	0.022
0.5ppb Multi			0.498	±	0.027		0.506	±	0.023

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AP101 Analysis OTF

May 17, 2000

Sample ID	Client ID	MDL µCi/ml	*Plutonium 240 Analyzed µCi/ml	*AMU 241 Analyzed µg/ml	*AMU 242 Analyzed µg/ml	*AMU 243 Analyzed µg/ml
00-001701PB	PROCESS BLANK	<3.0E-02	< 2.4E-03	< 0.011	< 0.010	< 0.0069
00-001701BS	BLANK SPIKE	<3.0E-02	< 3.1E-02	< 0.14	< 0.13	< 0.090
00-001701	AP-101-COMP	<3.0E-02	< 2.4E-03	< 0.011	< 0.010	< 0.0071
00-001701D	AP-101-COMP	<3.0E-02	< 2.4E-03	< 0.011	< 0.010	< 0.0072
00-001701T	AP-101-COMP	<3.0E-02	< 2.4E-03	< 0.011	< 0.010	< 0.0072
00-001701+spike Spike Recovery	AP-101-COMP	<3.0E-02	< 2.4E-03	< 0.011	< 0.010	< 0.0071
00-001701MS	AP-101-COMP	<3.0E-02	< 2.3E-03	< 0.010	< 0.0099	< 0.0068
Blank and CCV results are reported in ng/ml (ppb)						
1%HNO3			< 0.044	< 0.045	< 0.043	< 0.029
1%HNO3			< 0.041	< 0.042	< 0.040	< 0.028

*Calculated from response of different isotope. Should be considered semiquantitative.

5/10/00

AP101 Analysis

May 10, 2000

Sample ID	Client ID		U-233 Abundance	U-234 Abundance	U-235 Abundance	U-236 Abundance	U-238 Abundance
00-001701PB	PROCESS BLANK	Average	-4.24E-03	9.16E-03	1.20E-04	2.35E-03	9.88E-01
		stdev	9.56E-03	6.69E-03	6.77E-03	1.07E-02	2.18E-01
		%SD	-225.2%	73.1%	5657.7%	455.9%	22.0%
00-001701BS	BLANK SPIKE	Average	-6.68E-05	6.17E-03	1.31E-02	7.65E-04	9.80E-01
		stdev	1.13E-03	2.69E-03	9.78E-03	2.93E-03	2.66E-02
		%SD	-1691.0%	43.5%	74.7%	383.4%	2.7%
00-001701	AP-101-COMP	Average	9.75E-05	7.30E-05	8.32E-03	5.85E-04	9.91E-01
		stdev	6.79E-06	1.53E-05	9.00E-05	2.85E-05	5.45E-03
		%SD	7.0%	21.0%	1.1%	4.9%	0.5%
00-001701D	AP-101-COMP	Average	1.09E-04	7.44E-05	8.69E-03	6.04E-04	9.91E-01
		stdev	6.12E-06	9.09E-06	2.27E-04	3.48E-05	5.27E-03
		%SD	5.6%	12.2%	2.6%	5.8%	0.5%
00-001701T	AP-101-COMP	Average	9.15E-05	6.21E-05	8.41E-03	5.94E-04	9.91E-01
		stdev	8.74E-06	6.77E-06	2.62E-04	1.15E-05	4.22E-03
		%SD	9.5%	10.9%	3.1%	1.9%	0.4%
00-001701MS	AP-101-COMP	Average	9.32E-05	5.67E-05	8.31E-03	5.94E-04	9.91E-01
		stdev	3.21E-05	1.12E-05	3.12E-04	4.06E-05	2.48E-03
		%SD	34.5%	19.7%	3.8%	6.8%	0.3%
4321B		Average	6.25E-06	5.22E-05	7.08E-03	7.83E-06	9.93E-01
		stdev	1.12E-05	6.80E-06	2.80E-05	1.05E-05	1.32E-02
		%SD	178.8%	13.0%	0.4%	133.8%	1.3%
		True Value		5.29E-03	7.20E-01		9.93E+01
UO3O		Average	5.40E-06	1.91E-04	3.00E-02	1.97E-04	9.70E-01
		stdev	1.44E-05	1.53E-05	4.54E-04	6.85E-06	7.67E-03
		%SD	266%	8.0%	1.5%	3.5%	0.8%
		True Value		1.90E-04	3.05E-03	2.00E-04	9.69E-01

DATA REVIEW

Reviewed: O.J. Farmer III

Date: 10May00 Pages. 13of13

AP101 MDL's

Sample Number	Client Number	Li µg/ml	Be µg/ml	B µg/ml	V µg/ml	Co µg/ml	As µg/ml	Se µg/ml	Rb µg/ml	Mo µg/ml	Tc-99 µCi/ml	Sb µg/ml	Te µg/ml	Se-126 µCi/ml
00-001701	AP-101-COMP	0.063	0.004	0.16	0.007	0.012	0.063	2.3	0.011	0.013	2.6E-04	0.014	0.17	8.6E-04
00-001701D	AP-101-COMP	0.061	0.004	0.16	0.007	0.012	0.062	2.3	0.011	0.013	2.6E-04	0.014	0.16	8.6E-04
00-001701T	AP-101-COMP	0.059	0.004	0.15	0.007	0.011	0.059	2.3	0.011	0.012	2.6E-04	0.013	0.16	8.2E-04

Sample Number	Client Number	I-127 µg/ml	I-129 µCi/ml	Cs µg/ml	Ce µg/ml	Pr µg/ml	Eu µg/ml	Ta µg/ml	W µg/ml	Tl µg/ml	Pa-231 µCi/ml	Th µg/ml	U-233 µCi/ml	U-234 µCi/ml
00-001701	AP-101-COMP	0.037	6.7E-06	0.004	0.077	0.018	0.016	0.087	0.23	0.011	1.0E-04	0.011	8.8E-06	5.7E-06
00-001701D	AP-101-COMP	0.037	6.7E-06	0.004	0.075	0.017	0.016	0.089	0.22	0.011	1.1E-04	0.011	8.8E-06	5.7E-06
00-001701T	AP-101-COMP	0.033	6.0E-06	0.004	0.072	0.017	0.015	0.089	0.24	0.011	1.1E-04	0.011	8.8E-06	5.7E-06

Sample Number	Client Number	U-235 µCi/ml	U-236 µCi/ml	U µg/ml	Np-237 µCi/ml	Pu-239 µCi/ml	Pu-240 µCi/ml	AMU-241 µg/ml	AMU-242 µg/ml	AMU-243 µg/ml
00-001701	AP-101-COMP	6.8E-09	5.8E-08	0.090	5.4E-06	1.2E-03	2.4E-03	0.011	0.01	0.0071
00-001701D	AP-101-COMP	6.8E-09	5.8E-08	0.086	5.4E-06	1.2E-03	2.4E-03	0.011	0.01	0.0072
00-001701T	AP-101-COMP	6.8E-09	5.8E-08	0.094	5.5E-06	1.2E-03	2.4E-03	0.011	0.01	0.0072

Battelle PNNL/RPG/Inorganic Analysis ---Hg Report

WO/Project: W54906/29953
Client: D. Kurath

ACL Numbers: 00-01701
ASR Number 5778

Procedure: PNNL-ALO-131, "Mercury Digestion"
PNNL-ALO-201, "Mercury Analysis"

Analyst: J. J. Wagner

Digestion Date: May 10, 2000 **Analysis Date:** May 11, 2000

M&TE: Hg system (WD14126); Mettler AT400 Balance (360-06-01-029) See Chemical Measurement Center 98620 RIDS for Hg File for Calibration, Standards Preparations, and Maintenance Records.

Analyst: Jerry Wagner 5-15-00
Approval: ______________ Date 5-15-00

Final Results:

The samples were analyzed by cold vapor atomic absorption spectrophotometry for inorganic mercury as specified in ASR 5778. Four aliquots of 0.2ml including one for matrix spike, was processed and diluted to a final volume of 25ml per procedure ALO-131. No additional dilution was performed. Concentration of all sample aliquots measured were near instrument detection limit and several times lower than MRQ (1.5 µg/ml) listed in Table 2, "Supernate Analyses Required by Contract Specification 7 and Opportunistic Analytes". The mercury concentration results are presented in the table below.

Battelle PNNL/RPG/Inorganic Analysis ---Hg Report

Lab ID	Solid Sample ID	Aqueous ml	Aqueous Dig Fctr	Aqueous Anal Fctr	Hg ug/ml	RPD (%)
00-01701-PB	Reagent Process Blank	0.20	125	1	0.026	
00-01701	AP-101 COMP	0.20	125	1	<0.025	
00-01701DUP	AP-101 COMP	0.20	125	1	<0.025	
00-01701TRI	AP-101 COMP	0.20	125	1	0.032	N/A

RPD = Relative Percent Difference (between sample and duplicate/replicate)

"Sample volume" used for the process blank is an average volume of the samples.

N/A = RPD is not calculated when results are less than 5 x IDL

Notes:

1) "Final Results" have been corrected for all dilution performed on the sample during processing or analysis.
2) The low calibration standard is defined as the estimated detection limit (IDL) for the reported results and assumes non-complex aqueous matrices. Actual detection limits or quantitation limits for specific sample matrices may be determined, if requested.
3) Routine precision and bias is typically ± 15% or better for non-complex aqueous samples that are free of interference.

Q.C. Comments:

Following are results of quality control checks performed during Hg analyses. In general, quality control checks met the requirements of the governing QA Plan.

Working Blank Spike/Process Blank Spike: Process Blank Spike recovery is 100%, well within the acceptance criteria of 80% to 120%.

Matrix Spiked Sample: A matrix spike was prepared for the samples submitted under this ASR. Recovery of the matrix spike is 97%, well within the acceptance criteria of 75% to 125%.

Duplicate/replicates: RPD is not calculated since all replicate results are less than 5 x IDL.

Laboratory Control Sample (liquid): Sample recovery of mercury in SRM-1641d (certified by NIST to contain 1.60 ± 0.018 µg/ml) was recovered within acceptance criteria of 75% to 125%.

System Blank/Processing Blanks: A system blank was process during the analysis of the sample. The concentration measured was within about two times detection limit or less. Samples were about the same concentration as the process blank.

Quality Control Calibration Verification Check Standards: Six mid-range verification standards were analyzed throughout the analysis run. All were within the acceptance criteria of 80% to 120% recovery for the verification standard.

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Date May 18, 2000

To D. E. Kurath

From L. R. Greenwood

Subject <u>NH-3 Analyses for AP-101 Composite ASR 5778</u>

Ammonia was measured in triplicate sample aliquots of the composite from tank AP-101 (00-1701) using an ion selective electrode according to procedure PNL-ALO-226. The ammonia probe was calibrated using five standards spanning ammonia concentrations from 1.0E-2 to 1.0E-6 moles/liter. The method of standard additions was used to determine the ammonia concentrations by first taking a direct reading and then adding a known standard to each sample. The triplicate concentrations are in good agreement with an RSD of 6%. The method detection limit was estimated at 0.2 ug/ml, well below the requested MRQ value of 140 ug/ml.

Battelle Pacific Northwest Laboratory
Radiochemical Processing Group-325 Building
Chemical Measurements Center

00-1701
5/18/2000

Client : Kurath

Cognizant Scientist: L R Greenwood Date : 5/18/00

Concur : C. Soderquist Date : 5-19-00

Procedure: PNL-ALO-226

Measured Concentrations (ug/ml) with 1-sigma error

ALO ID Client ID	NH_3 Error %
00-1701 AP-101 Comp	1.83 9%
00-1701Dup AP-101 Comp	1.70 10%
00-1701 T AP-101 Comp	1.61 10%
RSD	6%
MDL	0.2

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Date May 19, 2000

To D. Kurath

From M. Urie

Subject Cyanide Results for AP-101 Sample

RPL Number	Sample ID	CN (µg / ml)	RPD (%)	RSD (%)	Spike Rec (%)
00-1701	AP-101 Sample	5.81	---	---	---
00-1701 D	AP-101 Duplicate	5.56	4.4	---	---
00-1701 T	AP-101 Triplicate	5.73	---	2.2	---
00-1701 MS	AP-101 Matrix Spike	---	---	---	95

The CN results for AP-101 composite samples analyzed on May 11, 2000 per ASR 5778 are reported in the Table above. The composite samples were transferred from the Shielded Analytical Laboratory and prepared for distillation and analyzed at the CN Workstation. The AP-101 samples were distilled with the addition of sulfamic acid to ensure there would be no interference from high nitrates present in the sample. The samples were analyzed using a Lachat QuickChem AE Autoanalyzer (WC36517). The reporting limits are estimated to be approximately 0.25 µg CN/ml based on the sample quantity distilled. No Quality Control or other measurement problems were encountered.

An independent mid-range calibration check solution run at the beginning, middle, and end of the analysis batch gave an average recovery of 100%. These calibration check standards ranged from 99% recovery to 100% recovery which is within the 85% to 115% acceptance criteria of the governing QA plan.

The AP-101 composite was analyzed in triplicate. The Relative Percent Difference (RPD) between the Sample and Duplicate was 4.4% and the Relative Standard Deviation (RSD) for the triplicates was 2.2%. Based on the RPD and RSD, the measurement precision meets the Quality Control criteria established by Table 4 of the ASR.

For the liquid AP-101 composite, the Laboratory Control Sample (LCS) was a distilled Blank Spike sample. The liquid LCS recovery was 101%, well within the Quality Control parameters established by Table 4 of the ASR. Beside the liquid LCS, as solid LCS was also processed. The solid LCS was analyzed at 112 µg/g and 165 µg/g, well within the certified advisory range of 77 µg/g to 301 µg/g. However, the solid LCS does not meet the ASR Quality Control criteria.

The spike recovery for the spiked AP-101 composite was 95%, well within the acceptance criteria of 75% to 125%.

All sample preparation sheets, standard preparation information, and analytical data are included with this report.

Memo File: CN ASR 5778 Kurath.doc   Spreadsheet File: ASR 5778 Kurath.xls

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