PNWD-3047
BNFL-RPT-025 Rev. 0

Development of an Alternative Treatment Scheme for Sr/TRU Removal: Permanganate Treatment of AN-107 Waste

R. T. Hallen
S. A. Bryan
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July 2000

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Prepared for BNFL, Inc.
under Contract W375-LC-98-4168

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Battelle, Pacific Northwest Division
Richland, Washington 99352

Summary

A number of Hanford tanks received waste containing organic complexants, which increase the solubility of Sr-90 and transuranic (TRU) elements. Wastes from these tanks require additional pretreatment to remove Sr-90 and TRU for immobilization as low activity waste (Waste Envelope C). The baseline pretreatment process for Sr/TRU removal was isotopic exchange and precipitation with added strontium and iron. However, studies at both Battelle and Savannah River Technology Center (SRTC) have shown that the Sr/Fe precipitates were very difficult to filter. This was a result of the formation of poor filtering iron solids. An alternate treatment technology was needed for Sr/TRU removal. Battelle had demonstrated that permanganate treatment was effective for decontaminating waste samples from Hanford Tank SY-101 and proposed that permanganate be examined as an alternative Sr/TRU removal scheme for complexant-containing tank wastes such as AN-107.

Battelle conducted preliminary small-scale experiments to determine the effectiveness of permanganate treatment with AN-107 waste samples that had been archived at Battelle from earlier studies. Three series of experiments were performed to evaluate conditions that provided adequate Sr/TRU decontamination using permanganate treatment. The final series included experiments with actual AN-107 diluted feed that had been obtained specifically for BNFL process testing. Conditions that provided adequate Sr/TRU decontamination were identified. A free hydroxide concentration of 0.5M provided adequate decontamination with added Sr of 0.05M and permanganate of 0.03M for archived AN-107. The best results were obtained when reagents were added in the sequence Sr followed by permanganate with the waste at ambient temperature. The reaction conditions for Sr/TRU removal will be further evaluated with a 1-L batch of archived AN-107, which will provide a large enough volume of waste to conduct crossflow filtration studies (Hallen et al. 2000a).

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1.0 Introduction

This report summarizes work performed for BNFL Inc. by Battelle in support of the Privatization Contract for treatment of Hanford underground storage tank wastes. The privatization work is part of the River Protection Project-Waste Treatment Plant (RPP-WTP). Under Part B-1 of the privatization effort, Battelle is conducting technology development and demonstration of various process flowsheet steps for BNFL with actual waste samples. Three candidate low-activity waste types have been identified for initial treatment: Envelope A, Envelope B, and Envelope C. Each of these represents compositional envelopes as defined in the privatization contract (Specification 7 of the TWRS privatization contract, http://www.hanford.gov/doe/contracts/de-ac06-96rl13308/index.html). Before the liquid (supernatant) fraction of Envelope C wastes (e.g., Tank 241-AN-107 waste) can be disposed of as low-activity waste, pretreatment is required to remove transuranic (TRU) elements and radioactive strontium. Because of the high concentration of organic complexants in this waste, conventional separation processes (e.g., ion exchange) are not effective.

During Part A-1 of the privatization effort, the Savannah River Technical Center (SRTC) developed a Sr/TRU removal process involving isotopic dilution and precipitation with added strontium and iron (SRTC 1997a-d). While this treatment process provided the necessary supernatant decontamination, the resulting precipitate could not be filtered. Tests with waste simulants identified the iron precipitate as causing the difficulty with filtration (SRTC 2000). The search began for an alternative treatment process. Battelle proposed permanganate be examined as an alternative because it had been demonstrated to work with waste from Hanford Tank SY-101, which also contains high levels of organic complexants (Orth et al. 1995).

Orth et al. (1995) examined the removal of radioactive Sr and TRU from complexant-containing (citrate, glycolate, EDTA, HEDTA, and NTA) tank waste by the addition of metal cations and chemical oxidant. Permanganate was examined as a chemical oxidant to promote destruction/defunctionalization of the complexing agents and possible flocculation by the manganese solids. Permanganate was found to oxidize chromium first; then organic carbon; and last, nitrite. A sample of 3:1 diluted SY-101 waste was treated with 0.15M permanganate and decontamination factors (DFs)[(a)] of >143 were obtained for Sr and 28.5 for Pu. Orth et al. recommended permanganate doses of 0.1M for treating complexant-containing wastes. For wastes such as in Tank SY-101, the chromium in the sludge consumes as much as half the permanganate. Waste in Tank AN-107 does not have the high chromium values in the sludge, so permanganate is expected to be effective at lower concentrations.

Permanganate is also used as a precursor to MnO_2 and/or $Mn(OH)_2$ coprecipitants via the "Method of Appearing Reagents" (Krot et al. 1996). This method requires that a chemical reductant such as formate or hydrazine be added to the waste to be treated. However, for Hanford wastes, it is not necessary because reductants are already present in the waste as organic complexing agents or their degradation products (e.g., formate). The resulting manganese solids are effective coprecipitants for Pu and other TRU elements, but generally not as effective as iron precipitates. Decontamination factors of >100 have been reported for various simulated waste streams.

The objective of the work reported here was to determine the potential use of permanganate for Sr/TRU removal and the optimal conditions for Sr/TRU decontamination. An archived sample of AN-107 waste was used because only a limited quantity of the actual AN-107 diluted feed was available. Tank waste simulants were not used for decontamination studies because the exact composition of organic complexants in the waste is not known, nor is the speciation of soluble Sr or TRU components. Proof-of-principle experiments were performed using approximately 20-mL samples of waste with

(a) The decontamination factor is defined as the amount of the contaminant in the waste before treatment divided by the amount present after treatment.

various amounts of permanganate, strontium, and/or other metal ions. Supernatant decontamination data were obtained from the test data. The Sr and TRU DFs were compared to determine the efficiency of the Sr/TRU removal process. Preferred conditions were identified for larger-scale testing using 1-L samples.

The proof-of-principle experiments, three series of small-scale Sr/TRU decontamination tests, are described in this report. Test conditions and experimental procedures are described in Section 2.0. Experimental results from the three series of tests are described in Section 3.0. The major conclusion and recommendations that evolved from this work are given in Section 4.0. The appendices contain the test instructions, data sheets, logbook entries, analytical data, calculation, and staff role/responsibilities for this work.

2.0 Test Conditions and Experimental Procedures

2.1 Description of Archived AN-107 and AN-107 Diluted Feed Samples

Prior to its use for the BNFL project, the archived AN-107 material was diluted, decanted from the settled solids, and treated by ion exchange to remove cesium (Hendrickson 1997). It was collected as 45 grab samples in 125-mL bottles taken during January 1997. Approximately 5.4-L of tank waste were then transferred to Hanford's 222-S Analytical Laboratory, and 0.53M sodium hydroxide was added to dilute the waste to 5M sodium and a free hydroxide concentration of 0.24M. The supernatant was not filtered prior to cesium ion exchange. Instead, the solids were allowed to settle, and the supernatant was decanted and sent through the crystalline silicotitanate loaded columns. Analysis of the waste after cesium removal indicated the free hydroxide was 0.126M. Following cesium removal the sample was transferred to Battelle in five 1-L plastic bottles where it has been stored in the Shielded Analytical Laboratory (SAL) hot cells in the Radiochemical Processing Laboratory (RPL).

In addition to the tests done with the archived AN-107 sample, three experiments were conducted with actual AN-107 diluted feed prepared specifically for the BNFL testing. The diluted feed was prepared and characterized at Battelle for integrated process testing (Urie et al. 1999). Waste samples retrieved from AN-107 were diluted and caustic adjusted to target concentrations of 7.7M sodium, and 1.0M free hydroxide for demonstration of the Sr/TRU removal process (Hallen et al. 2000b).

2.2 Development of Test Conditions

The Privatization Contract requires that the immobilized low-activity waste (ILAW) product contain less than 100 nCi/g TRU and less than 20 Ci/m^3 Sr-90. Supernatant from Envelope C waste contains levels of Sr and TRU too high to meet ILAW requirements. For AN-107 waste, DFs of approximately 10 for Sr-90 (90% removal) and 5 for TRU (80% removal) are needed to meet the ILAW disposal requirements. Since over 90% of the TRU in AN-107 is Am-241, a target DF of 5 was established for Am-241.

Experimental conditions were defined using the results from the earlier studies by Orth et al. and limited studies conducted with AN-107 waste simulant at Battelle and SRTC (1999). Based on these studies a permanganate treatment level of 0.05M was expected to yield good decontamination results. Also results by Orth and others suggested that increased free hydroxide concentration, and/or addition of other metal salt precipitants (calcium, strontium, and europium) could improve decontamination of Sr-90 and TRU. This information was used to construct the first test matrix (see Section 3.1). The target concentrations listed in the test matrix are based on the final composition after addition of all reagents. The quantity of each reagent to add to the waste to achieve these values, as well as the actual quantities that were used, can be found in the test instructions included in Appendix A. Two controls were added for calculating the DFs, one unfiltered containing entrained solids and the other filtered to remove the entrained solids.

The results of the first series of experiments were used to define the conditions for the second series of experiments (see Section 3.2). The most significant observation was the lack of free hydroxide in the starting waste; consequently, for the second series of experiments, sodium hydroxide was added to the waste before the experiments were started. Also, permanganate alone did not give as high as expected DF for Sr-90, so non-radioactive strontium addition at different concentrations was examined for isotopic dilution. The completed test instruction and experimental details of the second series of experiments are included in Appendix B.

Adequate Sr-90 and TRU decontamination was obtained for many conditions in the second series of experiments. The third series of experiments was conducted to verify these results, further optimize reagent concentration, and examine the preferred reaction conditions with samples of actual AN-107 diluted feed (see Section 3.3). The completed test instruction and experimental details of the third series of experiments are included in Appendix C.

The heater temperature, hold time, and addition sequence was varied for each series of experiments. The first series of experiments was heated to 40°C and held there for 1 hour after addition of all reagents. This was considered adequate for permanganate treatment, based on results of Orth et al. (1995) that permanganate oxidation was complete in a matter of minutes at 30°C. However, this was a lower temperature and shorter time than the conditions identified for Sr/Fe addition from Part A-1 experiments. As a result, the second series of experiments was heated to 50°C and held for 4 hours after reagent addition. The additional time was expected to allow more isotopic exchange of Sr-90 with added nonradioactive Sr. For the third series of experiments, the first reagent was added and the waste heated to 50°C and held for 2 hours. The second reagent was then added, and the waste heated to 50°C and held for an additional 2 hours, again to allow for more isotopic Sr exchange.

2.3 Experimental

Battelle had archived approximately 5 L of AN-107 waste that had previously been treated by ion exchange for cesium removal (Henderson 1997). The waste was reported to be 5M sodium and 0.1M hydroxide. Experiments were designed on the assumption that the composition had not changed. However, after the first series of experiments, no free hydroxide was found by titration of waste samples. Continued organic aging of this waste during storage most likely consumed the free hydroxide. Later tests all included the addition of hydroxide to ensure the presence of free hydroxide during treatment/precipitation. The composition of the other components in the archived AN-107 is reported in the literature; the key components of the initial waste were determined for each series of experiments as a control, and were used to calculate DFs for the treated waste.

The small-scale experiments were conducted in the SAL hot cells with samples of approximately 20 mL of tank waste. The reagents were added to the wastes with an adjustable pipette, in the order listed in the test matrix. The reagents were rapidly added to the waste at room temperature and mixed by swirling of the vials with the remote manipulator hand. For the first two series of experiments, the addition of all reagents was completed before the samples were heated in a heat block that had been preheated to the set temperature. The samples were held for the prescribed time at this temperature, removed, cooled, centrifuged, and filtered for analyses. Stock solutions of the reagents were prepared for addition to the waste. The first round of experiments used 0.4M potassium permanganate as the stock solution, and later experiments used 1M sodium permanganate as the stock solution. The metal addition solutions were made up as the nitrate salt in 1M concentration. Sodium hydroxide was added as solid pellets or 10-19M solution. The actual quantities of waste and reagents used are given in the test instructions included as Appendix A, B, and C of this report.

2.4 Chemical Analyses

All of the chemical analyses were conducted at Battelle. BNFL designated the analytes of interest and minimum reportable quantity in a test specification or guidance letter (BNFL 1999a,b). Because the archived AN-107 sample had most of the radioactive cesium removed, Am-241 concentration could be determined directly by gamma energy analysis (GEA), along with the Eu isotopes 154 and 155. Relatively high levels of Cs-137 raise the gamma background level in the detector through Compton scattering, thereby making it difficult to detect other, lower-level gamma emitters, especially those having gamma energies below that of Cs-137. For the AN-107 diluted feed samples, separation and alpha energy analysis (AEA) were required for Am-241 because of the high Cs-137 concentration. The Sr-90

concentration was determined by chemical separation followed by beta counting. Sodium concentration was determined by inductively couple plasma-atomic emission spectrometry (ICP-AES), as well as the other metals listed in the test instructions. Selected samples were also analyzed by titration to determine the free hydroxide concentration. All of the analytical results are included in Appendix D.

3.0 Results and Discussion

Each series of experiments involved multiple samples and each was analyzed to determine the change in waste composition upon treatment. Samples of the initial waste were analyzed with and without filtration (0.45 um) to examine the contribution of entrained solids to the overall treatment. The radionuclide composition of the treated samples was compared with the initial composition to determine the extent of decontamination. The initial waste composition varied for each series of experiments. The Decontamination Factor (DF) for a specific radionuclide is defined as the concentration of the component in the initial waste divided by the concentration after treatment, corrected by the amount of dilution that occurred:

$$DF = [A]_i/([A]*MD)$$

where $[A]_i$ is the concentration of component A per mass in the initial sample, [A] is the concentration of component A per mass in the treated sample, and MD is the mass dilution, final mass of treated solution divided by the initial mass of solution. The final mass is determined by summing up the mass of initial waste and all dilution, adjustments, and/or reagent additions.

3.1 The First Series of Proof-of-Principle Experiments

The first series of experiments focused on treatment with permanganate alone and in combination with added metal cations (Ca, Sr and Eu) using the waste as received (see Table 3.1). The archived AN-107 was expected to contain 5M Na and 0.12M free hydroxide. However, analyses of the starting material showed that there was no free hydroxide remaining in this waste. Where specified, sodium hydroxide was added as a 10M stock solution; metals cations were added as 1M nitrate solutions [$Ca(NO_3)_2$, $Sr(NO_3)_2$, and $Eu(NO_3)_3$]; and permanganate was added as 0.4M $KMnO_4$. The reagents were added in the order listed in Table 3.1. After addition of all reagents, the samples were heated to 40°C for 1 hour. The samples were removed from the heat block, cooled, and centrifuged. The supernatant was decanted from the centrifuged solids and filtered through a 0.45-um filter disk. Sample MN-01 was the initial waste and was not heated or filtered. Sample MN-02 was heated and filtered along with the other samples but no chemical reagents were added. Samples were acid digested and analyzed (ICP-AES, total alpha, GEA, and separation-beta counting for ^{90}Sr). The centrifuged solids from one experiment, MN-03, were acid digested and analyzed (results reported as MN-12 in Appendix D).

Table 3.1. Test Matrix for the First Series of Permanganate Addition Experiments.

Sample Number	NaOH Addition	Metal Addition	Target $[MnO_4^-]$	Comment
MN-01	none	none	none	initial waste-unfiltered
MN-02	none	none	none	initial waste-filtered
MN-03	none	none	0.05 M	base case test condition
MN-04	none	none	0.05 M	duplicate (of MN-03)
MN-05	none	none	0.03M	low $[MnO_4^-]$
MN-06	none	none	0.08 M	high $[MnO_4^-]$
MN-07	to 1M	none	0.05 M	high [OH-]
MN-08	to 1M	none	0.08 M	high $[MnO_4^-]$, high $[OH^-]$
MN-09	none	to 0.05M Ca	0.05 M	metal addition
MN-10	none	to 0.05M Sr	0.05 M	metal addition
MN-11	none	to 0.05M Eu	0.05 M	metal addition
MN-12				centrifuged solids from MN-03

The effectiveness of permanganate treatment for TRU removal can be seen by examining the DFs for total alpha and Am-241 shown in Figure 3.1. The target DF of 5 was obtained for many of the samples. Decontamination was much higher with added hydroxide, MN-07 and MN-08, and added calcium, MN-09. This is expected because of the high carbonate and lack of any free hydroxide in the starting waste (bicarbonate/carbonate complexes of TRU). The addition of strontium with permanganate increased the DF slightly over permanganate alone. Increasing the permanganate level from 0.03M to 0.05M to 0.08M continued to increase the DF in a near linear relationship. The addition of Eu was evaluated to help increase the TRU DF. Unfortunately, because the $Eu(NO_3)_3$ was acidic and the waste had no free hydroxide, the Eu addition just increased the conversion of carbonate to bicarbonate, decreasing the TRU DF compared with permanganate addition alone. Addition of free hydroxide had a greater effect on DF values, suggesting that 0.03M permanganate would be adequate for TRU decontamination with added free hydroxide.

Since over 90% of the TRU is Am-241, the good correlation between total alpha and Am-241 was expected. Decontamination factors for Eu-154 and Eu-155 are also shown in Figure 3.1 and varied similarly to Am-241 DFs, but were somewhat lower. Both Am and Eu were expected to be predominantly in the +3 oxidation state, and to have similar chemistries. No significant decontamination occurred for Co-60 or Cs-137.

Permanganate treatment of the waste removed iron from solution. Am-241 removal correlated with iron removal, as shown in Figure 3.2. Iron is known to be a good co-precipitant/flocculent for TRU, so the iron removal/precipitation may contribute to the high TRU removal. Data are also shown for MN-02, the filtered initial waste. This sample shows that approximately 10% of the Am-241 (and iron) removal was associated with filtration of the sample and removal of entrained solids. Manganese removal from solution showed a similar trend to Fe with the exception of MN-11, Eu addition. Because of the lack of free hydroxide, addition of the acidic Eu solution lowered the pH of the waste, and increased the soluble Mn.

The decontamination factors for Sr-90 are shown in Figure 3.3. Very little Sr decontamination occurred with permanganate addition, and little improvement occurred in going from 0.03M to 0.05M to 0.08M permanganate addition. The added free hydroxide only slightly improved the Sr DF. Calcium addition provided the highest Sr DF, but was still below the target DF of 10. Isotopic exchange with addition of nonradioactive strontium approximately doubled the Sr DF. This may be caused by the lower temperature and digest time used in these studies compared to the Part A-1 studies, which found Sr addition at 0.075M to be effective for decontamination of AN-107 (SRTC). Higher Sr DFs were expected for permanganate treatment based on the results from Orth et al. (1995). The much higher organic complexant concentration in AN-107 than SY-101 must be a significant factor in the low values. These tests indicate that different conditions for increased strontium decontamination are needed.

The ICP data in Appendix D for MN-09 and MN-10 indicate that the initial waste is below saturation in calcium and strontium. For MN-09, the calcium concentration increased from an initial value of 250 ug/g to 665 ug/g after addition of the $Ca(NO_3)_2$ and permanganate solutions. For MN-10, the total strontium concentration increased from an initial value of 1.2 ug/g to 125 ug/g after addition of the $Sr(NO_3)_2$ and permanganate solutions.

A comparison of MN-03 and MN-04, repeat experiments at the same conditions, shows that the procedure and analyses are reproducible; and the variability noted is caused by differences in reagent addition. This comparison is important since these experiments are difficult to conduct with actual waste in the hot cell; are conducted by remote manipulator; and reagent addition and stirring are difficult to repeat identically for every sample.

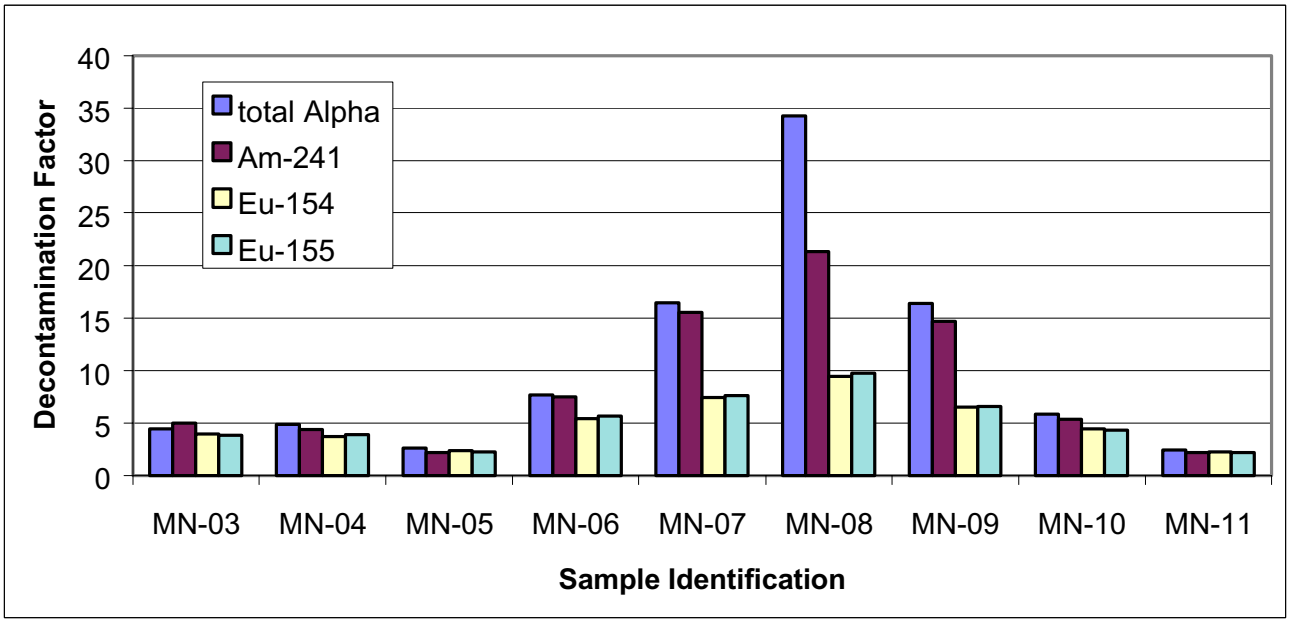


Figure 3.1. Decontamination Factors for Total Alpha, Am-241, Eu-154, and Eu-155.

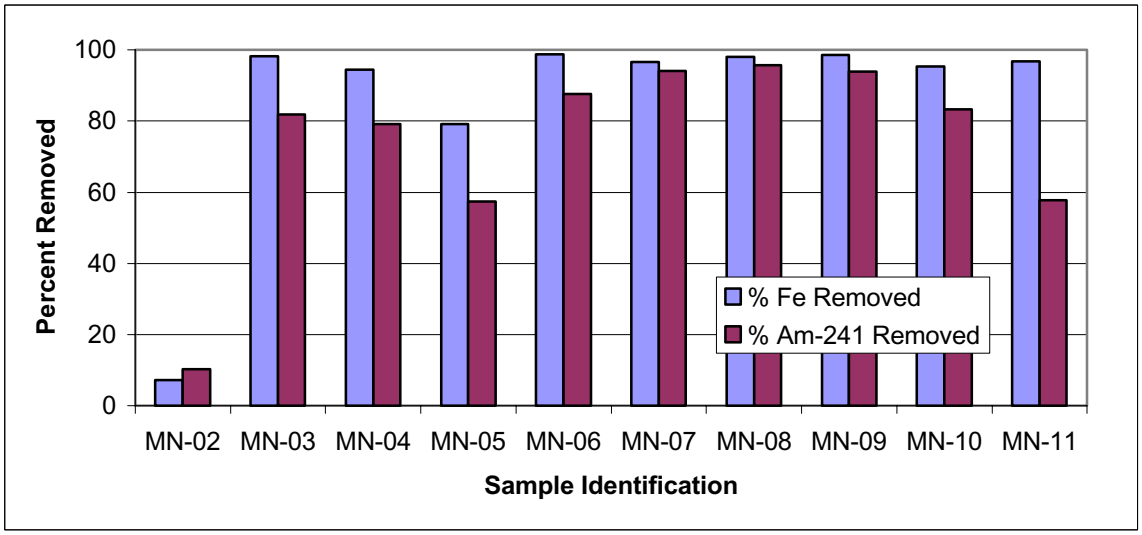


Figure 3.2. Percent Fe and Am-241 Removal.

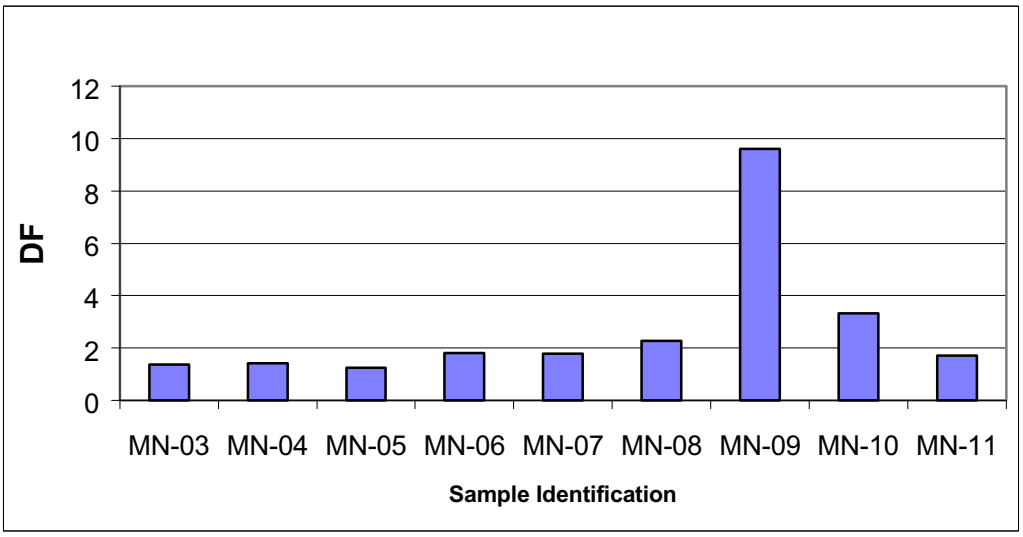


Figure 3.3. Strontium Decontamination Factors.

3.2 The Second Series of Proof-of-Principle Experiments

Because the first series of experiments showed the importance of free hydroxide for TRU decontamination, the second series of experiments was conducted with archived AN-107 that was adjusted to a calculated free hydroxide concentration of 1M. The second series of experiments, shown in Table 3.2, was designed to determine conditions for increased Sr DF. One test was added with permanganate at 0.16M, twice the highest concentration from the first series. A series of tests were also added with various combinations of Sr and permanganate addition. Calcium addition at very low concentration was examined at or below the predicted solubility limit. The calcium addition was kept low because simulant tests had shown that calcium precipitate greatly reduced the filterability of the waste. Tests were added to determine the effect of higher sodium concentration and reduced carbonate

concentration. A major change for all these experiments was the digest temperature, which was increased to 50°C, and the digest time, which was increased to 4 hours. These conditions were identified by SRTC for Sr/TRU removal with Sr and Fe addition, and were expected to increase the Sr decontamination by isotopic exchange/dilution and precipitation as $SrCO_3$.

The DFs for Am and Eu are presented in Figure 3.4. Results from duplicate experiments, PR-06 and PR-07, show good reproducibility. Samples PR-03 and PR-08 were sampled and analyzed twice; the duplicate results indicate good reproducibility of the analytical procedure. The differences between experiments were a result of the change in reagents and reaction conditions. The Am DFs were above the target value of 5 for all conditions except PR-08, high Sr and low permanganate test. The high concentration of Sr actually decreased the Am DF; compare PR-08 to PR-10. The large adverse impact of carbonate on Am (TRU) decontamination can be seen by comparing the results from PR-14 to PR-03, where the carbonate concentration had been reduced by approximately 50%. Results from this series of experiments confirm the requirement for free hydroxide to obtain adequate Am DF. This is likely related to the shift in carbonate/bicarbonate equilibrium caused by increasing the free hydroxide concentration. The small amount of Ca addition increased the Am DF, but the Am DFs were well above the target of 5 without the addition of Ca.

Table 3.2. Test Matrix for the Second Series of Permanganate Addition Experiments.

Sample Number	Other Addition	Target [Sr]	Target $[MnO_4^-]$	Comment
PR-01	none	none	none	initial waste-unfiltered
PR-02	none	none	none	initial waste-filtered
PR-03	none	none	0.05 M	repeat of MN-7
PR-04	none	none	0.08 M	repeat of MN-8
PR-05	none	none	0.16 M	2X $[MnO_4^-]$
PR-06	none	0.075 M	0.05 M	base case
PR-07	none	0.075 M	0.05 M	duplicate of base case
PR-08	none	0.075 M	0.03 M	low $[MnO_4^-]$
PR-09	none	0.05 M	0.05 M	low [Sr]
PR-10	none	0.05 M	0.03 M	low $[MnO_4^-]$ and [Sr]
PR-11	0.01 M Ca	0.05 M	0.03 M	Ca effect
PR-12	0.01 M Ca	0.075 M	0.05 M	Ca effect
PR-13	1.5 M Na*	0.075 M	0.05 M	Na effect
PR-14	1 M H^+**	none	0.05 M	$CO_3^=$ effect
PR-15				centrifuged solids from PR-06

* Sodium nitrate was added to increase sodium concentration.

** The initial waste was added to concentrated nitric acid to neutralize and reduce the carbonate concentration in half.

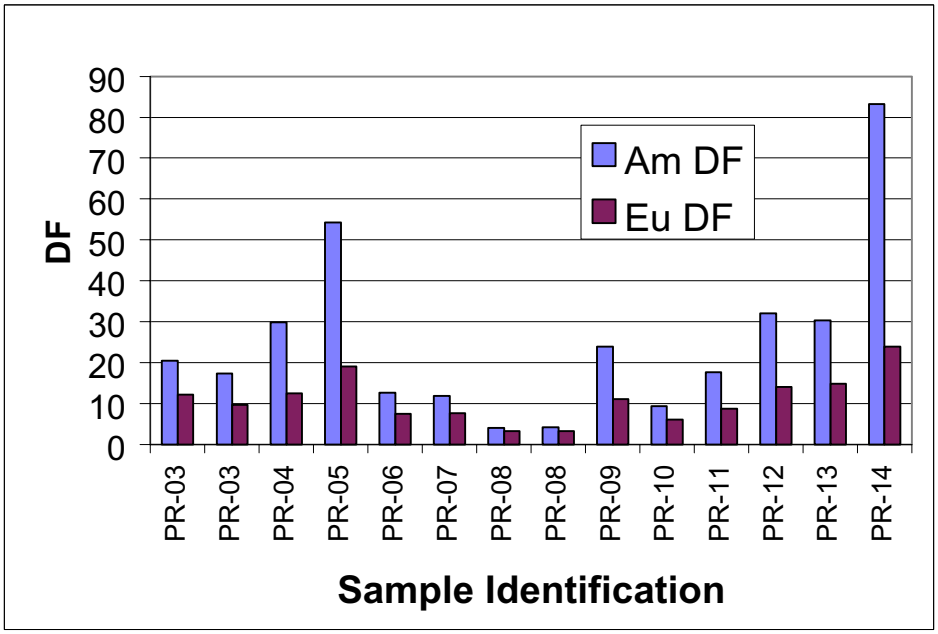


Figure 3.4. Decontamination Factors for Americium (241) and Europium (155).

The Sr-90 decontamination factors are presented in Figure 3.5. These results confirm that permanganate alone, even at a concentration as high as 0.16 M, will not provide adequate Sr decontamination. The changes made for the combined Sr and permanganate addition increased the Sr DF above the target of 10. The Sr DFs appear to be much more sensitive to reaction conditions; note the variability between PR-06 and PR-07, which are results for the same treatment conditions. Similar Sr-90 DFs results for PR-06, 07, 10, 11, 12, and 13 suggest that the Sr and permanganate mole ratio needs to be between 1.5 and 1.7 Sr/Mn, that lower concentration of reagents are effective, and Ca addition has no benefit. Decreasing the carbonate in the waste did not significantly improve the Sr DF; compare PR-03 to PR-14.

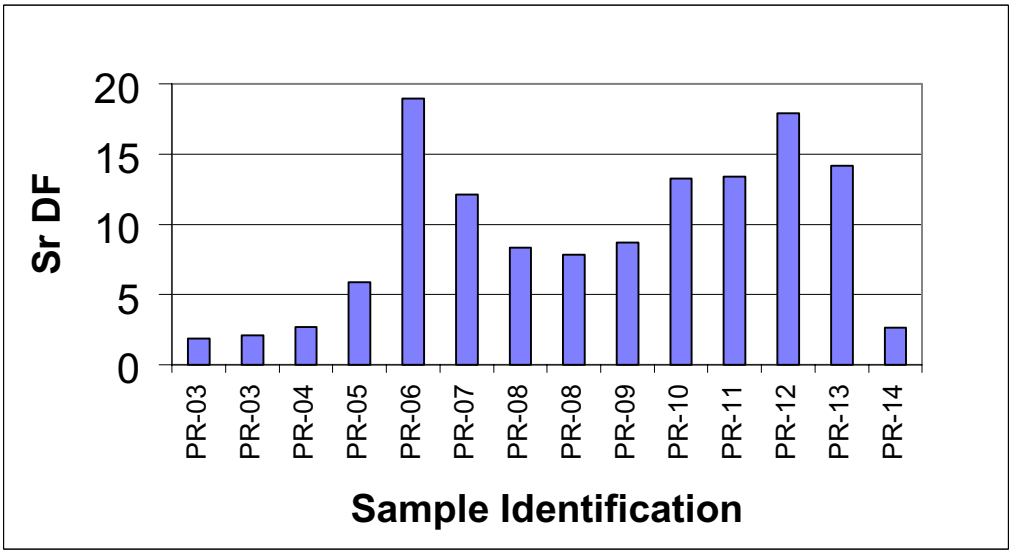


Figure 3.5. Strontium-90 decontamination factors for the second series of experiments.

In contrast to the Fe precipitation for TRU removal, permanganate treatment consumed very little of the added free hydroxide. Whereas iron consumed 3 mole of hydroxide per mole of added iron, permanganate consumed less than 1. Examining the titration data shows that Sr addition reduced the carbonate on a basis of 1 mole of carbonate per mole of added Sr, i.e., precipitation of $SrCO_3$.

3.3 The Third Series of Proof-of-Principle Experiments

The third series of experiments used samples of both archived AN-107 and AN-107 diluted feed. These tests, shown in Table 3.3, were conducted as a final confirmation of reaction conditions prior to conducting large-scale precipitation tests. The Sr and permanganate additions were at the lower concentration, and one experiment, OP-02, was a repeat of the earlier concentrations used PR-10. Reversing the order of addition, permanganate first followed by Sr, was examined (OP-05), as well as reduced free hydroxide concentration (LH-07). Because the change in reaction conditions was so successful for the second series, BNFL requested the conditions be changed for these tests also. After each chemical addition was completed, the samples were heated to 50°C and held for 2 hours. Before the second reagent was added, the samples were removed from the heater block and allowed to cool to make weighing easier (less balance drift). Then the second reagent was added, and the vials returned to the heating block for an additional 2 hours digestion at 50°C.

Table 3.3. Test Matrix for the Third Series of Permanganate Addition Experiments.

Sample Number	AN-107 Waste ID	Target [Sr]	Target $[MnO_4^-]$	Comment
OP-01	Archived, 1M OH + 1.5M Na	none	none	initial waste-filtered
OP-02	Archived, 1M OH	0.05	0.03	Repeat of PR-10
OP-03	Archived, 1M OH + 1.5M Na	0.05	0.03	low [Sr] and $[MnO_4^-]$
OP-04	Archived, 1M OH + 1.5M Na	0.05	0.03	Duplicate of OP-03
OP-05	Archived, 1M OH + 1.5M Na	0.05	0.03	Reverse addition order
LH-06	Archived, 0.5M OH + 1.5M Na	none	none	initial waste-filtered
LH-07	Archived, 0.5M OH + 1.5M Na	0.05	0.03	Low hydroxide
RW-08	Diluted feed*	none	none	initial waste-filtered
RW-09	Diluted feed*	0.05	0.03	low [Sr] and $[MnO_4^-]$
RW-10	Diluted feed*	0.05	0.03	Duplicate of RW-09
RW-11	Diluted feed*	0.075	0.05	High [Sr] and $[MnO_4^-]$

* See Urie et al. (1999), 7.5M sodium and 0.71M free hydroxide.

The Am-241 DFs are shown in Figure 3.6 for the third series of experiments. The DFs exceeded the target value of 5 for all of the archived AN-107 experiments. However, the DFs for Am-241 in the low concentration tests with AN-107 diluted feed, RW-09 and RW-10, were below 5. The AN-107 diluted feed is much more concentrated then the archived AN-107 which had been treated by ion exchange, and the higher reagent addition was necessary to obtain adequate Am decontamination. Examining the results from the experiments with archived AN-107, reversing the order of reagent addition, permanganate then Sr, appears to reduce the Am-241 decontamination. Reducing the free hydroxide addition from 1M to 0.5M had no impact on Am decontamination.

The strontium-90 DFs are shown in Figure 3.7. The Sr-90 DFs were all below the target values of 10. The lower DFs appear to be a result of the change in treatment conditions used for these experiments since OP-02, a repeat of the reagent concentrations used in experiment PR-10, had a lower DF. The reversed reagent addition order, OP-05, improved the Sr-90 value for these reaction conditions.

The decreased addition of free hydroxide from 1M to 0.5M had no effect on the Sr-90 DFs. The Sr-90 DFs for the AN-107 diluted feed were less than for the archived AN-107 samples, as was the case for Am-241 DFs. Sr-90 decontamination appears to be extremely sensitive to reaction conditions, and adequate Sr-90 decontamination is more difficult to obtain than Am-241 (TRU) decontamination.

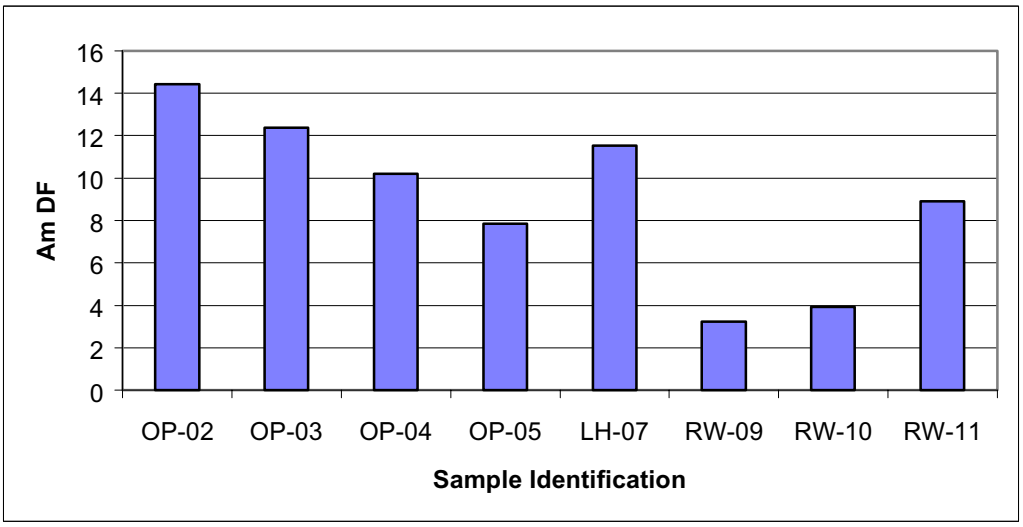


Figure 3.6. Americium-241 Decontamination Factors for the Third Series of Experiments.

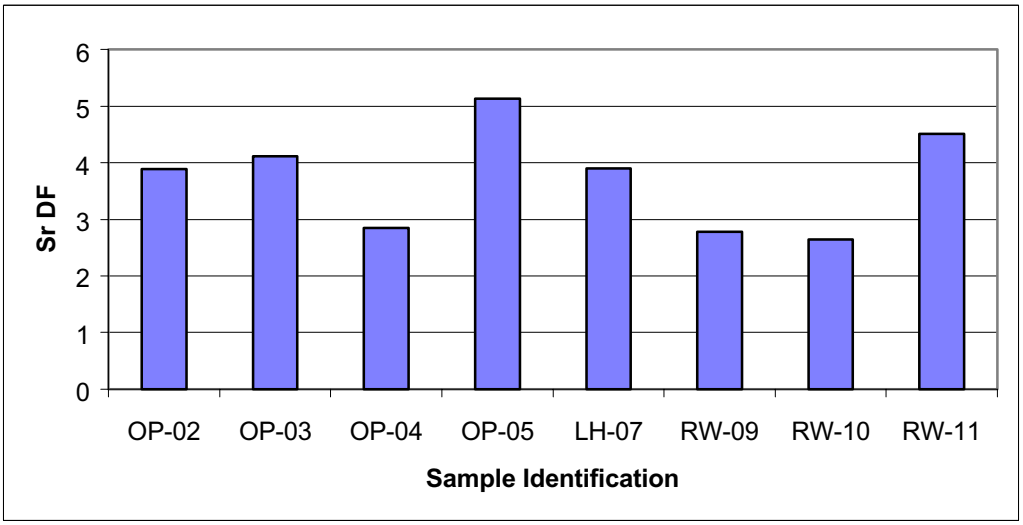


Figure 3.7. Strontium-90 Decontamination Factors for the Third Series of Experiments.

The AN-107 diluted feed samples were analyzed for Am-241 by separation followed by AEA. This analysis method also detects curium isotopes 242 and 243+244. The DFs for Cm were calculated and found to be equal to those obtained for Am-241.

4.0 Conclusion and Recommendations

The results of the proof-of-principle experiments showed that free hydroxide was needed for high TRU (Am-241) removal using permanganate. Similar results were obtained for calculated free hydroxide levels of 0.5 and 1.0M. Addition of permanganate alone could not achieve adequate Sr-90 decontamination, and isotopic dilution/precipitation with added nonradioactive strontium was required. Adequate levels of Sr-90 decontamination were more difficult to attain and more sensitive to treatment conditions. The highest strontium decontamination was obtained when reagents were added to the waste at ambient temperature in the order strontium then permanganate. Adequate Sr/TRU removal was obtained with addition of 0.05M strontium and 0.03M permanganate to samples of archived AN-107. However, because the AN-107 diluted feed is more concentrated, large-scale Sr/TRU removal tests should be conducted with 0.075M strontium and 0.05M permanganate.

The addition of low concentrations of calcium increased the Am DF, but had no impact on the Sr-90 decontamination. Since calcium was found to decrease the filterability of waste simulants, it is recommended that no calcium addition be used for the large-scale tests.

Additional tests should be run with AN-107 diluted feed on a larger scale with reduced reagent addition; free hydroxide 0.5M, Sr = 0.05M and permanganate = 0.03M. These tests should examine in detail the effects of temperature and digest time. Since $SrCO_3$ has retrograde solubility (decreases with increasing temperature), the digest temperature of 50°C may reduce the Sr-90 isotopic exchange because of the lower Sr solubility. The permanganate reaction is also rapid, complete in a manner of minutes, so the 4-hour digest time may not be required.

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APPENDIX A

Appendix A: Test Instruction TI-037 and Data Sheets

APPENDIX B

Appendix B: Test Instruction TI-040 and Data Sheets

APPENDIX C

Appendix C: Test Instruction TI-043

APPENDIX D

Appendix D: Analytical Data

APPENDIX E

Appendix E: Calculations

APPENDIX F

Appendix F: Staff Roles and Responsibilities

Staff Member	Role/Responsibility
Richard Hallen	Scientist/Technical Leader - Sr/TRU Removal
Sam Bryan	Scientist/Hot Cell Experiments - lead and direct hot cell experiments
Vaughn Hoopes	Technician/Hot Cell Experiments- conduct experiments and sample prep.

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APPENDIX A

Appendix A: Test Instruction TI-037 and Data Sheets

PNNL Test Instruction

Document No.: BNFL-TI-29953-037
Rev. No.: 0

Title: Sr/TRU Removal from AN-107, Permanganate Addition Scoping Studies

Work Location: RPL SFO HLRF

Page 1 of 10

Author: SA Bryan

Effective Date: New
Supersedes Date: New

Use Category Identification: Reference

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

Required Reviewers:
_x_ Author
_x_ Technical Reviewer
__ RPL Manager
__ Project Manager
__ RPG Quality Engineer
__ BNFL (not required for scoping studies)

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	Samuel A. Bryan	4/20/99
Technical Reviewer	Richard T. Hallen	4/20/99
SAL-RPL Representative	Rick T. Steele	4/20/99

Controlled Document

Applicability

This test instruction describes the procedure to be used for scoping studies to determining the efficiency of the Sr/TRU removal (decontamination factor) by permanganate addition. The work described herein will be performed in the Shielded Analytical Laboratory (SAL) hot cells located in the Radiochemical Processing Laboratory (RPL). This test instruction supports the Test Plan No. 29953-013.

Work is to be performed by hot cell technicians under the supervision of a cognizant scientist. The cognizant scientist shall be responsible for implementation and adherence to this test instruction. This instruction is specific to:

- Sr/TRU removal by permanganate addition to envelope C waste during part 1B of the privatization; AN-107 will be used as a representative envelope C sample,
- permanganate addition and precipitation of actual wastes in RPL hot cell facilities, and
- tests performed at Battelle in the RPL, by staff in the Environmental Technology Division.

DRD Reference: none

Schedule Reference: Additional work scope not in baseline.

Justification

This activity is a scoping study using actual AN-107 waste to evaluate the potential of permanganate addition for Sr/TRU removal (decontamination). The preferred method by BNFL, strontium and iron precipitation, has not provided the necessary performance based upon process design criteria.

Objective

Because of the recent problem with filtration of the iron precipitates from AN-107 simulant, a series of scoping experiments are needed to determine the ability of permanganate to obtain the necessary DF for Sr and TRU (primarily Am, ~92% of TRU on an activity basis). Permanganate has been examined as both an oxidant (decomplexing waste, solubilizing chromium, and oxidation of technetium species to pertechnetate) and a precursor to MnO_2 and/or $Mn(OH)_2$ coprecipitants via the "Method of Appearing Reagents," Krot et.al. Permanganate was found to preferentially oxidize chromium, followed by organic carbon, and lastly nitrite. For wastes such as SY-101, the chromium in the sludge consumes as much as half the permanganate.

Success Criteria

The BNFL flowsheet for AN-107 (Envelope C) requires the separation of the HLW Sr/TRU from the LLW supernate prior to incorporation into glass. BNFL in Phase 1A identified precipitation by strontium and iron addition as the preferred method for decontamination. Decontamination factors are needed to reduce Sr and TRU (primarily Am) to the low level limits. Sr and TRU decontamination factors of 5 or more are needed while minimizing the addition of chemical reagents.

These tests will generate results that can be used for comparison with Envelope C Criteria for Sr/TRU decontamination (DF 5 or more).

Background

Orth et al (1995) recommended permanganate doses of 0.1M for decomplexing SY-101 type wastes where high concentrations of chromium (approximately 0.4%) partly consumed permanganate prior to organic destruction. AN-107 does not have the high chromium values in the sludge compared to SY-101. Due to lower chromium values in AN-107, permanganate is expected to be effective at lower doses, with 0.05M a target treatment level. Reducing the amount of permanganate added will reduce the amount of HLW waste glass produced.

Spill Protection/Response

Hot cell technicians shall conduct tests in a manner to minimize the impact of a spill. In the event of a spill, the cognizant scientist shall be notified and a decision will be made to try to recover the sample or repeat the test condition.

Feed Description

The Sr/TRU removal scoping tests will use AN-107 supernatant previously treated for cesium removal (Envelope C). This feed was diluted and chemicals added such that the approximate final concentrations are: 4.9M sodium and 0.2M hydroxide. Approximately 2 L of diluted AN-107 supernatant is available for these scoping tests, of this approximately 200 mL will be needed.

Equipment Description

The permanganate addition tests will be conducted on a small scale, approximately 20 mL each. Appropriate glass vials or test tubes small be used, such that the samples can be heated to a temperature of 40°C. Some mixing/stirring of the samples after chemical addition should be provide, this may be as simple as swirling the samples. Reagents will be added slowly as liquids, and stirred/mixed/swirled after each reagent is added. Some experiments will require two different reagent to be added in the proper sequence as detailed in the test matrix.

Work Instructions

1.0 Applicability

This test instruction is to be used to perform scoping tests for Sr/TRU removal by permanganate addition. Approximately four (4) 1-L bottles of AN-107 supernatant previously treated by Cs ion exchange is available in SAL for these scoping tests. One bottle of the AN-107 waste will be used for these tests.

2.0 Supporting Documents

This test instruction is not a stand-alone document. Sr/TRU Precipitation and analytical requirements for all BNFL related work are contained in PNNL Test Plan No. BNFL-TP-29953-013. TP-29953-013 also contains an overall description of the project, ES&H compliance, emergency response, and the hazards assessment and mitigation.

3.0 Responsible Staff

The staff responsible for executing this test plan are as follows.

- Task Manager – Rich Hallen
- SFO Manager – Randy Thornhill (Rick Steele)
- Test Scientists – Sam Bryan, Rich Hallen

- Hot Cell Technician – Vaughn Hoops
- Radiological Control Technician

4.0 Materials, Equipment, Supplies and Reagents Needed

4.1 Materials Required

1. Twelve 20 mL glass scintillation vials for filtered, analytical samples, pre-labeled as follows: MN-01 through MN-12. And 11 vials or test tubes for conducting experiments.
2. A 1 liter polyethylene bottle or equivalent for waste.
3. 12 - disposable syringes and 0.45 micron syringe filters.
4. 9 - vessels (vials/test tubes) to conduct tests
5. AN-107 waste in SAL-cell. Use archived sample from "Tc Removal Flow Studies" (Project No. 25865). Archive sample # C3E3
6. heating device
7. Volume dispensing or measuring device, such as a graduated tube or cylinder, for determining the density of the AN-107 sample

4.2 Equipment

1. 100 gram balance
2. Hand held camera (if convenient)
3. Stop-watch
4. Calculator
5. Hot plate
6. Thermometer

4.3 Reagents Needed (see prep sheet)

1. 10 mL of 10M NaOH
2. 10 mL of 1M $Ca(NO_3)_2$, $Sr(NO_3)_2$ and $Eu(NO_3)_3$
3. 50 mL of 0.4M $KMnO_4$
4. Archive AN-107 sample # C3E3.

4.4 Other Supplies

1. BNFL-TI-29953-037 (this test instruction)
2. Laboratory Record Book (use Red Bound, BNFL lab notebook, BNW-13733)
3. BNFL-TP-29953-013 (Hallen 1999)

5.0 Test Instructions

The laboratory record book (LRB) shall be used to record other testing information as required by this test instruction and all test conditions not stated by this test instruction.

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 practical. Those tools that are reused should be washed and rinsed prior to reuse.

Keep all test materials in sealed containers as much as possible to prevent them from drying.

5.1 Prestart

5.1.1 Prepare solutions according to the attached preparation sheet.
5.1.2 Inventory materials, equipment, supplies, and reagents to ensure all required items are available. Assure that all materials have been modified for remote handling.

Record Unique ID # of reagents:

0.4M KMnO4 KMnO4.
10N NaOH Manufacture_____ Lot # prepared according to bench sheet
1M $Ca(NO_3)_2$ $Ca(NO_3)_2$.
1M $Sr(NO_3)_2$ $Sr(NO_3)_2$
1M $Eu(NO_3)_3$ $Eu(NO_3)_3$

5.1.3 Initial and date when each item is completed.

✓ Review the test matrix (Table 1) in the test instructions in BNFL-TI-29953-037. Note the calculation worksheet, which gives quantities of reagents to add. Reagents can be added as volume but always record the mass added.

5.1.4 Obtain the following information:

M&TE List:

✓ Balance 1: 3600601016 / Metler AE160
Calib ID ↓ Calib Exp Date 8/99
Location Cell 2 / SAL

✓ temperature reading device (thermometer or thermcouple/reader):
Calib ID 0059719-56 Calib Exp Date 2/25/00
Location Cell 6/SAL ← Cell 2/SAL (thermometer)
thermometer in cell 2 calibrated against thermocouple in cell 6 prior to test.

5.2 Operation

5.2.1 Determine the density of the AN-107 sample and record here data and results here:
mass_____; volume_____; density_____.

Review the test matrix shown below, Table 1. Record data in Table 2. Note to check each activity when complete. This should be done and verified by the cognizant scientist.

Table 1. Test Matrix.

Check when complete	Test #	Target [KMnO4]	Added NaOH	Metal Addition	Comment	Scientist Verification
✓	1	none	none	none	control-unfiltered	SAB
✓	2	none	none	none	control-filtered	SAB
✓	3	0.05 M	none	none	base case test condition	SAB
✓	4	0.05 M	none	none	duplicate (of # 3)	SAB
✓	5	0.03M	none	none	low [KMnO4]	SAB
✓	6	0.08 M	none	none	high [KMnO4]	SAB
✓	7	0.05 M	to 1M	none	high [OH-]	SAB
✓	8	0.08 M	to 1M	none	high [KMnO4], high [OH-]	SAB
✓	9	0.05 M	none	to 0.05M Ca	metal addition	SAB
✓	10	0.05 M	none	to 0.05M Sr	metal addition	SAB
✓	11	0.05 M	none	to 0.05M Eu	metal addition	SAB

4/20/99

It is preferable that the permanganate treated solution be heated to 40°C and held at this temperature for 1 hour. The permanganate oxidation reaction generates some heat but at these low volume additions, the sample is expected to reach about 30°C without external heating.

Table 2. Data Sheet.

Test #	Vial ID	Vial Tare Weight, g	Number Indicates Order of Reagent Addition								Test Complete (initial)
			1		2		3		4		
			AN-107 added		NaOH added		Metal added		MnO_4^- added		
			target mL	actual g	target mL	actual g	target mL	actual g	target mL	actual g	SAB
1	MN-01 set aside	24.9031	20	~ 50g	0	X	0	X	0	X	SAB
2	MN-02	24.8613	20	49.3119	0	X	0	X	0	X	SAB
3	MN-03	24.8178	20	49.1039	0	X	0	X	1.8	1.8810	SAB
4	MN-04	25.0212	20	50.1885	0	X	0	X	1.8	1.8795	SAB
5	MN-05	24.9138	20	50.852	0	X	0	X	1.1	1.1538	SAB
6	MN-06	24.9195	20	50.5740	0	X	0	X	3.1	3.2592	SAB
7	MN-07	24.8674	20	49.5249	2.2	2.9502	0	X	1.8	1.8720	SAB
8	MN-08	24.8986	20	50.0023	2.2	3.0409	0	X	3.1	3.2704	SAB
9	MN-09	24.9076	20	49.5991	0	X	1.05 (Ca)	1.2248	1.8	1.8783	SAB
10	MN-10	24.8933	20	49.7013	0	X	1.05 (Sr)	1.2320	1.8	1.8685	SAB
11	MN-11	24.8810	20	50.0922	0	X	1.05 (Eu)	1.3508	1.8	1.8867	SAB

4/29

MN-12 tare wt: 24.7257g vial

5.2.2 Record the weights of all vails, samples, additions, etc. After the reaction time of 1 hour at 40°C, the samples can be centrifuged to allow easier filtration prior to analytical analysis. If possible, record the volume of centrifuged solids. For the base case, (test 1, 0.05M MnO_4^-), the centrifuged solids may be submitted for solids analyses. Decant the supernate from this sample,

record the weight of solids/solution remaining; the solids will be submitted as is for acid digestion/analysis (see Table 3 below). Note that the AN-107 original "as is - without filtering" waste needs to be submitted for analyses and acid digest because it contains some solids; the "as received - filtrate" will be the same "as received" waste but treated as the other samples, and is a control sample (centrifuged then filtered the same manner as the other samples, syringe filter).

6.0 Sample Analysis

The point of contact for the sample analysis from these tests is Mike Urie and Rick Steele.

6.1 Chemical and Radiochemical Analysis

Table 3 below shows the sample analysis list. The table lists the analyses to be performed on samples generated from this test instruction.

Table 3. Samples and Their Required Analyses

Process Variable	Vial ID	ACL No.[a]	Sample Type	Sample Preparation	Analysis Description[b]
AN-107 as is	MN-01	99-01595	some solids	acid digest	Sr/Am/Total alpha, ICP
AN-107 as is	MN-02	99-01596	Filtrate	0.45 um dead end	Sr/Am/Total alpha, ICP, [OH^-]
0.05M Permanganate	MN-03	99-01597	Filtrate	0.45 um dead end	Sr/Am/Total alpha,ICP, [OH^-]
0.05M Permanganate(dup)	MN-04	99-01598	Filtrate	acid digest	Sr/Am/Total alpha, ICP
0.03 Permanganate	MN-05	99-01599	Filtrate	0.45 um dead end	Sr/Am/Total alpha
0.08 Permanganate	MN-06	99-01600	Filtrate	0.45 um dead end	Sr/Am/Total alpha
1M Hydroxide, 0.05M Permanganate	MN-07	99-01601	Filtrate	0.45 um dead end	Sr/Am/Total alpha
1M Hydroxide, 0.08M Permanganate	MN-08	99-01602	Filtrate	0.45 um dead end	Sr/Am/Total alpha
Ca Cation Addition	MN-09	99-01603	Filtrate	0.45 um dead end	Sr/Am/Total alpha
Sr Cation Addition	MN-10	99-01604	Filtrate	0.45 um dead end	Sr/Am/Total alpha
Eu Cation Addition	MN-11	99-01605	Filtrate	0.45 um dead end	Sr/Am/Total alpha
0.05M Permanganate	MN-12	99-01606	CentrifugeSolids	acid digest	Sr/Am/Total alpha, ICP

(a) Analytical Chemistry Laboratory (ACL) tracking number is a unique identification for these samples. The samples are submitted for analysis under the Analytical Service Request (ASR) number 5345.
(b) Descriptions of analyses are contained in Table 4.

Table 4. Description of Analyses

Constituent	Analysis Method	PNNL Procedure No.
Americium-241, Eu isotopes	GEA	PNL-ALO-450
Strontium-90 (Yttrium-90)	Separations and Beta Counting	PNL-ALO-476/431
Total Alpha	Gross Alpha	PNL-ALO-420/421
Hydroxide	EPA SW-846 Modified Method, 310(3)	PNL-ALO-228
Metal Ions (see list Table 5)	ICP-AES	PNL-ALO-211/280

Table 5. Analytical Requirements for Supernate/Filtrate and Centrifuged Solids

Analyte	Centrifuged Solids Minimum Reportable Quantity microCi/gm	Supernate/Filtrate Minimum Reportable Quantity microCi/ml	Analysis Method
Strontium-90	7.01E+01	1.5E-01	Chemical Separation & Beta Count
Americium-241	1.2E-03	7.2E-04	GEA
Total Alpha	1.0E-03	2.3E-01	Total Alpha
	microgm/gm	microgm/ml	
Al	3.3E+02	7.5E+01	Acid Digestion followed by ICP-AES
Ba	6.0E+02	7.8E+01	
Ca	1.8E+02	1.5E+02	
Cd	1.1E+01	7.5E+00	
Co	3.0E+00	3.0E+01	
Cr	1.2E+02	1.5E+01	
Cu	1.8E+01	1.7E+01	
Eu	NA	NA	
Fe	1.4E+02	1.5E+02	
K	1.5E+03	2.0E+02	
La	6.0E+01	3.5E+01	
Mg	5.4E+02	1.5E+02	
Mn	3.0E+02	1.5E+02	
Mo	6.0E+00	9.0E+01	
Na	1.5E+02	7.5E+01	
Ni	1.6E+02	3.0E+01	
Pb	6.0E+02	3.0E+02	
Si	3.0E+03	1.7E+02	
Sr	NA	NA	
Ti	1.5E+02	1.7E+01	
U	6.0E+02	6.0E+02	
Zn	6.0E+00	1.65E+01	
OH-		0.05M	

7.0 Calculation and Important Information

Density of AN-107 sample that has cesium removed = estimated 1.22 g/mL ← measured as 1.26 g/mL – 4/21/99 S4.3

Density of 0.4M $KMnO_4$ solution = 1.0361 g/mL (measured from bench sheet)

Density of 10M NaOH solution =1.33 g/mL (CRC)

Density of 1M $Ca(NO_3)_2$ solution = 1.116 g/mL (measured from bench sheet)

Density of 1M $Sr(NO_3)_2$ solution = 1.162 g/mL (measured from bench sheet)

Density of 1M $Eu(NO_3)_3$ solution = 1.277 g/mL (measured from bench sheet)

20 mL = 24.4 grams of AN-107 waste

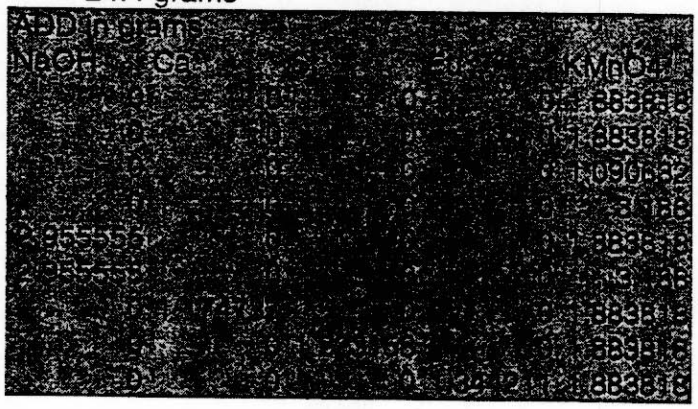
Mass of Solutions based on above density data. Densities (and masses) need to be verified based on actual solution densities. This will be performed after solutions are prepared in Step 4.3.

initial waste volume= 20 mL

test #	test Condition	ADD in mL NaOH	Ca	Sr	Eu	KMnO4
1	0.05 M	0	0	0	0	1.818182
2	0.05 M	0	0	0	0	1.818182
3	0.03M	0	0	0	0	1.052632
4	0.08 M	0	0	0	0	3.076923
5	0.05 M	2.222222	0	0	0	1.818182
6	0.08 M	2.222222	0	0	0	3.076923
7	0.05 M	0	1.052632	0	0	1.818182
8	0.05 M	0	0	1.052632	0	1.818182
9	0.05 M	0	0	0	1.052632	1.818182

initial waste mass= 24.4 grams

test #	test Condition
1	0.05 M
2	0.05 M
3	0.03M
4	0.08 M
5	0.05 M
6	0.08 M
7	0.05 M
8	0.05 M
9	0.05 M



8.0 References

Hallen, RT. 1999. "Sr/TRU Precipitation and Crossflow Filtration Test Plan." PNNL Test Plan No. TP-29953-013, Pacific Northwest National Laboratory, Richland Washington.

Krot, N, V Shilov, A Bessonov, N Budantseza, I Charushnikova, V Perminov, and L Astafuroza. "Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solutions by Method of Appearing Reagents." WHC-EP-0898, Institute of Physical Chemistry of the Russian Academy of Sciences.

Orth, RJ, AH Zacker, AJ Schmidt, MR Elmore, KR Elliott, GG Neuenschwander, and SR Gano. "Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant – FY 1995 Test Results." PNNL-10766, Pacific Northwest National Laboratory, Richland Washington.

BNW 13733 FVH 22

Metal Additions: Prep of Stock Solutions

Ca, Sr, or Eu need to be added to the waste for Sr/TRU decomtamination.
These solutions will be added before the permanganate.
cord all information and observations on prep sheet or in lab notebook.

Balance number: 36-06-01-046
Balance calibration: 8-99 .

Makeup Ca(NO3)2 solution 1 M
use Ca(NO3)2*4H2O
236.15 grams/mole (FW) (lot #07603BN)
Tare 25 mL volumetric flask 22.0877 grams
add 5.90375 grams Ca(NO3)2*4H2O flask + Ca(NO3)2 27.9935 grams
actual weight of Ca(NO3)2 added 5.9058 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
fill to volumetric line with Milli-Q water. Record total weight: 50.0018 grams
calculate actual [Ca] = actual weight/236.15/volume in Liters = 1.0003 M
calculate density of solution, weight of solution/volume = 1.1166 grams/mL
Transfer stock solution to bottle and label unique ID # Ca(NO3)2

Makeup Sr(NO3)2 solution 1 M
use Sr(NO3)2
211.63 grams/mole (FW) (lot #09319BF)
Tare ~~10~~ ~~25~~ mL volumetric flask 11.8460 grams
add ~~5.29075~~ 2.116 grams Sr(NO3)2 flask + Sr(NO3)2 13.9609 grams
actual weight of Sr(NO3)2 added 2.1149 grams
d approximately 1/2 the volume of Milli-Q water and swirl until dissolved
to volumetric line with Milli-Q water. Record total weight: 23.4676 grams
calculate actual [Sr] = actual weight/211.63/volume in Liters = 0.9993 M
calculate density of solution, weight of solution/volume = 1.1622 grams/mL
Transfer stock solution to bottle and label unique ID # Sr(NO3)2

Makeup Eu(NO3)3 solution 1 M
use Eu(NO3)3*6H2O
446.07 grams/mole (FW) (lot #03131 P4)
Tare ~~5~~ ~~25~~ mL volumetric flask 15.0372 grams
add ~~11.15175~~ 2.23 grams Eu(NO3)3*6H2O flask + Eu(NO3)3*6H2O 17.3811 grams
actual weight of Eu(NO3)3*6H2O add 2.2439 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
fill to volumetric line with Milli-Q water. Record total weight: 21.4243 grams
calculate actual [Eu] = actual weight/446.07/volume in Liters = 1.0061 M
calculate density of solution, weight of solution/volume = 1.2224 grams/mL
Transfer stock solution to bottle and label unique ID # Eu(NO3)3

Date prepared: 4-19-99
Prepared by: RTH
Work Package Number: WS-130c

Calculatations prepared by RT Hallen
Calculations checked by:

BNW/3733 FUH 23

Preparation of Stock Permanganate Solution

Permanganate needs to be added to the waste for Sr/TRU decomtamination.
This solution will be added after any other reagents, if needed.
Record all information and observations on prep sheet or in lab notebook.

Balance number: ~~362-06-01-047~~ 360-06-01-040
Balance calibration: ~~8-99~~ 8-99

Makeup stock KMnO4 solution 0.4 M
use KMnO4 99+%, ACS Reagent Grade
158.04 grams/mole (FW) (lot # 3616)
Tare 50 mL volumetric flask ~~31.8342~~ grams
add 3.1608 grams KMnO4 flask + KMnO4 34.9856 grams
actual weight of KMnO4 added 3.1614 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
add approximately .5 mL of 1N NaOH or 0.05mL of 10N NaOH to stabilize permanganate – (about 2 drops 10N-see solution below)
all will probably not dissolve because 0.4M is near saturation, add more water, repeat
fill to volumetric line with Milli-Q water. Record total weight: 83.6305 grams
calculate actual [MnO4] = actual weight/158.04/volume in Liters = 0.4001 M
calculate density of solution, weight of solution/volume = 1.0361 grams/mL
Transfer stock solution to bottle and label unique ID # $KMnO_4$

Date prepared: ~~4-14-99~~ 4-14-99
Prepared by:
Work Package Number: W5130C

60.30
~~24.4~~
tare weight ~~24.2550~~
Bottle+Olt 90.2914

Make up 30% NaOH (w/w)(10N)
in poly bottle add 30gram NaOH pellet ~~29.9858~~ grams added
then add 70grams water ~~70.0622~~ grams total weight = 160.3536

calculate 29.97 % NaOH (w/w)

LOT # 961969

Calculation Prepared by RT Hallen
Calculation checked by

Greenwood, Larry R

To: Hallen, Richard T
Cc: Bryan, Samuel A
Subject: RE: Sr-90 and GEA Results - ASR 5392 Revised

Rich - I have attached the density results - see the tabs labeled density on each worksheet. If you need anything else, just let me know.


99-1595.xls


99-2102.xls

Larry Greenwood Ph: 509-376-6918 Fax: 509-372-2156
mailto:larry.greenwood@pnl.gov

-----Original Message-----
From: Hallen, Richard T
Sent: Tuesday, August 10, 1999 11:10 AM
To: Greenwood, Larry R
Subject: RE: Sr-90 and GEA Results - ASR 5392 Revised

Larry, You are correct, ASR-5345 (99-1595, 4/30/99) data was all reported on a per gram basis. However, if density data is readily available, I would appreciate receiving it for this series of samples for completeness, Mn-01 to Mn-12 (99-1595 to 99-1606).

Also density data for ASR-5426 (99-2102 to 99-2112) would be nice.

Thanks, Rich Hallen

-----Original Message-----
From: Greenwood, Larry R
Sent: Friday, August 06, 1999 5:04 PM
To: Hallen, Richard T; Bryan, Samuel A
Cc: Urie, Michael W
Subject: Sr-90 and GEA Results - ASR 5392 Revised

Rich - I revised the reports to give you all data on a weight basis. The densities are shown on one tab; tabs with (g) mean that results are on a per gram basis. If any questions, just let me know. As far as I see, all results for ASR 5345 were already on a weight basis.

<< File: 99-1856.xls >>

Larry Greenwood Ph: 509-376-6918 Fax: 509-372-2156
mailto:larry.greenwood@pnl.gov

APPENDIX B

Appendix B: Test Instruction TI-040 and Data Sheets

PNNL Test Instruction	Document No.: BNFL-TI-29953-040 Rev. No.: 0
Title: Sr/TRU Removal from AN-107, Permanganate Optimization Studies	
Work Location: RPL SFO SAL	**Page** 1 of 13
Author: SA Bryan	**Effective Date: New** **Supersedes Date: New**
Use Category Identification: Reference	
Identified Hazards: ___ Radiological _x_ Hazardous Materials ___ Physical Hazards ___ Hazardous Environment ___ Other:	**Required Reviewers:** _x_ Author _x_ Technical Reviewer __ RPL Manager __ Project Manager __ RPG Quality Engineer __ BNFL (not required)

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	Samuel A. Bryan	5/24/99
Technical Reviewer	Richard T. Hallen	5/24/99
SAL-RPL Representative	Rick T. Steele	5/24/99

Controlled Document

RT Hallen comments - checks in blue ink.
RT Hallen 8/13/99

Applicability

This test instruction describes the procedure to be used for studies to determine the efficiency of the Sr/TRU removal (decontamination factor) by permanganate addition. The work described herein will be performed in the Shielded Analytical Laboratory (SAL) hot cells located in the Radiochemical Processing Laboratory (RPL). This test instruction supports the Test Plan No. 29953-013 and is a follow on of work conducted in Test Instruction No. 29953-037.

Work is to be performed by hot cell technicians under the supervision of a cognizant scientist. The cognizant scientist shall be responsible for implementation and adherence to this test instruction. This instruction is specific to:

- Sr/TRU removal by permanganate addition to envelope C; archived AN-107 (previously treated to remove Cs) will be used as a representative envelope C sample,
- permanganate addition and precipitation of actual wastes in RPL hot cell facilities, and
- tests performed at Battelle in the RPL, by staff in the Environmental Technology Division.

DRD Reference: none

Schedule Reference: Additional work scope not in baseline.

Justification

This activity is a study using archived AN-107 waste to evaluate the potential of permanganate addition for Sr/TRU removal (decontamination). The preferred method by BNFL, strontium and iron precipitation, has not provided the necessary performance based upon process design criteria.

Objective

The objective of this work is to optimize process conditions to obtain Sr and TRU decontamination with minimal reagent addition, and produce a precipitate that is easy to filter by cross-flow filtration.

Success Criteria

The BNFL flowsheet for AN-107 (Envelope C) requires the separation of the HLW Sr/TRU from the LLW supernate prior to incorporation into glass. BNFL in Phase 1A identified precipitation by strontium and iron addition as the preferred method for decontamination. Decontamination factors are needed to reduce Sr and TRU (primarily Am) to the low level limits. TRU/Am decontamination factors of 5 or more are needed while minimizing the addition of chemical reagents. Sr decontamination factors of greater than 10 are needed. Minimizing reagent addition will also reduce the cost of treatment.

Background

Because of the recent problem with filtration of the iron precipitates from AN-107 simulant, a series of scoping experiments were conducted to determine the ability of permanganate to obtain the necessary DF for Sr and TRU (primarily Am, ~92% of TRU on an activity basis). Permanganate has been examined as both an oxidant (decomplexing waste, solubilizing chromium, and oxidation of technetium species to pertechnetate) and a precursor to MnO_2 and/or $Mn(OH)_2$ coprecipitants via the "Method of Appearing Reagents," Krot et.al. Permanganate was found to preferentially oxidize chromium, followed by organic carbon, and lastly nitrite. In previous tests with archived AN-107, permanganate was successful in obtaining the necessary DFs for Am and TRU, but did not give adequate Sr DF (need a DF for Sr of greater than 10).

Orth et al (1995) recommended permanganate doses of 0.1M for decomplexing SY-101 type wastes where high concentrations of chromium (approximately 0.4%) partly consumed permanganate prior to organic destruction. AN-107 does not have the high chromium values in the sludge compared to SY-101. Due to lower chromium values in AN-107, permanganate was effective for TRU/Am removal at lower doses, 0.05M. Reducing the amount of permanganate added will reduce the amount of HLW waste glass produced. To increase the Sr DF, higher levels of $Sr(NO_3)_2$ we be added and the samples will be treated at a higher temperature, 50 C, for a longer period of time, 4 hours.

Spill Protection/Response

Hot cell technicians shall conduct tests in a manner to minimize the impact of a spill. In the event of a spill, the cognizant scientist shall be notified and a decision will be made to try to recover the sample or repeat the test condition.

Feed Description

The Sr/TRU removal tests will use archived AN-107 supernatant previously treated for cesium removal (Envelope C). This feed was diluted and chemicals added such that the approximate final concentrations are: 5M sodium and no hydroxide. Approximately 2.1 L of archived AN-107 supernatant is available for scoping/optimization tests, of this approximately 284 mL will be needed for these studies.

Equipment Description

The premanganate addition tests will be conducted on a small scale, approximately 20 mL each. Appropriate glass vials will be used, such that the samples can be heated in a sample block heater to a temperature of 50°C. Some mixing/stirring of the samples after chemical addition should be provided, this may be as simple as periodic swirling the samples. Reagents will be added slowly as liquids, and stirred/mixed/swirled after each reagent is added. Some experiments will require two or more different reagents to be added in the proper sequence as detailed in the test matrix.

Work Instructions

1.0 Applicability

This test instruction is to be used to perform tests for Sr/TRU removal by permanganate addition. Three (3) 1-L bottles of archived AN-107 supernatant previously treated by Cs ion exchange is available in SAL for these scoping tests. One bottle of the AN-107, C3E3, waste will be used for these tests.

2.0 Supporting Documents

This test instruction is not a stand-alone document. Sr/TRU Precipitation and analytical requirements for all BNFL related work are contained in PNNL Test Plan No. BNFL-TP-29953-013. TP-29953-013 also contains an overall description of the project, ES&H compliance, emergency response, and the hazards assessment and mitigation. These are follow on studies to TI-29953-037.

3.0 Responsible Staff

The staff responsible for executing this test plan are as follows.

- Task Manager – Rich Hallen
- SFO Manager – Randy Thornhill (Rick Steele)
- Test Scientists – Sam Bryan, Rich Hallen
- Hot Cell Technician – Vaughn Hoops
- Radiological Control Technician

4.0 Materials, Equipment, Supplies and Reagents Needed

4.1 Materials Required

1. Fifteen each 40 mL glass and plastic scintillation vials for filtered, analytical samples, pre-labeled as follows: PR-01 through PR-15. And 14, 40-mL glass scintillation vials for conducting experiments, labeled 1-14, with a 20 mL volume mark on each vial.
2. A 0.5 liter polyethylene bottle or equivalent to use for caustic adjustment to the waste. Mark a line at 300 mL on bottle and label, Archived AN-107 caustic adjusted to 1M.
3. 14 - disposable syringes and 0.45 micron syringe filters.
4. AN-107 waste in SAL-cell. Use archived sample from "Tc Removal Flow Studies" (Project No. 25865). Archive sample # C3E3
5. heating device
6. volume dispensing or measuring device, such as graduated tube or cylinder, for determining the density of the AN-107 sample

4.2 Equipment

1. 100 gram balance
2. Hand held camera (if convenient)
3. Stop-watch
4. Calculator
5. Hot plate
6. Thermometer

4.3 Reagents Needed In Hot Cell (see prep sheet)

1. 20 mL of 19M NaOH
2. 10 mL of 1M $Ca(NO_3)_2$
3. 25 mL of 1M $Sr(NO_3)_2$
4. 25 mL of 1M $NaMnO_4$
5. NaNO3 weighed in vial #13
6. HNO3 weighed in vial #14

4.4 Other Supplies

1. BNFL-TI-29953-040 (this test instruction)
2. Laboratory Record Book (use Red Bound, BNFL lab notebook, record number of book, BNW-13733)
3. BNFL-TP-29953-013 (Hallen 1999)

5.0 Test Instructions

The laboratory record book (LRB) shall be used to record other testing information as required by this test instruction and all test conditions not stated by this test instruction.

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 practical. Those tools that are reused should be washed and rinsed prior to reuse.

Keep all test materials in sealed containers as much as possible to prevent them from drying.

5.1 Prestart

5.1.1 Prepare solutions according to the attached preparation sheet. Calculate solution densities and record these values. All vials should be labeled and marked with the 20 mL line before they are taken into the hot cell. NOTE: Tare weigh bottle/vials with caps/lids. Keep lids on containers to minimize potential for spill, and to prevent evaporation.

For caustic adjustment to the archived AN-107: Outside of the hot cell a 0.5 Liter poly bottle should be marked with a line on the bottle at 300 mL and labeled "Archive AN-107, caustic adjusted to 1M OH." Tare the empty bottle, record tare weight. Add 12 grams of solid NaOH pellets, or 24 grams (16 mL) of 19M (50%) NaOH solution to poly bottle. Cap tightly for transfer into the hot cell. Transfer a second poly bottle marked with a line at 100mL to be used for 3 x 100mL additions to the "Archive AN-107, caustic adjusted to 1M OH." bottle. Weigh and record mass of the poly bottle before and after each 100mL addition.

Tare bottle 107.2775 g, bottle + NaOH 91.3976 g

Tare 100mL poly bottle _____ g,
bottle + addition 1 145.4571 g, bottle + addition 2 148.4668 g bottle + addition 3 145.0306 g
18.7326 19.1683 18.9197
Type of NaOH used 19M 50% Amount of NaOH added to bottle 24.1201 g

126.7245
129.2985
126.1109
382.1339 g

For test #13: Take vial #13, tare empty vial, add 2.55 grams of NaNO3 to the vial. Record the weight added to the vial, and set with other vials for transfer into the hot cell. Then treat as usual in hot cell with other samples.

Tare vial #13 24.9155 g, vial+NaNO3 27.4994 g

amount of NaNO3 added to vial #13 2.5839 g

For test #14: Before going into the hot cell, take vial #14, tare the empty vial, add 1.8 grams or 1.27 mL of concentrated Nitric Acid to vial, reweigh vial and record weight. Tightly cap vial and place with other for transfer into the hot cells.

Tare vial #14 24.9743 g, vial+HNO3 26.7815 g, amount of HNO3 added to vial #14 1.8070 g

5.1.2 Inventory materials, equipment, supplies, and reagents to ensure all required items are available. Assure that all materials have been modified for remote handling.

Record Unique ID # of reagents:

1M NaMnO4 _____.
19N NaOH _____.
1M $Ca(NO_3)_2$ _____.
1M $Sr(NO_3)_2$ _____.

382.1339 g / 1.265 g/mL = 303.2809 mL
24.1201 g / 1.519 g/mL = 15.9736 mL
406.2540 g 319.2544 mL
predicted density = 1.2725 g/mL

5.1.3 Initial and date when each item is completed.

ATC Review the test matrix (Table 1) in the test instructions in BNFL-TI-29953-040. Note the calculation worksheet, which gives quantities of reagents to add. Reagents can be added as volume but always record the mass added.

[OH] starting = 0.9506 M predicted
[Na] starting = 5.7005 M predicted

5.1.4 Obtain the following information:

M&TE List:

✓ Balance 1: (and Balance 2 if used) Bal. #2

Calib ID 360-06-01-040 Calib Exp Date 8/99 360-06-01-016 8/99

Location 201 Bench. Cell 2

_____ temperature reading device (thermometer or thermcouple/reader):

Calib ID _____ Calib Exp Date _____

Location _____

5.2 Operation

5.2.1 First, hydroxide adjustment must be done to the waste. It is preferred that this be completed a day in advance of the test matrix. In side the hot cell, transfer waste from bottle labeled "AN-107 - C3E3" to the 300 mL line of the poly bottle (now containing NaOH). Add 300 mL or 381 g of waste if NaOH pellets were used or add 284 mL or 360.7g of waste if 19M NaOH was used (density =1.27 g/mL). Record tare of bottle and weight after waste added.

Tare of bottle _____ g, bottle + waste _____ g, waste added 382.13 g

Replace cap tightly to keep from picking up CO_2 from the air. Invert bottle several times to well mix. Waste solution will warm with dissolution/dilution of the NaOH. This is the material to use for all of these experiments, with the exception of test #14 which has special instruction starting with the original AN-107 - C3E3 waste. Set this waste aside and allow to cool to cell temperature. After cool, use a volumetric flask (ball flask) to determine the new density of this solution. Record the density of the waste, and use this density to determine the weight of 20 mL of waste.

tare flask 9.7607 g, flask + waste 22.3944 g, waste mass 12.6337 g, flask volume 10 mL

density of AN-107 w/caustic 1.263 g/mL – Vol flask.

Record Hot Cell temperature 26 °C

For vial #14: This vial/sample should be prepared ahead of time with the hydroxide adjustment described above. After the hydroxide adjustment is complete and the bottle of AN-107-C3E3 is still available, take vial #14 (which now contains concentrated HNO_3) and record the tare weight. Then very slowly, drop wise, add AN-107 waste to vial #14 containing the nitric acid. The waste will react with the acid, foam and bubble, liberating carbon dioxide. Periodically swirl the vial to insure good mixing. The sample will also heat up because of the acid-base reaction. The waste is to be added slowly until approximately 10 mL is added and the bubbling/foaming has stopped. Then the additional 10 mL, up to the total volume of 20 mL of waste can be added. Record the weight of vial #14 with waste. Allow this sample to cool to cell temperature. Then add 1.11 mL or 1.47 grams of 19M (50%) NaOH. Record weight. Place vial #14 back with the other vials and treat with other samples as specified in test instructions.

Tare of vial 26.7965 g, vial + waste 51.5043 g, vial + waste + NaOH 56.7201 g

weight of waste added 22.81 g and weight of NaOH added 7.18 g

remove here waste was wrong vial was used

Review the test matrix shown below, Table 1. Record data in Table 2. Note to check each activity when complete. This should be done and verified by the cognizant scientist.

Table 1. Test Matrix.

Check complete	Test #	Target [MnO4]	Target [Sr]	Other Addition	Comment	Scientist Verification
/	1	none	none	none	control-unfiltered	
/	2	none	none	none	control-filtered	
/	3	0.05 M	none	none	repeat of MN-07[a]	
/	4	0.08 M	none	none	repeat of MN-08[a]	
/	5	0.16 M	none	none	2X [MnO4]	
/	6	0.05 M	0.075 M	none	base case	
/	7	0.05 M	0.075 M	none	duplicate of base case	
/	8	0.03 M	0.075 M	none	low [MnO4]	
/	9	0.05 M	0.05 M	none	low Sr	
/	10	0.03 M	0.05 M	none	low MnO4 and Sr	
/	11	0.03 M	0.05 M	0.05M Ca	Ca effect	
/	12	0.05 M	0.075 M	0.05M Ca	Ca effect	
/	13	0.05 M	0.075 M	1.5 M Na**	Na effect	
/	14	0.05 M	none	1 M H+**	CO3 effect	

** See special instruction for samples 13 and 14.
[a] Described in BNFL-TI-29953-037

The permanganate oxidation reaction generates some heat but at these low volume additions, the sample is expected to reach only about 30°C without external heating. After all of the chemical additions are complete to all of the vials, the vials (except for PR-01, control) should be heated to 50°C and held at this temperature for 4 hours. The vials should be periodically removed from the heat block and swirled to insure samples are mixed. Sample will not generate significant gas, or built up pressure at 50°C but vial caps do not need to be overly tight during heating.

Table 2. Data Sheet.

Test #	Vial ID	Vial Tare Weight, g	Number Indicates Order of Reagent Addition: 1 AN-107/OH added		2 Ca added		3 Sr added		4 MnO_4^- added		Test Complete (initial)
			target mL	actual g gross/net	target mL	actual g gross/net	target mL	actual g gross/net	target mL	actual g gross/net	
1	PR-01 set aside	24.8243	20	49.4175	0	×	0	×	0	×	SB
2	PR-02	24.9575	20	50.3622	0	×	0	×	0	×	SB
3	PR-03	24.8666	20	50.8044	0	×	0	×	1.05	51.9752	SB
4	PR-04	24.8342	20	49.7018	0	×	0	×	1.73	51.5653	SB
5	PR-05	24.9870	20	50.4443	0	×	0	×	3.80	54.5853	SB
6	PR-06	24.7558	20	50.2934	0	×	1.62	52.2358	1.05	53.3930	SB
7	PR-07	24.8320	20	50.0323	0	×	1.62	51.9513	1.05	53.1169	SB
8	PR-08	24.8983	20	50.8475	0	×	1.62	52.7592	0.61	53.4563	SB
9	PR-09	24.9962	20	50.7053	0	×	1.05	51.9557	1.05	~~53.4408~~ 53.1405	SB
10	PR-10	24.9180	20	50.1399	0	×	1.05	51.4949	0.61	52.2038	SB
11	PR-11	24.4422	20	49.8759	0.20	50.0919	1.05	51.3453	0.61	52.0323	SB
12	PR-12	24.9616	20	50.3058	0.20	50.5234	1.62	52.4478	1.05	53.6237	SB
13	PR-13	~~27.4986~~ 24.9155	20	52.0174	0	×	1.62	53.9580	1.05	55.1303	SB
14	PR-14	26.5477 ~~26.7147~~	20 AN-107 C3E3 (No [illegible])	49.7128	0	×	0	×	1.05	50.8888 *	SB 52.6887g

7 solids 31.3271

NO Heat filter.

added NaOH prior to NaOH wt after NaOH add

* Test ~~PR-14~~ — MnO_4^- added prior to NaOH — OH^- was added immediately following #

5.2.2 Record the weights (and volumes where appropriate) of all vails, samples, additions, and dilutions. After the reaction time of 4 hours at 50°C, the samples can be centrifuged to allow easier filtration prior to analytical preparation. If possible, record the volume of centrifuged solids. For the base case, (test PR-06 or PR-07 , 0.05M MnO_4^-,and 0.075 Sr) the centrifuged solids should be digested and submitted for analyses. Decant the supernate from this sample, record the weight of solids/solution remaining; the solids will be submitted "as is" for acid digestion/analysis (see Table 3 below). Note that the AN-107/OH "control - unfiltered" (PR-01) should not be heated, should not be filtered with the syringe filter, and needs to be acid digested "as is" (because it contains some solids) for analyses. The "AN-107/OH as is -

filtrate" (PR-02) will be the same "AN-107/OH" waste but treated as the other samples, i.e. heated and filtered with others samples (centrifuged then filtered the same manner as the other samples, syringe filter).

6.0 Sample Analysis

All sample dilution/digestions are to be recorded noting both volume and mass. The data for from preparation of the samples for analyses shall be recorded in a table format, or on a data sheet. The point of contact for the sample analyses from these tests is Rick Steele.

6.1 Chemical and Radiochemical Analysis

Table 3 below shows the sample analysis list. The table lists the analyses to be performed on samples generated from this test instruction.

Table 3. Samples and Their Required Analyses

Process Variable	Vial ID	Sample Type	Sample Preparation	Analysis Description[a]
caustic adjusted AN-107/OH as is	PR-01	some solids	acid digest	Sr/Am, ICP
AN-107/OH as is	PR-02	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH⁻][b]
0.05 M MnO4 only	PR-03	Filtrate	0.45 um disk/acid digest	Sr/Am,ICP
0.08 M MnO4 only	PR-04	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.16 M MnO4 only	PR-05	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.05 M MnO4 + Sr	PR-06	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH][b]
0.05 M MnO4+ Sr	PR-07	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.03 M MnO4+ Sr	PR-08	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.05 M MnO4+ Sr	PR-09	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.03 M MnO4+ Sr	PR-10	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.03 M MnO4+ Sr + Ca	PR-11	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.05 M MnO4+ Sr + Ca	PR-12	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH][b]
0.05 M MnO4+ Sr	PR-13	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
0.05 M MnO4	PR-14	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH][b]
solids from PR-06	PR-15	Centrifuge Solids	acid digest	Sr/Am, ICP

(a) Descriptions of analyses are contained in Table 4.
(b) Separate vial for [OH] analysis, filtered, but no acid digest treatment.

Table 4. Description of Analyses

Constituent	Analysis Method	PNNL Procedure No.
Americium-241, Eu isotopes	GEA	PNL-ALO-450
Strontium-90 (Yttrium-90)	Separations and Beta Counting	PNL-ALO-476/431
Hydroxide	EPA SW-846 Modified Method, 310(3)	PNL-ALO-228
Metal Ions (see Table 5 list)	ICP-AES	PNL-ALO-211/280

Table 5. Analytical Requirements for Supernate/Filtrate and Centrifuged Solids

Analyte	Centrifuged Solids Minimum Reportable Quantity microCi/gm	Supernate/Filtrate Minimum Reportable Quantity microCi/ml	Analysis Method
Strontium-90	7.01E+01	1.5E-01	Chemical Separation & Beta Count
Americium-241	1.2E-03	7.2E-04	GEA
	microgm/gm	microgm/ml	
Al	3.3E+02	7.5E+01	Acid Digestion followed by ICP-AES
Ba	6.0E+02	7.8E+01	
Ca	1.8E+02	1.5E+02	
Cd	1.1E+01	7.5E+00	
Co	3.0E+00	3.0E+01	
Cr	1.2E+02	1.5E+01	
Cu	1.8E+01	1.7E+01	
Eu	NA	NA	
Fe	1.4E+02	1.5E+02	
K	1.5E+03	2.0E+02	
La	6.0E+01	3.5E+01	
Mg	5.4E+02	1.5E+02	
Mn	3.0E+02	1.5E+02	
Mo	6.0E+00	9.0E+01	
Na	1.5E+02	7.5E+01	
Ni	1.6E+02	3.0E+01	
Pb	6.0E+02	3.0E+02	
Si	3.0E+03	1.7E+02	
Sr	3.0E+02	8.7E+01	
Ti	1.5E+02	1.7E+01	
U	6.0E+02	6.0E+02	
Zn	6.0E+00	1.65E+01	
OH-		0.05M	

7.0 Calculation and Important Information

Density of starting AN-107 sample that has cesium removed = 1.26 g/mL

Estimated density of AN-107/OH caustic adjusted to 1M = estimated 1.31 g/mL — actually 1.2639/mL

Density of 1M $NaMnO_4$ solution = 1.086 g/mL

Density of 19M NaOH solution =1.51 g/mL

Density of 1M $Ca(NO_3)_2$ solution = 1.117 g/mL (extrapolated from CRC data)

Density of 1M $Sr(NO_3)_2$ solution = 1.157 g/mL (extrapolated from CRC data)

20 mL = 26.2 grams of AN-107 caustic adjusted waste

Mass of Solutions based on above density data. Densities (and masses) need to be verified based on actual solution densities. This will be performed after solutions are prepared in Step 4.3.

		mL/20mL waste	grams/20mL waste	density
Three NaMnO4 levels	0.03 M	0.62 mL 1M NaMnO4	0.67 g 0.4M KMnO4	1.086
	0.05 M	1.05 mL 1M NaMnO4	1.14 g 0.4M KMnO4	1.086
	0.08 M	1.74 mL 1M NaMnO4	1.89 g 0.4M KMnO4	1.086
	0.16 M	3.81 mL 1M NaMnO4	4.14 g 0.4M KMnO4	1.086
one new OH level	1 M	1.11 mL 19N NaOH	1.68 g 19N NaOH	1.51
one Ca level	0.01 M	0.20 mL 1M Ca(NO3)2	0.23 g 1M Ca(NO3)2	1.12
two Sr levels	0.05 M	1.05 mL 1M Sr(NO3)2	1.22 g 1M Sr(NO3)2	1.16
	0.075 M	1.62 mL 1M Sr(NO3)2	1.88 g 1M Sr(NO3)2	1.16
NaNO	1.5 M		2.55 g of solids NaNO3	
HNO3	1 M	1.27 mL conc HNO3	1.80 g of conc HNO3	1.42

initial volume= 20 mL

test	Condition	Sr	Chemical	other	ADD in mL NaOH	Ca	Sr	NaMnO4
1	unfiltered control			0.00	0.00	0.00	0.00	0.00
2	filtered contol			0.00	0.00	0.00	0.00	0.00
3	0.05 M			0.00	0.00	0.00	0.00	1.05
4	0.08 M			0	0	0	0	1.74
5	0.16 M			0.00	0.00	0.00	0.00	3.81
6	0.05 M	0.075M		0.00	0.00	0.00	1.62	1.05
7	0.05 M	0.075M		0.00	0.00	0.00	1.62	1.05
8	0.03 M	0.075M		0.00	0.00	0.00	1.62	0.62
9	0.05 M	0.05M		0.00	0.00	0.00	1.05	1.05
10	0.03M	0.05M		0.00	0.00	0.00	1.05	0.62
11	0.03M	0.05M	0.01M	0.00	0.00	0.20	1.05	0.62
12	0.05 M	0.075M	0.01M	0.00	0.00	0.20	1.62	1.05
13	0.05 M	0.075M	NaNO3	2.55	0.00	0.00	1.62	1.05
14	0.05 M		HNO3	1.27	1.11	0.00	0.00	1.05
	volume needed				1.11	0.40	11.27	14.77

initial mass= 26.2 g

test	Condition	Sr	other	ADD g other	NaOH	Ca	Sr	NaMnO4
1	unfiltered control			0.00	0.00	0.00	0.00	0.00
2	filtered contol			0.00	0.00	0.00	0.00	0.00
3	0.05 M			0.00	0.00	0.00	0.00	1.14
4	0.08 M			0.00	0.00	0.00	0.00	1.89
5	0.16 M			0.00	0.00	0.00	0.00	4.14
6	0.05 M	0.075M		0.00	0.00	0.00	1.88	1.14
7	0.05 M	0.075M		0.00	0.00	0.00	1.88	1.14
8	0.03M	0.075M		0.00	0.00	0.00	1.88	0.67
9	0.05 M	0.05M		0.00	0.00	0.00	1.22	1.14
10	0.03M	0.05M		0.00	0.00	0.00	1.22	0.67
11	0.03M	0.05M	0.01M	0.00	0.00	0.23	1.22	0.67
12	0.05 M	0.075M	0.01M	0.00	0.00	0.23	1.88	1.14
13	0.05 M	0.075M	NaNO3	2.55	0.00	0.00	1.88	1.14
14	0.05 M		HNO3	1.80	1.68	0.00	0.00	1.14

8.0 References

Bryan, SA. 1999. "Sr/TRU Removal from AN-107, Permanganate Addition Scoping Studies." PNNL Test Plan BNFL-TI-29953-037, Pacific Northwest National Laboratory, Richland Washington.

Hallen, RT. 1999. "Sr/TRU Precipitation and Crossflow Filtration Test Plan." PNNL Test Plan No. TP-29953-013, Pacific Northwest National Laboratory, Richland Washington.

Krot, N, V Shilov, A Bessonov, N Budantseza, I Charushnikova, V Perminov, and L Astafuroza. "Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solutions by Method of Appearing Reagents." WHC-EP-0898, Institute of Physical Chemistry of the Russian Academy of Sciences.

Orth, RJ, AH Zacker, AJ Schmidt, MR Elmore, KR Elliott, GG Neuenschwander, and SR Gano. "Removal of Strontium and Transuranics from Hanford Tank Waste via Addition of Metal Cations and Chemical Oxidant – FY 1995 Test Results." PNNL-10766, Pacific Northwest National Laboratory, Richland Washington.

Preparation of 19M NaOH

19M NaOH is needed to adjust the waste to 1M OH-
This solution will be added the archived AN-107 before the optimization tests.
Record all information and observations on prep sheet or in lab notebook.

Balance number: 380-06-01-012
Balance calibration: 3-1-99 .

Makeup NaOH solution 19 M 19
use NaOH pellets/beads Aldrich reagent grade Lot # 06431MY
40 grams/mole (FW) (lot #
Tare 25 mL volumetric flas _____ grams
add 19 g NaOH flask + NaOH _____ grams
actual weight of NaOH add 18.94815 grams
add approximately 1/2 the volume of Milli-Q water and swirl to dissolve
solution/flask will get very hot, be careful. Allow to cool down.
add the other 1/2 the volume of Milli-Q water and swirl until all dissolves
Allow to cool to near room temperature, 20-25 C.
fill to volumetric line with Milli-Q water. Record total weight: 37.81147 grams
calculate actual [OH] = actual weight/40.00/volume in Liters = _____ M
calculate density of solution, weight of solution/volume = 1.5125 grams/mL
Transfer stock solution to bottle and label unique ID #

Date prepared: 5/20/99
Prepared by: JS Hall
Work Package Number: WS1702

Metal Additions: Prep of Stock Solutions

Ca, Sr, or Eu need to be added to the waste for Sr/TRU decomtamination.
These solutions will be added before the permanganate.
cord all information and observations on prep sheet or in lab notebook.

Balance number: 350-06-01-012
Balance calibration: 3-1-99

Makeup Ca(NO3)2 solution 1 M
use Ca(NO3)2*4H2O Fisher Scientific Cert. ACS
236.15 grams/mole (FW) (lot # 960308)
Tare 25 mL volumetric flask _____ grams
add 5.90375 grams Ca(NO3)2*4H2O flask + Ca(NO3)2 _____ grams
actual weight of Ca(NO3)2 added 5.90584 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
fill to volumetric line with Milli-Q water. Record total weight: 27.9226 grams
calculate actual [Ca] = actual weight/236.15/volume in Liters = _____ M
calculate density of solution, weight of solution/volume = _____ grams/mL
Transfer stock solution to bottle and label unique ID #

1.1169 g/mL

5/20/99
RT Hallen

Makeup Sr(NO3)2 solution 1 M
use Sr(NO3)2 Fisher-Scientific-Cert. ACS
211.63 grams/mole (FW) (lot # 984987)
Tare 25 mL volumetric flask _____ grams
add 5.29075 grams Sr(NO3)2 flask + Sr(NO3)2 _____ grams
actual weight of Sr(NO3)2 added 5.30386 grams
d approximately 1/2 the volume of Milli-Q water and swirl until dissolved
to volumetric line with Milli-Q water. Record total weight: 28.935 grams
calculate actual [Sr] = actual weight/211.63/volume in Liters = _____ M
calculate density of solution, weight of solution/volume = _____ grams/mL
Transfer stock solution to bottle and label unique ID #

1.1574 g/mL

Makeup Eu(NO3)3 solution 1 M
use Eu(NO3)3*6H2O
446.07 grams/mole (FW) (lot #)
Tare 25 mL volumetric flask _____ grams
add 11.15175 g Eu(NO3)3*6H2O flask + Eu(NO3)3*6H2O _____ grams
actual weight of Eu(NO3)3*6H2O add _____ grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
fill to volumetric line with Milli-Q water. Record total weight: _____ grams
calculate actual [Eu] = actual weight/446.07/volume in Liters = _____ M
calculate density of solution, weight of solution/volume = _____ grams/mL
Transfer stock solution to bottle and label unique ID #

Date prepared:
Prepared by:
Work Package Number:

Calculatations prepared by RT Hallen
Calculations checked by:

5/19/99

Preparation of Stock Permanganate Solution

Permanganate needs to be added to the waste for Sr/TRU decomtamination.
This solution will be added after any other reagents, if needed.
Record all information and observations on prep sheet or in lab notebook.
Note this is Na now!!

Balance number: 382-06-01-012
Balance calibration: 3-1-99.

Makeup stock NaMnO4 solution 1 M
use NaMnO4.1 H2O, 97+%, ACS Reagent Grade
159.94 grams/mole (FW) (lot # A010675901)
Tare 50 mL volumetric flask _____ grams
add 7.997 grams NaMnO4 flask + NaMnO4 _____ grams
actual weight of NaMnO4 added 7.9969 grams
add approximately 1/2 the volume of Milli-Q water and swirl until dissolved
~~add approximately .5 mL of 1N NaOH or 0.05mL of 10N NaOH to stabilize permanganate, 2 drops~~ do not add - already basic.
fill to volumetric line with Milli-Q water. Record total weight: 54.2840 grams
calculate actual [MnO4] = actual weight/159.94/volume in Liters = 1.00 M
calculate density of solution, weight of solution/volume = 1.0357 grams/mL
Transfer stock solution to bottle and label unique ID #

pH = 10.4 !

Date prepared: 5/20/99
Prepared by: KJ Haber
Work Package Number: W51302

APPENDIX C

Appendix C: Test Instruction TI-043

PNNL Test Instruction	Document No.: BNFL-TI-29953-043 Rev. No.: 0

Title: Sr/TRU Removal from AN-107 Archived Waste and Diluted Feed, Minimum Reagent Addition Studies

Work Location: RPL SFO SAL	**Page** 1 of 14
Author: SA Bryan	**Effective Date: New** **Supersedes Date: New**
Use Category Identification: Reference	
Identified Hazards: ___ Radiological _x_ Hazardous Materials ___ Physical Hazards ___ Hazardous Environment ___ Other:	**Required Reviewers:** _x_ Author _x_ Technical Reviewer __RPL Manager __Project Manager __RPG Quality Engineer __BNFL (not required)

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	Samuel A. Bryan	6/23/99
Technical Reviewer	Richard T. Hallen	6/23/99
SAL-RPL Representative	Rick T. Steele	6/23/99

Controlled Document

Applicability

This test instruction describes the procedure to be used for studies to determine the efficiency of the Sr/TRU removal (decontamination factor) by permanganate addition. The work described herein will be performed in the Shielded Analytical Laboratory (SAL) hot cells located in the Radiochemical Processing Laboratory (RPL). This test instruction supports the Test Plan No. 29953-013 and is a follow on of work conducted in Test Instruction No. 29953-037 and -040.

Work is to be performed by hot cell technicians under the supervision of a cognizant scientist. The cognizant scientist shall be responsible for implementation and adherence to this test instruction. This instruction is specific to:

- Sr/TRU removal by permanganate addition to envelope C; archived AN-107 (previously treated to remove Cs) and AN-107 diluted feed (remaining from leaching studies) will be used as a representative envelope C sample,
- permanganate addition and precipitation of actual wastes in RPL hot cell facilities, and
- tests performed at Battelle in the RPL, by staff in the Environmental Technology Division.

DRD Reference: none

Schedule Reference: Additional work scope not in baseline.

Justification

This activity is a study using archived AN-107 waste and actual AN-107 diluted feed to evaluate the potential of minimizing the amount of strontium and permanganate addition to achieve the necessary Sr/TRU removal (decontamination). The preferred method by BNFL, strontium and iron precipitation, has not provided the necessary performance based upon process design criteria.

Objective

The objective of this work is to optimize process conditions to obtain Sr and TRU decontamination with minimal reagent addition, and produce a precipitate that is easy to filter by cross-flow filtration.

Success Criteria

The BNFL flowsheet for AN-107 (Envelope C) requires the separation of the HLW Sr/TRU from the LLW supernate prior to incorporation into glass. BNFL in Phase 1A identified precipitation by strontium and iron addition as the preferred method for decontamination. Decontamination factors are needed to reduce Sr and TRU (primarily Am) to the low level limits. TRU/Am decontamination factors of 5 or more are needed while minimizing the addition of chemical reagents. Sr decontamination factors of greater than 10 are needed. Minimizing reagent addition will also reduce the cost of treatment.

Background

Because of the recent problem with filtration of the iron precipitates from AN-107 simulant, a series of scoping experiments were conducted to determine the ability of permanganate to obtain the necessary DF for Sr and TRU (primarily Am, ~92% of TRU on an activity basis). Permanganate has been examined as both an oxidant (decomplexing waste, solubilizing chromium, and oxidation of technetium species to pertechnetate) and a precursor to MnO_2 and/or $Mn(OH)_2$ coprecipitants via the "Method of Appearing Reagents," Krot et.al. Permanganate was found to preferentially oxidize chromium, followed by organic carbon, and lastly nitrite. In previous tests with archived AN-107, permanganate was successful in obtaining the necessary DFs for Am and TRU, but did not give adequate Sr DF (need a DF for Sr of greater than 10).

Orth et al (1995) recommended permanganate doses of 0.1M for decomplexing SY-101 type wastes where high concentrations of chromium (approximately 0.4%) partly consumed permanganate prior to organic destruction. AN-107 does not have the high chromium values in the sludge compared to SY-101. Due to lower chromium values in AN-107, permanganate was effective for TRU/Am removal at lower doses, 0.05M. Reducing the amount of permanganate added will reduce the amount of HLW waste glass produced. To increase the Sr DF, higher levels of $Sr(NO_3)_2$ we be added and the samples will be treated at a higher temperature, 50°C, for a longer period of time, 4 hours.

Spill Protection/Response

Hot cell technicians shall conduct tests in a manner to minimize the impact of a spill. In the event of a spill, the cognizant scientist shall be notified and a decision will be made to try to recover the sample or repeat the test condition.

Feed Description

The Sr/TRU removal tests will use archived AN-107 supernatant previously treated for cesium removal (Envelope C) with the free hydroxide adjusted to 1 and 0.5 M. AN-107 diluted feed left over from leaching studies will be used for the real waste tests. Approximately 100 mL of caustic adjusted, archived AN-107 (AN-107/OH) supernatant is available for these tests. At least 40 mL of archived AN-107 (C3E3) is left to prepare the samples at 0.5 M free hydroxide. Samples CL-1 and AQ-10 (40 mL each) will be combined and used as the AN-107 diluted feed.

Equipment Description

The premanganate addition tests will be conducted on a small scale, approximately 20 mL each. Appropriate glass vials will be used, such that the samples can be heated in a sample block heater to a temperature of 50°C. Some mixing/stirring of the samples after chemical addition should be provided, this may be as simple as periodic swirling the samples. Reagents will be added slowly as liquids, and stirred/mixed/swirled after each reagent is added. Experiments will require addition of two different reagents to be added in the proper sequence as detailed in the test matrix. The samples are to be heated for two hours in the sample block heater for 2 hours after the addition of each reagent.

Work Instructions

1.0 Applicability

This test instruction is to be used to perform tests for Sr/TRU removal by strontium and permanganate addition. The studies shall use approximately 100 mL of caustic adjusted, archived AN-107 (AN-107/OH), approximately 40 mL of achived AN-107 (bottle ID# C3E3), and approximately 80 mL of AN-107 diluted feed (combined CL-1 and ~~AQ~~-10 samples from Lumetta's leaching studies).

CL-2 R1 0

2.0 Supporting Documents

This test instruction is not a stand-alone document. Sr/TRU Precipitation and analytical requirements for all BNFL related work are contained in PNNL Test Plan No. BNFL-TP-29953-013. TP-29953-013 also contains an overall description of the project, ES&H compliance, emergency response, and the hazards assessment and mitigation. These are follow on studies to TI-29953-037 and TI-29953-040.

3.0 Responsible Staff

The staff responsible for executing this test plan are as follows.

- Task Manager – Rich Hallen
- SFO Manager – Randy Thornhill (Rick Steele)
- Test Scientists – Sam Bryan, Rich Hallen

- Hot Cell Technician – Vaughn Hoopes
- Radiological Control Technician

4.0 Materials, Equipment, Supplies and Reagents Needed

4.1 Materials Required

1. Eleven each 20 mL glass and plastic scintillation vials for filtered, analytical samples, pre-labeled as follows: OP-01 through OP-05, LH-06 and LH-07, and RW-08 through RW-11. And 11, 40-mL glass scintillation vials for conducting experiments, labeled 1-11, with a 20 mL volume mark on each vial.
2. A 100 mL polyethylene bottle or equivalent to use for adding NaNO3 to the caustic adjusted waste, labeled " archived AN-107 caustic adjusted to 1M plus 1.5 M sodium." A 50 mL vial/bottle to adjust C3E3 waste to 0.5M free hydroxide and additional 1.5 M sodium, labeled "archived AN-107 caustic adjusted to 0.5M plus 1.5 M sodium. A 100 mL bottle to combine AN-107 diluted feed from samples CL-I and ~~AQ-10~~ CL-2, labeled "AN-107 diluted feed combined sample."
3. 11 - disposable syringes and 0.45 micron syringe filters.
4. AN-107 wastes in SAL-cell. Archived AN-107 caustic adjusted to 1 M, archived sample from "Tc Removal Flow Studies" (Project No. 25865) bottle number C3E3, and AN-107 diluted feed from leaching studies, sample numbers CL-1 and ~~AQ-10~~ CL-2
5. heating device
6. volume measuring device, such as volumetric/ball flask, for determining the density of the AN-107 sample

4.2 Equipment

1. 100 gram balance
2. Hand held camera (if convenient)
3. Stop-watch
4. Calculator
5. Hot plate
6. Thermometer

4.3 Reagents Needed In Hot Cell (see prep sheet)

1. 2 mL of 19M NaOH (or 1 grams of NaOH pellets)
2. 10 mL of 1M $Sr(NO_3)_2$
3. 6 mL of 1M $NaMnO_4$
4. 16 grams reagent grade $NaNO_3$

4.4 Other Supplies

1. BNFL-TI-29953-043 (this test instruction)
2. Laboratory Record Book (use Red Bound, BNFL lab notebook, record number of book, BNW-13733)
3. BNFL-TP-29953-013 (Hallen 1999)

5.0 Test Instructions

The laboratory record book (LRB) shall be used to record other testing information as required by this test instruction and all test conditions not stated by this test instruction.

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 practical. Those tools that are reused should be washed and rinsed prior to reuse.

Keep all test materials in sealed containers as much as possible to prevent them from drying.

5.1 Prestart

5.1.1 Prepare solutions according to the attached preparation sheet. Calculate solution densities and record these values. All vials should be labeled and marked with the 20 mL line before they are taken into the hot cell. NOTE: Tare weigh bottle/vials with caps/lids. Keep lids on containers to minimize potential for spill, and to prevent evaporation.

For archived AN-107 caustic adjusted to 1 M OH^- plus 1.5 M sodium: Outside of the hot cell a 100 mL bottle should be marked with a line on the bottle at 80 mL and labeled "Archived AN-107 caustic adjusted to 1M OH plus 1.5M sodium." Tare the empty bottle, record tare weight. Add 10.2 grams of solid $NaNO_3$ bottle. Cap tightly for transfer into the hot cell. Based on BNFL-29953-040 – used C3E4 w 10.2 g $NaNO_3$ + 4.27 mL (6.40 g) 50% NaOH.

Tare bottle 24.1818 g, bottle + NaNO3 34.3843 g + NaOH 40.7863 g

For archived AN-107 caustic adjusted to 0.5 M OH^- plus 1.5 M sodium: Outside of the hot cell a 50 mL vial/bottle should be marked with a line at 40 mL and labeled "Archived AN-107 caustic adjusted to 0.5M OH plus 1.5M sodium." Tare the empty bottle, record tare weight. Add 5.1 grams of solid NaNO3 bottle. Add 1.68 grams of 19 M NaOH (50% by weight) (or 0.84 grams of NaOH pellets). Cap tightly for transfer into the hot cell.

Tare bottle 24.0993 g, bottle + NaNO3 29.1929 g + NaOH 30.9028 g

For AN-107 diluted feed: ~~Take a 100 mL vial/~~bottle into the hot cell for combining CL-1 and AQ-10 that is labeled AN-107 diluted feed combined sample. Not needed – used CL-1 & CL-2 combined – AQ-1 Not available –

5.1.2 Inventory materials, equipment, supplies, and reagents to ensure all required items are available. Assure that all materials have been modified for remote handling.

Record Unique ID # of reagents:

1M NaMnO4 _____.
19N NaOH 50% NaOH.
1M $Sr(NO_3)_2$ _____.

50% NaOH prepared –
Tare wt of flask 27.2047 g
Tare wt + NaOH 37.2465 g
+ NaOH + H_2O 47.2836 g
Balance # 360-06-01-040

5.1.3 Initial and date when each item is completed.

_____Review the test matrix (Table 1) in the test instructions in BNFL-TI-29953-043. Note the calculation worksheet, which gives quantities of reagents to add. Reagents can be added as volume but always record the mass added.

5.1.4 Obtain the following information:

M&TE List:

_____ Balance 1: (and Balance 2 if used)

Calib ID _____ Calib Exp Date_____

Location _____

_____ temperature reading device (thermometer or thermcouple/reader):

Calib ID _____ Calib Exp Date _____

Location _____

5.2 Operation

(Note: The sodium adjustment, caustic adjustment, and sample combining could all be completed a day in advance of the test matrix.)

used original AN-107 caustic adjusted 1M from BNFL 29953 for OP-02

5.2.1 First, 20 mL or 25.2 grams of waste (density = 1.26 g/mL) from the archived AN-107 caustic adjusted to 1 M must be transferred to vial # OP-02, record weight transferred in Table 2 below. After this is complete, transfer 80 mL or 100.8 grams of the caustic adjusted waste to the 100 mL bottle containing the NaNO3, Archived AN-107 caustic adjusted to 1 M plus 1.5 M sodium. Record data below: (If 80 mL of the caustic adjusted AN-107/OH is not available add all plus any additional "C3E3" waste as required to give 80 mL).

OP sample

C3E4 - used

Tare of bottle 40.7863 g, bottle + waste 132.1991 133.7753 g, waste added 92.9890 g

* from previous purge (Bottle + $NaNO_2$ + NaOH)

had to make up from C3E4 because not enough C3E3 available R7B

Replace cap tightly to keep from picking up CO_2 from the air. Invert bottle several times to well mix. Waste solution will warm with dissolution/dilution of the NaOH.

All solutions will have new density. If needed and after cool, a volumetric flask (ball flask) can be used to determine the new density of these solution. Record the density of the waste, and use this density to determine the weight of 20 mL of waste.

tare flask 9.3326 g, flask + waste 22.6402 g, waste mass 13.3076 g, flask volume 10.00 mL

new density of archived AN-107 1.3308 g/mL

used Sample OP-01 for density measurments - 6/5/99.

Record Hot Cell temperature 25°C

LH samples

Hydroxide and sodium adjustments must be done to the archived waste for tests LH-06 and LH-07. In the hot cell, transfer 40 mL of waste from bottle labeled "AN-107 - C3E3" to the vial/bottle labeled "archived AN-107 caustic adjusted to 0.5 M plus 1.5 M sodium (bottle containing NaOH and NaNO3). Add 40 mL or 50.4 g of waste (density =1.26 g/mL). Record tare of bottle and weight after waste added.

C3E4

Tare of bottle *30.9028 g, bottle + waste 79.5713 g, waste added 48.6685 g

* tare from previous purge (Bottle + NaOH + $NaNO_3$).

Replace cap tightly to keep from picking up CO_2 from the air. Invert bottle several times to well mix. Waste solution will warm with dissolution/dilution of the NaOH.

All solutions will have new density. If needed and after cool, a volumetric flask (ball flask) can be used to determine the new density of these solution. Record the density of the waste, and use this density to determine the weight of 20 mL of waste.

tare flask 9.4071 g, flask + waste 22.5401 g, waste mass 13.1330 g, flask volume 10.00 mL

LH-6 sample used for density measurment - 6/25/99 - after heating & centrifuging - sample shaken prior to density measurments

new density of archived AN-107 1.3133 g/mL

Record Hot Cell temperature 25 °C

RW Sept

For RW-08 to RW-11: AN-107 diluted feed from samples CL-1 and AQ-10 need to be combined. Record the tare weight vial/bottle used to combine these samples. Then add each sample and record the weights. (density should be 1.36 g/mL based on analytical report BNFL-RPT-003 Rev. 0)

Combined CL-1 into CL-2 container — no tare wts of container were available — or needed.

Tare of vial _____ g, vial + CL-1 _____ g, vial + CL-1 + AQ-10 _____ g

weight of CL-1 added _____ g and weight of AQ-10 added _____ g

Replace cap tightly to keep from picking up CO_2 from the air. Invert bottle several times to well mix.

The density should be 1.36 g/mL based on analytical report. If needed and after cool, a volumetric flask (ball flask) can be used to determine the new density of these solution. Record the density of the waste, and use this density to determine the weight of 20 mL of waste.

tare flask 12.8422 g, flask + waste 26.7627 g, waste mass 13.9205 g, flask volume 10.000 mL

new density of archived AN-107 1.392 g/mL (CL-2 - CL-1 mix)

Record Hot Cell temperature 25 °C

Review the test matrix shown below, Table 1. Record data in Table 2. Note to check each activity when complete. This should be done and verified by the cognizant scientist.

Table 1. Test Matrix.

Check complete	Test #	Test ID #	Target [MnO4]	Target [Sr]	AN-107 Waste ID	Comment	Scientis Verification
✓	1	OP-01	none	none	Archived 1M OH + 1.5M Na	control-filtered	
✓	2	OP-02	0.03	0.05	Archived, 1M OH	Repeat of PR-10	
✓	3	OP-03	0.03	0.05	Archived 1M OH + 1.5M Na	low Sr and MnO4	
✓	4	OP-04	0.03	0.05	Archived 1M OH + 1.5M Na	Duplicate of 3	
✓	5	OP-05	0.03	0.05	Archived 1M OH + 1.5M Na	Reverse addition	
✓	6	LH-06	none	none	Archived 0.5M OH + 1.5M Na	control-filtered	
✓	7	LH-07	0.03	0.05	Archived 0.5M OH + 1.5M Na	Low hydroxide	
✓	8	RW-08	none	none	Diluted feed	control-filtered	
✓	9	RW-09	0.03	0.05	Diluted feed	low Sr and MnO4	
✓	10	RW-10	0.03	0.05	Diluted feed	Duplicate of 9	
	11	RW-11	0.05	0.075	Diluted feed	High Sr and MnO4	

The reaction conditions are much different for these tests. The samples are to be heated to 50°C after each chemical addition is complete and held at this temperature for 2 hours. After the first 2 hours of heating the samples should be removed from the heater block and allowed to cool so weighing will be easier (less balance drift). Then add the second reagent and return vials to the heating block for an additional 2 hours. The vials should be periodically removed from the heat block and swirled to insure samples are mixed. Sample will not generate significant gas, or built up pressure at 50°C but vial caps do not need to be overly tight during heating.

1st heating - Started heating at 6:50 am 6/24/99 - Reached 50°C @ 7:05 AM Taken off heat at 9:55 am

Addn's of 1, 2, 3 (except OP-5) Then heated @ 50°C for 2 hrs (See Notes #1 & #2 below)

2nd heating started @ 10:10 after addn of #4 Reagent

(Exception #OP-05 addn of MnO4 both #3 prior to 2nd heating

Table 2. Data Sheet.

Test #	Vial ID	Vial Tare Weight, g	Number Indicates Order of Reagent Addition								Test Complete (initial)
			1		2		3		4		
			AN-107 waste added		MnO4- Added		Sr added		MnO_4^- added		
			target mL	actual g gross/net	Target ML	Actual g gross/net	arget mL	actual g gross/net	target mL	actual g gross/net	
1	OP-01	25.0405	20	52.6433	0	X	0	X	0	X	1 filter SATS
2	OP-02	24.8722	20	51.9494	0	X	1.05	53.1895	0.61	53.8377	SATS very easy to filter
3	OP-03	25.0317	20	51.8560	0	X	1.05	53.0909	0.61	53.7956	1 filter SATS filtered easy
4	OP-04	24.9225	20	51.9486	0	X	1.05	53.1779	0.61	53.8559	SATS filtered easy
5	OP-05	25.0383	20	52.9514	0.61	(*1) 53.6391	1.05	(*2) 54.5314	0	X	SATS 2 filters Sat filtered total
6	LH-06	25.1049	20	51.8138	0	X	0	X	0	X	SATS 1 filter
7	LH-07	25.0140	20	52.8324	0	X	1.05	54.0808	0.61	54.7626	SATS 1 filter - hard to filter
8	RW-08	25.2879	20	53.3228	0	X	0	X	0	X	SATS 3 filters each
9	RW-09	25.0788	20	53.3787	0	X	1.05	54.6123	0.61	55.2629	SATS 3 filters used
10	RW-10	25.0473	20	53.2996	0	X	1.05	54.5104	0.61	55.1658	SATS 2 filters
11	RW-11	24.9541	20	52.9673	0	X	1.62	54.4343	1.05	55.5941	SAT 2 filters

From OP-02 (*3) AN-107/OH-1M mix

1.5M HNO3

Mixture

heated 2 hrs @ 50°C

heated 2 hrs @ 50°C

*1 - MnO_4^- added to OP-5 prior to 1st heating - heated ~ 2 hrs @ 50°C

*2 - Addn of 1.05 mL $Sr(NO_3)_2$ after 1st heating - prior to 2nd heating -

*3 - AN-107/OH-1M used from BNFL-29953-040 prep - for OP-02 test.

5.2.2 Record the weights (and volumes where appropriate) of all vials, samples, additions, and dilutions. After the reagent additions and heating are complete, the samples can be centrifuged to allow easier filtration prior to analytical preparation. If possible, record the volume of centrifuged solids. Note that there is no "control - unfiltered" for these studies. The control-filtered (OP-01, LH-06, and RW-08) will be treated as the other samples, i.e. heated and filtered with others samples (centrifuged then filtered the same manner as the other samples, syringe filter).

#5 Very hard to filter. used 2 filters + still didn't filter All.
#2 Very Easy #7 hard to filter

RW-9, 10, 11 - had a light layer of ppt at bottom of vessel after centrifuging to a dark thick ~ 20% by volume layer above.

6.0 Sample Analysis

All sample dilution/digestions are to be recorded noting both volume and mass. The data for from preparation of the samples for analyses shall be recorded in a table format, or on a data sheet. The point of contact for the sample analyses from these tests is Rick Steele.

1 & 6 centrifuged/much easier than 8-11.
Filtered fast

6.1 Chemical and Radiochemical Analysis

Table 3 below shows the sample analysis list. The table lists the analyses to be performed on samples generated from this test instruction.

Table 3. Samples and Their Required Analyses

Process Variable	Vial ID	Sample Type	Sample Preparation	Analysis Description[a]
1M caustic adjusted AN-107 plus 1.5M Na	OP-01	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
Repeat of PR-10 (no Na)	OP-02	Filtrate	0.45 um disk/acid digest	Sr/Am
Low Sr and MnO4	OP-03	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP
Duplicate of OP-03	OP-04	Filtrate	0.45 um disk/acid digest	Sr/Am
Reverse addition	OP-05	Filtrate	0.45 um disk/acid digest	Sr/Am
0.05M caustic & 1.5M Na	LH-06	Filtrate	0.45 um disk/acid digest	Sr/Am
Low Sr and MnO4	LH-07	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH] [b]
Diluted Feed Combined	RW-08	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH] [b]
Low Sr and MnO4	RW-09	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH] [b]
Duplicate of RW-09	RW-10	Filtrate	0.45 um disk/acid digest	Sr/Am
High Sr and MnO4	RW-11	Filtrate	0.45 um disk/acid digest	Sr/Am, ICP, [OH] [b]

(a) Descriptions of analyses are contained in Table 4.
(b) Separate vial for [OH] analysis, filtered, but no acid digest treatment.

Table 4. Description of Analyses

Constituent	Analysis Method	PNNL Procedure No.
Americium-241, Eu isotopes	GEA	PNL-ALO-450
Strontium-90 (Yttrium-90)	Separations and Beta Counting	PNL-ALO-476/431
Hydroxide	EPA SW-846 Modified Method, 310(3)	PNL-ALO-228
Metal Ions (see Table 5 list)	ICP-AES	PNL-ALO-211/280

Table 5. Analytical Requirements for Supernate/Filtrate and Centrifuged Solids

Analyte	Centrifuged Solids Minimum Reportable Quantity microCi/gm	Supernate/Filtrate Minimum Reportable Quantity microCi/ml	Analysis Method
Strontium-90	7.01E+01	1.5E-01	Chemical Separation & Beta Count
Americium-241	1.2E-03	7.2E-04	GEA
	microgm/gm	microgm/ml	
Al	3.3E+02	7.5E+01	Acid Digestion followed by ICP-AES
Ba	6.0E+02	7.8E+01	
Ca	1.8E+02	1.5E+02	
Cd	1.1E+01	7.5E+00	
Co	3.0E+00	3.0E+01	
Cr	1.2E+02	1.5E+01	
Cu	1.8E+01	1.7E+01	
Eu	NA	NA	
Fe	1.4E+02	1.5E+02	
K	1.5E+03	2.0E+02	
La	6.0E+01	3.5E+01	
Mg	5.4E+02	1.5E+02	
Mn	3.0E+02	1.5E+02	
Mo	6.0E+00	9.0E+01	
Na	1.5E+02	7.5E+01	
Ni	1.6E+02	3.0E+01	
Pb	6.0E+02	3.0E+02	
Si	3.0E+03	1.7E+02	
Sr	3.0E+02	8.7E+01	
Ti	1.5E+02	1.7E+01	
U	6.0E+02	6.0E+02	
Zn	6.0E+00	1.65E+01	
OH-		0.05M	

7.0 Calculation and Important Information

Density of starting AN-107 sample from bottle "C3E3" that has cesium removed = 1.26 g/mL

Density of AN-107/OH caustic adjusted to 1M = 1.26 g/mL

Density of AN-107 diluted feed combined "CL-1+AQ-10" = estimated 1.36 g/mL

Density of 1M $NaMnO_4$ solution = 1.086 g/mL

Density of 19M NaOH solution (50% by weight) =1.51 g/mL

Density of 1M $Sr(NO_3)_2$ solution = 1.157 g/mL (extrapolated from CRC data)

20 mL = 25.2 grams of AN-107 caustic adjusted waste

Mass of Solutions based on above density data. Densities (and masses) need to be verified based on actual solution densities. This will be performed after solutions are prepared in Step 4.3.

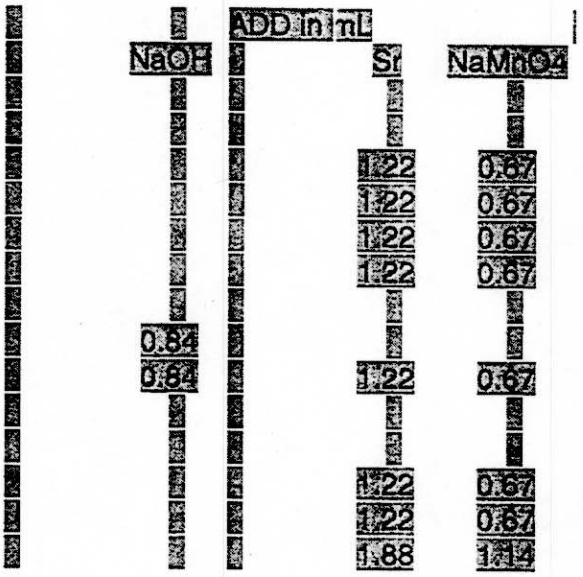
		mL/20mL waste	grams/20mL waste	density
Two NaMnO4 levels	0.03 M	0.62 mL 1M NaMnO4	0.67 g 1M NaMnO4	1.086
	0.05 M	1.05 mL 1M NaMnO4	1.14 g 1M NaMnO4	1.086
one new OH level	0.5 M	0.56 mL 19N NaOH	0.84 g 19N NaOH	1.51
two Sr levels	0.05 M	1.05 mL 1M Sr(NO3)2	1.22 g 1M Sr(NO3)2	1.16
	0.075 M	1.62 mL 1M Sr(NO3)2	1.88 g 1M Sr(NO3)2	1.16
NaNO3	1.5 M		2.55 g of solids NaNO3	

initial volume= 20 mL

test	sample ID#	Condition	[Sr]	[MnO4]	NaOH	ADD in mL Sr	NaMnO4
	OP = optimization						
1	OP-01	filtered control					
2	OP-02	repeat of PR-10	0.05M	0.03M		1.05	0.62
3	OP-03	low Sr and MnO4	0.05M	0.03M		1.05	0.62
4	OP-04	duplicate	0.05M	0.03M		1.05	0.62
5	OP-05	reverse addition	0.05M	0.03M		1.05	0.62
	LH =low hydroxide	0.5 M hydroxide					
6	LH-06	filtered control			0.55		
7	LH-07	0.03 M	0.05M	0.03M	0.55	1.05	0.62
	RW = real waste	diluted feed					
8	RW-08	filtered control					
9	RW-09	0.03M	0.05M	0.03M		1.05	0.62
10	RW-10	0.03M	0.05M	0.03M		1.05	0.62
11	RW-11	0.05 M	0.075M	0.05M		1.62	1.05
		volume needed			1.11	9.0	5.4

initial mass = 20 * density

test	sample ID#	Condition	[Sr]	[MnO4]
	OP = optimization			
1	OP-01	filtered control		
2	OP-02	repeat of PR-10	0.05M	0.03M
3	OP-03	low Sr and MnO4	0.05M	0.03M
4	OP-04	duplicate	0.05M	0.03M
5	OP-05	reverse addition	0.05M	0.03M
	LH =low hydroxide	0.5 M hydroxide		
6	LH-06	filtered control		
7	LH-07	0.03 M	0.05M	0.03M
	RW = real waste	diluted feed		
8	RW-08	filtered control		
9	RW-09	0.03M	0.05M	0.03M
10	RW-10	0.03M	0.05M	0.03M
11	RW-11	0.05 M	0.075M	0.05M



8.0 References

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Krot, N, V Shilov, A Bessonov, N Budantseza, I Charushnikova, V Perminov, and L Astafuroza. "Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solutions by Method of Appearing Reagents." WHC-EP-0898, Institute of Physical Chemistry of the Russian Academy of Sciences.

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APPENDIX D

Appendix D: Analytical Data

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

Project: 29953
Client: S. Bryan

ACL Number(s): 99-1595 through 99-1606

Client ID: "MN-01" through "MN-12"

ASR Number: 5345

Total Samples: 12

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

Analyst: J. J. Wagner

Analysis Date (Filename): 4-27-99 (A0525)

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

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

Jerry Wagner 5-3-99
Reviewed by

MW Thu 5-3-99
Concur

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

Twelve radioactive liquid samples, MN-01 through MN-12, were analyzed by ICPAES after preparation by the Sample Receiving and Preparation Laboratory (SRPL) using PNNL-ALO-128 Acid Digestion procedure. One ml of aqueous sample (also weighed) was digested and diluted to a final volume of 25 ml. Additional dilution, up to 30 fold, was necessary to quantify Mn and Na. All measurement results reported have been corrected for preparation and analytical dilution. Analytes of interest (ASR 5345) include Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Si, Ti, U, and Zn.

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

Five fold serial dilution:

(Solid samples)	--
(Aqueous samples)	All results are within tolerance limit of ≤ 10% after correcting for dilution.

Duplicate RPD (Relative Percent Difference):

(Solid samples)	--
(Aqueous samples)	No duplicate samples were prepared due to limit sample volume available.

Post-Spiked Samples (Group A):

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

Post-Spiked Samples (Group B):

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

Blank Spike:

(Solid samples)	--
(Aqueous samples)	A blank spike was not prepared.

Matrix Spiked Sample:

(Solid samples) --

(Aqueous samples) A matrix spike was not prepared due to limit sample volume available.

Quality Control Check Standards:

Concentration of all analytes of interest, with one exception, was recovered within tolerance of ± 10% accuracy in the standards: QC_MCVA, QC_MCVB, and QC_SSTMCV.

Silicon in QC_SSTMCV check standard measured high (+14%) one time and only +4% a second time. However, all Si concentrations measured in QC_MCVA were within tolerance. The concentration of Si in both check standards is similar in concentration. Therefore, Si measurements through out the analysis are assumed accurate.

High Calibration Standard Check:

Verification of the high-end calibration concentration for all analytes of interest was within tolerance of ± 5% accuracy, including Na at 1000 ug/ml.

Process Blank:

(Solid samples) --

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

Laboratory Control Standard:

(Solid samples) --

(Aqueous samples) LCS not prepared.

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

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

Comments:

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

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

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

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

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

FINAL REPORT

The attached report is sent for **final distribution** to the client.

Status these tests as sent to client -

ACL Numbers: (99-1595)-(99-016006)

ASR Number: 5345

Tests: ICP Report – REVISED

File in Project File -

Project Number: 29953 or ED Work Order: _____

or __ ACL Waste File, or P.E. File: _____

Distribution -

RT HALLEN
Date 9/8/99
Route _____
File TI-037
Copy _____

Send To	BY FAX	Send REPORT	Send DATA	Send SUPPORT	MSIN, Address, Fax Number (as req'd)
Sam Bryan		✓			
Rich Hallen		✓			

__ Special distribution instructions are attached.

Project Manager -

Signature: _____ Date: _____

Return copy of this coversheet to: _____

For LSO Use Only

Sent to client by: _____ Date: _____

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

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	25.0 / 99-1595-PB / Process Blank #1 / 4/27/99 / ug/g	19.7 / 99-1595 / MN-01 / 4/27/99 / ug/g	19.7 / 99-1596 / MN-02 / 4/27/99 / ug/g	20.0 / 99-1597 / MN-03 / 4/27/99 / ug/g	20.2 / 99-1598 / MN-04 / 4/27/99 / ug/g
0.015	Ag	--	--	--	--	--
0.060	Al	[7.2]	147	148	115	112
0.080	As	--	[1.7]	[1.6]	--	--
0.050	B	47.3	57.5	61.6	43.9	61.8
0.010	Ba	--	[1.5]	[1.5]	--	--
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	[3.6]	247	250	226	222
0.015	Cd	--	28.4	28.7	26.0	25.6
0.100	Ce	--	[11]	[11]	--	--
0.025	Co	--	[2.2]	[2.2]	[2.0]	[2.0]
0.020	Cr	--	62.8	62.4	36.8	37.3
0.015	Cu	--	12.9	13.1	11.9	11.6
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	--	543	517	9.04	28.6
2.000	K	--	696	702	1,580	1,750
0.025	La	--	13.1	13.2	7.63	7.33
0.005	Li	--	[0.28]	[0.25]	[0.17]	[0.23]
0.100	Mg	--	--	--	--	--
0.005	Mn	--	66.0	60.3	59.6	71.8
0.030	Mo	--	16.2	16.3	14.8	14.7
0.100	Na	55.1	90,300	89,700	84,600	82,200
0.100	Nd	--	37.2	36.8	[13]	[13]
0.030	Ni	--	236	238	218	216
0.100	P	--	211	212	188	185
0.060	Pb	--	153	152	103	101
0.300	Pd	--	[17]	[17]	--	--
0.300	Rh	--	--	--	--	--
0.075	Ru	--	16.9	16.9	[15]	[15]
0.050	Sb	--	--	--	--	--
0.050	Se	--	[1.5]	[1.4]	[1.3]	[1.5]
0.100	Si	75.1	81.4	94.7	60.4	86.4
1.000	Sn	--	--	--	--	--
0.005	Sr	--	1.23	1.24	[0.85]	[0.81]
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	--	1.83	1.70	[0.11]	[0.19]
0.250	Tl	--	--	--	--	--
2.000	U	--	[44]	[42]	--	--
0.015	V	--	--	--	--	--
0.500	W	--	[76]	[77]	[67]	[65]
0.010	Y	--	3.26	3.23	[1.5]	[1.5]
0.020	Zn	--	7.91	8.05	5.42	4.93
0.025	Zr	--	25.1	24.5	[4.2]	[4.9]

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

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

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

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

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	20.0 / 99-1599 / MN-05 / 4/27/99 / ug/g	20.4 / 99-1600 / MN-06 / 4/27/99 / ug/g	25.0 / 99-1601-PB @1 / Process Blank #2 / 4/27/99 / ug/g	19.9 / 99-1601 / MN-07 / 4/27/99 / ug/g	20.2 / 99-1602 / MN-08 / 4/27/99 / ug/g
0.015	Ag	–	–	–	–	–
0.060	Al	121	104	[4.6]	108	103
0.080	As	–	–	–	–	–
0.050	B	58.9	48.2	52.3	63.1	44.0
0.010	Ba	[0.30]	–	–	–	–
0.010	Be	–	–	–	–	–
0.100	Bi	–	–	–	–	–
0.100	Ca	232	213	[3.4]	197	187
0.015	Cd	26.7	24.6	–	23.3	22.0
0.100	Ce	[2.6]	–	–	–	–
0.025	Co	[2.1]	[1.9]	–	[1.8]	[1.7]
0.020	Cr	41.8	34.4	–	30.7	30.7
0.015	Cu	12.2	11.2	–	10.5	9.94
0.050	Dy	–	–	–	–	–
0.100	Eu	–	–	–	–	–
0.025	Fe	106	5.76	–	15.3	8.71
2.000	K	1,270	2,150	–	1,500	2,030
0.025	La	8.99	5.92	–	[1.1]	[0.85]
0.005	Li	[0.22]	[0.23]	–	[0.23]	[0.27]
0.100	Mg	–	–	–	–	–
0.005	Mn	60.3	50.6	–	33.4	20.7
.030	Mo	15.3	14.1	–	13.2	12.6
.100	Na	85,800	80,700	61.1	93,700	87,700
0.100	Nd	[19]	[9.2]	–	[3.2]	[2.4]
0.030	Ni	224	207	–	193	183
0.100	P	194	176	–	171	162
0.060	Pb	114	90.6	–	72.6	62.5
0.300	Pd	[7.8]	–	–	–	–
0.300	Rh	–	–	–	–	–
0.075	Ru	15.3	[14]	–	[13]	[13]
0.050	Sb	–	–	–	–	–
0.050	Se	[1.4]	[1.4]	–	[1.4]	[1.4]
0.100	Si	84.2	63.9	86.6	115	72.2
1.000	Sn	–	–	–	–	–
0.005	Sr	[0.95]	[0.67]	–	[0.57]	[0.47]
0.500	Te	–	–	–	–	–
0.800	Th	–	–	–	–	–
0.005	Ti	[0.41]	[0.11]	–	[0.16]	[0.14]
0.250	Tl	–	–	–	–	–
2.000	U	–	–	–	–	–
0.015	V	–	–	–	–	–
0.500	W	[68]	[61]	–	[61]	[58]
0.010	Y	[1.9]	[1.2]	–	[0.71]	[0.59]
0.020	Zn	5.59	4.69	–	4.22	4.12
0.025	Zr	8.45	[3.4]	–	[3.4]	[2.6]

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.
2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.
3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

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

Det. Limit (ug/mL)	Multiplier= ALO#= Client ID= Run Date= (Analyte)	20.4 99-1603 MN-09 4/27/99 ug/g	20.4 99-1604 MN-10 4/27/99 ug/g	20.3 99-1605 MN-11 4/27/99 ug/g	20.0 99-1606 MN-12 4/27/99 ug/g	
0.015	Ag	--	--	--	[0.63]	--
0.060	Al	104	112	102	179	--
0.080	As	--	--	[6.9]	[3.4]	--
0.050	B	60.0	45.9	57.6	60.5	--
0.010	Ba	--	--	--	3.96	--
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	665	182	212	235	--
0.015	Cd	24.2	25.2	25.6	26.8	--
0.100	Ce	--	--	--	28.4	--
0.025	Co	[1.9]	[1.9]	[2.0]	[2.2]	--
0.020	Cr	33.5	36.1	36.7	97.5	--
0.015	Cu	11.0	11.4	11.6	12.8	--
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	450	--	--
0.025	Fe	7.05	23.0	15.3	1,400	--
2.000	K	1,570	1,600	1,610	1,440	--
0.025	La	[1.8]	[4.7]	8.82	20.5	--
0.005	Li	[0.25]	[0.15]	[0.17]	[0.35]	--
0.100	Mg	--	--	--	--	--
0.005	Mn	13.9	50.0	159	4,100	--
0.030	Mo	13.9	14.4	14.6	15.2	--
0.100	Na	80,100	83,200	82,500	87,900	--
0.100	Nd	[3.8]	[9.4]	20.7	73.8	--
0.030	Ni	203	210	214	218	--
0.100	P	150	179	162	206	--
0.060	Pb	52.9	98.8	108	211	--
0.300	Pd	--	--	[6.6]	[33]	--
0.300	Rh	--	--	--	--	--
0.075	Ru	[14]	[14]	[14]	17.7	--
0.050	Sb	--	--	--	[1.4]	--
0.050	Se	[1.5]	[1.5]	[1.3]	[5.6]	--
0.100	Si	96.6	61.1	89.6	97.6	--
1.000	Sn	--	--	--	--	--
0.005	Sr	[0.18]	125	[0.67]	1.70	--
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	[19]	--
0.005	Ti	[0.14]	[0.16]	[0.12]	4.58	--
0.250	Tl	--	--	--	--	--
2.000	U	--	--	--	[54]	--
0.015	V	--	--	--	[0.71]	--
0.500	W	[62]	[63]	[61]	[77]	--
0.010	Y	[1.1]	[1.4]	[1.9]	5.85	--
0.020	Zn	[4.0]	5.12	5.04	11.6	--
0.025	Zr	[4.7]	[4.6]	5.72	57.9	--

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.
2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.
3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Battelle Pacific Northwest Laboratories
Analytical Chemistry Laboratory

EXHIBIT I
PAGE 1 of 1

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

Client name: Sam Bryan
Work Auth. Doc (WAD): ASR-5345
Tank/Core/Project:
Special Instructions:

Work package number: WS1300
Project number:
PNL QA plan:
PNL Impact level:
Prop. lab (SAL/SRPL/other):
Preparation batch number:

	ACL Sample ID	ACL order number or Client sample ID	Vial Identifier	Sample Volume / 1ml Sample Weight	Spike added Volume (ml)	Empty Vial Weight (g)	Final solution Volume (ml)	Process Factor (1)	Full Vial Weight/gms.
1	99-1595	MN-01	1	1ml. = 1.2700g.		24.7928	25 mls		50.7436
2	1596	-02	2	1.2664g.		24.8498			51.0310
3	1597	-03	3	1.2481g.		24.9224			51.2476
4	1598	-04	4	1.2348g.		25.1528			51.4983
5	1599	-05	5	1.2494g.		25.0280			51.7108
6	1600	-06	6	1.2231g.		24.7971			51.0970
7	PB-1595	Reagent Blank	7	—		25.0042			51.0026
8	99-1601	MN-07	8	1ml. = 1.2552g.		24.9808			51.4040
9	1602	-08	9	1.2377g.		24.8530			51.0881
10	1603	-09	10	1.2283g.		25.0884			51.6511
11	1604	-10	11	1.2273g.		24.8348			51.0524
12	1605	-11	12	1.2297g.		25.0337			51.5761
13	1606	-12	13	1.2484g.		24.8739			51.1554
14	PB-1601	Reagent Blank	14	—		25.0068			51.4313

Analyst's sample preparation comments: NOTE: A one ml. sample was diluted to ~20 mls with DI-H2O then digested per PNL-ALO-128. The final solution was taken to 25 mls then weighed. These samples were processed in 2 batches; therefore, there are two process blanks.

Pipette # 288618 @ 1ml - 22°C
0.9991
1.0044
1.0043
1.0068
1.0102

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

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

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

Analyst/Date: Lori P. Darnell 4-28-98 Reviewer/Date: Should be 99

Rev. 2.0 7-28-95 JMR

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

99-1595
8/10/1999

Client : S. Bryan

Cognizant Scientist: L R Greenwood Date : 8/10/99

Concur : C Soderquist Date : 8-10-99

ALO ID Client ID	Density g/ml
99-1595 Mn-01	1.2700
99-1596 Mn-02	1.2664
99-1597 Mn-03	1.2481
99-1598 Mn-04	1.2348
99-1599 Mn-05	1.2494
99-1600 Mn-06	1.2331
99-1601 Mn-07	1.2552
99-1602 Mn-08	1.2377
99-1603 Mn-09	1.2283
99-1604 Mn-10	1.2273
99-1605 Mn-11	1.2297
99-1606 Mn-12	1.2484

RT Hallen
RT HALLEN
Date 8/23/99
Route
File TI-037
Copy

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

99-1595
4/30/99

Client : S. Bryan

Cognizant Scientist: L R Greenwood Date : 4/30/99

Concur : T Trang-Le Date : 4/30/99

Measured Activities (uCi/g)

ALO ID Client ID	Sr-90 Error %
99-1595 PB Process Blank	2.29E-3 6%
99-1595 Mn-01	3.63E+1 3%
99-1596 Mn-02	3.62E+1 3%
99-1597 Mn-03	2.47E+1 3%
99-1598 Mn-04	2.36E+1 3%
99-1599 Mn-05	2.77E+1 3%
99-1600 Mn-06	1.78E+1 3%
99-1601 PB Process Blank	<2.E-4
99-1601 Mn-07	1.69E+1 3%
99-1602 Mn-08	1.29E+1 3%
99-1602 Rep Mn-08	1.24E+1 3%
99-1603 Mn-09	3.35E+0 3%
99-1604 Mn-10	9.69E+0 3%
99-1605 Mn-11	1.86E+1 3%
99-1606 Mn-12	5.09E+1 3%
Matrix Spike	127%
Blank Spike	96%
Blank	<2.E-4

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

99-1595
4/30/99

Client : S. Bryan

Cognizant Scientist: [signature] Date : 4/30/99

Concur : [signature] Date : 4/30/99

Total Hydroxide Concentration - PNL-ALO-228

ALO ID Client ID	OH^- Molarity	+/- 1 σ
99-1596 Mn-02	0.9954	+/-0.084
99-1596 Dup Mn-02	0.9872	+/-0.084
Average	0.9913	+/-0.059
99-1597 Mn-03	0.9252	+/-0.084
99-1597 Dup Mn-03	0.9397	+/-0.084
Average	0.9324	+/-0.059
Standard 0.1021 M NaOH	0.1031	

$CO_3^{=}$ - request rerun on autotitrator

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

99-1595
4/28/99

Client : S. Bryan

Cognizant Scientist: L R Greenwood Date : 4/28/99

Concur : T Trang-Le Date : 4/28/99

Measured Activities (uCi/g)

ALO ID Client ID	Co-60 Error %	Cs-137 Error %	Eu-154 Error %	Eu-155 Error %	Am-241 Error %
99-1595 PB Process Blank	<3.E-5	<3.E-5	<6.E-5	<7.E-5	<9.E-5
99-1595 Mn-01	6.63E-2 2%	1.96E-2 3%	2.62E-1 1%	1.91E-1 3%	2.40E-1 7%
99-1596 Mn-02	6.55E-2 2%	1.80E-2 4%	2.51E-1 1%	1.84E-1 3%	2.21E-1 7%
99-1597 Mn-03	5.99E-2 2%	1.52E-2 4%	5.94E-2 2%	4.47E-2 5%	4.13E-2 10%
99-1598 Mn-04	5.98E-2 2%	1.50E-2 4%	6.33E-2 2%	4.45E-2 4%	4.68E-2 10%
99-1599 Mn-05	6.10E-2 2%	1.60E-2 4%	1.01E-1 2%	7.78E-2 4%	9.56E-2 8%
99-1600 Mn-06	5.61E-2 2%	1.47E-2 3%	4.14E-2 2%	2.88E-2 6%	2.61E-2 13%
99-1601 PB Process Blank	<5.E-6	<6.E-6	<2.E-5	<2.E-5	<3.E-5
99-1601 Mn-07	5.27E-2 2%	1.40E-2 3%	2.84E-2 2%	2.02E-2 6%	1.19E-2 14%
99-1602 Mn-08	5.07E-2 2%	1.32E-2 3%	2.13E-2 3%	1.51E-2 6%	8.28E-3 16%
99-1603 Mn-09	5.61E-2 2%	1.43E-2 3%	3.44E-2 2%	2.48E-2 4%	1.34E-2 9%
99-1604 Mn-10	5.71E-2 2%	1.54E-2 3%	5.01E-2 2%	3.80E-2 4%	3.67E-2 6%
99-1605 Mn-11	5.74E-2 2%	1.53E-2 3%	9.96E-2 2%	7.41E-2 4%	9.09E-2 4%
99-1606 Mn-12	6.15E-2 2%	2.39E-2 4%	5.72E-1 1%	4.20E-1 3%	5.35E-1 3%

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

99-1595
4/27/99

Client : S. Bryan

Cognizant Scientist: L R Livermore Date : 4/27/99

Concur : T Trang-Le Date : 4/27/99

Measured Activities (uCi/g)

ALO ID Client ID	Alpha Error %
99-1595 PB Process Blank	<4.E-5
99-1595 Mn-01	2.63E-1 3%
99-1595 DUP Mn-01	2.60E-1 3%
RPD	1%
99-1596 Mn-02	2.44E-1 3%
99-1597 Mn-03	5.07E-2 6%
99-1598 Mn-04	4.68E-2 7%
99-1599 Mn-05	8.88E-2 5%
99-1600 Mn-06	2.81E-2 8%
99-1601 PB Process Blank	<4.E-5
99-1601 Mn-07	1.24E-2 13%
99-1602 Mn-08	5.69E-3 22%
99-1603 Mn-09	1.32E-2 14%
99-1604 Mn-10	3.73E-2 7%
99-1605 Mn-11	8.92E-2 5%
99-1606 Mn-12	5.89E-1 2%
Matrix Spike	102%
Blank Spike	103%
Blank	<5.E-5

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

ASR # 5345

File: L:\radchem\hydroxide\asr5345
Analysis Date: 5/18/99
Print Date: 5/19/99

Hydroxide and Alkalinity Determination
Governing Procedures: PNL-ALO-228: Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates
and Operation of Brinkman 636 Auto-Titrator
Equip # WB76843
Lab Loc. 525

Titrant	Molarity
HCl	0.2034

							CO3					HCO3			
							1st Equivalence Point					2nd Equivalence Point			
RPG #	Sample ID		Sample Volume (mL)	Sample Wt. (g)	Density g/mL	Initial pH reading	Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD	Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
99-1596	MN-02		0.500	0.6291	1.258	11.038	2.472	7.769	0.503	1.01		off curve	na		
99-1596D	MN-02	Replicate	0.300	0.3832	1.277	10.780	1.463	7.793	0.298	0.99	1.37%	2.897	4.725	0.292	0.97
99-1596D	MN-02	Replicate	0.300	0.3828	1.276	10.886	1.491	7.862	0.303	1.01	1.90%	2.977	4.697	0.302	1.01
99-1597	MN-03		0.300	0.3758	1.253	10.849	1.374	7.815	0.279	0.93		2.739	4.714	0.278	0.93
99-1597D	MN-03	Replicate	0.300	0.3741	1.247	10.854	1.369	7.803	0.278	0.93	0.36%	2.734	4.714	0.278	0.93
RB - 1596	Reagent Blank			5.00			No inflection point		na						
PB-1596	Process Blank			5.00			No inflection point		na						
									% Recovered						
Standard 1	0.1018 N NaOH		5.000			11.552	2.518	7.849	0.102	100.6%					
Standard 2	0.1018 N NaOH		5.000			11.342	2.528	7.852	0.103	101%					

Analyst: [signature] 5/19/99
Reviewer: [signature] 5/19/99

Performance checks

		Vol.	Wt.
Balance #	360--01-06-036		
Pipet #	H30973	5.0	4.9887
	C40043	0.5	0.49954
	C40043	0.3	0.30014

Prep record on 0.2034 M HCl is on following page.

Chem Rec_51a

Prep date: 4/18/99

Preparation of Standardized 0.2 M HCl

WP# W51300

Standardized O.1021 M NaOH will be re-checked and then used to standardized the ~ 0.1 M HCl solution. The 0.1021 M NaOH was prepared in Chem Rec_37 (see Chem Rec_37 --prep.date 2-25-98 for original data) and re-verified against NIST SRM84j Potassium Acid Phthalate KHC8H404 (KAP) = 204.23 g/mole -- Barcode # 52232 --- (see below verification check).
The re-standardized value of 0.1018 M NaOH was reassigned to this NaOH solution with a revised Expiration Date of Feb. 2000.
Prepared 1- liters of ~0.2 M HCl by diluting 100 mL of 1.029M HCl (Chemrec_10) to 0.5 L with DI. H2O.
20 mL aliquots of 0.2 M HCl were were neutralized to the phenopthalien endpoint using the re-standardized 0.1018 M NaOH. The volume of NaOH is accurate to +/- 0.02mL and the pipitting error is estimated to be < 1% @ 1s. Thus total error is < 3 % for the measurements

NaOH Molarity veification

Verification Test #	Wt. of KAP	Vol. of **0.1021M NaOH** to neutralize	NaOH Molarity =a * 1000 / b * 204.23	Molarity Error +/- @ 1 s
1	0.80894	38.95	0.1017	
2	0.80582	38.84	0.1016	
3	0.96233	46.12	0.1022	
		Ave=	**0.1018**	0.0003
			re-certified value	

Titration Id.	aliquot of sample	Vol. of **0.1018M NaOH** to neutralize	**Molarity of Acid** in Sample	Molarity Error +/- @ 1 s
1	20.00	39.88	0.2030	
2	20.00	39.92	0.2032	
3	20.00	40.04	0.2038	
		Ave Molarity HCl =	**0.2034**	0.00042

5-19-99

Analyst/Date

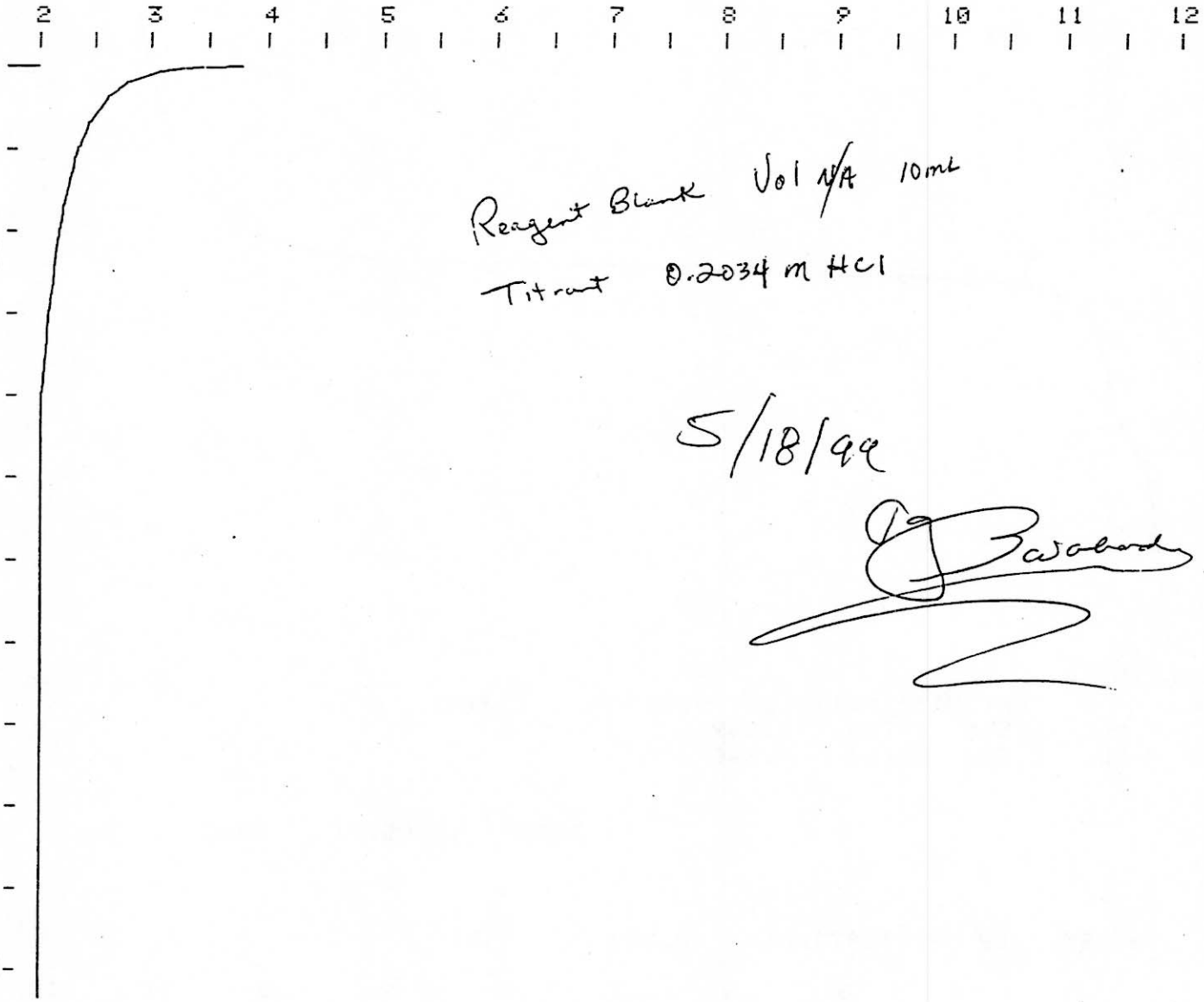
OH⁻ Alkalinity

DATE 18.05.99 NAME

1st Run with .2M HCl Titrant

Standized value 0.2034 M HCl

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



Reagent Blank Vol N/A 10mL

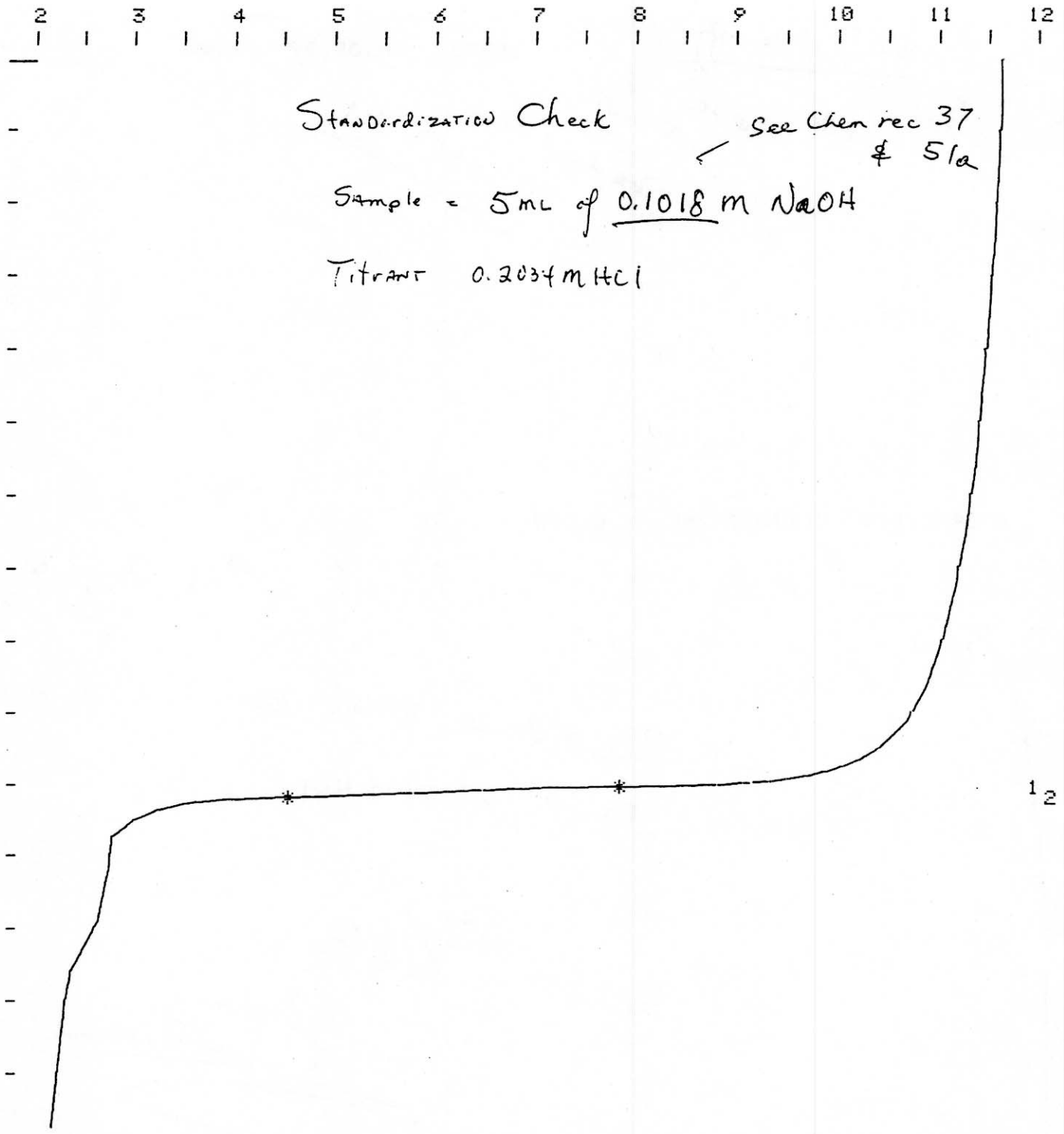
Titrant 0.2034 M HCl

5/18/99

ROUTINE # 101
7 PH(INIT) 3.798 V(TE)/ML 3.083

DATE 18.05.99 NAME

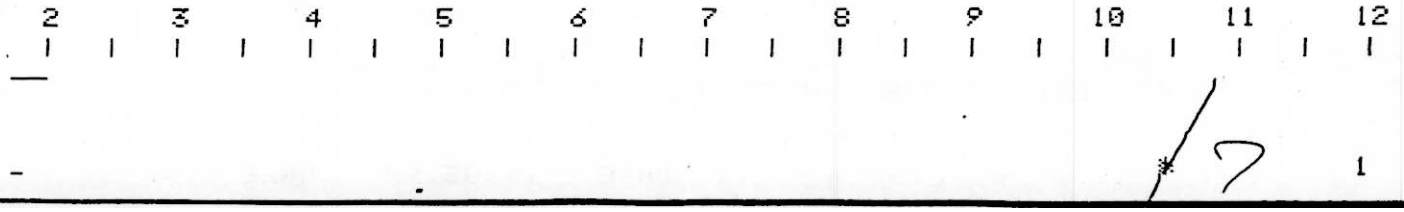
BRINKMANN EA-1121A CAT # 2025015-1



ROUTINE # 101
8 PH(INIT) 11.552 V(TE)/ML 3.905
1 V/ML 2.518 PH(M) 7.849
2 V/ML 2.556 PH(M) 4.545

DATE 18.05.99 NAME

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



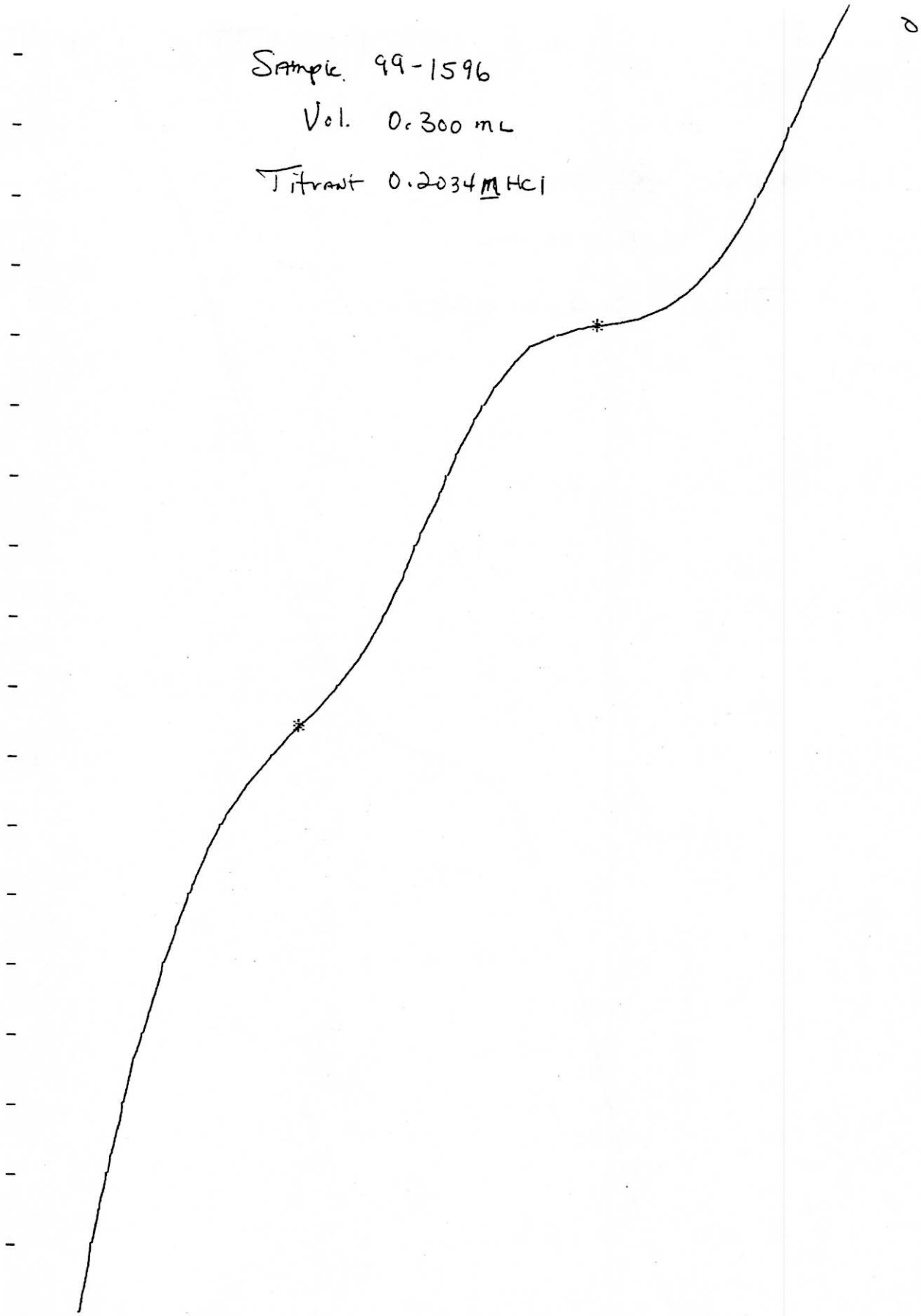
BRINKMANN EA-1 CAT # 2025015-1

054

Sample 99-1596

Vol. 0.300 mL

Titrant 0.2034 M HCl

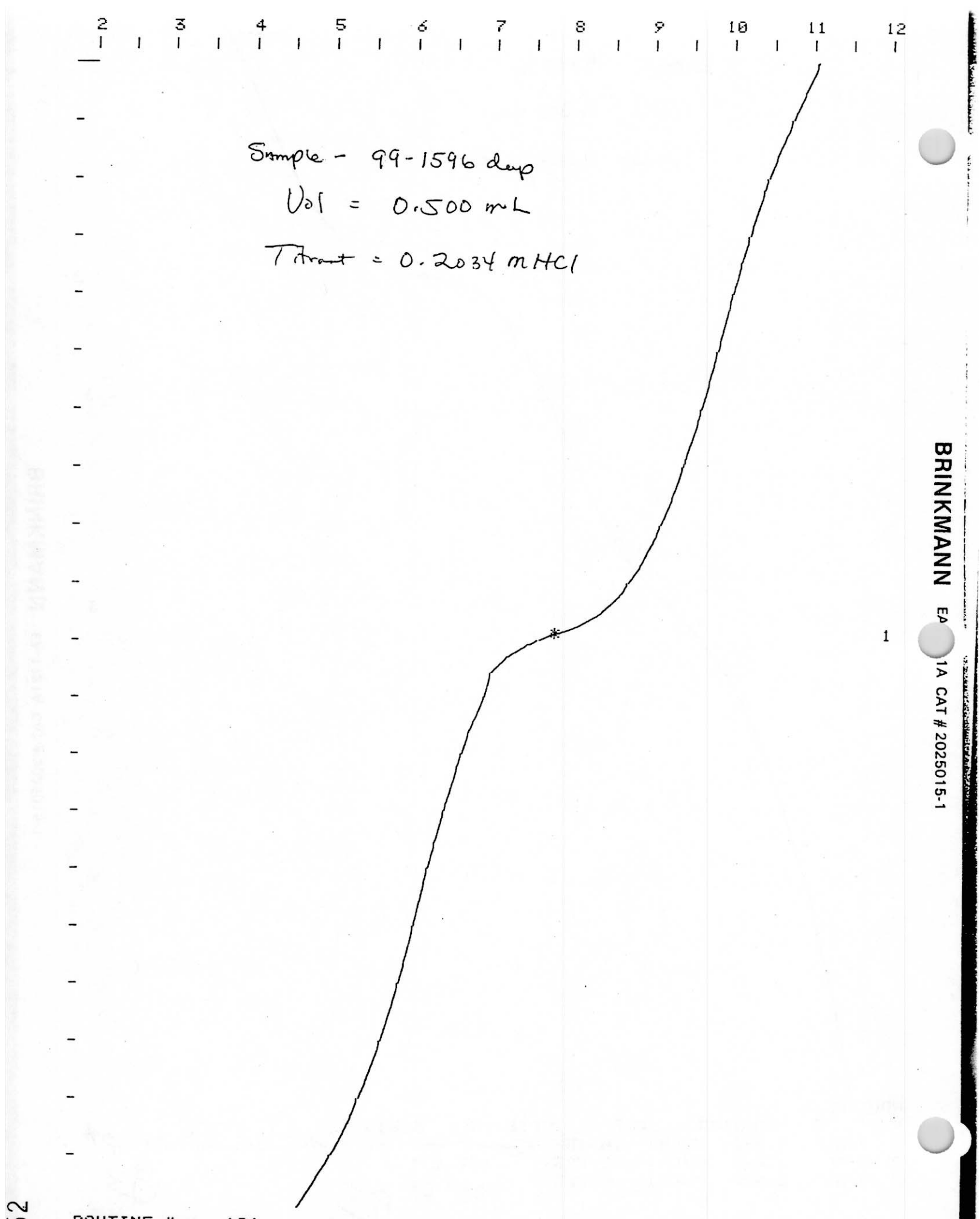


ROUTINE # 101

#	9	PH(INIT)	10.780	V(TE)/ML	5.000
1	V/ML	0.232	PH(M)	10.456	← not real inflection pt
2	V/ML	1.463	PH(M)	7.793	1st EP
3	V/ML	2.897	PH(M)	4.725	2nd EP

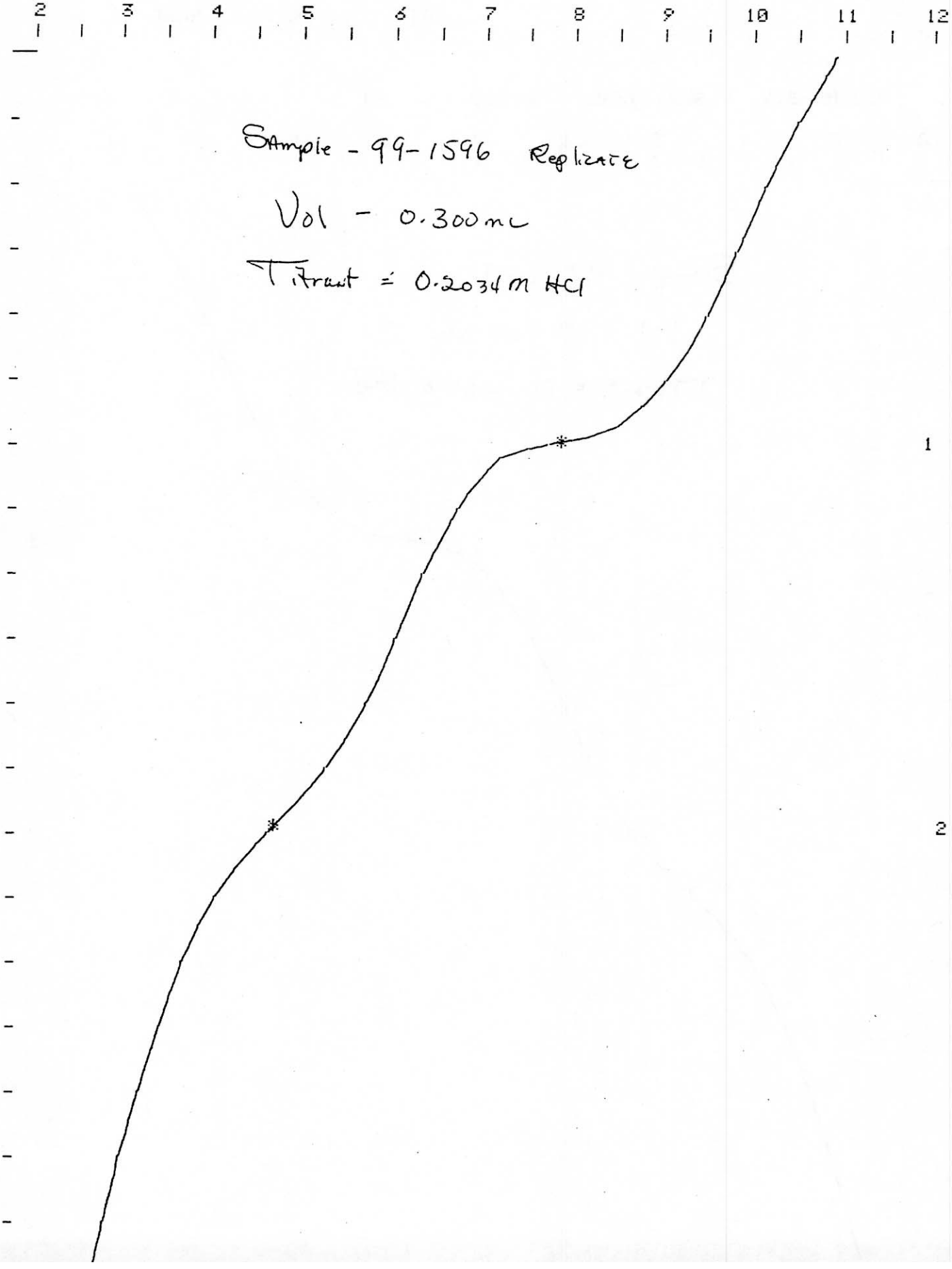
DATE 18.05.99 NAME

BRINKMANN EA-1121A CAT # 2025015-1


2 3 4 5 6 7 8 9 10 11 12
Sample - 99-1596 dup
Vol = 0.500 mL
Titrant = 0.2034 m HCl
BRINKMANN
1A CAT # 2025015-1
1
ROUTINE # 101
10 PH(INIT) 11.038 V(TE)/ML 5.000
PH(M) 7.769

DATE 18.05.99 NAME

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

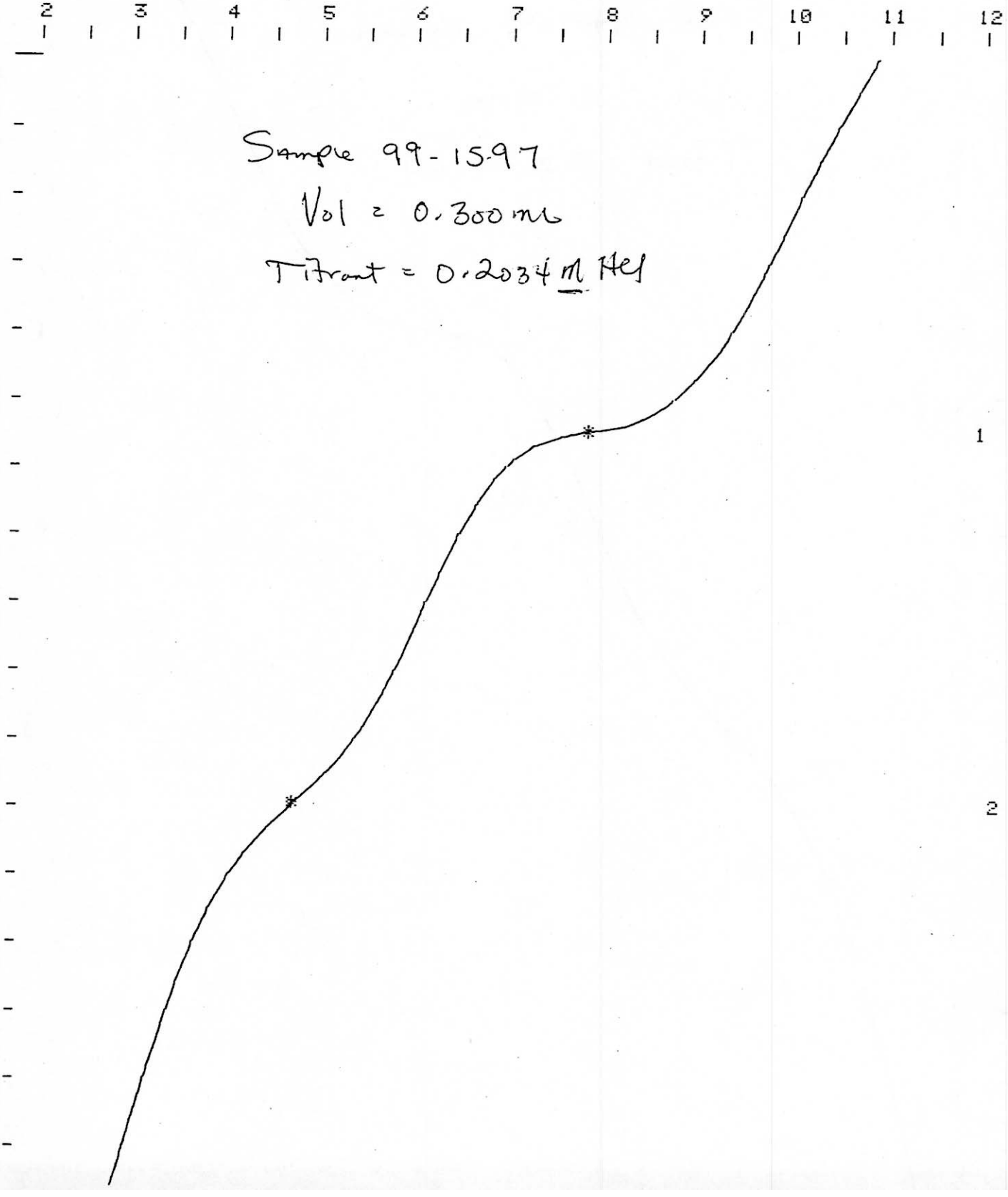


BRINKMANN EA-1121A CAT # 2025015-1

ROUTINE # 101
11 PH(INIT) 10.886 V(TE)/ML 5.000
1 V/ML 1.491 PH(M) 7.862
2 V/ML 2.977 PH(M) 4.697

DATE 18.05.99 NAME

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



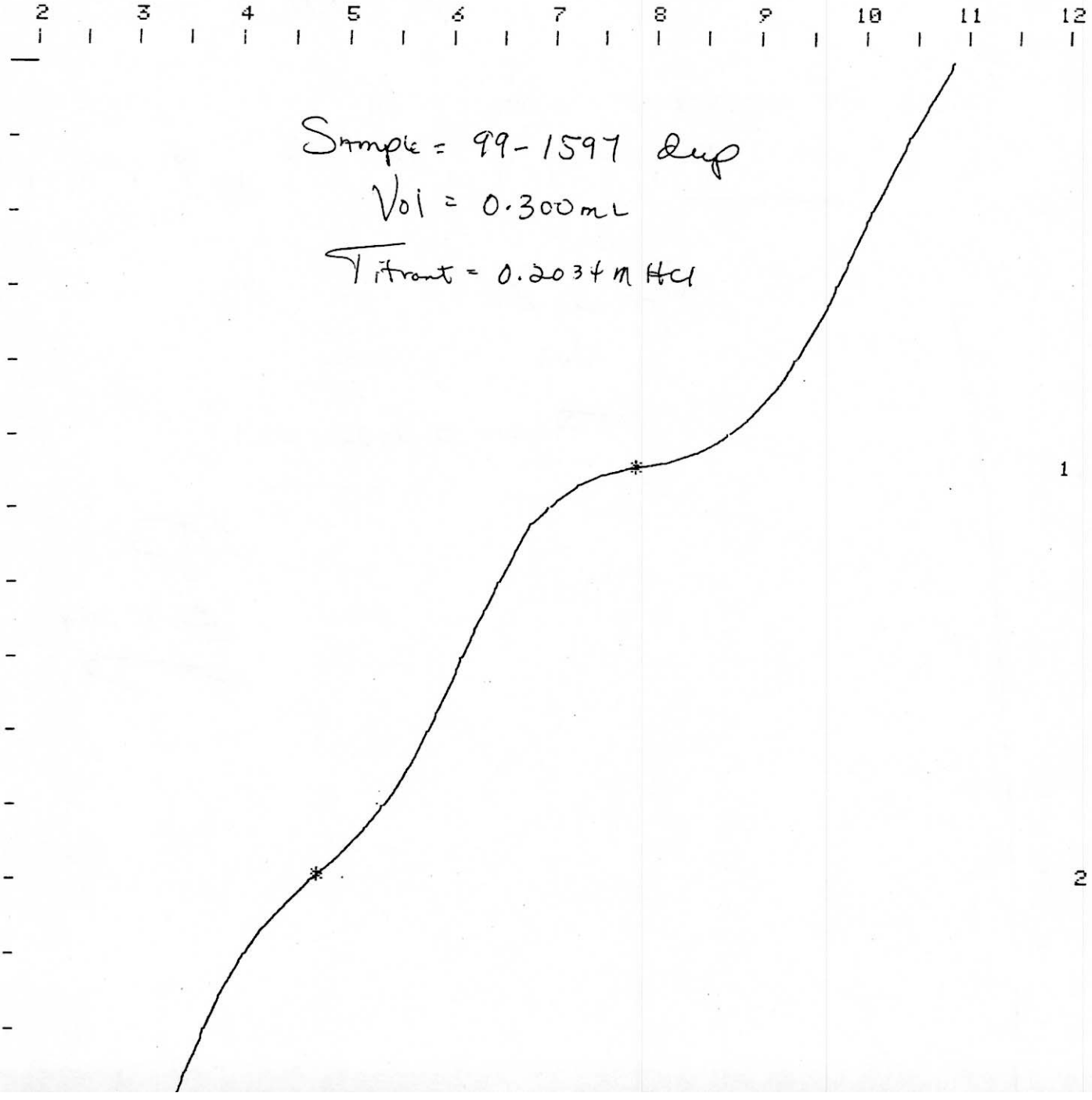
Sample 99-1597
Vol = 0.300 mL
Titrant = 0.2034 M HCl

BRINKMANN EA 1A CAT # 2025015-1

ROUTINE # 101
12 PH(INIT) 10.849 V(TE)/ML 5.000
1 V/ML 1.374 PH(M) 7.815
2 V/ML 2.739 PH(M) 4.714

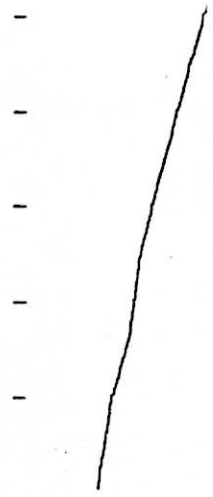
DATE 18.05.99 NAME

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



BRINKMANN EA-1121A CAT # 2025015-1

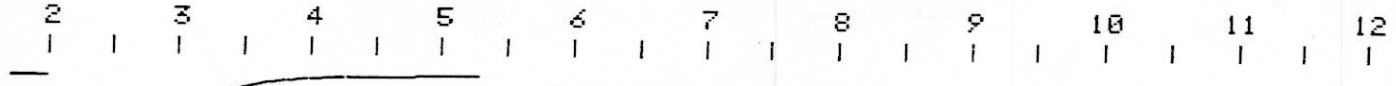
049

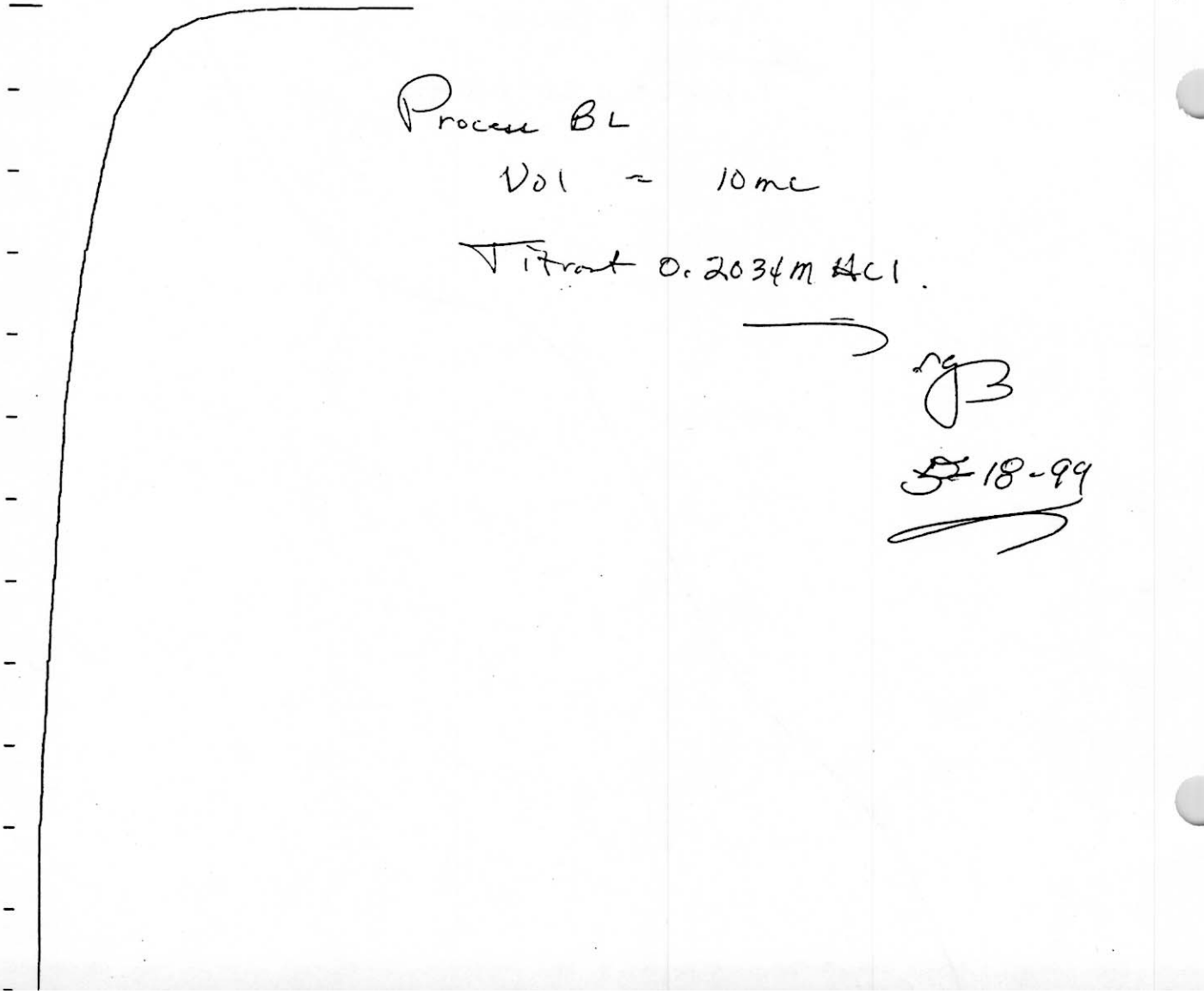


ROUTINE # 101
13 PH(INIT) 10.854 V(TE)/ML 5.000
1 V/ML 1.369 PH(M) 7.803
2 V/ML 2.734 PH(M) 4.714

DATE 18.05.99 NAME

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





Process BL

Vol ~ 10 mL

Titrant 0.2034 M HCl.

JB

5/18-99

EA-1121A CAL # 20250151

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

Project: 29953
Client: S. Bryan

UPDATED REPORT

ACL Number(s): 99-1856 through 99-1870

Client ID: "PR-01" through "PR-15"

ASR Number: 5392

Total Samples: 15

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

Analyst: J. J. Wagner

Analysis Date (Filename): 06-03-99 (A0527) & 06-04-99 (A0528)

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

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

Jerry Wagner 8-11-99
Reviewed by

8-11-99
Concur

8/11/99

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

Thirteen radioactive liquid samples, PR-02 (ACL# 99-1857) through PR-14 (ACL# 99-1869), were analyzed by ICPAES after sample preparation using PNNL-ALO-128 Acid Digestion procedure. Typically five ml of aqueous sample (also weighed) was digested and diluted to a final volume of 25 ml.

Two radioactive slurry samples, PR-01 (ACL# 99-1856) and PR-15 (ACL# 99-1870) were initially weighed into glass vials by SAL in the hot cell and moved to SRPL for processing. Approximately 2.5g of sample PR-01 was digested and diluted to a final volume of 25ml. Two aliquots of PR-15 (centrifuged solids) were prepared in duplicate by removing approximately half of the sample from the original vial received from SAL (hot cell) using a spatula and washed off the spatula with water into a second glass vial. The amount of material transferred was determined by weighing the original sample container before and after the aliquot was removed. Each aliquot of PR-15 weighed about 0.25g and each was diluted to 25ml after digestion.

Measurement results reported are in µg/g for the slurry sample, centrifuged solids sample and the liquid samples. All results have been corrected for preparation and analytical dilution. Analytes of interest requested include: Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Si, Sr, Ti, U, and Zn. Additional dilution, up to 30 fold, was sometimes necessary to quantify Na, Mn and/or Sr.

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

Five fold serial dilution:

(Solid samples) All results are within tolerance limit of ≤ 10% after correcting for dilution.

(Aqueous samples) All results are within tolerance limit of ≤ 10% after correcting for dilution except for Ba, Ca, and Sr in samples PR-08, PR-11 and PR-13. The dilution corrected values for these analytes are biased low by 11% to 12% in the data report based upon this test. The lower value is likely caused by the very high concentration of sodium in the samples.

Duplicate RPD (Relative Percent Difference):

(Solid samples) All results are within tolerance limit of ≤ 20% RPD for analytes of interest except Sr (+30% RPD).

(Aqueous samples) All results are within tolerance limit of ≤ 20% RPD for analytes of interest.

Post-Spiked Samples (Group A):

(Solid samples) --

(Aqueous samples) All analytes of interest tested were recovered within tolerance of 75% to 125% except Cr, K, Mo, and Pb in sample PR-14. Analyte recovery was low by 62%, 74%, 65% and 58% respectively. Sodium concentration in the sample was very high, approximately 118,000µg/g.

Post-Spiked Samples (Group B):

(Solid samples) --

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

Blank Spike:

(Solid samples) All analytes of interest tested were recovered within tolerance of 80% to 120%.

(Aqueous samples) All analytes of interest tested were recovered within tolerance of 80% to 120%.

Matrix Spiked Sample:

(Solid samples) Matrix spike was not prepared due to limited sample material.

(Aqueous samples) All analytes of interest tested were recovered within tolerance of 80% to 120% except Ba and Pb in samplePR-08 (ACL# 99-1863). The low recovery may be due to relatively high concentration of sulfate in the sample resulting in precipitation of Ba and Pb.

Quality Control Check Standards:

Concentration of all analytes of interest, with two exceptions, was recovered within tolerance of ± 10% accuracy in the standards: QC_MCVA, QC_MCVB, and QC_SSTMCV.

Strontium in QC_MCVA check standard measured slightly high (+12%) one out of 5 measurements. Silicon in QC_SSTMCV standard

measured high by 19% in one of two measurements. This may have been caused by sample carry-over from a previous sample.

High Calibration Standard Check:

Verification of the high-end calibration concentration for all analytes of interest measured in QC_SST was within tolerance of ± 5% except for Fe and Ni which were slightly low in recovery (-6% each). This should not affect measurement results of Fe and Ni since only the very high end concentration is affected while actual sample concentration was much lower in concentration.

Process Blank:

(Solid samples) All analytes of interest were within tolerance limit of ≤ EQL or < 5% of sample concentration except silicon. The concentration of silicon in the slurry samples was similar or slightly higher than that found in the process blank. Silicon contamination is probably due to labware (glass) used in transporting the sample material and use of glass digestion vessels to prepare and store the processed samples prior to analysis.

(Aqueous samples) All analytes of interest were within tolerance limit of ≤ EQL or < 5% of sample concentration except silicon. The concentration of silicon in the aqueous samples was below EQL and less than that found in the process blank. Silicon contamination is probably due to differences in leaching of the glass digestion vessels used to prepare the blank and samples.

Laboratory Control Standard:

(Solid samples) None prepared

(Aqueous samples) None prepared.

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

Comments:

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

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

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

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

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

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

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	9.7 99-1856-B Process Blank (129) 6/3/99 ug/g	9.7 99-1856 @1 PR-01 (ALO-129) 6/3/99 ug/g	102.0 99-1856-B Process Blank (129) 6/3/99 ug/g	102.0 99-1870 @1 PR-15 (ALO-129) 6/3/99 ug/g	101.5 99-1870-D @1 PR-15 Dup (ALO-12 6/3/99 ug/g
0.015	Ag	–	–	–	–	–
0.060	Al	[2.0]	136	[21]	185	189
0.080	As	–	[1.3]	–	–	–
0.050	B	19.4	39.2	205	299	203
0.010	Ba	–	1.44	–	[7.2]	[7.9]
0.010	Be	–	–	–	–	–
0.100	Bi	–	–	–	–	–
0.100	Ca	–	218	–	256	281
0.015	Cd	–	26.1	–	24.6	25.2
0.100	Ce	–	10.8	–	[32]	[40]
0.025	Co	–	[1.9]	–	–	–
0.020	Cr	–	56.7	–	126	143
0.015	Cu	–	11.8	–	[13]	[13]
0.050	Dy	–	–	–	–	–
0.100	Eu	–	–	–	–	–
0.025	Fe	–	502	–	1,520	1,730
2.000	K	–	657	–	[510]	[580]
0.025	La	–	12.2	–	32.8	38.0
0.005	Li	–	[0.26]	–	–	[0.58]
0.100	Mg	–	–	–	–	–
0.005	Mn	–	69.7	–	8,440	8,940
0.030	Mo	–	14.3	–	[14]	[15]
0.100	Na	23.2	105,000	245	96,800	96,400
0.100	Nd	–	35.5	–	[99]	114
0.030	Ni	–	206	–	204	206
0.100	P	–	192	–	195	200
0.060	Pb	–	135	–	278	309
0.300	Pd	–	[17]	–	–	[37]
0.300	Rh	–	[4.5]	–	–	–
0.075	Ru	–	15.5	–	[18]	[19]
0.050	Sb	–	–	–	–	–
0.050	Se	–	[0.93]	–	[9.0]	[12]
0.100	Si	42.5	70.5	449	532	504
1.000	Sn	–	–	–	–	–
0.005	Sr	–	1.25	–	4,830	6,540
0.500	Te	–	–	–	–	–
0.800	Th	–	–	–	–	–
0.005	Ti	–	1.76	–	5.41	6.35
0.250	Tl	–	–	–	–	–
2.000	U	–	[45]	–	–	–
0.015	V	–	[0.20]	–	–	–
0.500	W	–	67.9	–	[70]	[72]
0.010	Y	–	3.02	–	[7.8]	[8.9]
0.020	Zn	–	7.47	–	[13]	[15]
0.025	Zr	–	23.3	–	65.5	75.1

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

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

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

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

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	5.0 99-1857-B Proc Blk (ALO-128) 6/3/99 (ug/mL)	71.4 99-1857 @10 PR-02 ~~6/3/99~~ (ug/mL)	50.0 99-1858 @10 PR-03 ~~6/3/99~~ (ug/mL)	62.5 99-1858-D @10 PR-03 Dup ~~6/3/99~~ (ug/mL)	
0.015	Ag	–	–	–	–	–
0.060	Al	[1.2]	162	153	154	–
0.080	As	–	–	–	–	–
0.050	B	11.6	[27]	27.6	[30]	–
0.010	Ba	–	[1.5]	–	–	–
0.010	Be	–	–	–	–	–
0.100	Bi	–	–	–	–	–
0.100	Ca	–	361	279	281	–
0.015	Cd	–	32.0	32.9	33.0	–
0.100	Ce	–	[12]	–	–	–
0.025	Co	–	[2.6]	[2.6]	[2.7]	–
0.020	Cr	–	65.5	37.4	37.8	–
0.015	Cu	–	14.4	14.9	15.1	–
0.050	Dy	–	–	–	–	–
0.100	Eu	–	–	–	–	–
0.025	Fe	–	494	[9.9]	[10]	–
2.000	K	–	[840]	[900]	[940]	–
0.025	La	–	[14]	[1.7]	[2.0]	–
0.005	Li	–	[0.60]	[0.58]	[0.59]	–
0.100	Mg	–	[13]	–	–	–
0.005	Mn	–	54.9	17.8	18.0	–
0.030	Mo	–	[18]	19.3	19.5	–
.100	Na	14.2	122,000	129,000	131,000	–
0.100	Nd	–	[41]	–	–	–
0.030	Ni	–	267	279	282	–
0.100	P	–	223	240	240	–
0.060	Pb	–	159	91.6	92.9	–
0.300	Pd	–	[23]	–	–	–
0.300	Rh	–	–	–	–	–
0.075	Ru	–	[20]	[20]	[20]	–
0.050	Sb	–	–	–	–	–
0.050	Se	–	–	–	[3.4]	–
0.100	Si	24.6	[48]	[38]	[44]	–
1.000	Sn	–	–	–	–	–
0.005	Sr	–	[1.9]	[0.85]	[0.89]	–
0.500	Te	–	–	–	–	–
0.800	Th	–	–	–	–	–
0.005	Ti	–	[1.6]	–	–	–
0.250	Tl	–	–	–	–	–
2.000	U	–	–	–	–	–
0.015	V	–	–	–	–	–
0.500	W	–	[85]	[88]	[88]	–
0.010	Y	–	[3.6]	[0.79]	[0.86]	–
0.020	Zn	–	[8.4]	[6.0]	[6.1]	–
0.025	Zr	–	[18]	[3.6]	[3.8]	–

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

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

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

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

	Multiplier=	19.8	20.2	20.0	20.0	19.8
	ALO#=	99-1859 @5	99-1860 @5	99-1861 @5	99-1862 @5	99-1863 @5
	Client ID=	PR-04 (ALO-128)	PR-05 (ALO-128)	PR-06 (ALO-128)	PR-07 (ALO-128)	PR-08 (ALO-128)
Det. Limit	Run Date=	6/4/99	6/4/99	6/4/99	6/4/99	6/4/99
(ug/mL)	(Analyte)	ug/g	ug/g	ug/g	ug/g	ug/g
0.015	Ag	--	--	--	--	--
0.060	Al	115	109	105	112	112
0.080	As	--	--	--	--	--
0.050	B	23.3	20.9	20.5	21.0	19.9
0.010	Ba	--	--	--	--	[0.29]
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	208	183	136	142	149
0.015	Cd	25.7	23.5	23.5	24.8	24.3
0.100	Ce	--	--	--	--	[3.4]
0.025	Co	[1.8]	[1.7]	[1.7]	[1.8]	[1.8]
0.020	Cr	28.2	34.3	26.2	28.8	39.5
0.015	Cu	11.3	10.3	10.3	11.0	10.6
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	[4.9]	[2.2]	19.0	17.8	139
2.000	K	699	696	632	660	637
0.025	La	[0.85]	[0.56]	[0.91]	[0.85]	[1.7]
0.005	Li	[0.22]	[0.23]	[0.27]	[0.22]	[0.26]
0.100	Mg	--	--	--	--	--
0.005	Mn	8.41	5.10	14.3	4.61	24.3
0.030	Mo	14.1	13.0	12.9	13.7	13.4
0.100	Na	92,400	86,300	85,200	90,500	91,700
0.100	Nd	[2.0]	--	[3.1]	[2.8]	[6.7]
0.030	Ni	205	189	188	198	194
0.100	P	189	172	167	178	175
0.060	Pb	60.6	39.2	68.0	71.7	74.8
0.300	Pd	--	--	--	--	[7.3]
0.300	Rh	--	--	--	--	--
0.075	Ru	[14]	[13]	[13]	[14]	[14]
0.050	Sb	--	--	--	--	--
0.050	Se	--	--	--	--	--
0.100	Si	34.1	34.3	31.9	31.6	29.6
1.000	Sn	--	--	--	--	--
0.005	Sr	[0.40]	[0.18]	101	112	117
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	--	--	[0.11]	--	[0.41]
0.250	Tl	--	--	--	--	--
2.000	U	--	--	[40]	--	--
0.015	V	--	--	--	--	--
0.500	W	[66]	[59]	[62]	[65]	[63]
0.010	Y	[0.50]	[0.37]	[0.58]	[0.60]	[1.0]
0.020	Zn	4.14	[3.5]	4.06	4.34	4.62
0.025	Zr	[2.2]	[1.5]	[2.6]	[2.8]	6.31

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.
2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.
3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

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

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	19.6 / 99-1864 @5 / PR-09 (ALO-128) / 6/4/99 / ug/g	19.8 / 99-1865 @5 / PR-10 (ALO-128) / 6/4/99 / ug/g	19.9 / 99-1866 @5 / PR-11 (ALO-128) / 6/4/99 / ug/g	19.8 / 99-1867 @5 / PR-12 (ALO-128) / 6/4/99 / ug/g	19.6 / 99-1868 @5 / PR-13 (ALO-128) / 6/4/99 / ug/g
0.015	Ag	--	--	--	--	--
0.060	Al	109	108	108	108	106
0.080	As	--	--	--	--	--
0.050	B	21.0	19.6	20.9	22.1	21.4
0.010	Ba	--	--	--	--	--
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	159	156	246	218	133
0.015	Cd	24.5	24.2	24.0	23.6	23.1
0.100	Ce	--	--	--	--	--
0.025	Co	[1.8]	[1.8]	[1.8]	[1.7]	[1.7]
0.020	Cr	27.3	31.2	29.3	23.0	21.6
0.015	Cu	10.7	10.6	10.6	10.4	10.2
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	7.59	28.5	13.0	6.97	5.34
2.000	K	647	630	636	629	603
0.025	La	[0.84]	[1.1]	[0.87]	[0.60]	[0.58]
0.005	Li	[0.26]	[0.24]	[0.31]	[0.26]	[0.21]
0.100	Mg	--	--	--	--	--
0.005	Mn	13.4	15.2	8.31	15.6	14.4
0.030	Mo	13.4	13.3	13.3	13.1	12.9
0.100	Na	92,500	86,600	91,600	87,600	92,200
.100	Nd	[2.3]	[4.0]	[2.7]	--	--
.030	Ni	196	193	194	191	187
0.100	P	176	174	173	167	165
0.060	Pb	68.2	74.0	67.7	59.0	58.7
0.300	Pd	--	--	--	--	--
0.300	Rh	--	--	--	--	--
0.075	Ru	[14]	[14]	[14]	[13]	[13]
0.050	Sb	--	--	--	--	--
0.050	Se	--	--	[1.1]	--	--
0.100	Si	32.6	33.8	44.0	47.4	45.9
1.000	Sn	--	--	--	--	--
0.005	Sr	96.4	105	67.7	82.4	128
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	--	[0.13]	[0.11]	--	--
0.250	Tl	--	--	--	--	--
2.000	U	--	--	[41]	--	--
0.015	V	--	--	--	--	--
0.500	W	[64]	[63]	[63]	[62]	[61]
0.010	Y	[0.50]	[0.78]	[0.60]	[0.38]	[0.33]
0.020	Zn	4.19	4.29	4.63	[3.9]	[3.8]
0.025	Zr	[2.2]	[3.5]	[2.6]	[1.7]	[1.4]

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

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

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

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

Det. Limit (ug/mL)	Multiplier= / ALO#= / Client ID= / Run Date= / (Analyte)	19.8 / 99-1869 @5 / PR-14 (ALO-128) / 6/4/99 / ug/g				
0.015	Ag	--	--	--	--	--
0.060	Al	111	--	--	--	--
0.080	As	--	--	--	--	--
0.050	B	23.0	--	--	--	--
0.010	Ba	--	--	--	--	--
0.010	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.100	Ca	190	--	--	--	--
0.015	Cd	23.7	--	--	--	--
0.100	Ce	--	--	--	--	--
0.025	Co	[1.8]	--	--	--	--
0.020	Cr	13.6	--	--	--	--
0.015	Cu	10.6	--	--	--	--
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	6.47	--	--	--	--
2.000	K	631	--	--	--	--
0.025	La	--	--	--	--	--
0.005	Li	[0.23]	--	--	--	--
0.100	Mg	--	--	--	--	--
0.005	Mn	27.5	--	--	--	--
0.030	Mo	13.3	--	--	--	--
0.100	Na	93,100	--	--	--	--
0.100	Nd	--	--	--	--	--
0.030	Ni	194	--	--	--	--
0.100	P	176	--	--	--	--
0.060	Pb	38.1	--	--	--	--
0.300	Pd	--	--	--	--	--
0.300	Rh	--	--	--	--	--
0.075	Ru	[14]	--	--	--	--
0.050	Sb	--	--	--	--	--
0.050	Se	[1.1]	--	--	--	--
0.100	Si	47.2	--	--	--	--
1.000	Sn	--	--	--	--	--
0.005	Sr	[0.39]	--	--	--	--
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	--	--	--	--	--
0.250	Tl	--	--	--	--	--
2.000	U	--	--	--	--	--
0.015	V	--	--	--	--	--
0.500	W	[63]	--	--	--	--
0.010	Y	[0.27]	--	--	--	--
0.020	Zn	[3.3]	--	--	--	--
0.025	Zr	[1.2]	--	--	--	--

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).

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

99-1856
8/6/1999

Client : Sam Bryan

Cognizant Scientist: L L Greenwood Date : 8/6/99

Concur : C Soderquist Date : 8-6-99

ALO ID Client ID	Volume ml	Weight g	Density g/ml
99-1856 * PR-01		2.5875	
99-1857 PR-02	3.5	4.4466	1.270
99-1858 PR-03	5.0	6.3372	1.267
99-1858 DUP PR-03	4.0	5.0575	1.264
99-1859 PR-04	5.0	6.3219	1.264
99-1860 PR-05	5.0	6.2003	1.240
99-1861 PR-06	5.0	6.2597	1.252
99-1862 PR-07	5.0	6.2558	1.251
99-1863 PR-08	5.0	6.3100	1.262
99-1863MS (DUP) PR-08	2.9	3.6134	1.246
99-1864 PR-09	5.0	6.3933	1.279
99-1865 PR-10	5.0	6.3189	1.264
99-1866 PR-11	5.0	6.2919	1.258
99-1867 PR-12	5.0	6.3136	1.263
99-1868 PR-13	5.0	6.3681	1.274
99-1869 PR-14	5.0	6.3290	1.266
99-1870 * PR-15-SOL-(07)		0.2451	
99-1870 DUP * PR-15-SOL-(07)		0.2463	

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

99-1856
8/6/1999

Client : Sam Bryan

Cognizant Scientist: H L Greenwood Date : 8/6/99

Concur : C. Soderquist Date : 8-6-99

Gamma Energy Analysis Measured Activities (uCi/g)

ALO ID Client ID	Co-60 Error %	Cs-137 Error %	Eu-154 Error %	Eu-155 Error %	Am-241 Error %
99-1856 PR-01	6.33E-2 2%	1.94E-2 5%	2.60E-1 1%	2.01E-1 6%	2.31E-1 5%
99-1857 PR-02	6.35E-2 2%	1.78E-2 5%	2.31E-1 1%	1.72E-1 3%	1.93E-1 4%
99-1858 PR-03	5.28E-2 2%	1.36E-2 3%	1.94E-2 3%	1.25E-2 8%	8.52E-3 16%
99-1858 DUP PR-03	5.91E-2 2%	1.59E-2 3%	2.19E-2 3%	1.57E-2 8%	1.01E-2 22%
RPD	11%	15%	12%	23%	17%
99-1859 PR-04	5.61E-2 2%	1.54E-2 3%	1.67E-2 3%	1.19E-2 8%	5.68E-3 22%
99-1860 PR-05	5.43E-2 2%	1.52E-2 3%	1.03E-2 4%	7.29E-3 10%	2.95E-3 33%
99-1861 PR-06	5.48E-2 2%	1.46E-2 3%	2.45E-2 2%	1.89E-2 5%	1.30E-2 9%
99-1862 PR-07	5.51E-2 2%	1.51E-2 3%	2.51E-2 2%	1.86E-2 5%	1.39E-2 8%
99-1863 PR-08	5.63E-2 2%	1.44E-2 3%	6.05E-2 2%	4.46E-2 3%	4.14E-2 5%
99-1863MS (DUP) PR-08	5.71E-2 2%	1.52E-2 4%	6.34E-2 2%	4.50E-2 4%	4.04E-2 5%
RPD	2%	5%	5%	1%	2%
99-1864 PR-09	5.56E-2 2%	1.51E-2 3%	1.78E-2 3%	1.29E-2 6%	6.88E-3 14%
99-1865 PR-10	5.55E-2 2%	1.43E-2 3%	3.59E-2 2%	2.39E-2 4%	1.81E-2 7%
99-1866 PR-11	5.55E-2 2%	1.53E-2 3%	2.30E-2 2%	1.69E-2 5%	9.54E-3 12%
99-1867 PR-12	5.41E-2 2%	1.41E-2 3%	1.33E-2 3%	1.01E-2 6%	5.04E-3 17%
99-1868 PR-13	5.13E-2 2%	1.33E-2 3%	1.13E-2 3%	8.64E-3 7%	4.84E-3 17%
99-1869 PR-14	5.47E-2 2%	1.45E-2 3%	9.32E-3 4%	5.93E-3 13%	1.96E-3 55%
99-1870 PR-15-SOL-(07)	5.76E-2 4%	2.71E-2 14%	6.43E-1 2%	4.67E-1 4%	6.38E-1 6%
99-1870 DUP PR-15-SOL-(07)	5.77E-2 4%	2.68E-2 13%	7.41E-1 2%	5.33E-1 4%	7.01E-1 5%

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

99-1856
8/6/1999

Client : Sam Bryan

Cognizant Scientist: [signature] Date : 8/6/99

Concur : C Sidergno Date : 8-6-99

Corrected Report

Measured Activities (µCi/g)

ALO ID Client ID	Sr-90 ± 1s%
99-1856 Blank	2.03E-4 17%
99-1856 Process Blank	<6.E-5
99-1856 PR-01	3.54E+1 3%
99-1857 Process Blank	<5.E-5
99-1857 PR-02	3.31E+1 3%
99-1858 PR-03	1.70E+1 3%
99-1858 DUP PR-03	1.52E+1 3%
RPD	12%
99-1859 PR-04	1.15E+1 3%
99-1860 PR-05	4.94E+0 3%
99-1861 PR-06	1.57E+0 3%
99-1862 PR-07	2.45E+0 3%
99-1863 PR-08	3.64E+0 3%
99-1863 DUP PR-08	3.91E+0 3%
RPD	7%
99-1864 PR-09	3.44E+0 3%
99-1865 PR-10	2.32E+0 3%
99-1866 PR-11	2.29E+0 3%
99-1867 PR-12	1.64E+0 3%

ALO ID Client ID	Sr-90 ± 1s%
99-1868 PR-13	1.89E+0 3%
99-1869 PR-14	1.13E+1 3%
99-1870 PR-15-SOL-(07)	7.04E+1 3%
99-1870 DUP PR-15-SOL-(07)	8.63E+1 3%
RPD	20%
99-1870 Rep PR-15-SOL-(07)	7.00E+1 3%
RPD	1%
Matrix Spike	98%
Reagent Spike	89%

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

ASR # 5392

WP# W51300

File: L:\radchem\hydroxide\asr5392
Analysis Date: 6/3/99
Print Date: 6/4/99

Hydroxide and Alkalinity Determination
Governing Procedures: PNL-ALO-228: Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates and Operation of Brinkman 636 Auto-Titrator
Equip # WB76843
Lab Loc. 525

Analyst: [signature] 6/4/99
Reviewer: [signature] 6/4/99

Titrant	Molarity
HCl	0.2034

Std. & Spike	Molarity
NaOH	0.1018

RPG #	Sample ID		Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Initial pH reading	OH 1st Equivalence Point Titrant Vol. (mL)	OH 1st Equivalence Point pH	Found millimoles base	Molarity base	millimole RPD
99-1857	PR-02		0.100	0.1257	1.257	11.345	0.488	10.478	0.099	0.99	
99-1857D	PR-02	Replicate	0.200	0.2548	1.274	11.533	0.964	10.592	0.196	0.98	1.24%
99-1857D	PR-02	Replicate	0.300	0.3891	1.297	11.774	1.491	10.722	0.303	1.01	3.06%
99-1861	PR-06		0.300	0.3709	1.236	11.712	1.245	10.666	0.253	0.84	
99-1861D	PR-06	Replicate	0.300	0.3743	1.248	11.783	1.230	10.730	0.250	0.83	1.21%
99-1867	PR-12		0.300	0.3644	1.215	11.758	1.181	10.735	0.240	0.80	
99-1867D	PR-12	Replicate	0.300	0.3652	1.217	11.768	1.182	10.715	0.240	0.80	0.08%
99-1869	PR-14		0.300	0.3750	1.250	11.759	1.227	10.588	0.250	0.83	
99-1869D	PR-14	Replicate	0.300	0.3694	1.231	11.739	1.208	10.619	0.246	0.82	1.56%
RB - 5392	Reagent Blank			5.00		6.008	No inflection point		na		
PB-5392	Process Blank			5.00		4.94	No inflection point		na	% Recovered	
Standard 1	0.1018 N NaOH		5.000			11.763	2.483	7.947	0.1010	99.2%	
Standard 2	0.1018 N NaOH		5.000			11.828	2.485	7.987	0.1011	99.3%	
99-1857MS	PR-02	MS+ 2mL NaOH	0.100	0.1257	1.257	11.798	1.383	10.637	0.182	89.4%	
99-1861MS	PR-06	MS+ 2mL NaOH	0.100	0.1233	1.233	11.769	1.291	10.600	0.179	87.8%	
99-1867MS	PR-12	MS+ 2mL NaOH	0.100	0.1218	1.218	11.853	1.274	10.605	0.177	87.1%	
99-1859MS	PR-14	MS+ 2mL NaOH	0.100	0.1238	1.238	11.863	1.312	10.501	0.187	91.7%	

Buffer	VWR Lot #	CMS#	Expire Date
10	981659-24	144109	Jul-00
4	981583-24	144107	Jun-00
7	981894-24	144108	Aug-00

Performance checks

Balance # 360--01-06-037

		Vol.	Wt.
Pipet #	H30762	5.00	4.9841
Pipet #	288618	0.300	0.2997
Pipet #	120737	0.100	0.1002

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

ASR # 5392
WP# W51300

File: L:\radchem\hydroxide\asr5392
Analysis Date: 6/3/99
Print Date: 6/4/99

Hydroxide and Alkalinity Determination
Governing Procedures: PNL-ALO-228: Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates
and Operation of Brinkman 636 Auto-Titrator
Equip # WB76843
Lab Loc. 525

Analyst: [signature] 6/4/99
Reviewer: [signature] 6/4/99

Titrant	Molarity
HCl	0.2034

				CO3						HCO3				
				2nd Equivalence						3rd Equivalence				
RPG #	Sample ID		Sample Vol. (mL)	Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD		Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
99-1857	PR-02		0.100	0.927	7.634	0.089	0.893			1.411	4.542	0.098	0.98	
99-1857	PR-02	Replicate	0.200	1.856	7.825	0.181	0.907	1.58%		2.826	4.588	0.197	0.99	0.21%
99-1857D	PR-02	Replicate	0.300	2.826	7.958	0.272	0.905	0.22%		4.305	4.681	0.301	1.00	1.64%
99-1861	PR-06		0.300	2.288	7.959	0.212	0.707			3.437	4.691	0.234	0.78	
99-1861D	PR-06	Replicate	0.300	2.303	7.977	0.218	0.727	2.84%		3.442	4.762	0.232	0.77	0.87%
99-1867	PR-12		0.300	2.224	7.911	0.212	0.707			3.319	4.767	0.223	0.74	
99-1867D	PR-12	Replicate	0.300	2.214	7.899	0.210	0.700	1.06%		3.313	4.759	0.224	0.75	0.36%
99-1868	PR-14		0.300	1.966	7.940	0.150	0.501			2.774	4.846	0.164	0.55	
99-1868D	PR-14	Replicate	0.300	1.969	7.641	0.155	0.516	2.93%		2.770	4.801	0.163	0.54	0.87%
RB - 5392	Reagent Blank		5.00			No inflection point								
PB-5392	Process Blank		5.00			No inflection point								
Standard 1	0.1018 N NaOH		5.000	2.534	4.338									
Standard 2	0.1018 N NaOH		5.000	2.54	4.225		% Recovered							
99-1857MS	PR-02	M. Spk.	0.100	1.881	7.937	0.19404	95.3%			2.399	4.899			
99-1861MS	PR-06	M. Spk.	0.100	1.726	7.601	0.19543	96.0%			2.162	4.815			
99-1867MS	PR-12	M. Spk.	0.100	1.700	7.756	0.19231	94.5%			2.153	4.638			
99-1859MS	PR-14	M. Spk.	0.100	1.624	7.801	0.17987	88.3%			1.950	4.817			

Matrix spike recovery is calculated as follows:
Spike = 2.00 mL 0.1018 N NaOH was added to the 0..100-mL of sample for each matrix spilke.
SpikeTitrant vol. (sample @ .1mL + spike) - SampleTitrant vol. (average sample only equated to .1mL) * 0.2034 N (HCl titrant) = meq. OH
meq OH / 2.00 mL added = meq OH/mL found / 0.1018 N OH added * 100 = % recovered.

Prep record on 0.2034 M HCl is on following page.

Chem Rec_51a

Prep date: 4/18/99

Preparation of Standardized 0.2 M HCl

WP# WK51300

Standardized O.1021 M NaOH will be re-checked and then used to standardized the ~ 0.1 M HCl solution. The 0.1021 M NaOH was prepared in Chem Rec_37 (see Chem Rec_37 –prep.date 2-25-98 for original data) and re-verified against NIST SRM84j Potassium Acid Phthalate KHC8H404 (KAP) = 204.23 g/mole -- Barcode # 52232 — (see below verification check).
The re-standardized value of 0.1018 M NaOH was reassigned to this NaOH solution with a revised Expiration Date of Feb. 2000.
Prepared 1- liters of ~0.2 M HCl by diluting 100 mL of 1.029M HCl (Chemrec_10) to 0.5 L with DI. H2O.
20 mL aliquots of 0.2 M HCl were were neutralized to the phenopthalien endpoint using the re-standardized 0.1018 M NaOH. The volume of NaOH is accurate to +/- 0.02mL and the pipitting error is estimated to be < 1% @ 1s. Thus total error is < 3 % for the measurements

NaOH Molarity veification

Verification Test #	Wt. of KAP	Vol. of **0.1021M NaOH** to neutralize	NaOH Molarity =a * 1000 / b * 204.23	Molarity Error +/- @ 1 s
1	0.80894	38.95	0.1017	
2	0.80582	38.84	0.1016	
3	0.96233	46.12	0.1022	
		Ave=	**0.1018**	0.0003
			re-certified value	

Titration Id.	aliquot of sample	Vol. of **0.1018M NaOH** to neutralize	**Molarity of Acid** in Sample	Molarity Error +/- @ 1 s
1	20.00	39.88	0.2030	
2	20.00	39.92	0.2032	
3	20.00	40.04	0.2038	
		Ave Molarity HCl =	**0.2034**	0.00042

Analyst/Date 6/4/99

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

Project: 29953
Client: S. Bryan

ACL Number(s): 99-2102, 99-2104, 99-2108 through 99-2110, and 99-2112

Client ID: "OP-01" , "OP-03", "LH-07" through "RW-09", and "RW-11"

ASR Number: 5426

Total Samples: 6

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

Analyst: DR Sanders

Analysis Date (Filename): 07-21-99 (A0536)

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 8-12-99
Reviewed by

8-13-99
Concur

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

Six radioactive aqueous samples, OP-01 through RW-11 (ACL# 99-2102 through 99-2112), were analyzed by ICPAES after preparation by the Sample Receiving and Preparation Laboratory (SRPL). Samples were prepared by SRPL using PNL-ALO-128 acid digestion procedure. Approximately 3ml of sample (weighed) was processed and diluted to a final volume of 15ml. All liquid samples were caustic, salt solutions prior to processing. An additional 0.6 ml of concentrated nitric acid was added to each sample beyond the normal amount of acid required by PNL-ALO-128 procedure because of the caustic in the samples. Samples were filtered after being diluted to 15 ml using 0.45 um filter because all of the samples contained a small amount of white to clear grainy material after processing.

All results reported are in µg/g including liquid samples and corrected for preparation and analytical dilution. Volumes and weights have been recorded on bench sheets (included with raw data, etc.). Analytes of interest include Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Si, Sr, Ti, U, and Zn.

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

Five fold serial dilution:
(Aqueous samples) All results were within tolerance limit of ≤ 10% after correcting for dilution.

Duplicate RPD (Relative Percent Difference):
(Aqueous samples) All analytes of interest were recovered within tolerance limit of ≤ 20% relative percent difference (RPD).

Post-Spiked Samples (Group A):
(Aqueous samples) All analytes of interest were recovered within tolerance of 75% to 125%.

Post-Spiked Samples (Group B):
(Aqueous samples) All analytes of interest were recovered within tolerance of 75% to 125%.

Blank Spike:
(Aqueous samples) All analytes of interest in the blank spike were recovered within tolerance limit of 80% to 120%.

Matrix Spiked Sample:
(Aqueous samples) All analytes of interest in the matrix-spike were recovered within tolerance limit of 75% to 125% except for Ba and Pb. Matrix-spike recovery for barium in sample OP-03 was only about 7%. Lead recovery in the same sample was about 15%. Low recovery for these two analytes may be caused by moderately high concentration of sulfate in the sample. Post-spike recovery for all analytes of interest was recovered within tolerance limit of 75% to 125%.

Quality Control Check Standards:
Concentration of all analytes of interest was within tolerance limit of ± 10% accuracy in the standards: QC_MCVA and QC_MCVB. Calibration Blank (ICP98.0) concentration was less than two times IDL.

High Calibration Standard Check:
Verification of the high-end calibration accuracy for all analytes of interest except potassium was within ± 5% tolerance. The high-end calibration accuracy for potassium was slightly high, +5.5%. This will cause the potassium results to be slightly high by about the same amount since most of the potassium results in the samples were near the concentration test value.

Process Blank:
(Aqueous samples) All analytes of interest were within tolerance limit of ≤ EQL or < 5% of sample concentration except Si, which was equivalent to about 13% to 93% of that reported in the samples. The concentration of silicon reported in the samples were all below MRQ=170 µg/ml (or µg/g).

Laboratory Control Standard (LCS):
(Aqueous samples) No LCS was prepared for PNL-ALO-128 acid digested samples.

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

8/12/99

Comments:

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

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

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

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

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

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

Det. Limit (ug/mL)	Multiplier= / Run Date= (Analyte)	3.8 99-2102-PB *Process Blank* 7/21/99 ug/g	18.8 99-2102 @5 *OP-01* 7/21/99 ug/g	18.8 99-2102-DUP @5 *OP-01* 7/21/99 ug/g	19.1 99-2104 @5 *OP-03* 7/21/99 ug/g	19.3 99-2108 @5 *LH-07* 7/21/99 ug/g
	ALO#=					
	Client ID=					
0.015	Ag	--	--	--	--	--
0.060	Al	[1.9]	119	121	99.4	95.7
0.080	As	--	--	--	--	--
0.050	B	22.8	35.0	32.8	38.5	31.0
0.010	Ba	--	[1.2]	[1.2]	--	--
0.005	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.250	Ca	[1.0]	207	208	148	153
0.015	Cd	--	23.9	24.0	22.2	21.9
0.100	Ce	--	[9.4]	[9.1]	--	--
0.025	Co	--	[1.7]	[1.7]	[1.6]	[1.7]
0.020	Cr	--	50.8	51.1	32.2	31.4
0.015	Cu	--	10.3	10.3	9.34	9.22
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	[0.15]	431	435	15.9	15.0
2.000	K	--	581	573	555	558
0.025	La	--	10.3	10.3	[0.95]	[1.5]
0.020	Li	--	--	--	--	--
0.100	Mg	[0.75]	--	[2.2]	--	--
0.005	Mn	--	44.2	44.5	5.61	3.84
0.030	Mo	--	12.9	12.9	12.0	12.0
0.100	Na	30.2	112,000	112,000	111,000	101,000
[illegible]	Nd	--	30.0	30.0	[3.3]	[4.2]
[illegible]	Ni	--	189	190	177	177
0.100	P	--	160	160	158	157
0.060	Pb	--	126	126	69.5	72.8
0.300	Pd	--	[16]	[15]	--	[6.6]
0.300	Rh	--	--	--	--	--
0.075	Ru	--	[14]	[14]	[12]	[12]
0.050	Sb	--	--	--	--	--
0.050	Se	--	[1.00]	--	--	[1.1]
0.100	Si	22.4	73.1	74.6	76.3	57.7
1.000	Sn	--	--	--	--	--
0.005	Sr	--	[0.94]	0.942	113	114
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	--	1.09	1.11	[0.11]	[0.13]
0.250	Tl	--	--	--	--	--
2.000	U	--	[43]	[38]	--	[44]
0.015	V	--	--	--	--	--
0.500	W	--	[61]	[63]	[57]	[56]
0.010	Y	--	2.73	2.74	[0.67]	[0.79]
0.020	Zn	[0.083]	6.22	6.31	3.93	[3.7]
0.025	Zr	--	5.52	5.77	[1.8]	[2.3]

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).

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

Det. Limit (ug/mL)	Multiplier= ALO#= Client ID= Run Date= (Analyte)	18.1 99-2109 @5 RW-08 7/21/99 ug/g	18.4 99-2110 @5 RW-09 7/21/99 ug/g	18.7 99-2112 @5 RW-11 7/21/99 ug/g		
0.015	Ag	--	--	--	--	--
0.060	Al	2,730	2,610	2,510	--	--
0.080	As	[2.7]	[3.1]	[2.9]	--	--
0.050	B	33.3	34.6	36.3	--	--
0.010	Ba	2.55	[0.60]	--	--	--
0.005	Be	--	--	--	--	--
0.100	Bi	--	--	--	--	--
0.250	Ca	319	237	200	--	--
0.015	Cd	33.3	32.2	31.2	--	--
0.100	Ce	18.7	[5.1]	[2.0]	--	--
0.025	Co	[2.3]	[2.3]	[2.2]	--	--
0.020	Cr	102	65.3	50.6	--	--
0.015	Cu	14.1	13.8	13.4	--	--
0.050	Dy	--	--	--	--	--
0.100	Eu	--	--	--	--	--
0.025	Fe	806	206	66.6	--	--
2.000	K	803	788	774	--	--
0.025	La	14.5	[4.3]	[2.2]	--	--
0.020	Li	--	--	--	--	--
0.100	Mg	[2.8]	[2.0]	--	--	--
0.005	Mn	88.7	29.1	23.1	--	--
0.030	Mo	18.0	17.7	17.2	--	--
0.100	Na	117,000	117,000	114,000	--	--
0.100	Nd	46.5	[14]	[6.1]	--	--
0.030	Ni	261	256	250	--	--
0.100	P	327	330	321	--	--
0.060	Pb	174	109	87.5	--	--
0.300	Pd	[28]	[11]	[6.2]	--	--
0.300	Rh	--	--	--	--	--
0.075	Ru	18.5	17.1	16.1	--	--
0.050	Sb	--	--	--	--	--
0.050	Se	[1.6]	[1.7]	[1.5]	--	--
0.100	Si	32.5	26.2	24.1	--	--
1.000	Sn	--	--	--	--	--
0.005	Sr	1.73	109	140	--	--
0.500	Te	--	--	--	--	--
0.800	Th	--	--	--	--	--
0.005	Ti	[0.40]	[0.15]	--	--	--
0.250	Tl	--	--	--	--	--
2.000	U	[61]	[50]	[44]	--	--
0.015	V	[0.30]	--	--	--	--
0.500	W	[87]	[84]	[82]	--	--
0.010	Y	7.56	3.15	[1.8]	--	--
0.020	Zn	11.1	7.50	6.39	--	--
0.025	Zr	[3.9]	[3.0]	[1.6]	--	--

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.
2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.
3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Battelle Pacific Northwest Laboratories
Analytical Chemistry Laboratory

EXHIBIT I
PAGE 1 of 1

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

Client name: Sam Bryan
Work Auth. Doc (WAD): ASR-5426
Tank/Core/Project:
Special Instructions

Work package number: W51302
Project number: 27753
PNL QA plan: MCS-033
PNL Impact level:
Prep. lab (SAL/SRPL/other):
Preparation batch number:

	ACL Sample ID	ACL order number or Client sample ID	Sample Mass Identifier (Vial # 7/9/99 JMD)	Sample Volume (ml)	Spike added Volume (ml)	Spike added Weight (g)	Final solution Volume (ml)	Process Factor (1)
1	99-2102	OP-01	3.9890	3 mls			15 mls	
2	Dup-2102	OP-01 Dup	3.9876					
3	99-2103	OP-02	3.7970					
4	99-2104	OP-03	3.9178					
5	99-2105	OP-04	3.9018					
6	99-2106	OP-05	3.9211					
7	99-2107	LH-06	3.9480					
8	99-2108	LH-07	3.8832					
9	99-2109	RW-08	4.1513					
10	99-2110	RW-09	4.0680					
11	99-2111	RW-10	4.0514					
12	99-2112	RW-11	4.0159					
13	MS-2104	OP-03 Spiked	3.9115		0.3 ml part A 0.3 ml part B			
14	BS-2102	DI-H2O Spiked	3.0057		0.3 ml part A 0.3 ml part B			

Analyst's sample preparation comments: All samples were weighed prior to the digestion, - see sample Mass above! TCLP spiking solutions #990305 Tclp Part-A and #990629 Tclp Part-B were used with 0.3ml of each per spiked sample used. All of the samples were basic, salty solutions that reacted with the addition of 0.6 ml conc. trace metals grade HCl and reacted further with the addition of 0.6 ml. conc. trace metals grade HNO_3. An additional 0.6 mls. of conc. trace metals grade HNO_3 was used and several samples were dried pH'ed to verify acidity prior to the digestion.

Spike source: Standard Stock
PNL spike ID number: See Notes
Anal. balance M&TE: 360-06-01-03
Sample filtered (yes/no): 0.45 HCl

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

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

See Pg. 2 ...

Analyst/Date: Lori P. Darnell 7/8/99 Reviewer/Date:

Battelle Pacific Northwest Laboratories
Analytical Chemistry Laboratory

EXHIBIT I
PAGE 1 of 1

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

Client name: Sam Bryan
Work Auth. Doc (WAD): ASR-5426
Tank/Core/Project:
Special Instructions

Work package number: W51302
Project number: 29953
PNL QA plan: MCS033
PNL Impact level:
Prep. lab (SAL/SRPL/other):
Preparation batch number:

	ACL Sample ID	ACL order number or Client sample ID	~~Vial~~ Sample identifier	Sample Volume (ml)	Spike added Volume (ml)	Spike added Weight (g)	Final solution Volume (ml)	Process Factor (1)
1	BL-2102	DI-H2O	3.0020	3 ml.			15 ml	
2				3.9 ml				
3								
4								
5								
6								
7	pipette #	H30754 @ 3 ml (21°C)			Pipette #	288618 @	0.3 ml (21°C)	
8	2.9978	g.			0.2994	g.		
9	2.9990				0.2992			
10	2.9996				0.2998			
11	3.0005				0.3002			
12	2.9984	↓			0.3005	↓		
13								
14								

Analyst's sample preparation comments: Upon completion of the digestion the samples were diluted to 15 mls and allowed to set overnight. Samples #99-2102, 99-2102 dup, 99-2107, 99-2109, 99-2110, 99-2111 and 99-2112 all contained a small amount of white to clear grainy material. All samples were filtered to 0.45 µm.

Spike source: See pg. 1.
PNL spike ID number:
Anal. balance M&TE:
Sample filtered (yes/no):

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

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

Analyst/Date: Lori P. Darnell 7-8-99 Reviewer/D

Rev. 2. .95 JMR

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

99-2102
8/10/99

Client : Sam Bryan

Cognizant Scientist: _____ Date : _____

Concur : _____ Date : _____

ALO ID Client ID	**Density g/ml**
99-2102 **OP-01**	1.330
99-2103 **OP-02**	1.266
99-2104 **OP-03**	1.306
99-2105 **OP-04**	1.301
99-2106 **OP-05**	1.307
99-2107 **LH-06**	1.316
99-2108 **LH-07**	1.294
99-2109 **RW-08**	1.384
99-2110 **RW-09**	1.356
99-2111 **RW-10**	1.351
99-2112 **RW-11**	1.339

requested density information

RT HALLEN
Date 8/10/99
Route
File T1-043
Copy - electronic file

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

99-2102
8/10/99

Client : Sam Bryan

Cognizant Scientist: _____ Date : _____

Concur : _____ Date : _____

Measured Activities (µCi/g)

ALO ID Client ID	Sr-90 Error %	Am-241 Error %	Cm-243+ Cm-244 Error %	Cm-242 Error %	--- Gamma Emitters --- Co-60 Error %	Cs-137 Error %	Eu-154 Error %	Eu-155 Error %	Am-241 Error %
99-2102 **OP-01**	2.79E+1 3%				5.32E-2 2%	1.52E-2 7%	2.08E-1 2%	1.52E-1 4%	1.87E-1 5%
99-2103 **OP-02**	7.97E+0 3%				5.68E-2 2%	1.45E-2 3%	2.82E-2 2%	2.16E-2 4%	1.25E-2 10%
99-2103 DUP **OP-02**	7.94E+0 3%								
RPD	0.4%								
99-2104 **OP-03**	6.32E+0 3				5.00E-2 2%	1.36E-2 3%	2.84E-2 2%	2.00E-2 4%	1.41E-2 9%
99-2105 **OP-04**	9.16E+0 3%				5.02E-2 2%	1.35E-2 3%	2.98E-2 2%	2.16E-2 4%	1.71E-2 8%
99-2106 **OP-05**	5.09E+0 3%				4.88E-2 2%	1.34E-2 3%	3.96E-2 2%	2.92E-2 4%	2.23E-2 6%
99-2107 **LH-06**	2.91E+1 3				5.38E-2 2%	1.72E-2 3%	2.11E-1 1%	1.60E-1 3%	1.95E-1 4%
99-2108 **LH-07**	6.98E+0 3%				5.04E-2 2%	1.42E-2 3%	3.10E-2 2%	2.32E-2 4%	1.58E-2 8%
99-2109 **RW-08**	4.71E+1 3%	2.63E-1 5%	5.25E-3 8%	6.68E-4 20%					
99-2110 **RW-09**	1.59E+1 3%	7.63E-2 5%	1.87E-3 7%	2.07E-4 15%					
99-2111 **RW-10**	1.67E+1 3%	6.27E-2 5%	1.40E-3 7%	1.38E-4 18%					
99-2111 REP **RW-10**		6.31E-2 5%	1.56E-3 7%	1.33E-4 19%					
99-2112 **RW-11**	9.41E+0 3%	2.66E-2 6%	2.28E-4 24%	4.80E-5 57%					
BI-2102	6.91E-4 4%				<3.E-5	2.00E-5 45%	<6.E-5	<6.E-5	<6.E-5
Matrix Spike	87%	67%							
Blank Spike	95%	95%							
Blank	<4.E-5	<2.E-6	<2.E-7	<2.E-7					

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

ASR # **5426**

WP# **W51302**

File: L:\radchem\hydroxide\asr5421
Analysis Date: 7/9/99
Print Date: 7/12/99

Hydroxide and Alkalinity Determination
Governing Procedures: **PNL-ALO-228:** Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates and Operation of Brinkman 636 Auto-Titrator
Equip # **WB76843**
Lab Loc. 525

Analyst: [signature] 7/12/99
Reviewer: [signature] 7/12/99

Titrant	Molarity
HCl	**0.2034**

Std. & Spike	Molarity
NaOH	**0.1018**

									OH				
									1st Equivalence				
RPG #	Sample ID		Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Titrator Routine #	Initial pH reading		Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
99-2108	**LH-07**		0.050	0.0658	1.316	4	10.982		0.127	10.354	0.026	0.52	
99-2108	**LH-07**	Replicate	0.200	0.2676	1.338	5	11.427		0.486	10.637	0.099	0.49	4.43%
99-2109	**RW-08**		0.100	0.1434	1.434	6	11.344		0.345	10.717	0.070	0.70	
99-2109	**RW-08**	Replicate	0.100	0.1401	1.401	7	11.419		0.344	10.705	0.070	0.70	0.29%
99-2110	**RW-09**		0.100	0.1421	1.421	8	11.505		0.294	10.848	0.060	0.60	
99-2110	**RW-09**	Replicate	0.100	0.1396	1.396	9	11.459		0.295	10.809	0.060	0.60	0.34%
99-2112	**RW-11**		0.100	0.1417	1.417	10	11.456		0.310	10.716	0.063	0.63	
99-2112	**RW-11**	Replicate	0.100	0.1337	1.337	11	11.500		0.307	10.679	0.062	0.62	0.97%
QC Data:													
Reag. Blk.			5.00			1	5.366					**OH % Recovery, Accur**	
Standard 1	0.1018 N NaOH		5.000	5.0149	1.003	2	11.891		2.599	7.908	0.5286	**103.9%**	standard
Standard 2	0.1018 N NaOH		5.000	5.0305	1.006	3	12.031		2.468	7.906	0.5020	**98.6%**	standard
99-2108MS	LH-07 + 2mL 0.1N NaOH		0.100	0.1318	1.318	12	11.576		1.186	10.664	0.241	**93.7%**	matrix spk
99-2109MS	RW-08 + 2mL 0.1N NaOH		0.100	0.146	1.460	13	11.947		1.262	10.809	0.257	**91.7%**	matrix spk
99-2110MS	RW-09 + 2mL 0.1N NaOH		0.100	0.1401	1.401	14	11.894		1.203	10.748	0.245	**90.8%**	matrix spk
99-2112MS	RW-11 + 2mL 0.1N NaOH		0.100	0.1399	1.399	15	11.916		1.127	10.767	0.229	**81.8%**	matrix spk

* -- Volume restrictions existed

Buffer	VWR Lot #	CMS#	Expire Date
10	981659-24	144109	Jul-00
4	981583-24	144107	Jun-00
7	981894-24	144108	Aug-00

Performance checks

Balance # 360--01-06-037

		Vol.	Wt.
Pipet #	H30762	5.00	5.0084
Pipet #	288618	0.200	0.2004
Pipet #	120737	0.100	0.0998

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

ASR # 5426
WP# W51302

File: L:\radchem\hydroxide\asr5421
Analysis Date: 7/9/99
Print Date: 7/12/99

Hydroxide and Alkalinity Determination
Governing Procedures: PNL-ALO-228: Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates
and Operation of Brinkman 636 Auto-Titrator
Equip # WB76843
Lab Loc. 525

Analyst: [signature] 7/12/99
Reviewer: L.D. Greenwood 7/12/99

Titrant	Molarity
HCl	0.2034

				CO3						HCO3				
				2nd Equivalence Point						3rd Equivalence Point				
RPG #	Sample ID		Sample Vol. (mL)	Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD		Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	millimole RPD
99-2108	LH-07	0	0.050	0.322	7.660	0.040	0.793			0.556	4.293	0.048	0.95	
99-2108	LH-07	Replicate	0.200	1.292	7.814	0.164	0.820	3.28%		2.160	4.616	0.177	0.88	7.54%
99-2109	RW-08	0	0.100	1.290	7.459	0.192	1.922			2.066	4.704	0.158	1.58	
99-2109	RW-08	Replicate	0.100	1.253	7.589	0.185	1.849	3.88%		2.028	4.664	0.158	1.58	0.1%
99-2110	RW-09	0	0.100	1.150	7.691	0.174	1.741			1.857	4.770	0.144	1.44	
99-2110	RW-09	Replicate	0.100	1.153	7.517	0.175	1.745	0.23%		1.838	4.733	0.139	1.39	3.16%
99-2112	RW-11	0	0.100	1.077	7.601	0.156	1.560			1.708	4.808	0.128	1.28	
99-2112	RW-11	Replicate	0.100	1.007	7.800	0.142	1.424	9.13%		1.639	4.681	0.129	1.29	0.16%
cy							CO3 % Recovered							
Standard 1	0.1018 N NaOH		5.000	2.674	4.109	0.01525	0.003	sample						
Standard 2	0.1018 N NaOH		5.000	2.541	3.999	0.01485	0.003	sample				HCO3 % recovered		
99-2108MS	LH-07 + 2mL 0.1N NaOH		0.100	1.624	7.874	0.08909	**110.5%**	sample		2.079	4.749	0.0925	**100.9%**	sample
99-2109MS	RW-08 + 2mL 0.1N NaOH		0.100	2.273	7.694	0.20564	**109.1%**	sample		3.126	4.734	0.1735	**110.0%**	sample
99-2110MS	RW-09 + 2mL 0.1N NaOH		0.100	2.116	7.398	0.1857	**106.5%**	sample		2.850	4.669	0.1493	**105.5%**	sample
99-2112MS	RW-11 + 2mL 0.1N NaOH		0.100	1.982	7.676	0.17391	**116.6%**	sample		2.716	4.713	0.1493	**116.2%**	sample

Matrix spike recovery is calculated as follows:
Spike = 2.00 mL 0.1018 N NaOH was added to the 0..100-mL of sample for each matrix spilke.
SpikeTitrant vol. (sample @ .1mL + spike) - SampleTitrant vol. (average sample only equated to .1mL) * 0.2034 N (HCl titrant) = meq. OH
meq OH / 2.00 mL added = meq OH/mL found / 0.1018 N OH added * 100 = % recovered.

Prep record on 0.2034 M HCl is on following page.

Chem Rec_51a

Prep date: 4/18/99

Preparation of Standardized 0.2 M HCl

WP# K51300

Standardized O.1021 M NaOH will be re-checked and then used to standardized the ~ 0.1 M HCl solution. The 0.1021 M NaOH was prepared in Chem Rec_37 (see Chem Rec_37 --prep.date 2-25-98 for original data) and re-verified against NIST SRM84j Potassium Acid Phthalate KHC8H404 (KAP) = 204.23 g/mole -- Barcode # 52232 --- (see below verification check).
The re-standardized value of 0.1018 M NaOH was reassigned to this NaOH solution with a revised Expiration Date of Feb. 2000.
Prepared 1- liters of ~0.2 M HCl by diluting 100 mL of 1.029M HCl (Chemrec_10) to 0.5 L with DI. H2O.
20 mL aliquots of 0.2 M HCl were were neutralized to the phenopthalien endpoint using the re-standardized 0.1018 M NaOH. The volume of NaOH is accurate to +/- 0.02mL and the pipitting error is estimated to be < 1% @ 1s. Thus total error is < 3 % for the measurements

NaOH Molarity veification

Verification Test #	Wt. of KAP	Vol. of **0.1021M NaOH** to neutralize	NaOH Molarity =a * 1000 / b * 204.23	Molarity Error +/- @ 1 s
1	0.80894	38.95	0.1017	
2	0.80582	38.84	0.1016	
3	0.96233	46.12	0.1022	
		Ave=	**0.1018**	0.0003
			re-certified value	

Titration Id.	aliquot of sample	Vol. of **0.1018M NaOH** to neutralize	**Molarity of Acid** in Sample	Molarity Error +/- @ 1 s
1	20.00	39.88	0.2030	
2	20.00	39.92	0.2032	
3	20.00	40.04	0.2038	
		Ave Molarity HCl =	**0.2034**	0.00042

Analyst/Date 7/12/99

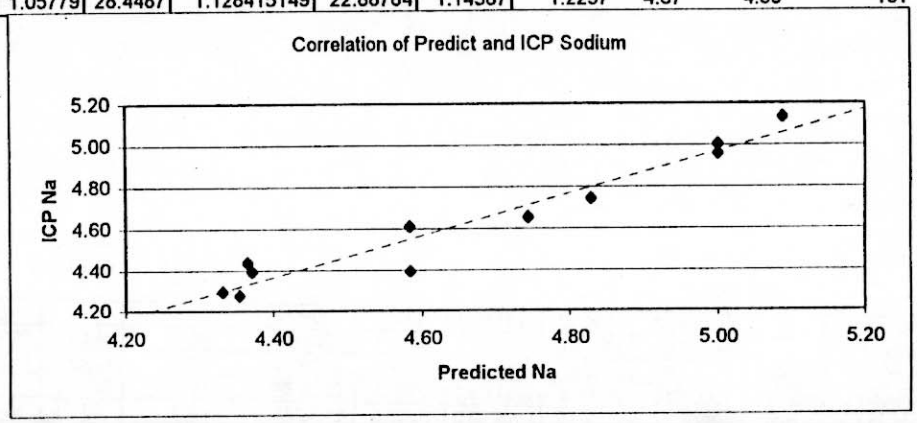
APPENDIX E

Appendix E: Calculations

The MN series were the first run. It was assumed that the archived AN-107 had 5M sodium and 0.2M OH (report said .24 target but only got 0.126).
The waste was titrated and found to have no free hydroxide. So only Mn-7 and 8 had any free hydroxide.

								0.4M KMnO4												
density				1.26		1.33		1.0361		1.116		1.162								
Sample	ID	sam&vial	vial tar	waste wei	waste vol	OH weig	OH vol	MnO4 w	MnO4 v	Ca weig	Ca vol	Sr/Eu we	Sr /Eu vo	Final Ma	Mass correction	final volum	vol correc	density	predicted	ICP. M	ICP(g/L)
1	Mn-01																	1.27	5.00	5.00	115
2	Mn-02																	1.2664	5.00	4.96	114
3	Mn-03	49.9639	24.82	25.1461	19.95722	0		1.881	1.8155	0		0		27.0271	1.074802852	21.77268	1.09097	1.2481	4.58	4.61	106
4	Mn-04	50.1885	25.02	25.1673	19.97405	0		1.8795	1.814	0		0		27.0468	1.07468024	21.78806	1.09082	1.2348	4.58	4.39	101
5	Mn-05	50.7552	24.91	25.8414	20.50905	0		1.1538	1.1136	0		0		26.9952	1.044649284	21.62265	1.0543	1.2494	4.74	4.65	107
6	Mn-06	50.574	24.92	25.6545	20.36071	0		3.2592	3.1456	0		0		28.9137	1.127042039	23.50636	1.1545	1.2331	4.33	4.29	98.7
7	Mn-07	49.5249	24.87	24.6575	19.56944	2.9502	2.218	1.872	1.8068	0		0		29.4797	1.195567272	23.59442	1.20568	1.2552	5.09	5.13	118
8	Mn-08	50.0023	24.9	25.1037	19.92357	3.0409	2.286	3.2704	3.1565	0		0		31.415	1.251409155	25.36641	1.27319	1.2377	4.83	4.74	109
9	Mn-09	49.5991	24.91	24.6915	19.59643	0		1.8783	1.8129	1.2248	1.0975	0		27.7946	1.125674827	22.50678	1.14851	1.2283	4.35	4.28	98.3
10	Mn-10	49.7093	24.89	24.816	19.69524	0		1.8685	1.8034	0		1.232	1.06024	27.9165	1.124939555	22.55888	1.1454	1.2273	4.37	4.44	102
11	Mn-11	50.0922	24.88	25.2112	20.00889	0		1.8867	1.821	0		1.3508	1.05779	28.4487	1.128415149	22.88764	1.14387	1.2297	4.37	4.39	101
											Eu den	1.277									

	mass c	total Alph	Am-24	Eu-154	Eu-155	Sr-90	DFs	total Alp	Am-241	Eu-154	Eu-155	Sr-90
Mn-01	1	0.2615	0.24	0.262	0.191	36.3	Mn-01	1	1	1	1	1
Mn-02	1	0.244	0.221	0.251	0.184	36.2	Mn-02	1.07172	1.086	1.0438	1.038	1.00276
Mn-03	1.0748	0.0507	0.041	0.0594	0.0447	24.7	Mn-03	4.79883	5.4067	4.1038	3.9755	1.36735
Mn-04	1.0747	0.0468	0.047	0.0633	0.0445	23.6	Mn-04	5.19932	4.7718	3.8514	3.9939	1.43125
Mn-05	1.0446	0.0888	0.096	0.101	0.0778	27.7	Mn-05	2.81896	2.4032	2.4832	2.3501	1.25446
Mn-06	1.127	0.0281	0.026	0.0414	0.0288	17.8	Mn-06	8.25706	8.1589	5.6151	5.8844	1.80945
Mn-07	1.1956	0.0124	0.012	0.0284	0.0202	16.9	Mn-07	17.6391	16.869	7.7163	7.9088	1.79658
Mn-08	1.2514	0.00569	0.008	0.0213	0.0151	12.65	Mn-08	36.7249	23.162	9.8293	10.108	2.29307
Mn-09	1.1257	0.0132	0.013	0.0344	0.0248	3.35	Mn-09	17.5989	15.911	6.766	6.8418	9.62607
Mn-10	1.1249	0.0373	0.037	0.0501	0.038	9.69	Mn-10	6.23209	5.8132	4.6487	4.4681	3.33007
Mn-11	1.1284	0.0892	0.091	0.0996	0.0741	18.6	Mn-11	2.59799	2.3398	2.3312	2.2843	1.72952
MN-12	solids	0.589	0.535	0.572	0.42	50.9						



For the PR series of experiments, the target [OH] concentration was 1M. So all of the waste was caustic adjusted except for PR-14 which first had acid added.
From TI-040, 382.1339 g of C3E3, d=1.26g/mL and 24.1201 grams of 50% NaOH (d=1.5g/mL) was added. Final density of 1.263g/mL.

Na

			number indicates order of addition																			
			1				2				3				4							
			AN-107/OH		density, g/mL =	1.263	Ca added		Ca(NO3)2 density, g/mL =	1.1169	Sr added		Sr(NO3)2 density, g/mL =	1.1574	1 M NaMnO4 added		MnO4- density, g/mL =	1.0857				
test #	Vial ID	Vial tare wt, g	target mL	gross wt	net wt of addition	volume, mL	target mL	gross wt	net wt of addition	volume, mL	target mL	gross wt	net wt of addition	volume, mL	target mL	gross wt	net wt of addition	volume, mL	Sum of volumes	Sum of net wts	calculated density	Mass Correction
1	PR-01	24.8243	20	49.4175	24.5932	19.4721	0	49.418	0	0	0	49.4175	0	0	0	49.4175	0	0	19.4721	24.5932	1.263	1
2	PR-02	24.9575	20	50.3622	25.4047	20.1146	0	50.362	0	0	0	50.3622	0	0	0	50.3622	0	0	20.1146	25.4047	1.263	1
3	PR-03	24.8606	20	50.8044	25.9438	20.5414	0	50.804	0	0	0	50.8044	0	0	1.05	51.9752	1.1708	1.078383	21.6198	27.1146	1.254156	1.045128
4	PR-04	24.8342	20	49.7018	24.8676	19.6893	0	49.702	0	0	0	49.7018	0	0	1.73	51.5653	1.8635	1.716404	21.4057	26.7311	1.248783	1.074937
5	PR-05	24.987	20	50.4443	25.4573	20.1562	0	50.444	0	0	0	50.4443	0	0	3.8	54.5853	4.141	3.814129	23.9703	29.5983	1.234788	1.162665
6	PR-06	24.7558	20	50.2934	25.5376	20.2198	0	50.293	0	0	1.62	52.2358	1.9424	1.6782	1.05	53.393	1.1572	1.065856	22.9639	28.6372	1.247053	1.121374
7	PR-07	24.832	20	50.0323	25.2003	19.9527	0	50.032	0	0	1.62	51.9513	1.919	1.658	1.05	53.1169	1.1656	1.073593	22.6844	28.2849	1.24689	1.122403
8	PR-08	24.8983	20	50.8475	25.9492	20.5457	0	50.848	0	0	1.62	52.7592	1.9117	1.6517	0.61	53.4563	0.6971	0.642074	22.8395	28.558	1.250379	1.100535
9	PR-09	24.9962	20	50.7053	25.7091	20.3556	0	50.705	0	0	1.05	51.9557	1.2504	1.0804	1.05	53.1405	1.1848	1.091278	22.5272	28.1443	1.249347	1.094721
10	PR-10	24.918	20	50.1399	25.2219	19.9698	0	50.14	0	0	1.05	51.4949	1.355	1.1707	0.61	52.2038	0.7089	0.652943	21.7935	27.2858	1.252015	1.08183
11	PR-11	24.9422	20	49.8759	24.9337	19.7416	0.2	50.092	0.216	0.1934	1.05	51.3453	1.2534	1.0829	0.61	52.0323	0.687	0.632771	21.6508	27.0901	1.251231	1.086485
12	PR-12	24.9616	20	50.3058	25.3442	20.0667	0.2	50.523	0.2176	0.1948	1.62	52.4478	1.9244	1.6627	1.05	53.6237	1.1759	1.08308	23.0073	28.6621	1.245785	1.130914
13	PR-13	27.4981	20	52.0174	24.5193	19.4135	0	52.017	0	0	1.62	53.958	1.9406	1.6767	1.05	55.1303	1.1723	1.079764	22.1700	30.2161		1.232339
14	PR-14	26.5477	20	51.5127	24.965	19.7664	0	51.513	0	0	0	51.5127	0	0	1.05	52.6887	1.176	1.083172	20.8496	27.9480		1.119487

In addition to reagents PR-13 had NaNO3 added	2.5839	grams		26.548	49.713	50.89	52.6887		51.513	52.6887				
In addition to reagents PR-14 had HNO3 added	1.8070				23.165	1.176	1.7999		24.965					

ALO ID	Co-60	Cs-137	Eu-154	Eu-155	Am-241	vol c	t	Am DF	Eu DF	Am DF (mass)	Eu DF (mass)	mass c
PR-01	6.33E-2	1.94E-2	2.60E-1	2.01E-1	2.31E-1		1	1	1	1	1	
PR-02	8.07E-2	2.26E-2	2.93E-1	2.18E-1	2.45E-1		1	1	1	0.94	0.92	1
PR-03	6.69E-2	1.73E-2	2.46E-2	1.58E-2	1.08E-2		1.0525	22	13	20	12	1.045128
PR-03	7.47E-2	2.01E-2	2.77E-2	1.99E-2	1.28E-2		1.0525	18	10	17	10	1.045128
PR-04	7.09E-2	1.95E-2	2.11E-2	1.50E-2	7.18E-3		1.0865	31	13	30	12	1.074937
PR-05	6.73E-2	1.89E-2	1.28E-2	9.04E-3	3.66E-3		1.19	56	20	54	19	1.162665
PR-06	6.86E-2	1.83E-2	3.07E-2	2.37E-2	1.63E-2		1.1335	13	8	13	8	1.121374
PR-07	6.90E-2	1.89E-2	3.14E-2	2.33E-2	1.74E-2		1.1335	12	8	12	8	1.122403
PR-08	7.10E-2	1.82E-2	7.64E-2	5.63E-2	5.23E-2		1.1115	4	3	4	3	1.100535
PR-08	7.12E-2	1.89E-2	7.90E-2	5.61E-2	5.04E-2		1.1115	4	3	4	3	1.100535
PR-09	7.11E-2	1.93E-2	2.27E-2	1.65E-2	8.80E-3		1.105	25	12	24	11	1.094721
PR-10	7.02E-2	1.81E-2	4.54E-2	3.02E-2	2.29E-2		1.083	10	7	9	6	1.08183
PR-11	6.98E-2	1.92E-2	2.90E-2	2.13E-2	1.20E-2		1.093	19	9	18	9	1.086485
PR-12	6.83E-2	1.78E-2	1.68E-2	1.27E-2	6.37E-3		1.1435	34	15	32	14	1.130914
PR-13	6.54E-2	1.69E-2	1.44E-2	1.10E-2	6.16E-3		1.1335	35	17	30	15	1.232339
PR-14	6.92E-2	1.84E-2	1.18E-2	7.50E-3	2.48E-3		1.116	89	26	83	24	1.119487
PR-15-SOL-(07)	5.76E-2	2.71E-2	6.43E-1	4.67E-1	6.38E-1							
PR-15-SOL-(07)	5.77E-2	2.68E-2	7.41E-1	5.33E-1	7.01E-1							

ALO ID	Sr-90	Vol correction	Sr DF (mass)	Mass correction	
PR-01	3.52E-1	1	1	1	PR-01
PR-02	4.17E-1	1	1	1	PR-02
PR-03	2.14E-1	1.0525	2	1.045128316	PR-03
PR-03	1.91E-1	1.0525	2	1.045128316	PR-03
PR-04	1.45E-1	1.0865	3	1.074936866	PR-04
PR-05	6.09E-2	1.19	6	1.16266454	PR-05
PR-06	1.96E-2	1.1335	19	1.121373974	PR-06
PR-07	3.06E-2	1.1335	12	1.122403305	PR-07
PR-08	4.56E-2	1.1115	8	1.100534891	PR-08
PR-08	4.84E-2	1.1115	8	1.100534891	PR-08
PR-09	4.37E-2	1.105	9	1.094721324	PR-09
PR-10	2.91E-2	1.083	13	1.08182968	PR-10
PR-11	2.86E-2	1.093	13	1.086485359	PR-11
PR-12	2.06E-2	1.1435	18	1.130913582	PR-12
PR-13	2.39E-2	1.1335	14	1.232339422	PR-13
PR-14	1.42E-1	1.116	3	1.119487282	PR-14
PR-15-SOL-(07)	6.99E-1				
PR-15-SOL-(07)	8.57E-1				
PR-15-SOL-(07)	6.95E-1				

The third series or Phase 3 experiments were to optimize treatment, and see if conditions from PR-10, minimal reagent addition would work.
However, the client also asked that we change the treatment scheme. Add Sr first, cook for 2 hours, then add MnO4 and cook for additional 2 hours.
Four different wastes used. OP-01, OP-03 to OP-05 all used C3E4 with 1M OH and 1.5M NaNO3. OP-02 was a repeat of PR-10 and used C3E3 caustic adjusted to 1M, same as PR-01.
LH-06 and LH-07 used C3E4 with 0.5M NaOH and 1.5M NaNO3. RW-08 to RW-11 used combined CL-1 and CL-2, AN-107 diluted feed from Lumetta's task/studies.

			number indicates order of addition																			
			1				2				3				4							
			AN-107/OH		density, g/mL =	1.3308	MnO4 added		MnO4- density, g/mL =	1.0857	Sr added		Sr(NO3) 2 density, g/mL =	1.1574	MnO4- added		MnO4- density, g/mL =	1.0857					
test #	Vial ID	Vial tare wt, g	target mL	gross wt	net wt of addition	volume, mL	target mL	gross wt	net wt of addition	volume, mL	target mL	gross wt	net wt of addition	volume, mL	target mL	gross wt	net wt of addition	volume, mL	Sum of volumes	Sum of net wts	calculated density	Volume correction factor	Weight correction factor
control	OP-01		20																		1.3308		
	OP-03	25.0317	20	51.856	26.8243	20.157	0			0	1.05	53.0909	1.2349	1.067	0.61	53.7956	0.7047	0.649074	21.8726	28.7639	1.315068	1.0851355	1.072308
	OP-04	24.9225	20	51.9486	27.0261	20.308	0				1.05	53.1779	1.2293	1.0621	0.61	53.8559	0.678	0.624482	21.9948	28.9334	1.315468	1.0830505	1.070573
	OP-05	25.0383	20	52.9514	27.9131	20.975	0.61	53.6391	0.6877	0.6334	1.05	54.8314	1.1923	1.0302					22.6382	29.7931	1.316052	1.0793133	1.067352
control	PR-02					1.263																	
	OP-02	24.8722	20	51.9494	27.0772	21.439	0				1.05	53.1895	1.2401	1.0715	0.61	53.8377	0.6482	0.597034	23.1073	28.9655	1.263 1.253522	1.0778256	1.069738
control	LH-06	25.1019	20			1.3133															1.3133		
	LH-07	25.014	20	52.8324	27.8184	21.182	0				1.05	54.0808	1.2484	1.0786	0.61	54.7626	0.6818	0.627982	22.8887	29.7486	1.299709	1.0805685	1.069386
control	RW-08		20			1.392															1.392		
	RW-09	25.0788	20	53.3787	28.2999	20.33	0				1.05	54.6123	1.2336	1.0658	0.61	55.2629	0.6506	0.599245	21.9955	30.1841	1.372287	1.0819011	1.06658
	RW-10	25.0473	20	53.2996	28.2523	20.296	0				1.05	54.5104	1.2108	1.0461	0.61	55.1658	0.6554	0.603666	21.946	30.1185	1.372392	1.0812864	1.066055
	RW-11	24.9541	20	52.5673	27.6132	19.837	0				1.62	54.4343	1.867	1.6131	1.05	55.5941	1.1598	1.068251	22.5184	30.64	1.360664	1.1351686	1.109614

Vial ID	Sr DF	Am DF	control #
OP-01			control
OP-02	3.89	14.4334	PR-02
OP-03	4.117	12.3681	
OP-04	2.845	10.2148	
OP-05	5.135	7.8565	
LH-07	3.899	11.541	LH-06
RW-09	2.777	3.23175	RW-08
RW-10	2.646	3.92216	
RW-11	4.511	8.9105	

		Sr-90	Am-241		Sr DF	Sr DF with ES		Am DF	AM DF with ES
AN-107 with entrained solids		62.7	0.384						
ES removed	RW-08	47.1	0.263						
Treated Samples	RW-09	15.9	0.0763		2.77735	3.6972		3.2318	4.7186
Treated Samples	RW-10	16.7	0.0629		2.6456	3.5219		3.9222	5.7267
Treated Samples	RW-11	9.41	0.0266		4.51086	6.0049		8.9105	13.01

APPENDIX F

Appendix F: Staff Roles and Responsibilities

Staff Member	Role/Responsibility
Richard Hallen	Scientist/Technical Leader - Sr/TRU Removal
Sam Bryan	Scientist/Hot Cell Experiments - lead and direct hot cell experiments
Vaughn Hoopes	Technician/Hot Cell Experiments- conduct experiments and sample prep.

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