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PETER MAGGIORE
Secretary

VIA FACSIMILE: (202)586-4403

September 24, 1998

The Honorable Bill Richardson
Secretary of Energy
U.S. Department of Energy
Washington D.C. 20585

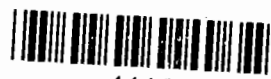
RE: Approval of Confirmatory Sampling and Analysis Plan, Revision 2, for Waste Stream TA-55-43, Lot No. 1.

Dear Secretary Richardson:

The New Mexico Environment Department (NMED) has reviewed the Confirmatory Sampling and Analysis Plan, Revision 2, (SAP, Rev. 2) submitted by the Department of Energy (DOE) on September 13, 1998. The original Sampling and Analysis Plan was received by NMED on July 27, 1998 and was submitted by DOE in order to provide a methodology for sampling and chemical analysis of Waste Stream TA-55-43. This confirmatory sampling is required to demonstrate that Waste Stream TA-55-43, Lot No.1 does not contain hazardous waste and may, therefore, be disposed at the Waste Isolation Pilot Plant (WIPP) without a hazardous waste permit.

NMED determined the original Plan to be inadequate because it failed to address the four requisite elements of an SAP (see NMED letter of August 26, 1998). DOE responded by submitting the first revision to the SAP on September 8, 1998, and, after receiving an NMED request for information dated September 9, 1998, submitted the SAP, Rev. 2.

NMED's review of the SAP, Rev. 2, is presented in the enclosed attachment, "Review of the Los Alamos Confirmatory Sampling and Analysis Plan for Waste Stream TA-55-43, Lot No. 1, Revision 2". Based on this review, NMED has determined to approve SAP, Rev. 2, with the conditions specified below. Please be advised that this approval does not represent a final agency



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decision with regard to a determination of whether TA-55-43 is non-hazardous and whether TA-55-43, Lot No. 1 is subject to the requirements of the New Mexico Hazardous Waste Act. NMED will make that determination after review of all sampling and analytical results.

The Los Alamos National Laboratory (LANL) shall implement the following conditions for the Sampling and Analysis Plan, Revision 2:

1. LANL/DOE shall incorporate, into the sampling design, reassessment of the sample selection process to address differences in weight distributions of the waste matrices whenever any matrix distribution exceeds a 10% change from that assumed in the SAP, Rev. 2;
2. LANL/DOE may use the "cold" HEPA metal analysis in proportion to its relative contribution to the total metals category only under the condition that the "cold" HEPA analysis exhibits TC metals in higher concentration than the other "hot" metals analyzed. LANL/DOE shall use the results of the "hot" metal analysis, shall apply these results to the entire metals category, and shall apply the highest metal analyses values to the HEPA metals if the "hot" metals analytical results are higher than the "cold" HEPA analytical results;
3. LANL/DOE shall submit, upon completing the implementation of the SAP, Rev. 2, a final report which details the implementation of the SAP, Rev. 2 and demonstrates that each condition for approval has been achieved. LANL/DOE shall include with the final sampling report provided to NMED a) step-wise calculations used to derive the optimal sample numbers to demonstrate the correct application of the statistical approach, including calculations for the optimal sample number n , weighted means and standard deviations; b) all analytical results for each sample collected; c) all supporting documentation on the analytical results (i.e., raw analytical data); d) all information and data on samples and/or materials in the sampled population which were excluded from the final calculations and an explanation of why they were excluded; and e) documentation and demonstration of the maintenance of sample "representativeness" throughout all sampling and subsampling procedures;
4. LANL/DOE shall calculate scenarios for Lot No. 1 assuming the various weight percent distributions and highest analytical values necessary to perform "worst case" analysis. These calculations are required if LANL/DOE determines the waste to be non-hazardous, and is necessary to ensure this determination holds true regardless of weight distribution, as LANL/DOE has indicated this distribution could change;
5. LANL/DOE shall calculate means and variances to determine whether the waste is hazardous using only "hot" data sampling results, except if "cold" HEPA results can be used (see Condition 2);
6. LANL/DOE shall provide documentation and an explanation regarding the exclusion of any drum that was originally selected for sampling and then subsequently excluded from the sampling set; and
7. NMED approval of the final report is required prior to shipment of Waste Stream TA-55-43, Lot No. 1 for disposal at the Waste Isolation Pilot Plant. NMED may require the submittal of additional information as necessary to approve the final report.

If you have any questions, or would like to meet regarding this approval, please call either Susan McMichael or Ed Kelley of my staff at (505)827-2855.

Sincerely,



Peter Maggiore, Secretary
New Mexico Environment Department

PM/cjm

cc w/att:

The Honorable Senator Domenici
The Honorable Senator Bingaman
The Honorable Congressman Skeen
The Honorable Congressman Redmond
The Honorable Congresswoman Wilson
The Honorable Governor Johnson
The Honorable Tom Udall, Attorney General, State of New Mexico
The Honorable Janet Reno, Attorney General of the United States, U.S.
Department of Justice
Carol Browner, Administrator, Environmental Protection Agency
Gregg Cooke, Regional Administrator, Environmental Protection Agency
Jennifer Salisbury, Secretary of Energy, Minerals & Natural Resources
Department
W. John Arthur III, Asst. Manager, Albuquerque Area Office
Mike McFadden, Manager, Carlsbad Area Office

bc w/out att:

Ed Kelley, Director of Water and Waste Management Division,
Environment Department
Benito Garcia, Bureau Chief, HRMB, Environment Department
Susan McMichael, Asst. General Counsel, Environment Department
John McKay, Asst. General Counsel, Environment Department
Connie Walker, Techlaw

**REVIEW OF THE LOS ALAMOS
CONFIRMATORY SAMPLING AND ANALYSIS PLAN
FOR WASTE STREAM TA-55-43, LOT NO. 01
REVISION 2**

Prepared for

the New Mexico Environment Department

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Prepared by

TechLaw, Inc.
300 Union Street Suite 600
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September 24, 1998

**REVIEW OF THE CONFIRMATORY SAMPLING
AND ANALYSIS PLAN FOR
TA-55-43, LOT NO. 1
REVISION 2**

The Los Alamos National Laboratory (LANL) has proposed disposal of waste stream TA-55-43, Lot No. 01, which LANL has determined to be non-hazardous, at the Waste Isolation Pilot Plant (WIPP). The New Mexico Environment Department (NMED) requested confirmatory sampling on July 10, 1998, to assess the non-hazardous nature of the waste. LANL responded on July 27, 1998 by submitting for NMED review Revision 2 of the Confirmatory Sampling and Analysis Plan (SAP) for TA-55-43, Lot No. 1. NMED reviewed the SAP and, in an August 26, 1998 letter to the Department of Energy (DOE), found it to be unsatisfactory because the SAP failed to meet the four requisite elements for sampling and analysis presented in the August 26, 1998 letter to the DOE. In the same letter, NMED provided comments on the SAP and suggested alternatives.

LANL responded on September 8, 1998 by revising the SAP to address NMED suggestions and concerns, and provided this response as the SAP, Revision 1. NMED performed a preliminary review of the SAP, Rev. 1 and raised additional questions in a September 9, 1998 letter. LANL then revised the SAP, Rev. 1, to create the SAP, Rev. 2, submitted on September 14, 1998, which incorporates information addressing NMED questions on the SAP, Rev. 1 (NMED questions and LANL responses are included as Attachment C to the SAP, Rev. 2).

NMED contracted TechLaw, Inc. to review the SAP. This Review evaluates each section of the SAP, Rev. 2, for technical adequacy, and incorporates review of public comment(s) received prior to September 23, 1998 in the administrative record for the disposal of Waste Stream TA-55-43, Lot No. 1 at WIPP. Each section includes a brief synopsis of the information presented in the SAP, Rev. 2, as well as a summary analysis of the information presented in the SAP, Rev. 2. In addition, the SAP, Rev. 2, was reviewed with respect to concerns raised by commentators, and an analysis of comments relative to specific technical issues in the SAP, Rev. 2, is also included in the applicable section-by-section review.

I. SUMMARY

The Los Alamos National Laboratory Sampling and Analysis Plan, Revision 2 (SAP Rev.2) includes a summary section that describes the overall statistical approach presented in the document, sample weight/size selection, and sample integrity. Refer to comments on Sections V, VI, and VIII of this Review regarding these technical elements. Because of ALARA¹ concerns, the Summary also proposes a reduction in sample size from 100 to 10 grams, exclusion of standard waste boxes from inclusion in the statistically sampled population, and exclusion of some

¹ ALARA is an acronym for "As Low As Reasonably Achievable" and refers to DOE guidance regarding the minimization of exposure to workers from radioactivity.

large metal objects from sampling due to difficulties associated with sample collection in a glove box. The Summary goes on to state that the stratified random sampling approach in the SAP, Rev.1, is consistent with the NMED's recommendations and with requirements in SW-846. The Summary also states the statistical analysis is based upon concentrations derived from "cold" rather than "hot" samples, and the results of the statistical analysis show that two samples (total) are required for confirmation of the non-mixed status of the waste. However, the SAP, Rev. 2, states that LANL conservatively proposes to collect two samples from each of the five matrices (ten samples in total), and one additional sample of the rust-colored material.

The overall statistical approach proposed in the SAP, Rev. 2, differs in some aspects from that recommended by the NMED (refer to Section V for a more detailed discussion of these differences). However, when the data used in the SAP, Rev. 2, approach is statistically evaluated using the somewhat different approach proposed by NMED, the number of samples that must be collected is consistent between both approaches.

Reduction of the sample size to 10 grams is consistent with the intent of SW-846, which suggests a 100 gram sample size but also indicates that the sample size need only be that necessary to meet the needs of the method (refer to Section VIII.B for additional discussion). It is also consistent with the Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste, 62 FR 62070-62094; November 20, 1997. Sample integrity information referenced in the SAP, Rev. 2, indicates that QA/QC, analytical chemistry, and chain of custody procedures are in place. The exclusion of standard waste boxes from the sample population does not significantly reduce the sample population, and sampling of the standard waste boxes would pose serious ALARA concerns (refer to Section V for additional discussion). The exclusion of some metal objects from the sample pool (e.g. metal HEPA filter casings) is reasonable in light of the significant difficulties associated with sampling the material, and sufficient metal population is available for sampling without the need to sample metal HEPA filter casings. (Refer to Section V.B.2 for additional discussion.)

III. WASTE STREAM DESCRIPTION

The SAP, Rev. 2, presents a brief summary of the TA-55-43 Lot No. 1 waste stream origin and contents, and assesses whether this waste stream includes any materials that would render it hazardous (i.e., ignitable, toxic, etc.). The information presented in this section is consistent with information presented in the Acceptable Knowledge Summary Report (TWCP-1042) and the Waste Determination Report for Waste Stream TA-55-43, Lot No. 1 (TWCP-1253).

IV. OBJECTIVES

The SAP, Rev. 2, page 5 states that the objective of the SAP, Rev. 2 is to describe the proposed statistical sampling and analysis approach and analytical procedures for confirming that TA-55-43, Lot No. 01 is non-mixed waste. The SAP, Rev. 2, then presents eight elements which address the SAP objectives.

V. STATISTICAL SAMPLING PLAN

V.A. Population of Drums to be Sampled

The SAP, Rev. 2, discusses how the waste from the TA-55-43 waste stream was initially bagged and 36 drums from this process were selected for preparation for disposal at WIPP. Contents of the 36 "parent drums" were briefly discussed. The SAP, Rev. 2, then states that the 36 parent drums underwent repackaging, creating daughter or progeny drums (repackaging was performed to address the thermal limits for transportation). As part of this repackaging, items labeled as Process Code R8 were removed from the TA-55-43 waste stream. In addition, containerized ashes from thermal decomposition of rags were removed from this waste stream. Waste from plutonium-pellet dissolution were also removed. The SAP, Rev. 2; states that eleven of the daughter drums are no longer available for sampling due to the potential for unacceptably high radiation exposures during sampling. These eleven daughter drum contents were placed in standard waste boxes. The SAP, Rev. 2, then presents Table 1, which summarizes the number of bags and progeny drums. No confirmatory data for Table 1 is provided.

The SAP, Rev. 2, also states that the sample unit will be based on bags in the parent drums, as bags are numbered and can be used in statistical analysis. The use of bags rather than drums reduces the area from which a grab sample would be collected (i.e., from a bag rather than an entire drum), but the sampling approach in Section V.G is random and grab samples will be composite samples from many locations in a randomly selected bag. The grab sample is generated by collecting many samples from sample matrices within a selected bag.

V.B. Waste Matrices to Sample

The weight estimates presented and used in SAP, Rev. 2, calculations are representative of the waste stream contents at the time that the SAP, Rev. 2, was prepared and include the reduction in generator estimates when a repackaged drum or material was removed from the waste stream, as well as the addition of material such as plastic and cheesecloth when repackaging occurs. The waste stream percent composition estimates could change as repackaging progresses. When asked by NMED (see Question #6, Attachment C of the SAP, Rev. 2) how this would impact the statistical analysis, which is based on the estimated weight percent, LANL responded that the weight distributions will be assessed as the repackaging continues, and updated estimates will be used in the sample size calculations to determine if additional samples are needed as part of the adaptive sampling and analysis plan. LANL also indicated, in the SAP, Rev. 2, that the impact on sample number from changes in weight distributions are expected to be small because of the expected sample concentration relative to regulatory thresholds.

V.B.1 Plastic Items

The SAP, Rev. 2, presents a brief discussion of the plastic materials present within the waste stream and the current estimated percent of the waste stream comprised of plastic material. The

weight percent is consistent with that which can be calculated using information presented in Table A-2. The discussion is consistent with the other acceptable knowledge descriptions of plastic materials in the waste stream (see TWCP 1042 and 1253). The SAP, Rev. 2, indicates that 3 grab samples will be randomly collected within a bag and composited to make a single composite plastic sample. (Note that two plastic samples will be collected and each plastic sample will be comprised of 3 grab samples randomly collected and composited to make an individual sample). The NMED asked how the specific grab samples were going to be collected (see Question #3, Attachment C, SAP, Rev. 2). LANL indicated that the grab sample will be made by cutting small pieces from a variety of "representative" locations on the item (i.e. for a glove, the grab would consist of several pieces cut from that glove). LANL also indicated that if discolored or degraded spots were noted, these would be preferentially sampled.

V.B.2 HEPA Filters

The SAP, Rev. 2, includes a brief discussion of the HEPA filter use and origin that is consistent with the other acceptable knowledge documentation (TWCP 1042 and 1253), and the current estimated weight percent. The weight percent is consistent with that which can be calculated using information presented in Table A-2. The SAP goes on to discuss components of the HEPA filters, explaining that the membranes of the HEPA filters will be sampled via three grab samples that will consist of small 8-10 gram sub-samples because of the small amount of membrane available (70-100 mg).

When asked by NMED whether the HEPA casing will be sampled (SAP, Rev. 2, Attachment C, Question #5), LANL indicated that sampling of HEPA metals is very difficult and poses a danger to workers cutting the HEPA casing in a glove box; instead "cold" HEPA metal samples will be collected, the results of which will be mathematically combined with other "hot" analysis to determine the content of the metal waste stream. Also, unless otherwise indicated by "cold" analysis, it is highly unlikely that the HEPA casing is, in and of itself, hazardous, and it is also unlikely that the casing would have acquired or become contaminated with hazardous waste based on the configuration of the metal casing being contained within the framework of the vent system. Analysis of "cold" HEPA filters will further confirm the non-hazardous nature of this material. The SAP, Rev. 2, indicated that the "cold" HEPA metal data be added to the "hot" data for a total metal concentration.

V.B.3 Metal Items

The SAP, Rev. 2, includes a brief discussion of the metal waste origin that is consistent with the other acceptable knowledge documentation (TWCP 1042 and 1253). The weight percent is consistent with that which can be calculated using information presented in Table A-2. The SAP, Rev. 2, states that metal samples will be collected by compositing a variety of metals to create the "grab" sample (three grab samples will be collected and further composited to create a large composite sample; two larger composite samples, in total, will be collected for each matrix, including metal items). The SAP, Rev. 2 also indicates that metal items that are not amenable to

cutting will be excluded from sampling. NMED questioned the criteria by which a metal would be considered not amenable to cutting (SAP, Rev. 2, Attachment C, Question #5), and LANL responded by indicating that metal bolts, tools, piping, and similar materials cannot be cut in a glove box for sample collection, as well as the rubber used to seal glove boxes. In addition, LANL indicated that HEPA metal material will not be sampled because it is unlikely to be hazardous based on where/how it was used and because it is very difficult to cut this metal in a glove box.

V.B.4 Rags and Combustible Items

The SAP, Rev. 2, includes a brief discussion of the rags and combustible waste origin that is consistent with the other acceptable knowledge documentation (TWCP 1042 and 1253), and the current estimated weight percent. The weight percent is consistent with that which can be calculated using information presented in Table A-2.

V.B.5 Rubber Items

The SAP, Rev. 2, includes a brief discussion of the rubber item waste origin that is consistent with the other acceptable knowledge documentation (TWCP 1042 and 1253), and the current estimated weight percent. The weight percent is consistent with that which can be calculated using information presented in Table A-2.

V.B.6 Glass Items

The SAP, Rev. 2, includes a brief discussion of the glass waste origin which is generally consistent with other more detailed acceptable knowledge documentation (TWCP 1042 and 1253), and the current estimated weight percent. The SAP, Rev. 2, indicates that glovebox window glass was the primary glass source in the waste. TWCP-1042 indicated that the glass waste consisted of broken glass, discarded labware, windows, and bottles (pg 8). The SAP, Rev. 2, proposes no sampling of glass because the glass material within the waste is unleaded and is not a characteristic waste under 40 CFR or RCRA and comprises a very small percentage of the waste stream.

V.B.7 Rust-Colored Powder

The SAP, Rev. 2, includes a brief discussion of the rust-colored material, indicating that preliminary analysis shows it to be rust (i.e. iron oxide). The SAP, Rev. 2, proposes to confirm this through Inductively Coupled Plasma Arc Spectrometry/Mass Spectrometry (ICP/MS) analysis. However, there is not enough of this material to prepare the two composite samples proposed for other material categories. The SAP, Rev. 2, therefore proposes to collect a single sample of this material, and to include in this sample a non-randomly collected sample from Drum

57042. This sample will be composited with material contaminated with the rust-colored powder from the randomly selected drums to ensure an adequate sample size is collected for analyses.

V.C Statistical Approach

The statistical approach used in the SAP, Rev. 2, uses a weighted mean and weighted standard deviation based upon a 10 gram sample size. A summary of the SAP, Rev. 2, statistical approach is as follows:

1) Matrix specific means and standard deviations were calculated from available 100 gram "cold" sample results that represent the actual waste components.

2) Weighted means and standard deviations were calculated for each metal. The weighting for each waste component was based upon the composition percentages presented in Table 2 of the SAP.

3) The weighted standard deviation was then adjusted to account for a reduction in the sample size from 100 grams to 10 grams. A decrease in the sample size results in a proportional increase in the variance associated with the samples. Therefore, a ten-fold decrease of the sample size results in a ten-fold increase in the sample variance. The resultant increase in the standard deviation for each weighted standard deviation would be the square root of 10, or approximately 3.14. All weighted standard deviations were therefore multiplied by 3.14 to account for the decrease in sample size.

4) The optimum sample number for each metal was iteratively calculated based upon Equation 3 in the SAP. The process is iterative because the n term used to calculate the student's t value is not initially known. The n value indicates the number of measurements and is used to calculate the degrees of freedom according to the formula:

$$\text{Degrees of Freedom} = n - 1$$

5) Evaluation of the student's t table indicates that as the number of measurements (and subsequently the degrees of freedom) is increased, the t test value decreases. A decrease in the t value would cause a decrease in n if the mean and standard deviation remained unchanged. The impact of decreasing the t value on Equation 3 in the SAP is to reduce the number of required samples. Therefore, determining the optimal value for n is critical. The approach used was to start with a sample size of 2, with a subsequent degrees of freedom equal to 1. The sample size would be appropriate if the calculated n on the left hand side of Equation 3 in the SAP was less than the chosen sample size. An n of 2 was found to be the optimal sample size.

6) The actual n is then calculated based upon Equation 3 in the SAP. All calculated n results were increased by 1 sample to account for the initial iteration needed to determine the appropriate t test value.

7) The optimal number of samples per matrix was then determined through the ratio of the matrix specific standard deviation to the 10 gram sample sum of standard deviations for all matrices (as found in Equation 4 of the SAP). Use of this method allocates more samples to the matrices that demonstrate greater variability in the results. The optimum number of samples for all metals in all matrices was found to be less than 2.

8) The number of samples collected for each matrix for each metal was increased to 2 based upon SW-846 guidance suggesting that additional samples should be collected to protect against poor initial estimates of the mean and variance.

9) The true n value will then be recalculated according to Equation 4 of the SAP based upon actual analytical results from the two "hot" samples collected and analyzed from each matrix. Iteration of the number of samples, as performed when determining the initial n value, is not required when recalculating the n value using actual "hot" data because the initial n value of 2, used to determine the t test value, is known. If calculation of the revised n value based on actual analytical results is higher than 2, then the additional samples indicated by the calculated n will be collected and analyzed. This process will be repeated until the calculated n for each metal is less than the actual number of samples collected.

10) When an appropriate number of samples are collected and analyzed, the confidence interval of the mean concentration for each metal will be determined. The waste will be considered hazardous for a metal if the upper confidence interval is greater than the regulatory threshold.

The statistical approach presented in the SAP generally reflects the approach recommended by NMED with some deviations. Equation 3 of the SAP determines a total number of samples based upon the weighted mean concentration and weighted variance for all the matrices to determine a total number of samples. The number of samples collected for each matrix are then determined based upon the ratio of a matrix specific standard deviation to the sum of the standard deviation for each metal matrix. The approach presented by NMED indicated that the number of samples should be calculated on a matrix specific basis and a calculated number of samples should be collected for each matrix. The proportional weighting of each matrix would then be accounted for when calculating the confidence interval of each metal.

The optimum sample size derived using the NMED approach was calculated and compared with that derived using the SAP, Rev. 2, approach. The optimum number of samples calculated using the NMED approach was determined based upon the following assumptions:

- All non-detected results would be reported at the full instrument detection limit (IDL).
- The initial "hot" sample number, n , would be initially set at 2, thereby providing an initial degrees of freedom of 1 to be used in establishing the t test value. As a result, the optimum number of samples will be increased by one in all matrices as opposed to only the total. Also, 1 was added to the calculated n number to be consistent with the approach presented in Step 6, above.

- A 10 gram sample would be used.
- The matrix specific means used to calculate the weighted mean and deviation for each TC metal were conservatively estimated as the upper confidence bounds to account for matrix-specific variance, as represented by the following equation and presented in Table V.C-1:

$$x_{\text{mean}} = x_{\text{mean}} + t_{2, n-1} \sqrt{((w_i \cdot s_i) / n_i)}$$

Table V.C-1
Comparison of NMED and SAP, Rev. 2, Matrix Specific Mean Concentrations (ppm)

	Waste Element	HEPA Filter	Metal	Plastics	Rubber	Combustibles
NMED	Lead	0.020	0.048	0.387	0.094	0.046
SAP, Rev. 2 (100 g)		0.012	0.005	0.22	0.044	0.011
NMED	Barium	5.852	0.466	0.423	0.076	0.241
SAP, Rev. 2 (100 g)		5.76	0.188	0.248	0.028	0.136
NMED	Cadmium	0.010	0.027	0.114	0.011	0.029
SAP, Rev. 2 (100 g)		0.007	0.002	0.037	0.003	0.002
NMED	Chromium	0.037	0.087	0.106	0.024	0.029
SAP, Rev. 2 (100 g)		0.026	0.015	0.044	0.011	0.010

Table V.C-2 presents the calculated optimum sample numbers using both the NMED and SAP, Rev. 2 approaches. The differences in the optimal sample numbers reported in the SAP, Rev. 2, and calculated by NMED and shown on Table V.C-2 are attributable to how the waste stream is viewed. LANL evaluated the waste stream (including all matrices) as a single entity, while the NMED approach evaluated each matrix as a separate entity. As a result, when the iterative nature of the statistical analysis is taken into account (i.e., addition of 1 to the calculated n value), in the NMED approach, the optimum minimum number of samples is determined on a *matrix* and parameter basis. In the SAP, Rev. 2 approach, however, the optimum minimum number of samples is determined on a *waste stream* and parameter basis. The SAP, Rev. 2, and NMED

values presented in Table V.C-2 cannot be directly compared. However, the optimum minimal sample number derived using these values is less than 2 for both the NMED and SAP, Rev. 2, approaches. Therefore, when both the SAP and NMED values are raised to the next integer that allows for the calculation of a variance, the result of both approaches is the collection of two samples for each matrix.

The purpose of calculating the optimal sample numbers for each scenario is to meet a conditional test of an iterative calculation of n . If the calculated value of n was less than the assigned n value (2 is the minimum assigned number that is allowable), then the assigned n value is the correct minimum number of samples. In both scenarios, the initial assigned n value was 2 samples. The calculated optimal number of samples was less than 2 in all circumstances, which indicates that the actual required number of samples for both scenarios in all matrices was 2 samples.

Table V.C-2
Comparison of the Optimal Number of Samples Using the
NMED and SAP, Rev. 2, Approaches¹

	Waste Element	HEPA Filter	Metal	Plastics	Rubber	Combustibles
NMED ²	Lead	1.00001	1.00001	1.043	1.0007	1.00095
SAP, Rev. 2 ²		0.01	0.03	0.97	0.13	0.04
NMED	Barium	1.0005	1.00006	1.00011	1.000001	1.000008
SAP, Rev. 2		0.5	0.18	0.23	0.03	0.06
NMED	Cadmium	1.00001	1.00004	1.053	1.00001	1.00004
SAP, Rev. 2		0.02	0.03	1.11	0.01	0.04
NMED	Chromium	1.00005	1.000113	1.00073	1.000004	1.000085
SAP, Rev. 2		0.14	0.22	0.56	0.04	0.03

1 The optimal sample numbers were calculated as non-integers. The actual number of required samples will be rounded to the next available integer that allows for the calculation of an analytical variance. In this case, the first available integer for all submatrices in the NMED and SAP approach is 2.

2 Using the SAP, Rev. 2, approach, a total number of samples is calculated for the entire waste stream for each metal. The number of samples for each matrix presented in Table V.C-2 is a portion of the total waste stream number and were determined based upon the weight component percentage and the ratio of the standard deviation of one matrix to the overall standard deviation for the waste stream. For example, the total SAP, Rev. 2 lead value is 1.18, meaning that the sum of the lead values for each of the five media yields the number of samples/matrix that must be collected and analyzed for lead (i.e., 1.18 samples). The NMED numbers are calculated differently in that each matrix is treated as a separate waste entity, and the sample numbers per matrix are not additive (i.e., 1.001 HEPA samples must be collected and analyzed for lead).

The approach provided in the SAP, Rev. 2, is consistent with SW-846 and is statistically valid. However, the following should have been considered: 1) the iterative calculation to determine n is designed to establish the appropriate integer value or number of samples to collect and not to generate a non-integer sample number; use of the non-integer value to calculate the ideal number of samples for each sub-matrix is not entirely correct, 2) the formula for estimating the number of samples for each submatrix $n(i)$ is more accurately represented by the following equation:

$$n(i) = n((w_i \cdot s_i) / (\sum (w_i \cdot s_i)))$$

This equation factors in the relative composition of each matrix and the error (standard deviation) of each matrix, and 3) the conservative iteration of all sample matrices to 2 samples should be to ensure that a minimum number of samples necessary to calculate a variance are collected and not to provide additional samples based on the uncertainty of the preliminary means and deviations. When data are evaluated taking these suggestions into consideration, however, the optimum sample size of two per media per matrix is still obtained.

Also, the SAP, Rev. 2, calculation of the matrix specific mean, variance, weighted mean and variance, and 10 gram weighted mean and variance were verified and found to be correct based upon the information provided in Table 2 and Table R-2 (Attachment C) of the SAP. The weighted averages would be subject to change if the composition percentages are modified. Changes in required sample numbers based upon modification in the component weights would likely only occur if one or more of the components was found to contain significant contamination of a TC metal in comparison to the cold component results.

V.D. Available Data that Support the Optimal Sample Design

The SAP, Rev. 2, proposes the use of “cold” sample Toxicity Concentration Leaching Procedure (TCLP) surrogate information to generate a sample design for the waste media. The SAP, Rev. 2, states that neither radiolysis nor the presence of impurities in the plutonium oxide have a significant effect on the RCRA constituent concentrations because the extreme refractory nature of high fired plutonium oxide renders chromium and barium nonexistent in the “hot” samples. The SAP, Rev. 2, also states that the adaptive sampling scheme of this Plan will directly correct for deficiencies in this assumption by requiring further sampling of observed concentrations if relative standard deviations from the waste stream are greater than expected.

The Waste Determination Report (TWCP 1253), which provided background material for the SAP, Rev. 2, states the waste in Lot No. 01 is debris resulting from cleaning, repairs, and normal every-day operations during the fabrication of the heat sources and fuel recovery. The SAP, Rev. 2, Section III “Waste Stream Description”, also states that waste stream TA-55-43 was generated from the fabrication of heat sources and the recovery of plutonium oxide from heat sources. In addition, this section states that the primary ALARA concern with this waste is the dispersability of the plutonium-238. It seems plausible that the chromium and barium would be present in plutonium metal that has not been fired and that would be leachable. Therefore, the validity of using cold sample surrogates was assessed because it is possible that “hot” material would contribute to the source material, rendering the cold surrogate samples nonrepresentative. Specifically, the use of cold sample surrogate metal values to provide the initial number of samples to be collected was evaluated, as well as whether the number of samples to be collected would increase if the analytical values of known impurities of Toxicity Characteristic (TC) metals in the feed stock were added to the cold surrogate values (TCLP value x 20 for totals values) to create an “artificial” sample that would hypothetically include additional contamination from Pu238.

The Waste Determination Report indicates that chromium is the impurity present in highest concentration within plutonium oxide, and hence this analysis focused on assessing the impact that additional chromium "in" the cold sample would have on the calculated *n* value. The worst case concentration of chromium (Cr) impurity measured analytically in the feed stock material was 4050 ppm Cr in PuO₂, as presented in the Waste Determination Report, Attachment B: Detailed Constituent Calculations, Table B-2, which shows the average concentration of Cr to be about 270 ppm. The corresponding TCLP concentration for this chromium value is 202.5 ppm, created by dividing the totals analytical value by 20 to account for the 20 time dilution associated with the TCLP analysis procedures. The highest plutonium economic discard limit for ²³⁸Pu in waste is 18.6 g Pu per kg waste associated with the combustibles waste matrix (page 35 of the "Waste Determination Report For Waste Stream TA-55-43 Lot No. 1"). Therefore, the maximum total chromium content in combustible waste with the maximum plutonium content (amount of plutonium does not exceed the economic discard limit) is 85 ppm, as shown in the following:

$$\text{ppmCr in waste} = \frac{(4050 \text{ ppm total Cr in PuO}_2) * (18.6 \text{ g Pu/kg waste})}{(1000 \text{ g/kg}) * (0.882 \text{ g Pu/g PuO}_2)} = 85 \text{ ppm (totals)}$$

To assess how much of this chromium might be present in combustible material, the quantity of chromium present in the special nuclear material (SNM) found in combustible material was assessed based on the total weight of the combustible waste material and the weight of special nuclear material (i.e. plutonium oxide, SNM) associated with combustible materials, as presented in Table A-1, Attachment A of the Confirmatory Sampling and Analysis Plan. The equation used to assess this is as follows:

$$\begin{aligned} \text{ppm Cr combustible waste} &= \frac{(4050 \text{ ppm total Cr in PuO}_2) * (8.9 \text{ g SNM/112.08 kg waste})}{(1000 \text{ g/kg}) * (0.882 \text{ g Pu/g PuO}_2)} \\ &= 0.365 \text{ total chromium} \end{aligned}$$

Approximate equivalent TCLP value = 0.018 ppm Cr

When 0.018 ppm Cr is added to the 0.010 mean "cold" chromium concentration in combustible materials as shown in Table 4 of the SAP, Rev. 2, (see calculation for determining mean concentrations in SW-846 for simple random sampling), the total mean value becomes 0.028 ppm. Considering that the regulatory threshold for chromium in waste is 5.0 ppm, even if the worst case quantity of chromium based on a maximum possible concentration in the feed lots to the PuO₂ process is added to the "cold" values, the sample does not approach the TC regulatory threshold.

If the average chromium concentration were considered instead of the worst case, this would result in 0.024 ppm total chromium, which is equivalent to a 0.0012 ppm TCLP value. Again, this value is well below the TC regulatory threshold of 5.0 ppm. The optimal number of samples to be collected (i.e. "n" value) based on the added chromium from plutonium oxide could not be calculated because the individual data points for all measurements taken on the plutonium oxide for this waste stream were not provided. The complete set of data points for all analyses would be necessary to establish a variance for calculating the optimal number of samples for making a non-hazardous waste determination. However, in the case of combustible material, for example,

when the highest average mean TCLP value of 0.0012 ppm is added to the estimated mean of 0.01 ppm Cr found in the combustible surrogate samples (see Table 4 of the sampling plan), the new average becomes 0.0112 ppm. This new value, when rounded to an equivalent number of significant figures, is equivalent to 0.01 ppm Cr, which is the same number that was used in the SAP, Rev. 2 to determine the number of samples to be collected for this sampling initiative. Therefore, assuming that the variance remains unchanged, adding the average chromium impurity concentration from plutonium oxide to the cold surrogate chromium concentration will not change the cold surrogate chromium concentration. Consequently, the calculated optimal number of samples to be collected will not change.

This same analysis was performed for the constituent with the lowest Toxicity Characteristic regulatory level. Mercury has the lowest TC regulatory level at 0.2 ppm, and selenium and cadmium have the next lowest regulatory levels at 1.0 ppm. However, neither mercury nor selenium were detected in any of the cold surrogate samples and neither metal was analyzed for in the feed streams because they were apparently not introduced into the raw feed material at the Savannah River site where the plutonium oxide feed was generated. Cadmium was detected in the cold surrogate samples and was analyzed in the raw feed stream material, and was therefore assessed to determine the impact of a compound with a low TC regulatory level. The equation for total cadmium in the combustible waste matrix is as follows:

$$\begin{aligned} \text{ppm Cd combustible waste} &= \frac{(10 \text{ ppm total Cd in PuO}_2) * (8.9 \text{ g SNM} / 112.08 \text{ kg waste})}{(1000 \text{ g/kg}) * (0.882 \text{ g Pu/g PuO}_2)} \\ &= 0.00090 \text{ total cadmium} \end{aligned}$$

$$\text{Approximate equivalent TCLP value} = 0.000045 \text{ ppm Cd}$$

Therefore, even considering a metal with a low regulatory threshold such as cadmium, the highest concentration of cadmium in the waste would result in only a very limited amount of cadmium in a TCLP extract, and when added to the mean concentration of the cold surrogate samples, would not significantly alter the number of samples needed for collection to support a statistically based sampling effort.

The toxicity characteristic regulatory level for chromium, cadmium or other TC metals would not be exceeded in this waste stream based on the hypothetical waste stream composition created by adding the “cold” surrogate analysis and the amount of chromium contained in the plutonium oxide. The small amount of chromium, cadmium, or any other TC metal added by impurities in the plutonium to the cold surrogate sample concentration would also not be sufficient to increase the statistically calculated sample numbers presented in the sampling plan. In other words, while the sample number n is based on “cold” rather than actual “hot” analytical results, simulated “hot” analyses developed by adding “cold” results with calculated TC metal concentrations does not result in sample concentrations near the regulatory threshold. As with chromium, addition of the plutonium oxide cadmium TCLP value 0.000045 ppm to the estimated mean cadmium concentration of 0.002 ppm in the surrogate combustible samples yields a concentration of 0.002045 ppm. Assuming that the variance remains the same, the optimal number of samples calculated would not change based on the new additive mean cadmium concentration of 0.002045

ppm because this value, when rounded up, is equivalent to that used in the SAP, Rev.2, calculations (i.e. 0.002).

NMED questioned whether missing selenium values were available, and also how "0" and "<" values were used in mean calculations (SAP, Rev. 2, Attachment C, Question #1). LANL responded by discussing data use and providing new and updated data tables. The viability of data presented in Table 3 and R-2 were also assessed, as this information was used to determine "cold" surrogate sample concentrations. These tables presented and used actual sample results below instrument detection limits, however, these actual analytical values below the instrument detection limit (IDL) cannot be readily distinguished from inherent instrument variability and are inappropriate for use. Therefore, the results should be reported at the instrument detection limit. The impact of this practice is negligible because the results reported at the detection limits are still significantly below the regulatory thresholds as presented in RCRA Part 261.24.

The sample means and variances were recalculated assuming non-detected results at the IDL, one half the IDL, and zero, to determine the variability that would occur with different reporting scenarios for non-detected results. The tabulated results demonstrate that there is no significant difference between the mean and variance calculated at each of the three data presentation options. Therefore, the data, as presented and used in Table 3 and R-2, and used to calculate analyte mean and standard deviations, are acceptable. The mean and variance at each of the three non-detect options are presented in Table V.D-1 and V.D-2 below.

Table V.D-1
Verified Mean Values at Zero, Half IDL, and Full IDL Presentation

	Ag	Ba	Cd	Cr	As	Se	Hg	Pb
Plastic								
Zero Option	0.000	0.248	0.037	0.044	0.000	0.000	0.000	219.000
Half IDL Option	0.002	0.248	0.037	0.044	25.000	1.200	0.016	220.000
Full IDL Option	0.004	0.248	0.037	0.044	50.000	2.400	0.032	221.000
HEPA								
Zero Option	0.000	5.763	0.007	0.026	0.000	0.000	0.000	12.000
Half IDL Option	0.002	5.763	0.007	0.026	24.000	1.000	0.016	12.000
Full IDL Option	0.004	5.763	0.007	0.026	48.000	2.000	0.032	12.000
Combustibles								
Zero Option	0.000	0.136	0.001	0.010	0.000	0.000	0.000	10.000
Half IDL Option	0.002	0.136	0.002	0.010	24.000	1.000	0.016	11.000
Full IDL Option	0.004	0.136	0.003	0.010	47.000	2.000	0.032	12.000
Rubber								
Zero Option	0.001	0.028	0.002	0.011	1.000	0.000	0.000	45.000
Half IDL Option	0.002	0.028	0.002	0.011	24.000	1.000	0.016	45.000
Full IDL Option	0.004	0.028	0.003	0.011	48.000	2.000	0.032	46.000
Metals								
Zero Option	0.000	0.188	0.001	0.015	0.000	0.000	0.000	5.000
Half IDL Option	0.002	0.188	0.002	0.015	24.000	1.000	0.016	7.000
Full IDL Option	0.004	0.188	0.002	0.015	47.000	2.000	0.032	9.000

Table V.D-2
Verified Estimated Standard Deviations at the Zero, Half IDL, and Full IDL Options

	Ag	Ba	Cd	Cr	As	Se	Hg	Pb
Plastic								
Zero Option	0.000	0.115	0.004	0.002	0.000	0.000	0.000	97854.000
Half IDL Option	0.000	0.115	0.004	0.002	270.000	0.178	0.000	97272.000
Full IDL Option	0.000	0.115	0.004	0.002	1079.000	0.711	0.000	96695.000
HEPA								
Zero Option	0.000	0.518	0.000	0.000	0.000	0.000	0.000	20.000
Half IDL Option	0.000	0.518	0.000	0.000	363.000	0.000	0.000	20.000
Full IDL Option	0.000	0.518	0.000	0.000	1452.000	0.000	0.000	20.000
Combustibles								
Zero Option	0.000	0.009	0.000	0.000	0.000	0.000	0.000	152.000
Half IDL Option	0.000	0.009	0.000	0.000	385.000	0.000	0.000	124.000
Full IDL Option	0.000	0.009	0.000	0.000	1541.000	0.000	0.000	102.000
Rubber								
Zero Option	0.000	0.002	0.000	0.000	3.000	0.000	0.000	1832.000
Half IDL Option	0.000	0.002	0.000	0.000	283.000	0.000	0.000	1780.000
Full IDL Option	0.000	0.002	0.000	0.000	1197.000	0.000	0.000	1731.000
Metals								
Zero Option	0.000	0.064	0.000	0.000	0.000	0.000	0.000	75.000
Half IDL Option	0.000	0.064	0.000	0.000	385.000	0.000	0.000	48.000
Full IDL Option	0.000	0.064	0.000	0.000	1541.000	0.000	0.000	27.000

It should be noted that the regulatory thresholds presented in Table 3 and R-2 of the SAP, Rev. 2, for arsenic, selenium, mercury, and lead are incorrect. The actual regulatory limit for arsenic is 5 ppm, not 0.2 ppm (200 ppb), as presented in Table R-2. The actual regulatory limit for selenium is 1 ppm, not 5 ppm (5000 ppb). The actual regulatory limit for mercury is 0.2 ppm, not 5 ppm (5000 ppb). The actual regulatory limit for lead is 5 ppm, not 1 ppm (1000 ppb). Verification of the optimal sample numbers indicated that the correct regulatory thresholds were used in calculating the optimum number of lead samples. Mercury, arsenic, and selenium optimum sample numbers were not calculated by LANL because all or nearly all sample results were non-detected. Therefore, the regulatory limits in Table R-2 for mercury, lead, arsenic, and selenium appear to be a typographical error that did not impact the actual calculations used to calculate the

optimum number of samples in Table 7 of the SAP. See Section IX for discussion of the proposed analytical suites.

V.E Optimal Sample Size Calculations

Section V.E provides the actual tabulated calculations for determining the optimal sample size based upon the strategy presented in Section V.C of the SAP, Rev. 2. The results presented in this section were consistent with the sampling strategy. Verification of the calculation used to determine the optimal number of samples indicated that the matrix specific standard deviations were not corrected for the 10 gram sample size. A comparison of the matrix specific sample sizes based upon a 10 gram and 100 gram matrix specific standard deviations and using the SAP, Rev. 2, statistical analysis method, are presented in Table V.E-1. However, the error in calculation did not result in the need to collect any additional samples.

**Table V.E-1
Comparison of the Optimal Number of Samples Using 10 gram and 100 gram Matrix
Specific Standard Deviations**

Waste Category		HEPA Filter	Metal	Plastics	Rubber	Combustibles
Lead	10 gram	0.013	0.013	0.833	0.112	0.027
	100 gram	0.01	0.02	0.99	0.13	0.03
Barium	10 gram	0.499	0.173	0.23	0.027	0.064
	100 gram	0.5	0.18	0.23	0.03	0.06
Cadmium	10 gram	0.143	0.22	0.558	0.039	0.039
	100 gram	0.02	0.03	1.11	0.01	0.04
Chromium	10 gram	0.013	0.027	0.916	0.01	0.027
	100 gram	0.14	0.22	0.56	0.04	0.03

V.F. PROCESS FOR SELECTING SAMPLES

The SAP, Rev. 2, process for selecting samples consists of the following sampling strategy:

- 1) Select a parent drum at random.

- 2) List the progeny drums if the drum has been repackaged. Otherwise list the bags within original parent drums. Select a subsampling unit from among the bags or progeny drums.
- 3) If the subsampling unit does not contain at least one matrix for which samples are required, pass the drum and select another drum randomly.
- 4) Obtain 3 grab samples to make a composite for each available matrix. Sampling will be performed across submatrices if available. Sample matrix that appears to be discolored or degraded will be selected if available.
- 5) If further samples are needed to collect the minimum number of samples for each matrix then an additional parent drum will be randomly chosen.
- 6) As data are collected and analyzed, iteratively update the mean, variance, and required number of samples to evaluate the need to take additional samples.

The SAP, Rev. 2, indicates that additional samples may be collected for waste component matrices that have already been sampled completely. The SAP, Rev. 2, did not indicate the circumstances under which additional samples had been collected. NMED requested additional information to clarify the conditions under which additional samples will be collected for a matrix. The SAP, Rev. 2, indicates that samples may be collected to serve as additional samples in the event the sample populations are elevated due to higher than expected means or standard deviations. These contingency samples would be collected to preclude the opening of any additional drums. Clarification of the criteria under which additional samples will be collected for a waste component matrix are not critical because the SAP, Rev. 2, as presented, indicates that an appropriate number of samples will be collected for each waste component matrix.

Public comments have suggested that the contents of every container must be sampled and analyzed to ensure that the waste stream is non-hazardous. However, this approach is not endorsed by EPA in its 1992 guidance document entitled Characterizing Heterogenous Wastes: Methods and Recommendations (1992), which was specifically written to present methods for characterizing heterogenous waste contaminated with radionuclides and hazardous waste. In this document, complete waste stream analysis is not endorsed, and generators are encouraged to develop sampling and analysis plans that determine an appropriate number of samples to be taken by considering the sample matrix and contaminants. The preferred sampling design must be "practical and achievable", and should take into consideration serious health and safety considerations unique to sampling radioactive waste. The document emphasizes that in the case of radioactive hazardous waste (mixed waste), the optimal sample design should aspire to collect as much information as necessary to characterize the waste from a *very limited number* of samples, with an emphasis on the use of acceptable knowledge and non-invasive processes.

In the case of TA-55-43, Lot. No. 1, the SAP, Rev. 2, uses a statistically-based method for determining sample collection that reduces sample bias, allows for the optimal number of samples to be collected based upon waste analysis, and requires the continual reassessment of the sample number based upon actual analytical data.

The methods and philosophies presented in the 1992 EPA document are also reflected in the Joint EPA/NRC Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste, (1997). This 1997 document emphasizes the use of process knowledge rather than sampling and analysis of mixed waste wherever possible, and offers sample strategies to help maintain exposures as low as reasonably achievable (ALARA), which includes use of small sample size, the use of surrogate samples, and select (i.e. not complete) sampling of drums to collect analytical information. Again, the SAP, Rev. 2, follows guidelines suggested in this 1997 document.

Further, RCRA regulations 40 CFR §§264.13 and 265.13, while for permitted and interim status facilities, respectively, reflect the EPA's intent that sites should collect representative samples, and that analysis of each and every container of waste intended for disposal is not required. In summary, the SAP, Rev. 2, presents a statistically based sample collection method that will provide the appropriate number of samples, as determined statistically, to assess the hazardous nature of the TA-55-43, Lot. No. 1 waste stream. As such, complete analysis of each the contents of each container is not required.

V.G SAMPLE SELECTION

The SAP, Rev. 2, provides the list of sample units to be sampled based on the statistical number of samples to be collected and random sample selection from the eligible sample unit population. The SAP, Rev. 2, indicates that individual bags within parent and some progeny drums are numbered, and the actual sample population can be based on these sample units. The SAP, Rev. 2, allows for random sample selection and reduces the need to open all bags within a drum if, for example, a drum (larger sample unit) were selected. Also, the drums and subsequent subsampling units selected for sampling are adequate to collect the minimum number of samples specified in the SAP, Rev. 2. In addition, with the exception of drum 55696, all of the randomly selected drums were different than those proposed in the original SAP. Drum 55696 was one of the two available HEPA filter drums and, as a result, was selected under the sampling strategy originally proposed and the strategy proposed in Revision 1.0 of the SAP. Therefore, there is no indication of selection bias based upon previously proposed sampling drums.

VI. QUALITY PROCEDURES, INCLUDING CHAIN-OF-CUSTODY

VI.C Chain of Custody

The Chain of Custody procedures meet the requirements of SW-846 and are adequate to meet the sample identification, control, and transfer requirements for control of the samples and the production of data.

VI.C.1 Samples of forms, labels, container descriptions

Given that the samples proposed in the SAP, Rev. 2, will be collected solely to provide confirmatory analyses for Lot No. 1 of Waste Stream TA-55-43, the sample forms, labels, and container descriptions meet the EPA's SW-846 methods and quality requirements.

VII. DECONTAMINATION BETWEEN ITEM SAMPLING

The SAP, Rev. 2, proposes minimal decontamination between sample collection of the various matrices. The technical basis for this proposal includes: 1) samples are already cross contaminated from common glovebox packaging and repackaging operations, 2) decontamination would create additional waste for disposal, and 3) decontamination procedures would increase the risk of radiation exposures to workers.

The purpose of the SAP, Rev. 2, is to confirm that Lot No. 01 of waste stream TA-55-43, as a whole, is not a RCRA-regulated hazardous waste. Any cross contamination that might occur as a result of sampling would not ultimately affect this determination because the material is being sampled and evaluated on a waste stream basis. Decontamination is typically performed to ensure that clean samples are not contaminated; lack of decontamination would bias the samples in that uncontaminated samples might become contaminated during sampling because no decontamination took place. This could potentially result in more samples being contaminated and would bias the sampling toward a hazardous waste determination. In addition, ALARA concerns posed by the further handling and waste generation associated with decontamination procedures warrant limiting decontamination activities in light of the fact that the decontamination activities do not add value to the data generated, nor would decontamination allow any additional information regarding the waste stream to be obtained.

VIII. SAMPLING PROCEDURES

The SAP, Rev. 2, describes the sampling procedures used to collect the samples, and references a specific procedure, TWCP-DTP-1.2-046, which provides specific instructions to the sampling personnel concerning the sampling process. The procedure provides a description for identifying the sample matrix, collecting and compositing the sample, field QC sample collection, sample size and quantity to be collected, sample labeling, sample containers, sample preservation, and sample packaging/shipment.

The sampling procedures, in general, are well defined and documented, with one minor exception. The exception concerns the subsampling of the composite sample to get a representative 10 gram sample for analysis. The NMED submitted questions concerning the SAP, Rev. 1, regarding the selection of these samples, and the SAP, Rev. 2, Attachment C indicates that 15-20 grams of sample will be collected for the grab samples, and also discusses how submatrices will be selected to ensure a non-biased sample selection. The SAP, Rev. 2, indicates that each of the two required samples/matrix will consist of a composite sample generated by compositing three grab

samples. If three submatrices were available, each of the grab samples will consist of a representative sample of one of the submatrices. In the event more than three submatrices are present, then the submatrices will be chosen randomly by assigning a letter to each submatrix and choosing three random letters that correspond to the waste submatrix. If two submatrices are present, one grab will be collected from each submatrix and the third grab will be randomly selected from one of the two matrices. In the event that a single submatrix is available, all three grabs will occur within the submatrix.

VIII.A Size Reduction Criteria

The SAP, Rev. 2, indicates that the samples need not undergo size reduction to meet the Method 1311 sample size of less than 9.5 mm because 1 gram of each material in the "cold" samples passed the size criteria; i.e. one gram of each material had a surface area greater than 3.1 cm². Therefore, the SAP, Rev. 2, meets the TCLP criteria for exclusion from particle size reduction and further size reduction is not warranted.

VIII.B Sample Size Collected

The Confirmatory Sampling and Analysis Plan, Rev. 2, proposes collecting 25 grams of HEPA filter material and 50 grams for the remaining waste types. A 10 gm aliquot will be used in the analysis. The plan also stated that a 20:1 ratio of leachate to sample will be maintained for the analysis.

The sample size of 100 grams listed in the TCLP method is only a recommendation. The only requirement of the method in this regards is that a 20:1 leachate to sample ratio be maintained. Therefore, the sample size reduction proposed by the sampling plan meets the method requirements and facility requirements for limitations on radioactivity in the laboratory while reducing waste generation and radioactivity exposure potentials.

IX. ANALYSES TO BE PERFORMED

The SAP, Rev. 2, proposes to analyze samples for a specific list of RCRA metals by TCLP. The rust-colored powder will be analyzed by Inductively Coupled Plasma Arc Spectrometry/ Mass Spectrometry (ICP/MS) to identify the composition of this powder. No other analyses are proposed in the SAP, Rev. 2.

The proposal in the SAP, Rev. 1, to analyze all of the composite samples for all of the RCRA toxicity characteristic metals is reasonable and appropriate to confirm that the waste is not a TC RCRA-regulated waste. Public comment has suggested that the analysis should include benzene and vinyl chloride, but analysis of radiolytic gas generation data presented in the SAP, Rev. 2, Attachment B indicate that these compounds could not accumulate to TC levels (refer to Section XII for additional analysis).

Public comment has also suggested that waste should be analyzed for corrosivity and reactivity. Examination of radiolytic waste generation information presented by commentators and in the SAP, Rev. 2, indicate that radiolysis has not created a waste characteristic for corrosivity; refer to Section XII for more discussion. With regard to reactivity, commentators suggested that because headspace gas might be physically displaced, the expelled gas would make the waste stream characteristic for reactivity. However, physical gas displacement does not constitute a reactive condition as defined in §264.23(a)(1-7), and analysis for reactivity on this basis is unfounded. Public comment also suggests that ignitability is of concern, but, again, headspace gas data do not indicate that ignitable conditions will develop within the waste containers; refer to Section XII for additional information.

The rust-colored powder has undergone x-ray fluorescence analysis, which preliminarily indicates it to be rust material, as stated on page 12 of the SAP, Rev. 2. Further analysis through the proposed ICP/MS method would provide confirmation that this powder is not a hazardous waste.

The SAP, Rev. 2, proposes to eliminate the requirement to perform volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) analyses on the HEPA filter membranes. Reasons given include: 1) the volatility of these compounds (particularly at high temperatures such as the 110°C as recorded at the waste storage unit), 2) MSDS sheets showing that the filters are made from fibrous glass and are fibrous and paperlike and therefore are not made to retain organic vapors, 3) data showing that no RCRA VOCs or SVOCs are found within the HEPA matrix itself, 4) documented analytical difficulties in performing zero-headspace extraction for a TCLP analysis on ²³⁸Pu contaminated media, 5) acceptable knowledge showing that no regulated VOC or SVOC compounds were used in the fabrication of the heat sources, and 6) acceptable knowledge documenting that during the heating phases in the heat source production processes, the Lot No. 1 HEPA filters were bypassed.

This waste stream has been stored for a number of years (apparently up to 6 years) at temperatures that have reached as high as 110°C. Furthermore, as stated in the QAPP (DOE, 1996), the HEPA filters are not designed to retain organic vapors, only particulates. There is no reason to believe from a technical standpoint that the organic vapors (VOC or SVOC) would be retained on the filters. Also, any vapors that might have been caught on the filters would evaporate from the fibrous, paperlike filter material, especially under elevated temperatures. Additionally, the filters were bypassed during the heating phases in the production processes, making it unlikely that any VOC or SVOCs that might have been present in the glovebox would have been volatilized to the extent that the vapors would reach the HEPA filters and also making it unlikely that they would be present at the filter in sufficient quantities to be retained and found in a TCLP extract several years later. Process knowledge further suggests that the metal parts used in the plutonium heat source fabrication were cleaned using either water or acids. Furthermore, it is unlikely that semi-volatile compounds would have been useful in the heat source production process, based on the materials and events that were employed in the production processes and as presented in available information (TWCP-1042 and 1053). There is no reason to believe that VOC compounds could be retained on a filter, much less retained under higher temperatures for the six year storage period in a vented container.

TA-55-43, Lot. No. 1 contains volatile organic constituents in headspace gas that are present in typical F-listed waste. The SAP, Rev. 2, states that acceptable knowledge indicates no F-listed waste was introduced to the waste stream. However, VOCs can be generated by radiolysis and other sources, such as off-gasing from adhesives and glues contained in the tapes listed as part of the plastics matrix in the SAP, Rev. 2. Although the SAP, Rev. 2, indicates that radiolysis can generate the quantities of VOCs detected in headspace gas, some question can be raised as to whether the maximum calculated VOC gas generation rate will be the actual generation rate, given that the gas generation via radiolysis was assessed based on experimental results that artificially optimized gas generation. In spite of this uncertainty, the lack of definitive evidence that VOCs were managed in the waste generating process, coupled with the possibility of VOC off-gasing and some radiolytic origin lead to the conclusion that sampling for VOCs in waste material would not yield meaningful information as to the F-listed nature of the waste. In fact, the most likely candidate for such sampling would be cellulosic/rag material, but even if VOCs were detected in this material their presence would not be a direct indication that F-listed wastes were present on the material because off-gassed VOCs could also have sorbed to the material.

X. DATA ANALYSIS AND CONFIRMATION TESTING

The SAP, Rev. 2, proposes to use an adaptive sampling approach to iteratively assess whether additional samples should be collected. The SAP, Rev. 2, indicates that the sample assessment could include only the "hot" samples or both the "hot" and "cold" sample results when assessing the number of samples to be collected, and the SAP, Rev. 2, includes a five-step data analysis process. This process includes a final step wherein the upper confidence limit of the means of each analyte for the total waste stream is compared to regulatory thresholds to determine whether the waste stream, as a whole, is hazardous. The approach used to determine if additional samples are needed and if the sample results indicate that the waste is hazardous based on exceedance of the upper confidence limit of the mean concentration is generally consistent with the approach recommended by NMED.

XI. RADIOLYTIC ORIGIN OF VOCs

The SAP, Rev. 2, states that the presence of methanol, acetone, methylene chloride, methyl ethyl ketone, benzene, toluene, and methane can be demonstrated to be caused by radiolysis of plastic and rubber in the waste. Attachment B of the SAP, Rev. 2, provided calculated acetone concentrations assuming radiolysis. The SAP also stated that the VOCs detected in headspace gas are not artifacts of the laboratory analyses, as blanks, field blanks, and field duplicate QA/QC samples did not indicate the presence of trace VOCs.

Appendix B of the SAP, Rev. 2, was examined to assess LANL's determination of acetone concentration via radiolysis. This Appendix does not directly address development of methanol, methylene chloride, methyl ethyl ketone, benzene, toluene, or methane, presumably because acetone is the compound of most interest as it is present in measurable quantities above the PRQL and its presence could indicate the presence of an F-listed waste.

LANL's calculations are based on work by Reed and Molecke (1994) who conducted experiments designed to assess the impact of gas generation via radiolysis in terms of performance assessment. The experiments were intentionally designed to maximize the gas generation potential, which was appropriate for the purpose of the analysis - to determine whether radiolysis would contribute significant quantities of gas that must be accounted for in the 10,000 year performance assessment calculations.

The SAP, Rev. 2, presented a G value of 0.012 for acetone, the G value being the number of molecules of a specific material produced per 100 electron volts (eV) of energy deposited via radiolysis on that material. The G value calculations are based upon experimental concentrations (ppmv) of acetone determined by Reed and Molecke, as well as the known experimental dose rate and reaction vessel volume. The calculations are accurate, assuming that the input values are accurate (there is no way of assessing the accuracy of these data, as they are the premise of the experiments and must be assumed to be accurate).

Using the calculated G value and calculated eV dose over a six year period, the SAP, Rev. 2, Attachment B, then determines the quantity of acetone (in ppmv) that would be generated over a six year period (which is presumably the time period since the TA-55-43 Lot No. 1 wastes have been in existence). In this analysis, the SAP, Rev. 2, assumes that "all alpha particles effectively deposit their energy into the plastic". That is, it is assumed that all alpha particles present in the waste are proximal to a plastic, and have their energy deposited upon waste for subsequent acetone liberation. While the waste stream is comprised of over 50% plastics and rubber, it is not realistic to assume that all alpha radiation energy will be adsorbed by these materials. Hence, the calculated total energy deposited on the waste is probably too high, although it is not possible to determine by how much. The calculations presented in the SAP, Rev. 2, to determine the total ppmv acetone generated over a six year period are not inappropriate mathematically, although, as indicated above, the 12,000 ppmv acetone quantity is probably higher than what would actually be the case. To demonstrate the importance of the eV value, if it is assumed that the total deposited energy is 5.5×10^{20} instead of 5.5×10^{23} , the total quantity of acetone generated is decreased by three orders of magnitude (i.e. from 12,000 ppmv to 12 ppmv). Clearly, the effective energy deposited upon the material is very important to overall VOC generation.

The SAP, Rev. 2, then presents calculations to determine the actual acetone that would remain in the drums assuming that these drums have been vented. This is done by first assessing the quantity of hydrogen generated, and comparing this with the actual quantity of hydrogen present in sample drum 55614. There are three orders of magnitude difference between the calculated and measured examine drum hydrogen content. Using the molecular weight of acetone and hydrogen to determine a relative diffusion ratio, the SAP, Rev. 2, indicates that acetone will diffuse out of a drum 0.18 times that of hydrogen, resulting in an acetone diffusion factor of 180 (i.e. the calculated maximum concentration would be divided by 180 to determine how much acetone remains in the container after diffusion). These calculations are simplistic and are not based on actual filter performance, but do offer a measure of scale comparison. It must be emphasized that the amount of VOCs in headspace gas must be reconciled with diffusion from the container to obtain an accurate assessment of the amount of radiolytically derived material present in the container. The SAP, Rev. 2, did not indicate that actual duration of drum venting, although

site safety considerations would dictate the need for such venting throughout the life of the drum to avoid gas pressurization.

The SAP, Rev. 2, concludes that the measured concentration of acetone in drum headspace gas can be acquired solely through radiolytic degradation. As indicated above, however, while radiolytic gas generation certainly accounts for much of the acetone present, uncertainties in energy deposition relative to waste arrangement could reduce the actual quantity of acetone generated radiolytically very significantly. Therefore, it cannot be concluded with 100% certainty that all acetone present in headspace gas is due to radiolytic decay, although certainly a large part of this gas could be generated via this process.

The possible presence and consequences of non-radiolytic acetone requires examination. While acetone can occur in F003 waste as a spent solvent, it's primary reason for being listed is for ignitability (see U002). If acetone was used only as acetone (i.e. as a pure cleaning solvent), then it would not be a F003 waste if the waste did not exhibit the characteristic of ignitability or any other characteristic. This interpretation is based on EPA guidance discussed in question RCRA-100, "Dilution of F003 Wastes", presented in RCRA Regulations and Key Words (Elsevier Science Inc., 1997). This question asked EPA whether an F003 waste can be treated by dilution. EPA stated that this could be performed for an F003 waste, because wastes listed solely for ignitability (i.e. acetone) and not toxicity "may be mixed with solid wastes and subsequently avoid regulation under RCRA via the Mixture Rule".

This is allowed under 40 CFR 261.3(a)(2)(iii) which states that a mixture of solid waste and hazardous waste "that is listed in Subpart D solely because it exhibits one or more of the characteristics of hazardous waste identified in Subpart C", is a hazardous waste. The EPA therefore concluded that if an F003 waste which is solely listed for the characteristic of ignitability (i.e. isn't toxic) and if it is no longer ignitable upon mixture with a solid waste, it is no longer regulated by RCRA. The presence of acetone does not make the TA-55-43, Lot No. 1 waste stream ignitable (refer to Section XII, Item 2). Even if a small quantity of spent acetone exists on debris or rags, the waste is not ignitable; therefore, and as allowed by regulation, the TA-55-43, Lot No. 1 waste stream need not be considered an F003 listed waste.

XII. RESPONSES TO ADDITIONAL TECHNICAL QUESTIONS FROM NMED

Public comments pertaining to the SAP, Rev. 0 were provided to the NMED for consideration. NMED developed technical questions about the SAP raised in public comment.

1. The potential of vinyl chloride and benzene in Waste Stream TA-55-43, Lot. No. 1 in excess of toxicity characteristic limits under 40 CFR 264.24 due to the radiolysis of plastics [should be addressed in the revised SAP].

The SAP, Rev. 2, states that because experimental data in Reed and Molecke show no vinyl chloride development, there will be no radiolytically produced vinyl chloride in TA-55-43, Lot. No. 1. The SAP, Rev. 2, goes on to indicate that even if vinyl chloride were present it would be

in a gaseous phase and would escape the container via the carbon filter, mitigating build-up to a toxic level. Also, vinyl chloride is a gas and does not meet the definition of a solid waste and would not be present in the liquid leachate of a representative sample in sufficient quantities to meet the regulatory definition of toxicity. The SAP, Rev. 2, asserts the same argument for benzene.

Public comments presented by the Southwest Research and Information Center (SRIC) are from Bernd Franke and Hisham Zerriffi with the Institute for Energy and Environmental Research (IEER). Drs. Franke and Zerriffi calculate the maximum benzene concentration in waste first by determining the G value of .00062 for benzene. Checking this value with that which could be derived using the formulas presented in Appendix B of the SAP, Rev. 2, the value used by IEER is consistent with that which can be calculated using SAP information (app. 0.0005). IEER assumes that 2.2×10^{16} MeV/g are generated per year; this value is calculated by IEER to result in 1.2×10^{17} molecules of benzene per gram of PVC waste. The origin of the MeV/g value assumed by the IEER is not presented, nor could this value be exactly duplicated by using values in the SAP, Rev. 2. Using SAP, Rev. 2, values of 6×10^{23} eV/day for 2.4 g of heat source material in a typical container, the calculated MeV/year is 2.2×10^{20} MeV/year.

The IEER comment implies that a correction based on PVC fraction has somehow been made, which could account for the difference, but this correction factor is not discussed in public comments. The values presented in the IEER comments were checked using information from the SAP, Rev. 2, in terms of total special nuclear material mass, total mass of plastic, and total eV/gram for the special nuclear material. Calculations show that assuming 50% of the approximately 485 kg of TA-455-43 Lot No. 1 waste is plastic, and approximately 50 grams of nuclear material is available with a dose rate of about 6×10^{23} eV/day, the estimated number of molecules of benzene generated per gram of plastic is roughly consistent with that presented in public comments. However, this also assumes that 50% of the total dose is available to plastic material, and does not take into account source distribution that could reduce the total energy deposited on plastic to generate VOCs.

Using the mass of a benzene molecule and the total number of benzene molecules, the IEER determined that 18 mg of benzene would be generated per kg of waste. Assuming totals analysis with a TC limit of .5 mg/l and corresponding totals limit of 10 mg/l, if all of the evolved benzene were present in the waste in an amenable form for regulation, public comments assert that the TC limit for the waste would be exceeded.

Evaluation of SAP, Rev. 2, and IEEL information has been conducted. The IEEL calculations, while mathematically correct based on general data, do not consider important, fundamental aspects of the waste that significantly impact the potential development of toxicity characteristic waste. These are:

- 1) The drums are vented, which would lead to a significant decrease in the headspace gas concentration due to diffusion. The SAP, Rev. 2, (page 43) suggests that the diffusion rate of 160 could be expected for benzene (this value is consistent with that derived using the molecular weight of hydrogen and benzene as shown in SAP, Rev. 2, formula 20). If approximately 3×10^{22}

molecules of benzene could be created (assuming the number of molecules generated in the IEEL comment and the assumption that 50% of the TA-55.43 Lot No. 1 waste stream is plastic) and using the formulas 10-13 in the SAP, Rev. 2, (page 41), roughly 5500 ppmv benzene could be generated. However, if this were allowed to diffuse, approximately 34 ppmv would remain. Likewise, the total "grams" would be reduced by a similar order of magnitude, and the total "grams" available to render the waste toxic is reduced such that it could not, mathematically, be toxic relative to benzene.

2) The Reed and Molecke experiments found benzene to be generated only when PVC was irradiated. The entire plastic population is not comprised of PVC, and therefore it is not realistic to assume that the entire plastic mass, once irradiated, would generate benzene. It is assumed that IEEL used approximately 50% of the total mass of the waste stream to determine their values, as calculations generally confirm their values using this assumption. Exact PVC amounts in the waste stream were not specified in the SAP, Rev. 2, and it is unknown whether IEEL had additional information unavailable to NMED that indicates a quantity of PVC present in waste. Further, self absorption and other factors that would reduce eV available for gas production have not been addressed, which would further reduce the quantities of VOCs generated via radiolysis.

3) There is no information to indicate that vinyl chloride is generated via radiolysis of those wastes that underwent experiment. This is not to say that vinyl chloride can't be generated, but available experimental data on typical waste stream plastic does not indicate its presence. Assuming vinyl chloride will be generated at TC levels is not supported by experimental evidence, and the simple analogy that vinyl chloride may leach from PVC is not sufficient information to indicate that vinyl chloride is present in TA-55-43, Lot No. 1 at TC levels.

4) Benzene gas is not a regulated solid waste. Benzene, present as material in/on solid waste could be regulated if present in sufficient quantities to render that waste toxic. The presence of benzene in headspace gas does not indicate that sufficient quantities are present within the waste itself to render the waste toxic and regulated as a RCRA waste. As correctly pointed out by the SAP, Rev. 2, radiolytically derived benzene would exist as a gas, and does not require the presence of a liquid benzene reservoir since the material is volatile by nature, expelled as a gas via radiolysis, and is probably maintained as a gas via actual heat within the TRU containers. The SAP, Rev. 2, correctly points out that the headspace gas concentration would have to be in excess of 50,000 ppm for liquid benzene to be present; headspace gas calculations show the maximum possible ppmv to be about an order of magnitude less than this concentration without even considering the concentration reduction afforded by drum venting. Further, RTR, VE and repackaging activities have not indicated the presence of free liquid benzene in the waste, which the IEEL report infers is present.

The NMED questioned whether rags and plastics should be sampled for benzene and vinyl chloride using a totals analysis (Attachment C, Question #9). LANL responded by indicating that it is inappropriate to sample plastics and rags because it is the benzene/vinyl chloride generated through radiolysis, not the rags, that would be hazardous. Also, LANL indicated that the benzene and vinyl chloride gas are not in a solid waste, and no liquid waste is present. In addition, LANL believed that total rather than TCLP analysis is inappropriate because the wastes in question are

gaseous. From a technical perspective, LANL did not believe that vinyl chloride would be present, and vinyl chloride (if present) and benzene would be present as gases and would not sorb to plastics. LANL also pointed out that the assumed thermal energy used by commentators to determine the amount of benzene developed via radiolysis would be much lower in progeny drums, which are repackaged to decrease the internal wattage; hence, evolved benzene and vinyl chloride concentrations would be much lower than the commentator's calculated concentration. LANL also believes repackaging would decrease the benzene and vinyl chloride concentrations well below any potential TC level. The explanations offered by LANL are technically correct and support the analysis in items 1-4, above, that vinyl chloride and benzene are not present in excess of TC limits.

2. The potential for Waste Stream TA-55-43, Lot. No. 1 to exhibit the characteristic of ignitability due to the presence of acetone or other volatile organic constituents in headspace gas [should be assessed].

The potential for Waste Stream TA-55-43, Lot No. 1 to exhibit the characteristic of ignitability due to the presence of acetone or other volatile organic constituents in headspace gas was assessed in the SAP, Rev. 2. LANL concluded that the waste stream could not exhibit the characteristic of ignitability because it does not have the required flashpoint, it is incapable of causing fire under container conditions, is not a compressed gas, and is not oxidizer.

The definition of the characteristic of ignitability would only apply if the waste was capable, under standard temperature and pressure, of causing a fire through friction, absorption of moisture, or spontaneous chemical changes. The waste could not meet any other portion of the definition because it is not a liquid, is not a compressed gas or contain any compressed gasses, nor does this waste stream contain oxidizers. Therefore, this question can only be evaluated in light of the potential of causing a fire through friction, absorption of moisture, or spontaneous chemical change due to the presence of small amounts of VOCs detected in the headspace gas. The volatile organic compounds that were detected are listed along with the highest concentration that were detected as follows: methanol - 79 ppmv; acetone - 150 ppmv; methylene chloride - 4 ppmv; methyl ethyl ketone - 50 ppmv; cyclohexane - 5 ppmv; benzene - 5 ppmv; and toluene - 12 ppmv. In addition, hydrogen and methane gases were detected, with the highest concentrations found for each being 0.69 ppmv and 0.12 ppmv, respectively. However, these compounds are evaluated for the characteristic of ignitability by SW-846 method 1010 or 1020, the Pensky-Martens Closed-Cup Method For Determining Ignitability or Setaflash Closed-Cup Method For Determining Ignitability, respectively. These methods quantify the Lower-Explosive-Limit (LEL) for organic compounds. The LELs for the VOCs found in the headspace gas are as follows: methanol - 6.7% by volume or 67,000 ppmv; acetone - 2.6% by volume or 26,000 ppmv; methylene chloride - 13% by volume or 130,000 ppmv; methyl ethyl ketone - 2 % by volume or 20,000 ppmv; cyclohexane - 1.3% by volume or 13,000 ppmv; benzene - 1.3% by volume or 13,000 ppmv; and toluene - 1.1% by volume or 11,000 ppmv. Additionally, the drums and standard waste boxes are vented. All of the detected constituents are well below their LELs, and drums are vented so that VOC and other gas concentrations do not build up within waste containers. It is reasonable to conclude that the waste containers do not contain VOCs or gases in sufficient quantities to produce an ignitable condition and, therefore, the waste is not a RCRA

hazardous waste by the definition of ignitability. See Section XI. Radiolytic Origin Of VOCs for a discussion of generation of VOCs, in particular for acetone and the diffusion rate of acetone and hydrogen.

3. The potential for Waste Stream TA-55-43, Lot No. 1 to exhibit the characteristic of corrosivity due to the radiolysis of plastic, and due to the possible presence of non-liquid corrosive material [should be assessed].

The SAP, Rev. 2, indicates that since no liquid water is present in waste, corrosivity cannot be assessed. However, public comment points out that Method 9045C can be used to determine the corrosivity of a aqueous non-liquid. Public comment asserts that rags used to clean gloveboxes, equipment, etc. may contain acids, and that these rags should be tested using Method 9045C for corrosivity.

In addition, public comments imply that radiolysis of plastics will result in hydrogen chloride liberation in sufficient quantities to render the waste corrosive, citing experimental results from Arakawa, et.al regarding radiolytic hydrochloric acid gas and hydrogen generation via gamma radiolysis. Public comments assert that because hydrogen gas will be liberated, "It is therefore likely that chlorinated plastic material in TA-55 waste will release enough hydrogen chloride so that it exhibits the corrosivity characteristic".

Public comment is correct in stating that corrosivity of non liquid materials can be assessed, as evidenced by EPA policy compendium information. This comment is also correct that an EPA approved method is available for use. However, other considerations must be taken into account before requiring such analysis, including ALARA concerns and the mass of the questioned waste material with respect to the entire waste stream. According to Table A-1 of the SAP, Containers 55400, 55401, and 55403 are the only containers, thus far, that contain rags. However, for these containers, the rags are associated with more special nuclear material than any other component (in fact, rags are "hotter" than most components in TA-55-43 waste), thus bringing to question whether ALARA concerns should be taken into consideration when assessing the need to sample this material. In addition, the rags comprise less than 1% of the total waste weight. If the assumption were made that rags contained enough corrosive material in the extract to render the rags a corrosive waste (i.e. typical laboratory acid with a pH of 2, for example), hypothetical combination of the rag extract (pH of 2) with the extract of a non-corrosive material would result in an overall non-hazardous designation for the waste, as the hydrogen ions in the rag extract would "dilute" throughout the non-hazardous extract, rendering the overall pH greater than 2.

Relative to hydrogen chloride generation, experimental evidence does indicate that hydrogen and chloride ions will be liberated via radiolysis. In addition, radiolysis within the TA-55-43 Lot 1 containers has generated hydrogen gas, as stated in the SAP, Rev. 2, page 42. Based on SAP, Rev. 2, information, greater than .01 moles of hydrogen have been generated per kilogram of waste which, according to the commentator, would apparently combine with chlorine gas to generate hydrogen chloride and impart an overall pH to the waste of less than 2. However, the commentator fails to consider numerous factors that bring to question this interpretation:

1) The containers are vented, so the calculated worst case hydrogen gas/hydrogen chloride gas development cannot occur. Actual measured data from TRU waste container 55614 indicate that 1.4 liters of hydrogen are present in the container, which is much less than the total amount of hydrogen that could be generated via radiolysis (1.3×10^3 liters). The difference in the amount of hydrogen present and hydrogen generated is because most of the hydrogen generated was vented from the container.

2) If the 1.3×10^3 liters of hydrogen gas is equivalent to about 60 moles, approximately .06 moles remains in the headspace gas, which is above the .01 mole "trigger" cited by the commentator. However, this .01 value cited by the commentator is based upon hydrogen within water liberated through performance of Method 9045C analysis; it is not based on the presence of hydrogen in a gaseous phase. The assumption cannot be made that the quantity of hydrogen within headspace gas is "equal" to the available hydrogen ion within solids and renders the solid corrosive, because hydrogen within a plastic material that has not undergone radiolysis is chemically bonded and not necessarily available to corrode material. Radiolysis would liberate gaseous hydrogen and chlorine that would probably not be maintained within the plastic; hence, hydrogen and chlorine would not be retained within or on the plastic material to render it corrosive.

3) A one-to-one ratio between hydrogen and chlorine to generate hydrogen chloride cannot be assumed. The presence of chlorine depends directly upon the type of material undergoing radiation; plastic in the TA-55-43 waste is of varying composition and the direct correlation cannot be made.

NMED questioned the need to assess non-liquid pH of rags and plastics, and the possibility of radiolytic generation of HCl to render the waste characteristic (D002) (Attachment C, Question #10). LANL responded by stating that the only regulatorily recognized method for determining corrosivity is Method 9040, which requires >20% of the waste be aqueous. LANL also points to more recent EPA Policy Compendium information than that cited by the commentator, which references the regulation (§264.22) for the definition of aqueous. Additionally, EPA Policy Compendium information is cited which states that corrosivity is intended to apply to liquid/aqueous wastes unless EPA promulgates a definition for solids, which it has not done. LANL also believes that Method 9045C is amenable to materials that exist as homogenous media, not the TA-55-43 Lot No. 1 waste stream. LANL also does not believe that HCl could be generated in sufficient quantities to generate HCl liquid, and hydrogen chloride would escape through filter vents long before it could accumulate.

LANL's technical statements regarding the generation of HCl liquid and venting of HCl gas are technically valid. Although arguments have been made that Method 9045C could be used to assess corrosivity, EPA policy in this regard does not indicate that corrosivity of heterogeneous debris material is the intended use of this method. Therefore, the explanations provided by LANL are correct and support the conclusions drawn in Items 1-3, above.

Therefore, the presence of evolved hydrogen does not indicate that corrosive conditions will develop in the waste; nor does its presence in headspace gas indicate that the actual waste material being regulated is subsequently corrosive.

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Southwest Research and Information Center (SRIC) Comments on the Los Alamos Sampling and Analysis Plan, including all attachments such as letter(s) from the Institute for Energy and Environmental Research, Bernd Franke to Geoffrey Fettus (Assistant Attorney General, State of NM) titled, "Review of Documents Relating to the Proposed Shipments of LANL TA-53-43 Wastes to the Waste Isolation Pilot Plant," dated July 7, 1998, and associated references.

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