SAMPLING AND ANALYSIS VALIDATES ACCEPTABLE KNOWLEDGE ON LANL TRANSURANIC, HETEROGENEOUS, DEBRIS WASTE
OR
"CUTTING THE GORDIAN KNOT THAT BINDS WIPP"

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ABSTRACT

King Gordius tied a knot that was so intricate that an oracle proclaimed that whoever could undo it would be the next ruler of Asia. Alexander the Great cut it with his sword to claim the kingdom. By analogy, a Gordian knot has bound the Waste Isolation Pilot Plant (WIPP). The Los Alamos National Laboratory (LANL) and the Department of Energy (DOE) recently took one step closer to cutting this knot.

Through sampling and toxicity characteristic leaching procedure (TCLP) analyses, LANL and the DOE validated that a LANL transuranic (TRU) waste (TA-55-43, Lot No. 01) was not a Resource Recovery and Conservation Act (RCRA) hazardous waste. This paper describes the sampling and analysis project as well as the statistical assessment of the analytical results. The analyses were conducted according to the requirements and procedures in the sampling and analysis plan (1) approved by the New Mexico Environment Department (2). The plan used a statistical approach that was consistent with the stratified, random sampling requirements of SW-846 (3).

LANL adhered to the plan during sampling and chemical analysis of randomly selected items of the five major types of materials in this heterogeneous, radioactive, debris waste. To generate portions of the plan, LANL analyzed a number of non-radioactive items that were representative of the mix of items present in the waste stream. Data from these "cold" surrogates were used to generate means and variances needed to optimize the design. Based on statistical arguments alone, only two samples from the entire waste stream were deemed necessary, however a decision was made to analyze at least two samples of each of the five major waste types. To obtain these samples, nine TRU waste drums were opened. Sixty-six radioactively contaminated and four non-radioactive grab samples were collected. Portions of the samples were composited for chemical analyses. In addition, a radioactively contaminated sample of rust-colored powder of interest to the New Mexico Environment Department (NMED) was collected and qualitatively identified as rust.

The waste stream does not contain hazardous metals at or above regulated concentrations. The chemical TCLP analytical results for most of the RCRA metals were two to three orders of magnitude below the regulatory limits. Only cadmium, chromium, and barium were detected frequently enough to warrant statistical calculation of the upper confidence limits as required by

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SW-846. The individual measurements and upper confidence limits were all well below the regulatory limits. As an example, the barium upper confidence limit was 0.58 ppm whereas the regulatory limit is 100 ppm. These data (generated from TA-55-43, Lot No. 01 waste) validated an earlier determination based on Acceptable Knowledge characterization (4) that neither the RCRA nor the New Mexico Hazardous Waste Act (NMHWA) regulates the TA-55-43 waste stream. The NMED concurred (5) with this LANL and DOE assessment (6).

DISCUSSION

Introduction

Based on Acceptable Knowledge (AK) characterization, LANL and the DOE determined that the TRU waste identified as Lot No. 01 of waste stream TA-55-43 from LANL Technical Area (TA) 55 was not a hazardous waste as defined and regulated by RCRA or the NMHWA. The AK characterization relied on knowledge of the waste generation processes and waste materials and on existing data concerning the characteristics of the materials and waste. This determination was presented in detail in the Acceptable Knowledge Summary Report (4) and the Waste Determination Report for Waste Stream TA-55-43, Lot No. 01 (7). These reports described the processes that generated the waste in TA-55-43, Lot No. 01, relevant sampling and analytical data on the materials used in those processes, information on the characterization process, and other pertinent information on the waste lot.

The TRU waste that constitutes this waste lot is heterogeneous, radioactive debris. All steps in the waste generation process, as well as all resulting wastes, were extensively documented by LANL. In addition, LANL had detailed information on feedstock, additional introduced materials, changes that may have occurred to materials, and generated materials associated with the processes.

Data collection, inspections, audits, and analyses based on real-time radiography, visual examination, headspace gas analysis, repackaging, gamma spectroscopy, and neutron radioassay confirmed the characterization of this waste lot.

LANL and the DOE performed confirmatory sampling and analysis to enable the NMED to determine that this waste stream is adequately characterized as non-mixed waste. LANL and the DOE submitted a confirmatory sampling and analysis plan that was approved by the NMED in revised form (1). As required by the plan, randomly selected drums and items were collected and analyzed for RCRA metals.

Waste Stream Description

TRU waste stream TA-55-43 was generated at the TA-55 plutonium facility during the fabrication of heat sources containing plutonium-238 (^{238}Pu) and the recovery of plutonium oxide from heat sources. This isotope of plutonium is about 280 times more radioactive than ^{239}Pu, making it useful for thermoelectric power generation. Heat sources were produced using a ^{238}Pu feedstock consisting of plutonium-oxide (PuO_2) powder received from the DOE's Savannah River Site (SRS).

The fabrication processes for these heat sources consisted of ^{238}Pu feedstock introduction, an oxygen-exchange stage, a milling and granulation stage, pellet pressing, and a cladding and decontamination stage. All processing stages were conducted in a line of ^{238}Pu gloveboxes that were, and continue to be, separated from all other TA-55 operations. During the course of these operations, a variety of waste materials were generated and placed in the drums that are now being prepared for shipment to WIPP as non-mixed waste. Five general categories of waste material types (matrices) were produced: plastics, rubber, metal, HEPA filters, and combustibles comprised mainly of rags and paper. In addition, a small amount of rust-colored powder was observed in the waste stream.

In all of the above processes, no materials were ever introduced at any time that would produce a listed waste, e.g., as a solvent fitting a listed description. Also, no materials that exhibit the qualities of ignitability, corrosivity, reactivity, or toxicity were introduced into the processes. Therefore, the materials introduced into the process would not result in the generation of a characteristic waste. In addition, the types of waste materials generated from these processes did not come into contact with any feedstock, additional introduced material, or converted material that would cause the waste to be hazardous and regulated by RCRA.

Description of Sample Collection Procedure

TA-55-43 waste stream items were initially placed into individual bags that were taped, numbered, and placed into lined drums. Thirty-six "parent" drums were chosen from this waste stream for preparation for shipment to WIPP. Each parent drum contained 1-15 plastic bags of waste, and each bag contained the waste materials removed from a glove box during manufacturing operations. These materials may have included plastics, rags, rubber o-rings, metal cans, and other similar heterogeneous debris contaminated with ^{238}Pu.

The 36 parent drums were repackaged (8) to prepare them for shipment to WIPP. The primary purpose of repackaging is to reduce the amount of nuclear material in every drum so that the thermal limits for transportation in the TRUPACT-II container are met. The thermal limits are imposed to assure that flammable concentrations of hydrogen are not generated during the 60-day period that the TRUPACT-II can be sealed without venting. During repackaging, some, or all of the contents of a parent drum are placed into one or more "daughter" drums as illustrated in Figure 1. If a daughter drum does not meet the thermal limits for transportation, its contents may be distributed among two or more "granddaughter" drums. The result of this process is final progeny drums that meet the transportation and other requirements imposed for shipment to WIPP.

Some of the progeny drums were no longer available for sampling because they were placed in standard waste boxes (SWBs) and were removed from the sample selection process. When the plan was developed, about half of the parent drums had been repackaged. Therefore, a two stage sampling process was used to select drums. First, a parent drum was randomly selected. Next, a subsampling unit consisting of either one bag from the parent drum or one of the final progeny drums was selected. This process was repeated until approximately 20 drums were listed in the random order selected. The contents of these drums were then listed in detail. Each waste material type (matrix) present in a subpopulation unit was considered available for sampling. A determination of how many units needed to be sampled to obtain at least 2 samples of each waste matrix was then performed. If the next random drum under consideration offered no new waste matrices, or if the quota (two samples/matrix) was already filled, it was skipped.

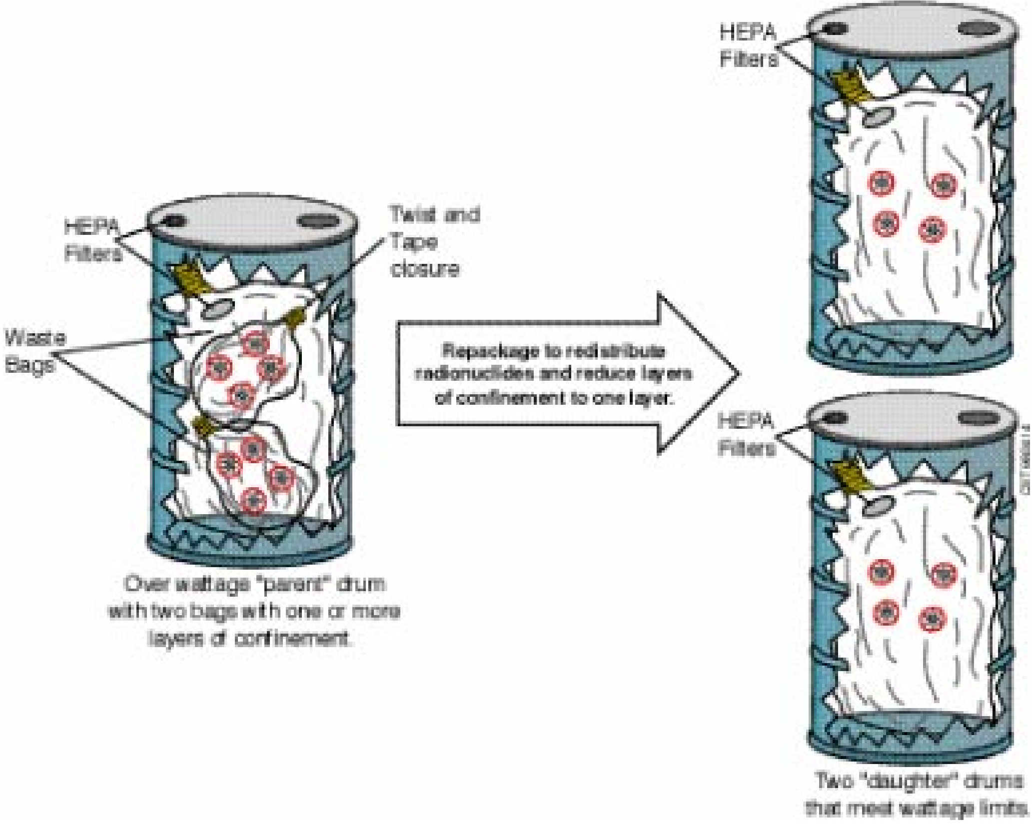

Figure 1. Illustration of Repackaging Process.

Table I provides a listing of the parent drum and subsampling unit pairs that were selected by this process. In some cases, subsampling units are progeny drums, which, like parent drums, are identified by five digit numbers. Parent drums that had not been repackaged contain bags as their subsampling units that are identified with an alphabetic prefix.

Table I.
Randomly Selected Sample Units and Matrices Available for Sampling

Parent Drum	Selected Bag or Progeny	Plastic	Rubber	Metal	HEPA Filter	Combustibles / Rags
55631	RUB-7	No[a]	rubber in can in plastic bag	can	No	No
56225	PLSP159	plastic	No	No	No	No
55614	PLS-215	plastic in can in bag	No	can	No	No
55452	57220	1/2 of PLS-150, drum liner bag from parent	No	steel can	No	Repackaging cheesecloth
56000	RUBPI17	No	rubber in can in bag	can	No	No
56090	57269	parts of plastic bottles, plastic, glove, glovebag	No	No	No	Repackaging cheesecloth
56053	57031	No	No	No	2 HEPA filters	No
55696	57008	No	No	No	HEPA filter	No

[a] A "No" in the table indicates that these matrices were not originally targeted for collection in the drum. After the primary targeted matrices were collected, these could be collected if they were available in the waste item.

Table I presents the waste type materials that were expected to be found in the sampling units. As specified in the sampling plan (1), sampling was considered to be complete when six grab samples and three backup grab samples for each type of waste matrix had been collected. All grab samples were nominally 15 gram. The order in which the drums were to be opened was the same as their listing in Table I. The following illustrates the sampling process for drum #55631.

Drum #55631
Date sampled: 28 September 1998
Material types originally targeted for collection: rubber and metal
Material types collected: rubber, metal, and plastic; and backup samples for rubber and metal
Drum condition comments: no rust

As seen in Table I, the primary waste type materials originally targeted for sampling from waste item RUB-7 in drum #55631 were rubber and metal. The "No" in the columns for other materials indicates that those materials were not targeted for collection from that drum. However, once the primary material types were obtained, additional matrix types were collected if they were present as specified in the sampling plan. NMED observers were present and agreed to this process. Grab samples of metal from a can and rubber from "O-rings" were collected from waste item RUB-7. After these grab samples were collected, grab samples of plastic from a bag in RUB-7 were taken. In addition, backup grab samples of rubber and metal were collected. In summary, the waste type matrices collected from RUB-7 were rubber, metal, and plastic, and backup grab samples of rubber and metal. The remaining contents of drum #55631 were repackaged into two daughter drums (#57505 and #57506) for shipment to the WIPP.

Other drums were similarly sampled to complete the collection of the required material types for analysis. In addition, non-radioactive (i.e., "cold") grab samples of metal from HEPA filter housings and aluminum baffles were obtained from two non-radioactive HEPA filters randomly selected from three that were available.

In summary, nine waste drums were opened. Sixty-six radioactively contaminated grab samples (this includes backup samples) were collected for the TCLP analyses of the five matrices. Portions of these grab samples were composited to form 13 radioactive samples for chemical analysis. One radioactively contaminated sample and one backup sample were collected for qualitative identification of the rust-colored powder. Four nonradioactive samples of HEPA filter metals were collected for analysis. The grand total of samples collected numbered seventy-two.

LANL and the NMED personnel documented (via notes and photographs) the entire sample collection process. Figures 2a and 2b show several of the LANL personnel that were present during the sampling process. Typically, LANL sampling personnel consisted of two sampling technicians, the principal investigator, one or two quality specialists, a repackaging specialist recording sampling field notes, and a radiation control technician (RCT). There was a minimum of one NMED observer during sample collection, and at times, as many as three. There were one or two DOE observers present during the sample collection process.

The materials were collected in the radioactive glovebox shown in Figure 2a. The required amounts of the materials were cut up with various hand tools and placed in prelabeled sample bottles (Figure 2c). Three grab samples of about 15 gram of each material type were collected and placed into separate collection bottles. During the collection process, grab samples that appeared (by visual assessment) to be radiolyticaly degraded were collected as were grab samples with lesser visual evidence of degradation. When an adequate number of sample collection bottles had been filled, they were lowered into a sealed bag through a port on the bottom of the glovebox. These were sealed with twist and tape closures to form bag-offs as required for radiation control. They were then removed from the glovebox by personnel using special, full-face respirators (Figure 2d). The RCT verified radionuclide containment prior to allowing normal operations to resume in the work area.

As shown in Figure 2e, tamper seals were applied to the two twist and tape closures of each bag. Additional radiation monitoring was done (Figure 2f) to obtain information required to allow the samples to be shipped from the sampling facility at LANL TA-50 to the chemistry facility (LANL CMR Building).

The sample bag-offs were placed inside a pipe container (about 5" diameter and 23" long) known as a "2R" that was placed inside a baffled drum for shipment (Figure 2g). The drum (referred to at this point in the process as a 6M container) was sealed, monitored again, and appropriately labeled for transportation. The chain of custody forms were transferred to the transportation crew.

Upon receipt of the drums (samples) at the LANL CMR building, the chain of custody forms were transferred from the transportation crew to the sample receiving group at the CMR Building. Chain of custody was transferred to the analysts. Portions of grab samples from each of the three sample jars for a matrix were combined to form a composite sample for that waste matrix as required by the sampling and analysis plan (1).

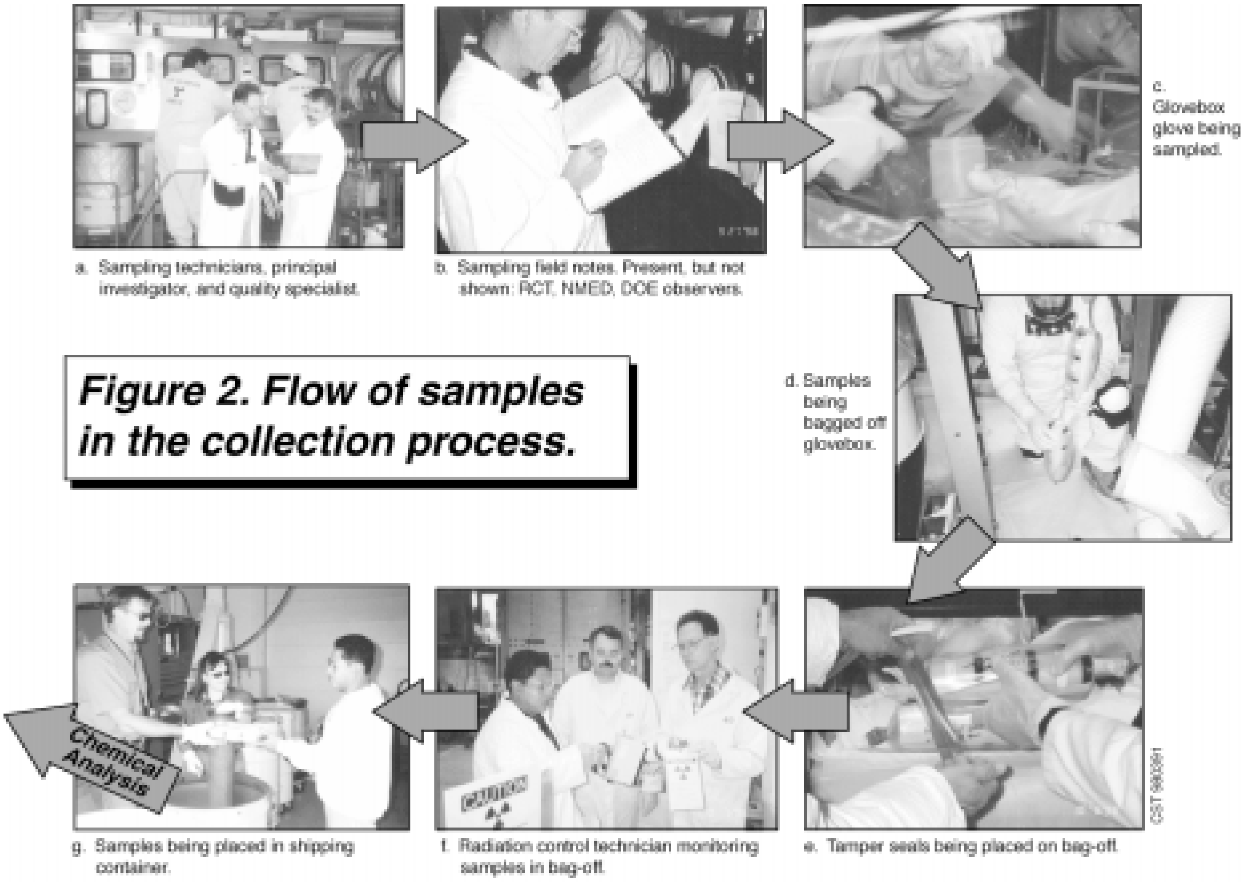
Figure 2. Flow of samples in the collection process.

a. Sampling technicians, principal investigator, and quality specialist.

b. Sampling field notes. Present, but not shown: RCT, NMED, DOE observers.

c. Glovebox glove being sampled.

d. Samples being bagged off glovebox.

e. Tamper seals being placed on bag-off.

f. Radiation control technician monitoring samples in bag-off.

g. Samples being placed in shipping container.

The composited samples were tumbled in a 12-position TCLP tumbler. After appropriate chemical processing, e.g., acidification and microwave digestion, the TCLP metals were analyzed by ICP/AES, and cold vapor atomic fluorescence for mercury. Required matrix spikes, matrix spike duplicates, laboratory control samples, blanks, and laboratory duplicates were analyzed along with the samples and reviewed to ensure appropriate quality controls.

The data were reported using the Contract Lab Program (CLP) format. In addition, data validation (9) was performed at the data generation level. The final analytical data are provided in the next section of this paper. The qualified data on the analyses for TCLP metals for all of the composited samples were assessed by the statisticians to determine whether calculations in the plan (1) concerning the number of samples needed for analysis were correct, whether additional samples needed to be analyzed, and whether the observed metal concentrations exceeded the TCLP regulatory limits. The statistical assessment is discussed subsequently in this paper.

TCLP METAL DATA

Samples from five matrix categories (plastic, rubber, combustible/rags, HEPA filter, and metal) were collected for TCLP analysis. The metal samples were further categorized as nonradioactive, i.e., "cold," metal (HEPA housings and bafflings only) or radioactive, i.e., "hot," metal. The concentration values for these samples are presented in Table II along with the detection limits (DLs) and, for comparison, the RCRA regulatory thresholds.

The data in Table II, for nearly all of the TCLP metal concentrations, are well below (often two to three orders of magnitude) their regulatory thresholds. Most of the metals were not detectable at detection limits, which are well below the TCLP limits. The only instances for which metals had reported concentrations that were within one order of magnitude of the regulatory threshold are cadmium in samples Plastic I, Combustibles and Rags I, HEPA Filter I and HEPA Filter II; chromium in samples HEPA Filter I and HEPA Filter II; and lead in sample Combustibles and Rags II. Nevertheless, all metal concentrations are well below the regulatory thresholds in all samples.

RUST-COLORED POWDER QUALITATIVE ANALYSIS

A sample of the rust-colored powder that was adhering to plastic in a drum was collected and analyzed by ICP/MS. The powder was removed from the plastic substrate with a plastic utensil. Previously (1), the powder was reported to be common rust as determined via x-ray fluorescence (XRF) analysis. This conclusion was based on the relatively large iron content and the apparent origin of the powder (i,e, oxidation of ferrous metals in the waste drum). The ICP/MS analysis confirms the XRF analysis as indicated by an iron content of 45% by weight (average based on two samples). The amount of iron in rust samples will vary depending upon the extent of oxidation and the oxygen stoichiometry. Based on the observed iron content (45%), the contents of the drum where the rust-colored powder was collected, its texture and color, and its high iron content, we concluded that the material is common iron oxide (rust).

TABLE II.

RESULTS OF TCLP LEACHATE ANALYSES*

Description	**Silver**	**Arsenic**	**Barium**	**Cadmium**	**Chromium**	**Lead**	**Selenium**	**Mercury**
Detection limit[a]	**0.022**	**0.33**	**0.0055**	**0.022**	**0.055**	**0.22**	**0.55**	**0.0001**
Regulatory Thresholds	**5**	**5**	**100**	**1**	**5**	**5**	**1**	**0.2**
Metal I	0.031	[-0.046]	0.14	[-0.030]	[-0.029]	[-0.077]	[-0.29]	0.0003[b]
Metal II	[-0.005][c]	[0.13]	0.17	[-0.012]	[-0.06][c]	[-0.056]	[0.093]	0.005
Plastic I	[-0.011]	[-0.204]	0.62	0.44	[0.008]	[0.075]	[0.025]	[-0.0001][b]
Plastic II	[0.017][c]	[0.065]	0.39	[0.001]	0.093[c]	[0.04]	[-0.107]	0.0002
Plastic III	[0.015][c]	[-0.068]	0.24	[0.003]	0.21[c]	[-0.008]	[-0.27]	0.0002
Rubber I	[0.02]	[0.097]	1.8	[0.018]	0.099	[0.089]	[-0.092]	[-0.0001][b]
Rubber II	[-0.004][c]	[-0.084]	0.34	[-0.002]	0.071[c]	[-0.13]	[-0.095]	0.0002
Combustibles and rags I	[-0.004][c]	[-0.056]	0.32	0.057	[0.047][c]	[-0.076]	[-0.038]	0.0002
Combustibles and rags II	[-0.008][c]	[-0.035]	0.37	0.101	0.079[c]	2.1	[-0.11]	0.0006
HEPA filter I	[-0.064][c]	[-0.07]	1.5	0.11	1.2[c]	[-0.25]	[-0.204]	0.0001
HEPA filter II	[-0.055][c]	[-0.408]	1.4	0.83	2.7[c]	[0.083]	[-0.23]	0.0495
HEPA ALB	[-0.001]	[-0.12]	0.006	[0.001]	0.058	[-0.14]	[-0.19]	[-0.0001][b]
HEPA SSH	[0.005]	[0.32]	0.009	[-0.002]	0.062	[-0.19]	[0.23]	[-0.0002][b]

All concentrations are reported in ppm and were those provided to the NMED on November 16, 1998. Additional analyses were done, but didn't alter the conclusions.

a Detection limit represents the instrument detection limit multiplied by a dilution factor.

b Detection limit is 0.0003 ppm for these samples.

c These data have been qualified during data validation.

*Concentrations in [ ] represent concentration values less than the detection limit.

STATISTICAL EVALUATION AND INTERPRETATION OF ANALYTICAL RESULTS

The sampling and analysis plan (1) presented data from previous sampling of cold matrices similar to those included in TA-55-43, Lot No. 01. Arsenic and selenium were never detected in the cold matrices, and silver and mercury were only detected once each. The sample size calculations focused on the remaining four metals — barium, cadmium, chromium and lead — that were detected frequently. Similar results were expected from the analyses of the samples collected and analyzed during this confirmatory sampling effort.

The data collected to support this effort are presented in Table II. As expected, arsenic and selenium were never detected. The detection limits (DLs) for these elements are much lower than the regulatory threshold concentrations, and it is reasonable to conclude that concentrations of these metals are far below regulatory levels. Because no measurable concentrations of these analytes were detected, these metals are not used for sample size verification, and upper confidence limits cannot be reasonably estimated.

Silver was reported at a concentration value exceeding the nominal detection limit in only one of the 13 samples for which results are available. The DL for silver (0.022 ppm) is more than two orders of magnitude less than the regulatory threshold (5 ppm). In addition, the single detected value is only slightly greater than the DL. Further statistical analysis strongly suggests that silver is not present in any of the samples Considering these results and the results from cold matrices presented in the sampling and analysis plan (1), it is reasonable to conclude that concentrations of silver are far below regulatory levels. As with arsenic and selenium, silver is not used for sample size verification and upper confidence limits are not presented because standard deviations cannot be reasonably estimated for all matrices. In addition, the observed concentrations and the DL are very low compared to the regulatory threshold concentration.

It should be noted that a detection limit does not determine the presence or absence of a chemical. It is used to establish a threshold below which it is more difficult to distinguish the reportable result from random noise. Consequently, sometimes a value can be reported below a detection limit when the chemical is present, and sometimes a value can be reported above a detection limit when the chemical is not present. A useful statistical metric for measuring random noise is to compare the uncensored data with a normal distribution centered at zero concentration.

Mercury was detected in nine of the 13 samples collected. The DL for mercury (0.1 ppb) is orders of magnitude below the regulatory threshold (200 ppb), and most of the detected values are reported at levels only slightly greater than the detection limit. At the level of sensitivity indicated by the analytical method it is possible that these reported concentrations, which are in the parts per trillion range, are the result of laboratory contamination. The one exception was a HEPA filter sample in which a mercury concentration of 0.0495 ppm was reported. Based on the data, it is reasonable to conclude that concentrations of mercury are far below regulatory levels. As for silver, mercury is not used for sample size verification, and upper confidence limits are not presented because standard deviations cannot be reasonably estimated for many of the matrices. The observed concentrations and the sample-specific DLs are very low compared to the regulatory threshold concentration.

Lead was detected only once in the 13 samples collected. The DL for lead (0.22 ppm) is considerably lower than the regulatory threshold (5 ppm), and the single detected value is only slightly greater than the DL. The current data indicate that lead is not present in the waste stream at concentrations near regulatory levels. Due to the paucity of values observed above the detection limit, it was not appropriate to perform a statistical sample size verification or to estimate an upper confidence limit.

In contrast, the remaining three metals (barium, cadmium, and chromium) were detected relatively frequently. Statistical analysis can be performed reasonably to calculate optimal sample sizes and upper confidence limits. Because they were detected relatively frequently, these three analytes require the greatest sample sizes (number of samples) and provide the greatest potential for upper confidence limit estimates that might approach regulatory levels. For arsenic, selenium, silver, mercury and lead, it is appropriate to directly compare maximum observed concentrations (or DLs for those analytes that were never detected) with the regulatory threshold concentration. Consequently, much of the remainder of this section focuses on barium, cadmium, and chromium.

The following subsections present:

A. comparison of the "hot" and "cold" metals samples to determine if the cold sample results should be included in the statistical analysis;

B. comparison of data across matrices to determine if the stratification was beneficial;

C. revised sample size (number of samples) calculations based on the new data; and,

D. estimation of upper confidence limits.

Analysis of "Hot" and "Cold" Metal Samples

Due to technical and safety considerations, an agreement was reached with the NMED to perform an analysis of TCLP metals on the metal components of nonradioactive (i.e., "cold") HEPA filters, to avoid the hazards associated with trying to cut filter housings and baffling inside a glove box. However, the NMED indicated (2) that they would only allow the results from these "cold" analyses to be included if the measured values were higher then in "hot" metal samples collected from the waste lot (e.g., metal cans). All eight analytes (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) were analyzed from two "hot" metal samples and two "cold" metal samples.

The analytical results are given in Table II. The TCLP concentration values obtained from the "cold" HEPA metal samples were compared to the TCLP values obtained from the "hot" metal samples. The results for all analytes from all metal samples were either detected near the detection limits or not detected at all. In general, inclusion or exclusion of the "cold" HEPA results did not affect the conclusions. For four of the analytes (arsenic, cadmium, lead, and selenium), all results showed non-detectable levels for both "hot" and "cold" metal samples. For the remaining metals:

- Silver was detected in one of the "hot" metal samples and not in either of the "cold" HEPA housing metal samples.

- Mercury was detected in the "hot" metal samples and not in the "cold" HEPA housing metal samples.

- Barium was detected in all the metals samples, but the concentrations of barium in the "hot" metals samples were greater than those from the "cold" HEPA housing metal samples.

- Chromium was not detected in the "hot" metal samples but was detected near the detection limit in both of the two "cold" metal samples.

Consequently, chromium is the only analyte for which the "cold" HEPA results are factored into the calculation of the mean concentration.

Confirmation that Stratification is Appropriate to this Waste Stream

Stratified random sampling was used to select samples for characterization of the waste stream. The results clearly show that the observed concentrations are so much lower than the regulatory threshold that the form of the stratification has no effect on the final conclusions. However, this stratification scheme had the benefit of ensuring that all major waste matrices were represented in the confirmatory sampling.

In addition, differences in concentration results, including detection status and magnitude or variability of detected concentrations, were evaluated. Clear differences were observed between the various waste categories sampled for some of the analytes (see Table II). The differences between analyte concentrations in the waste categories indicate that the waste stream is non-randomly heterogeneous in terms of its chemical properties.

Calculation of Optimal Sample Sizes

For this sampling activity, the optimal total sample size for three of the analytes (barium, cadmium, and chromium) was calculated. A stratified random sampling design was used as described in SW-846, Chapter Nine (3), and was approved by the NMED (2). The adaptive sampling plan (1) called for updating sample sizes throughout the project. Final evaluations of the required sample sizes were calculated using the sample results given in Table II. As noted at the beginning of this section, optimal sample sizes were calculated only for barium, cadmium, and chromium. These were used because four of the remaining five metals were not detected frequently enough to allow a reasonable calculation, and, in the case of mercury, the reported concentration values were too low compared to the regulatory threshold to warrant further statistical analysis. Given the observed results for all the metals, the three metals selected are more limiting (i.e., will have the greatest impact on the results) both for sample size calculations and for estimation of upper confidence limits.

The mean and variance inputs for each TCLP metal in each waste matrix were combined using weights that reflect the relative contribution of each of the waste categories to the overall waste Lot No. 01.
Table III provides the relative weights () for this waste lot based on the mass percent of each of the matrices of interest. The relative weights presented in Table III reflect the mass percents of each waste matrix following the repackaging of all but six of the original "parent" drums. Further repackaging of the remaining drums is extremely unlikely to change the weight percentages by more than 10%.

Means and standard deviations for each of the three metals selected for each of the five matrices (strata) of interest ($\bar{x}_k$ and s_k, where the subscript *k* represents, in turn, each of the five matrices) were calculated. Instrument readings were used in calculating the means and variances that are reported in Tables IV and V, including for those measurements that were reported as less than the instrument detection limit (DL). This was done in order to avoid the problem of underestimating variances, which often results from substituting detection limits in place of instrument readings below the level of detection. The instrument readings are shown in Table II. The effect on optimal sample size (number of samples) calculations of using instrument values as opposed to substituting DLs for non detects was evaluated and the results were provided to the NMED. Substituting Dls for NDs was determined to have no effect on the final conclusions.

Table III.

Waste Categories and Weight Distribution in Lot No. 01†

Waste Category	HEPA Filters	Metal	Plastics	Rubber	Rags, and Combustibles	Rust-Colored Powder
Estimated Weight %	1%*	30%	44%	9%	16%	Trace

†Estimates of weight percent were updated during repackaging activities because some of these activities added plastic and rags to the waste stream.
* From the boron membrane of the filter. The metal portions of the filter contribute to the percentage of metal items in the waste stream.

For chromium, the "cold" metals samples were also included in the calculations. To properly account for these samples, the metal waste category was separated into HEPA filter metal components and other metals. These categories make up 19 and 11 weight percent of the waste stream, respectively. These percents were used for calculation of weighted means and variances for chromium.

The weighted means and variances for each RCRA constituent are calculated using equations 1 and 2.

(Eq. 1)
$$\bar{x} = \sum_{k=1}^{5} w_k \bar{x}_k$$

(Eq. 2)
$$s^2 = \sum_{k=1}^{5} w_k s_k^{2}$$

The weighted standard deviation, *s*, is calculated by taking the square-root of the weighted variance. Tables IV and V show the estimates from the five waste matrices.

Table IV.
Estimated Means of Sample Results by Waste Matrix (in ppm)

Waste *Category*	DL	*HEPA Filters*	Metal	*Plastics*	*Rubber*	Combustibles and Rags	Weighted Mean
Barium	0.0055	1.43	0.15	0.50	1.06	0.35	0.43
Cadmium	0.022	0.47	[-0.021]	0.22	[0.008]	0.08	0.05
Chromium*	0.055	1.91	[0.02]	[0.05]	0.09	0.06	0.01

*cold HEPA filter metal results included in Metal category
[ ] results in brackets are less than DLs

Table V.
Estimated Standard Deviations of Sample Results by Waste (in ppm)

Waste Category	HEPA Filters	Metal	Plastics	Rubber	Combustibles and Rags	Weighted Standard Deviation
Barium	0.10	0.02	0.16	1.03	0.04	0.33
Cadmium	0.50	0.01	0.31	0.01	0.03	0.21
Chromium	1.06	0.01	0.06	0.02	0.02	0.11

Based on these estimates and the use of a 20% significance level (i.e., 80% confidence level) as recommended in SW-846 (3), an optimal total number of samples, *n*, can be calculated using Equation 3. RT represents the regulatory threshold for the RCRA constituent of interest, and $t_{n-1,0.20}$ represents the 90th percentile of the standard *t*-distribution with *n*-1 degrees of freedom. The 90th percentile is used because the significance level as presented in SW-846 corresponds to a two-sided hypothesis test. This equation is equivalent to Equation 8 of SW-846, Chapter Nine, Table 9-1 (3). Note that Equation 3 contains *n* on both sides of the equation, indicating that iteration is required to determine the optimal *n*.

(Eq. 3)

$$\mathbf{n} = \frac{\left(\mathbf{t}^2_{\mathbf{n}-1,0.20}\right)\mathbf{s}^2}{\left(\mathbf{RT} - \bar{\mathbf{x}}\right)^2}$$

After calculation of a total sample size, allocation of samples across the matrices must be performed. The allocation of samples to the strata is performed consistently with the guidance provided in SW-846 and uses the relative contribution to the overall uncertainty or variability of each of the strata. That is, the samples are allocated in direct proportion to the standard deviation estimates for each matrix. Equation 4 represents this relationship and is consistent with page NINE-18 of SW-846 (3).

(Eq. 4)

$$\mathbf{n_k} = \mathbf{n}\frac{\mathbf{s_k}}{\sum\limits_{\mathbf{k}=1}^{5}\mathbf{s_k}}$$

The nature of the classical statistical sampling technique used guarantees that the minimum possible number of samples is two, after rounding up the calculated fractional value. Equation 3 is solved at the point where the number of samples on the left hand side is one greater than the degrees of freedom term on the right hand side (allowing for the unit difference of *n* compared with *n*-1). This match is achieved at numbers for each of the three RCRA metals that are only slightly greater than one (see Table VI). The optimal sample sizes are rounded up to two. The implication is that concentration levels of the RCRA metals in the waste of TA-55-43, Lot No. 01 are so far below the regulatory thresholds that only two samples are needed from the entire waste lot for confirmation.

Table VI.
Optimal Number of Samples and Allocation of Samples for All Waste Categories

Waste Category	TOTAL	HEPA filters	Metal	Plastics	Rubber	Combustibles and Rags
Barium	1.22	0.09	0.02	0.149	0.037	0.927
Cadmium	1.67	0.965	0.025	0.594	0.06	0.026
Chromium	1.32	1.169	0.035	0.066	0.025	0.022

In accordance with the sampling plan, at least two samples were taken from each of the waste matrix categories. Thus, the overall sample size collected and analyzed is more conservative, i.e., much larger, than that required by the optimal sample size calculation and is more than adequate for determining that this waste stream is not hazardous.

Comparison of Each RCRA Analyte to the Associated Regulatory Threshold

According to the NMED (2) and SW-846 guidance (3), the appropriate value to compare to the regulatory threshold is the upper confidence limit of the mean based on 80% confidence. The upper confidence limits on the means ($CI_{0.80}$) are calculated using equation 5:

(Eq. 5)

$$CI_{0.80} = \bar{x} + t_{n-1,0.20}\frac{s}{\sqrt{n}}$$

For all results, including results below the DLs, the instrument readings were used for calculation of the mean and variance of the waste category. The means and variances for the waste categories (presented in Tables IV and V) were used in the formulas for the means and variances based on stratified sampling (Equations 1 and 2).

Table VII.
Upper Confidence Limits on Means of Analytes in Waste Stream

Analyte	DL	Mean	$CI_{0.80}$ (ppm)	RCRA threshold (ppm)
Barium (ppm)	0.0055	0.43	0.58	100
Cadmium (ppm)	0.022	0.11	0.20	1
Chromium (ppm)	0.055	0.07	0.11	5

For barium and chromium, the means and confidence limits on the means are at least an order of magnitude lower than the corresponding RCRA threshold TCLP limits (Table VII). For cadmium, the upper confidence limit is closer to the regulatory threshold, but is still considerably lower. The findings for cadmium are driven primarily by the HEPA filter membrane sample results.

The results confirm that, to the required degree of confidence, the mean concentrations of all RCRA constituents in the waste stream of Lot No.1 are far below the regulatory thresholds. In addition, the discussion in the previous section indicates that more than a sufficient number of samples has been collected to justify the conclusions. Similar conclusions are justified for the remaining five metals because of the infrequency of their detection and the large difference between the regulatory thresholds and the few reported detections or the DLs.

CONCLUSIONS

Chemical analyses of a large number of randomly selected items from the five major waste matrices in the waste stream show that TA-55-43, Lot No. 01 waste does not contain hazardous metals at or above regulated concentrations for any of the five major waste type materials. This conclusion validates the earlier AK determination (4) that LANL and the DOE provided to the NMED on waste stream TA-55-43. The chemical TCLP analytical results presented are two to three orders of magnitude below the regulatory limits for most of the RCRA metals. As stated above, only cadmium, chromium, and barium were detected frequently enough to warrant statistical calculation of the upper confidence limits. As provided in Table VII, the upper confidence limit for barium was 0.58 ppm to be compared with the regulatory limit of 100 ppm, the upper confidence limit of cadmium was 0.20 ppm to be compared with the regulatory limit of 1 ppm, and the upper confidence limit of chromium was 0.11 ppm to be compared with the regulatory limit of 5 ppm. These levels are all well below the regulatory limits. Based on these analysis results, it is concluded (6) that the waste in TA-55-43, Lot No. 01 was not regulated by either the Resource Recovery and Conservation Act (RCRA) or the New Mexico Hazardous Waste Act (NMHWA). The NMED concurred with this assessment (5).

Statistical analyses of the chemical data confirm that comparison of concentrations by matrices is appropriate for this waste stream. In addition, new optimal sample sizes were calculated based on these data, and it was confirmed that the original sample sizes in the plan (1) were more than adequate.

Finally, the rust-colored powder was chemically analyzed and concluded to be common rust.

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