ATTACHMENT ~~B~~ C2

STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS

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STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS

Introduction

The ~~Permittees U.S. Department of Energy Carlsbad Field Office (DOE)~~ Permittees shall require generator/storage sites (**sites**) to use the following statistical methods for sampling and analysis of TRU mixed waste which is managed, stored, or disposed at WIPP, unless determined unnecessary by ~~the Permittees~~ the U.S. Department of Energy (**DOE**) as a result of an Acceptable Knowledge (AK) Sufficiency Determination. These statistical methods include methods for selecting waste containers for totals analysis, selecting waste containers for headspace gas sampling and analysis, and setting the upper confidence limit.

~~B~~C2-1 Approach for Selecting Waste Containers for Statistical Sampling

~~B~~C2-1a Statistical Selection of Containers for Totals Analysis

The statistical approach for characterizing retrievably stored and newly generated homogeneous solids (S3000) and soil/gravel (S4000) waste and repackaged or treated S3000 waste relies on using acceptable knowledge to segregate waste containers into relatively homogeneous waste streams. Using acceptable knowledge, generator/storage sites will classify the entire waste stream as hazardous or nonhazardous rather than individual waste containers. Individual waste containers serve as convenient units for characterizing the combined mass of waste from the waste stream of interest. Once segregated by waste stream, random selection and sampling of the waste containers followed by analysis of the waste samples shall be performed to ensure that the resulting mean contaminant concentration provides an unbiased representation of the true mean contaminant concentration for each waste stream. ~~The Permittees~~ ~~DOE~~ The Permittees shall require each site project manager to verify that the samples collected from within a waste stream were selected randomly.

An end use of analytical results for retrievably stored homogeneous solids and soil/gravel is for assigning the Environmental Protection Agency (**EPA**) hazardous waste numbers associated with toxicity characteristic waste (D-numbers) that apply to each mixed waste stream. The toxicity characteristic D-numbers are indicators that the waste exhibits the toxicity characteristic for specific contaminants under the Resource Conservation and Recovery Act (**RCRA**). The RCRA-toxicity determination is made on the basis of sampling and analysis of waste streams and on whether or not the waste stream includes F-number wastes. If a waste stream includes one or more RCRA F-numbers identified via acceptable knowledge, toxicity characteristic contaminants associated with the F-number waste(s) are not included in the RCRA-toxicity characteristic determination. That is, the F-numbers take precedence over RCRA-toxicity D-number, and the waste stream is assumed hazardous regardless of the concentration. Therefore, toxicity characteristics contaminants associated with F-numbers for a waste stream shall be omitted from all calculations for determining the number of containers to sample because these wastes streams are assumed to be hazardous. In addition, each toxicity characteristic contaminant associated with the F-number(s) shall be excluded from evaluation of analytical results to determine D-numbers. Contaminants of interest for the sampling, analysis, and RCRA-toxicity determination of a waste stream, then, excludes contaminants associated with F-numbers that have been assigned to the waste stream.

The sampling and analysis strategy is illustrated in Figure ~~B~~ C2-1. Preliminary estimates of the mean concentration and variance of each RCRA regulated contaminant in the waste will be used to determine the number of waste containers to select for sampling and analysis. Preliminary estimates will be based on a minimum of five samples selected randomly from the waste stream. If the entire waste stream is not accessible for sampling then a minimum of five preliminary samples will be selected randomly from the accessible population. As the rest of the waste stream is retrieved or generated, additional selected containers will be sampled as provided below and the analytical results will be reported to ~~the Permittees~~ ~~DOE~~ the Permittees. Samples collected to establish preliminary estimates that are selected, sampled, and analyzed using a ~~Permittee~~ DOE approved laboratory in accordance with applicable provisions of the WAP may be used as part of the required number of samples to be collected. The applicability of the preliminary estimates to the waste stream to be sampled shall be justified and documented. The preliminary estimates will be determined in accordance with the following equations:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad (\text{~~B~~C2-1})$$

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2 \qquad (\text{~~B~~C2-2})$$

Where:

$\bar{x}$ = the calculated mean.
s^2 = the calculated concentration variance.
n = the number of samples analyzed.
x_i = the concentration determined in the *ith* sample.
i = an index from 1 to n.

Based upon the preliminary estimates of $\bar{x}$ and s^2 for each chemical contaminant of concern, estimate the appropriate minimum number of samples (*n*) to be collected for each contaminant using the following formula from SW-846 (EPA 1996):

$$n = \frac{t^2_{\alpha,n_0-1}\, s^2}{\left(RT - \bar{x}\right)^2} \qquad (\text{~~B~~C2-3})$$

Where:

n_0 = the initial number of samples used to calculate the preliminary estimates.
n = the calculated minimum number of samples to be collected.
$t_{\alpha,n-1}$ = the 90th percentile for the *t* distribution with n_0-1 degrees of freedom.
RT = the Regulatory Threshold of the contaminant (TC limit for toxicity characteristic wastes, PRQL for listed wastes)

The number of samples to be collected will be based upon the largest *n* calculated for each of the contaminants of concern. The actual number of samples collected shall be adjusted as necessary to ensure that an adequate number of samples are collected to allow for acceptable levels of completeness.

Non-integer results of calculations for the required sample size should be rounded up to the next integer. A minimum of five containers shall be sampled and analyzed in each waste stream. If there are fewer containers than the minimum or required number of samples in a waste stream, one or more randomly selected containers shall be sampled more than once to obtain the number of needed samples of the waste. Otherwise any one container may be selected for sampling only once.

The calculated total number of required waste containers will then be randomly sampled and analyzed using a ~~Permittee~~ DOE approved laboratory. Waste container samples from the preliminary mean and variance estimates may be counted as part of the total number of calculated required samples if and only if:

- There is documented evidence that the waste containers for the preliminary estimate samples were selected in the same random manner as is chosen for the required samples.

- There is documented evidence that the method of sample collection in the preliminary estimate samples were identical to the methodology to be employed for the required samples.

- There is documented evidence that the method of sample analysis in the preliminary estimate samples were identical to the analytical methodology employed for the required samples.

- There is documented evidence that the validation of the sample analyses in the preliminary estimate samples were comparable to the validation employed for the required samples. In addition, the validated samples results shall indicate that all sample results were valid according to the analytical methodology.

If only a portion of a waste stream is accessible for sampling (e.g., the remainder of the waste stream will be recovered from storage at the generator/storage site, or only a portion of the waste stream has been repackaged, treated, or generated), the calculated number of samples will be randomly selected from the accessible portion of the waste stream. A minimum of five randomly selected samples will be obtained and analyzed from the accessible portion of the waste stream. ~~The Permittees~~ DOE may approve the WSPF and authorize the generator/storage site to begin shipping the waste stream to WIPP once the analytical data for the randomly selected samples from the accessible portion of the waste stream have been obtained.

The generator/storage site will also randomly select the calculated number of sample locations from the waste stream as a whole. A minimum of five randomly selected sample locations will be selected from the waste stream as a whole. As those randomly selected locations (e.g., buried or newly generated waste containers) become accessible for sampling, samples will be obtained and analyzed.

For those waste streams where the population of the waste stream as a whole is indeterminate (e.g., continually generated waste streams from ongoing processes) or to facilitate waste processing, the generator/storage site may divide the waste stream into lots. In this case, a minimum of five randomly selected sample locations will be selected from within each subsequent lot. As those randomly selected locations (e.g., buried or newly generated waste containers) become accessible, samples will be obtained and analyzed. As with sampling from the waste stream as a whole, the generator/storage site may ship waste from the lot being generated or retrieved prior to completing sampling and analysis of the lot.

The generator/storage site will use the data to update the UCL_{90} values for the waste stream as described in Section ~~B~~ C2-2a and assign EPA hazardous waste numbers as appropriate. The generator/storage sites will submit the analytical data from subsequent sampling to ~~the Permittees~~ ~~DOE~~ the Permittees for inclusion in the WIPP facility operating record upon completion of project level data validation in Permit Attachment ~~B~~ C3, Section ~~B~~ C3-10b. If changes to EPA hazardous waste numbers are required as a result of subsequent sampling, the generator/storage site will notify ~~the Permittees~~ ~~DOE~~ the Permittees and shipments of the affected waste stream shall be suspended until ~~the Permittees~~ DOE approves a revised WSPF for the affected waste stream.

Upon collection and analysis of the preliminary samples, or at any time after the preliminary samples have been analyzed, the generator/storage site may presumptively assign hazardous waste numbers to a waste stream even if the calculated number of required samples is greater than the preliminary number of samples collected. For waste streams with calculated upper confidence limits below the regulatory threshold, the site shall collect the required number of samples if the site intends to establish that the constituent is below the regulatory threshold.

~~B~~C2-1b Statistical Selection of Containers for Headspace Gas Analysis

Headspace gas sampling of a waste stream may be done on a randomly selected portion of containers in the waste stream. The minimum number of containers, *n*, that must be sampled is determined by taking an initial VOC sample from ten randomly selected containers. These samples are analyzed for all the target analytes analytes using a ~~Permittee~~ DOE approved laboratory. The standard deviation, *s*, is calculated for each of the nine VOCs in ~~Module IV~~ Part 4, Table ~~IV.D.1~~ 4.4.1. The value of *n* is determined as the largest number of samples (not to exceed the number of containers in the waste stream or waste stream lot) calculated using the following equation:

$$n_{voc_i} = \frac{t^2_{\alpha,n-1} s^2 e_{voc_i}}{E^2_{voc_i}} \qquad (\text{~~B~~C2-4})$$

Where:

n_{voci} = the number of samples needed to representatively sample the waste stream for the VOC_i from Table ~~IV.D.1~~ 4.4.1

$t_{\alpha,n-1}$ = the 90th percentile of the *t* distribution with *n*-1 degrees of freedom

s_{evoci} = the estimated standard deviation, based on the initial *n* samples, for VOC_i from Table ~~IV.D.1~~ 4.4.1

E_{voci} = the allowable error determined as 1 percent of the limiting concentration for VOC_i from Table ~~IV.D.1~~ 4.4.1

Non-integer results of calculations for the required sample size should be rounded up to the next integer. A minimum of ten containers shall be sampled and analyzed in each waste stream. If there are fewer containers than the minimum or required number of samples in a waste stream, then each container should be sampled once.

The calculated total number of required waste containers will then be randomly sampled and analyzed. Waste container samples from the preliminary mean and variance estimates may be counted as part of the total number of calculated required samples if and only if:

- There is documented evidence that the waste containers for the preliminary estimate samples were selected in the same random manner as is chosen for the required samples.
- There is documented evidence that the method of sample collection in the preliminary estimate samples were identical to the methodology to be employed for the required samples.
- There is documented evidence that the method of sample analysis in the preliminary estimate samples were identical to the analytical methodology employed for the required samples.
- There is documented evidence that the validation of the sample analyses in the preliminary estimate samples were comparable to the validation employed for the required samples. In addition, the validated samples results shall indicate that all sample results were valid according to the analytical methodology.

The mean and standard deviation calculated after sampling *n* containers can be used to calculate a UCL_{90} for each of the headspace gas VOCs using the methodology presented in Section ~~B~~ C2-2b.

If only a portion of a waste stream is accessible for sampling (e.g., the remainder of the waste stream will be recovered from storage at the generator/storage site or only a portion of the waste stream has been repackaged or treated), the calculated number of samples will be randomly selected from the accessible portion of the waste stream. A minimum of ten randomly selected samples will be obtained and analyzed from the accessible portion of the waste stream. ~~The Permittees~~ DOE may approve the WSPF and authorize the generator/storage site to begin shipping the waste stream to WIPP once the analytical data for the randomly selected samples from the accessible portion of the waste stream has been obtained.

The generator/storage site will also randomly select the calculated number of sample locations from the waste stream as a whole. A minimum of ten randomly selected sample locations will be selected from the waste stream as a whole. As those randomly selected locations (e.g., buried or newly generated waste containers) become accessible for sampling, samples will be obtained and analyzed.

For those waste streams where the population of the waste stream as a whole is indeterminate (e.g., continually generated waste streams from ongoing processes) or to facilitate waste processing, the generator/storage site may divide the waste stream into lots. In this case, a minimum of ten randomly selected containers will be selected from within each subsequent lot. As those randomly selected containers (e.g., buried or newly generated waste containers) become accessible, samples will be obtained and analyzed. As with sampling from the waste stream as a whole, the generator/storage site may ship waste from the lot being generated or retrieved prior to completing sampling and analysis of the lot.

The generator/storage site will use the data to update the UCL_{90} values for the waste stream as described in Section ~~B~~ C2-2b and assign EPA hazardous waste numbers as appropriate. The generator/storage sites will submit the analytical data from subsequent sampling to ~~the Permittees~~ ~~DOE~~ the Permittees for inclusion in the WIPP facility operating record upon completion of project level data validation in Permit Attachment ~~B~~ C3, Section ~~B~~ C3-10b. If changes to EPA hazardous waste numbers are required as a result of subsequent sampling, the generator/storage site will notify ~~the Permittees~~ ~~DOE~~ the Permittees, and shipments of the affected waste stream shall be suspended until ~~the Permittees~~ DOE approves a revised WSPF for the affected waste stream.

Upon collection and analysis of the preliminary samples, or at any time after the preliminary samples have been analyzed, the generator/storage site may presumptively assign hazardous waste numbers to a waste stream even if the calculated number of required samples is greater than the preliminary number of samples collected. For waste streams with calculated upper confidence limits below the regulatory threshold, the site shall collect the required number of samples if the site intends to establish that the constituent is below the regulatory threshold.

~~B~~C2-2 Upper Confidence Limits for Statistical Sampling

~~B~~C2-2a Upper Confidence Limit for Statistical Solid Sampling

Upon completion of the required sampling, final mean and variance estimates and the UCL_{90} for the mean concentration for each contaminant shall be determined. The observed sample *n** shall be checked against the preliminary estimate for the number of samples (n) to be collected before proceeding, where n* is:

$$n^* = \frac{t^2_{\alpha,n-1}\, s^2}{\left(RT - \bar{x}\right)^2} \qquad (\text{~~B~~C2-5})$$

and the right-side terms in the equation are as defined in Section ~~B~~ C2-1a.

If the observed sample *n** estimate results in greater than 20 percent or more required samples than were originally calculated, then the additional samples required to fulfill the revised sample estimate shall be collected and analyzed. The determination of *n** is an iterative process that follows the collection and analysis of any additional samples and continues until the difference between *n** and the previous sample size determination is less than 20 percent.

Once sufficient sampling and analysis has occurred, the waste characterization will proceed. The assessment will be made at the 90 percent confidence level. The UCL_{90} for the mean concentration of each contaminant will be calculated using the following equation from OSWER 9285.6-10 (EPA 2002):

$$UCL_{90} = \bar{x} + \frac{t_{\alpha,n-1}s}{\sqrt{n}} \qquad (\text{~~B~~C2-6})$$

If the UCL_{90} for the mean concentration is less than the regulatory threshold limit, the waste stream is not required to be assigned the hazardous waste number for the associated contaminant. If the UCL_{90} is greater than or equal to the regulatory threshold limit, the waste stream will be assigned the hazardous waste number for the associated contaminant.

~~B~~C2-2b Upper Confidence Limit for Statistical Headspace Gas Sampling

A UCL_{90} concentration for each of the headspace gas VOCs must be calculated from the sample data collected. The observed sample n^* shall be checked against the estimate for the number of samples (n) to be collected before proceeding, where n* is:

$$n^* = \frac{t^2_{\alpha,n-1}s^2}{E^2} \qquad (\text{~~B~~C2-7})$$

where E is as defined in Section ~~B~~ C2-1b and the remaining right-side terms in the equation are defined in Section ~~B~~ C2-1a. When composite headspace gas sample results are used, the mean, standard deviation, and t-statistic are based on the number of composite samples analyzed, rather than the number of containers sampled.

If the observed sample n^* estimate results in greater than 20 percent or more required samples than were originally calculated, then the additional samples required to fulfill the revised sample estimate shall be collected and analyzed. The determination of n^* is an iterative process that follows the collection and analysis of any additional samples and continues until the difference between n^* and the previous sample size determination is less than 20 percent. The UCL_{90} is then calculated using equation ~~B~~ C2-6. In this case, UCL_{90} is the 90 percent upper confidence limit for the mean VOC concentration, $\bar{x}$ is the calculated sample mean VOC concentration and s is the calculated sample standard deviation. The value of $t_{(\alpha,n-1)}$ is found in Table 9-2 of Chapter 9 of SW-846 (EPA, 1996).

References

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FIGURES

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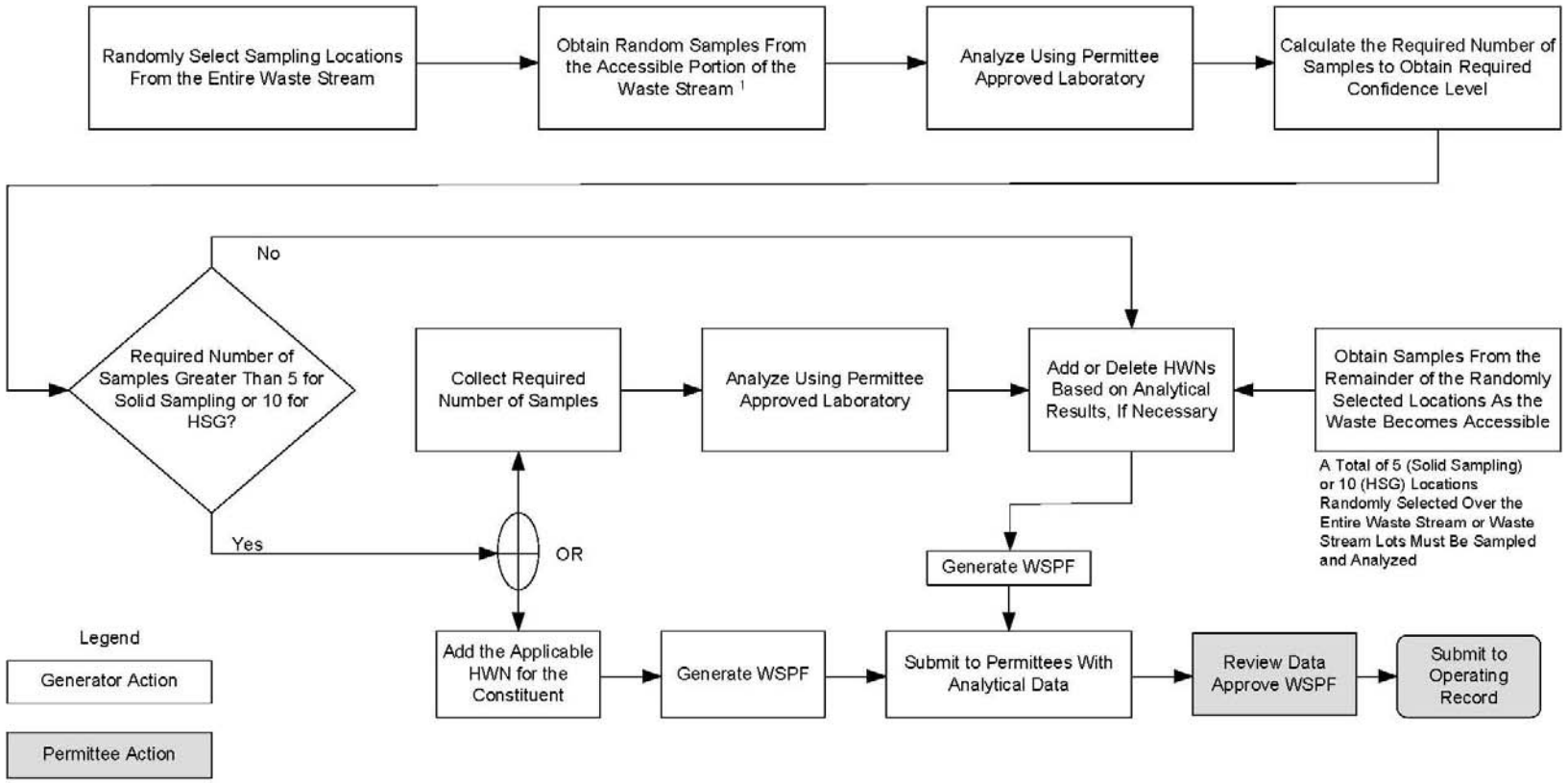

[1] Samples Are Obtained From the First Five Accessible Random Locations for Solid Sampling and the First Ten Accessible Random Locations for Headspace Gas Sampling

Figure ~~B~~ C2-1
Approach for Solid and Headspace Gas Sampling and Analysis to Obtain Additional Waste Characterization Information

1