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Utilizing Statistics to Determine How Much Sampling and Analysis is Warranted to Support Savannah River Site (SRS) High Level Waste (HLW) Sludge Batch Preparation

B. Hamm, T. Edwards, S. Reboul, and P. Hill

Washington Savannah River Company
Aiken, SC 29808

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Abstract

Accelerated cleanup initiatives at the SRS include expediting radioactive sludge processing. Sludge is the highest risk component of waste since it contains the highest concentrations of long-lived radionuclides. The sludge is staged into 'batches' that are then the feed material to the Defense Waste Processing Facility (DWPF) which vitrifies the waste into a safe form for permanent disposal. The preparation of each batch includes sampling and analysis of the slurried material. The results of the characterization are used as the bases for batch blending and processing decisions. Uncertainty is inherent in the information used for planning. There is uncertainty in the quantity of sludge contained in a tank, the waste composition, and the waste physical properties.

The goal of this analysis is to develop the basis for the number of physical samples that should be taken from the slurried waste tank and the number of replicates of laboratory measurements that should be performed in order to achieve a specified uncertainty level. Recommendations for sampling and analysis strategies are made based on the results of the analysis.

Introduction

Approximately thirty-six million gallons of HLW are stored at the SRS Tank Farm, awaiting disposition processing at the DWPF and the Salt Waste Processing Facility (SWPF). This waste can be separated into three discrete phases: 1) a sludge phase, comprised primarily of solid precipitated oxides/hydroxides of iron and aluminum; 2) a saltcake phase, comprised primarily of solid precipitated sodium salts (largely sodium nitrate and sodium nitrite); and 3) a supernatant phase, comprised primarily of sodium salts (also largely sodium nitrate and sodium nitrite) dissolved in aqueous alkaline solution.

Of the three phases, the sludge is considered the most challenging to characterize, due to inherently large variations in composition and physical properties. Although process knowledge of tank inputs has provided adequate sludge characterization information for safety basis determinations, it has proved problematic with respect to planning of DWPF sludge batch characteristics and canister production (Nguyen, 2006). DWPF has processed four large batches of sludge to date, and the actual mass of sludge in each batch as measured by waste immobilized in the vitrified wasteform trends consistently higher than the amount that would be predicted based on site records and tank volume measurements. Consequently, there is renewed interest in the possibility of improving sludge characterization via sampling and analysis.

As attempts are made to develop sampling plans, concerns arise as to the efficacy of the resulting plans from a statistical perspective. What is the relationship between number of samples and analysis replicates to the level of certainty for a given sampling plan for slurried sludge? What number of samples and analysis replicates provide the best value? The purpose of this paper is to explore these two questions.

Savannah River Site High Level Waste Sludge

The SRS HLW sludge is stored in large (from 0.75 to 1.3 million gallons) underground waste tanks until it can be removed and processed at the DWPF. The sludge is highly radioactive, which makes it both difficult and expensive to sample and analyze. In addition, the solids are comprised primarily of precipitated oxides/hydroxides of iron and aluminum. As such, they settle to the bottom of the waste tanks and do not mix without the input of multiple high powered mixers.

Sampling of the slurried waste is conducted using 'grab sampling'. The tank contents are thoroughly mixed and then a stainless steel bottle is lowered into the sludge and allowed to fill. The bottle is retrieved and placed into a special container for transport to a 'hot cell' where it can be opened and the contents characterized. The type of characterization can vary from very simple, such as a few physical property measurements to an extensive study of the sludge composition and behavior.

Principles of Discovery Sampling

Even a small amount of experience with sampling provides the engineer or scientist with the start of an intuitive understanding of the 'principles of sampling'. Most of us learn them the hard way, by collecting samples and then being unsure of how to interpret or apply the results. Naturally, the investigator then turns to the field of statistics to gain some tools for understanding their data. Unfortunately, the literature of statistics can be highly theoretical and difficult to apply.

This is in part due to the different applications of discovery sampling. A major branch of statistics focuses on the use of sampling as an auditing tool. The purpose is to provide documentation that some large inventory of items complies with some predetermined criteria. A representative sample is drawn from the inventory and then evaluated for compliance with the criteria. Items that fail compliance (defective items) are then tabulated and often some corrective action is initiated. The auditor expects to find only a small number of defective items. Therefore, the size of the sample has to be large enough to detect the defects. The auditor is very precise in reporting the level of confidence of his conclusion, such as “The inventory of 10,000 items contains no more than 100 defective items with a confidence of 90%”.

The application of sampling in waste tanks is significantly different. Sampling is used to determine a given physical measurement and is expressed using a statement about the probable size of the potential error of the measurement; that is, the amount of difference between the ‘true’ value (the ***unknown*** value) and the average of the measured samples. The magnitude of this difference is derived from the confidence interval for the mean and may be described by the half-width of this interval around the sample mean of the results. A small half-width indicates that the uncertainty associated with the average measured value is small and likewise, a large half-width indicates that the uncertainty is large.

Using information that will be developed in the next section, an example of how this is expressed is “ The mean of the analyte concentration of the sludge based on results from seven samples with a RSD of 20% and two determinations for each with a RSD of 10% has a 95% chance of being within 30% of the true value.”

Two important points that can not be over emphasized are that the sampling has to actually be representative of the material being sampled and it has to be random. The conditions necessary to ensure that sampling is both representative and random have been fully investigated by Pierre Gy. Gy (born in 1924), graduated in chemical engineering from the Paris School of Physics and Chemistry in 1946. Gy went to work as a research engineer for a large mining company, a field for which good sampling is necessary to ensure that profits are maximized and losses minimized. Gy focused on developing a working approach to identifying and applying the requirements for ‘correct sampling’. His first paper on the subject of the theory of sampling appeared in 1951. Since that first publication, Gy has published nine books, 175 papers, given more than 200 lectures, workshops and courses in addition to working as a private consultant. Gy’s theory provides a structured approach for breaking down sampling problems into component parts and basic principles to be applied to any sampling situation.

A well-written, easy to read, and highly useful book with applicability to the area of the sampling of solids, liquids and gases is “A Primer for Sampling Solids, Liquids, and Gases; Based on the Seven Sampling Errors of Pierre Gy” by Patricia Smith [2].

Statistical Concepts and Equations

As previously mentioned, confidence intervals are used to estimate the difference between the ‘true’ value and the average of the sample values for an analyte of interest. The magnitude of this difference may be described by the half-width of the confidence interval for the true mean that is determined for the sample mean of the results. A small half-width indicates that the uncertainty associated with the measured value is small and likewise, a large half-width indicates that the uncertainty is large.

The half-width of the Confidence Interval (CI) is calculated using the equation;

$$HW(n, r) = t_{(\alpha/2, n-1)} \sqrt{\frac{\sigma_n^{\ 2}}{n} + \frac{\sigma_r^{\ 2}}{n \times r}} \quad \text{(Eq. 1)}$$

where,

n	is the number of independent, representative and random samples collected from the tank
r	is the number of times the analysis is performed (replicated)
t (α/2, n-1)	is the α/2 tail of the Student's t distribution with n-1 degrees of freedom
σ_n^2	is an estimate of the variance associated with the sampling
σ_r^2	is an estimate of the variance associated with the analytical measurements

If σ_n^2 and σ_r^2 are replaced by their corresponding % relative standards deviations, RSD_n and RSD_r, respectively, then the half-width (HW) of the confidence interval will be expressed as a percentage of the mean of the sample results, as follows

$$HW(n, r) = t_{(\alpha/2, n-1)} \sqrt{\frac{\%RSD_n^{\ 2}}{n} + \frac{\%RSD_r^{\ 2}}{n \times r}} \quad \text{(Eq. 2)}$$

The numbers n and r are in the denominator of equations 1 and 2. Therefore, the HW decreases as n and r increase. The number of samples, n, has the most influence because it appears in both terms.

The value of t(α/2, n-1) can be determined from a table found in most statistics texts. The t-values are shown in Table 1 for the 95% CI (α = 0.05). Examination of the table shows us that there is a large difference in the critical value for degrees of freedom (n-1) of one through four and that the impact is less as the degrees of freedom increase.

Table 1. Critical Values of "Student's" t Statistic at α=0.05

Degrees of Freedom	*n-1*	*1*	*2*	*3*	*4*	*5*	*10*	*15*	*20*
Critical Value	T (α/2, n-1)	12.71	4.30	3.18	2.78	2.57	2.23	2.13	2.09

Results from Various Combinations of Sample Size, Replicates and RSDs

This paper does not use a particular set of data, therefore relative standard deviations of the results will be hypothetical. However, since the tanks in this study are well-mixed and the samples are pulled before any appreciable settling takes place, it is likely that the sample RSD deviation would be on the order of 25% at the very best and 100% or more for sampling that is not carefully performed. The analyses performed for physical and chemical characterization will have an RSD on the order of 10% for those that are easy to analyze and abundant in the sludge, to about 50% or more for those that require difficult sample preparation and measurements.

Various exercises will be performed in this section to illustrate the effect of changes in sample number, replicate number, and RSD on HW. All of the analyses are performed for the 95% CI ($\alpha = 0.05$).

Note that a single sample is not one of the options, because that would result in zero degrees of freedom for estimating the sampling variance component.

Half-Width Size in Relation to Relative Standard Deviation

Exercise 1. Effect of Increasing Replicates

Three sets of data are shown in Table 2, with the objective of showing how increasing replicates affects HW. In this exercise, the RSD of both the sampling and the replicates are held constant at 25%. The number of samples is held constant at either 2, 3, or 4 while the number of replicates is varied.

Table 2. Half-Width for Various Combinations of Samples and Analysis Replicates

Sample Variation		**Analytical Measurement Variation**		**HW %**
Number of Samples n	***% RSD***	***Number of Replicates r***	***% RSD***	95% CI (α = 0.05)
2	25%	2	25%	275%
2	25%	3	25%	259%
2	25%	4	25%	251%
3	25%	2	25%	76%
3	25%	3	25%	72%
3	25%	4	25%	69%
4	25%	2	25%	49%
4	25%	3	25%	46%
4	25%	4	25%	44%

Increasing the number of replicates has only a small effect on reducing the HW.

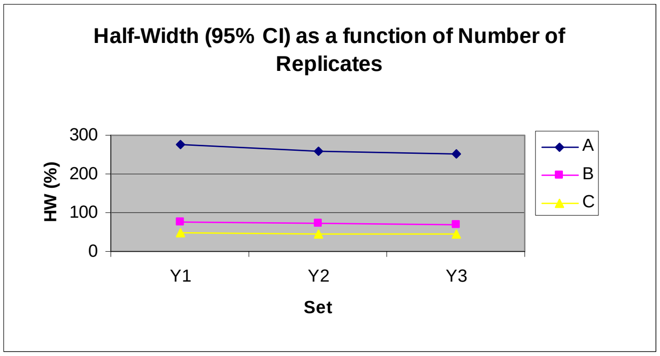

Figure 2. Increasing Replicates Effect on Half-Width of Confidence Interval

Exercise 2. Effect of Increasing Samples

Three sets of data are shown in Table 3, with the objective of showing how increasing samples affects HW. In this exercise, the RSD of both the sampling and the replicates are equal and are shown at 50%, 25%, and 10%. The number of samples is equal to the number of replicates (although we know from exercise 1 that this does not have a large effect).

Table 3. Half-Width for Various Combinations of Samples and Analysis Replicates

Sample Variation		Analytical Measurement Variation		HW %
Number of Samples n	***% RSD***	***Number of Replicates r***	***% RSD***	95% CI ($\alpha = 0.05$)
2	50%	2	50%	550
2	25%	2	25%	275
2	10%	2	10%	110
3	50%	3	50%	143
3	25%	3	25%	72
3	10%	3	10%	29
4	50%	4	50%	89
4	25%	4	25%	44
4	10%	4	10%	18

The results are shown in Figure 4.

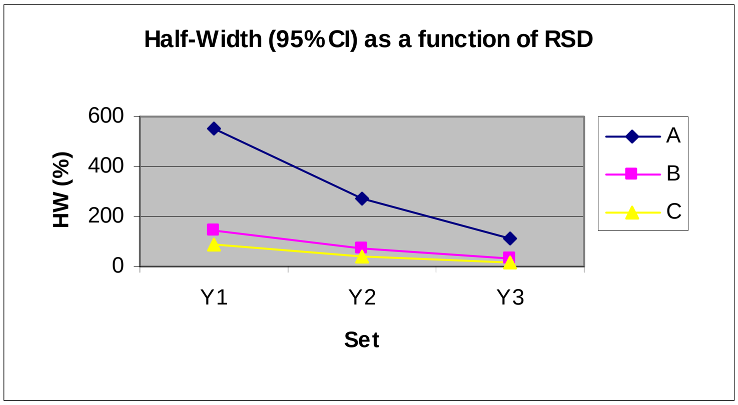

Figure 4. Increasing Replicates Effect on Half-Width of Confidence Interval

Exercise 3. Expressing the Level of Confidence in a Sample Result

The information discussed in this section is shown in Table 4. In this section we look at how to express the results of the calculations as documented in the table.

Table 4. Half-Width for Various Combinations of Samples and Analysis Replicates

Sample Variation		Analytical Measurement Variation		HW %
Number of Samples n	***% RSD***	***Number of Replicates r***	***% RSD***	95% CI (α = 0.05)
7	50%	2	30%	50%
5	50%	2	30%	30%
5	25%	2	10%	32%
4	25%	2	10%	41%
3	25%	2	10%	65%
2	25%	2	10%	233%

If there are seven samples taken from a well slurried waste tank with a expected RSD of 50%, and they are analyzed twice for aluminum with a RSD of 30%, then the deviation of the sample result mean and the true mean can be characterized by the following statement-

"The mean of aluminum results from seven samples with a RSD of 50% and two determinations for each with a RSD of 30% has a 95% chance of being within 25% of the true value."

If the number of samples is reduced to five, and there are still two determinations of aluminum for each, with the same RSD as before, then the statement becomes:

"The mean of aluminum results from five samples with a RSD of 50% and two determinations for each with a RSD of 30% has a 95% chance of being within 33.5% of the true value."

The last statement illustrates one of the key findings of this study. The number of samples is the most important factor in terms of reducing uncertainty by reducing the HW.

Sampling a minimum of three times, even with only one replication, decreases the half-width to 67%. This rather dramatic reduction shows that the third sample is well worth taking. This analysis shows that the best use of sampling dollars is to increase the number of individual samples, even if it has to be at the expense of replicates of the analyses.

Conclusions and Recommendations

The purpose of this paper is to explore the following two questions;

- What is the relationship between number of samples and analysis replicates to the level of certainty for a given sampling plan for slurried sludge?
- What number of samples and analysis replicates provide the best value?

The results of this analysis consist of the following conclusions and recommendations:

1. Grab sampling of sludge that has been homogenized can be considered representative and random provided that the tank is very well mixed (four slurry pumps) and the sample has been collected before any appreciable settling has taken place. The sample results can be used in order to characterize the tank waste.

2. The distribution of the means of the sample results from the grab sampling will be approximately normal. When the number of samples is low (less than 25, as would be expected for typical SRS sludge sampling events), the 'Student's t-statistic' should be used when performing half-width calculations.

3. Three samples, even with only a single analysis, provide a large benefit over two samples, due to the considerable decrease in the half width of the confidence interval of the sample results. Therefore, it is recommended that the minimum number of samples taken should be three. Four samples continue to provide improvements in HW, and should be performed if budget constraints allow. Five or more samples provide diminishing returns and are therefore not recommended.

References

[1] Q. L. Nguyen, "Sludge Characterization Proposal," Savannah River Site, LWO-PIT-2006-00019, Rev. 0, August 2006.

[2] P. L. Smith, *A Primer for Sampling Solids, Liquids, and Gases: Based on the Seven Sampling Errors of Pierre Gy*, American Statistical Association, Alexandria, VA, and the Society for Industrial and Applied Mathematics, Philadelphia, PA, 2001.

[3] J. G. Peatman, *Introduction to Applied Statistics,* Harper & Row, 1963