A Probabilistic Strategy for Compositing Samples for Waste Analysis

by

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SAMPLES FOR WASTE ANALYSIS**

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ABSTRACT

A probabilistic strategy for sample compositing was developed to minimize the volume of waste sample analyses. Disposable waste must have a contaminant concentration below an acceptance limit L . A composite of N different samples must have a contaminant concentration below L/N , to assure that no individual sample is unacceptable. Unacceptable samples are eventually identified by analyses of successive splits composited with $N/2$, $N/4$, ..of the original samples. The probable number of such analyses is derived using conservative log-Normal distributions to model the concentration probabilities. A minimum number of analyses result when $N \approx L/a$, where a is the average contaminant concentration expected for the sample. The approximation is useful for $L/a \geq 5$. Experimental composites from 880 samples with $L/a = 41.8$ are consistent with the calculated predictions.

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A Probabilistic Strategy for Compositing Samples for Waste Analysis

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INTRODUCTION

Because of the growing emphasis on waste disposal impact to the environment, the analysis volume for waste samples has increased dramatically in recent years. At the Savannah River Site, the demand for establishing acceptable radionuclide levels for offplant waste disposal has resulted in strategies for compositing samples to help alleviate the analysis load. A strategy based on probabilistic methods is examined; it should have broad application in areas of waste certification. This method is a variation of sequential statistical analysis (1,2), which minimizes the required measurements in batch appraisals.

THEORY

General Method. Environmental standards for waste typically require that the contaminant concentration, c , be below some limit, L . Normally, the contents of waste containers are homogenized, and then individual samples are taken and analyzed. If N waste samples from different containers are equally mixed as a single composite sample, this sample must have $c < L/N$, to ensure that no individual component sample of the composite contains the entire contamination at a level exceeding L . If measurements on any composite sample yielded $c > L/N$, then two recomposites would be made, each from a different $N/2$ samples included in the original composite. Each of these recomposites would be tested against the criteria that $c < L/[N/2]$ or $c < 2L/N$. This recompositing process would continue as necessary, until (1) all recomposites have satisfied $c < 2^j L/N = L$, at some j th recomposite level and (2) any individual component samples

with $c > L$ have been identified. Because each recomposite will split the preceding composite by a factor of 2, it is recommended that $N = 2^n$, where n is an integer. With this choice of N the j th recomposite limit is given by

$$L_j = 2^{j-n} L \quad [1]$$

This recompositing scheme requires some knowledge of the probabilities of exceeding the limits L_j , to project how many sample analyses are needed for a given N . Suppose some large number of samples, S , must be appraised relative to compliance with the limit L . Then, the initially composited samples will require A_0 analyses, as given by

$$A_0 = S/N = 2^n S \quad [2]$$

A total of $A_0 P(c_0 > L_0)$ analyses would fail the compliance criteria, requiring analysis of A_1 recomposited samples, which are composed of paired splits from the first composites. Here, $P(c_0 > L_0)$ is the probability that an initial composite sample has $c_0 > L_0$. More explicitly, A_1 is given by

$$\begin{aligned} A_1 &= 2 A_0 P(c_0 > L_0) \\ &= 2^{1-n} S P(c_0 > L_0) \end{aligned} \quad [3]$$

Continuing this procedure, it is readily observed that the number A_j of j th recomposite analyses will be given by

$$\begin{aligned} A_j &= 2 A_{j-1} P(c_{j-1} > L_{j-1}) \\ &= 2^{j-n} S \prod_{i=1}^j P(c_{i-1} > L_{i-1}) \end{aligned} \quad [4]$$

Thus, the total number A of expected analyses is obtained by summing the A_j , viz

$$A = \sum_{j=0}^n A_j \quad [5]$$

where in summary

$$A_j = 2^{j \cdot n} S \prod_{i=0}^j P_i$$

$$P_i = 1 \text{ for } i = 0$$

$$= P(c_{i-1} > L_{i-1}) \text{ for } i > 0$$

$$L_1 = 2^{i \cdot n} L$$

Probability Assignment . The preceding treatment defines the general formalism; however, the probabilities P_i must be defined to obtain results. These probabilities may be deduced from measurements; however, it is desirable to have useful guidelines before detailed probability data are developed. It will be shown that log-Normal distributions provide reasonable estimates of the P_i .

In general, waste is expected to be generated from a variety of sources with contamination levels, c , that depend on numerous multiplicative factors which are randomly distributed. As a statistical variable, c is given as

$$c = X_1 X_2 X_3 \dots X_k \quad [6]$$

where each X_i is a randomly distributed factor of a large total of k factors. By taking the log of both sides of the equation

$$\log(c) = \sum_{i=1}^k \log(X_i) = \sum_{i=1}^k Y_i = k \left[\sum_{i=1}^k Y_i / k \right] \quad [7]$$

Here the Y_i are also randomly distributed and their sum or average should be distributed as a Gaussian distribution, according to the Central Limit Theorem (3). Thus, $\log(c)$ also has a Gaussian distribution, and accordingly c has a log-Normal distribution.

An initial trial log-Normal distribution for c can be approximated with data from preliminary analyses. A conservative approximation, which uses larger P_i , should be favored. The present work assumes an average $c = a$ is available but that the sigma s is unknown. Conservatively assuming that s is comparable to the average c , a value of $s = a$ is assigned. Corresponding log-Normal parameters are derived as

$$\begin{aligned}\text{Log concentration} &= \log(c) = x \\ \text{Log-Normal average} &= \log(a) = u \\ \text{Log-Normal sigma} &= \log(a+s) - \log(a) = \log(2)\end{aligned}\tag{8}$$

Thus, for this conservative case, the probabilities may be written as

$$\begin{aligned}P_i &= 1 \text{ for } i = 0 \\ P_i &= P(c_{i-1} > L_{i-1}) = G(x > \log L_{i-1}) \text{ for } i > 0 \\ &= G(x - u > \log[L_{i-1}/a]) \\ &= G(Z > \log[L/a]/\log[2] + i - n - 1)\end{aligned}\tag{9}$$

where $G(Z > Z_L)$ is the integrated Gaussian probability for $Z > Z_L$, and the Z values are normalized to the standard deviation (i.e., $Z = [x - u]/\log[2]$). No distinction has been made between the c_i and c , which is also a conservatism because the distributions of sample composites should be narrower than those of individual samples.

CALCULATIONS AND MEASUREMENTS

A BASIC code COMPOSE was written to calculate the projected number of analyses A from Equation 5, using the conservative log-Normal probability estimates of Equation 9.

Calculation of A is straight forward, once the P_i are determined. The P_i are determined by interpolation of 5-place Gaussian data which are encoded (4).

Figure 1 plots A vs N (or 2^n) for various L/a values. The A analyses are expressed in percent of total samples S . The L/a range is from 0 to 50. For $L/a = 0$, all $P_i = 1$ and this represents the worst possible situation. The plots indicate that there is no advantage in compositing samples for $L/a \leq 2$, as all analyses yield A 's that exceed 100% of the total samples S . For $L/a \geq 5$ compositing does become noticeably advantageous, and an optimum choice of N can be selected. Here, as N increases from 1, a minimum A is reached near $N \approx L/a$; then A rises very little as N increases further. This shows that N must only exceed some minimum value to yield a near-optimum A ; however, Figure 2 illustrates that it is ridiculous to use arbitrarily large N . In this figure, P_1 for the first recomposite is plotted against N ; for higher N values P_1 approaches 1, and thus it is ridiculous to analyze composite samples that are virtually assured of being recomposited. Thus, an N that corresponds to both low A and low P_1 is preferred, and this occurs near the minimum A value deduced from Figure 1.

COMPOSE can print all A_i and P_i values corresponding to an A calculation. These results illustrate that $P_1 > P_2 > \dots > P_n$, and that each of these probabilities also increases toward 1 as N increases beyond its optimum value. Figure 3 illustrates this behavior for $L/a = 41.8$, which corresponds to experimental data discussed next.

Composite data from a recent radioassay for paint/solvent waste serve to illustrate the usefulness of the method. In this work, the total radioactive concentration for the paint/solvent waste had to be less than $L = 2$ nCi/g to comply with DOT regulations for offplant shipment (5). Here, $S = 880$ drums of liquid waste were sampled and composited as 44 samples, each with $N = 20$ drum samples per composite. Of these, $A_1 = 4$ and $A_2 = 2$ recomposite analyses were required. A geometric mean of the samples was 0.0478 nCi/g, yielding L/a of 41.8. Table I shows that results for the experimental data are reasonably consistent with the calculated projections.

In this comparison, an experimental $N = 20 \neq 2^n$ is used, and the corresponding calculated values are interpolated using Figure 3 and Equation 4. Ideally $N = 2^n$ should have been selected for the analyses, and subsequent work is now incorporating such N . As these subsequent measurements evolve into comparably large data sets (e.g., $S \approx 1000$), additional appraisals will be made.

SUMMARY

These studies show that a probabilistic approach is useful in predicting sample compositing strategies for waste certification. The conservative log-Normal probability assignments are useful as initial guidelines for the compositing strategy, as evidenced by comparison with the experimental data in Table I. Even though the calculations project a somewhat larger number of analyses than observed in the experimental measurements, the compositing strategies deduced from either calculations or experiment are comparable.

Some simplified general guidelines can be derived from the conservative calculations plotted in Figures 1 and 2. These plots demonstrate that $N = N_m = 2^m \approx L/a$ corresponds to the minimum number A of analyses, for $L/a \geq 5$. Mathematically, the value of N_m can be determined as

$$N_m = 2^m = 2^{\text{Integer}[\log(L/a)/\log(2) + 0.5]} \quad [10]$$

or N_m is the factor of 2 nearest L/a . Typically, this optimum N_m yields $P_1 \approx 0.5$, although this conservative log-Normal treatment causes this value to be somewhat high. However, because such a large P_1 can require a fair amount of bookkeeping for addressing sample recompositing, it may be wise to select $N = 2^{m-1}$, where $P_1 \approx 0.15$ and the corresponding A is only slightly above the optimum value. A choice of $N = 2^{m-2}$ yields a very low $P_1 \approx 0.03$; however, the corresponding A is noticeably greater.

The data of Table I provide an example of this guideline. Equation 10 projects $N_m = 32$ from the experimental L/a of 41.8, but with corresponding $P_1 = 0.350$. With $N = 2^{m-1} = 16$, the P_1 is reduced to 0.083. Thus, the experimental choice of $N = 20$ is quite reasonable as it projects $P_1 = 0.135$; however, as mentioned earlier, an $N = 2^n$ should be favored when possible.

These considerations identify the variables that must be appraised in selecting a compositing strategy. It is likely that more accurate (less conservative) probability assignments can be modeled into the analysis as data for specific types of waste are developed. However, the present conservative model can always offer a general method for selecting an initial compositing strategy.

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Table I. Comparison of Calculations and Measurements

Data are for S = 880 paint/solvent waste-drum samples grouped as S/N initial composites. The experimental average concentration of a = 0.0478 nCi/g is compared to an L = 2.0 nCi/g, yielding L/a = 41.8.

	N=16 <u>calculated</u>	N=20 <u>calculated</u> ^a	N=20 <u>measured</u> ^b	N=32 <u>calculated</u>	N=64 <u>calculated</u>
A	64.297	56.356	50±3	50.007	50.278
A ₀	55.000	44.000	≅44	27.500	13.750
A ₁	9.141	11.880	4±2	19.252	20.087
A ₂	0.157	0.475	2±2	3.200	14.063
A ₃	0.000	0.001	0	0.055	2.337
A ₄	0.000	0.000	0	0.000	0.040
A ₅	-	-	-	0.000	0.000
A ₆	-	-	-	-	0.000
P ₀	1.00000	1.000	≅1.000	1.00000	1.00000
P ₁	0.08310	0.135	0.045±0.017	0.35004	0.73045
P ₂	0.00857	0.020	0.250±0.250	0.08310	0.35004
P ₃	0.00036	0.001	0.0	0.00857	0.08310
P ₄	0.00000	0.000	0.0	0.00036	0.00857
P ₅	-	-	-	0.00000	0.00036
P ₆	-	-	-	-	0.00000

a Values are interpolated using calculations from Figure 3 and Equation 4.

b Experimental measurement errors are estimated as follows:

- 2±1 composites of 44 needed to be recomposited for 4±2 analyses, and yield $P_1 = (2±1)/44$.
- 1±1 recomposites from 4 needed to be recomposited for 2±2 analyses, and yield $P_2 = (1±1)/4$.
- Error in A accumulates from A_i errors.
- The adoption of ±1 for each recomposite number is approximated from small number Poisson statistics.

FIGURE 1. Sample analyses A for $S = 100\%$ samples when first composites have $N = 2^n$ samples each, for various limit/average ratios L/a . Conservative log-Normal probabilities are used.

FIGURE 2. First recomposite probability P_1 when first composites have $N = 2^n$ samples each, for various limit/average ratios L/a . Note also that the minimum analyses A for $n = m$ situations are identified. Conservative log-Normal probabilities are used.

FIGURE 3. Dependence of i th recomposite probability P_i on initial samples $N = 2^n$ composited, for limit/average ratio $L/a = 41.8$.