

CHAPTER NINE

SAMPLING PLAN

9.1 DESIGN AND DEVELOPMENT

The initial -- and perhaps most critical -- element in a program designed to evaluate the physical and chemical properties of a solid waste is the plan for sampling the waste. It is understandable that analytical studies, with their sophisticated instrumentation and high cost, are often perceived as the dominant element in a waste characterization program. Yet, despite that sophistication and high cost, analytical data generated by a scientifically defective sampling plan have limited utility, particularly in the case of regulatory proceedings.

This section of the manual addresses the development and implementation of a scientifically credible sampling plan for a solid waste and the documentation of the chain of custody for such a plan. The information presented in this section is relevant to the sampling of any solid waste, which has been defined by the EPA in its regulations for the identification and listing of hazardous wastes to include solid, semisolid, liquid, and contained gaseous materials. However, the physical and chemical diversity of those materials, as well as the dissimilarity of storage facilities (lagoons, open piles, tanks, drums, etc.) and sampling equipment associated with them, preclude a detailed consideration of any specific sampling plan. Consequently, because the burden of responsibility for developing a technically sound sampling plan rests with the waste producer, it is advisable that he/she seek competent advice before designing a plan. This is particularly true in the early developmental stages of a sampling plan, at which time at least a basic understanding of applied statistics is required. Applied statistics is the science of employing techniques that allow the uncertainty of inductive inferences (general conclusions based on partial knowledge) to be evaluated.

9.1.1 Development of Appropriate Sampling Plans

An appropriate sampling plan for a solid waste must be responsive to both regulatory and scientific objectives. Once those objectives have been clearly identified, a suitable sampling strategy, predicated upon fundamental statistical concepts, can be developed. The statistical terminology associated with those concepts is reviewed in Table 9-1; Student's "t" values for use in the statistics of Table 9-1 appear in Table 9-2.

9.1.1.1 Regulatory and Scientific Objectives

The EPA, in its hazardous waste management system, has required that certain solid wastes be analyzed for physical and chemical properties. It is mostly chemical properties that are of concern, and, in the case of a number of chemical contaminants, the EPA has promulgated levels (regulatory thresholds) that cannot be equaled or exceeded. The regulations pertaining to the management of hazardous wastes contain three references regarding the

TABLE 9-1. BASIC STATISTICAL TERMINOLOGY APPLICABLE TO SAMPLING PLANS FOR SOLID WASTES

Terminology	Symbol	Mathematical Equation (Equation)
• Variable (e.g., barium or endrin)	x	—
• Individual measurement of variable	x_i	—
• Mean of possible measurements of variable (population mean)	μ	$\mu = \frac{\sum_{i=1}^N x_i}{N}, \text{ with } N = \text{number of possible measurements} \quad (1)$
• Mean of measurements generated by sample (sample mean)	\bar{x}	<p><u>Simple random sampling and systematic random sampling</u></p> $\bar{x} = \frac{\sum_{i=1}^n x_i}{n}, \text{ with } n = \text{number of sample measurements} \quad (2a)$ <p><u>Stratified random sampling</u></p> $\bar{x} = \sum_{k=1}^r W_k \bar{x}_k, \text{ with } \bar{x}_k = \text{stratum mean and } W_k = \text{fraction of population represented by Stratum } k \text{ (number of strata } [k] \text{ range from 1 to } r) \quad (2b)$
• Variance of sample	s^2	<p><u>Simple random sampling and systematic random sampling</u></p> $s^2 = \frac{\sum_{i=1}^n x_i^2 - (\sum_{i=1}^n x_i)^2/n}{n - 1} \quad (3a)$ <p><u>Stratified random sampling</u></p> $s^2 = \sum_{k=1}^r W_k s_k^2, \text{ with } s_k^2 = \text{stratum variance and } W_k = \text{fraction of population represent by Stratum } k \text{ (number of strata } [k] \text{ ranges from 1 to } r) \quad (3b)$

TABLE 9-1. (continued)

Terminology	Symbol	Mathematical Equation	(Equation)
• Standard deviation of sample	s	$s = \sqrt{s^2}$	(4)
• Standard error (also standard error of mean and standard deviation of mean) of sample	$s_{\bar{x}}$	$s_{\bar{x}} = \frac{s}{\sqrt{n}}$	(5)
• Confidence interval for μ^a	CI	$CI = \bar{x} \pm t_{.20} s_{\bar{x}}$, with $t_{.20}$ obtained from Table 2 for appropriate degrees of freedom	(6)
• Regulatory threshold ^a	RT	Defined by EPA (e.g., 100 ppm for barium in elutriate of EP toxicity)	(7)
• Appropriate number of samples to collect from a solid waste (financial constraints not considered)	n	$n = \frac{t_{.20}^2 s^2}{\Delta^2}$, with $\Delta = RT - \bar{x}$	(8)
• Degrees of freedom	df	$df = n - 1$	(9)
• Square root transformation	---	$X_i + \frac{1}{2}$	(10)
• Arcsin transformation	---	Arcsin p; if necessary, refer to any text on basic statistics; measurements must be converted to percentages (p)	(11)

^aThe upper limit of the CI for μ is compared with the applicable regulatory threshold (RT) to determine if a solid waste contains the variable (chemical contaminant) of concern at a hazardous level. The contaminant of concern is not considered to be present in the waste at a hazardous level if the upper limit of the CI is less than the applicable RT. Otherwise, the opposite conclusion is reached.

TABLE 9-2. TABULATED VALUES OF STUDENT'S "t" FOR EVALUATING SOLID WASTES

Degrees of freedom (n-1) ^a	Tabulated "t" Value ^b
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.393
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289
	1.282

^a Degrees of freedom (df) are equal to the number of samples (n) collected from a solid waste less one.

^b Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.20 (the same values are applicable to a one-tailed confidence interval and a probability of 0.10).

sampling of solid wastes for analytical properties. The first reference, which occurs throughout the regulations, requires that representative samples of waste be collected and defines representative samples as exhibiting average properties of the whole waste. The second reference, which pertains just to petitions to exclude wastes from being listed as hazardous wastes, specifies that enough samples (but in no case less than four samples) be collected over a period of time sufficient to represent the variability of the wastes. The third reference, which applies only to ground water monitoring systems, mandates that four replicates (subsamples) be taken from each ground water sample intended for chemical analysis and that the mean concentration and variance for each chemical constituent be calculated from those four subsamples and compared with background levels for ground water. Even the statistical test to be employed in that comparison is specified (Student's t-test).

The first of the above-described references addresses the issue of sampling accuracy, and the second and third references focus on sampling variability or, conversely, sampling precision (actually the third reference relates to analytical variability, which, in many statistical tests, is indistinguishable from true sampling variability). Sampling accuracy (the closeness of a sample value to its true value) and sampling precision (the closeness of repeated sample values) are also the issues of overriding importance in any scientific assessment of sampling practices. Thus, from both regulatory and scientific perspectives, the primary objectives of a sampling plan for a solid waste are twofold: namely, to collect samples that will allow measurements of the chemical properties of the waste that are both accurate and precise. If the chemical measurements are sufficiently accurate and precise, they will be considered reliable estimates of the chemical properties of the waste.

It is now apparent that a judgment must be made as to the degree of sampling accuracy and precision that is required to estimate reliably the chemical characteristics of a solid waste for the purpose of comparing those characteristics with applicable regulatory thresholds. Generally, high accuracy and high precision are required if one or more chemical contaminants of a solid waste are present at a concentration that is close to the applicable regulatory threshold. Alternatively, relatively low accuracy and low precision can be tolerated if the contaminants of concern occur at levels far below or far above their applicable thresholds. However, a word of caution is in order. Low sampling precision is often associated with considerable savings in analytical, as well as sampling, costs and is clearly recognizable even in the simplest of statistical tests. On the other hand, low sampling accuracy may not entail cost savings and is always obscured in statistical tests (i.e., it cannot be evaluated). Therefore, although it is desirable to design sampling plans for solid wastes to achieve only the minimally required precision (at least two samples of a material are required for any estimate of precision), it is prudent to design the plans to attain the greatest possible accuracy.

The roles that inaccurate and imprecise sampling can play in causing a solid waste to be inappropriately judged hazardous are illustrated in Figure 9-1. When evaluating Figure 9-1, several points are worthy of consideration. Although a sampling plan for a solid waste generates a mean concentration (\bar{x}) and standard deviation (s_x , a measure of the extent to which individual sample concentrations are dispersed around \bar{x}) for each chemical contaminant of concern, it is not the variation of individual sample concentrations that is of ultimate concern, but rather the variation that characterizes \bar{x} itself. That measure of dispersion is termed the standard deviation of the mean (also, the standard error of the mean or standard error) and is designated as $s_{\bar{x}}$. Those two sample values, \bar{x} and $S_{\bar{x}}$, are used to estimate the interval (range) within which the true mean (μ) of the chemical concentration probably occurs, under the assumption that the individual concentrations exhibit a normal (bell-shaped) distribution. For the purposes of evaluating solid wastes, the probability level (confidence interval) of 80% has been selected. That is, for each chemical contaminant of concern, a confidence interval (CI) is described within which μ occurs if the sample is representative, which is expected of about 80 out of 100 samples. The upper limit of the 80% CI is then compared with the appropriate regulatory threshold. If the upper limit is less than the threshold, the chemical contaminant is not considered to be present in the waste at a hazardous level; otherwise, the opposite conclusion is drawn. One last point merits explanation. Even if the upper limit of an estimated 80% CI is only slightly less than the regulatory threshold (the worst case of chemical contamination that would be judged acceptable), there is only a 10% (not 20%) chance that the threshold is equaled or exceeded. That is because values of a normally distributed contaminant that are outside the limits of an 80% CI are equally distributed between the left (lower) and right (upper) tails of the normal curve. Consequently, the CI employed to evaluate solid wastes is, for all practical purposes, a 90% interval.

9.1.1.2 Fundamental Statistical Concepts

The concepts of sampling accuracy and precision have already been introduced, along with some measurements of central tendency (\bar{x}) and dispersion (standard deviation [s] and s_x) for concentrations of a chemical contaminant of a solid waste. The utility of \bar{x} and s_x in estimating a confidence interval that probably contains the true mean (μ) concentration of a contaminant has also been described. However, it was noted that the validity of that estimate is predicated upon the assumption that individual concentrations of the contaminant exhibit a normal distribution.

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. Sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the population (e.g., every location in a lagoon used to store a solid waste) has a theoretically equal chance of being sampled and measured. Consequently, statistics generated by the sample (e.g., \bar{x} and, to a lesser degree, $S_{\bar{x}}$) are unbiased (accurate) estimators of true population parameters (e.g., the CI for μ). In other words, the sample is representative of the population. One of the commonest methods of selecting a random sample is to divide the

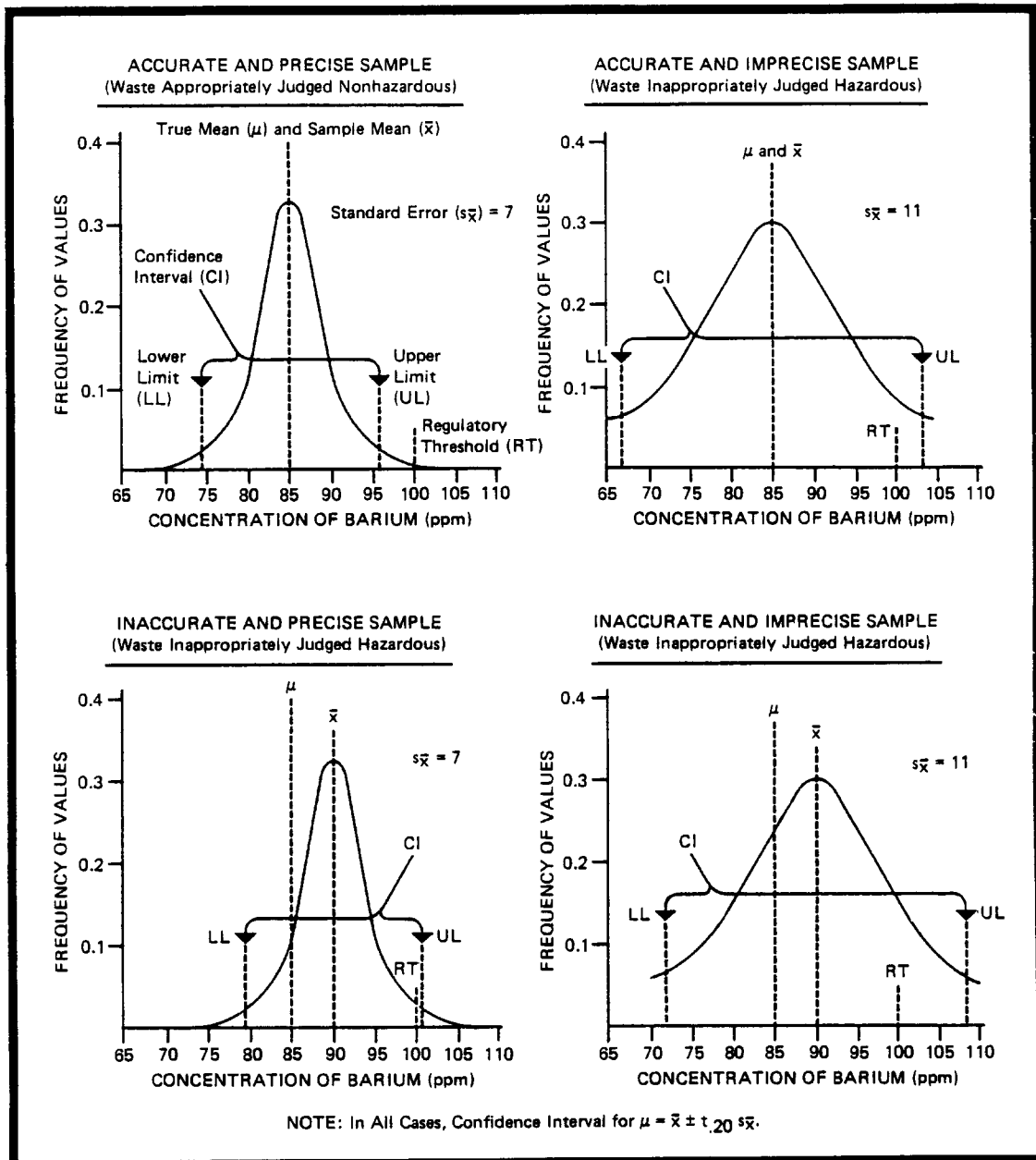


Figure 9-1. - Important theoretical relationships between sampling accuracy and precision and regulatory objectives for a chemical contaminant of a solid waste that occurs at a concentration marginally less than its regulatory threshold. In this example, barium is the chemical contaminant. The true mean concentration of barium in the elutriate of the EP toxicity test is 85 ppm, as compared to a regulatory threshold of 100 ppm. The upper limit of the confidence interval for the true mean concentration, which is estimated from the sample mean and standard error, must be less than the regulatory threshold if barium is judged to be present in the waste at a nonhazardous level.

population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers (units) to be sampled through the use of a random-numbers table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population.

Sampling precision is most commonly achieved by taking an appropriate number of samples from the population. As can be observed from the equation for calculating $S_{\bar{x}}$, precision increases ($S_{\bar{x}}$ and the CI for μ decrease) as the number of samples (n) increases, although not in a 1:1 ratio. For example, a 100% increase in the number of samples from two to four causes the CI to decrease by approximately 62% (about 31% of that decrease is associated with the critical upper tail of the normal curve). However, another 100% increase in sampling effort from four to eight samples results in only an additional 39% decrease in the CI. Another technique for increasing sampling precision is to maximize the physical size (weight or volume) of the samples that are collected. That has the effect of minimizing between-sample variation and, consequently, decreasing $s_{\bar{x}}$. Increasing the number or size of samples taken from a population, in addition to increasing sampling precision, has the secondary effect of increasing sampling accuracy.

In summary, reliable information concerning the chemical properties of a solid waste is needed for the purpose of comparing those properties with applicable regulatory thresholds. If chemical information is to be considered reliable, it must be accurate and sufficiently precise. Accuracy is usually achieved by incorporating some form of randomness into the selection process for the samples that generate the chemical information. Sufficient precision is most often obtained by selecting an appropriate number of samples.

There are a few ramifications of the above-described concepts that merit elaboration. If, for example, as in the case of semiconductor etching solutions, each batch of a waste is completely homogeneous with regard to the chemical properties of concern and that chemical homogeneity is constant (uniform) over time (from batch to batch), a single sample collected from the waste at an arbitrary location and time would theoretically generate an accurate and precise estimate of the chemical properties. However, most wastes are heterogeneous in terms of their chemical properties. If a batch of waste is randomly heterogeneous with regard to its chemical characteristics and that random chemical heterogeneity remains constant from batch to batch, accuracy and appropriate precision can usually be achieved by simple random sampling. In that type of sampling, all units in the population (essentially all locations or points in all batches of waste from which a sample could be collected) are identified, and a suitable number of samples is randomly selected from the population. More complex stratified random sampling is appropriate if a batch of waste is known to be nonrandomly heterogeneous in terms of its chemical properties and/or nonrandom chemical heterogeneity is known to exist from batch to batch. In such cases, the population is stratified to isolate the known sources of nonrandom chemical heterogeneity.

After stratification, which may occur over space (locations or points in a batch of waste) and/or time (each batch of waste), the units in each stratum are numerically identified, and a simple random sample is taken from each stratum. As previously intimated, both simple and stratified random sampling generate accurate estimates of the chemical properties of a solid waste. The advantage of stratified random sampling over simple random sampling is that, for a given number of samples and a given sample size, the former technique often results in a more precise estimate of chemical properties of a waste (a lower value of s_x) than the latter technique. However, greater precision is likely to be realized only if a waste exhibits substantial nonrandom chemical heterogeneity and stratification efficiently "divides" the waste into strata that exhibit maximum between-strata variability and minimum within-strata variability. If that does not occur, stratified random sampling can produce results that are less precise than in the case of simple random sampling. Therefore, it is reasonable to select stratified random sampling over simple random sampling only if the distribution of chemical contaminants in a waste is sufficiently known to allow an intelligent identification of strata and at least two or three samples can be collected in each stratum. If a strategy employing stratified random sampling is selected, a decision must be made regarding the allocation of sampling effort among strata. When chemical variation within each stratum can be estimated with a great degree of detail, samples should be optimally allocated among strata, i.e., the number of samples collected from each stratum should be directly proportional to the chemical variation encountered in the stratum. When detailed information concerning chemical variability within strata is not available, samples should be proportionally allocated among strata, i.e., sampling effort in each stratum should be directly proportional to the size of the stratum.

Simple random sampling and stratified random sampling are types of probability sampling. Which, because of a reliance upon mathematical and statistical theories, allows an evaluation of the effectiveness of sampling procedures. Another type of probability sampling is systematic random sampling, in which the first unit to be collected from a population is randomly selected, but all subsequent units are taken at fixed space or time intervals. An example of systematic random sampling is the sampling of a waste lagoon along a transect in which the first sampling point on the transect is 1 m from a randomly selected location on the shore and subsequent sampling points are located at 2-m intervals along the transect. The advantages of systematic random sampling over simple random sampling and stratified random sampling are the ease with which samples are identified and collected (the selection of the first sampling unit determines the remainder of the units) and, sometimes, an increase in precision. In certain cases, for example, systematic random sampling might be expected to be a little more precise than stratified random sampling with one unit per stratum because samples are distributed more evenly over the population. As will be demonstrated shortly, disadvantages of systematic random sampling are the poor accuracy and precision that can occur when unrecognized trends or cycles occur in the population. For those reasons, systematic random sampling is recommended only when a population is essentially random or contains at most a modest stratification. In such cases, systematic random sampling would be employed for the sake of convenience, with little expectation of an increase in precision over other random sampling techniques.

Probability sampling is contrasted with authoritative sampling, in which an individual who is well acquainted with the solid waste to be sampled selects a sample without regard to randomization. The validity of data gathered in that manner is totally dependent on the knowledge of the sampler and although valid data can sometimes be obtained, authoritative sampling is not recommended for the chemical characterization of most wastes.

It may now be useful to offer a generalization regarding the four sampling strategies that have been identified for solid wastes. If little or no information is available concerning the distribution of chemical contaminants of a waste, simple random sampling is the most appropriate sampling strategy. As more information is accumulated for the contaminants of concern, greater consideration can be given (in order of the additional information required) to stratified random sampling, systematic random sampling, and, perhaps, authoritative sampling.

The validity of a CI for the true mean (μ) concentration of a chemical contaminant of a solid waste is, as previously noted, based on the assumption that individual concentrations of the contaminant exhibit a normal distribution. This is true regardless of the strategy that is employed to sample the waste. Although there are computational procedures for evaluating the correctness of the assumption of normality, those procedures are meaningful only if a large number of samples are collected from a waste. Because sampling plans for most solid wastes entail just a few samples, one can do little more than superficially examine resulting data for obvious departures from normality (this can be done by simple graphical methods), keeping in mind that even if individual measurements of a chemical contaminant of a waste exhibit a considerably abnormal distribution, such abnormality is not likely to be the case for sample means, which are our primary concern. One can also compare the mean of the sample (\bar{x}) with the variance of the sample (s^2). In a normally distributed population, \bar{x} would be expected to be greater than s^2 (assuming that the number of samples [n] is reasonably large). If that is not the case, the chemical contaminant of concern may be characterized by a Poisson distribution (\bar{x} is approximately equal to s^2) or a negative binomial distribution (\bar{x} is less than s^2). In the former circumstance, normality can often be achieved by transforming data according to the square root transformation. In the latter circumstance, normality may be realized through use of the arcsine transformation. If either transformation is required, all subsequent statistical evaluations must be performed on the transformed scale.

Finally, it is necessary to address the appropriate number of samples to be employed in the chemical characterization of a solid waste. As has already been emphasized, the appropriate number of samples is the least number of samples required to generate a sufficiently precise estimate of the true mean (μ) concentration of a chemical contaminant of a waste. From the perspective of most waste producers, that means the minimal number of samples needed to demonstrate that the upper limit of the CI for μ is less than the applicable regulatory threshold (RT). The formula for estimating appropriate sampling effort (Table 9-1, Equation 8) indicates that increased sampling effort is generally justified as s^2 or the " $t_{.20}$ " value (probable error rate) increases

and as $\Delta(RT - \bar{x})$ decreases. In a well-designed sampling plan for a solid waste, an effort is made to estimate the values of \bar{x} and s^2 before sampling is initiated. Such preliminary estimates, which may be derived from information pertaining to similar wastes, process engineering data, or limited analytical studies, are used to identify the approximate number of samples that must be collected from the waste. It is always prudent to collect a somewhat greater number of samples than indicated by preliminary estimates of \bar{x} and s^2 since poor preliminary estimates of those statistics can result in an underestimate of the appropriate number of samples to collect. It is usually possible to process and store the extra samples appropriately until analysis of the initially identified samples is completed and it can be determined if analysis of the additional samples is warranted.

9.1.1.3 Basic Sampling Strategies

It is now appropriate to present general procedures for implementing the three previously introduced sampling strategies (simple random sampling, stratified random sampling, and systematic random sampling) and a hypothetical example of each sampling strategy. The hypothetical examples illustrate the statistical calculations that must be performed in most situations likely to be encountered by a waste producer and, also, provide some insight into the efficiency of the three sampling strategies in meeting regulatory objectives.

The following hypothetical conditions are assumed to exist for all three sampling strategies. First, barium, which has an RT of 100 ppm as measured in the EP elutriate test, is the only chemical contaminant of concern. Second, barium is discharged in particulate form to a waste lagoon and accumulates in the lagoon in the form of a sludge, which has built up to approximately the same thickness throughout the lagoon. Third, concentrations of barium are relatively homogeneous along the vertical gradient (from the water-sludge interface to the sludge-lagoon interface), suggesting a highly controlled manufacturing process (little between-batch variation in barium concentrations). Fourth, the physical size of sludge samples collected from the lagoon is as large as practical, and barium concentrations derived from those samples are normally distributed (note that we do not refer to barium levels in the samples of sludge because barium measurements are actually made on the elutriate from EP toxicity tests performed with the samples). Last, a preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago identified values of 86 and 90 ppm for material collected near the outfall (in the upper third) of the lagoon and values of 98 and 104 ppm for material obtained from the far end (the lower two-thirds) of the lagoon.

For all sampling strategies, it is important to remember that barium will be determined to be present in the sludge at a hazardous level if the upper limit of the CI for μ is equal to or greater than the RT of 100 ppm (Table 9-1, Equations 6 and 7).

9.1.1.3.1 Simple Random Sampling

Simple random sampling (Box 1) is performed by general procedures in which preliminary estimates of \bar{x} and s^2 , as well as a knowledge of the RT, for each chemical contaminant of a solid waste that is of concern are employed to estimate the appropriate number of samples (n) to be collected from the waste. That number of samples is subsequently analyzed for each chemical contaminant of concern. The resulting analytical data are then used to conclude definitively that each contaminant is or is not present in the waste at a hazardous concentration or, alternatively, to suggest a reiterative process, involving increased sampling effort, through which the presence or absence of hazard can be definitively determined.

In the hypothetical example for simple random sampling (Box 1), preliminary estimates of \bar{x} and s^2 indicated a sampling effort consisting of six samples. That number of samples was collected and initially analyzed generating analytical data somewhat different from the preliminary data (s^2 was substantially greater than was preliminarily estimated). Consequently, the upper limit of the CI was unexpectedly greater than the applicable RT, resulting in a tentative conclusion of hazard. However, a reestimation of appropriate sampling effort, based on statistics derived from the six samples, suggested that such a conclusion might be reversed through the collection and analysis of just one more sample. Fortunately, a resampling effort was not required because of the foresight of the waste producer in obtaining three extra samples during the initial sampling effort, which, because of their influence in decreasing the final values of \bar{x} , $S_{\bar{x}}$, $t_{.20}$, and, consequently, the upper limit of the CI -- values obtained from all nine samples -- resulted in a definitive conclusion of nonhazard.

9.1.1.3.2 Stratified Random Sampling

Stratified random sampling (Box 2) is conducted by general procedures that are similar to the procedures described for simple random sampling. The only difference is that, in stratified random sampling, values of \bar{x} and s^2 are calculated for each stratum in the population and then integrated into overall estimates of those statistics, the standard deviation (s), $s_{\bar{x}}$, and the appropriate number of samples (n) for all strata.

The hypothetical example for stratified random sampling (Box 2) is based on the same nine sludge samples previously identified in the example of simple random sampling (Box 1) so that the relative efficiencies of the two sampling strategies can be fully compared. The efficiency generated through the process of stratification is first evident in the preliminary estimate of n (Step 2 in Boxes 1 and 2), which is six for simple random sampling and four for stratified random sampling. (The lesser value for stratified sampling is the consequence of a dramatic decrease in s^2 which more than compensated for a modest increase in Δ .) The most relevant indication of sampling efficiency is the value of $S_{\bar{x}}$, which is directly employed to calculate the CI. In the case of simple random sampling, $S_{\bar{x}}$ is calculated as 2.58 (Step 9 in Box 1), and, for stratified random sampling, $S_{\bar{x}}$ is determined to be 2.35 (Steps 5 and 7 in Box 2). Consequently, the gain in efficiency attributable to stratification is approximately 9% ($0.23/2.58$).

BOX 1. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SIMPLE RANDOM SAMPLING

Step

General Procedures

1. Obtain preliminary estimates of \bar{x} and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2a and 3a (Table 9-1).
2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.
3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of \bar{x} and s^2). Maximize the physical size (weight or volume) of all samples that are collected.
4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data for obvious departures from normality.
5. Calculate \bar{x} , s^2 , the standard deviation (s), and $s_{\bar{x}}$ for each set of analytical data by, respectively, Equations 2a, 3a, 4, and 5 (Table 9-1).
6. If \bar{x} for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of μ , the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which \bar{x} is greater than s^2 , perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if \bar{x} is about equal to s^2) or the arcsine transformation (if \bar{x} is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).
7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2 , employ the newly calculated (not preliminary) values of \bar{x} and s^2 . If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.
9. Repeat the basic operations described in Steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of \bar{x} and s^2 are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} = \frac{86 + 90 + 98 + 104}{4} = 94.50, \text{ and} \quad (\text{Equation 2a})$$

$$s^2 = \frac{\sum_{i=1}^n x_i^2 - (\sum_{i=1}^n x_i)^2/n}{n - 1} \quad (\text{Equation 3a})$$

$$= \frac{35,916.00 - 35,721.00}{3} = 65.00.$$

2. Based on the preliminary estimates of \bar{x} and s^2 as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t_{.20}^2 s^2}{\Delta^2} = \frac{(1.638^2) (65.00)}{5.50^2} = 5.77. \quad (\text{Equation 8})$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is six. That number of samples (plus three extra samples for protection against poor preliminary estimates of \bar{x} and s^2) is collected from the lagoon by a single randomization process (Figure 9-2). All samples consist of the greatest volume of sludge that can be

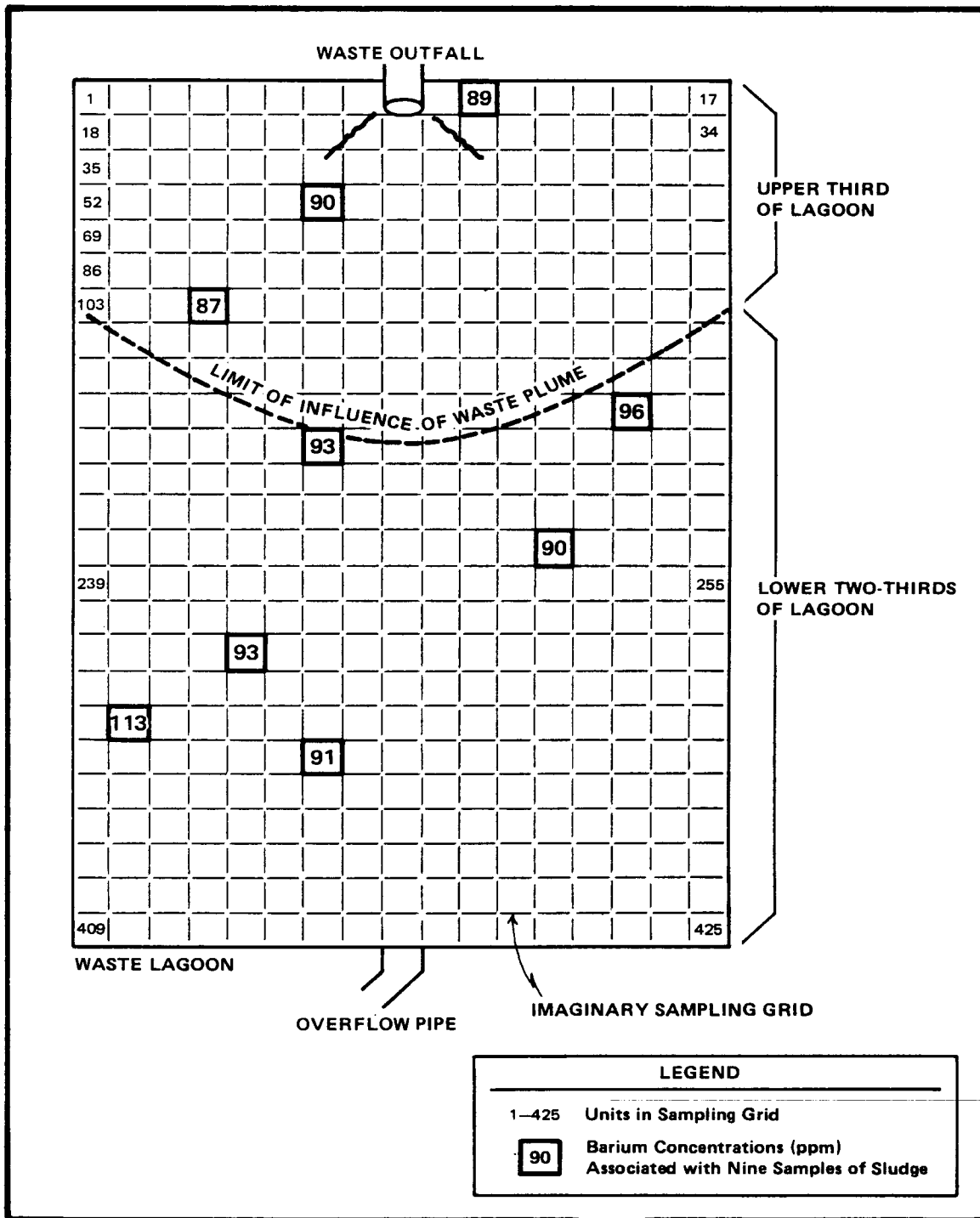


Figure 9-2. Hypothetical sampling conditions in waste lagoon containing sludge contaminated with barium. Barium concentrations associated with samples of sludge refer to levels measured in the elutriate of EP toxicity tests conducted with the samples.

practically collected. The three extra samples are suitably processed and stored for possible later analysis.

4. The six samples of sludge (n_1) designated for immediate analysis generate the following concentrations of barium in the EP toxicity test: 89, 90, 87, 96, 93, and 113 ppm. Although the value of 113 ppm appears unusual as compared with the other data, there is no obvious indication that the data are not normally distributed.
5. New values for \bar{x} and s^2 and associated values for the standard deviation (s) and $s_{\bar{x}}$ are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} = \frac{89 + 90 + 87 + 96 + 93 + 113}{6} = 94.67, \quad (\text{Equation 2a})$$

$$s^2 = \frac{\sum_{i=1}^n x_i^2 - (\sum_{i=1}^n x_i)^2/n}{n - 1} \quad (\text{Equation 3a})$$

$$= \frac{54,224.00 - 53,770.67}{5} = 90.67,$$

$$s = \sqrt{s^2} = 9.52, \text{ and} \quad (\text{Equation 4})$$

$$s_{\bar{x}} = s/\sqrt{n} = 9.52/\sqrt{6} = 3.89. \quad (\text{Equation 5})$$

6. The new value for \bar{x} (94.67) is less than the RT (100). In addition, \bar{x} is greater (only slightly) than s^2 (90.67), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

$$7. \quad CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 94.67 \pm (1.476)(3.89) \quad (\text{Equation 6})$$

$$= 94.67 \pm 5.74.$$

Because the upper limit of the CI (100.41) is greater than the applicable RT (100), it is tentatively concluded that barium is present in the sludge at a hazardous concentration.

8. n is now reestimated as:

$$n_2 = \frac{t_{.20}^2 s^2}{\Delta^2} = \frac{(1.476^2) (90.67)}{5.33^2} = 6.95. \quad (\text{Equation 8})$$

The value for n_2 (approximately 7) indicates that an additional ($n_2 - n_1 = 1$) sludge sample should be collected from the lagoon.

9. The additional sampling effort is not necessary because of the three extra samples that were initially collected from the lagoon. All extra samples are analyzed, generating the following levels of barium for the EP toxicity test: 93, 90, and 91 ppm. Consequently, \bar{x} , s^2 the standard deviation (s), and $s_{\bar{x}}$ are recalculated as:

$$\bar{x} = \frac{\sum_{i=1}^n X_i}{n} = \frac{86 + 90 + \dots + 91}{9} = 93.56, \quad (\text{Equation 2a})$$

$$s^2 = \frac{\sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2/n}{n-1} \quad (\text{Equation 3a})$$

$$= \frac{79,254.00 - 78,773.78}{8} = 60.03,$$

$$s = \sqrt{s^2} = 7.75, \text{ and} \quad (\text{Equation 4})$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.75/\sqrt{9} = 2.58. \quad (\text{Equation 5})$$

The value for \bar{x} (93.56) is again less than the RT (100), and there is no indication that the nine data points, considered collectively, are abnormally distributed (in particular, \bar{x} is now substantially greater than s^2). Consequently, CI, calculated with nontransformed data, is determined to be:

$$CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 93.56 \pm (1.397)(2.58) \quad (\text{Equation 6})$$

$$= 93.56 \pm 3.60.$$

The upper limit of the CI (97.16) is now less than the RT of 100. Consequently, it is definitively concluded that barium is not present in the sludge at a hazardous level.

BOX 2. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - STRATIFIED RANDOM SAMPLING

Step General Procedures

1. Obtain preliminary estimates of \bar{x} and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2b and 3b (Table 9-1).
2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.
3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of \bar{x} and s^2). If s_k for each stratum (see Equation 3b) is believed to be an accurate estimate, optimally allocate samples among strata (i.e., allocate samples among strata so that the number of samples collected from each stratum is directly proportional to s_k for that stratum). Otherwise, proportionally allocate samples among strata according to size of the strata. Maximize the physical size (weight or volume) of all samples that are collected from the strata.
4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data from each stratum for obvious departures from normality.
5. Calculate \bar{x} , s_2 , the standard deviation (s), and $\bar{x}s$ for each set of analytical data by, respectively, Equations 2b, 3b, 4, and 5 (Table 9-1).
6. If \bar{x} for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of μ , the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which \bar{x} is greater than s^2 , perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if \bar{x} is about equal to s^2) or the arcsine transformation (if \bar{x} is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).
7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2 , employ the newly calculated (not preliminary) values of \bar{x} and s^2 . If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.
9. Repeat the basic operations described in steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of \bar{x} and s^2 are calculated as:

$$\bar{x} = \sum_{k=1}^r W_k \bar{x}_k = \frac{(1)(88.00)}{3} + \frac{(2)(101.00)}{3} = 96.67, \text{ and} \quad (\text{Equation 2b})$$

$$s^2 = \sum_{k=1}^r W_k s_k^2 = \frac{(1)(8.00)}{3} + \frac{(2)(18.00)}{3} = 14.67. \quad (\text{Equation 3b})$$

2. Based on the preliminary estimates of \bar{x} and s^2 as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t_{.20}^2 s^2}{\Delta^2} = \frac{(1.368^2)(14.67)}{3.33^2} = 3.55. \quad (\text{Equation 8})$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is four. However, for purposes of comparison with simple random sampling (Box 1), six samples (plus three extra samples for protection against poor preliminary estimates of \bar{x} and s^2) are collected from the lagoon by a two-stage randomization process (Figure 2). Because s_k for the upper (2.12 ppm) and lower (5.66 ppm) strata are not believed to be very accurate estimates, the nine samples to be collected from the lagoon are not optimally allocated between the two strata (optimum allocation would require two and seven samples to be

collected from the upper and lower strata, respectively). Alternatively, proportional allocation is employed: three samples are collected from the upper stratum (which represents one-third of the lagoon), and six samples are taken from the lower stratum (two-thirds of the lagoon). All samples consist of the greatest volume of sludge that can be practically collected.

4. The nine samples of sludge generate the following concentrations of barium in the EP toxicity test: upper stratum -- 89, 90, and 87 ppm; lower stratum -- 96, 93, 113, 93, 90, and 91 ppm. Although the value of 113 ppm appears unusual as compared with the other data for the lower stratum, there is no obvious indication that the data are not normally distributed.
5. New values for \bar{x} and s^2 and associated values for the standard deviation (s) and $s_{\bar{x}}$ are calculated as:

$$\bar{x} = \sum_{k=1}^r W_k \bar{x}_k = \frac{(1)(88.67)}{3} + \frac{(2)(96.00)}{3} = 93.56 , \quad (\text{Equation 2b})$$

$$s^2 = \sum_{k=1}^r W_k s_k^2 = \frac{(1)(2.33)}{3} + \frac{(2)(73.60)}{3} = 49.84 , \quad (\text{Equation 3b})$$

$$s = \sqrt{s^2} = 7.06, \text{ and} \quad (\text{Equation 4})$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.06/\sqrt{9} = 2.35. \quad (\text{Equation 5})$$

6. The new value for \bar{x} (93.56) is less than the RT (100). In addition, \bar{x} is greater than s^2 (49.84), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

$$\begin{aligned} 7. \quad CI &= \bar{x} \pm t_{.20} s_{\bar{x}} = 93.56 \pm (1.397)(2.35) && (\text{Equation 6}) \\ &= 93.56 \pm 3.28. \end{aligned}$$

The upper limit of the CI (96.84) is less than the applicable RT (100). Therefore, it is concluded that barium is not present in the sludge at a hazardous concentration.

9.1.1.3.3 Systematic Random Sampling

Systematic random sampling (Box 3) is implemented by general procedures that are identical to the procedures identified for simple random sampling. The hypothetical example for systematic random sampling (Box 3) demonstrates the bias and imprecision that are associated with that type of sampling when unrecognized trends or cycles exist in the population.

9.1.1.4 Special Considerations

The preceding discussion has addressed the major issues that are critical to the development of a reliable sampling strategy for a solid waste. The remaining discussion focuses on several "secondary" issues that should be considered when designing an appropriate sampling strategy. These secondary issues are applicable to all three of the basic sampling strategies that have been identified.

9.1.1.4.1 Composite Sampling

In composite sampling, a number of random samples are initially collected from a waste and combined into a single sample, which is then analyzed for the chemical contaminants of concern. The major disadvantage of composite sampling, as compared with noncomposite sampling, is that information concerning the chemical contaminants is lost, i.e., each initial set of samples generates only a single estimate of the concentration of each contaminant. Consequently, because the number of analytical measurements (n) is small, $s_{\bar{x}}$ and $t_{.20}$ are large, thus decreasing the likelihood that a contaminant will be judged to occur in the waste at a nonhazardous level (refer to appropriate equations in Table 9-1 and to Table 9-2). A remedy to that situation is to collect and analyze a relatively large number of composite samples, thereby offsetting the savings in analytical costs that are often associated with composite sampling, but achieving better representation of the waste than would occur with noncomposite sampling.

The appropriate number of composite samples to be collected from a solid waste is estimated by use of Equation 8 (Table 9-1), as previously described for the three basic sampling strategies. In comparison with noncomposite sampling, composite sampling may have the effect of minimizing between-sample variation (the same phenomenon that occurs when the physical size of a sample is maximized), thereby reducing somewhat the number of samples that must be collected from the waste.

9.1.1.4.2 Subsampling

The variance (s^2) associated with a chemical contaminant of a waste consists of two components in that:

$$s^2 = s_s^2 + \frac{s_a^2}{m}, \quad (\text{Equation 12})$$

BOX 3. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES
ARE PRESENT AT HAZARDOUS LEVELS - SYSTEMATIC RANDOM SAMPLING

Step

General Procedures

1. Follow general procedures presented for simple random sampling of solid wastes (Box 1).

Step

Hypothetical Example

1. The example presented in Box 1 is applicable to systematic random sampling, with the understanding that the nine sludge samples obtained from the lagoon would be collected at equal intervals along a transect running from a randomly selected location on one bank of the lagoon to the opposite bank. If that randomly selected transect were established between Units 1 and 409 of the sampling grid (Figure 9-2) and sampling were performed at Unit 1 and thereafter at three-unit intervals along the transect (i.e., Unit 1, Unit 52, Unit 103, ... , and Unit 409), it is apparent that only two samples would be collected in the upper third of the lagoon, whereas seven samples would be obtained from the lower two-thirds of the lagoon. If, as suggested by the barium concentrations illustrated in Figure 9-2, the lower part of the lagoon is characterized by greater and more variable barium contamination than the upper part of the lagoon, systematic random sampling along the above-identified transect, by placing undue (disproportionate) emphasis on the lower part of the lagoon, might be expected to result in an inaccurate (overestimated) and imprecise characterization of barium levels in the whole lagoon, as compared with either simple random sampling or stratified random sampling. Such inaccuracy and imprecision, which are typical of systematic random sampling when unrecognized trends or cycles occur in the population, would be magnified if, for example, the randomly selected transect were established solely in the lower part of the lagoon, e.g., between Units 239 and 255 of the sampling grid.

where s_s^2 = a component attributable to sampling (sample) variation, s_a^2 = a component attributable to analytical (subsample) variation, and m = number of subsamples. In general, s_a^2 should not be allowed to exceed one-ninth of s_s^2 . If a preliminary study indicates that s_a^2 exceeds that threshold, a sampling strategy involving subsampling should be considered. In such a strategy, a number of replicate measurements are randomly made on a relatively limited number of randomly collected samples. Consequently, analytical effort is allocated as a function of analytical variability. The efficiency of that general strategy in meeting regulatory objectives has already been demonstrated in the previous discussions of sampling effort.

The appropriate number of samples (n) to be collected from a solid waste for which subsampling will be employed is again estimated by Equation 8 (Table 9-1). In the case of simple random sampling or systematic random sampling with an equal number of subsamples analyzed per sample:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}, \quad (\text{Equation 13})$$

where \bar{x}_i = sample mean (calculated from values for subsamples) and n = number of samples. Also,

$$s^2 = \frac{\sum_{i=1}^n \bar{x}_i^2 - (\sum_{i=1}^n \bar{x}_i)^2/n}{n-1} \quad (\text{Equation 14})$$

The optimum number of subsamples to be taken from each sample ($m_{opt.}$) is estimated as:

$$m_{(opt.)} = \frac{s_a}{s_s} \quad (\text{Equation 15})$$

when cost factors are not considered. The value for s_a is calculated from available data as:

$$s_a = \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^m x_{ij}^2 - (\sum_{i=1}^n x_{ij})^2/m}{n(m-1)}}, \quad (\text{Equation 16})$$

and s_s , which can have a negative characteristic, is defined as:

$$s_s = \sqrt{s^2 - \frac{s_a^2}{m}}, \quad (\text{Equation 17})$$

with s_2 calculated as indicated in Equation 14.

In the case of stratified random sampling with subsampling, critical formulas for estimating sample size (n) by Equation 8 (Table 9-1) include:

$$\bar{x} = \sum_{k=1}^r W_k \bar{x}_k, \quad (\text{Equation 2b})$$

where \bar{x}_k = stratum mean and W_k = fraction of population represented by Stratum K (number of strata, k, ranges from 1 to r). In Equation 2b, \bar{x}_k for each stratum is calculated as the average of all sample means in the stratum (sample means are calculated from values for subsamples). In addition, s^2 is calculated by:

$$s^2 = \sum_{k=1}^r W_k s_k^2, \quad (\text{Equation 3b})$$

with s_k^2 for each stratum calculated from all sample means in the stratum. The optimum subsampling effort when cost factors are not considered and all replication is symmetrical is again estimated as:

$$m_{(opt.)} = \frac{S_a}{S_s}, \text{ with} \quad (\text{Equation 15})$$

$$S_a = \sqrt{\frac{\sum_{k=1}^r \sum_{i=1}^n \sum_{j=1}^m X_{kij}^2 - (\sum X_{kij})^2 / m}{rn(m-1)}}, \text{ and} \quad (\text{Equation 18})$$

$$S_s = \sqrt{S^2 - \frac{S_a^2}{m}}, \quad (\text{Equation 17})$$

with s^2 derived as shown in Equation 3b.

9.1.1.5 Cost and Loss Functions

The cost of chemically characterizing a waste is dependent on the specific strategy that is employed to sample the waste. For example, in the case of simple random sampling without subsampling, a reasonable cost function might be:

$$C_{(n)} = C_0 + C_1 n, \quad (\text{Equation 19})$$

where $C_{(n)}$ = cost of employing a sample size of n , C_0 = an overhead cost (which is independent of the number of samples that are collected and analyzed), and C_1 = a sample-dependent cost. A consideration of $C_{(n)}$ mandates an evaluation of $L_{(n)}$, which is the sample-size-dependent expected financial loss related to the erroneous conclusion that a waste is hazardous. A simple loss function is:

$$L_{(n)} = \frac{\alpha s^2}{n}, \quad (\text{Equation 20})$$

with α = a constant related to the cost of a waste management program if the waste is judged to be hazardous, s^2 = sample variance, and n = number of samples. A primary objective of any sampling strategy is to minimize $C_{(n)} + L_{(n)}$. Differentiation of Equations 19 and 20 indicates that the number of samples (n) that minimize $C_{(n)} + L_{(n)}$ is:

$$n = \sqrt{\frac{\alpha s^2}{C_1}}. \quad (\text{Equation 21})$$

As is evident from Equation 21, a comparatively large number of samples (n) is justified if the value of α or s^2 is large, whereas a relatively small number of samples is appropriate if the value of C_1 is large. These general conclusions are valid for any sampling strategy for a solid waste.

9.2 IMPLEMENTATION

This section discusses the implementation of a sampling plan for the collection of a "solid waste," as defined by Section 261.2 of the Resource Conservation and Recovery Act (RCRA) regulations. Due to the uniqueness of each sampling effort, the following discussion is in the general form of guidance which, when applied to each sampling effort, should improve and document the quality of the sampling and the representativeness of samples.

The following subsections address elements of a sampling effort in a logical order, from defining objectives through compositing samples prior to analysis.

9.2.1 Definition Of Objectives

After verifying the need for sampling, those personnel directing the sampling effort should define the program's objectives. The need for a sampling effort should not be confused with the objective. When management, a regulation, or a regulatory agency requires sampling, the need for sampling is established but the objectives must be defined.

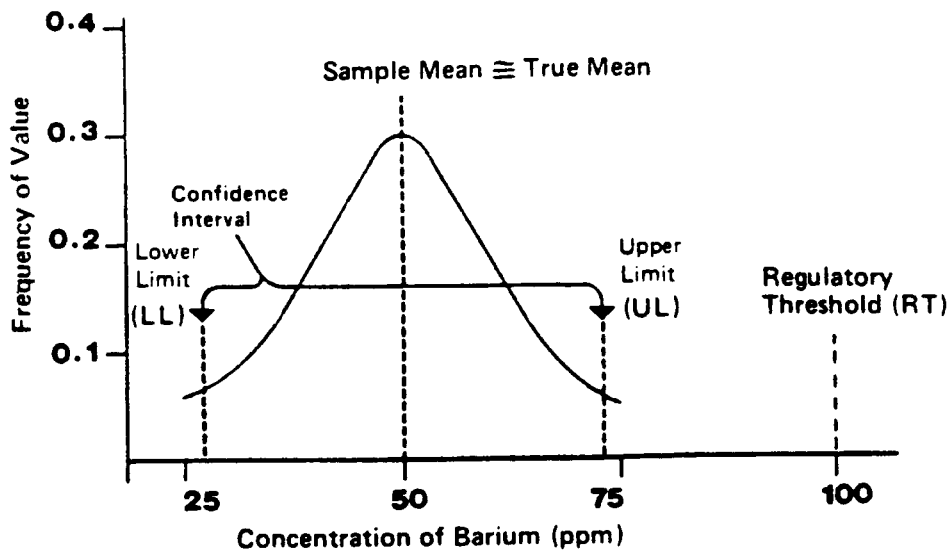
The primary objective of any waste sampling effort is to obtain information that can be used to evaluate a waste. It is essential that the specific information needed and its uses are defined in detail at this stage. The information needed is usually more complex than just a concentration of a specified parameter; it may be further qualified (e.g., by sampling location or sampling time.) The manner in which the information is to be used can also have a substantial impact on the design of a sampling plan. (Are the data to be used in a qualitative or quantitative manner? If quantitative, what are the accuracy and precision requirements?)

All pertinent information should be gathered. For example, if the primary objective has been roughly defined as "collecting samples of waste which will be analyzed to comply with environmental regulations," then ask the following questions:

1. The sampling is being done to comply with which environmental regulation? Certain regulations detail specific or minimum protocols (e.g., exclusion petitions as defined in §260.22 of the RCRA regulations); the sampling effort must comply with these regulatory requirements.
2. The collected samples are to be analyzed for which parameters? Why those and not others? Should the samples be analyzed for more or fewer parameters?
3. What waste is to be sampled: the waste as generated? The waste prior to or after mixing with other wastes or stabilizing agents? The waste after aging or drying or just prior to disposal? Should waste disposed of 10 years ago be sampled to acquire historical data?
4. What is the end-use of the generated data base? What are the required degrees of accuracy and precision?

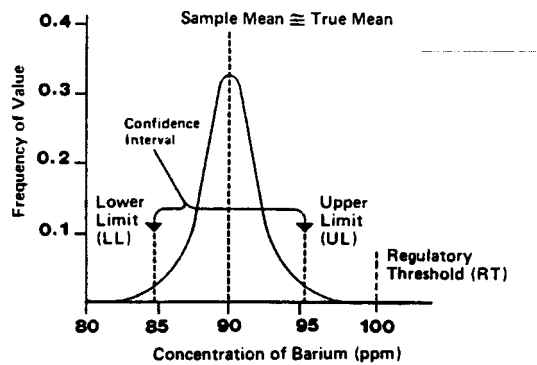
By asking such questions, both the primary objective and specific sampling, analytical, and data objectives can be established.

Two sampling efforts could have identical primary objectives but different specific objectives. For example, consider two situations in which the primary objective is to determine if the concentration of barium is less than the regulatory threshold of 100 ppm. The specific objectives will vary and have a substantial effect on sampling. (This situation is presented graphically in Figures 9-3 and 9-4.) In Figure 9-3, under the assumption that the true distribution of barium concentrations throughout the waste of interest is as shown, limited information has indicated that the average concentration is approximately 50 ppm. In Figure 9-4, assume that historical data indicated an average concentration of 90 ppm and the true distribution of barium concentrations is as shown. Therefore, the specific data objective for the latter case is to generate a data base that can discriminate between 90 and 100 ppm, whereas in the former case the data objective is to discriminate between 50 and 100 ppm. Greater accuracy and precision are required to discriminate between 90 and 100 ppm; this fact will affect the number, size, and degree of compositing of samples collected and analyzed.



Distance of true value from regulatory threshold requires less accuracy and precision.

Figure 9-3. Distribution of barium concentration removed from a regulatory threshold.



Proximity of true value from regulatory threshold requires more accuracy and precision.

Figure 9-4. Distribution of barium concentration near a regulatory threshold.

The form in Figure 9-5 can be used to document primary and specific objectives prior to development of a sampling plan. Once the objectives of a sampling effort are developed, it is important to adhere to them to ensure that the program maintains its direction.

9.2.2 Sampling Plan Considerations

The sampling plan is usually a written document that describes the objectives and details the individual tasks of a sampling effort and how they will be performed. (Under unusual circumstances, time may not allow for the sampling plan to be documented in writing, e.g., sampling during an emergency spill. When operating under these conditions, it is essential that the person directing the sampling effort be aware of the various elements of a sampling plan.) The more detailed the sampling plan, the less the opportunity for oversight or misunderstanding during sampling, analysis, and data treatment.

To ensure that the sampling plan is designed properly, it is wise to have all aspects of the effort represented. Those designing the sampling plan should include the following personnel:

1. An end-user of the data, who will be using the data to attain program objectives and thus would be best prepared to ensure that the data objectives are understood and incorporated into the sampling plan.
2. An experienced member of the field team who will actually collect samples, who can offer hands-on insight into potential problems and solutions, and who, having acquired a comprehensive understanding of the entire sampling effort during the design phase, will be better prepared to implement the sampling plan.
3. An analytical chemist, because the analytical requirements for sampling, preservation, and holding times will be factors around which the sampling plan will be written. A sampling effort cannot succeed if an improperly collected or preserved sample or an inadequate volume of sample is submitted to the laboratory for chemical, physical, or biological testing. The appropriate analytical chemist should be consulted on these matters.
4. An engineer should be involved if a complex manufacturing process is being sampled. Representation of the appropriate engineering discipline will allow for the optimization of sampling locations and safety during sampling and should ensure that all waste-stream variations are accounted for.
5. A statistician, who will review the sampling approach and verify that the resulting data will be suitable for any required statistical calculations or decisions.
6. A quality assurance representative, who will review the applicability of standard operating procedures and determine the number of blanks, duplicates, spike samples, and other steps required to document the accuracy and precision of the resulting data base.

Sampling Site: _____

Address: _____

Description of Waste to be Sampled: _____

Primary Objective: _____

Specific Sampling Objectives: _____

Specific Analysis Objectives: _____

Specific Data Objectives: _____

Figure 9-5. Form for Documenting Primary and Specific Objectives

At least one person should be familiar with the site to be sampled. If not, then a presampling site visit should be arranged to acquire site-specific information. If no one is familiar with the site and a presampling site visit cannot be arranged, then the sampling plan must be written so that it can address contingencies that may occur.

Even in those cases in which a detailed sampling plan is authored and a comprehensive knowledge of the site exists, it is unusual for a sampling plan to be implemented exactly as written. Waste-stream changes, inappropriate weather, sampling equipment failure, and problems in gaining access to the waste are some reasons why a sampling plan must be altered. Thus it is always necessary to have at least one experienced sampler as a member of a sampling team.

The sampling plan should address the considerations discussed below.

9.2.2.1 Statistics

A discussion of waste sampling often leads to a discussion of statistics. The goals of waste sampling and statistics are identical, i.e., to make inferences about a parent population based upon the information contained in a sample.

Thus it is not surprising that waste sampling relies heavily upon the highly developed science of statistics and that a sampling/analytical effort usually contains the same elements as does a statistical experiment. Analogously, the Harris pollster collects opinions from randomly chosen people, whereas environmental scientists collect waste at randomly chosen locations or times. The pollster analyzes the information into a useable data base; laboratories analyze waste samples and generate data. Then the unbiased data base is used to draw inferences about the entire population, which for the Harris pollster may be the voting population of a large city, whereas for the environmental scientist the population may mean the entire contents of a landfill.

During the implementation of a waste sampling plan or a statistical experiment, an effort is made to minimize the possibility of drawing incorrect inferences by obtaining samples that are representative of a population. In fact, the term "representative sample" is commonly used to denote a sample that (1) has the properties and chemical composition of the population from which it was collected, and (2) has them in the same average proportions as are found in the population.

In regard to waste sampling, the term "representative sample" can be misleading unless one is dealing with a homogeneous waste from which one sample can represent the whole population. In most cases, it would be best to consider a "representative data base" generated by the collection and analysis of more than one sample that defines the average properties or composition of the waste. A "representative data base" is a more realistic term because the evaluation of most wastes requires numerous samples to determine the average properties or concentrations of parameters in a waste. (The additional samples needed to generate a representative data base can also be used to determine the variability of these properties or concentrations throughout the waste population.)

Statisticians have developed a number of strategies to obtain samples that are unbiased and collectively representative of a population. A detailed discussion of these strategies is presented in Section 9.1 of this chapter. The following discussion of statistical considerations is a less technical summary of these strategies. It was written to complement Section 9.1 and will be most useful after Section 9.1 is read and studied.

Section 9.1 describes three basic sampling strategies: simple random, stratified random, and systematic random sampling. It should be noted that the word random has more than one meaning. When used in statistical discussions, it does not mean haphazard: it means that every part of a waste has a theoretically equal chance of being sampled. Random sampling, which entails detailed planning and painstaking implementation, is distinctly different from haphazard sampling, which may introduce bias into the collection of samples and the resulting data.

Systematic random sampling and authoritative sampling strategies require a substantial knowledge of the waste to ensure that: (1) a cycle or trend in waste composition does not coincide with the sampling locations: or (2) in the case of authoritative sampling, all or most of the assumptions regarding waste composition or generation are true. Because the variabilities of waste composition and the waste generation process are often unknown, systematic random and authoritative sampling strategies are usually not applicable to waste evaluation.

Therefore, for waste sampling, the usual options are simple or stratified random sampling. Of these two strategies, simple random sampling is the option of choice unless: (1) there are known distinct strata divisions) in the waste over time or in space: (2) one wants to prove or disprove that there are distinct time and/or space strata in the waste of interest; or (3) one is collecting a minimum number of samples and desires to minimize the size of a hot spot (area of high concentration) that could go unsampled. If any of these three conditions exists, it may be determined that stratified random sampling would be the optimum strategy. To explain how these strategies can be employed, a few examples follow:

Example 1: Simple Random Sampling of Tanks

A batch manufacturing process had been generating a liquid waste over a period of years and storing it in a large open-top tank. As this tank approached capacity, some of the waste was allowed to overflow to a smaller enclosed tank. This smaller tank allowed for limited access through an inspection port on its top.

Because the on-site tank storage was approaching capacity, it was determined that the waste would have to be disposed of off-site.

The operators of the facility had determined that the waste was a nonhazardous solid waste when the RCRA regulations were first promulgated. However, upon recent passage of more stringent state regulations and concerns of potential liability, the operators determined that they should perform a more comprehensive analysis of the waste.

Because the waste was generated in a batch mode over a period of years, the operators were concerned that the waste composition might have varied between batches and that stratification might have occurred in the tank at unknown and random depths. Based on their knowledge, the operators knew that a grab sample would not suffice and that a sampling program would have to be designed to address the heterogeneity of the waste.

Because the operators intended to dispose of the entire contents of the tank and lacked any specific information regarding stratification and variability of the waste, it was decided that a simple random strategy would be employed. (If the operators had treated portions of the waste differently or had been aware of distinct strata, then stratified random sampling might have been more appropriate.)

The large, unenclosed tank had a diameter of 50 ft, a height of 20 ft, and an approximate volume of 295,000 gal allowed. It was encircled and traversed by catwalks (refer to Figure 9-6), which allowed access to the entire waste surface. The smaller tank had a diameter of 10 ft, a height of 10 ft, and an approximate volume of 6,000 gal: an inspection port located on the top allowed limited access. It was determined that the different construction of the two tanks would require different simple random sampling approaches.

In the case of the large tank, it was decided that vertical composite samples would be collected because the operators were interested in the average composition and variability of the waste and not in determining if different vertical strata existed. It was decided to select points randomly along the circumference (157 ft) and along the radius (25 ft). These numbers, which would constitute the coordinates of the sampling locations, were chosen from a random-number table by indiscriminately choosing a page and then a column on that page. The circumference coordinates were then chosen by proceeding down the column and listing the first 15 numbers that are greater than or equal to 0, but less than or equal to 157. The radius coordinates were chosen by continuing down the column and listing the first 15 numbers that are greater than or equal to 0, but less than or equal to 25. These numbers were paired to form the coordinates that determined the location of the 15 randomly chosen sampling points. These coordinates were recorded in the field notebook (refer to Table 9-3). Because no precision data on waste composition existed prior to sampling, the number of samples (15) was chosen as a conservative figure to more than allow for a sound statistical decision.

The actual samples were collected by employing a sampling device, which was constructed on site from available materials, and a weighted bottle. This device, which was used to access more remote areas of the tank, consisted of a weighted bottle, a rope marked off at 1-ft increments, and a discarded spool that originally contained electrical wire (refer to Figure 9-7).

Samples were collected by a three-person team. The person controlling the weighted bottle walked to the first circumference coordinate (149 ft), while the two persons holding the ropes attached to the spool walked along opposing catwalks toward the center of the tank. The person controlling the

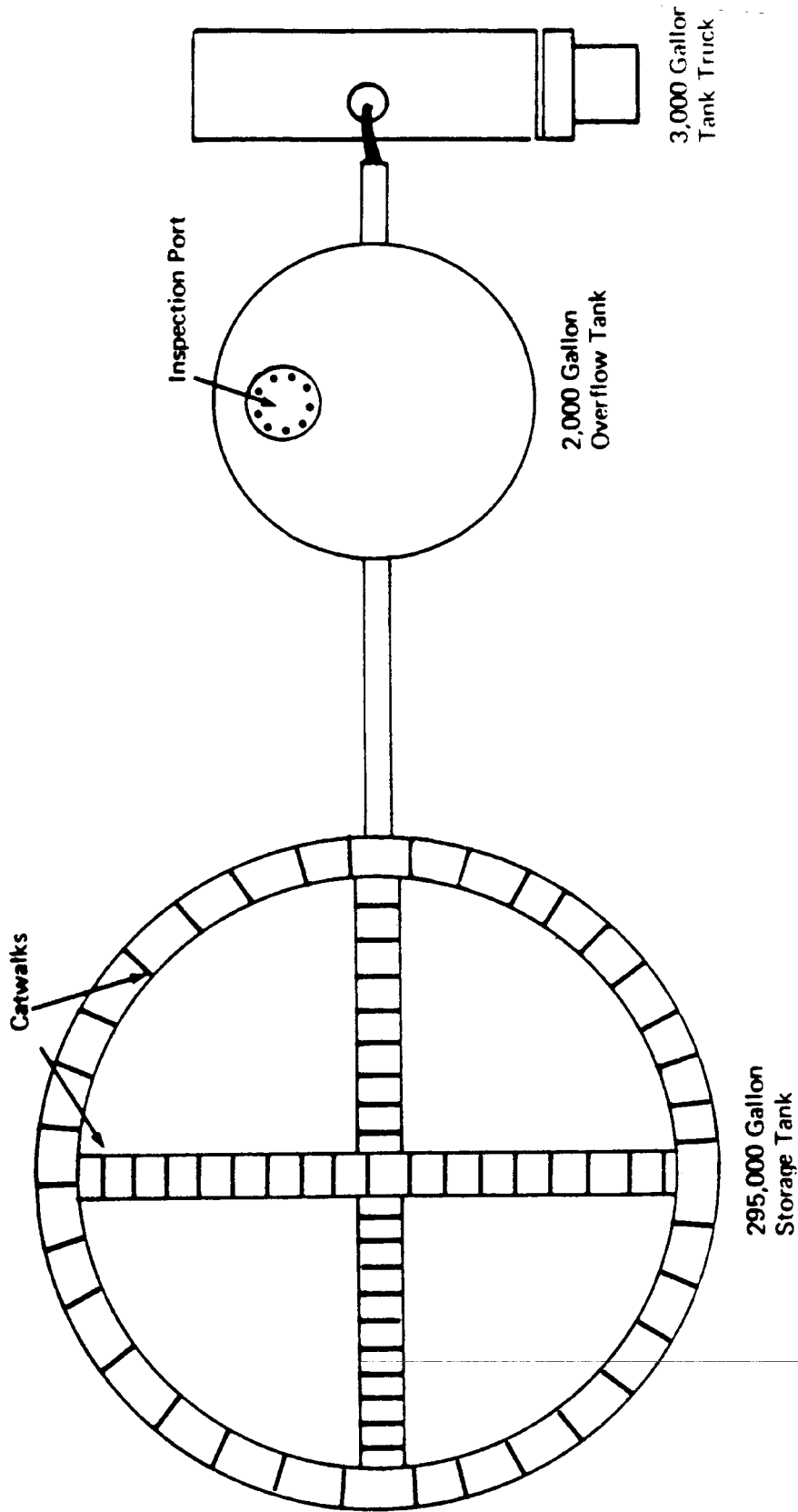


Figure 9-6. Bird's eye view of waste tank, overflow tank, tank truck and connecting plumbing.

TABLE 9-3. RANDOM COORDINATES FOR 295,000-GAL TANK

Sampling Point	Circumference	Radius
1	149	4
2	86	22
3	94	13
4	99	0
5	23	10
6	58	2
7	52	22
8	104	16
9	23	25
10	51	4
11	77	14
12	12	5
13	151	15
14	83	23
15	99	18

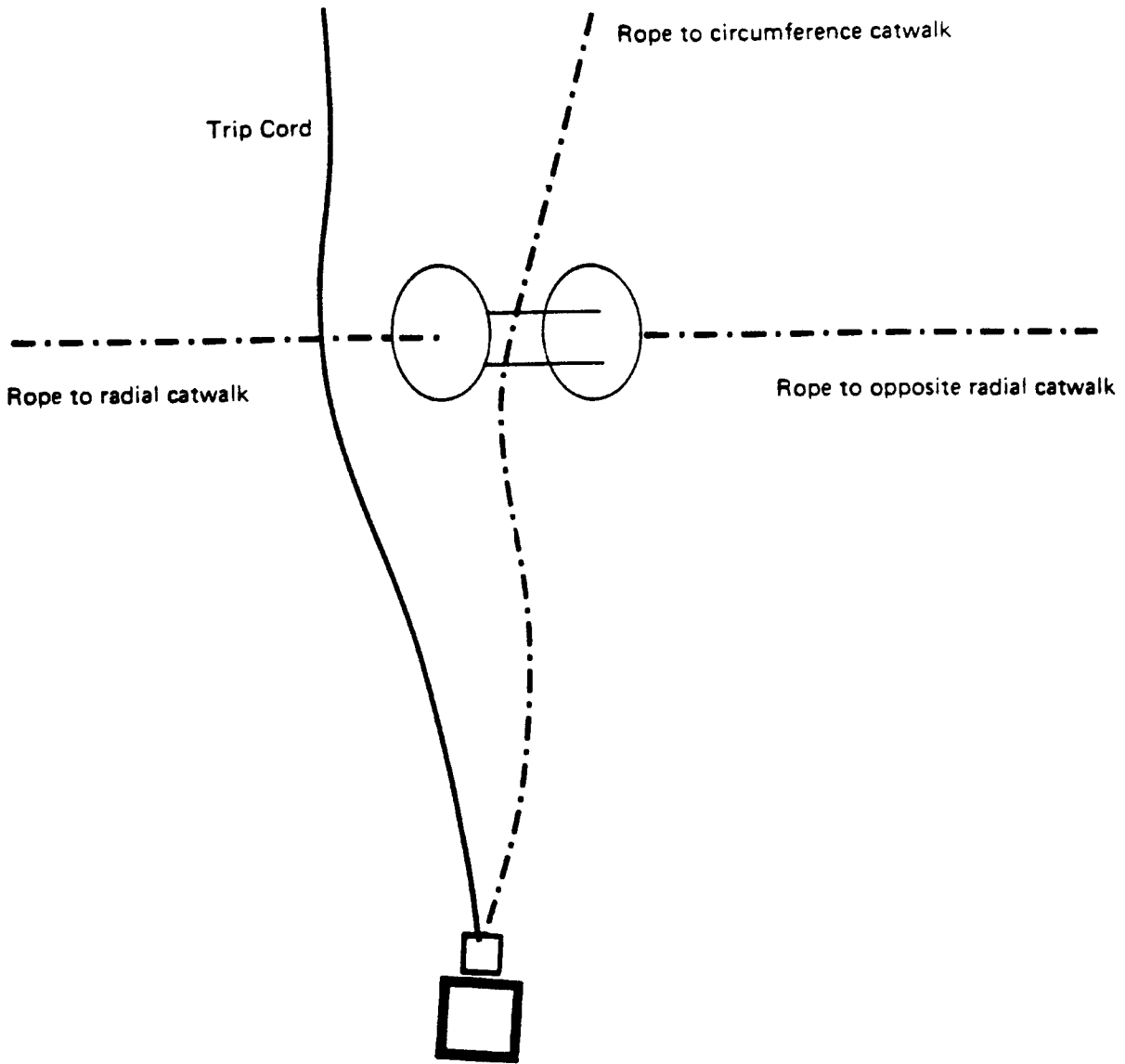


Figure 9-7. Device used to collect sample from the open tank.

weighted bottle measured off the radius coordinate (4 ft). The spool was then centered in the quadrant, the weighted bottle was lowered to the surface, and a sample was collected from the first 2 ft of waste. This sample was then transferred into a large, labeled sample container, which was used for compositing. This same process was repeated nine more times at the same location at different 2-ft depth intervals, resulting in the collection of a total of 10 component depth samples that were compiled in the field into one sample for that sampling point. This process was repeated at the remaining 14 sampling points, resulting in the collection of 15 vertical composite samples. These vertical composite samples were taken to address any vertical stratification that may have occurred.

The samples were properly preserved and stored, chain-of-custody procedures were completed, and the samples were submitted to the laboratory. A cost/benefit decision was made to composite aliquots of the samples into five composite samples that were submitted for analysis. (Following analysis, Equation 8 of Section 9.1 of this chapter was employed to determine if enough samples were analyzed to make a statistically sound decision. If the number of samples analyzed was not sufficient, then the samples would be recomposited to a lesser degree or analyzed individually.)

Because there was no information to prove that the waste in the smaller tank was the same as that in the larger tank, the operators decided that the smaller tank must also be sampled. The different construction of the smaller, enclosed tank mandated that a different sampling plan be designed. The only access to the tank was through a small inspection port on the top of the tank. This port would allow sampling only of a small portion of the tank contents; thus, to make a decision on the entire contents of the tank, one would have to assume that the waste in the vicinity of the inspection port was representative of the remainder of the tank contents. The operators were not willing to make this assumption because they determined that the liability of an incorrect decision overrode the convenience of facilitating the sampling effort.

To randomly sample the entire contents of the tank, a different plan was designed. This plan exploited the relatively small volume (approximately 6,000 gal) of the tank. A decision was made to rent two tank trucks and to sample the waste randomly over time as it drained from the tank into the tank trucks.

It was calculated that at a rate of 20 gal/min, it would take 300 min to drain the tank. From the random-number tables, 15 numbers that were greater than or equal to 0, but less than or equal to 300, were chosen in a manner similar to that employed for the larger tank. These numbers were recorded in the field notebook (refer to Table 9-4) at the time that they were encountered in the random-number table and were then assigned sampling point numbers according to their chronological order.

The 15 samples were collected at the previously chosen random times as the waste exited from a drainage hose into the tank trucks. These samples were collected in separate labeled containers, properly preserved and stored; chain-of-custody procedures were employed for transferral of the samples to the laboratory.

TABLE 9-4. RANDOM TIMES FOR 6,000-GAL TANK

Sampling point	Time (min)
11	153
10	122
8	85
6	55
5	46
15	294
12	195
1	5
13	213
9	99
2	29
4	41
7	74
3	31
14	219

The above example employed simple random sampling to determine the average composition and variance of the waste contained in the two tanks. The contents of the large tank were sampled randomly in space, whereas the contents of the smaller tank were sampled randomly over time.

The following example will involve the use of stratified random sampling, which is used when: (1) distinct strata are known to exist or (2) it is not known whether different strata exist, but an objective of the sampling effort is to discover the existence or nonexistence of strata.

A variation of this second reason for employing stratified random sampling is when cost considerations limit the number of samples that can be collected (e.g., when the budget allows for the collection of only six samples in a 40-acre lagoon). In this situation, where little is known about the composition of the waste, a concern exists that an area of the lagoon may be highly contaminated and yet may not be sampled. The smaller the number of samples, the greater the probability that an area of high contamination (a distinct stratum) could be missed, and the greater the probability that the sampling accuracy will suffer. Under such circumstances, a sampling plan may employ stratified random sampling to minimize the size of a highly contaminated area that could go unsampled.

For example, consider the situation where the budget allows only for the collection of six samples in a 40-acre lagoon. If simple random sampling is employed with such a small number of samples, there is a certain probability that large areas of the lagoon may go unsampled. One approach to minimizing the size of areas that may go unsampled is to divide the lagoon into three strata of equal size and randomly sample each stratum separately. This approach decreases the size of an area that can go unsampled to something less than one-third of the total lagoon area.

The following example details more traditional applications of stratified random sampling.

Example 2: Stratified Random Sampling of Effluents and Lagoons

A pigment manufacturing process has been generating wastes over a number of years. The pigment is generated in large batches that involve a 24-hr cycle. During the first 16 hr of the cycle, an aqueous sludge stream is discharged. This waste contains a high percentage of large-sized black particulate matter. The waste generated during the remaining 8 hr of the manufacturing cycle is an aqueous-based white sludge that consists of much smaller-sized particles than those found in the sludge generated in the first 16 hr of the batch process. This waste has been disposed of over the years into a 40-acre settling lagoon, allowing the particulate matter to settle out of solution while the water phase drains to an NPDES outfall at the opposite end of the lagoon. The smaller white pigment particles released in the last 8 hr of the batch process settle more slowly than the much larger black particles generated in the previous 16 hr. This settling pattern is quite apparent from the distinct colors of the wastes. The sludge in the quadrant closest to the waste influent pipe is black; the next quadrant is a light gray color, resulting from settling of both waste streams. The last two quadrants contain a pure white sludge, resulting from the settling of the small pigment particles.

Eventually, the facility operators decided that the settled particulate matter had to be removed to keep the settling lagoon functioning. In the past, this residual lagoon waste was found to be a hazardous waste due to its leachable barium content. Further studies determined that the source of the barium was a certain raw material that was released during the first 16 hr of batch process.

To minimize present disposal costs, the operators wanted to determine if the white sludge in the last two quadrants and the light gray waste were nonhazardous. Also, the operators had recently changed raw materials, with the intention of removing the source of barium in an attempt to minimize future disposal costs. Thus, the operators were interested in determining whether the currently generated waste was hazardous. If the altered waste stream was not hazardous, future lagoon sludge could be disposed of more economically as a solid waste. If the waste generated during the first 16 hr of the process remained hazardous but the waste generated during the following 8 hr was nonhazardous, the operators were willing to shift this latter waste to a second lagoon reserved for nonhazardous wastes. By sequestering the waste streams in this manner, the operators intended to decrease the amount of hazardous waste by precluding generation of additional amounts of hazardous waste under the "mixture rule."

To decide how the lagoon sludge should be handled, the operators arranged to have the lagoon sludge sampled. The objectives of sampling the lagoon sludge were to determine the average concentration and variance of leachable barium for the sludge in the entire lagoon and for each of the different sludges.

The dimensions of the 40-acre square lagoon were calculated to be 1,320 ft on a side, with the black and the gray sludge each covering a quadrant measuring 1,320 ft by 330 ft, and the white sludge covering the remaining area of the lagoon, which measured 1,320 ft by 660 ft (refer to Figure 9-8). The sludge had settled to a uniform thickness throughout the lagoon and was covered with 2 ft of water.

Because the leachable barium was assumed to be associated with the black sludge, which was concentrated in the first quadrant, a stratified random sampling approach was chosen. (Because of the obvious strata in the lagoon sludge, the stratified sampling strategy was expected to give a more precise estimate of the leachable barium, in addition to giving information specific to each stratum.)

When the actual sampling was being planned, it was decided that the hazards presented by the lagoon waste were minimal, and, that if proper precautions were employed, a stable and unsinkable boat could be used to collect samples. The samples were collected with a core sampler at random locations throughout each stratum. Because the cost of collecting samples was reasonable and no historical data were available to help determine the optimum number of samples, the operators decided to collect a total of 10 samples from each of the smaller strata and a total of 20 samples from the larger strata. They had confidence that this number of samples would allow them to detect a small significant difference between the mean concentration of leachable barium and the applicable regulatory threshold.

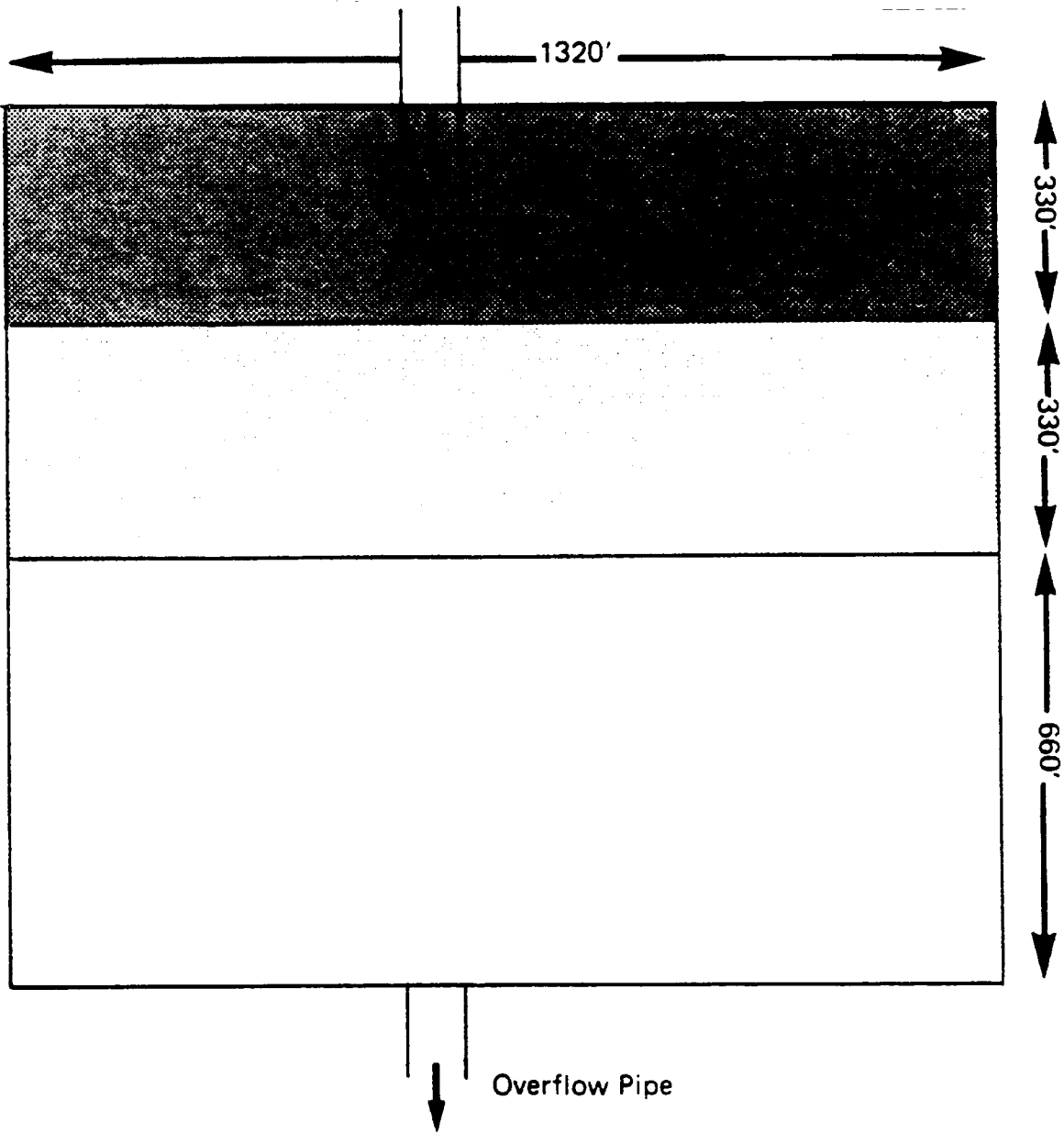


Figure 9-8. Schematic of the 40-acre settling lagoon displaying strata generated by a waste stream.

The locations of the random sampling points were determined by selecting length and width coordinates from a random-number table. This was done by indiscriminately choosing a page from the random-number tables and then a column on that page. The width coordinates of the two smaller quadrants were then chosen by proceeding down the column and listing the first 20 numbers that were greater than or equal to 0, but less than or equal to 330. The width coordinate for the third and largest stratum was chosen by proceeding down the column and selecting the first 20 numbers that were greater than or equal to 0, but less than or equal to 660. Because the lengths of the three quadrants were all 1,320 ft, the length coordinates were chosen by listing the first 40 numbers that were greater than or equal to 0 but less than or equal to 1,320. These coordinates were recorded in the field notebook (refer to table 9-5).

The samples were collected by a four-person team. Two people remained onshore while two maneuvered the boat and collected the samples. The first sample in the first quadrant was collected by launching the boat at a distance of 41 ft from the corner, which was designated the origin, 0 ft. The boat proceeded out into the lagoon perpendicular to the long side of the quadrant. The person onshore released 134 ft of a measured rope, which allowed the boat to stop at the first sampling point (41, 134). The sample was then collected with a core sampler and transferred to a sample container. This process was repeated for all sampling points in the three strata. The samples were properly preserved and stored, and the chain-of-custody records documented the transfer of samples to the laboratory.

Aliquots of the samples were composited into five composite samples for each stratum. The mean and variance of each stratum were calculated by Equations 2(a) and 3(a), respectively. The mean and variance for the total lagoon were calculated by using Equations 2(b) and 3(b), respectively. Equation 6 was used to calculate a confidence interval for the leachable barium concentration, and the upper limit of this interval was compared with the regulatory threshold. (See Table 9-1, Section 9.1 of this chapter, for equations.)

As previously mentioned, the operators had recently changed their raw materials and were also interested in discovering if the currently generated waste was nonhazardous or if portions of this waste stream were nonhazardous. As described above, the waste effluent for the first 16 hr of the day was different from that discharged during the last 8 hr. However, because the same large plumbing system was used for both waste streams, there were two 2-hr periods during which the discharged waste was a mixture of the two different wastes.

With the above objectives in mind, the operators decided to employ stratified random sampling with four strata occurring over time, as opposed to the strata in space that were employed for sampling the lagoon. The four time strata were from 6:00 to 8:00 hr, from 8:00 to 20:00 hr, from 20:00 to 22:00 hr, and from 22:00 to 6:00 hr the following day. The two 2-hr strata were those time periods during which the waste was a mixture of the two different waste streams. The 12-hr stratum was the time period during which the large-sized particulate black waste was being discharged. The smaller particulate white waste was being discharged during the 8-hr stratum.

TABLE 9-5. RANDOM COORDINATES FOR EACH STRATUM
IN THE 40-ACRE SETTLING LAGOON

	Sampling Point	Length (ft)	Width (ft)
<u>Stratum #1</u> (Black)	1	41	134
	2	271	51
	3	968	32
	4	129	228
	5	472	137
	6	1,198	56
	7	700	261
	8	286	8
	9	940	26
	10	151	121
<u>Stratum #2</u> (Gray)	1	1,173	109
	2	277	2
	3	438	302
	4	780	5
	5	525	135
	6	50	37
	7	26	127
	8	1,207	149
	9	1,231	325
	10	840	32
<u>Stratum #3</u> (White)	1	54	374
	2	909	434
	3	1,163	390
	4	1,251	449
	5	1	609
	6	1,126	140
	7	717	235
	8	1,155	148
	9	668	433
	10	66	642
	11	462	455
	12	213	305
	13	1,220	541
	14	1,038	644
	15	508	376
	16	1,293	270
	17	30	38
	18	114	52
	19	1,229	570
	20	392	613

The flow rate was constant throughout the 24-hr period, and there were no precision data available for the waste. Therefore, it was decided that the number of samples collected in the 8- and 12-hr strata would be proportional to time. Because the 2-hr periods were times during which the composition of the waste was changing, it was decided to collect more samples to get a more precise estimate of the average composition of the waste during these time strata. Thus a total of 28 samples was collected.

The samples were collected at randomly chosen times within each time stratum. The random sampling times were chosen by employing a random-number table. After indiscriminately selecting a starting point, the first four numbers greater than or equal to 0, but less than or equal to 120 were selected for the 120-min strata from 6:00 to 8:00 hr. These minutes were then added to the starting time to determine when the four samples would be collected. In similar fashion, the remaining 24 sampling times were chosen. The random-number data were recorded in a laboratory notebook (refer to Table 9-6).

The samples were collected from the waste influent pipe with a wide-mouth bottle at the randomly chosen sampling times. The samples were properly preserved and stored and shipped to the laboratory, along with chain-of-custody records. The samples were subjected to analysis, and the data were evaluated in a manner similar to that employed for the samples of sludge collected in the different strata of the lagoon.

9.2.2.2 Waste

The sampling plan must address a number of factors in addition to statistical considerations. Obviously, one of the most important factors is the waste itself and its properties. The following waste properties are examples of what must be considered when designing a sampling plan:

1. Physical state: The physical state of the waste will affect most aspects of a sampling effort. The sampling device will vary according to whether the sample is liquid, gas, solid, or multiphasic. It will also vary according to whether the liquid is viscous or free-flowing, or whether the solid is hard or soft, powdery, monolithic, or clay-like.

Wide-mouth sample containers will be needed for most solid samples and for sludges or liquids with substantial amounts of suspended matter. Narrow-mouth containers can be used for other wastes, and bottles with air-tight closures will be needed for gas samples or gases adsorbed on solids or dissolved in liquids.

The physical state will also affect how sampling devices are deployed. A different plan will be developed for sampling a soil-like waste that can easily support the weight of a sampling team and its equipment than for a lagoon filled with a viscous sludge or a liquid waste.

TABLE 9-6. RANDOM TIMES FOR THE WASTE EFFLUENT

	Sampling Point	Random Minute	Time
<u>Stratum #1</u> (6:00 to 8:00 hours)	1	28	6:28
	2	62	7:02
	3	99	7:39
	4	112	7:52
<u>Stratum #2</u> (8:00 to 20:00 hours)	1	11	8:11
	2	107	9:47
	3	156	10:36
	4	173	10:53
	5	296	12:56
	6	313	13:13
	7	398	14:38
	8	497	16:17
	9	555	17:15
	10	600	18:00
	11	637	18:37
	12	706	19:46
<u>Stratum #3</u> (20:00 to 22:00 hours)	1	13	20:13
	2	52	20:52
	3	88	21:28
	4	108	21:48
<u>Stratum #4</u> (22:00 to 6:00 hours)	1	48	22:48
	2	113	23:53
	3	153	24:33
	4	189	1:09
	5	227	1:47
	6	290	2:49
	7	314	3:14
	8	474	5:44

The sampling strategy will have to vary if the physical state of the waste allows for stratification (e.g., liquid wastes that vary in density or viscosity or have a suspended solid phase), homogenization or random heterogeneity.

2. Volume: The volume of the waste, which has to be represented by the samples collected, will have an effect upon the choice of sampling equipment and strategies. Sampling a 40-acre lagoon requires a different approach from sampling a 4-sq-ft container. Although a 3-ft depth can be sampled with a Coliwasa or a drum thief, a weighted bottle may be required to sample a 50-ft depth.
3. Hazardous properties: Safety and health precautions and methods of sampling and shipping will vary dramatically with the toxicity, ignitability, corrosivity, and reactivity of the waste.
4. Composition: The chosen sampling strategy will reflect the homogeneity, random heterogeneity, or stratification of the waste in time or over space.

9.2.2.3 Site

Site-specific factors must be considered when designing a sampling plan. A thorough examination of these factors will minimize oversights that can affect the success of sampling and prevent attainment of the program objectives. At least one person involved in the design and implementation of the sampling plan should be familiar with the site, or a presampling site visit should be arranged. If nobody is familiar with the site and a visit cannot be arranged, the sampling plan must be written to account for the possible contingencies. Examples of site-specific factors that should be considered follow:

1. Accessibility: The accessibility of waste can vary substantially. Some wastes are accessed by the simple turning of a valve; others may require that an entire tank be emptied or that heavy equipment be employed. The accessibility of a waste at the chosen sampling location must be determined prior to design of a sampling plan.
2. Waste generation and handling: The waste generation and handling process must be understood to ensure that collected samples are representative of the waste. Factors which must be known and accounted for in the sampling plan include: if the waste is generated in batches; if there is a change in the raw materials used in a manufacturing process; if waste composition can vary substantially as a function of process temperatures or pressures; and if storage time after generation may vary.
3. Transitory events: Start-up, shut-down, slow-down, and maintenance transients can result in the generation of a waste that is not representative of the normal waste stream. If a sample was unknowingly collected at one of these intervals, incorrect conclusions could be drawn.

4. Climate: The sampling plan should specify any clothing needed for personnel to accommodate any extreme heat or cold that may be encountered. Dehydration and extensive exposure to sun, insects, or poisonous snakes must be considered.
5. Hazards: Each site can have hazards -- both expected and unexpected. For example, a general understanding of a process may lead a sampling team to be prepared for dealing with toxic or reactive material, but not for dealing with an electrical hazard or the potential for suffocation in a confined space. A thorough sampling plan will include a health and safety plan that will counsel team members to be alert to potential hazards.

9.2.2.4 Equipment

The choice of sampling equipment and sample containers will depend upon the previously described waste and site considerations. For the following reasons, the analytical chemist will play an important role in the selection of sampling equipment:

1. The analytical chemist is aware of the potential interactions between sampling equipment or container material with analytes of interest. As a result, he/she can suggest a material that minimizes losses by adsorption, volatilization, or contamination caused by leaching from containers or sampling devices.
2. The analytical chemist can specify cleaning procedures for sampling devices and containers that minimize sample contamination and cross contamination between consecutive samples.
3. The analytical chemist's awareness of analyte-specific properties is useful in selecting the optimum equipment (e.g., choice of sampling devices that minimize agitation for those samples that will be subjected to analysis for volatile compounds).

The final choice of containers and sampling devices will be made jointly by the analytical chemist and the group designing the sampling plan. The factors that will be considered when choosing a sampling device are:

1. Negative contamination: The potential for the measured analyte concentration to be artificially low because of losses from volatilization or adsorption.
2. Positive contamination: The potential for the measured analyte to be artificially high because of leaching or the introduction of foreign matter into the sample by particle fallout or gaseous air contaminants.
3. Cross contamination: A type of positive contamination caused by the introduction of part of one sample into a second sample during sampling, shipping, or storage.

4. Required sample volume: For physical and/or chemical analysis.
5. "Ease of use" of the sampling device and containers under the conditions that will be encountered on-site. This includes the ease of shipping to and from the site, ease of deployment, and ease of cleaning.
6. The degree of hazard associated with the deployment of one sampling device versus another.
7. Cost of the sampling device and of the labor for its deployment.

This section describes examples of sampling equipment and suggests potential uses for this equipment. Some of these devices are commercially available, but others will have to be fabricated by the user. The information in this section is general in nature and therefore limited.

Because each sampling situation is unique, the cited equipment and applications may have to be modified to ensure that a representative sample is collected and its physical and chemical integrity are maintained. It is the responsibility of those persons conducting sampling programs to make the appropriate modifications.

Table 9-7 contains examples of sampling equipment and potential applications. It should be noted that these suggested sampling devices may not be applicable to a user's situation due to waste- or site-specific factors. For example, if a waste is highly viscous or if a solid is clay-like, these properties may preclude the use of certain sampling devices. The size and depth of a lagoon or tank, or difficulties associated with accessing the waste, may also preclude use of a given device or require modification of its deployment.

The most important factors to consider when choosing containers for hazardous waste samples are compatibility with the waste, cost, resistance to breakage, and volume. Containers must not distort, rupture, or leak as a result of chemical reactions with constituents of waste samples. Thus, it is important to have some idea of the properties and composition of the waste. The containers must have adequate wall thickness to withstand handling during sample collection and transport to the laboratory. Containers with wide mouths are often desirable to facilitate transfer of samples from samplers to containers. Also, the containers must be large enough to contain the optimum sample volume.

Containers for collecting and storing hazardous waste samples are usually made of plastic or glass. Plastics that are commonly used to make the containers include high-density or linear polyethylene (LPE), conventional polyethylene, polypropylene, polycarbonate, Teflon FEP (fluorinated ethylene propylene), polyvinyl chloride (PVC), or polymethylpentene. Teflon FEP is almost universally usable due to its chemical inertness and resistance to breakage. However, its high cost severely limits its use. LPE, on the other hand, usually offers the best combination of chemical resistance and low cost when samples are to be analyzed for inorganic parameters.

TABLE 9-7. EXAMPLES OF SAMPLING EQUIPMENT FOR PARTICULAR WASTE TYPES

Waste Type	Waste Location or Container								
	Drum	Sacks and Bags	Open-bed Truck	Closed-Bed Truck	Storage Tanks or Bins	Waste Piles	Ponds, Lagoons, & Pits	Convey-or Belt	Pipe
Free-flowing liquids and slurries	Coliwasa	N/A	N/A	Coliwasa	Weighted bottle	N/A	Dipper	N/A	Dipper
Sludges	Trier	N/A	Trier	Trier	Trier	a	a		
Moist powders or granules	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	Dipper
Dry powders or granules	Thief	Thief	Thief	Thief	a	Thief	Thief	Shovel	Dipper
Sand or packed powders and granules	Auger	Auger	Auger	Auger	Thief	Thief	a	Dipper	Dipper
Large-grained solids	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Trier	Dipper

^a This type of sampling situation can present significant logistical sampling problems, and sampling equipment must be specifically selected or designed based on site and waste conditions. No general statement about appropriate sampling equipment can be made.

Glass containers are relatively inert to most chemicals and can be used to collect and store almost all hazardous waste samples, except those that contain strong alkali and hydrofluoric acid. Glass soda bottles are suggested due to their low cost and ready availability. Borosilicate glass containers, such as Pyrex and Corex, are more inert and more resistant to breakage than soda glass, but are expensive and not always readily available. Glass containers are generally more fragile and much heavier than plastic containers. Glass or FEP containers must be used for waste samples that will be analyzed for organic compounds.

The containers must have tight, screw-type lids. Plastic bottles are usually provided with screw caps made of the same material as the bottles. Buttress threads are recommended. Cap liners are not usually required for plastic containers. Teflon cap liners should be used with glass containers supplied with rigid plastic screw caps. (These caps are usually provided with waxed paper liners.) Teflon liners may be purchased from plastic specialty supply houses (e.g., Scientific Specialties Service, Inc., P.O. Box 352, Randallstown, Maryland 21133). Other liners that may be suitable are polyethylene, polypropylene, and neoprene plastics.

If the samples are to be submitted for analysis of volatile compounds, the samples must be sealed in air-tight containers.

Prior to sampling, a detailed equipment list should be compiled. This equipment list should be comprehensive and leave nothing to memory. The categories of materials that should be considered are:

1. Personnel equipment, which will include boots, rain gear, disposable coveralls, face masks and cartridges, gloves, etc.
2. Safety equipment, such as portable eyewash stations and a first-aid kit.
3. Field test equipment, such as pH meters and Draeger tube samplers.
4. An ample supply of containers to address the fact that once in the field, the sampling team may want to collect 50% more samples than originally planned or to collect a liquid sample, although the sampling plan had specified solids only.
5. Additional sampling equipment for use if a problem arises, e.g., a tool kit.
6. Shipping and office supplies, such as tape, labels, shipping forms, chain-of-custody forms and seals, field notebooks, random-number tables, scissors, pens, etc.

Composite Liquid Waste Sampler (Coliwasa)

The Coliwasa is a device employed to sample free-flowing liquids and slurries contained in drums, shallow tanks, pits, and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases.

The Coliwasa consists of a glass, plastic, or metal tube equipped with an end closure that can be opened and closed while the tube is submerged in the material to be sampled (refer to Figure 9-9).

Weighted Bottle

This sampler consists of a glass or plastic bottle, sinker, stopper, and a line that is used to lower, raise, and open the bottle. The weighted bottle samples liquids and free-flowing slurries. A weighted bottle with line is built to the specifications in ASTM Methods D270 and E300. Figure 9-10 shows the configuration of a weighted-bottle sampler.

Dipper

The dipper consists of a glass or plastic beaker clamped to the end of a two- or three-piece telescoping aluminum or fiberglass pole that serves as the handle. A dipper samples liquids and free-flowing slurries. Dippers are not available commercially and must be fabricated (Figure 9-11).

Thief

A thief consists of two slotted concentric tubes, usually made of stainless steel or brass. The outer tube has a conical pointed tip that permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample dry granules or powdered wastes whose particle diameter is less than one-third the width of the slots. A thief (Figure 9-12) is available at laboratory supply stores.

Trier

A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and to loosen soil. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier. Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter are available at laboratory supply stores. A large trier can be fabricated (see Figure 9-13).

Auger

An auger consists of sharpened spiral blades attached to a hard metal central shaft. An auger samples hard or packed solid wastes or soil. Augers are available at hardware and laboratory supply stores.

Scoops and Shovels

Scoops and shovels are used to sample granular or powdered material in bins, shallow containers, and conveyor belts. Scoops are available at laboratory supply houses. Flat-nosed shovels are available at hardware stores.

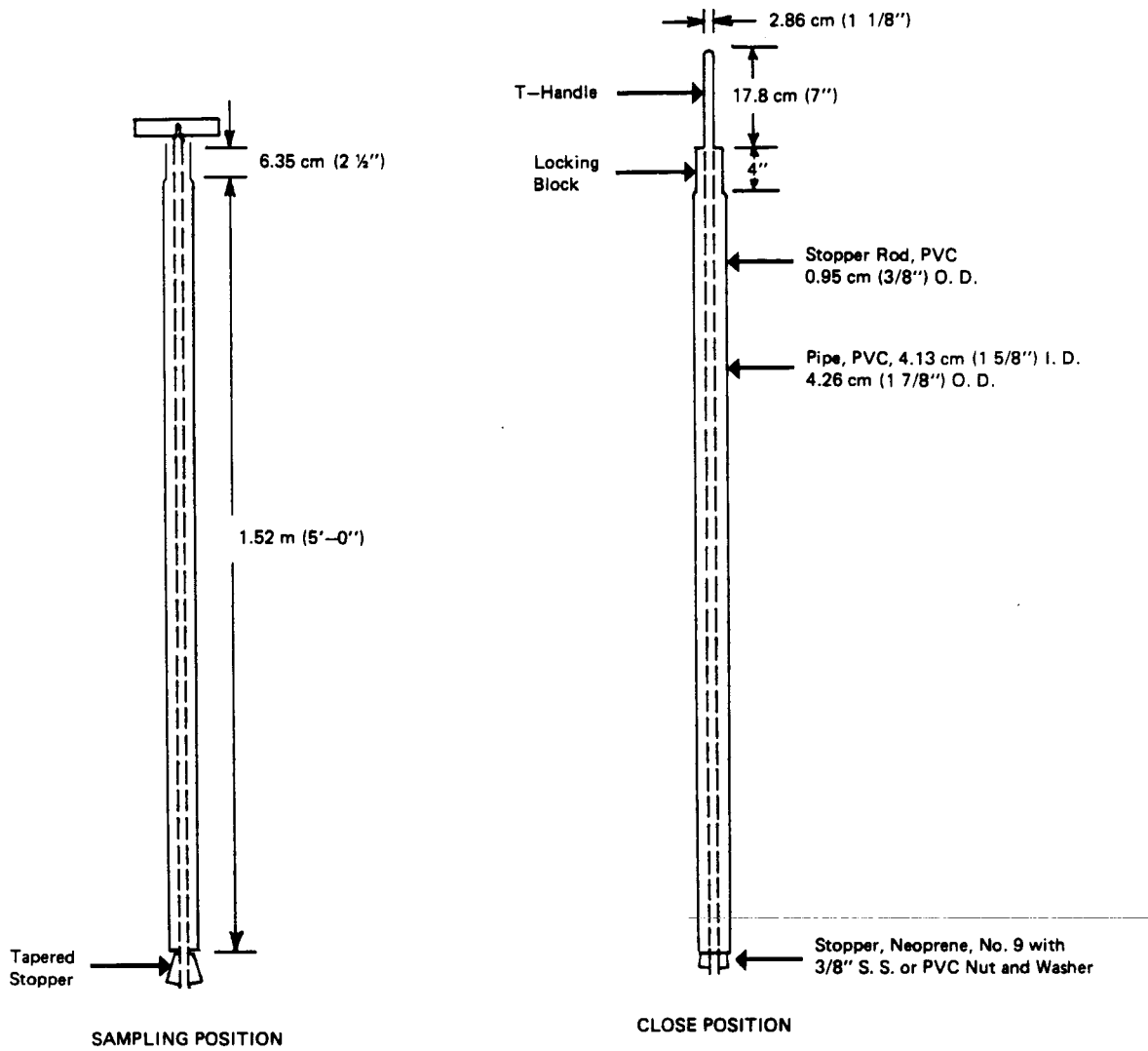


Figure 9-9. Composite liquid waste sampler (Coli-wasa).

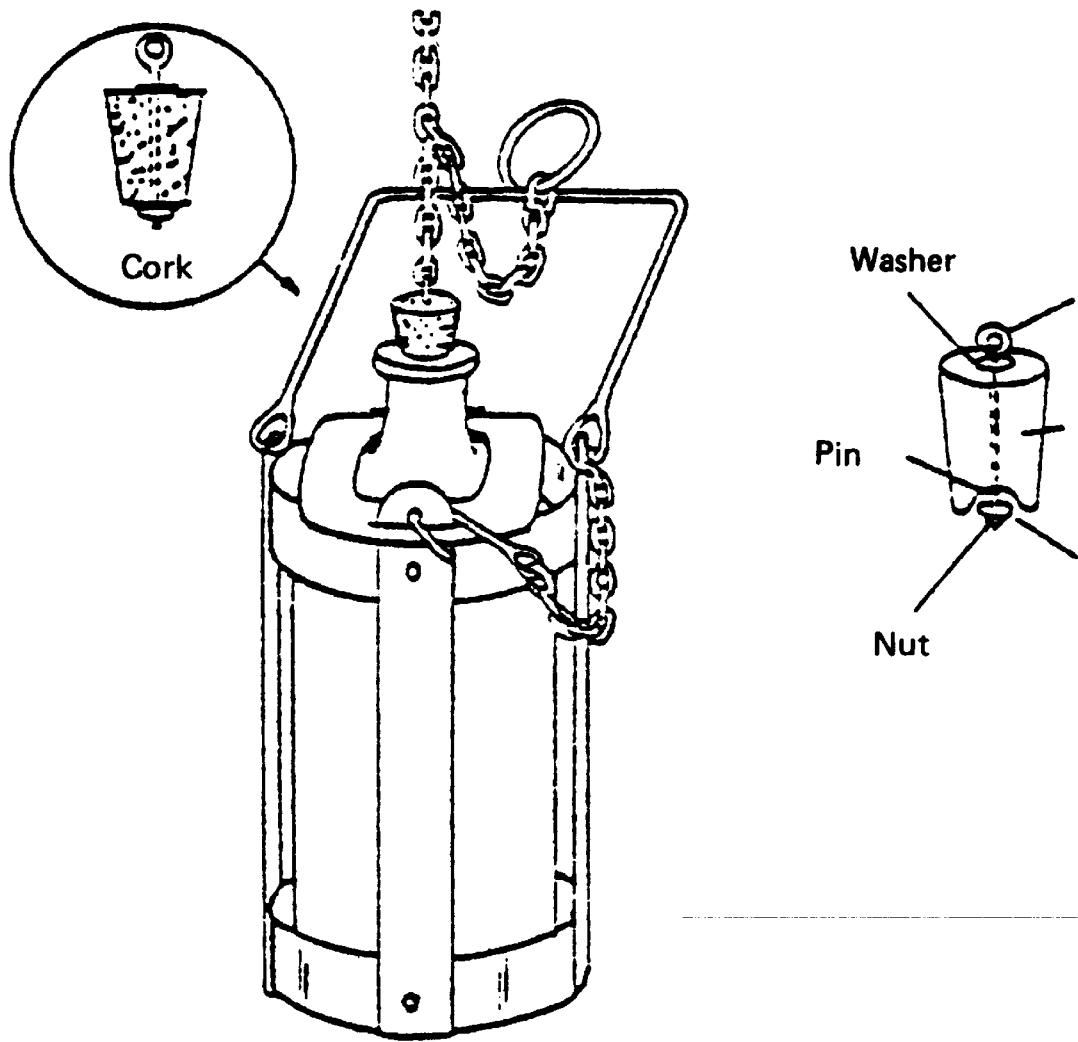


Figure 9-10. Weighted bottle sampler.

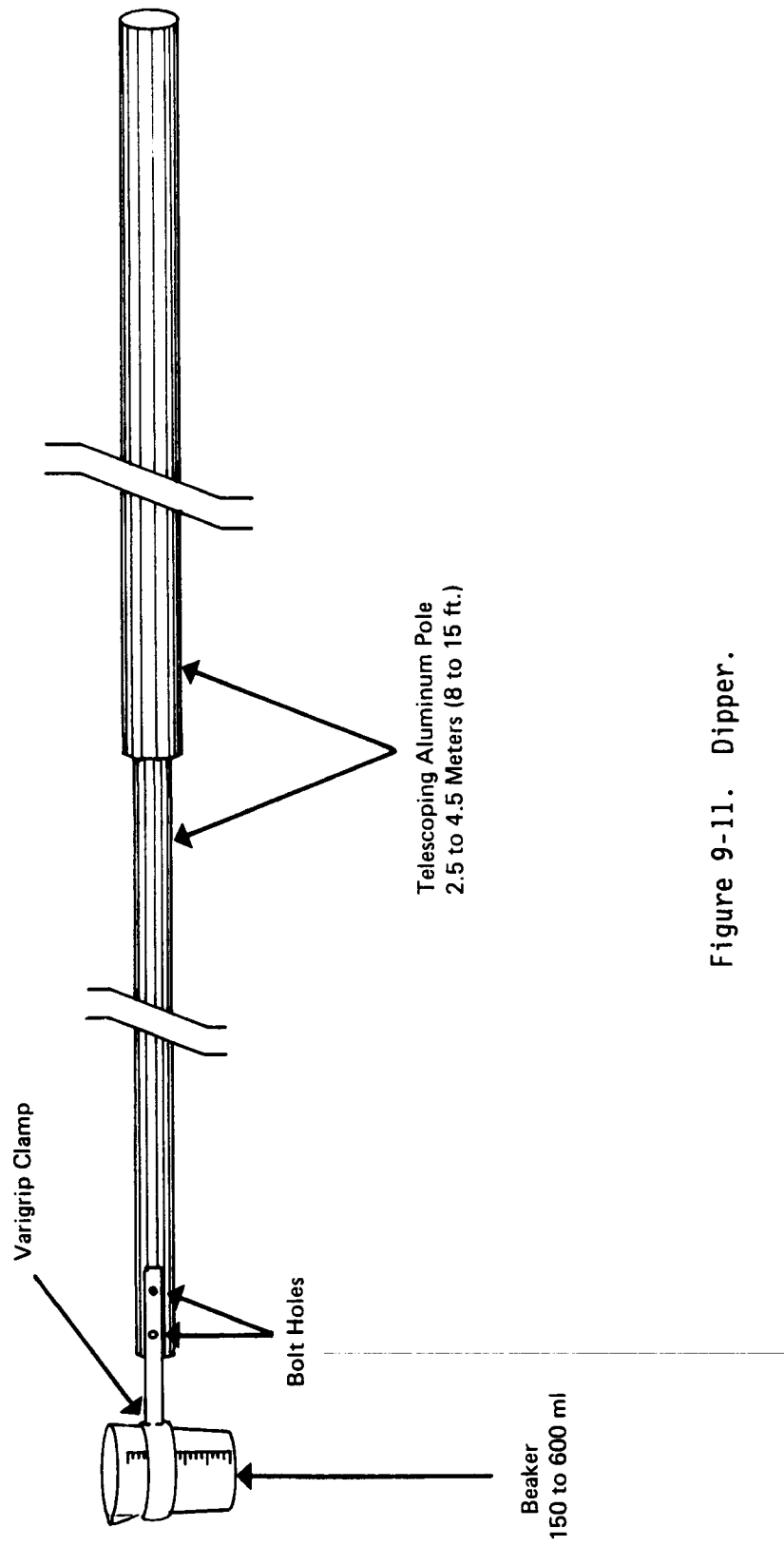


Figure 9-11. Dipper.

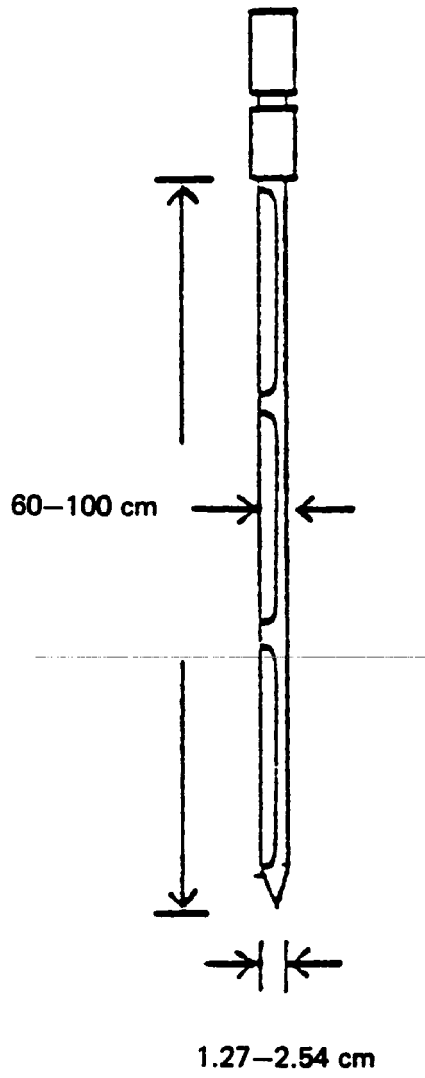


Figure 9-12. Thief sampler.

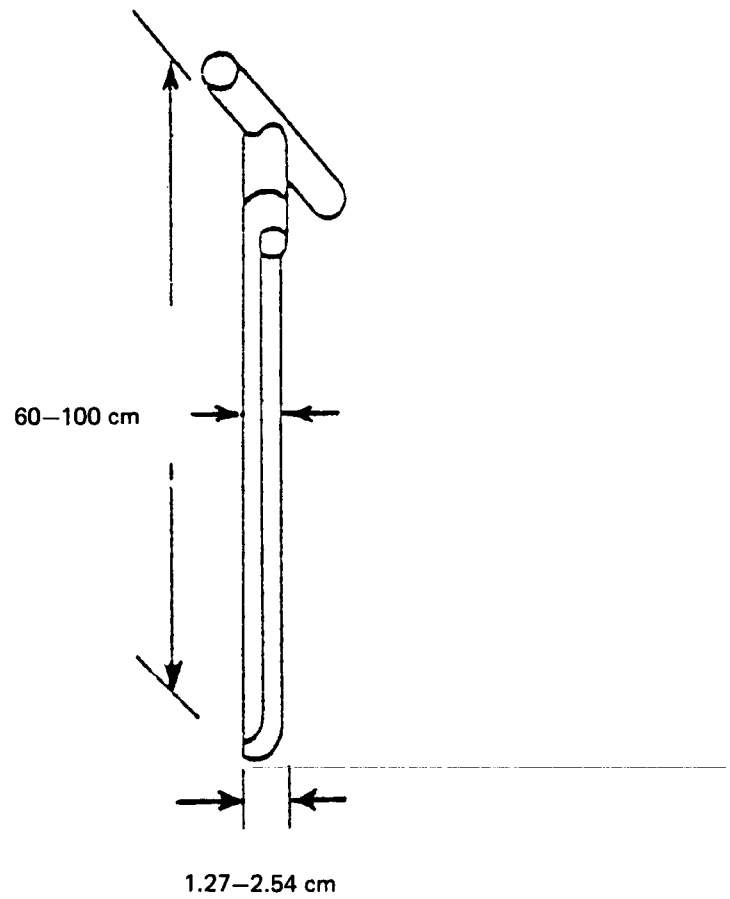
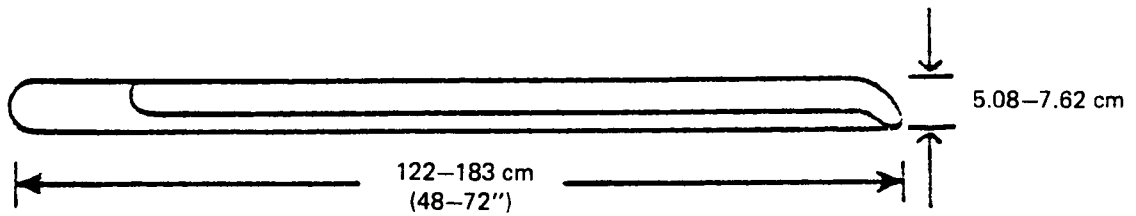


Figure 9-13. Sampling triers.

Bailer

The bailer is employed for sampling well water. It consists of a container attached to a cable that is lowered into the well to retrieve a sample. Bailers can be of various designs. The simplest is a weighted bottle or basally capped length of pipe that fills from the top as it is lowered into the well. Some bailers have a check valve, located at the base, which allows water to enter from the bottom as it is lowered into the well. When the bailer is lifted, the check valve closes, allowing water in the bailer to be brought to the surface. More sophisticated bailers are available that remain open at both ends while being lowered, but can be sealed at both top and bottom by activating a triggering mechanism from the surface. This allows more reliable sampling at discrete depths within a well. Perhaps the best known bailer of this latter design is the Kemmerer sampler.

Bailers generally provide an excellent means for collecting samples from monitoring wells. They can be constructed from a wide variety of materials compatible with the parameter of interest. Because they are relatively inexpensive, bailers can be easily dedicated to an individual well to minimize cross contamination during sampling. If not dedicated to a well, they can be easily cleaned to prevent cross contamination. Unfortunately, bailers are frequently not suited for well evacuation because of their small volume.

Suction Pumps

As the name implies, suction pumps operate by creating a partial vacuum in a sampling tube. This vacuum allows the pressure exerted by the atmosphere on the water in the well to force water up the tube to the surface. Accordingly, these pumps are located at the surface and require only that a transmission tube be lowered into the well. Unfortunately, their use is limited by their reliance on suction to depths of 20 to 25 ft, depending on the pump. In addition, their use may result in out-gassing of dissolved gases or volatile organics and is therefore limited in many sampling applications. In spite of this, suction methods may provide a suitable means for well evacuation because the water remaining in the well is left reasonably undisturbed.

A variety of pumps that operate on this principle are available, but the ones most commonly suggested for monitoring purposes are the centrifugal and peristaltic pumps. In the centrifugal pump, the fluid is displaced by the action of an impeller rotating inside the pump chamber. This discharges water by centrifugal force. The resulting pressure drop in the chamber creates a suction and causes water to enter the intake pipe in the well. These pumps can provide substantial yields and are readily available and inexpensive. The disadvantages are that they require an external power source and may be difficult to clean between sampling events. In addition, the materials with which these pumps are constructed may frequently be incompatible with certain sample constituents. However, their substantial pumping rates make them suitable for well evacuation.

Peristaltic pumps operate in a manner similar to centrifugal pumps but displace the fluid by mechanical peristalsis. A flexible transmission line is mounted around the perimeter of the pump chamber, and rotating rollers compress the tubing, forcing fluid movement ahead (the peristaltic effect) and inducing suction behind each roller. This design isolates the sample from the moving part of the pump and allows for easy cleaning by removal and replacement of the flexible tubing. Unfortunately, peristaltic pumps are generally capable of providing only relatively low yields. They are, therefore, not ideally suited to well evacuation.

Positive Displacement Pumps

A variety of positive displacement pumps are available for use in withdrawing water from wells. These methods utilize some pumping mechanism, placed in the well, that forces water from the bottom of the well to the surface by some means of positive displacement. This minimizes the potential for aerating or stripping volatile organics from the sample during removal from the well.

The submersible centrifugal pump is one common example of a positive displacement pump. It works in a manner similar to the centrifugal suction lift pump previously described, except that, in this case, both the pump and electric motor are lowered into the well. As the impeller rotates and fluid is brought into the pump, fluid is displaced up the transmission line and out of the well. These pumps are capable of providing a high yield. However, they require an external source of power and are frequently constructed with materials and contain lubricants incompatible with certain sample constituents, particularly organics. They also require considerable equipment and effort to move from well to well. Cleaning between sampling events is difficult as well, and, until recently, they have not been available for well diameters smaller than 3 in.

Piston-driven or reciprocating piston pumps are another example of common positive displacement pumps. These pumps consist of a piston in a submerged cylinder operated by a rod connected to the drive mechanism at the surface. A flap valve or ball-check valve is located immediately above or below the piston cylinder. As the piston is lowered in the cylinder, the check valve opens, and water fills the chamber. On the upstroke, the check valve closes, and water is forced out of the cylinder, up into the transmission line, and to the surface. The transmission line or piston contains a second check valve that closes on the downstroke, preventing water from re-entering the cylinder. These pumps are capable of providing high yields. However, moving these pumps from well to well is difficult, and their use in monitoring programs may require that a pump be dedicated to each well. Many of these pumps may not be constructed with materials compatible with monitoring certain constituents.

A special adaptation of this pump has recently become available for use in ground water monitoring. These piston pumps use compressed gas, rather than a rod connected to a driving mechanism at the surface, to drive the pistons. This provides a much more convenient and portable means for collecting samples from monitoring wells. Compressed-gas pumps provide good yields and can be constructed with materials compatible with many sampling programs.

Another positive displacement pump applicable for monitoring purposes is the gas-operated squeeze pump. This pump was originally developed by R. F. Middleburg of the U.S.G.S. and consequently is referred to as the Middleburg pump. It consists principally of a collapsible membrane inside a long, rigid housing, a compressed gas supply, and appropriate control valves. When the pump is submerged, water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and membrane, forcing the water upward through a sampling tube. When the pressure is released, the top check valve prevents the sample from flowing back down the discharge line, and water from the well again enters the pump through the bottom check valve.

Gas-operated squeeze pumps offer a number of advantages for use in ground water monitoring programs. They can be constructed in diameters as small as 1 in. and from a wide variety of materials. They are also relatively portable and are capable of providing a fair range of pumping rates. Most important, the driving gas does not contact the water sample, so that possible contamination or gas stripping does not occur. However, they do require a gas source, and withdrawal of water from substantial depths may require large gas volumes and long pumping cycles.

Jet pumps, a common type of submersible pump used in small domestic water wells, may in some cases be suggested for use in monitoring wells. These pumps operate by injecting water through a pipe down into the well. A venturi device is located at the intake portion of the pump. As the water injected from the surface passes through the constricted portion of the venturi, the velocity increases and pressures decrease according to Bernoulli's principle. If the discharge velocity at the nozzle is great enough, the pressure at this point will be lowered sufficiently to draw water into the venturi assembly through the intake and to bring it to the surface with the original water injected into the well. This additional increment of water is then made available at the surface as the pump's output. Because jet pumps require priming with water and because the water taken from the well mixes with water circulating in the system, they are clearly not applicable to collecting samples for monitoring purposes. For similar reasons, their use is not recommended for well evacuation.

Pressure-Vacuum Lysimeters

The basic construction of pressure-vacuum lysimeters (Wood, 1973), shown in Figure 9-14, consists of a porous ceramic cup, with a bubbling pressure of 1 bar or greater, attached to a short piece of PVC pipe of suitable diameter. Two tubes extend down into the device, as illustrated. Data by Silkworth and Grigal (1981) indicate that, of the two commercially available sampler sizes (2.2 and 4.8 cm diameter), the larger ceramic cup sampler is more reliable, influences water quality less, and yields samples of suitable volume for analysis.

Detailed installation instructions for pressure-vacuum lysimeters are given by Parizek and Lane (1970). Significant modification may be necessary to adapt these instruments to field use when heavy equipment is used. To prevent channelling of contaminated surface water directly to the sampling device, the sampler may be installed in the side wall of an access trench. Because random placement procedures may locate a sampler in the middle of an

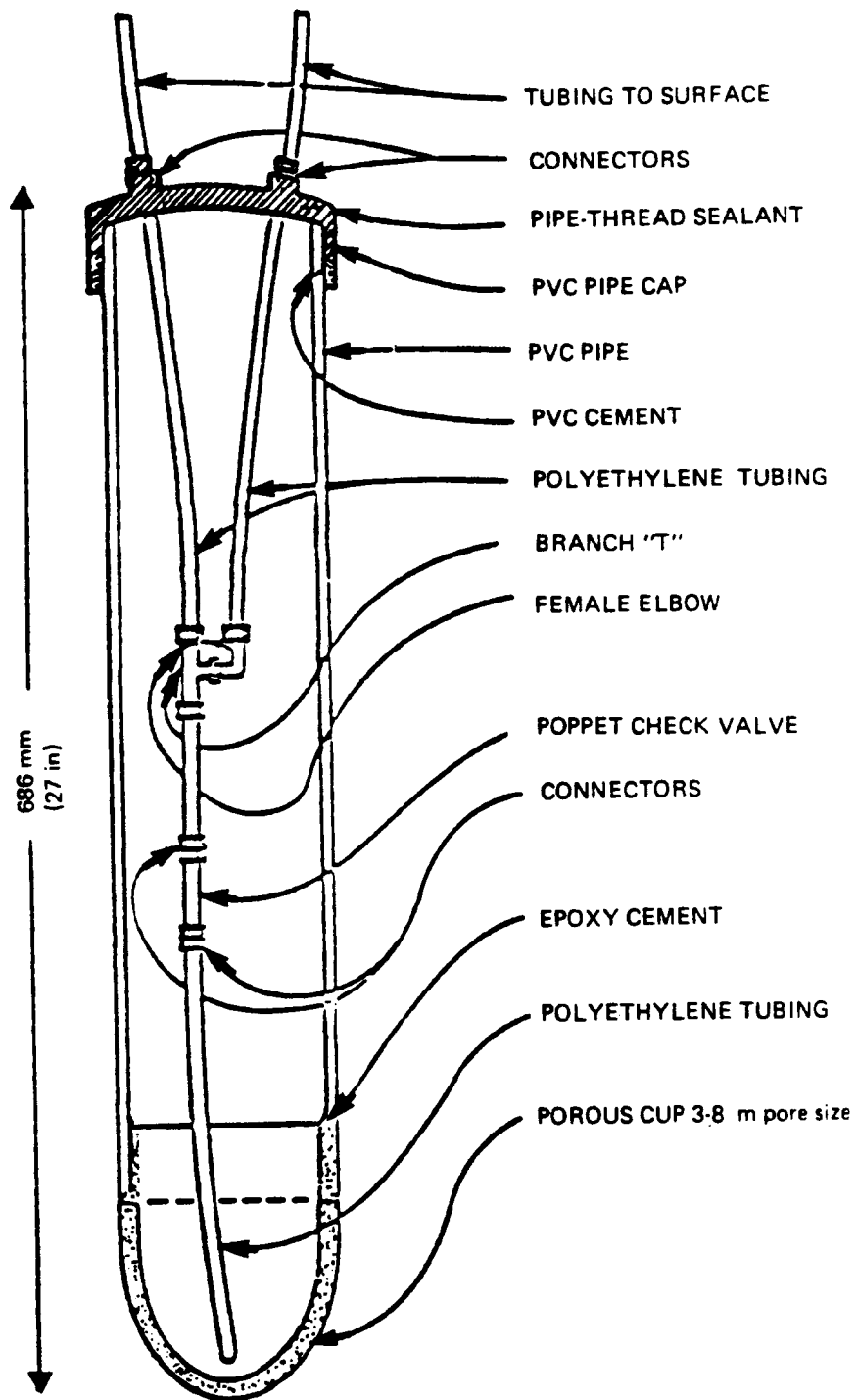


Figure 9-14. One example of a pressure-vacuum lysimeter (Wood, 1973).
 Reprinted by permission of the American Geophysical Union.

active area, the sample collection tube should be protected at the surface from heavy equipment by a manhole cover, brightly painted steel cage, or other structure. Another problem associated with such sampler placement is that its presence may alter waste management activities (i.e., waste applications, tilling, etc., will avoid the location): therefore, the sampler may not yield representative leachate samples. This problem may be avoided by running the collection tube horizontally underground about 10 m before surfacing.

For sampling after the unit is in place, a vacuum is placed on the system and the tubes are clamped off. Surrounding soil water is drawn into the ceramic cup and up the polyethylene tube. To collect the water sample, the vacuum is released, and one tube is placed in a sample container. Air pressure is applied to the other tube, forcing the liquid up the tube and into the sample container. Preliminary testing should ensure that waste products can pass into the ceramic cup. If sampling for organics, an inert tubing, such as one made of Teflon, should be substituted for the polyethylene pipe to prevent organic contamination.

The major advantages of these sampling devices are that they are easily available, relatively inexpensive to purchase and install, and quite reliable. The major disadvantage is the potential for water quality alterations due to the ceramic cup; this possible problem requires further testing. For a given installation, the device chosen should be specifically tested using solutions containing the soluble hazardous constituents of the waste to be land treated. This device is not recommended for volatiles unless a special trap device is used (Hazardous Waste Land Treatment, SW-874).

Vacuum Extractor

Vacuum extractors were developed by Duke and Haise (1973) to extract moisture from soils above the ground water table. The basic device consists of a stainless steel trough that contains ceramic tubes packed in soil. The unit is sized not to interfere with ambient soil water potentials (Corey, 1974); it is installed at a given depth in the soil with a slight slope toward the collection bottle, which is in the bottom of an adjacent access hole. The system is evacuated and moisture is moved from the adjacent soil into the ceramic tubes and into the collection bottle, from which it can be withdrawn as desired. The advantage of this system is that it yields a quantitative estimate of leachate flux as well as provides a water sample for analysis. The volume of collected leachate per unit area per unit time is an estimate of the downward movement of leachate water at that depth. The major disadvantages to this system are: it is delicate; it requires a trained operator; it estimates leachate quantity somewhat lower than actual field drainage; and it disturbs the soil above the sampler. Further details about the use of the vacuum extractor are given by Trout et al. (1975). Performance of this device when installed in clay soils is generally poor.

Trench Lysimeters

Trench lysimeters are named for the large access trench, or caisson, necessary for operation. Basic installation, as described by Parizek and Lane (1970), involves excavating a rather large trench and shoring up the side walls, taking care to leave open areas so that samplers can be placed in the side walls. Sample trays are imbedded in the side walls and connected by tubing to sample collection containers. The entire trench area is then covered to prevent flooding. One significant danger in using this system is the potential for accumulation of hazardous fumes in the trench, possibly endangering the health and safety of the person collecting the samples.

Trench lysimeters function by intercepting downward-moving water and diverting it into a collection device located at a lower elevation. The intercepting agent may be an open-ended pipe, sheet metal trough, pan, or other similar device. Pans 0.9 to 1.2 m in diameter have been successfully used in the field by Tyler and Thomas (1977). Because there is no vacuum applied to the system, only free water in excess of saturation is sampled. Consequently, samples are plentiful during rainy seasons but are nonexistent during the dry season.

Another variation of this system is to use a funnel filled with clean sand inserted into the sidewall of the trench. Free water will drain into a collection chamber, from which a sample is periodically removed by vacuum. A small sample collection device such as this may be preferable to the large trench because the necessary hole is smaller, so that installation is easier (Figure 9-15).

9.2.2.5 Quality Assurance and Quality Control

Quality assurance (QA) can briefly be defined as the process for ensuring that all data and the decisions based on these data are technically sound, statistically valid, and properly documented. Quality control (QC) procedures are the tools employed to measure the degree to which these quality assurance objectives are met.

A data base cannot be properly evaluated for accuracy and precision unless it is accompanied by quality assurance data. In the case of waste evaluation, these quality assurance data result from the implementation of quality control procedures during sampling and analysis. Quality control requirements for specific analytical methods are given in detail in each method in this manual: in this subsection, quality assurance and quality control procedures for sampling will be discussed.

Quality control procedures that are employed to document the accuracy and precision of sampling are:

1. Trip Blanks: Trip blanks should accompany sample containers to and from the field. These samples can be used to detect any contamination or cross-contamination during handling and transportation.
2. Field Blanks: Field blanks should be collected at specified frequencies, which will vary according to the probability of

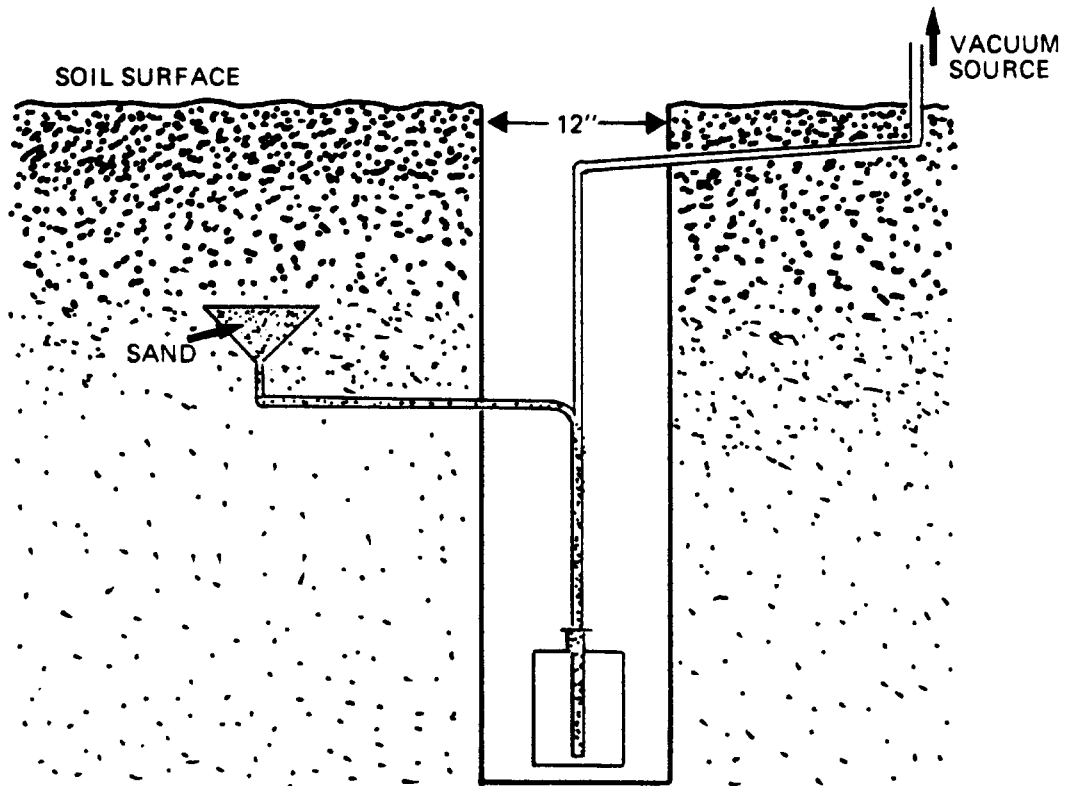


Figure 9-15. Schematic diagram of a sand filled funnel used to collect leachate from the unsaturated zone.

contamination or cross-contamination. Field blanks are often metal- and/or organic-free water aliquots that contact sampling equipment under field conditions and are analyzed to detect any contamination from sampling equipment, cross contamination from previously collected samples, or contamination from conditions during sampling (e.g., airborne contaminants that are not from the waste being sampled).

3. Field Duplicates: Field duplicates are collected at specified frequencies and are employed to document precision. The precision resulting from field duplicates is a function of the variance of waste composition, the variance of the sampling technique, and the variance of the analytical technique.
4. Field Spikes: Field spikes are infrequently used to determine the loss of parameters of interest during sampling and shipment to the laboratories. Because spiking is done in the field, the making of spiked samples or spiked blanks is susceptible to error. In addition, compounds can be lost during spiking, and equipment can be contaminated with spiking solutions. To eliminate these and other problems, some analysts spike blanks or matrices similar to the waste in the laboratory and ship them, along with sample containers, to the field. This approach also has its limitation because the matrix and the handling of the spike are different from those of the actual sample. In all cases, the meaning of a low field-spike recovery is difficult to interpret, and thus, field spikes are not commonly used.

In addition to the above quality control samples, a complete quality assurance program will ensure that standard operating procedures (SOPs) exist for all essential aspects of a sampling effort. SOPs should exist for the following steps in a sampling effort:

1. Definition of objectives (refer to Section 9.2.1).
2. Design of sampling plans (refer to Section 9.2.2).
3. Preparation of containers and equipment (refer to the specific analytical methods).
4. Maintenance, calibration, and cleaning of field equipment (refer to instrument manuals or consult a chemist for cleaning protocols).
5. Sample preservation, packaging, and shipping (refer to the analytical methods and to Section 9.2.2.7).
6. Health and safety protocols (refer to Section 9.2.2.6).
7. Chain-of-custody protocols (refer to Section 9.2.2.7).

In addition to the above protocols, numerous other QA/QC protocols must be employed to document the accuracy of the analytical portion of a waste evaluation program.

9.2.2.6 Health and Safety

Safety and health must also be considered when implementing a sampling plan. A comprehensive health and safety plan has three basic elements: (1) monitoring the health of field personnel; (2) routine safety procedures; and (3) emergency procedures.

Employees who perform field work, as well as those exposed to chemicals in the laboratory, should have a medical examination at the initiation of employment and routinely thereafter. This exam should preferably be performed and evaluated by medical doctors who specialize in industrial medicine. Some examples of parts of a medical examination that ought to be performed are: documentation of medical history; a standard physical exam; pulmonary functions screening; chest X-ray; EKG; urinalysis; and blood chemistry. These procedures are useful to: (1) document the quality of an employee's health at the time of matriculation; (2) ensure the maintenance of good health; and (3) detect early signs of bodily reactions to chemical exposures so they can be treated in a timely fashion. Unscheduled examinations should be performed in the event of an accident, illness, or exposure or suspected exposure to toxic materials.

Regarding safety procedures, personnel should be aware of the common routes of exposure to chemicals (i.e., inhalation, contact, and ingestion) and be instructed in the proper use of safety equipment, such as Draeger tube air samplers to detect air contamination, and in the proper use of protective clothing and respiratory equipment. Protocols should also be defined stating when safety equipment should be employed and designating safe areas where facilities are available for washing, drinking, and eating.

Even when the utmost care is taken, an emergency situation can occur as a result of an unanticipated explosion, electrical hazard, fall, or exposure to a hazardous substance. To minimize the impact of an emergency, field personnel should be aware of basic first aid and have immediate access to a first-aid kit. Phone numbers for both police and the nearest hospital should be obtained and kept by each team member before entering the site. Directions to the nearest hospital should also be obtained so that anyone suffering an injury can be transported quickly for treatment.

9.2.2.7 Chain of Custody

An essential part of any sampling/analytical scheme is ensuring the integrity of the sample from collection to data reporting. The possession and handling of samples should be traceable from the time of collection through analysis and final disposition. This documentation of the history of the sample is referred to as chain of custody.

Chain of custody is necessary if there is any possibility that the analytical data or conclusions based upon analytical data will be used in litigation. In cases where litigation is not involved, many of the chain-of-custody procedures are still useful for routine control of sample flow. The components of chain of custody -- sample seals, a field logbook, chain-of-custody record, and sample analysis request sheet -- and the procedures for their use are described in this section.

A sample is considered is considered to be under a person's custody if it is (1) in a person's physical possession, (2) in view of the person after taking possession, and (3) secured by that person so that no one can tamper with it, or secured by that person in an area that is restricted to authorized personnel. A person who has samples in custody must comply with the following procedures.

(The material presented here briefly summarizes the major aspects of chain of custody. The reader is referred to NEIC Policies and Procedures, EPA-330/9/78/001-R [as revised 1/82], or other manual, as appropriate, for more information.)

Sample labels (Figure 9-16) are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate and should include at least the following information:

- Sample number.
- Name of collector.
- Date and time of collection.
- Place of collection.

Labels should be affixed to sample containers prior to or at the time of sampling and should be filled out at the time of collection.

Sample seals are used to detect unauthorized tampering of samples following sample collection up to the time of analysis. Gummed paper seals may be used for this purpose. The paper seal should include, minimally, the following information:

- Sample number. (This number must be identical with the number on the sample label.)
- Name of collector.
- Date and time of sampling.
- Place of collection.

The seal must be attached in such a way that it is necessary to break it in order to open the sample container. (An example of an official sample seal is shown in Figure 9-17.) Seals must be affixed to containers before the samples leave the custody of sampling personnel.

All information pertinent to a field survey or sampling must be recorded in a logbook. This should be bound, preferably with consecutively numbered pages that are 21.6 by 27.9 cm (8-1/2 by 11 in.). At a minimum, entries in the logbook must include the following:

- Location of sampling point.
- Name and address of field contact.
- Producer of waste and address, if different from location.
- Type of process producing waste (if known).
- Type of waste (e.g., sludge, wastewater).
- Suspected waste composition, including concentrations.
- Number and volume of sample taken.

Collector _____ Sample No. _____

Place of Collection _____

Date Sampled _____ Time Sampled _____

Field Information _____

Figure 9-16. Example of Sample Label

NAME AND ADDRESS OF ORGANIZATION COLLECTING SAMPLES

Person Collecting Sample _____ Sample No. _____
(signature)

Date Collected _____ Time Collected _____

Place Collected _____

Figure 9-17. Example of Official Sample Seal

Purpose of sampling (e.g., surveillance, contract number).
Description of sampling point and sampling methodology.
Date and time of collection.
Collector's sample identification number(s).
Sample distribution and how transported (e.g., name of laboratory, UPS, Federal Express).
References, such as maps or photographs of the sampling site.
Field observations.
Any field measurements made (e.g., pH, flammability, explosivity).
Signatures of personnel responsible for observations.

Sampling situations vary widely. No general rule can be given as to the extent of information that must be entered in the logbook. A good rule, however, is to record sufficient information so that anyone can reconstruct the sampling without reliance on the collector's memory. The logbook must be stored safely.

To establish the documentation necessary to trace sample possession from the time of collection, a chain-of-custody record should be filled out and should accompany every sample. This record becomes especially important if the sample is to be introduced as evidence in a court litigation. (A chain-of-custody record is illustrated in Figure 9-18.)

The record should contain, minimally, the following information:

Sample number.
Signature of collector.
Date and time of collection.
Place and address of collection.
Waste type.
Signature of persons involved in the chain of possession.
Inclusive dates of possession.

The sample analysis request sheet (Figure 9-19) is intended to accompany the sample on delivery to the laboratory. The field portion of this form is completed by the person collecting the sample and should include most of the pertinent information noted in the logbook. The laboratory portion of this form is intended to be completed by laboratory personnel and to include, minimally:

Name of person receiving the sample.
Laboratory sample number.
Date and time of sample receipt.
Sample allocation.
Analyses to be performed.

The sample should be delivered to the laboratory for analysis as soon as practicable -- usually within 1 or 2 days after sampling. The sample must be accompanied by the chain-of-custody record (Figure 9-18) and by a sample analysis request sheet (Figure 9-19). The sample must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

SAMPLING ANALYSIS REQUEST

Part I: Field Section

Collector _____ Date Sampled _____ Time _____ hours

Affiliation of Sampler _____

Address _____
 number street city state zip

Telephone (____) _____ Company Contact _____

LABORATORY

SAMPLE NUMBER	COLLECTOR'S SAMPLE NO.	TYPE OF SAMPLE*	FIELD INFORMATION**
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Analysis Requested _____

Special Handling and/or Storage _____

PART II: LABORATORY SECTION**

Received by _____ Title _____ Date _____

Analysis Required _____

* Indicate whether sample is soil, sludge, etc.

** Use back of page for additional information relative to sample location.

Figure 9-19. Example of hazardous waste sample analysis sheet.

Any material that is identified in the DOT Hazardous Material Table (49 CFR 172.101) must be transported as prescribed in the table. All other hazardous waste samples must be transported as follows:

1. Collect sample in a 16-oz or smaller glass or polyethylene container with nonmetallic Teflon-lined screw cap. For liquids, allow sufficient air space, approximately 10% by volume) so that the container is not full at 54°C (130 °F). If collecting a solid material, the container plus contents should not exceed 1 lb net weight. If sampling for volatile organic analysis, fill VOA container to septum but place the VOA container inside a 16-oz or smaller container so that the required air space may be provided. Large quantities, up to 3.785 liters (1 gal), may be collected if the sample's flash point is 23°C (75°F) or higher. In this case, the flash point must be marked on the outside container (e.g., carton or cooler), and shipping paper should state that "Flash point is 73°F or higher."
2. Seal sample and place in a 4-mil-thick polyethylene bag, one sample per bag.
3. Place sealed bag inside a metal can with noncombustible, absorbent cushioning material (e.g., vermiculite or earth) to prevent breakage, one bag per can. Pressure-close the can and use clips, tape, or other positive means to hold the lid securely.
4. Mark the can with:

Name and address of originator.
"Flammable Liquid, N.O.S. UN 1993."
(or, "Flammable Solid, N.O.S. UN 1325".)

NOTE: UN numbers are now required in proper shipping names.

5. Place one or more metal cans in a strong outside container such as a picnic cooler or fiberboard box. Preservatives are not used for hazardous waste site samples.
6. Prepare for shipping: The words "Flammable Liquid, N.O.S. UN 1993" or "Flammable Solid, N.O.S. UN 1325"; "Cargo Aircraft Only" (if more than 1 qt net per outside package); "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight ____" or "Net Volume ____" (of hazardous contents) should be indicated on shipping papers and on the outside of the outside shipping container. The words "This Side Up" or "This End Up" should also be on container. Sign the shipper certification.

7. Stand by for possible carrier requests to open outside containers for inspection or to modify packaging. (It is wise to contact carrier before packing to ascertain local packaging requirements.) Remain in the departure area until the carrier vehicle (aircraft, truck, etc.) is on its way.

At the laboratory, a sample custodian should be assigned to receive the samples. Upon receipt of a sample, the custodian should inspect the condition of the sample and the sample seal, reconcile the information on the sample label and seal against that on the chain-of-custody record, assign a laboratory number, log in the sample in the laboratory logbook, and store it in a secured sample storage room or cabinet until it is assigned to an analyst for analysis.

The sample custodian should inspect the sample for any leakage from the container. A leaky container containing a multiphase sample should not be accepted for analysis. This sample will no longer be a representative sample. If the sample is contained in a plastic bottle and the container walls show that the sample is under pressure or releasing gases, the sample should be treated with caution because it may be explosive or release extremely poisonous gases. The custodian should examine whether the sample seal is intact or broken, because a broken seal may mean sample tampering and would make analysis results inadmissible as evidence in court. Any discrepancies between the information on the sample label and seal and the information that is on the chain-of-custody record and the sample analysis request sheet should be resolved before the sample is assigned for analysis. This effort might require communication with the sample collector. Results of the inspection should be noted on the sample analysis request sheet and on the laboratory sample logbook.

Incoming samples usually carry the inspector's or collector's identification numbers. To identify these samples further, the laboratory should assign its own identification numbers, which normally are given consecutively. Each sample should be marked with the assigned laboratory number. This number is correspondingly recorded on a laboratory sample log book along with the information describing the sample. The sample information is copied from the sample analysis request sheet and cross-checked against that on the sample label.

In most cases, the laboratory supervisor assigns the sample for analysis. The supervisor should review the information on the sample analysis request sheet, which now includes inspection notes recorded by the laboratory sample custodian. The technician assigned to analysis should record in the laboratory notebook the identifying information about the sample, the date of receipt, and other pertinent information. This record should also include the subsequent testing data and calculations. The sample may have to be split with other laboratories in order to obtain all the necessary analytical information. In this case, the same type of chain-of-custody procedures must be employed while the sample is being transported and at the other laboratory.

Once the sample has been received in the laboratory, the supervisor or his/her assignee is responsible for its care and custody. That person should be prepared to testify that the sample was in his/her possession or secured in the laboratory at all times, from the moment it was received from the custodian until the analyses were performed.

9.2.3 Sample Plan Implementation

Prior to implementing a sampling plan, it is often strategic to walk through the sampling plan mentally, starting with the preparation of equipment until the time when samples are received at the laboratory. This mental excursion should be in as much detail as can be imagined, because the small details are the ones most frequently overlooked. By employing this technique, items not included on the equipment list may be discovered, as well as any major oversight that could cause the sampling effort to fail. During this review of the sampling plan, an attempt should be made to anticipate what could go wrong. A solution to anticipated problems should be found, and, if necessary, materials needed for solving these problems should be added to the equipment list.

The remainder of this section discusses examples of sampling strategies for different situations that may be encountered.

Containers

Prior to discussing the sampling of containers, the term must be defined. The term container, as used here, refers to receptacles that are designed for transporting materials, e.g., drums and other smaller receptacles, as opposed to stationary tanks. Weighted bottles, Coliwassas, drum thieves, or triers are the sampling devices that are chosen for the sampling of containers. (See Section 9.2.2.4 for a full discussion of sampling equipment.)

The sampling strategy for containers varies according to (1) the number of containers to be sampled and (2) access to the containers. Ideally, if the waste is contained in several containers, every container will be sampled. If this is not possible due to the large number of containers or to cost factors, a subset of individual containers must be randomly selected for sampling. This can be done by assigning each container a number and then randomly choosing a set of numbers for sampling.

Access to a container will affect the number of samples that can be taken from the container and the location within the container from which samples can be taken. Ideally, several samples should be taken from locations displaced both vertically and horizontally throughout the waste. The number of samples required for reliable sampling will vary depending on the distribution of the waste components in the container. At a minimum with an unknown waste, a sufficient number and distribution of samples should be taken to address any possible vertical anomalies in the waste. This is because contained wastes have a much greater tendency to be nonrandomly heterogeneous in a vertical rather than a horizontal direction due to (1) settling of solids and the denser phases of liquids and (2) variation in the content of the waste as it enters the container. Bags, paper drums, and open-headed steel drums (of which the entire top can be removed) generally do not restrict access to the waste and therefore do not limit sampling.

When access to a container is unlimited, a useful strategy for obtaining a representative set of samples is a three-dimensional simple random sampling strategy in which the container is divided by constructing an imaginary three-dimensional grid (see Figure 9-20), as follows. First, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the container is large. (Cylindrical containers can be divided into imaginary concentric circles, which are then further divided into grids of equal size.) Each section is assigned a number. The height of the container is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are then assigned numbers. Specific levels and grid locations are then selected for sampling using a random-number table or random-number generator. (an alternative means of choosing random sampling locations using circumference and diameter dimensions is discussed in Section 9.2.2.1.)

Another appropriate sampling approach is the two-dimensional simple random sampling strategy, which can usually yield a more precise sampling when fewer samples are collected. This strategy involves (1) dividing the top surface of the waste into an imaginary grid as in the three-dimensional strategy, (2) selecting grid sections for sampling using random-number tables or random-number generators, and (3) sampling each selected grid point in a vertical manner along the entire length from top to bottom using a sampling device such as a drum thief or Coliwasa.

Some containers, such as drums with bung openings, limit access to the contained waste and restrict sampling to a single vertical plane. Samples taken in this manner can be considered representative of the entire container only if the waste is known to be homogenous or if no horizontal stratification has occurred. Precautions must be taken when sampling any type of steel drum because the drum may explode or expel gases and/or pressurized liquids. An EPA/NEIC manual, "Safety Manual for Hazardous Waste Site Investigation," addresses these safety precautions.

Tanks

Tanks are essentially large containers. The considerations involved in sampling tanks are therefore similar to those for sampling containers. As with containers, the goal of sampling tanks is to acquire a sufficient number of samples from different locations within the waste to provide analytical data that are representative of the entire tank contents.

The accessibility of the tank contents will affect the sampling methodology. If the tank is an open one, allowing unrestricted access, then usually a representative set of samples is best obtained using the three-dimensional simple random sampling strategy, as described for containers (see also Section 9.2.2.1). This strategy involves dividing the tank contents into an imaginary three-dimensional grid. As a first step, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the tank is large.

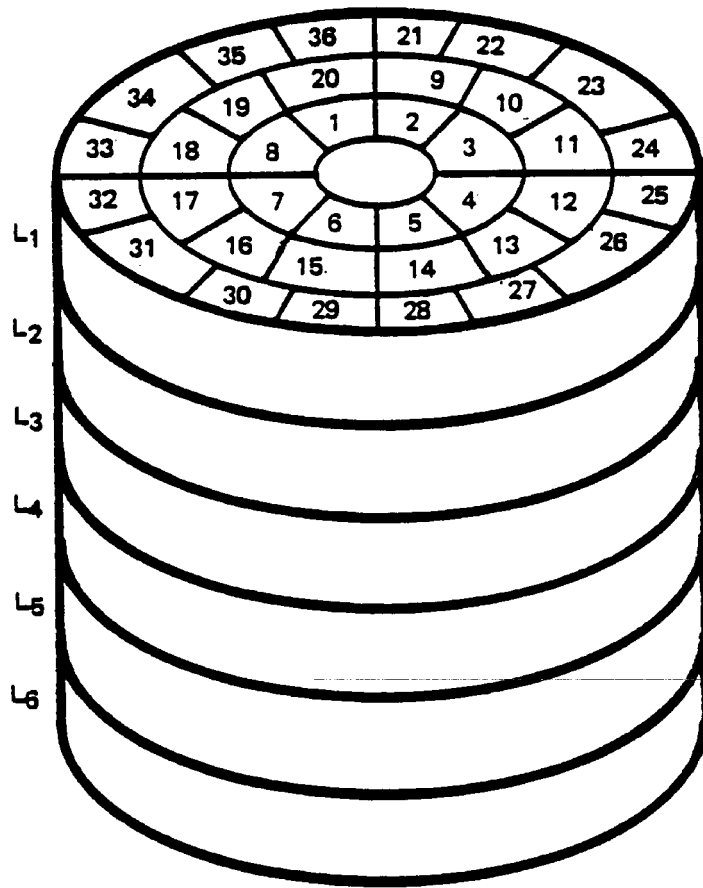


Figure 9-20. Container divided into an imaginary three-dimensional grid.

(Cylindrical tanks can be divided into imaginary concentric circles, which are then further divided into grids of equal size.) Each section is assigned a number. The height of the tank is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are assigned numbers. Specific levels and grid locations are then selected for sampling using a random-number table or random-number generator.

A less comprehensive sampling approach may be appropriate if information regarding the distribution of waste components is known or assumed (e.g., if vertical compositing will yield a representative sample). In such cases, a two-dimensional simple random sampling strategy may be appropriate. In this strategy, the top surface of the waste is divided into an imaginary grid; grid sections are selected using random-number tables or random-number generators; and each selected grid point is then sampled in a vertical manner along the entire length from top to bottom using a sampling device such as a weighted bottle, a drum thief, or Coliwasa. If the waste is known to consist of two or more discrete strata, a more precise representation of the tank contents can be obtained by using a stratified random sampling strategy, i.e., by sampling each stratum separately using the two- or three-dimensional simple random sampling strategy.

Some tanks permit only limited access to their contents, which restricts the locations within the tank from which samples can be taken. If sampling is restricted, the sampling strategy must, at a minimum, take sufficient samples to address the potential vertical anomalies in the waste in order to be considered representative. This is because contained wastes tend to display vertical, rather than horizontal, nonrandom heterogeneity due to settling of suspended solids or denser liquid phases. If access restricts sampling to a portion of the tank contents (e.g., in an open tank, the size of the tank may restrict sampling to the perimeter of the tank; in a closed tank, the only access to the waste may be through inspection ports), then the resulting analytical data will be deemed representative only of the accessed area, not of the entire tank contents unless the tank contents are known to be homogeneous.

If a limited access tank is to be sampled, and little is known about the distribution of components within the waste, a set of samples that is representative of the entire tank contents can be obtained by taking a series of samples as the tank contents are being drained. This should be done in a simple random manner by estimating how long it will take to drain the tank and then randomly selecting times during drainage for sampling.

The most appropriate type of sampling device for tanks depends on the tank parameters. In general, subsurface samples (i.e., pond samplers) are used for shallow tanks, and weighted bottles are usually employed for tanks deeper than 5 ft. Dippers are useful for sampling pipe effluents.

Waste Piles

In waste piles, the accessibility of waste for sampling is usually a function of pile size, a key factor in the design of a sampling strategy for a waste pile. Ideally, piles containing unknown wastes should be sampled using a three-dimensional simple random sampling strategy. This strategy can be employed only if all points within the pile can be accessed. In such cases, the pile should be divided into a three-dimensional grid system, the grid sections assigned numbers, and the sampling points then chosen using random-number tables or random-number generators.

If sampling is limited to certain portions of the pile, then the collected sample will be representative only of those portions, unless the waste is known to be homogenous.

In cases where the size of a pile impedes access to the waste, a set of samples that are representative of the entire pile can be obtained with a minimum of effort by scheduling sampling to coincide with pile removal. The number of truckloads needed to remove the pile should be estimated and the truckloads randomly chosen for sampling.

The sampling devices most commonly used for small piles are thieves, triers, and shovels. Excavation equipment, such as backhoes, can be useful for sampling medium-sized piles.

Landfills and Lagoons

Landfills contain primarily solid waste, whereas lagooned waste may range from liquids to dried sludge residues. Lagooned waste that is either liquid or semisolid is often best sampled using the methods recommended for large tanks. Usually, solid wastes contained in a landfill or lagoon are best sampled using the three-dimensional random sampling strategy.

The three-dimensional random sampling strategy involves establishing an imaginary three-dimensional grid of sampling points in the waste and then using random-number tables or random-number generators to select points for sampling. In the case of landfills and lagoons, the grid is established using a survey or map of the area. The map is divided into two two-dimensional grids with sections of equal size. (An alternative way of choosing random sampling locations is presented in the second example described in Section 9.2.2.1) These sections are then assigned numbers sequentially.

Next, the depth to which sampling will take place is determined and subdivided into equal levels, which are also sequentially numbered. (The lowest sampling depth will vary from landfill to landfill. Usually, sampling extends to the interface of the fill and the natural soils. If soil contamination is suspected, sampling may extend into the natural soil.) The horizontal and vertical sampling coordinates are then selected using random-number tables or random-number generators. If some information is known about the nature of the waste, then a modified three-dimensional strategy may be more appropriate. For example, if the landfill consists of several cells, a more precise measurement may be obtained by considering each cell as a stratum and employing a stratified three-dimensional random sampling strategy (see Section 9.1).

Hollow-stem augers combined with split-spoon samplers are frequently appropriate for sampling landfills. Water-driven or water-rinsed coring equipment should not be used for sampling because the water can rinse chemical components from the sample. Excavation equipment, such as backhoes, may be useful in obtaining samples at various depths; the resulting holes may be useful for viewing and recording the contents of the landfill.

9.2.4 Sample Compositing

The compositing of samples, is usually done for cost-saving reasons, involves the combining of a number of samples or aliquots of a number of samples collected from the same waste. The disadvantage of sample compositing is the loss of concentration variance data, whereas the advantage is that, for a given analytical cost, a more representative (i.e., more accurate) sample is obtained.

It is usually most expedient and cost effective to collect component samples in the field and to composite aliquots of each sample later in the laboratory. Then, if after reviewing the data any questions arise, the samples can be recomposited in a different combination, or each component sample can be analyzed separately to determine better the variation of waste composition over time and space, or to determine better the precision of an average number. The fact that this recompositing of samples can occur without the need to resample often results in a substantial cost savings.

To ensure that recompositing can be done at a later date, it is essential to collect enough sample volume in the field so that, under normal circumstances, enough component sample will remain following compositing to allow for a different compositing scheme or even for an analysis of the component samples themselves.

The actual compositing of samples requires the homogenization of all component samples to ensure that a representative subsample is aliquoted. The homogenization procedure, and the containers and equipment used for compositing, will vary according to the type of waste being composited and the parameters to be measured. Likewise, the composite sample itself will be homogenized prior to the subsampling of analytical aliquots.

9.2.5 References

1. Corey, P.R., Soil Water Monitoring, Unpublished Report to Dept. of Agr. Eng., Colorado State University, Fort Collins, Colorado, 1974.
2. Duke, H.R. and H.R. Haise, Vacuum Extractors to Assess Deep percolation Losses and Chemical Constituents of Soil Water, Soil Sci, Soc, Am. Proc. 37, 963-4 (1973)
3. Parizek, R.R. and B.E. Lane, Soil-Water Sampling Using Pan and Deep Pressure-Vacuum Lysimeters, J.Hydr. 11, 1-21 (1970).

4. Silkworth, D.R. and D.F. Grigal, Field Comparison of Soil Solution Samplers, Soil Sci. Soc. Am. J. 45, 440-442 (1981).
5. Trout, T.J., J.L. Smith, and D.B. McWhorter, Environmental Effects of Land Application of Digested Municipal Sewage Sludge, Report submitted to City of Boulder, Colorado, Dept. of Agr. Engr., Colorado State Univ., For Collins, Colorado, 1975.
6. Tyler, D.D. and G.W. Thomas, Lysimeter Measurements of Nitrate and Chloride Losses and No-tillage Corn, J. Environ. Qual. 6, 63-66 (1977).
7. U.S. Department of Transportation, Hazardous Materials Table, 49 CFR 172.101.
8. U.S. EPA, Office of Solid Waste and Emergency Response, Hazardous Waste Land Treatment, Washington, D.C., SW-874, 1983.
9. U.S. EPA, NEIC Policies and Procedures, 330/9/78/001-R, 1982.
10. Wood, W.W., A Technique Using Porous Cups for Water Sampling at Any Depth in the Unsaturated Zone, Water Resources Research 9, 486-488 (1973).