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**CONSIDERATIONS FOR SAMPLING
NUCLEAR MATERIALS FOR
SNM ACCOUNTING MEASUREMENTS**

**R. J. Brouns F. P. Roberts
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ABSTRACT

This report presents principles and guidelines for sampling nuclear materials to measure chemical and isotopic content of the material. Development of sampling plans and procedures that maintain the random and systematic errors of sampling within acceptable limits for SNM accounting purposes are emphasized.

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CONSIDERATIONS FOR SAMPLING NUCLEAR MATERIALS FOR SNM ACCOUNTING MEASUREMENTS

1.0 INTRODUCTION

Measurement control is a necessary element in special nuclear materials (SNM) control and accounting. To be fully effective, a formal measurement control program must consider all sources of errors, including those arising from sampling of materials for chemical and isotopic analyses. Sampling is unique as a source of measurement error. It does not lend itself to the usual test of accuracy, namely, measurement of a physical standard in parallel with unknowns. Yet any errors in sampling and any errors introduced in preparing samples for analysis are imposed directly on the composition measurements that follow. In effect, the results of the analyses can be no better than the samples. It is important, therefore, that the sources of sampling errors and techniques for minimizing and monitoring sampling errors at each SNM measurement point in a facility be understood.

The objective of this report is to present general principles of good sampling practice and specific guidelines for the monitoring and control of sampling error. These principles and guidelines are considered an essential part of a quality control program for SNM accounting measurements.

2.0 GENERAL CONSIDERATIONS

2.1 BACKGROUND

The process of sampling consists of drawing a relatively small number of individual items or portions from a large number of items or a quantity of material, i.e., a "population". The purpose is to describe the population based on the information obtained from measurements of the individual samples. In the nuclear industry the population of interest is usually a lot, or some subdivision of a lot (sublot, batch or container), of SNM. In this report the process of sampling is considered to include all preparatory

operations required prior to making the desired measurements. These operations may include preparing the bulk material for sampling (e.g., blending), taking the sample increments, packaging and storing, and preparing the sample(s) for making the measurements (e.g., pulverizing, blending and subsampling).

The items or portions taken from the population, which we will refer to as sample increments, may be analyzed individually, or may be composited into one or more gross samples from which analytical samples are selected. Figure 1 illustrates a simple pattern for selecting and compositing increments. Each step may be replicated. The pattern shows two alternatives for analyzing the gross sample. The first provides for a quantity reduction (division or splitting) before preparing analytical samples, and the second omits splitting, providing for analyses which do not require sample division. The manner of selecting the analytical samples can vary according to the type of material involved, the degree of homogeneity, the stability of the material and other factors. Grab or dip sampling, thief sampling, and riffing (e.g., spinning disk riffler) are common sampling techniques whose applicability depends upon the properties of the material to be sampled.

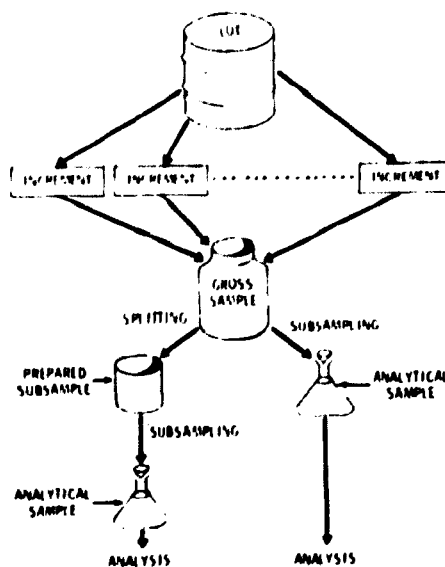


FIGURE 1. A Typical Sampling Pattern

The process of sampling and preparing samples for analysis may involve several other steps beside selecting the increments, compositing and splitting. Examples are drying, blending, particle-size reduction (grinding, milling or crushing) and screening. Particle-size reduction, screening and blending may either precede or follow splitting^(1,2) (see Section 2.2.6).

Sampling procedures are, to a great extent, process dependent, and specific procedures often are applicable to only a particular facility. Differences in equipment and processes often preclude simple transfer of a successful sampling procedure from one facility to another. An understanding of the properties of a material and, particularly, its degree of homogeneity is necessary before a sampling procedure can be established.

Many subjects in this report are treated only briefly because adequate detailed treatments are available in the literature to which references are given. References 1 through 7 may be consulted for greater detail in sampling theory and principles.

2.1.1 Terminology

The following terms will be used frequently in this report:

- Lot

A definite quantity of material relatively uniform in composition and produced under comparable conditions of production. Lot structure is usually predetermined by process batching practices, which, in turn, are dictated by such factors as blending equipment capacity, lot structure of the feed material, operating continuity and administrative requirements (e.g., product specifications).

- Batch

A quantity of material that has been or will be treated as a single entity; generally a subplot.

- Increment

A quantity of material taken in a single sampling action; i.e., a single portion.

- Gross Sample

A sample that represents a lot, batch, container or other specified quantity of material, frequently obtained by combining several increments, in which case it may also be called a composite sample.

- Prepared Sample

A sample that has been processed according to an established procedure, such as blending, pulverizing and splitting, and placed in a container, labeled, and readied for the laboratory. It may also be called a laboratory sample.

- Splitting of Samples

The process of subdividing a gross sample to obtain several lesser quantities of material representative of the gross sample. Splitting also often involves pulverizing, sieving, and blending and may be carried out in several stages. Common splitting techniques are coning and quartering, alternate-shovel splitting, spinning disk riffing, and chute riffing^(2,3,8) (see Section 2.2.6).

- Analytical Sample

A measured portion of a prepared sample that is used (often destructively) for an analysis. The analytical sample may be dissolved and separate aliquots of the solution used for each of several tests or analyses.

2.1.2 Common Sampling Techniques

Techniques for taking sample increments vary from simple dip or grab sampling to the use of sophisticated mechanical devices which, for example, select a fraction of the entire cross section of material in a container or flowing stream. The choice of sampling technique depends on the physical characteristics of the material (e.g., physical state, stability and, for powders, the particle size distribution and surface energy), the material variability relative to the required measurement precision, the kind and number of items or containers to be sampled, accessibility, and safety hazards involved. Materials encountered in the nuclear industry frequently

are not sufficiently homogeneous to permit reliance on arbitrary sample selection methods such as grab sampling from easily accessible parts of a lot. Therefore, random sampling or the closest practical approach to random sampling is usually used. This requires that sample increments be selected in such a way that every possible increment in the population has a finite and predictable chance of selection.

Techniques and devices in common use for sampling liquids and powders, and adaptable to random sampling are:

1) Liquid Thief Probe

A closed bottle or tube that can be opened for filling at any desired level in the liquid.

2) Powder Thief Probe

A closed tube that is inserted into a material, and then opened to allow filling at the desired place in the powder (usually along the full length of the probe).

3) Vacuum or Pneumatic Probe

An open-ended tube which can be evacuated to draw a powder or liquid through the tube and into a sample receiver. The tube is inserted into the material at the same rate the material flows up the tube.

4) Core Sampler

An open-ended tube for insertion into material that is sufficiently viscous or cohesive that it remains in the tube when the tube is withdrawn.

5) Dip Tube

Similar to a core sampler, i.e., a simple, open-ended, small-diameter tube inserted slowly into a liquid, then closed at the top to prevent flow-out when the tube is withdrawn.

6) Auger Sampling Probe

A sheathed auger that draws the material up the tube while it is being inserted (analogous to a vacuum probe).

7) Flowing-Stream Sampler

A stream splitter that withdraws either continuously or periodically a portion of the moving material. This type of sampler is readily automated, and many variations of this type of design are used in powder and liquid sampling⁽³⁾ (see spinning disk sampler below).

8) Outlet Sampling

Manual or mechanical withdrawal of a portion from a conveyor or mixer outlet. In the case of liquids the withdrawal may be from the drain line.

9) Petcock Sampling

Withdrawal of liquid sample from a flowing stream, a tank, or a recirculating line on a tank through a fixed tube and valve.

10) Spinning Disk Sampler^(7,8)

A rotating device that captures a small increment (a complete cross-sectional portion) of a flowing stream at frequent intervals during the time the material is flowing.

2.2 SAMPLING PLANS

A sampling plan describes a procedure for providing test units (samples) from which some property of the material sampled can be determined within a desired limit of error. The procedure used to select samples of a material can be very simple if the material is uniform throughout in the properties of interest. Because this is often not the case, sampling procedures need to be designed so that samples and sample composites reliably represent the average quality or composition of the batch of material being sampled. In addition, the procedures need to be designed so that they can provide the desired information within known and reproducible limits of error and at a reasonable cost. Consequently, successful sampling requires that sampling be done according to a plan that provides control over all parameters that may affect the quality of a sample.

Preparing a sampling plan involves specifying the population (and sub-populations, if any) to be sampled, the sampling units from which increments will be selected, and the specific physical and statistical sampling techniques (e.g., frequency or schedule, compositing and subsampling patterns, and sampling and analysis replication patterns) to be used, in accordance with predetermined measurement objectives. Key steps in developing and applying a sampling plan include:⁽⁴⁾

- 1) Making the purpose of the sampling clear; i.e., defining the population and the specific information desired,
- 2) Knowing the characteristics of the population,
- 3) Determining the measurement and sampling errors, including the process variances (e.g., within-lot and between-lot variances),
- 4) Preparing clearly written sampling instructions,
- 5) Testing the procedure thoroughly,
- 6) Training the sampling personnel and monitoring their work,
- 7) Periodically rechecking the procedures.

It is obvious that most of the following information will be very helpful, if not absolutely necessary, in preparing an effective sampling plan:

- The physical and chemical properties of the material to be sampled, including its stability,
- The lot and/or batch structure,
- The locations of the material to be sampled,
- The inherent homogeneity of the material and its potential for stratification, particularly as it may be affected by processing variations, conveying, and transporting,
- The availability of means for mixing the material prior to sampling,
- The accessibility of all items or containers for sampling, and
- The use to be made of the sampling and measurement results, and the precision and accuracy required to accomplish the desired ends.

2.2.1 Probability Sampling

Samples for SNM accounting measurements are taken by random selection procedures according to known probabilities so that the mean and process variance^(a) estimates for the sample characteristics can be used to derive unbiased estimates of the mean and variance of the corresponding characteristics of the population. Probability sampling requires that 1) every portion of the population have a finite chance of selection, 2) the probabilities of selection be known, and 3) the measured values be weighted in inverse proportion to the probabilities of selection, either in sample compositing or in the computations.⁽⁵⁾ Grab or dip sampling is acceptable only if the material sampled is homogeneous, as demonstrated by a test of between-sample variability which should be sufficiently small to have a negligible effect on the overall measurement error.

Probability sampling may be performed by simple random sampling, stratified sampling, or systematic sampling.^(1,2,4,5) Simple random sampling consists of selecting a finite number of units out of the population such that every unit of that size in the population has an equal chance of being chosen. The selections are made by using random number lists or by drawing cards from a bowl--not by haphazard or subjective means. In sampling liquid or bulk solid materials (i.e., from a population of an essentially continuous medium rather than discrete items) multiple stage sampling (subsampling) is usually applied (see Figure 1). To reduce the possibility of sampling error in the subsampling stages, the samples are thoroughly blended between stages.

In stratified sampling the items in the population are grouped into two or more classes called strata, each of which is independently sampled. For example, a population of N units is divided into subpopulations of N_1, N_2, \dots, N_L units, respectively. These subpopulations have no elements in common and together are the complete population ($N_1 + N_2 + \dots + N_L = N$). If a simple random sample is taken in each stratum, the procedure is called stratified random sampling. The probabilities of selection need not be the same from stratum to stratum. For example, if N_1, N_2, \dots and N_L are of unequal size, one may select more sample increments from larger strata than from

(a) We use process variance to refer to the variability between increments within the population, not including the measurement variance.

from smaller strata so that the sampling error affecting the mean values of the measured characteristics is smaller for the larger strata than for the smaller strata. If the data from several strata are to be combined and the probabilities of selection of individual items or increments are not equal, the quantity of material from each stratum included in the composite sample should be proportional to the probability of selection, or each stratum composite should be analyzed separately and the measurement data obtained should be weighted proportionally in combining the results.

Systematic sampling (also called interval sampling) consists of taking increments in a repetitive pattern such as every n th item in a lot or at fixed time intervals from a continuous process. This is often done when the population has a known order, such as the sequence in which containers are filled. Systematic sampling from such a population is performed by selecting a unit at random from the first k units and every k th unit thereafter. The selection of the first unit determines the selection of all other units; therefore, it must be selected at random unless it is known that the variability from unit to unit is negligible. Systematic sampling, in effect, stratifies the population into n strata, each of k units.

Systematic sampling can result in bias if the population characteristics vary systematically in the sequence. If the population characteristic varies in a cyclic manner, the sample increments chosen may, by chance, come predominantly from the same part of the cycle. However, systematic sampling is often simpler to perform and less subject to operator error than either simple random sampling or stratified sampling

Some of the common sampling devices listed in Section 2.1.2 have limitations with respect to random sampling. Thief, core and probe sampling devices usually cannot take a portion of a material close to the bottom of a container. Sampling along the sides is precluded in some techniques. For example, a common drum-sampling procedure⁽⁹⁾ involves insertion of thief sampler probes through a template with three holes, 120° apart at three radial distances from the axis. With this technique, rotational positioning is random and the three sample portions are cross sections of the drum contents, top-to-bottom, but radial positions are fixed. Allen and Khan⁽⁸⁾ compared several methods of sampling powder by determining their sampling variances and made the following recommendations:

- 1) Preferably, the sample should be taken from a moving stream of the powder.
- 2) All of the powder should pass through the sampling device.
- 3) It is preferable to take all of the powder stream for many short intervals of time rather than to take a part of the stream for all of the time.

Sampling at fixed locations is sometimes unavoidable. For example, in tanks of radioactive liquids the sampling tubes are usually permanently installed near the bottom of the tank. In this case, thorough mixing of the tank contents is required to insure that the contents are sufficiently homogeneous to obtain a representative sample, i.e., a sample whose expected composition equals the mean composition of the population (sometimes called a random sample).

2.2.2 Number of Basic Units or Increments

Sampling error caused by nonhomogeneity of material may be reduced by compositing a number of randomly selected increments.^(a) The number of increments needed can be calculated as follows:⁽¹⁰⁾

$$E = \frac{s_s}{\sqrt{n}}, \text{ or } n = \frac{s_s^2}{E^2},$$

where E = the desired standard deviation of sampling
 n = the number of increments in the composited gross sample, and
 s_s = the estimated standard deviation of the sampling process (the between-increments variability).

The value of E may have some practical lower limit affected by the precision achievable in analysis because the errors of sampling and analysis, together, make up the total composition measurement error. The standard deviation of the composition value obtained, considering random errors only, is estimated by:

$$s = \left(\frac{s_s^2}{n} + \frac{s_a^2}{m} \right)^{1/2},$$

^(a)The gross sample or composite must be either used as a single analytical sample or blended, and possibly pulverized to a finer powder, to avoid a sampling error when subsampling for analysis.

where s_a^2 is the analytical process variance, and m is the number of analyses made per gross sample. There is usually no advantage in reducing the sampling variance component (s_s^2/n) to less than about one-fourth that of an analytical process variance. For that case, a reasonable value for n can be estimated by:

$$n = \frac{4m s_s^2}{s_a^2}$$

A more sophisticated treatment of sampling may involve the principle of optimization of resources. If one considers the problem of sampling k out of N containers, taking m independent samples from each container, and performing N analyses per sample, one can select values of k , m and n that result in the smallest variance for a given amount of time or cost by a statistical technique such as that described by Stewart⁽¹¹⁾ or Bicking.⁽⁴⁾ Gutmacher and co-authors describe the application of sampling optimization techniques for determining the mean plutonium and uranium compositions of plutonium dioxide and uranium dioxide, respectively.⁽¹²⁾ Further guidelines for choosing sample increments are given in References 2, 3, 4, 5, and 12.

2.2.3 Amount of Sample

2.2.3.1 Sizes of Increments

The quantity of sample taken may be dependent upon such parameters as equipment size (e.g., thief sampler capacity), number of portions composited from a stream, number of containers sampled, and the physical form of the material. When a gross sample is much larger than can be conveniently accommodated in the laboratory, the material is blended, pulverized if necessary, and reduced or split to obtain a smaller representative portion for preparing the analytical sample (see Figure 1).

When coarse particulate material is sampled, the sampling device must be sufficiently large and of proper geometric design, so that the largest particles in a material can be freely accepted by the device. ASTM Standard E-300⁽³⁾ prescribes that the width of the cup, scoop or other sampling device should be at least three times the diameter of the largest particles being sampled. Table 1 gives a set of recommended sample increment scoop sizes as a function of the maximum particle size in the population sampled for very coarse material.⁽²⁾ Below 1000 microns any practical scoop size is satisfactory.

TABLE 1. Scoop Sizes for Powder Sampling^(a)

Maximum Particle Size ^(b) (mm)	Scoop Dimensions ^(c)			Scoop Capacity (cm ³)
	w (mm)	d (mm)	l (mm)	
150	350	140	350	16,000
100	250	110	250	7,000
75	200	100	200	4,000
50	150	75	150	1,700
20	80	45	80	300
10	60	35	60	125
5	50	30	50	75
1	30	15	30	13

^(a) See Reference 2 for further details.

^(b) Determined by the size of the screen that retains 5% of the material.

^(c) A rectangular scoop (with open front) with dimensions of width, depth and length (w, d, l).

2.2.3.2 Sizes of Gross Samples and Subsamples

In general, the quantity of gross sample is at least three times the quantity required for all usual analyses and tests. If a sample is to be sent to a shipper or receiver, or to a referee laboratory, the quantity of sample taken may need to be increased accordingly. A further consideration is the quantity of material required to obtain a random sample with negligible error due to particle variability. Theoretically, liquid samples can be microscopically small because liquids are continuous media and can be made perfectly homogeneous. However, solids are only macroscopically homogeneous even perfectly randomized. When the composition of the material may vary between particulate species in a mixture, the minimum size of sample required will be affected by the size of the largest particles in the mixture.

The statistical variability of samples drawn from mixtures of particulate material is predicted by a formula developed by applying the Bernoulli equation to sampling from a binary population.⁽¹³⁾ Assume that a powder mixture consists of two constituents, A and B, and p is the weight fraction of A in the mixture. If

equal-sized samples are drawn at random from the mixture, the number of particles of A per sample will fluctuate around a mean value, np , where n is the average number of total particles in a sample. According to the binary population distribution the standard deviation of the value for the number, np , of particles of A in a sample will be:

$$\sigma = \sqrt{np(1-p)} \quad (1)$$

Thus the sampling standard deviation of A is primarily a square-root function of the number of particles of A in a sample. This, in turn, is directly proportional to the sample size and inversely proportional to the average particle sizes A and B. The standard deviation of sampling is reduced by increasing the sample size or by reducing the particle sizes of A and B (constituent B is involved because n is the total number of particles per sample).

To illustrate, assume the simple case of a thoroughly blended binary mixture in which p is 0.1 and A and B have the same average particle diameter of 140 μ . Also assume that each constituent has a particle density of 3 g/cc and that one-gram samples are taken. The average mass per particle is estimated by:

$$\begin{aligned} m &= \frac{4}{3} \pi \left(\frac{d}{2}\right)^3 \rho \\ &= 4.31 \times 10^{-6} \text{ g,} \end{aligned} \quad (2)$$

and the average number of particles per one gram sample is the reciprocal of m , or 2.32×10^5 . Therefore, the standard deviation of the quantity of A per sample is estimated by equation (1):

$$\begin{aligned} \sigma &= \sqrt{(2.32 \times 10^5) (0.1) (0.9)}, \\ &= 1.44 \times 10^2 \text{ particles.} \end{aligned} \quad (3)$$

This corresponds to relative standard deviation (RSD) of 0.62%^(a) as given by:

$$\frac{100\sigma}{np}, \text{ or } 100 \sqrt{\frac{1-p}{np}}. \quad (4)$$

^(a)This RSD is only that component of error due to the statistical behavior of a mixture of two particulate materials assumed to have been well blended, i.e., a random mixture. Sampling error due to nonhomogeneity in a mixture is not involved, but is, of course, another possible component of the sampling error.

Equations 1-4 may also be used to calculate the minimum sample size needed to achieve a desired precision in sampling particulate material. Examples of minimum sample sizes to yield 0.1% relative standard deviation in the measured value of the concentration of a constituent (A) in a simple mixture are given in Table 2 for several concentrations and for two different average particle sizes.

TABLE 2. Estimated Sample Size in Grams for a Relative Standard Deviation of 0.1% in Constituent A (two component mixtures of uniform particle size and a particle density of 3 g/cc)

Percent of A in Mixture	Required Sample Size, g	
	0.0140 cm ^(a) (140 μm)	0.007 cm ^(b) (70 μm)
1	430	53
3	140	17
10	39	5
20	17	2
50	4	0.5

(a) Average particle diameter for a particle size range passing a 100 mesh and retained by a 140 mesh U.S. Standard sieve.

(b) Average particle diameter for a particle size range passing a 200 mesh and retained by a 230 mesh U.S. Standard sieve.

The theory has been extended to binary mixtures whose constituents have different particle densities and where an element of interest, X, is present in both constituent particle types. (6,7,13,14) A typical form of the equation is:

$$\sigma_x = \frac{d_A d_B}{d^2} (P_A - P_B) \sqrt{\frac{p(1-p)}{n}} \quad (5)$$

where

σ_x = the absolute standard deviation of the percent of x in the mixture.

d_A = the density of the A particles

d_B = the density of the B particles

d = the weighted average density of all particles assuming that all have the same volume.

- p_A = the percent of x in A particles
- p_B = the percent of x in B particles
- p = the fractional number of total particles that are type A
- n = the total number of particles in a sample.

Application to mixtures of constituents with different particle size ranges has also been studied.⁽¹⁵⁾ The well-known size-weight ratio rules governing aggregate size reductions before riffing and subsampling, found in the ASTM sampling standards (see, for example, ASTM Standard D75-71), are derived from the statistical principles embodied in equations (1) and (5).

This method of estimating sample size is idealized in two ways. First, it is assumed that only two components, A and B, are present. If more are present, the desired result may be approximated by classifying all fractions rich in constituent x as one fraction, A, and by classifying all other fractions as a second fraction. Second, it is assumed that all particles are the same size and are spherical. In practice, the average volume (or mass) of particles can be estimated from particle size range measurements (screening, sedimentation or microscopy). Errors due to such estimation of the size range as well as to nonsphericity of the particles are not serious.^(13,14) Grant and Pelton have tested the theory experimentally.⁽¹⁴⁾ In all cases, the theory serves as a rough guide, subject to experimental verification.

This theory illustrates a potential source of sampling error that may occur with some SNM bearing materials in the nuclear industry. However, most nuclear fuel materials are processed as very fine powders.

2.2.4 Time of Sampling

Since compositional analyses are correlated to a bulk measurement (mass or volume), samples are taken preferably at the same time the bulk measurement is made. Some leeway in this practice is possible if the material is sufficiently stable that no significant changes in composition, mass or volume occur in the time interval between sampling and bulk measurement. Such leeway may allow samples to be taken at times most efficient or convenient for operators, or by mechanical devices such as proportioning or

continuous samplers on flowing streams during loading, unloading, or filling operations. Such techniques often provide the most consistently representative samples.

2.2.5 Compositing

Frequently sample increments are combined and blended to form a gross sample for analysis. The increments are usually equal in size but may be varied to accomplish weighting in proportion to some variable in the population such as quantity of material per container.^(a) Compositing reduces analysis costs but forfeits all information about the variability between increments. This can be unimportant if the variability is already known or if a knowledge of the variability from one part of a lot to another is irrelevant, as may be the case if the material is to be thoroughly mixed later.

Compositing is usually done only if the material is relatively uniform in composition. Useful considerations are: 1) whenever, on the basis of experience or processing information, a between-batch variance would be expected to be significantly greater than within-batch variance, a gross sample should not include material from more than one batch; 2) if appreciable container-to-container variability can occur, the sampling plan should provide for tests of such containers. If between-container variability is excessive, each container should be sampled and assayed separately.

2.2.6 Splitting Samples

Gross samples may need to be split to obtain smaller subsamples for processing in the laboratory. Homogeneous material may be subsampled by simple dip sampling without introducing bias. However, homogeneity may be difficult to achieve except with liquids. The common splitting techniques such as quartering and coring or use of riffling devices^(2,3,4,7,13) are designed to divide samples of powders by a random process that ensures representative subsamples. Inhomogeneous material may best be subdivided by means of a spinning disk riffler. Representative samples often are not obtained by other sampling and subsampling techniques.^(7,16)

^(a) Sample increments of liquids and powders are usually made equal in volume. If there is an appreciable density difference between increments, as may be the case for nonhomogeneous mixtures of solids or slurries, equal-volume compositing may not give a representative gross sample.

As indicated by theory (see Section 2.2.3.2) powders that are not already finely divided may need to be pulverized before splitting or subsampling to insure that the size of the subsample is not below the minimum requirements for the precision desired. Finely divided powders are also less likely to segregate by particle size during handling.^(4,13) Some finely divided powders tend to agglomerate during mixing. Sufficient energy is required during mixing these types of powders to assure that the agglomerates are broken and thorough blending is achieved. Several stages of pulverizing, screening, blending, and splitting may be used for large samples to reduce the amount of material that needs to be put through the fine screens of the last stage.

3.0 MONITORING AND CONTROLLING SAMPLING ERROR

3.1 SOURCES OF ERROR IN SAMPLING

Sampling can contribute to material accounting measurement errors.

Potential sources of sampling errors are:

- Excessive variability in the properties, including composition, of the material or variability not random with respect to the method of sampling.
- Changes in composition of samples during the sample increment selections, during compositing, splitting and preparing analytical samples, and while awaiting analysis.
- Contamination or dilution of samples in sampling equipment such as from residual liquid in sampling lines from previous samplings or from purging with water or steam.
- Contamination during the sample reduction process from wearing of the surfaces of grinding equipment.
- In the case of liquids, the presence of suspended solids or multiple liquid phases.
- In the case of powders, use of an increment size or equipment size that is too small relative to the particle size distribution of the material (see Section 2.2.3).
- Segregation among powder fractions during sampling, mixing, splitting and subsampling because of particle size or density differences.

- Improper design or malfunctioning of sampling and mixing equipment.
- Failure of operators to follow prescribed procedures.

A portion taken from any part of a homogeneous lot should have a composition that is not measurably different from the average lot composition.^(a) However, homogeneity can be demonstrated only by testing. One may be convinced that the material is "thoroughly mixed" and hence sampling from any portion (even the top layer) is adequate, but in the absence of careful tests such assumptions are risky and often lead to incorrect results.

Sampling error caused by nonhomogeneity of a material will be a random error, in the long term, if the sampling process is random. If the sampling standard deviation is excessive, it can be reduced by compositing many increments of sample. When the sampling process is not random, a systematic error can result from nonhomogeneous material. Stratified material or material varying in a systematic or cyclic pattern can be especially troublesome if systematic sampling (see definition in Section 2.2.1) or grab sampling is used. For example, if samples are usually taken from the same part of a batch, such as from the first container, or the top layer of each container or from the same part of a flowing stream, a sampling bias can occur when the material composition varies in a systematic way.

Homogeneity is usually more easily achieved with simple liquids than powders or multiphase systems such as liquids containing suspended solids. A material cannot always be well mixed before sampling because of equipment size or criticality limitations. The extent of nonhomogeneity in a material can be determined by measuring the variability in composition among replicate samples.^(7,8,17)

Some powder mixtures have a tendency to segregate by particle size, particle density, other characteristics, during mixing or conveying operations. Blending such powders by the common rolling, tumbling, or stirring methods is sometimes ineffective in achieving a physically random mixture.^(8,16,17)

^(a)The term "homogeneous" is applied here in a macroscopic sense. A powder mixture is never strictly homogeneous and a more exact description for a perfectly blended mixture is "random mixture": i.e., one in which the probability of finding a particle of a given component is the same at all points in the mixture.

Segregation can occur as a result of handling, vibration during transportation to the laboratory, and even the blending, splitting and subsampling operations in the laboratory. Such a behavior can affect measurement results because chemical composition among the particle size fractions of a powder may differ (because of different rates of reaction toward oxygen or moisture, for example).

The usual ways to reduce sampling error with nonhomogeneous powders are:

- Random selection of multiple increments.
- Use of flowing stream sampling, with each increment being a complete and proportional cross-sectional portion of the stream.
- Use of the spinning riffler technique.⁽⁷⁾
- Dissolution of the total gross or subgross sample, followed by subsampling the solution for analysis.

Sampling of heterogeneous process materials, such as liquid-solid mixtures, scrap, and waste materials, may give large errors even when multiple increments are taken. Data reported by Reilly⁽¹⁸⁾ comparing chemical assay and NDA results for such materials illustrate the problem. Such errors can be minimized by:

- Subdividing and blending the material, when possible, by such means as incinerating and/or grinding.
- Leaching or dissolving the SNM-bearing fractions, analyzing the liquid samples and testing the solid residue by NDA for presence of undissolved SNM.
- Analyzing whole items by NDA methods to avoid the necessity of sampling.

Sample integrity can be lost if the samples are not adequately protected from contamination and from composition changes by evaporation, precipitation, polymer formation (e.g., of plutonium polymer in liquid samples), hydration or dehydration, and oxidation or deoxidation during and after sampling. Sample containers that are not clean and dry may cause excessive contamination or dilution of samples. In addition, samples may be altered or diluted if the pipes and valves of sampling systems are not preflushed with the process material

to ensure that they are free of previously sampled material or water.^(a) Such sources of error are likely to be consistently in one direction, resulting in bias.

3.2 MONITORING RANDOM ERROR

The random error of sampling may be determined by analyzing duplicate samples and estimating the standard deviation by the method of paired differences.⁽¹⁹⁾ This will give an estimate of the combined error of sampling and analysis and the analytical component must be removed to obtain the sampling error. If the random error of the analyses is not known from other sources, an appropriate combination of duplicate sample and duplicate analysis data will permit separation of these two error components by an analysis of variance.⁽¹⁹⁾ To achieve a valid estimate of sampling error by measurement of paired samples, all sources of error that may affect routine measurements need to be applicable with equal probability to the duplicate samples. Therefore, the duplicate samples are taken as independently as possible and by the same procedure, including all mixing and handling steps, as routine samples. It may be necessary to select the person who takes the samples and the time of sampling at random because a group of replicate samples taken at one time, or by one person, is likely to have less variability between samples than would be observed if the samples were taken at different times by different persons. The monitoring is also distributed throughout the period of process application. This has two advantages: 1) it provides continual verification of the state of statistical control of the sampling process, and 2) it allows random error standard deviation estimates to be matched with sets of process data for the same period.

3.3 MONITORING SYSTEMATIC ERROR

Bias in sampling is detected by performing mixing and sampling tests. The initial testing of a system is generally done to develop mixing and sampling procedures that yield negligible bias, although application of a bias correction for sampling is not out of the question. Mixing and sampling tests are repeated periodically to monitor the procedures and to determine if sampling bias has changed significantly. The uncertainty of the bias estimate

^(a)The sampling equipment commonly used for remote liquid sampling in nuclear processing facilities includes considerable piping plus flush lines, steam or air jets, and retaining cups.

is derived by statistical evaluation of the measurement variability for the test samples (see examples by Jaech).⁽¹⁹⁾

Methods for determining sampling bias and its uncertainty by experimental testing are:

- 1) Comparing the measurement data from samples taken by the method under test with data from samples taken by an independent sampling procedure known to be substantially unbiased. Possible "unbiased" sampling procedures are:
 - Composite many sample increments taken at random locations in a vessel or from a flowing stream.
 - Composite several large sample increments that make up a large fraction (say 10% or more) of the population being sampled.
 - One of the above after an extensive effort at homogenizing the population.
 - Sample with a spinning riffler, progressively subdividing the entire population to a suitably sized sample. (See Sections 2.2.3 and 2.2.6).
- 2) Determining the effect of variations in a mixing and sampling procedure on sample composition, including such effects as mixing time, mixing and sampling technique, time delay before analysis, and ambient conditions. A mixing and sampling procedure having a negligible bias is designed on the basis of the test results. In this case it is necessary to take steps to ensure that all potential sources of bias are tested and that the span of testing conditions is adequate (see Section 3.1, Sources of Error in Sampling). If a selected condition can be varied with no observable change in the measured composition, this is an indication that there is no bias attributable to the condition being tested.
- 3) Testing the sampling equipment and process using known synthetic mixtures. This is commonly done in pilot plant studies to aid in the design of a sampling system and sampling procedures.

3.4 ROUTINE TESTS OF SAMPLE RELIABILITY

Routine analysis of replicate samples and periodic special tests like those mentioned above are the usual ways of monitoring the suitability of a

sampling process. In addition, tests of sample reliability may be made before the prescribed analyses are attempted to provide a high degree of assurance that the samples are valid or that the batch homogeneity is satisfactory. This may be accomplished by testing for agreement among replicate samples by measuring one or two characteristics, such as density and uranium concentration, before going ahead with the rest of the analyses. Although the samples are usually chosen at random from a lot or batch, systematically selected samples (such as the first and last of a run) are sometimes used on the premise that the heads and tails of a quantity of material are usually the most deviant.

A procedure developed for control of product solution sampling at the Idaho Chemical Processing Plant⁽²⁰⁾ is an example of sampling quality control. The product, a concentrated uranyl nitrate solution stored in banks of critically safe tanks is thoroughly mixed by recirculation and is then withdrawn in batches of 10 bottles. Two samples are taken from each bottle, one each from the top and bottom. One of each pair of samples is randomly selected to test for homogeneity. The specific gravity is determined for each of the 10 samples; and in addition, the samples from each of the first, second and tenth bottles are analyzed for U and ²³⁵U. The analytical results are then tested by comparison with range controls based upon the known precisions of the measurements as established through a quality control program. If, for example, agreement between the results from the first and second bottles is not satisfactory, the remaining sample (top or bottom) from the first bottle is analyzed to test for homogeneity within that bottle. If necessary, the bottle is further mixed by tumbling and resampled. Similar tests are then applied to the results from the second and tenth bottles and, successively, other bottles in the series. When and if agreement between the specific gravity values on all remaining bottles and the U and ²³⁵U values on the end bottles are all within limits, the analytical work is terminated and the average analytical values for the end bottles (1, 2, 9, 10) are accepted as the values for the group. If agreement between bottles is not satisfactory, the samples from each bottle are analyzed and reported, and each result is identified with its corresponding bottle.⁽²⁰⁾

Sampling reliability can also be protected by monitoring the mechanical performance and condition of the mixing and sampling equipment. The equipment

may be inspected frequently and, where feasible, automatic recording of equipment operation (e.g., time-on and time-off, pumping rate, or power consumption) used. In addition, the performance of the operating personnel should be monitored by supervision through observation and audits. It is important that samples be routinely inspected in the laboratory before analysis to detect abnormalities such as precipitates or plutonium polymerization, multiple phases, spillage, contamination, and incomplete, contradictory or ambiguous labeling. Generally, samples that show evidence of any abnormality are rejected, or investigated by special procedures that have been established for testing, evaluating or analyzing such samples.

3.5 PROTECTING SAMPLE COMPOSITION

Samples can change composition while awaiting analysis if they are not adequately protected. Possible composition changes that may occur were discussed in Section 3.1. To minimize error, the sample exposure conditions, such as temperature and humidity and the time delay before analysis, may need to be controlled. A knowledge of the chemical and physical behavior of the material is helpful in developing sample handling and packaging procedures that reduce the effects of sample instability to acceptably low levels.

Evaporation of solutions can be prevented by the use of proper containers. Plastic bottles with polyethylene-lined screw caps are satisfactory if solutions are to be held for only a few weeks, but glass bottles with conical plastic inserts in the caps are necessary if the solutions are to be retained longer. (12,21,22,23) Pressure will build up in sealed containers of highly radioactive solutions because hydrogen and oxygen are released by the radiolytic decomposition of water. For safety reasons, this phenomenon should be considered if solutions of plutonium or irradiated fuels with high specific activities are to be retained in sealed containers for more than a few days.

Powder samples can change composition as the humidity varies, and most powder samples need to be protected from air by means of tightly sealed containers. Such samples may even be sensitive to changes in glove-box atmospheres. (12) Plutonium dioxide absorbs moisture from air at a rate that is affected by the ambient relative humidity, the specific surface area of the oxide, and by properties related to the firing temperature of the oxide. Low-fired, high specific surface area oxide is quite hygroscopic. Samples of PuO_2 and mixtures

containing PuO_2 can be sealed, and all operations on gross samples, such as sieving, mixing, grinding, subsampling, and weighing can be performed in controlled-atmosphere gloved boxes. (12,24,25)

Sometimes sample containers are weighed immediately upon sampling and again upon subsampling for analysis, to detect weight changes. However, the absence of a measurable weight change doesn't rule out appreciable water absorption on the exposed top layer of powder; a grab sample obtained from the top portion of a powder bed may yield biased results. For material known to be unstable, the sample weight or volume can be measured at the time of sampling, and the entire quantity used in the analytical sample. Alternatively, a known quantity of a tracer material may be added to a measured amount of sample at the time of sampling to serve as an internal standard.

UO_2 may oxidize significantly in air, the rate being affected by the specific surface area, calcining temperature and ambient temperature. (26,27) UO_2 powder also absorbs moisture, but not as rapidly as PuO_2 or UO_3 . Calcined UO_2 is less reactive and is ordinarily stable enough for exposure to air for short periods of time.

UO_3 not sealed from air is particularly difficult to maintain at constant weight. Samples are taken immediately after batch blending and quickly sealed in glass containers. Davison and co-authors (25) reported a procedure at Windscale which specifies that UO_3 be sampled, homogenized, and subsampled for analysis within 30 min of the time the UO_3 drum is opened.

Plutonium (IV) polymer may be present in plutonium solutions that have not been kept at a sufficiently high acidity. Polymer formation rates also depend on temperature, plutonium concentration and other factors. (22,28,29) As a rule, polymer will not form at acidities above 2 M, but an acidity above 4 M is required to depolymerize the plutonium at a reasonable rate if it has formed. When the acidity of a plutonium solution sample is less than about 4 M, tests are made for the presence of polymer. (22) If present, ordinarily the bulk solution is resampled. If polymer is present in the process solution, the plutonium in that solution should be depolymerized before further processing or sampling.

Precipitates may form in samples upon the cooling of saturated solution or by the coagulation of colloids or other suspended material. This situation is not uncommon with waste solution and uranyl nitrate concentrates. The presence of any precipitate casts doubt on the validity of the sample as representative of the bulk material. However, if a sample containing a precipitate is to be analyzed, the usual procedures are:

- Redissolve the precipitate by heating, diluting or treating chemically before taking the analytical sample, or
- Separate the phases by filtering, determine the proportion of each component, and analyze each component separately.

4.0 DEVELOPING MIXING AND SAMPLING PROCEDURES

Each sampling situation requires the experimental development of a specific procedure designed to achieve the purposes of the sampling, within the constraints imposed by economic, process and equipment limitations. In many cases, mixing the material is an integral part of sampling. The development of the sampling procedure should include both mixing and sampling tests. In addition, sample stability may be a problem, and establishing the steps necessary to protect the sample up to the time of analysis needs to be part of the procedure development. The initial development is conducted and verified before plant startup, when feasible, such as in a pilot plant, to simplify revision of facilities and equipment if that proves to be necessary. Periodic retests with actual processes and equipment, not mockups or small scale equipment, are needed to monitor the procedures, using such methods as were discussed in Sections 3.2 and 3.3.

The main purposes of mixing and sampling procedure development are to establish methods which introduce the least possible error into the measurement, and to gather data from which the uncertainty of the sampling bias estimate can be derived.^(a) The experimental tests conducted in sampling

^(a) Even if the experimental tests lead to the ~~conclusion~~ conclusion that there is no sampling bias, there is a degree of uncertainty about that conclusion because of the limitations of the tests made. A set of limits can be established which bound the possible sampling bias that may occur.

development are evaluated for the quantitative effects of varying the experimental conditions. The experiments may be designed to determine such effects as:

- Varying the mixing rate and time.
- Using alternative mixing procedures: e.g., air sparging versus recirculation of a liquid; mechanical stirring versus tumbling of a powder.
- Changing material properties that may vary between batches, such as particle size distribution and wetness or, for liquids, viscosity and density.
- Changing ambient conditions such as humidity and temperature.
- Changing the length of time between sampling and analysis.

Ideally, sampling procedures will be sufficiently insensitive to variations that can be reasonably anticipated in material characteristics, equipment performance, ambient conditions and other parameters that the errors of sampling will not be appreciably affected by such variations. The potential sources of error in each sampling method should be determined experimentally so that the conditions that cause error can be guarded against in the application of the procedures. (See the discussion of the common sources of sampling error in Section 3.1.)

Examples of mixing and sampling procedures currently used in the nuclear industry and general methods used to develop procedures applicable to specific sampling problems follow.

4.1 MIXING AND SAMPLING LIQUIDS

4.1.1 Measurement and Storage Tanks

Low-level radioactive wastes and uranium and plutonium solutions that do not contain fission products can be sampled by simple techniques, such as use of a petcock on a tank or recirculation loop. However, closed systems for filling sample bottles, such as hypodermic needles inserted through rubber diaphragm closures, are often used to avoid spreading radioactive material.

Process solutions in high radiation zones are sampled using systems built into the shielded processing facilities in such a way that the person who draws samples is protected from exposure to radiation. Most of the mixing and sampling operations of such vessels are controlled remotely. Sampling usually involves use of recirculation lines from the vessel to a small receptacle (in a hood or glove box) that is accessible to an operator, and from which analytical samples can be taken. Examples of such sampling systems are described in Reference 9. The sampling points in such vessels are usually at a fixed position in a vessel, and the randomness of sample increment selection results from the mixing. Mixing and sampling tests are relied on to establish procedures that ensure randomness or, ideally, solution homogeneity before sampling. Tests should be made periodically to test the adequacy of mixing and the representativeness of samples taken by the routine procedures because solution compositions and equipment performance can change from time to time.

When the sampling station is at a much higher elevation than the vessel, injection of air into the suction leg of the sampler is often required to provide additional lift, especially for hot or dense liquids. Therefore, sampling error caused by excessive evaporation during the sampling process should be avoided by precooling the liquid, presaturating the air, minimizing the amount of air used, or minimizing the lift needed (a design factor).

Critically-safe vessels present a special mixing problem because of their unusual geometries. For example, a typical assembly consists of a number of cylinders about 5 in. in diameter and up to 40 ft tall, arranged in a cluster with interconnecting piping such that the cluster functions as a single tank. The contents of the tanks usually are mixed by recirculation and sampled from a bypass loop in the recirculating system to a sampling hood or glove box. Replicate samplings with intervening recirculation are used to test solution homogeneity. Such tests are repeated periodically as part of a measurement control program.

The kind of experimentation required to establish suitable mixing conditions is illustrated by a series of theoretical and experimental studies performed by Harrell and Perona^(30,31) and Dunn.⁽³²⁾ In these studies the uniformity of the solution composition was tested as a function of circulation time and rate, and type of flow (laminar or turbulent). Flow distributor and

baffle designs, the presence of suspended solids and immiscible organic solvent, and the use of air sparging instead of recirculation by pumping also were studied. It is clear from the descriptions of these studies that flow rates, flow times and other mixing conditions necessary to achieve solution homogeneity may be unique for each system, and that a universal procedure for general applicability cannot be established.

4.1.2 Shipping Containers

The mixing of liquid UF_6 for sampling has been studied extensively because of its importance in the nuclear industry. Reports resulting from these studies describe procedures and apparatus used in DOE facilities.⁽³³⁻³⁷⁾ The procedures were developed by conducting experimental tests with each size and type of container to establish the minimum required time to liquefy and thoroughly mix the UF_6 . Mixing is required because impurities are stratified by sublimation and condensation of volatile components in the vapor spaces in the cylinders, and by settling of solid impurities.

The recommended mixing and sampling procedure for cylinders of UF_6 consists of maintaining the cylinder of UF_6 at 200°F for a prescribed period of time.⁽⁹⁾ For cylinders of less than 2.5 tons capacity, the liquified UF_6 is further mixed by rocking or inverting the cylinder at least five times. After mixing, the sample is drawn off as a liquid into a previously purged and evacuated sample container.

Plutonium and enriched uranium feed and product solutions are moved from plant to plant in critically safe bottles with capacities from about 3 to 12L. The contents of the smaller containers may be mixed by tumbling or rocking and then sampled by pouring or pipetting. Larger containers can be sampled by a thief tube. Unless steps are taken to ensure that the solution is perfectly homogeneous, several samples from different depths are taken and composited.

Mixing in the larger critically safe bottles is done with a propeller stirrer or an air sparger. Neither method is very efficient in such containers because they are long, narrow cylinders. In addition, contamination spread is difficult to avoid. Therefore, proportional sampling of the solution during transfer may be a preferred alternative. Sampling can be accomplished via a bypass or tee in the transfer line or by vacuum transfer to a sample tube

directly from the receiving tank, taking either many random increments or a continuous proportional sample.

Systematic studies of mixing and sampling techniques and of sampling error for plutonium nitrate solution shipments have been described by Byrne and coworkers and by Miner and Byrne.^(29,38) Similar experimental studies for enriched uranyl nitrate product have been made at the Idaho Chemical Processing Plant,⁽²⁰⁾ resulting in the technique described previously in Section 3.4.

4.2 MIXING AND SAMPLING POWDERS

Significant variability of composition within containers, within batches, and within lots is more common with powders than liquids. When such variability could occur, either the bulk material is mixed until randomly distributed (see Section 3.1) or a sampling plan is developed that ensures random samples (see Section 2.2). The latter may consist of collecting many increments of material according to either a random or systematic plan and combining these increments into a gross sample.

4.2.1 Mixing Powders

Powder mixing is accomplished with mechanical equipment such as rolling drum mixers, ribbon blenders, V-blenders (twin-shell blenders), ball mills, and rifflers.^(7,8,9,16) The effectiveness of a mixing operation is affected by the physical characteristics of the material (such as surface area, particle sizes and distribution, particle shape and density, and tendency to cake) and the characteristics of the mixer (such as size, shape, rate of motion, and configurations of baffles and blades).^(7,8,16,17)

An adequate mixing procedure to achieve representative sampling for a specific material is developed by a series of experimental tests. Mixing times, rotation or stirring rates and other parameters are varied and the effects of the variables on the uniformity of the mixture is tested by determining the sample standard deviation.

4.2.2 Sampling Powders

The manner in which sample increments of powder are taken (i.e., increment size, number of increments per sample and the kind of sampling device used)

varies according to the material's physical and chemical characteristics, and location. These may include:

1) Form and Characteristics:

- particle size distribution
- flow behavior
- reactivity toward moisture or oxygen
- chemical stability
- variability of composition

2) Location:

- containers (cans or drums, bins, or mixers)
- conveyors (flowing or interrupted stream)
- falling stream

Powder compositions often vary appreciably within lots, batches and even containers, and blending can be hampered by such constraints as equipment sizes and criticality limits. Therefore, probability sampling plans should be carefully developed in accordance with the principles discussed in Section 2.2.1.

It is easier to obtain a random sample from a flowing stream while a material is being loaded or unloaded than from containers.⁽⁸⁾ Sampling errors caused by differences in composition from position to position across a flowing stream and from time to time during a run are avoided by taking many increments at random times and by taking a portion across the entire stream for each increment.^(4,8) This is often done by hand with a dipper or scoop (recommended scoop dimensions and increment sizes were given in Section 2.2.3), but mechanical splitters or scoops can yield more consistent samples by removing the human element from the operation.

A spinning riffler^(7,8) is a very useful device for both sampling and splitting powders. Thief probe and core samplers are suitable and convenient for taking increments from random locations in containers but common weaknesses of such devices are:

- The probes cannot obtain an increment from the bottom-most layer in the container.
- Thief and core probes usually distort the layer pattern, if any exists, in the bed of material as they are forced into position.

- Auger and vacuum probe types of samplers are subject to a possible sampling error if the probe is not inserted at the same rate as the rate of flow of material into the auger or evacuated tube.

When a powder cannot be blended thoroughly before sampling, or when it has a tendency to segregate during processing, mixing or other handling (see Section 3.1), special efforts are made to compensate for the process variance (variability of composition within the population) by such techniques as taking a large number of increments by random selection or taking continuous proportional samples from a flowing stream.

Care is necessary to minimize bias in splitting or subsampling the gross sample. Minimizing random and systematic errors is just as important in preparing the analysis portion as it is in the primary sampling of the process material. When achieving homogeneity is difficult, subsampling error is minimized by such techniques as:

- Taking many small increments at random to make up the portion for a sample analysis (see Section 2.2.2).
- Dissolving the entire sample and taking the analytical sample from a homogeneous solution.
- Pulverizing the gross sample to the point that segregation tendencies disappear (usually smaller than 75 microns) (see Section 2.2.3).

4.3 SAMPLING FUEL PELLETS

A fuel pellet sample increment is an entire pellet. A rejected or damaged pellet is not a representative sample of product. When between-item variance exists (as discussed in Section 2.2.2), the number of pellets taken from a gross lot sample is determined by the statistical principles involved in sampling items to determine batch or lot characteristics.⁽¹⁰⁾ For example, if the standard deviation for uranium content is 0.05 gram, the number of pellet samples, n , needed to obtain a lot mean standard deviation of 0.01 gram is $n = \frac{0.05^2}{0.01}$, or 25 (neglecting analytical error).

Pellet samples may be taken continually from a production or testing line or by random selection from containers. When the former procedure is used, a

systematic method involving a uniform sampling rate (e.g., by time interval or flow rate) after a randomly selected starting point is convenient. Use of randomized selection of the time or unit sampled and of the specific pellet taken may avoid systematic sampling error such as that due to periodicity in product quality.

4.4 SAMPLING WASTES AND SCRAP

Common wastes and scrap in nuclear material processing operations are:

- Mixtures of waste liquids and solids or immiscible liquids.
- Aggregate material such as broken or rejected fuel pellets.
- Impure powder mixtures such as hood, furnace and gloved box sweepings, and grinding sludge.
- Contaminated organic material such as gloves, paper, rags and plastic.
- Contaminated tools, equipment and leached fuel element shells, ends and chips.

Many of these materials are quite heterogeneous and are difficult to blend. If only a small quantity of SNM is contained in the bulk material, a large sampling error is usually tolerable.

Sampling error can generally be reduced by batching waste and scrap materials according to type and uniformity of composition, and by pulverizing or ashing and blending materials before sampling. Tests for systematic error in sampling heterogeneous materials can be made periodically by such techniques as:

- Analysis of many random sample increments or a composite of the increments for comparison with routine sample data.
- Extensive leaching of the entire lot or of several sublots to dissolve the SNM, followed by sampling and analysis of the resultant leach solution or of a homogenized slurry.
- Analysis of the dissolver solutions in subsequent waste or scrap recovery processing of the material.

Following are some general sampling procedures applicable to wastes and scrap (see also Section 3.1).

4.4.1 Liquid Wastes

Liquid wastes that are single-phase solutions present no unusual mixing and sampling problems, but if two or more phases are present, such as two immiscible liquids (aqueous and organic) or liquid plus solid, representative sampling is more difficult. Precipitate in liquid waste is common in processing operations and in evaporation or settling ponds.

When a solid-liquid mixture is encountered, the alternatives for sampling are:

- Treat the mixture in a suitable manner to convert it all to one phase, such as by dissolving the precipitate.
- Separate the phases, determine the weight proportion of each, and sample them separately.
- Stir the mixture vigorously enough to obtain a uniform suspension of the precipitated material and sample the mixture while stirring.

In the last alternative, uniformity of the suspension may not be achievable. Sampling from various depths in the liquid may be required to test the uniformity of the suspension. If not uniform, multiple samples from various depths may be combined for a gross sample that represents the average concentration. Sediment in ponds or lagoons must usually be core sampled because vertical stratification is expected. Areal stratification can also occur, as affected by the inflow and outflow patterns and settling rates. Therefore, random selections of many coring positions on a grid pattern over the pond may also be necessary. The best procedure will be obtained only through a systematic testing process.

4.4.2 Scrap Materials

This category may include reject pellets, impure powders, grinder sludge and other material that may contain recoverable amounts of SNM. Sampling error can be substantial, since considerable within-container and between-container variability are common. Sampling error may often be avoided by using non-destructive assay for such material. If sampling is required, a procedure that minimizes sampling error can be developed experimentally. Possible experimental approaches are:

- Selecting many sample increments at random from each container to obtain container composites.
- Blending the contents before sampling by pulverizing or other vigorous mixing techniques.
- Converting the material to a solution before sampling.

4.4.3 Miscellaneous Solid Waste and Contaminated Equipment

Usually NDA is employed to obtain estimates of the amount of SNM in solid wastes and contaminated equipment (see Regulatory Guide 5.11).⁽³⁹⁾ Often there is no practical way to sample such material until it is dissolved or acid-leached to the point that all significant amounts of SNM are in solution or slurry form.

5.0 SUMMARY

Practical guidelines for developing sampling plans and procedures have been given in Sections 3 and 4. Measurement control programs should provide for routine monitoring of sampling to ensure that measurement errors occurring in the sampling process are kept within acceptable limits. Random error is normally monitored by measurements of sample replicates, but systematic error determinations require experimental testing. The usual test consists of comparing measurement data from samples taken by the method under test with data from samples taken by another sampling procedure known to be substantially unbiased (see Section 3.3).

Samples should always be taken by random selection procedures. When strictly random sampling is not possible, frequent monitoring for error is particularly important. In addition each sampling procedure should be based on a plan that takes into account the predicted characteristics of the material, such as homogeneity, stability, and state of subdivision, the lot or batch makeup, accessibility of the material and process or equipment parameters that may affect the reliability of a sampling procedure.

6.0 REFERENCES

1. "Probability Sampling of Materials," Standard E-105-58, Annual Book of ASTM Standards, Part 30, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA.
2. General Rules for Methods of Sampling Bulk Materials, Japanese Industrial Standard JIS-M-8100-1973, Japanese Standards Association, Revised March 1, 1974.
3. "Sampling Industrial Chemicals," ASTM Standard E-300-70, Annual Book of Standards, Part 30, American Society for Testing and Materials (see Reference 1 for source).
4. C. A. Bicking, "The Sampling of Bulk Materials," Materials Research and Standards, March 1967, pp. 95-116.
5. W. G. Cochran, Sampling Techniques, John Wiley and Sons, Inc., New York, Second Edition, 1963.
6. H. A. Laitinen, "Sampling," Chapter 27, Chemical Analysis, McGraw Hill, 1960.
7. R. Charlier and W. Grossens, "Sampling a Heterogeneous Powder Using a Spinning Riffler," Powder Tech., 4, 351-9 (1970).
8. T. Allen and A. A. Khan, "Critical Examination of Powder Sampling Techniques," The Chemical Engineer, 238, 108-12, May 1970.
9. C. J. Rodden (Ed.), Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, USAEC Report TID-7029, National Technical Information Service, 1972, Chapter 3.
10. "Choice of Sample Size to Estimate the Average Quality of a Lot or Process," ASTM Standard E-122-72, Annual Book of ASTM Standards, Part 15, American Society for Testing and Materials (see Reference 1 for source).
11. K. B. Stewart, "Statistical Techniques for Enhancing the Role of Material Balance Accounting in Safeguards," Chapter VII, Safeguards Systems Analysis of Nuclear Fuel Cycles, USAEC Report WASH-1140, October 1969.
12. R. G. Gutmacher et al., Methods for the Accountability of Plutonium Dioxide, USAEC Report WASH-1335, 1974; and Methods for the Accountability of Uranium Dioxide, Report NUREG-75/010, 1975.
13. A. A. Benedetti-Pichler, Essentials of Quantitative Analysis, Chapter 19, The Ronald Press Co., New York, NY (1956); or see W. M. Berl (Ed.), Physical Methods in Chemical Analysis, Volume 3, p.183, Academic Press, Inc., New York, 1956.

14. C. L. Grant and P. A. Pelton, "Role of Homogeneity in Powder Sampling," ASTM Special Technical Publication 540, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA, 1973.
15. N. Harnby, "The Estimation of the Variance of Samples Withdrawn from a Random Mixture of Multisized Particles," The Chemical Engineer, 270-271, December 1967.
16. J. C. Williams and M. I. Kahn, "The Mixing and Segregation of Particulate Solids of Different Particle Size," The Chemical Engineer, 269, 19-25, January 1973.
17. H. Harnby, "The Statistical Analysis of Particulate Mixtures, Part 1. The Sampling of Mixtures and the Resultant Precision of Estimates," Powder Tech., 5, 81-86 (1972).
18. T. D. Reilly, "Assay Experience with MONAL at Oak Ridge," Nuclear Materials Management, Vol. 1, No. 3, 246-65, September 1972 (also USAEC Report LA-DC-72-604).
19. J. L. Jaech, Statistical Methods in Nuclear Material Control, TID-26298, U.S. Atomic Energy Commission, Technical Information Center, Office of Information Services, 1973, Section 3.
20. Nuclear Materials Control in Irradiated Fuel Processing, USAEC Report TID-12100, January 1961, Section B.8, p.39.
21. G. J. Curtis, J. E. Rein and S. S. Yamamura, "Comparative Study of Different Methods of Packing Liquid Reagents," Anal. Chem., 45, 996 (1973).
22. R. G. Gutmacher et al., Methods for the Accountability of Plutonium Nitrate Solutions, USAEC Report WASH-1282, February 1974.
23. C. D. Bingham (Dir.), Annual Progress Report for the Period July 1970 Through June 1971, USAEC Report NBL-262, January 1972, p. 47.
24. J. T. Byrne et al., Measurements Involved in Shipping Plutonium Oxide, USAEC Report RFP-502, August 1965.
25. A. S. Davidson et al., "Plant Measurement, Sampling and Analysis for Accountancy Purposes with Particular Reference to Separation Plants at Windscale," Paper SM-67153 in Proceedings of the Symposium on Nuclear Materials Management, IAEA, Vienna, August 30 - September 3, 1965, Int. Atomic Energy Agency, 1966.
26. E. H. P. Cordfunke, The Chemistry of Uranium, Elsevier Publishing Co., New York, 1969 (p. 76, "Properties of UO_2 ").
27. M. J. Bannister, "The Storage Behavior of Uranium Dioxide Powders-- Review Articles," J. of Nucl. Matls., 26, 174-84 (1968).

28. J. M. Cleveland, "Solution Chemistry of Plutonium," Chapter 13 in Plutonium Handbook, Vol. 1, O. J. Wick (Ed), Gordon and Breach Science Publication, New York, 1967.
29. J. T. Byrne et al., Measurements of Plutonium Nitrate Shipping Solutions, USAEC Report RFP-436, October 1964.
30. J. E. Harrell, Jr. and J. J. Perona, "Mixing of Fluids in Tanks of Large Length-to-Diameter Ratio by Recirculation," I and EC Process Design and Development, 7, No. 3, 464-68 (1968).
31. J. E. Harrell, Jr., Mixing and Sampling Enriched U-235 Fluids in Cylindrical Storage Containers, USAEC Report Y-1561, January 1967.
32. J. Dunn, 234-5 Bank Tank Circulation Studies, USAEC Report BNWL-CC-594, April 1966.
33. Procedures for Handling and Analysis of Uranium Hexafluoride, USAEC Report ORO-671-1, April 1972, Vol. 1.
34. Uranium Hexafluoride: Handling Procedures and Container Criteria, USAEC Report ORO-651, Rev. 3 (revised periodically).
35. R. J. Wertz, Sampling Influence on Uranium Hexafluoride Analysis, USAEC Report KL-6323, September 1973.
36. R. F. Smith, Isotopic Integrity for UF₆ Field Samples, USAEC Report K-626, January 1971.
37. A. H. Wernecke, UF₆ Sampling and Shipping Facility, USAEC Report GAT-T-1330, June 1968.
38. F. J. Miner and J. T. Byrne, "Plutonium Nitrate Shipping Investigation," pp. 1-11, in Presentations of AEC-Contractor Nuclear Materials Management Meeting, Idaho Falls, Idaho, October 16-18, 1963, USAEC Report IDO-16925, 1963.
39. Nondestructive Assay of Special Nuclear Material Contained in Scrap and Waste, Regulatory Guide 5.11, October 1973.

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