APPENDIX F
LABORATORY SUBSAMPLING

F.1 Introduction

In most cases a sample that arrives at the laboratory cannot be analyzed in its entirety. Usually only a small subsample is taken for analysis, and the analyte concentration of the subsample is assumed to be approximately equal to that of the sample itself. Obviously a subsample cannot be perfectly representative of a heterogeneous sample. Improper subsampling may introduce a significant bias into the analytical process. Even when done properly, subsampling increases the variability of the measured result. There are simple methods for controlling the bias, but estimating and controlling the random variability is less straightforward.

French geologist Pierre Gy has developed a theory of particulate sampling for applications in mining exploration and development (Gy, 1992), and his work has been promoted in the United States by Francis Pitard (Pitard, 1993). The basic concept of the theory is that the variability in the analyte concentration of a laboratory sample depends on the mass of the sample and the distribution of particle types and sizes in the material sampled. The particulate sampling theory developed by Gy is applicable to the sampling of soils and radioactive waste (EPA, 1992a and 1992b). In this appendix, the theory is applied in qualitative and quantitative approaches to the subsampling of particulate solids in the radiation laboratory.

There are many examples of the use of Gy's theory in the mining industry (Assibey-Bonsu, 1996; Stephens and Chapman, 1993; Bilonick, 1990; Borgman et al., 1996), and a computer program has been developed for its implementation (Minkkinen, 1989). The theory has recently been adapted for use in environmental science. To date, most environmental applications have been in laboratory and field sampling for hazardous chemicals in Superfund cleanups (Borgman et al., 1994; Shefsky, 1997), and there are several applications of the theory that involve mixed radioactive and hazardous wastes (Tamura, 1976).

In principle, particulate sampling theory applies to materials of any type, since even gases and liquids are composed of particles (molecules). However, sampling large numbers of randomly distributed molecules in a fluid presents few statistical difficulties; so, the theory is more often applied to particulate solids.

One of the most likely applications of Gy's theory in the radiation laboratory is the subsampling of soils. Natural soils are complex mixtures of different particle types, shapes, densities, and sizes. Soil particles range from

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fine clays at less than 4 µm diameter to coarse sand that ranges over 2 mm in diameter, spanning about 4 orders of magnitude. Contaminants may be absorbed or chemically combined into the soil matrix, adsorbed onto the surfaces of particles, or may occur in discrete particles that are not bound to the soil matrix. Contaminant particles in soil can vary in size from fine airborne deposits of less than 1 µm diameter to relatively large pellets. These factors and others, including radionuclide half-lives, significantly affect the sampling problem.

F.2 Basic Concepts

This appendix applies Gy's sampling theory to subsampling. To avoid confusion, the terms "lot" and "sample" will be used here instead of "sample" and "subsample," respectively. There may be several subsampling stages at the laboratory, and all of the stages must be considered. At any stage of sampling, the *lot* is the collection of particles from which a portion is to be taken, and the *sample* is the portion taken to represent the lot.

In Gy's theory, the chemical or physical component whose proportion in a lot is of interest is called the *critical component*. In the context of radiochemistry, the critical component may be a radionuclide, but, if the chemical form of the radionuclide is known, it may be more useful to consider the critical component to be a chemical compound. Certain applications of Gy's theory require knowledge of the density, so the physical form of the compound may also be important. In the limited context of this appendix, however, the critical component will be identified with the *analyte*, which is usually a radionuclide.

The proportion of critical component by mass in a lot, sample, or particle is called the *critical content*. In the context of radiochemistry, the critical content is directly related to the activity concentration of the analyte, but it is expressed as a dimensionless number between 0 and 1. Many of the mathematical formulas used in Gy's sampling theory are equally valid if the critical content is replaced everywhere by analyte concentration. All the formulas in this appendix will be expressed in terms of analyte concentration, not critical content.

The *sampling error* of a sample S is defined, for our purposes, as the relative error in the analyte concentration of the sample, or $(z_S - z_L) / z_L$, where z_S is the analyte concentration of the sample and z_L is the analyte concentration of the lot. If the sample is the entire lot, the sampling error is zero by definition.

A lot may be heterogeneous with respect to many characteristics, including particle size, density, and analyte concentration. Of these, analyte concentration is most important for the purposes of this appendix. A lot may be considered perfectly homogeneous when all particles have the same concentration of analyte.

The term "heterogeneity" is commonly used with more than one meaning. Gy attempts to clarify the concepts by distinguishing between two types of heterogeneity. The *constitutional heterogeneity* of a lot is determined by variations among the particles without regard to their locations in the lot. It is an intrinsic property of the lot itself, which cannot be changed without altering individual particles. The *distributional heterogeneity* of a lot depends not only on the variations among particles but also on their spatial distribution.[1] Thus, the distributional heterogeneity may change, for example, when the material is shaken or mixed. In Gy's theory, both constitution heterogeneity and distributional heterogeneity are quantitative terms, which are defined mathematically.

Heterogeneity is also sometimes described as either "random" or "nonrandom" (ASTM D5956). *Random heterogeneity* is exhibited by well-mixed material, in which dissimilar particles are randomly distributed. *Nonrandom heterogeneity* occurs when particles are not randomly distributed, but instead are stratified. There is a natural tendency for a randomly heterogeneous lot to become more stratified when shaken, bounced, or stirred. The same material may exhibit both random and nonrandom heterogeneity at different times in its history.[2]

In MARLAP's terminology, the *representativeness* of a sample denotes the closeness of the analyte concentration of the sample to the analyte concentration of the lot. A sample is representative if its analyte concentration is close to the analyte concentration of the lot, just as a measured result is accurate if its value is close to the value of the measurand. Representativeness may be affected by bias and imprecision in the sampling process, just as accuracy may be affected by bias and imprecision in the measurement process.[3]

The concept of representativeness is related to the question of heterogeneity. If a lot is completely homogeneous, then any sample is perfectly representative of the lot, regardless of the sampling strategy, but as the degree of heterogeneity increases, it becomes more difficult to select a representative sample.

F.3 Sources of Measurement Error

The total variance of the result of a measurement is the sum of the variances of a series of error components, including errors produced in the field and in the laboratory. Errors in the laboratory may be characterized as those associated with (sub)sampling and those associated with sample preparation and analysis.

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[1] ASTM D5956 uses the terms "compositional heterogeneity" and "distributional heterogeneity."

[2] A state of random heterogeneity exists when the distributional heterogeneity is zero. A state of nonrandom heterogeneity exists when the distributional heterogeneity is positive.

[3] The term "representativeness" is also like "accuracy" inasmuch as it is used with different meanings by different people. The definition provided here is MARLAP's definition.

Note that the practical significance of any error, including sampling error, depends on its magnitude relative to the other errors. If a crude analytical procedure is used or if there is a relatively large counting uncertainty, the sampling error may be relatively unimportant. In other cases the sampling error may dominate. If the standard uncertainty from either source is less than about one-third of the standard uncertainty from the other, the smaller uncertainty component contributes little to the combined standard uncertainty.

This appendix focuses only on sampling errors, which include:

- Sampling bias;
- The fundamental error; and
- Grouping and segregation errors.

The following sections define the three types of sampling errors and present methods for controlling or quantifying them. (See Chapter 19, *Measurement Uncertainty*, for a more general discussion of laboratory measurement errors.)

F.3.1 Sampling Bias

Sampling bias is often related to distributional heterogeneity. When there is a correlation between the physical properties of a particle and its location in the lot, care is required to avoid taking a biased sample. For example, if the analyte is primarily concentrated at the bottom of the lot, the analyte concentration of a sample taken from the top will be biased low. Situations like this may occur frequently in environmental radiochemical analysis, since anthropogenic radionuclides are often concentrated in some of the smallest particles, which tend to settle to the bottom of the container.

Sampling bias can be controlled by the use of "correct" sampling procedures. A sampling procedure is called "correct" if every particle in the lot has the same probability of being selected for the sample. As a practical rule, a sample is guaranteed to be unbiased only if the sampling procedure is correct.

RULE 1: A sample is guaranteed to be unbiased only if every particle in the lot has the same probability of selection.

The preceding rule is not being followed, for example, if particles on the bottom or in recesses of the container are never selected.

Actually the rule stated above is only approximately true.[4] It is invalid if the sample consists of only a few particles, or if only a few particles in the lot contain most of the mass. Therefore, a second practical rule of sampling is that the sample must be many times larger (by mass) than the largest particle of the lot.

RULE 2: The sample must be many times larger (by mass) than the largest particle of the lot.

Grouping of particles should also be minimized. If the particles form clumps, the effective number of particles in the lot is actually the number of clumps. For this reason, it is usually necessary to do some preparation of the material before sampling. Typical preparation steps in the laboratory include drying, grinding, sieving, and mixing, as described in Chapter 12.

F.3.2 Fundamental Error

When a sample is taken, the existence of constitutional heterogeneity in a lot leads to an unavoidable sampling error, called the *fundamental error*. Its variance, called the *fundamental variance*, is a property of the lot and the size of the sample. It represents the smallest sampling variance that can be achieved without altering individual particles or taking a larger sample. The fundamental variance is not affected by homogenizing, or mixing, and exists even when the sampling procedure is correct. It cannot be eliminated, but it can be reduced either by increasing the size of the sample or by reducing the particle sizes before sampling (e.g., by grinding).

RULE 3: The fundamental variance may be reduced by:

- Taking a larger sample or
- Reducing the particle sizes (grinding) before sampling

This theoretical minimum sampling variance is only achieved in practice when the lot is in a state of pure random heterogeneity (and the sampling is performed correctly). If there is nonrandom heterogeneity at the time of sampling, the total sampling variance will be larger than the fundamental variance.

Either method for reducing the fundamental variance may be difficult or costly to implement in some situations. When large objects or consolidated materials are contained in the lot, particle size reduction for every lot may be unrealistically expensive. Not all materials are amenable to particle size reduction (e.g., steel). If available, knowledge of the expected contamination types and distributions may be used to reduce the need for particle size reduction. For example, it may

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[4] A sample is unbiased if $E(Z_S / m_S) = z_L$, where Z_S is the total analyte activity in the sample, m_S is the sample mass, z_L is the analyte activity concentration of the lot, and $E(\cdot)$ denotes expected value. Equal selection probabilities guarantee only that $E(Z_S) / E(m_S) = z_L$.

be known that large objects in the lot are relatively free of analyte. If so, then such objects might be removed or analyzed separately using different methods, depending on the project objectives.

When particle size reduction is required and trace levels of contamination are expected in the lot, complete decontamination of grinding or milling equipment is required to avoid the possibility of cross-sample contamination. The equipment should be constructed of non-contaminating materials that are compatible with the chemical components of the lot. Glass, ceramic and stainless steel are typical materials. Particle size reducers, such as ball mills and ceramic plate grinders, require dried samples and thorough decontamination. Mechanical splitters may be difficult to decontaminate. A grinding blank may be analyzed to check for contamination of the grinding equipment (see Section 12.3.1.4, "Subsampling")

Contamination from airborne sources (e.g., stack releases or incinerator emissions), leaching (e.g., stored mill tailings), or from weathering of contaminated surfaces tends to be dispersed and deposited as many fine particles. In these cases, as long as the particles of the matrix are small relative to the sample size (Rule 2), grinding the material is unlikely to make dramatic differences in the fundamental variance, but the variance tends to be small because of the large number of contaminant particles.

If the lot contains only a few contaminant particles, all of which are very small, the fundamental variance may remain large even after extensive grinding. However, the analytical procedure may be amenable to modifications that permit larger samples to be processed. For example, dissolution of a large solid sample may be followed by subsampling of the solution to obtain the amount needed for further analysis. Since liquid solutions tend to be more easily homogenized than solids, subsampling from the solution contributes little to the total sampling error.

If neither reducing the particle size nor increasing the sample size is feasible, more innovative analytical techniques may have to be considered.

F.3.3 Grouping and Segregation Error

Since the analyte is often more closely associated with particles having certain characteristics (e.g., small or dense), it may become concentrated in one portion of the lot or in clumps spread throughout the lot. Such effects tend to increase distributional heterogeneity.

The existence of distributional heterogeneity leads to a sampling error called the *grouping and segregation error*. The grouping and segregation variance is not as easily quantified as the fundamental variance, but there are methods for reducing its magnitude.

Although the traditional approach to reducing the grouping and segregation error is mixing, or homogenizing, the material, Gy and Pitard warn that homogenizing heterogeneous materials is often difficult, especially if a large quantity is involved. Using improper methods, such as stirring, may actually tend to increase segregation, and, even if a degree of homogeneity is achieved, it is likely to be short-lived, because of the constant influence of gravity. Agitation of particulate matter during transport and handling also tends to produce segregation of particles by size, shape, and density. During these processes, the denser, smaller, and rounder particles tend to settle to the bottom of the container, while less dense, larger, and flatter particles tend to rise to the top.

RULE 4: The effects of homogenizing heterogeneous solid material tend to be short-lived because of the constant influence of gravity. Denser, smaller, and rounder particles tend to settle to the bottom of a container, while less dense, larger, and flatter particles tend to rise to the top.

Some homogenization of solid material is usually required before sampling to reduce clumping. However, since complete homogenization is difficult and likely to be short-lived at best, Gy and Pitard recommend sampling procedures to reduce not the distributional heterogeneity itself, but its effects on the grouping and segregation error. Gy classifies sampling procedures into two categories: (1) increment sampling, and (2) splitting. Increment sampling involves extracting a number of small portions, called *increments*, from the lot, which are combined to form the sample. Splitting involves dividing the lot into a large number of approximately equal-sized portions and recombining these portions into a smaller number of potential samples. One of the potential samples is then randomly chosen as the actual sample.

A sample composed of many increments will generally be more representative than a sample composed of a single increment. For example, if a 25-gram sample is required, it is better to take five 5-gram increments, selected from different locations in the sample, than to take a single 25-gram increment.

RULE 5: A sample composed of many increments taken from different locations in the lot is usually more representative than a sample composed of a single increment.

The variance reduction achievable by increment sampling depends on the distributional heterogeneity of the lot. If the lot is in a state of pure random heterogeneity, increment sampling provides no benefit. On the other hand, if the lot is highly stratified, the standard deviation of the analyte concentration of a small composite sample formed from n independent increments may be smaller by a factor of $1/\sqrt{n}$ than the standard deviation for a sample composed of a single increment.[5] Variance reductions intermediate between these two extremes are most likely in practice.

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[5] This statement assumes the stratification is such that a single large increment is likely to have no more constitutional heterogeneity than any of the n smaller increment.

Figures F.1 and F.2 illustrate what Gy calls "increment delimitation error" and "increment extraction error," respectively. One method for extracting increments is the one-dimensional "Japanese slab-cake" method (Gy, 1992; Pitard, 1993). First, the material in the lot is spread out into an elongated pile with roughly constant width and height. Then a scoop or spatula is used to delimit and extract evenly spaced cross-sections from the pile. A flat-bottomed scoop should be used for this purpose to avoid leaving particles at the bottom of the pile. Ideally it should also have vertical sides, as shown in Figure F.3, although such scoops may not be commercially available. If a spatula is used, its width must be much larger than the largest particles to be sampled, since particles will tend to fall off the edges (Figure F.2).

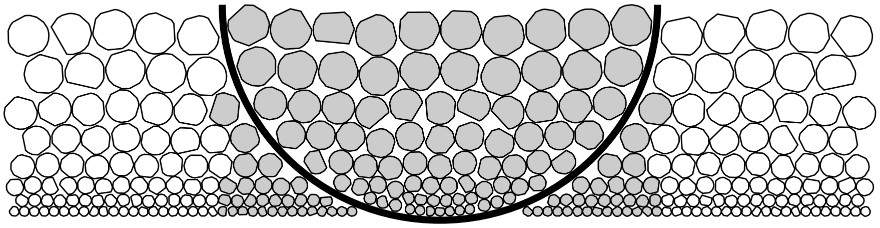

FIGURE F.1 — Incorrect increment delimitation using a round scoop

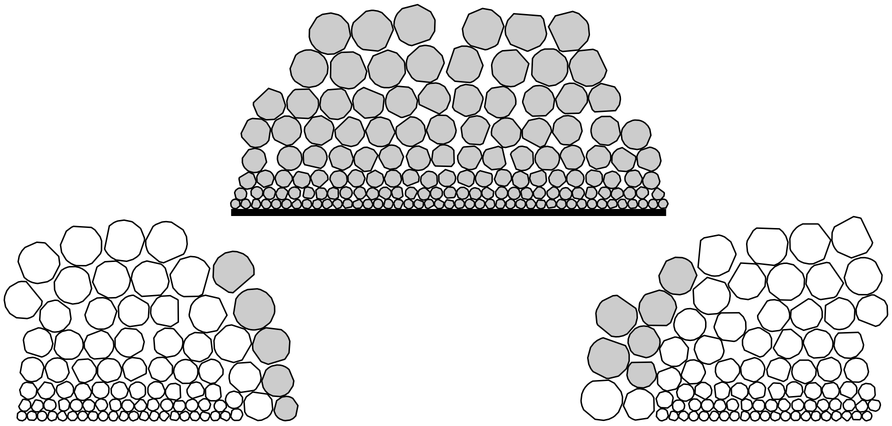

FIGURE F.2 — Incorrect increment extraction using a spatula

Splitting may be performed correctly by mechanical splitters, such as riffle splitters and sectorial splitters, or it may be performed manually by "fractional shoveling" (or "fractional scooping" in the laboratory). Fractional shoveling involves removing small portions of equal size from the lot and depositing them into two or more empty containers (or piles), cycling through the containers in order, and repeating the process until all the material has been deposited. When this process is complete, one container is chosen at random to be the sample.

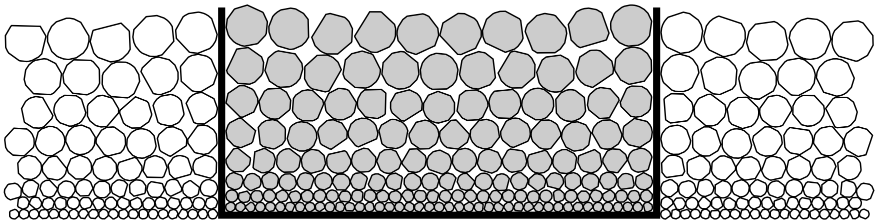

FIGURE F.3 — Correct increment delimitation using a rectangular scoop

The traditional "coning and quartering" method for splitting, although correct, is not recommended because it produces a subsample from too few increments. With this method, the material is mixed by forming it into a cone, adding a fraction of the sample at a time to the apex of the cone. After the entire sample is mixed in this way, the cone is flattened into a circular layer. Next the circular layer of material is divided into quarters and two opposite quarters are discarded. This process may be repeated until a suitable sample size is obtained (Shugar and Dean, 1990).

Homogenization may also be achieved with some types of grinding equipment, such as a ring-and-puck mill.

According to Gy, small quantities of solid material, up to a few kilograms, can be homogenized effectively in the laboratory. He recommends the use of a jar-shaker for this purpose and states that immediately after the lot is shaken, the sample may be taken directly from the jar using a spatula (Gy, 1992). Although Pitard recognizes the possibility of homogenizing small lots in the laboratory using a mechanical mixer that rotates and tumbles a closed container, he also states that homogenizing heterogeneous materials is often "wishful thinking" and recommends the one-dimensional Japanese slab-cake procedure instead (Pitard, 1993).

F.4 Implementation of the Particulate Sampling Theory

DISCLAIMER: *Gy's theory is currently the best-known and most completely developed theory of particulate sampling, but the problem is a difficult one, and the mathematical approaches offered may not give satisfactory results for all purposes. Quantitative estimates of the fundamental variance are often crude. Conservative assumptions are sometimes needed to permit mathematical solutions of the equations, leading to upper bounds for the fundamental variance which may be significantly overestimated. It appears that the theory has not been applied previously to sampling for radiochemical analysis, and no data are available to demonstrate the* *limits of its applicability. Until such data are available, MARLAP recommends the theory only for rough estimates of the uncertainty due to subsampling and as a guide to the factors that are important in subsampling and how their impact on the uncertainty might be mitigated.*

F.4.1 The Fundamental Variance

Gy's sampling theory leads to the following equation for the fundamental variance σ_{FE}^2 (Gy, 1992; Pitard, 1993):

$$\sigma_{\mathrm{FE}}^2 = \left(\frac{1}{m_{\mathrm{S}}} - \frac{1}{m_{\mathrm{L}}} \right) \sum_{i=1}^{N} \frac{(z_i - z_{\mathrm{L}})^2}{z_{\mathrm{L}}^2} \frac{m_i^2}{m_{\mathrm{L}}} \tag{F.1}$$

Here

m_{S}	is the mass of the sample;
m_{L}	is the mass of the lot;
N	is the number of particles in the lot;
z_i	is the analyte concentration of the i^{th} particle;
z_{L}	is the analyte concentration of the lot; and
m_i	is the mass of the i^{th} particle.

Equation F.1 is usually of only theoretical interest because it involves quantities whose values cannot be determined in practice; however, it is the most general formula for the fundamental variance and serves as a starting point for the development of more useful approximation formulas, which are derived using known or assumed properties of the lot.

F.4.2 Scenario 1 – Natural Radioactive Minerals

Gy has derived a practical formula for the fundamental variance based on the following assumptions (Gy, 1992):

- The analyte concentration (actually the critical content) of a particle does not depend on its size. More precisely, if the lot is divided into fractions according to particle size and density, the analyte concentration of each fraction is a function of particle density but not size.

- The distribution of particle sizes is unrelated to density. That is, if the lot is divided into fractions by density, each fraction has approximately the same distribution of particle diameters.

The first of these assumptions is often violated when environmental samples are analyzed for anthropogenic radionuclides, because in these cases, the analyte concentration of a particle tends to be inversely related to its size. The second assumption may also be violated when nonnatural materials are involved. However, when natural materials are analyzed for naturally occurring radionuclides, both assumptions may be valid.

Under the two stated assumptions, the fundamental standard deviation σ_{FE} is related to the mass of the lot m_{L}, the mass of the sample m_{S}, and the maximum particle diameter d by the equation

$$\sigma_{\mathrm{FE}} = \sqrt{\left(\frac{1}{m_{\mathrm{S}}} - \frac{1}{m_{\mathrm{L}}}\right) k d^{3}} \tag{F.2}$$

where the value of the coefficient k depends on the characteristics of the material.[6] The "maximum" diameter d is defined as the length of the edge of a square mesh that retains no more than a specified fraction of oversize by mass. Thus, it is *not* the size of the largest particle in the lot. Gy has found it most convenient to let d be the size of a square mesh that retains only 5 percent oversize, and his definition will be assumed here. According to Gy, this value of d also tends to be the approximate size of the largest particles that are easily identifiable by sight.

When m_{S} is much smaller than m_{L}, which is often the case, the fundamental standard deviation is given more simply by

$$\sigma_{\mathrm{FE}} = \sqrt{\frac{k d^{3}}{m_{\mathrm{S}}}} \tag{F.3}$$

This formula implies that, to reduce the fundamental standard deviation by half, one may either increase the sample size m_{S} by a factor of 4 or reduce the maximum particle size d by a factor of $0.5^{2/3} = 0.63$.[7]

F.4.3 Scenario 2 – Hot Particles

As noted, the assumptions of Scenario 1 are often violated when environmental media are analyzed for anthropogenic radionuclides, because there is usually a correlation between particle size and radionuclide concentration. However, another approximation formula (not due to Gy) may be used if the analyte occurs only in a minuscule fraction of the particles (i.e., "hot particles").

It is assumed that:

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[6] Gy (1992) and Pitard (1993) provide more information about the coefficient k. MARLAP presents only a brief summary of Scenario 1 because of the difficulty of estimating k.

[7] Equation F.3 also may be understood to say that the fundamental standard deviation is inversely proportional to the square root of the number of particles in the sample.

- The maximum analyte concentration of a particle $z_{\max}$ is known;
- Every particle in the lot has concentration 0 or $z_{\max}$ (approximately); and
- The high-activity particles make up a small fraction of the lot both by number and by mass.

Under these assumptions the fundamental standard deviation σ_{FE} is described by the equation[8]

$$\sigma_{\mathrm{FE}} = k\sqrt{\left(\frac{1}{m_{\mathrm{S}}} - \frac{1}{m_{\mathrm{L}}}\right)\frac{z_{\max}\,\varrho_{\mathrm{H}}\,d_{\mathrm{H}}^{3}}{2z_{\mathrm{L}}}} \tag{F.4}$$

where

m_{S} is the sample mass;
m_{L} is the mass of the lot;
ϱ_{H} is the average density of a high-activity particle;
d_{H} is the maximum diameter of a high-activity particle, defined as in Scenario 1; and
k is a dimensionless factor.

The value of the factor *k* depends on the distribution of sizes of the high-activity particles but is most likely to lie between 0.5 and 1.[9]

When m_{S} is much smaller than m_{L}, Equation F.4 reduces to

$$\sigma_{\mathrm{FE}} = k\sqrt{\frac{z_{\max}\,\varrho_{\mathrm{H}}\,d_{\mathrm{H}}^{3}}{2z_{\mathrm{L}}\,m_{\mathrm{S}}}} \tag{F.5}$$

If all the high-activity particles have approximately the same mass and the sample mass is much smaller than the mass of the lot, then Equation F.5 may be rewritten in the simple form

$$\sigma_{\mathrm{FE}} \approx \sqrt{\frac{m_{\mathrm{L}}}{m_{\mathrm{S}}\,n_{\mathrm{L}}}} \tag{F.6}$$

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[8] A more complete formula is $\sigma_{\mathrm{FE}} = \left[\left(\frac{1}{m_{\mathrm{S}}} - \frac{1}{m_{\mathrm{L}}}\right)\frac{z_{\max} - z_{\mathrm{L}}}{2z_{\max}}\left(\frac{z_{\max} - z_{\mathrm{L}}}{z_{\mathrm{L}}}\,\varrho_{\mathrm{H}}k_{\mathrm{H}}^{2}d_{\mathrm{H}}^{3} + \varrho_{\mathrm{G}}k_{\mathrm{G}}^{2}d_{\mathrm{G}}^{3}\right)\right]^{1/2}$, where ϱ_{G}, k_{G}, and d_{G} describe the zero-activity particles. Equation F.4 is obtained when $z_{\max}$ is much greater than z_{L}, which happens when the mass of high-activity material is very small.

[9] The factor *k* equals the square root of Gy's "size distribution factor" *g*. Gy recommends the value $g = 0.25$ by default for most uncalibrated materials of interest in the mining industry, but no assumption is made here that the same default value is appropriate for hot particles. If all the particles have the same size, $g = 1$.

where n_L is the number of hot particles in the lot. Equation F.6 can also be derived from the fact that the number of hot particles in a small sample can be modeled by a Poisson distribution, whose mean and variance are numerically equal (Chapter 19, *Measurement Uncertainty*). The fundamental standard deviation equals the coefficient of variation of the Poisson distribution, which is large when the mean is small.

EXAMPLE F.1

A 1-kilogram lot of soil contains approximately $1\ \mathrm{Bq/g}$ of ^{240}Pu occurring as hot particles of relatively pure plutonium dioxide ($^{240}\mathrm{PuO}_2$, density $\varrho_H = 11.4\ \mathrm{g/cm^3}$, specific activity $z_{\max} = 7.44 \times 10^9\ \mathrm{Bq/g}$) with "maximum" diameter $d_H = 10^{-3}$ cm (10 µm). Assume the distribution of particle sizes is such that $k \approx 0.5$. What is the fundamental standard deviation for a 1-gram sample?

According to Equation F.5,

$$\sigma_{FE} = 0.5\sqrt{\frac{(7.44\times 10^9\ \mathrm{Bq/g})(11.4\ \mathrm{g/cm^3})(10^{-3}\ \mathrm{cm})^3}{2\times(1\ \mathrm{Bq/g})\times(1\ \mathrm{g})}} \approx 3.3$$

Thus, the fundamental standard deviation is about 330 percent, indicating that a 1-gram sample probably is inadequate.

If all the hot particles had the same size, then k would equal 1 and the fundamental standard deviation would be about 650 percent.

When the presence of a small number of hot particles makes it impossible to reduce the fundamental standard deviation to an acceptable value by ordinary means (grinding the material or increasing the sample size), then more innovative methods may be required. For example, the entire lot may be spread into a thin layer and an autoradiograph made to locate the hot particles. Then, if necessary, a biased sample containing essentially all of the hot particles may be taken and analyzed, and the measured result corrected for sample size to obtain the average analyte concentration of the lot.

F.4.4 Scenario 3 – Particle Surface Contamination

A third approximation formula may be used if the contaminant occurs in tiny particles (e.g., colloidal particles or molecules) which adhere *randomly* to the surfaces of larger host particles of the matrix and cannot be selected without their hosts. In this case the total mass of the contaminant particles is assumed to be negligible. If the contaminant particles are also extremely numerous, so that many of them adhere to a typical host particle, then the analyte concentration of a particle tends to be inversely proportional to its diameter. In this case the fundamental variance depends primarily on the characteristics of the host particles.[10]

Under the stated assumptions, the fundamental standard deviation σ_{FE} for typical soils is given by

$$\sigma_{\mathrm{FE}} = k\sqrt{\left(\frac{1}{m_{\mathrm{S}}} - \frac{1}{m_{\mathrm{L}}}\right)\frac{\varrho d^3}{2}} \tag{F.7}$$

where

m_{S} is the sample mass;
m_{L} is the mass of the lot;
ϱ is the average particle density;
d is the "maximum" particle diameter, as defined for Scenario 1; and
k is a dimensionless factor.

The value of the factor *k* may vary from lot to lot but is always less than 1 and is usually less than 0.5.

When the sample mass is small, Equation F.7 reduces to

$$\sigma_{\mathrm{FE}} = k\sqrt{\frac{\varrho d^3}{2m_{\mathrm{S}}}} \tag{F.8}$$

The fundamental standard deviation σ_{FE} calculated using Equation F.8 is never greater than $\sqrt{\varrho d^3 / 2m_{\mathrm{S}}}$, which is the square root of the ratio of the "maximum" particle mass $\varrho d^3 / 2$ to the mass of the sample m_{S}. *So, as long as the sample is much heavier than the heaviest particle in the lot, the fundamental variance in Scenario 3 tends to be small.* As in Scenario 1, reducing the fundamental standard by half requires either increasing the sample mass m_{S} by a factor of 4 or reducing the particle diameter by a factor of 0.63. However, note that grinding may cause the assumptions underlying Equation F.8 to be violated if the contaminant is not redistributed onto the newly created particle surfaces.

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[10] The formula for σ_{FE} given here describes the variability of the total surface area in a sample. A more complete expression includes a term for the variability of the analyte concentration per unit area, but this term is negligible if the number of contaminant particles is sufficiently numerous.

EXAMPLE F.2

Suppose a 1-kilogram lot of soil contains ^{90}Sr, which is expected to adhere randomly to the surfaces of the particles. The maximum particle diameter d is found to be approximately 0.2 cm. If nothing more is known about the distribution of particles sizes, what is the maximum fundamental standard deviation for a 1-gram sample?

Assuming the density of the soil particles is $\varrho = 2.675\ \text{g/cm}^3$, Equation F.8 with $k = 1$ gives the solution

$$\sigma_{\text{FE}} = \sqrt{\frac{(2.675\ \text{g/cm}^3)(0.2\ \text{cm})^3}{2\times(1\ \text{g})}} = 0.10 \ \text{ or } \ 10\ \text{percent.}$$

Note that since k is usually less than 0.5, the fundamental standard deviation is more likely to be less than 5 percent.

F.5 Summary

Results derived from particulate sampling theory provide sampling protocols that help to control sampling errors, including sampling bias, fundamental error, and grouping and segregation errors. Some of the important conclusions are listed below.

- For most practical purposes, a sample is guaranteed to be unbiased only if all particles in the lot have the same probability of selection.

- The sample mass should be many times greater than the heaviest particle in the lot, and clumping of particles should be minimized (e.g., by drying and sieving).

- The fundamental variance, which is considered to be the minimum achievable sampling variance, may be reduced by increasing the size of the sample or reducing the particle sizes (grinding) before sampling.

- Grouping and segregation of particles, which occur because of the particles' differing physical characteristics and the influence of gravity, tend to increase the sampling variance.

- Grouping and segregation errors can be reduced by increment sampling or by splitting. The more increments, the better.

- Correct sampling requires tools and procedures that ensure each particle in the lot has the same probability of selection. Any sampling tool or procedure that prefers certain particles (e.g., because of their density, size, or shape) may produce a sampling bias.

- Small quantities of particulate material can be homogenized effectively in the laboratory using mechanical mixers that rotate and tumble a closed container, but the effects of mixing tend to be short-lived.

- Estimation of the fundamental variance requires either knowledge or assumptions about the characteristics of the material being analyzed. Quantitative estimates may be crude.

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