

# 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, 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 fine clays at less than 4  $\mu\text{m}$  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

34 discrete particles that are not bound to the soil matrix. Contaminant particles in soil can vary in  
35 size from fine airborne deposits of less than 1  $\mu\text{m}$  diameter to relatively large pellets. These  
36 factors and others, including radionuclide half-lives, significantly affect the sampling problem.

## 37 **F.2 Basic Concepts**

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

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

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

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

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

64 The term “heterogeneity” is commonly used with more than one meaning. Gy attempts to clarify  
65 the concepts by distinguishing between two types of heterogeneity. The *constitution hetero-*  
66 *geneity* of a lot is determined by variations among the particles without regard to their locations  
67 in the lot. It is an intrinsic property of the lot itself, which cannot be changed without altering  
68 individual particles. The *distribution heterogeneity* of a lot depends not only on the variations  
69 among particles but also on their spatial distribution.<sup>1</sup> Thus, the distribution heterogeneity may  
70 change, for example, when the material is shaken or mixed. In Gy’s theory, both constitution  
71 heterogeneity and distribution heterogeneity are quantitative terms, which are defined  
72 mathematically.

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

79 In MARLAP’s terminology, the *representativeness* of a sample denotes the closeness of the  
80 analyte concentration of the sample to the analyte concentration of the lot. A sample is  
81 representative if its analyte concentration is close to the concentration of the lot, just as a  
82 measured result is accurate if its value is close to the value of the measurand. Representativeness  
83 may be affected by bias and imprecision in the sampling process, just as accuracy may be  
84 affected by bias and imprecision in the measurement process.<sup>3</sup>

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

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<sup>1</sup>ASTM D5956 uses the terms “compositional heterogeneity” and “distributional heterogeneity.”

<sup>2</sup>A state of random heterogeneity exists when the distribution heterogeneity is zero. A state of nonrandom heterogeneity exists when the distribution heterogeneity is positive.

<sup>3</sup>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.

89 **F.3 Sources of Measurement Error**

90 The total variance of the result of a measurement is the sum of the variances of a series of error  
91 components, including errors produced in the field and in the laboratory. Errors in the laboratory  
92 may be divided into those associated with sampling and those associated with sample preparation  
93 and analysis.

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

100 This appendix focuses only on sampling errors, which include the following:

- 101 • Sampling bias;
- 102 • The fundamental error; and
- 103 • Grouping and segregation errors.

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

107 **F.3.1 Sampling Bias**

108 Sampling bias is often related to distribution heterogeneity. When there is a correlation between  
109 the physical properties of a particle and its location in the lot, care is required to avoid taking a  
110 biased sample. For example, if the analyte is primarily concentrated at the bottom of the lot, the  
111 analyte concentration of a sample taken from the top will be biased low. Situations like this may  
112 occur frequently in environmental radiochemical analysis, since non-natural radioactive materials  
113 often tend to be concentrated in the smallest particles, which tend to settle to the bottom of the  
114 container.

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

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

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

123 Actually the rule stated above is only approximately true.<sup>4</sup> It is invalid if the sample consists of  
124 only a few particles, or if only a few particles in the lot contain most of the mass. Therefore, a  
125 second practical rule of sampling is that the sample must be many times larger (by weight) than  
126 the largest particle of the lot.

127 RULE 2: The sample must be many times larger than the largest particle of the lot.

128 Grouping of particles should also be minimized. If the particles form clumps, the effective  
129 number of particles in the lot is actually the number of clumps.

### 130 F.3.2 Fundamental Error

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

138 RULE 3: The fundamental variance may be reduced by:

- 139 • Taking a larger sample
- 140 • Reducing the particle sizes before sampling

141 This theoretical minimum sampling variance is only achieved in practice when the lot is in a state  
142 of pure random heterogeneity (and the sampling is performed correctly). If there is nonrandom

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<sup>4</sup>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  $E()$  denotes expected value. Equal selection probabilities guarantee only that  $E(Z_S) / E(M_S) = z_L$ .

143 heterogeneity at the time of sampling, the total sampling variance will be larger than the  
144 fundamental variance.

145 Either method for reducing the fundamental variance may be difficult or costly to implement in  
146 some situations. When large objects or consolidated materials are contained in the lot, particle  
147 size reduction for every lot may be unrealistically expensive. Not all materials are amenable to  
148 particle size reduction (e.g., steel). If available, knowledge of the expected contamination types  
149 and distributions may be used to reduce the need for particle size reduction. For example, it may  
150 be known that large objects in the lot are relatively free of analyte. If so, then such objects might  
151 be removed or analyzed separately using different methods, depending on the project objectives.

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

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

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

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

### 174 F.3.3 Grouping and Segregation Error

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

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

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

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

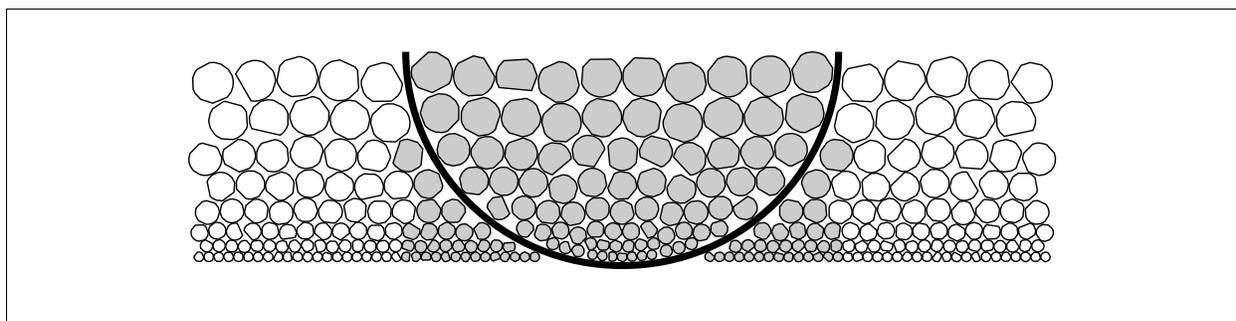
194 As an alternative to homogenizing, Gy and Pitard recommend sampling procedures to reduce not  
195 the distribution heterogeneity itself, but its effects on the grouping and segregation error. Gy  
196 classifies sampling procedures into two categories: (1) increment sampling, and (2) splitting.  
197 Increment sampling involves extracting a number of small portions, called *increments*, from the  
198 lot, which are combined to form the sample. Splitting involves dividing the lot into a large  
199 number of approximately equal-sized portions and recombining these portions into a smaller  
200 number of potential samples. One of the potential samples is then randomly chosen as the actual  
201 sample.

202 A sample composed of many increments will generally be more representative than a sample  
203 composed of a single increment. For example, if a 25 g sample is required, it is better to take five  
204 5 g increments, selected from different locations in the sample, than to take a single 25 g  
205 increment.

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

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

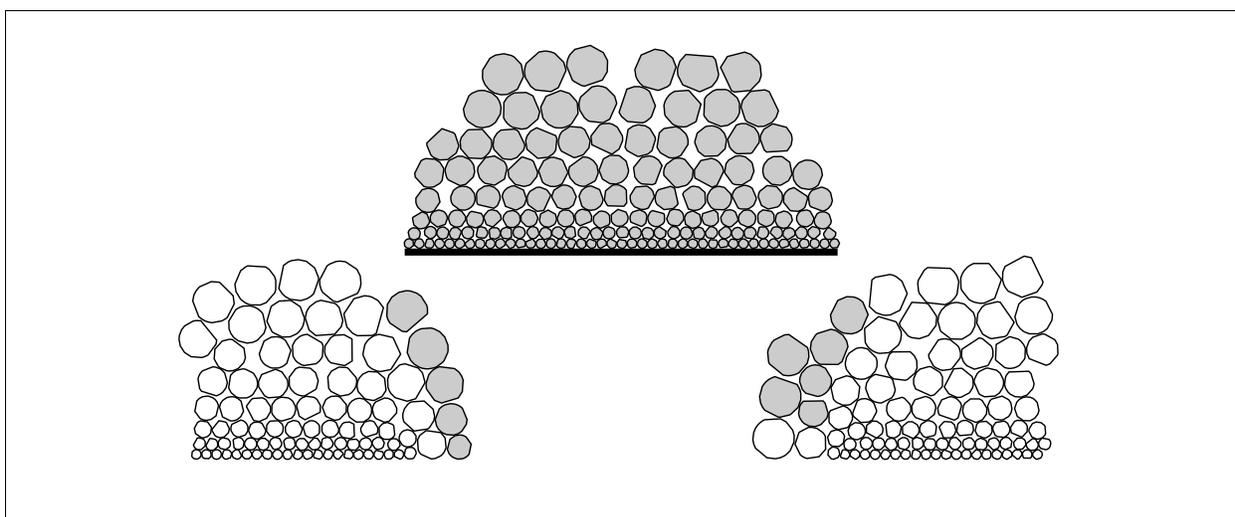
215 Figures F.1 and F.2 illustrate what Gy calls “increment delimitation error” and “increment  
216 extraction error,” respectively. One method for extracting increments is the one-dimensional  
217 “Japanese slab-cake” method (Gy 1992, Pitard 1993). First, the material in the lot is spread out  
218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



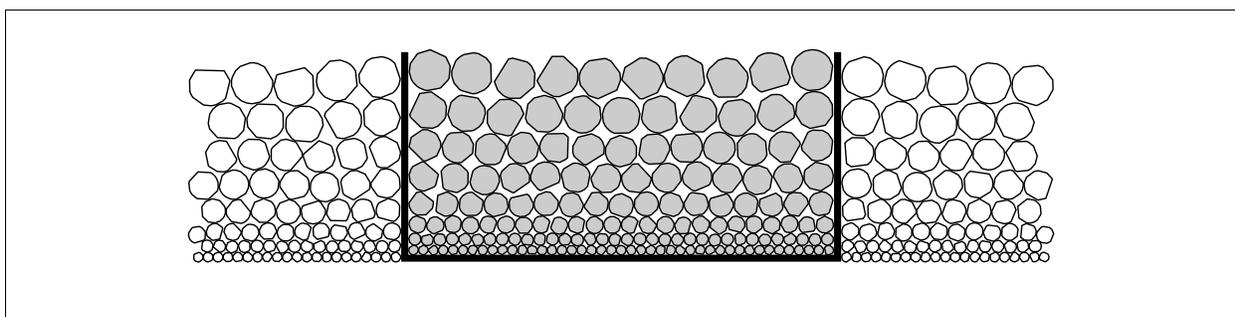
**FIGURE F.1 — Incorrect increment delimitation using a round scoop**

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<sup>5</sup>This statement assumes the stratification is such that a single large increment is likely to have no more constitution heterogeneity than any of the  $n$  smaller increment.



**FIGURE F.2 — Incorrect increment extraction using a spatula**



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

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

230 The traditional “coning and quartering” method for splitting, although correct, is not recommen-  
 231 ded because it produces a subsample from too few increments. With this method, the material is

232 mixed by forming it into a cone, adding a fraction of the sample at a time to the apex of the cone.  
233 After the entire sample is mixed in this way, the cone is flattened into a circular layer. Next the  
234 circular layer of material is divided into quarters and two opposite quarters are discarded. This  
235 process may be repeated until a suitable sample size is obtained (Shugar and Dean, 1990).

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

238 According to Gy, small quantities of solid material, up to a few kilograms, can be homogenized  
239 effectively in the laboratory. He recommends the use of a jar-shaker for this purpose and states  
240 that immediately after the lot is shaken, the sample may be taken directly from the jar using a  
241 spatula (Gy, 1992). Although Pitard recognizes the possibility of homogenizing small lots in the  
242 laboratory using a mechanical mixer that rotates and tumbles a closed container, he also states  
243 that homogenizing heterogeneous materials is often “wishful thinking” and recommends the one-  
244 dimensional Japanese slab-cake procedure instead (Pitard, 1993, §14.4.3).

## 245 **F.4 Implementation of the Particulate Sampling Theory**

246 *DISCLAIMER: Gy’s theory is currently the best-known and most completely developed theory of*  
247 *particulate sampling, but the problem is a difficult one, and the mathematical approaches*  
248 *offered may not give satisfactory results for all purposes. Quantitative estimates of the*  
249 *fundamental variance are often crude. Conservative assumptions are sometimes needed to*  
250 *permit mathematical solutions of the equations, leading to upper bounds for the fundamental*  
251 *variance which may be significantly overestimated. It appears that the theory has not been*  
252 *applied previously to sampling for radiochemical analysis, and no data are available to*  
253 *demonstrate the limits of its applicability. Until such data are available, MARLAP recommends*  
254 *the theory only for crude estimation.*

### 255 **F.4.1 The Fundamental Variance**

256 Gy’s sampling theory leads to the following equation for the fundamental variance  $\sigma_{FE}^2$  (Gy 1992,  
257 Pitard 1993):

$$\sigma_{FE}^2 = \left( \frac{1}{M_S} - \frac{1}{M_L} \right) \sum_{i=1}^N \frac{(z_i - z_L)^2}{z_L^2} \frac{m_i^2}{M_L} \quad (\text{F.1})$$

258 Here  
259  $M_S$  is the mass of the sample (g)

260  $M_L$  is the mass of the lot (g)  
 261  $N$  is the number of particles in the lot  
 262  $z_i$  is the analyte concentration of the  $i^{\text{th}}$  particle  
 263  $z_L$  is the analyte concentration of the lot  
 264  $m_i$  is the mass of the  $i^{\text{th}}$  particle (g)

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

#### 269 **F.4.2 Scenario 1 – Natural Radioactive Minerals**

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

- 272 • The analyte concentration (actually the critical content) of a particle does not depend on its  
 273 size. More precisely, if the lot is divided into fractions according to particle size and density,  
 274 the analyte concentration of each fraction is a function of particle density but not size.
- 275 • The distribution of particle sizes is unrelated to density. That is, if the lot is divided into  
 276 fractions by density, each fraction has approximately the same distribution of particle  
 277 diameters.

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

283 Under the two stated assumptions, the fundamental standard deviation  $\sigma_{\text{FE}}$  is related to the mass  
 284 of the lot  $M_L$ , the mass of the sample  $M_S$ , and the maximum particle diameter  $d$  by the equation

$$\sigma_{\text{FE}} = k \sqrt{\left( \frac{1}{M_S} - \frac{1}{M_L} \right) d^3} \quad (\text{F.2})$$

285 where  $k$  is a constant of proportionality.<sup>6</sup> The “maximum” diameter  $d$  is defined as the length of  
286 the edge of a square mesh that retains no more than a specified fraction of oversize by mass.  
287 Thus, it is *not* the size of the largest particle in the lot. Gy has found it most convenient to let  $d$  be  
288 the size of a square mesh that retains only 5% oversize, and his definition will be assumed here.  
289 According to Gy, this value of  $d$  also tends to be the approximate size of the largest particles that  
290 are easily identifiable by sight.

291 When  $M_S$  is much smaller than  $M_L$ , which is often the case, the fundamental standard deviation is  
292 given more simply by

$$\sigma_{FE} = k \sqrt{\frac{d^3}{M_S}} \quad (\text{F.3})$$

293 This formula implies that, to reduce the fundamental standard deviation by half, one may either  
294 increase the sample size  $M_S$  by a factor of 4 or reduce the maximum particle size  $d$  by a factor of  
295  $0.5^{2/3} = 0.63$ .<sup>7</sup>

### 296 F.4.3 Scenario 2 – Hot Particles

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

302 It is assumed that:

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

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<sup>6</sup>Gy (1992) and Pitard (1993) provide more information about the constant  $k$ . MARLAP presents only a brief summary of Scenario 1 because of the difficulty of estimating  $k$ .

<sup>7</sup>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.

306 Under these assumptions the fundamental standard deviation  $\sigma_{FE}$  is described by the equation<sup>8</sup>

$$\sigma_{FE} = k \sqrt{\left(\frac{1}{M_S} - \frac{1}{M_L}\right) \frac{z_{\max} \delta_H d_H^3}{2z_L}} \quad (\text{F.4})$$

307 where

308  $M_S$  is the sample mass (g)

309  $M_L$  is the mass of the lot (g)

310  $\delta_H$  is the average density of a high-activity particle (g / cm<sup>3</sup>)

311  $d_H$  is the maximum diameter of a high-activity particle, defined as in Scenario 1

312  $k$  is a constant of proportionality.

313 The proportionality constant  $k$  depends on the distribution of sizes of the high-activity particles  
314 but is most likely to lie between 0.5 and 1.<sup>9</sup>

315 When  $M_S$  is much smaller than  $M_L$ , Equation F.4 reduces to

$$\sigma_{FE} = k \sqrt{\frac{z_{\max} \delta_H d_H^3}{2z_L M_S}} \quad (\text{F.5})$$

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

$$\sigma_{FE} \approx \sqrt{\frac{M_L}{M_S n_L}} \quad (\text{F.6})$$

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<sup>8</sup>A more complete formula is  $\sigma_{FE} = \left[ \left( \frac{1}{M_S} - \frac{1}{M_L} \right) \frac{z_{\max} - z_L}{2z_{\max}} \left( \frac{z_{\max} - z_L}{z_L} \delta_H k_H^2 d_H^3 + \delta_G k_G^2 d_G^3 \right) \right]^{1/2}$ , where  $\delta_G$ ,  $k_G$ , 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.

<sup>9</sup>The constant  $k$  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,  $g = 1$ .

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

323 **EXAMPLE 1**

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

329 According to Equation F.5,

330 
$$\sigma_{\text{FE}} = 0.5 \sqrt{\frac{(7.44 \times 10^9)(11.4)(10^{-3})^3}{2(1)(1)}} \approx 3.3$$

331 Thus, the fundamental standard deviation is about 330%, indicating that a 1 g sample probably  
332 is inadequate.

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

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

342 **F.4.4 Scenario 3 – Particle Surface Contamination**

343 A third approximation formula may be used if the contaminant occurs in tiny particles, or even  
344 molecules, which adhere *randomly* to the surfaces of larger host particles of the matrix and

345 cannot be selected without their hosts. In this case, the total mass of the contaminant particles is  
 346 assumed to be negligible. If the contaminant particles are also extremely numerous, so that many  
 347 of them adhere to a typical host particle, then the analyte concentration of a particle tends to be  
 348 inversely proportional to its diameter. In this case the fundamental variance depends primarily on  
 349 the characteristics of the host particles.<sup>10</sup>

350 Under the stated assumptions, the fundamental standard deviation  $\sigma_{FE}$  for typical soils is given by

$$\sigma_{FE} = k \sqrt{\left( \frac{1}{M_S} - \frac{1}{M_L} \right) \frac{\delta d^3}{2}} \quad (\text{F.7})$$

351 where

352  $M_S$  is the sample mass (g)

353  $M_L$  is the mass of the lot (g)

354  $k$  is a constant of proportionality

355  $\delta$  is the average particle density (g/cm<sup>3</sup>)

356  $d$  is the “maximum” particle diameter (cm), as defined for Scenario 1

357 The factor  $k$  may vary from lot to lot but is always less than 1 and is usually less than 0.5.

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

$$\sigma_{FE} = k \sqrt{\frac{\delta d^3}{2M_S}} \quad (\text{F.8})$$

359 The fundamental standard deviation  $\sigma_{FE}$  calculated using Equation F.8 is never greater than  
 360  $\sqrt{\delta d^3 / 2M_S}$ , which is the square root of the ratio of the “maximum” particle mass  $\delta d^3 / 2$  to the  
 361 mass of the sample  $M_S$ . *So, as long as the sample is much heavier than the heaviest particle in*  
 362 *the lot, the fundamental variance in Scenario 3 tends to be small.* As in Scenario 1, reducing the  
 363 fundamental standard by half requires either increasing the sample mass  $M_S$  by a factor of 4 or  
 364 reducing the particle diameter by a factor of 0.63. However, note that grinding may cause the

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<sup>10</sup>The formula for  $\sigma_{FE}$  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.

365 assumptions underlying Equation F.8 to be violated if the contaminant is not redistributed onto  
366 the newly created particle surfaces.

367 **EXAMPLE 2**

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

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

$$\sigma_{\text{FE}} = \sqrt{\frac{(2.675)(0.2)^3}{(2)(1)}} = 0.10 \text{ or } 10\% .$$

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

377 **F.5 Summary**

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

- 381 • For most practical purposes, a sample is guaranteed to be unbiased only if all particles in the  
382 lot have the same probability of selection.
- 383 • The sample mass should be many times greater than the heaviest particle in the lot, and  
384 clumping of particles should be minimized.
- 385 • The fundamental variance, which is considered to be the minimum achievable sampling  
386 variance, may be reduced by increasing the size of the sample or reducing the particle sizes  
387 before sampling.
- 388 • Grouping and segregation of particles, which occur because of the particles' differing  
389 physical characteristics and the influence of gravity, tend to increase the sampling variance.

- 390 • Grouping and segregation errors can be reduced by increment sampling or by splitting. The  
391 more increments, the better.
- 392 • Correct sampling requires proper tools and procedures.
- 393 • Small quantities of particulate material can be homogenized effectively in the laboratory  
394 using mechanical mixers that rotate and tumble a closed container, but the effects of mixing  
395 tend to be short-lived.
- 396 • Estimation of the fundamental variance requires either knowledge or assumptions about the  
397 characteristics of the material being analyzed. Quantitative estimates may be crude.

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*Laboratory Subsampling*

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