

Appendix D

Determination of Appropriate Particle Size of PE Samples

D.1. Homogeneity and Sampling Errors.

Three ways to reduce sampling errors described below include:

- Sample matrix and method.
- Sample size and consistency.
- Particle size.

D.1.1. Sample Matrix and Method. Homogenization of PE samples is most likely the least controlled and error prone step in an analytical chain. It is especially critical in preparation of individual PE samples subsampled from bulk, solid materials because of direct effects on sample integrity. Homogeneity of PE samples of single-phase liquid matrices is not a problem unless analyte loss to container walls is a concern. Shaking and mixing just prior to analysis are usually sufficient to ensure homogeneity of bulk, aqueous PE sample materials. This appendix therefore focuses on homogeneity of solid PE samples.

D.1.2. Sample Size and Consistency. Solid PE samples should be as finely ground and homogeneous as possible. Smaller, more manageable quantities of PE samples can then be shipped. If laboratory proficiency in subsampling is to be tested, a coarse sample should be shipped. However, sufficient quantities must be furnished to allow execution of proper sampling technique. For example, several kilogram quantities may be necessary for samples with maximum particle size of 0.5 cm. If sufficient quantities are not shipped, the laboratory cannot follow proper sampling technique and achieve analyses that are representative of the lot of PE samples. For obvious reasons, proficiency testing in subsampling can be very expensive, logistically difficult, and is normally not included in the USACE PE Program.

D.1.3. Particle Size. The particle size and the subsample size of solid PE sample materials play important roles in determining sampling errors on contaminant concentrations. Because there is little room to change the method-specified subsample size, the particle size is the variable that can be adjusted to minimize sampling errors. Pierre Gy's Sampling Theory presents a method of estimating sampling precision of particulate materials at specific particle sizes. The theory describes how errors are generated; how they can be eliminated or reduced; and how the residual error can be estimated. The details on Pierre Gy's Sampling Theory are presented in several reference books and are beyond the scope of this appendix. This appendix will focus on "fundamental error" and "grouping and segregation error," which are directly applicable to heterogeneity problems with PE sample materials.

D.2. Pierre Gy's Sampling Theory.

D.2.1. Fundamental Error (FE). According to *Pierre Gy's Sampling Theory and Sampling Practice*, FE results from the constitution heterogeneity of PE sample materials. Constitution heterogeneity, related to individual particles of PE sample materials, is an intrinsic property of the PE sample materials and cannot be varied, unless processed with a comminution. Mixing and homogenization of PE sample materials have no influence on constitution heterogeneity. PE samples prepared by subsampling a bulk PE sample material are affected by an error specifically related to constitution heterogeneity. This error is known as the FE. For PE samples of a given weight, FE is an incompressible minimum depending on intrinsic properties of PE sample materials. FE is the only error that can never be canceled out even with perfect sampling operations. It is also the only error that can be estimated beforehand. FE is related to the sample size and particle size. It can be minimized for each PE sample material through reduction in particle size of PE sample materials.

D.2.2. Grouping and Segregation Error (GE). GE results from the distribution heterogeneity of PE sample materials. When preparing individual PE samples, individual particles making up PE samples are not collected strictly at random or one by one. Increments that are likely made of many particles are collected to make up individual PE samples. Statistically speaking, a PE sample is not made of strictly random particles, but only of random groups of particles. When all groups of particles that may be subsampled have the same average composition, a PE sample material is homogeneous in practice. Otherwise, the PE sample material has a heterogeneous distribution that leads to GE. The distribution heterogeneity is directly proportional to constitution heterogeneity and grouping and segregation factors that are naturally introduced by sampling process and gravitational force. Distribution heterogeneity can be minimized by mixing; however, there is always a residual heterogeneity that never goes to zero and is a characteristic of the PE sample material itself. GE is often negligible with major constituents but could become important with minor constituents. According to Gy, when optimizing sampling protocol, one may always assume that the GE is equal to FE. The overall sampling error is therefore the sum of FE and GE.

D.2.3. Estimating Sampling Errors. Major sample preparation efforts, including reduction in particle size and distribution heterogeneity, are designed to minimize FE and GE. The relationship between FE, sample size, and particle size is as follows.

$$S^2 = \frac{18 \times f \times e \times d^3}{M_s}$$

where: S^2 = relative variance of contaminant concentration due to FE
 S = relative standard deviation of contaminant concentration due to FE
 f = a dimensionless factor related to particle shape (a typical value is 0.5)
 e = average density in grams per cubic centimeter (ca. 2.5 g/cm³ for soil)
 d = diameter of the largest particle in centimeters
 M_s = sample mass in grams

D.2.4. Maximum Allowable Particle Size. Using the above assumptions for density and shape factor, this equation can be rearranged to calculate the largest particle size that can be representatively accommodated by a given subsample mass and FE.

$$d = \sqrt[3]{\frac{M_s \times S^2}{22.5}}$$

If the density of bulk PE sample materials being sampled varies significantly from 2.5 g/cm³, the actual density should be used. If PE sample material does not have a typical spherical shape, the factors in Table D-1 can be substituted for the f factor of 0.5.

Table D-1. “f” Values for Different Particle Shapes

Particle Shape	f
Cubic	1
Spheres	0.5
Flakes	0.1
Soft solids shaped by mechanical stress	0.2
Needles	>1 to # 10

Table D-2 lists the maximum allowable particle size in centimeters that can be accommodated by a given subsample mass at varying FE. The tighter the required precision, the larger the sample mass and/or the smaller the particle size. This table assumes that the soil particle has a typical spherical shape and serves as an example how the maximum allowable particle size changes as a function of these parameters. For proficiency testing, if limited amounts of PE samples are

EM 200-1-7
1 Feb 01

shipped, keep the total sampling errors including FE and GE as low as practically feasible but no larger than 15%.

Table D-2. Maximum Allowable Particle Size That Can Be Accommodated by a Given Subsample Mass at Various Percent Relative Standard Deviation (RSD)

Recommended Subsample Mass (g)	U.S. Standard Sieve No.	Nominal Sieve Opening (cm)	Maximum Allowable Particle Size (cm)		
			5% RSD	10% RSD	15% RSD
0.01	70	0.0212	0.010	0.016	0.022
0.02	60	0.0250	0.013	0.021	0.027
0.03	50	0.0300	0.015	0.024	0.031
0.05	45	0.0355	0.018	0.028	0.037
0.1	40	0.0425	0.022	0.035	0.046
0.2	35	0.0500	0.028	0.045	0.059
0.3	30	0.0600	0.032	0.051	0.067
0.5	25	0.0710	0.038	0.061	0.079
1	18	0.100	0.048	0.076	0.100
2	16	0.118	0.061	0.096	0.126
3	14	0.140	0.069	0.110	0.144
5	12	0.170	0.082	0.131	0.171
10	10	0.200	0.104	0.164	0.215
20	8	0.236	0.131	0.207	0.271
30	7	0.280	0.149	0.237	0.311
50	6	0.335	0.177	0.281	0.368
100	5	0.400	0.223	0.354	0.464