

Sample Size and Meaningful Gold Analysis

By H. EDWARD CLIFTON, RALPH E. HUNTER, FREDERICK J. SWANSON,
and R. LAWRENCE PHILLIPS

SHORTER CONTRIBUTIONS TO ECONOMIC GEOLOGY

GEOLOGICAL SURVEY PROFESSIONAL PAPER 625-C

*A technique for estimating the size of
sample required to provide a representative
sample for analysis for gold and other
particulate heavy metals and minerals*



UNITED STATES DEPARTMENT OF THE INTERIOR

WALTER J. HICKEL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

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SAMPLE SIZE AND MEANINGFUL GOLD ANALYSIS

By H. EDWARD CLIFTON, RALPH E. HUNTER, FREDERICK J. SWANSON, and R. LAWRENCE PHILLIPS

ABSTRACT

A sample of geologic material is of adequate size for gold analysis if it is large enough to insure that the analysis will have a specified degree of precision. It can be shown mathematically that, if (1) gold particle mass is uniform, (2) gold particles make up less than 0.1 percent of all the particles, (3) the sample contains at least 1,000 particles of all kinds, (4) analytical errors are absent, and (5) the gold particles are randomly distributed through the deposit being sampled, the precision is determined solely by the number of gold particles in the sample. The precision afforded by 20 particles per sample is deemed sufficient for most purposes. A graph has been devised by which one can determine, for different combinations of gold grade and particle size, the weight of sample expected to contain 20 particles. Modifications of this graph allow its use for determining sample sizes necessary for other degrees of precision, for determining to what extent field samples require preconcentration for gold analysis, and for determining sample sizes for heavy minerals other than gold.

In addition to variability in the number of gold particles per sample, variability in gold particle size is a major cause of imprecision in gold analysis. Several methods may be used to determine sample size where particle size varies. Analysis of a natural sand sample demonstrates the use of the procedures for determining adequate sample size.

INTRODUCTION

The collection of an adequate sample constitutes the first step for any analysis of geologic material. To be meaningful, the sample must accurately represent a larger entity—a deposit or some portion of a deposit. A sample too small to be representative of this entity is without value. The problem of sample size is particularly acute in the analysis for gold, which occurs significantly in trace amounts, parts per million, commonly represented by only a few particles per sample. The problem is further complicated by the size of the laboratory specimen ultimately analyzed; it may be much smaller than the initial field sample.

For example, atomic-absorption techniques, currently used by the U.S. Geological Survey for routine analysis for gold (Lakin and Nakagawa, 1965), utilize only 10 g (gram) of material. If the field sample contains relatively few gold particles, random selection

of the analytical portion may not provide a portion that is representative of the field sample. In such cases, the gold in the initial sample must be concentrated into the analytical portion (Clifton and others, 1967) or the sample must be reduced by grinding to produce a greater number of gold particles; otherwise, the most careful field sampling may prove futile.

The purpose of this paper is to provide simple workable means of establishing the minimum sample size adequate and to indicate the circumstances wherein concentration prior to analysis is necessary. Consideration is given mainly to analysis for gold by atomic-absorption techniques; the principles, however, apply to any kind of analysis for particulate trace elements.

The problems of determining sample size for mineral or chemical analyses have been studied in recent years by Becker (1964a, 1964b, 1965a, 1965b, 1966) and Gy (1954, 1956, 1967). Their results are applicable to sampling problems in general, whereas the present approach is based on assumptions that seem appropriate for the special problem of sampling for gold analysis. Consequently, the mathematical derivations presented here are less complex than those of Becker and Gy.

The results given in this paper can be shown to be essentially the same as those of Gy if the restrictions made in the present study are introduced into his equation relating the variance of analytical results to factors such as sample size (Gy, 1967, p. 51, eq 4.98; Ottley, 1966, p. 42). The present results are also essentially the same as those of de Magnée (1956) and Prigogine (1961), who made restrictions similar to those in this study. However, the graphs presented here are perhaps more easily grasped intuitively than are the equations of Gy, de Magnée, and Prigogine. They assume a form very similar to those shown by Gy (1956, p. 95, 97), but give sample sizes containing the expected number of gold particles.

The approach of this paper also differs from the work of Gy, de Magnée, and Prigogine in its use of relative errors determined from the binomial and Poisson distributions. This approach gives more complete infor-

mation about the distribution of analytical results than is given by the equations of Gy, de Magnée, and Prigogine for the variance of analytical results. The more complete information is especially useful for relatively small samples containing few gold particles.

The writers have profited greatly from the work of Gy and Prigogine, who have treated the problems of sampling in much greater detail than we have here. The reader is referred to their papers for additional information as well as to Krumbein and Graybill (1965) and Miesch (1967b) for discussions of the basic philosophy and methods of sampling geologic materials.

We wish to acknowledge that the analytical work was carried out by Kam Leong and Arthur Hubert, assisted by Oliver Roman, and that T. R. Alpha assisted in the field and laboratory.

ADEQUATE SAMPLE SIZE

In order to determine adequate sample size, the precision expected in the analysis of gold content must be quantitatively defined. The precision of a gold analysis can be defined by two numbers. First, the true gold content of the deposit is expected to be within a certain range of values surrounding the value obtained by chemical analysis of a sample. For example, we will require here that the true gold content be no more than approximately 50 percent larger or smaller than the gold content obtained by chemical analysis of a sample. However, because of random variation in gold content from sample to sample, it is impossible to be completely certain that the true gold content will be within a given range of values. Therefore, one must specify a second number, the confidence, or probability that the true gold content will be within the required range of values. For example, we will require here that it be 95 percent probable that the true gold content of the deposit be no more than approximately 50 percent larger or smaller than the gold content obtained by chemical analysis of a sample. The number, 50 percent, will be referred to as the relative error.

In the following discussion, a basic assumption will be made concerning the deposit from which the sample is taken. It will be assumed that its variability in gold content from point to point is due entirely to random spacing of the individual gold particles and that there are no systematic variations in gold content in any direction across the deposit. Most actual geologic deposits do not approach this ideal, instead they contain gold preferentially concentrated in layers, veins, or pockets. However, the ideal may be approached by limited portions of geologic deposits, which can be considered separate entities or deposits themselves.

If systematic trends in gold content do occur in a deposit, the precision of the gold analysis may be less than that predicted for the ideal type of deposit assumed here. The undesirable effect of systematic trends in gold content can be reduced by a proper sampling plan, but such procedures are beyond the scope of this paper. Sampling plans are treated in detail by Krumbein and Graybill (1965) and by Miesch (1967b).

It can be shown mathematically (see the section "Mathematical analysis") that the number of gold particles in the sample is the only factor controlling the precision of the chemical analysis if, in addition to assuming that the gold particles are distributed randomly, it is also assumed that (1) gold particle mass is uniform, (2) gold particles make up less than 0.1 percent of all the particles, (3) the sample contains at least 1,000 particles of all kinds, and (4) analytical errors are absent. The relation between precision and number of gold particles in the sample is shown in figure 1, which indicates that the degree of precision specified in this study will be attained if the sample contains 20 particles of gold. A sample has the minimum adequate size then if it is large enough that it can be expected to contain 20 particles of gold. For reconnaissance studies, a smaller sample containing fewer particles of gold may suffice. It is important, however, to note that as the expected number of particles per sample falls below five, the chance of having no gold particles in a given sample greatly increases (fig. 5).

Unfortunately, it is seldom, if ever, possible to count the number of gold particles in order to determine if a sample is of adequate size. However, in any material, an interrelationship exists between the number of particles of a particular component per unit mass of sample, the masses of these individual particles, and the grade or concentration by weight of the component. If the particle masses and their concentration are known, the number of particles can be determined. If particle mass is assumed to be uniform, the general relationship between these factors can be shown on a simple graph (fig. 2 or Clifton, 1967) or chart (Miesch, 1967a). The density and particle shape of any specific component relate the particle mass to particle size. Figure 2 applies specifically to gold in the grain-size relationships shown on the right margin of the figure. Grain size is shown in terms of both spheres and flakes of the shape that gold particles commonly exhibit. The ranges of particle mass and grade shown in the figure are limited to the field occupied by most deposits of detrital gold; the relationships can readily be extrapolated to cover particle masses and grades beyond the scope of the figure.

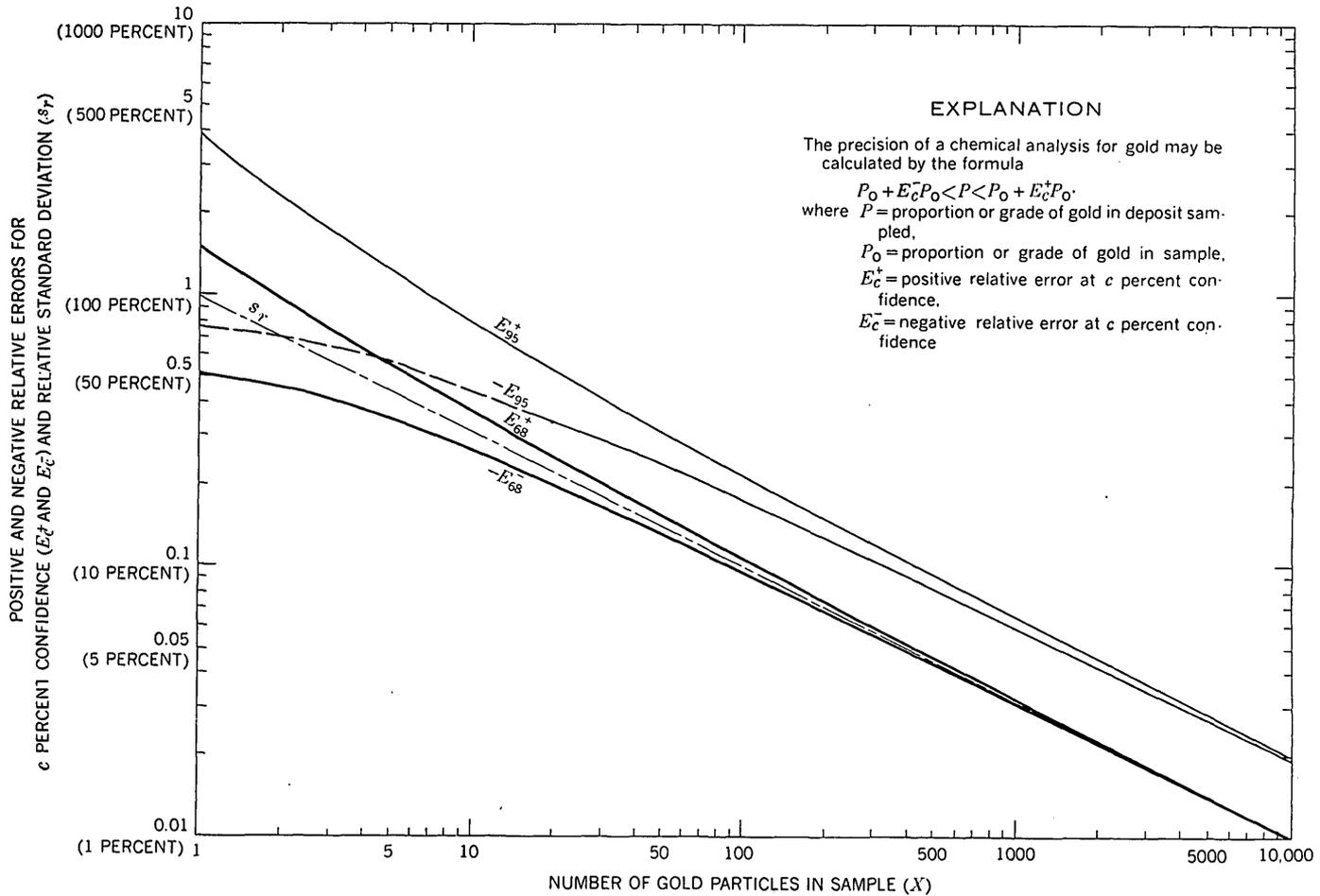


FIGURE 1.—Relative errors and relative standard deviation in relation to number of gold particles in sample. The relative errors for 68 and 95 percent confidence are shown. Note that the negative relative errors have negative values. The dashed portion of the E_{95}^- curve was calculated on the basis of the Poisson distribution. An example of how to use figure 1: Suppose that a sample is found by analysis to have a gold content (P_0) of 1.00 ppm and that the sample size and gold particle size are such that the number of gold particles, X , is calculated to be 20. At 95-percent confidence, what limits can be placed on the gold content of the deposit from which the sample was taken? From the figure, $E_{95}^+ = 0.54$ and $E_{95}^- = -0.34$. Therefore, one can be 95 percent confident that the gold content (P) is between $(1.00 - 0.34)$ ppm and $(1.00 + 0.54)$ ppm, or between 0.66 ppm and 1.54 ppm.

The size of sample required to provide the desired particle-per-sample ratio can be determined from figure 3, which is derived from figure 2. The ratio depends on both the mass and concentration of the particles. In figure 2, a 1-kg (kilogram) sample contains 20 particles at any of the mass-grade combinations intersected by the 20-particle vertical line. Likewise, a 500-g sample will contain 20 particles at any of the combinations intersected by the vertical line in the figure at which 1 kg contains 40 particles. The grade to grain-size relationships which provide 20 particles for samples of other sizes can be similarly calculated. In this way, figure 3 is derived; it shows the sample sizes that contain 20 par-

ticles per sample at various combinations of grade and particle mass.

Figure 2 also can readily be used to determine sample-size requirements to provide other particle-per-sample ratios. For example, to obtain 40 particles per sample for any particle mass-grade combination in figure 3, the indicated sample size should be doubled. To obtain 10 particles per sample the indicated size should be halved. Figure 4 indicates the changes necessary to modify the base of figure 3 to apply to specifically desired particle-per-sample ratios and relative errors.

Use of figure 3 requires that the sampler have some idea of the grade and particle mass likely to be encoun-

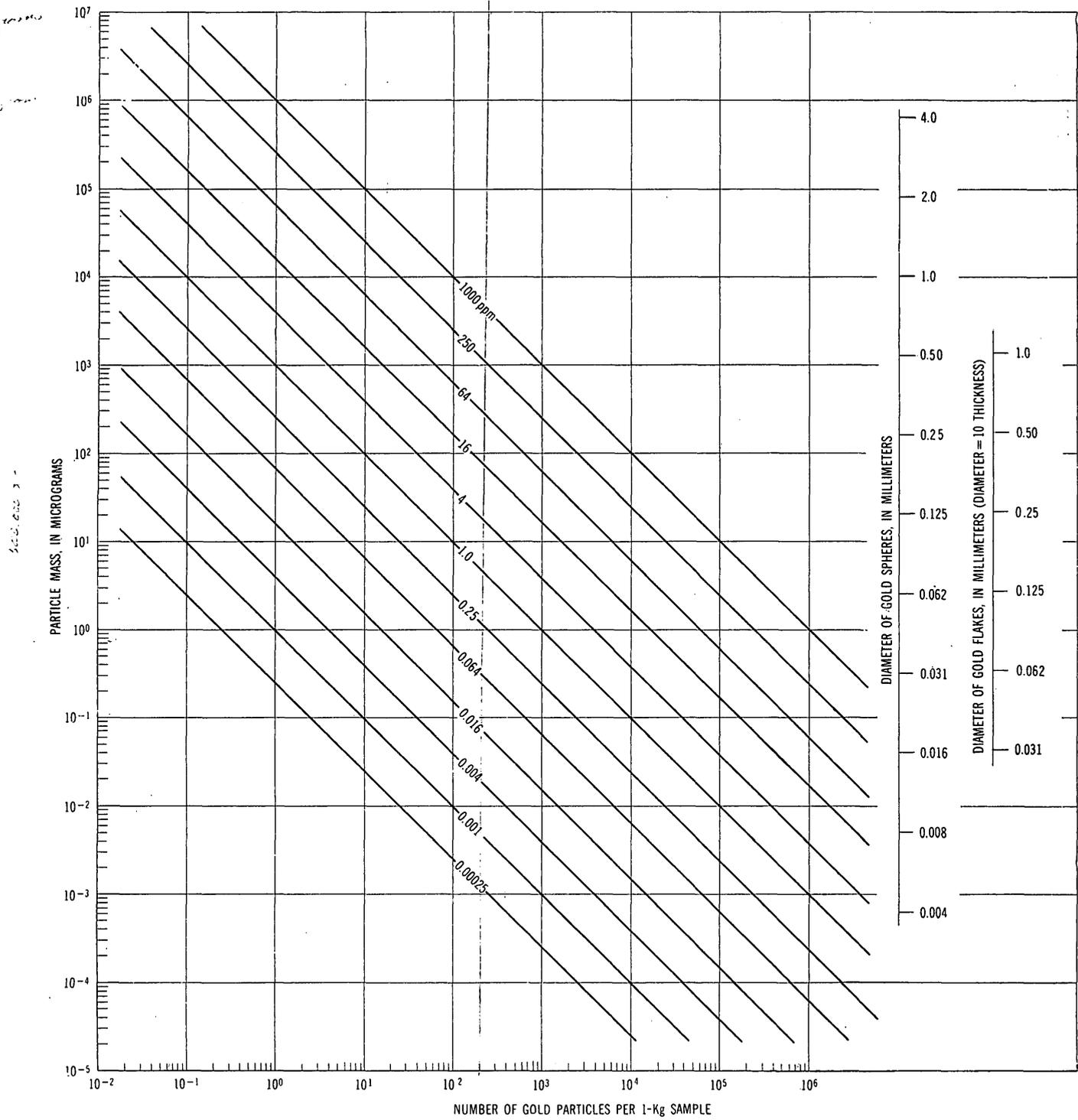


FIGURE 2.—Relationship between number of particles per 1-kg sample, particle mass (assuming all particles to be of uniform mass), and grade or tenor of the sample in parts per million. Scales to right relate grain size of gold spheres and flakes to particle mass.

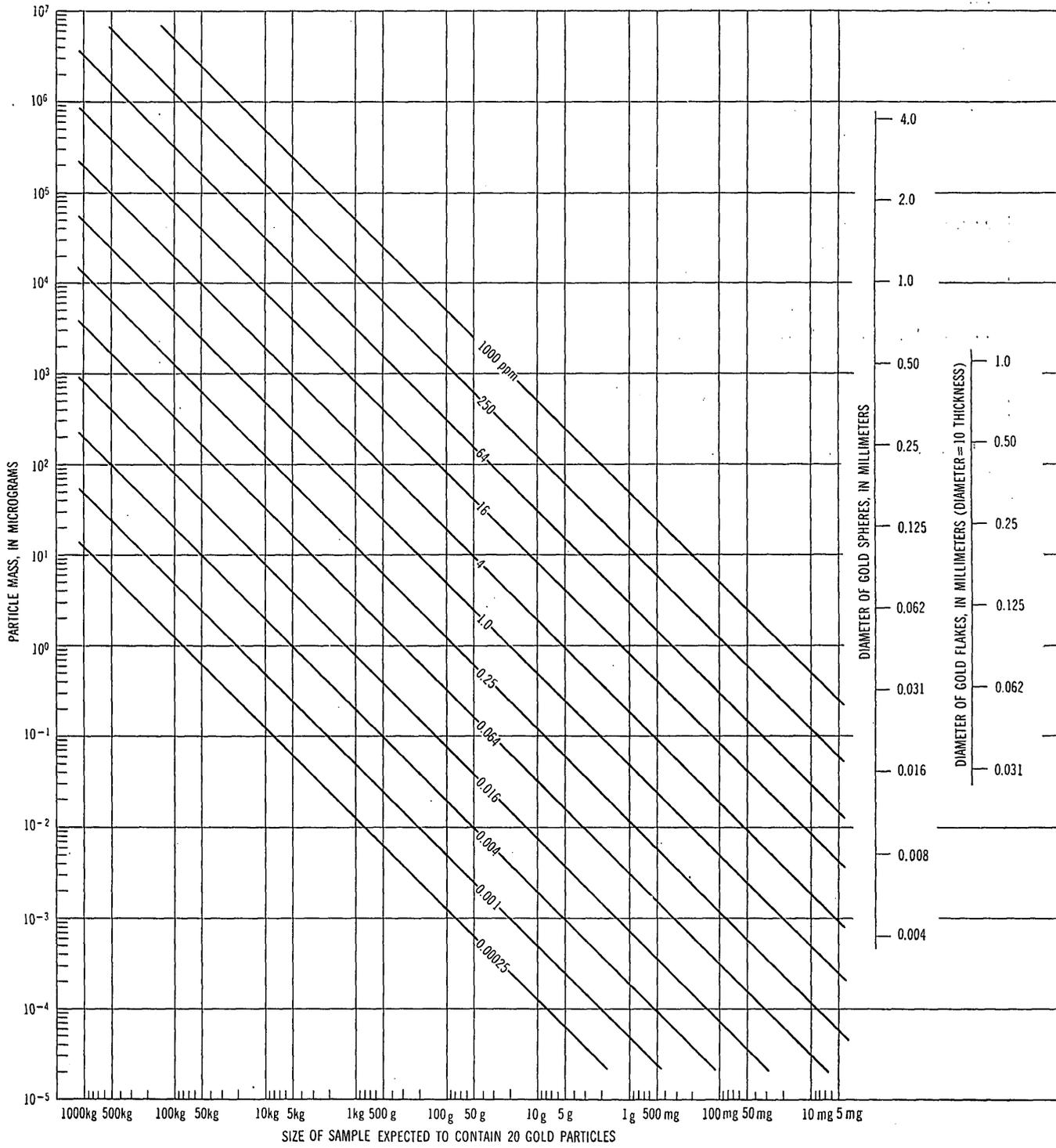


FIGURE 3.—Size of sample required to contain an expected 20 particles of gold as a function of the combination of gold particle size and grade, assuming all gold particles to be of uniform size and randomly distributed in the deposit.

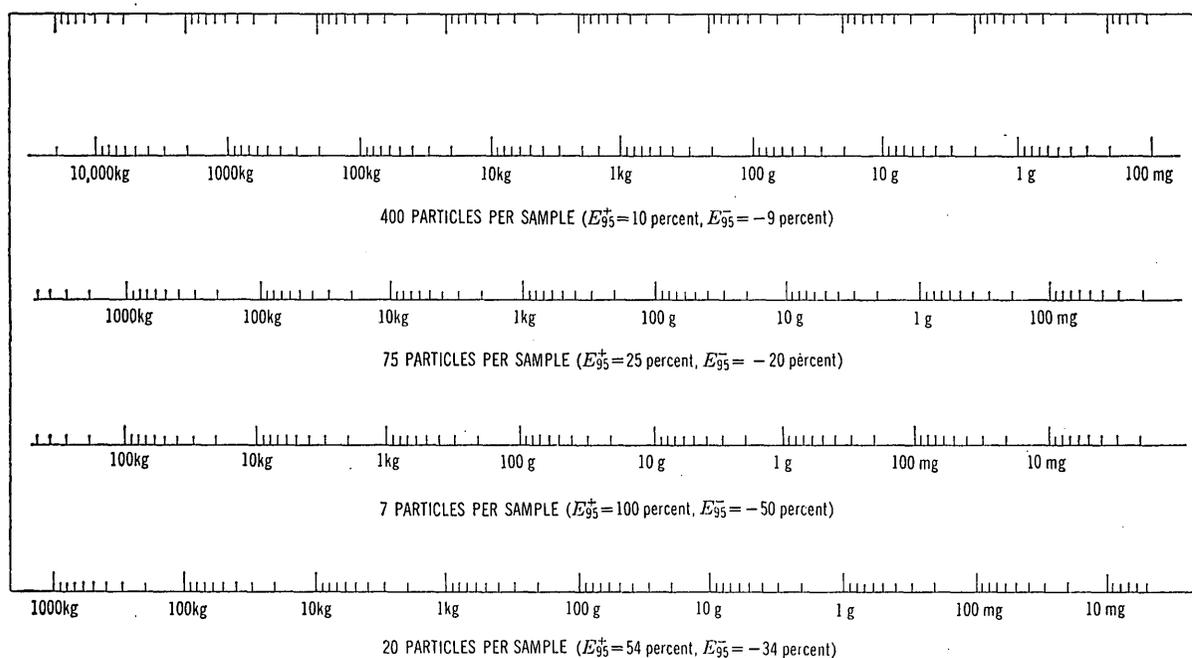


FIGURE 4.—Scales to convert sample size as indicated by figure 3 for 20 particles per sample to sample sizes for other particle-per-sample ratios (7, 75, and 400). E_{95}^+ and E_{95}^- show the positive and negative relative errors at 95 percent confidence for each of the ratios. For example, if the precision given by 400 particles per sample is required and the grain size-grade combination in figure 3 indicates a sample of 1 kg for 20 particles per sample, conversion shows that a sample of about 30 kg is needed. The conversion scale can also be applied to figure 6 to establish preconcentration requirements consistent with the degrees of precision shown.

tered. This may be estimated from the expected range for the type of deposit, established by preliminary analyses of selected size fractions, or estimated by a procedure described in a following section of this paper.

PRECONCENTRATION REQUIREMENTS

The foregoing discussion describes how to select a sample large enough to adequately represent the deposit. Analysis of such samples, however, may be meaningless if made only on a randomly selected portion of the original sample. For example, assume that a 2-kg sample of gold containing 20 particles of gold averaging 0.1 mg (milligram) each is brought from the field. The sample has a gold concentration of 1.0 ppm (parts per million). It is to be analyzed by an atomic-absorption process that utilizes a 10-g analytical portion. The hypothetical sample can be divided into 200 analytical portions but contains only 20 particles of gold; the chances are only about 1 in 10 that any randomly split analytical portion will contain 1 or more gold particles. If a particle did occur in the sample, the analysis would indicate a misleading 10.0 ppm, compared to the true concentration in the sample of 1.0 ppm.

Such a problem results from the particle-sparsity effect (Clifton and others, 1967), whereby the analysis for

a component such as gold, based on a split of unprocessed sample, depends more upon the chance occurrence of particles in the analytical portion than upon the actual concentration within the sample. Figure 5, based on calculations described in the section "Mathematical analysis" graphically illustrates the particle-sparsity effect. In the hypothetical sample described above, for example, the expected number of gold particles in each 10-g analytical portion is 20/200, or 0.1. Figure 5 shows that, for this value of expected number of gold particles, slightly more than 90 percent of all the possible analytical portions would contain no gold particles.

As the hypothetical sample has a gold value of economic interest, about \$1.00 per ton, a 90-percent chance of finding no gold by analysis is intolerable. Even if the gold particles were only one-tenth as large, weighing 0.01 mg apiece, a gold concentration of 1.0 ppm would lead to only 1.0 gold particles expected in a 10-g analytical portion. Figure 5 shows that, for this value of expected number of gold particles, the chances of an analysis finding no gold would be 37 percent, still an intolerably high figure.

The particle-sparsity effect pertains to some degree whenever the analytical portion contains fewer than the number of particles required for a given degree of

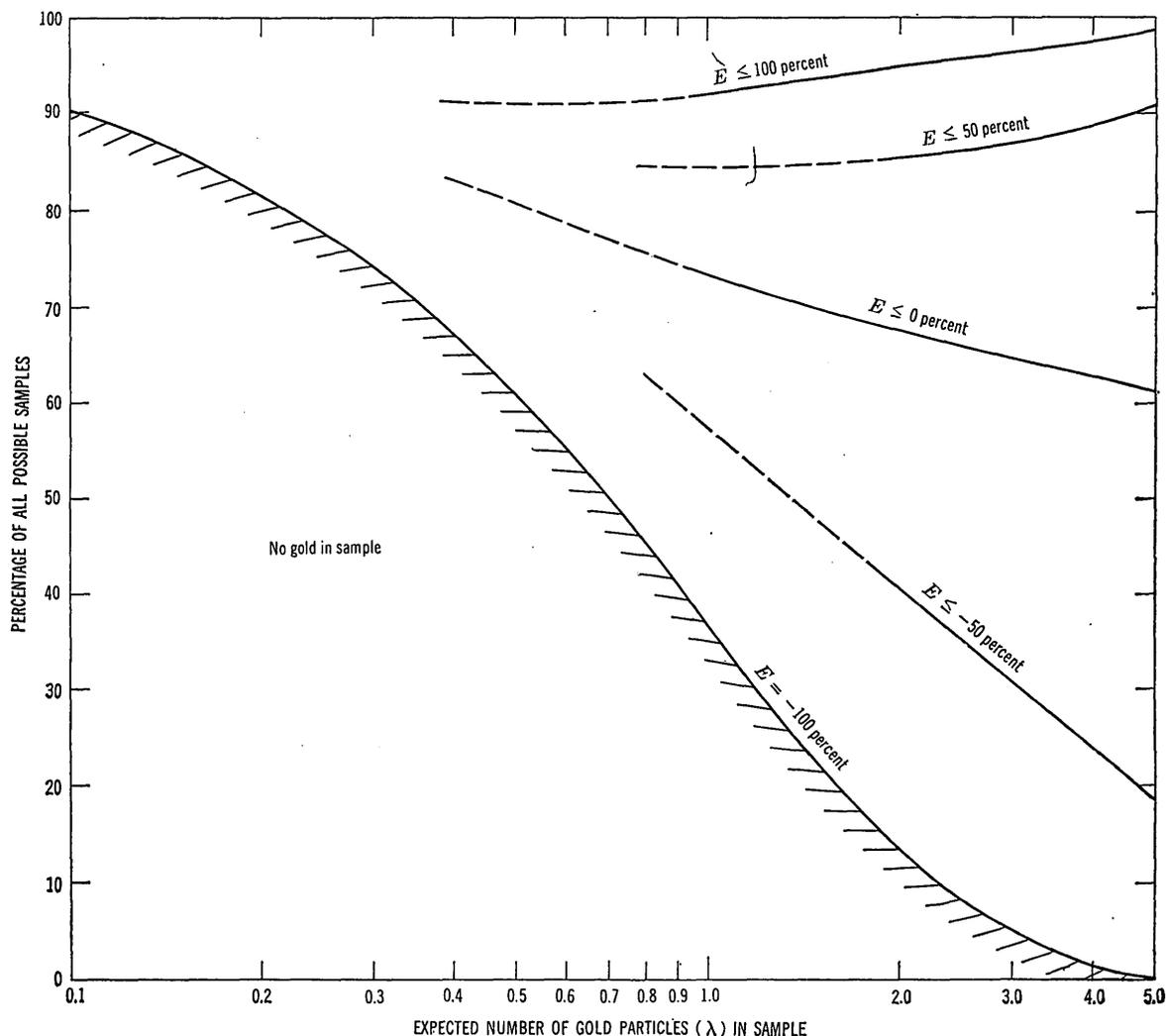


FIGURE 5.—Percent of all possible samples in which the relative error (E) is less than or equal to -100 , -50 , 0 , $+50$, and $+100$ percent, plotted in relation to the expected number of gold particles (λ) in the sample. The curve for which $E = -100$ percent shows, for a given value of λ , the percentage of all possible samples that will contain no gold. The curve for which $E \leq +100$ percent shows the percentage of all possible samples in which the observed gold content will be no more than twice the gold content of the deposit. Similarly, the curves for which $E \leq +50$ percent, $E \leq 0$, and $E \leq -50$ percent show the percentages of all possible samples in which the observed gold content will be no more than 1.5, 1.0, or 0.5 times the gold content of the deposit. For example, if the grain size-grade combination of the deposit is such that a sample of given size is expected to contain 1 gold particle, then 37 percent of all possible samples of that size will contain no gold, 74 percent of the samples will have gold analyses equal to or less than the grade of the deposit, and 93 percent of the samples will have gold analyses no more than twice the grade of the deposit.

precision. The effect can largely be overcome by concentrating all of the gold in a sample into the analytical portion or portions prior to analysis (a procedure referred to herein as "preconcentration"). Figure 6 shows those combinations of grade and grain size which necessitate preconcentration. It also distinguishes those samples that need to be preconcentrated, not to produce a representative analytical portion, but to increase the

grade of gold to the level of detectability by atomic-absorption techniques. Distinction between these two purposes is important. In the small range below the level of detectability it is possible to analyze samples without preconcentration to determine whether or not gold is present at the limit of detectability. Elsewhere in the field of the graph, preconcentration is required for even this decision.

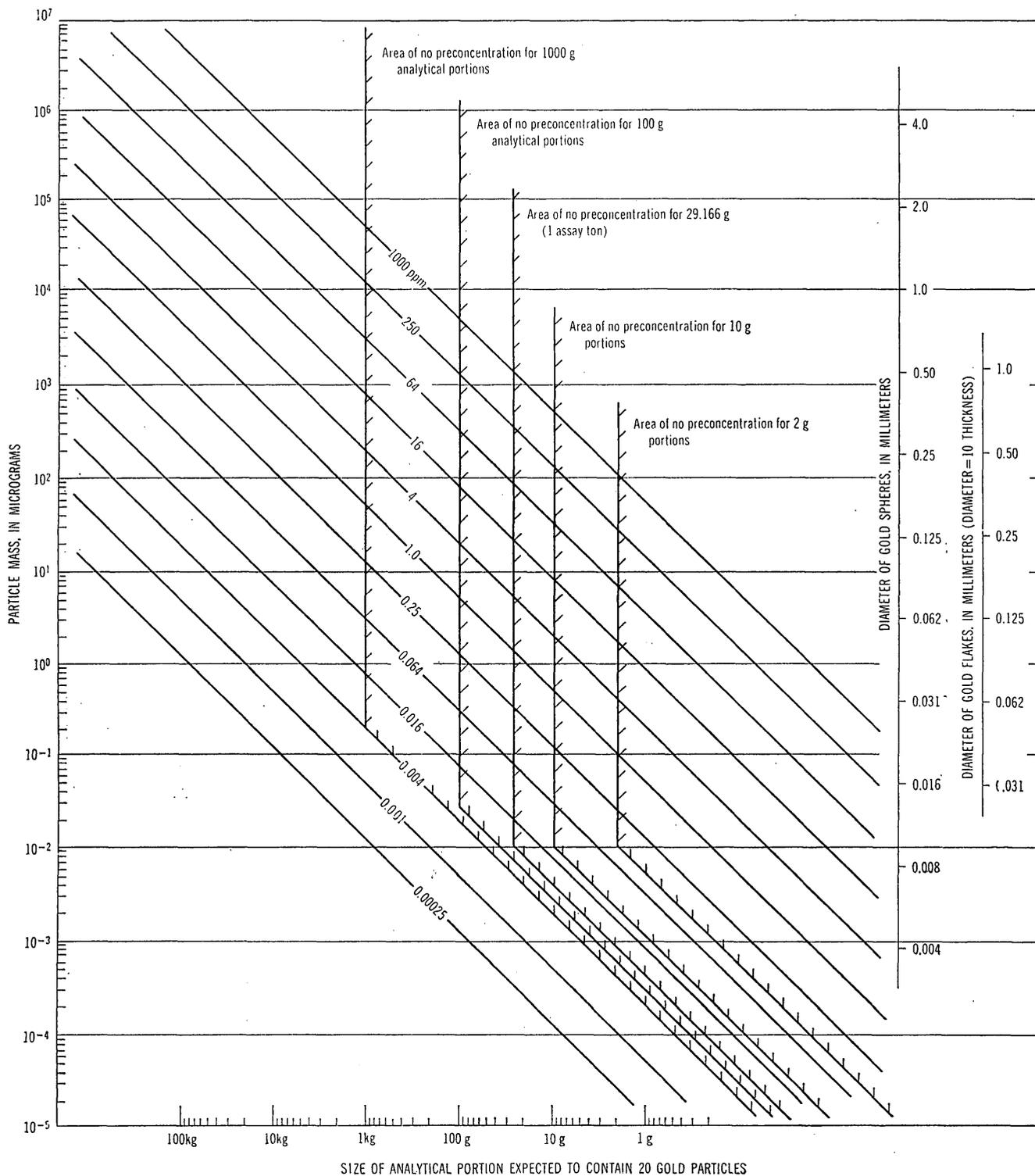


FIGURE 6.—Relation of gold grain size and grade to preconcentration requirements for some common sizes of analytical portions. (For explanation see opposite page.)

PARTICLE-SIZE VARIABILITY

The assumption has been made that the gold to be sampled is of uniform size. In practice, gold particles almost certainly range across a size spectrum, although in some deposits this range may be relatively restricted (Clifton and others, 1967). The variation in the sizes of gold particles is another source of error which must be considered when selecting adequate sample size. As the size range of the particles increases, the relative errors of the analyses will increase, even if the number of gold particles per sample remains the same. Therefore, the relative errors for samples in which the particle size varies will be greater than indicated in figure 1, and larger samples will have to be taken in order to maintain a specified precision.

The effects of nonuniform particle size can be taken into account by assuming that the gold particles have some uniform mass larger than the average mass per gold particle in the sample. By average mass per gold particle, we mean the total mass of gold in the sample divided by the number of gold particles in the sample. If an adequate sample size is determined from figure 3, assuming that the mass per gold particle is larger than the average mass, the sample would actually contain more than 20 gold particles. If the proper mass per gold particle is chosen, the sample could be said to contain effectively 20 gold particles, in the sense that the precision of the gold analysis would be the same as that predicted by figure 1 for a sample containing 20 gold particles of uniform size. This proper mass per gold particle will be termed the "effective" mass per gold particle.

Gy (1967, p. 51, eq 4.96) and Prigogine (1961, p. 22, eq 32b) have shown that, if the grain-size distribution

of the particles is known, the measure of grain size that can be used to calculate the effective gold-particle mass, and which therefore may be called the effective grain size or diameter, d_e , is calculated by the equation

$$d_e = \left(\sum_j \frac{M_j}{M} d_j^3 \right)^{1/3}$$

where M_j is the mass of gold in size grade j , d_j is the midpoint diameter of size grade j , and M is the total mass of gold in all size grades. Gy (1967, p. 33, eq 3.6) shows that the proper value for d_j^3 is one-half the sum of the cubes of the sieve openings bounding size grade j . The effective grain diameter, d_e , may be converted to the effective particle mass by use of the vertical scales in figure 2 or 3.

Preliminary analysis of unsized splits provides another means of estimating effective particle size. For example, a 1-kg sample could be split randomly into a hundred 10-g portions, each of which is independently analyzed. The variability in the analytical values, as measured by the relative standard deviation or coefficient of variation (table 1), gives an estimate of the effective number of gold particles in the sample (fig. 1 and table 1). Note that the value of the relative standard deviation is intermediate between the values of positive and negative relative errors at 68-percent confidence (fig. 1). If gold is not detected in some of the analyses, the percent of the analyses in which it is not detected may be compared with the percent of all possible analyses in which no gold particles are present (fig. 5) to give another estimate of the number of gold particles (table 1).

EXPLANATION OF FIGURE 6

Preconcentration is required for any combination of grain size and grade to the left of the areas indicated. For example, a sample containing gold particles that are uniformly 10 mg in mass and 4 ppm in grade need not be concentrated prior to analysis in 100 or 1,000 g portions but would require concentration prior to being analyzed in one of the smaller sized portions shown. The preconcentration specified here maintains the degree of precision given by 20 particles per sample provided the particle size is assumed to be uniform. Vertical boundaries are located by grain size-grade combinations that will produce 20 particles in the analytical portion indicated. Diagonal boundaries are located by the minimum detectability for each size of analytical portion. Below the diagonal boundaries, preconcentration is required, not to provide a statistically representative analytical portion but to increase the grade of the portion to the level of detectability. The detectable limits shown apply specifically to the atomic-absorption analytical methods described by VanSickle and Lakin (1968), as modified, for 1,000 g portions, by K. W. Leong. The limits of detectability may differ slightly depending on the instrument used and the nature of the material to be analyzed (K. W. Leong, oral commun., 1968). For different requirements of precision, the conversion scales given by figure 4 may be used.

TABLE 1.—*Estimate of effective number of gold particles from distribution of analytical values*

Distribution of analytical values	Effective number of gold particles per analyzed subsample
Gold detected in all analyses, very to fairly uniform values ($s_r < 0.22$) ¹	>20
Gold detected in all analyses, some variation ($s_r = 0.22-0.50$)	4-20
Gold detected in most analyses, much variation ($s_r = 0.50-1.0$)	1-4
Gold detected in less than half of the analyses, much variation ($s_r > 1.0$)	<1
Gold not detected in any of the analyses	0

¹ The relative standard deviation, or coefficient of variation, s_r , is the standard deviation of the gold values divided by the mean of all the values. The standard deviation, s , may be calculated by the equation

$$s = \sqrt{\frac{\sum_{i=1}^N A_i^2 - \frac{(\sum_{i=1}^N A_i)^2}{N}}{N-1}}$$

where A_i is the value of the gold analysis of the i th subsample and N is the number of analyzed subsamples (Dixon and Massey, 1957, p. 19).

The estimate of effective number of particles per kilogram may be plotted in figure 2 against the average grade produced by the combination of the analyses of all the splits. The intersection of these two parameters gives an estimate of the effective size of gold particles in the sample. The accuracy of the estimate improves as the number of analyzed splits is increased, but the method can be used even with a small number of splits.

If the size distribution of the gold particles is uncertain and analyses of splits are not available, adequate sample size can be determined on the assumption that all of the gold in the sample is uniformly as large as the maximum significant size. By maximum significant size is meant the size near the coarse end of the size frequency curve, a size beyond which coarser particles contribute only insignificantly to the total gold content. The coarsest gold particles, if by chance occurring in a sample, will produce a misleadingly high analytical value; however, their likelihood of occurrence is directly proportional to their significance within the deposit.

Once the gold-particle-size distribution is roughly established or estimated, the maximum significant size can be defined in accordance with the requirements of the study. In our studies we have arbitrarily considered the coarsest 5 percent (by weight) of the gold to be insignificant. Adequate sample size can then be determined by applying the estimated maximum significant gold size rather than the estimated effective gold size to figure 3. The assumption that all of the gold in a sample is uniformly as large as the coarsest significant gold provides an added safety factor in determining adequate sample size and should help to ensure a representative sample.

APPLICABILITY TO NATURAL SAMPLES

Detailed analysis of a single sample demonstrates the application of figures 2 and 3 to natural samples. A sample weighing 80 pounds was taken from magnetite-rich beach sand north of Gold Beach, Oreg. The sample was thoroughly mixed and then split into analytical fractions through a Jones-type sample splitter in order to avoid the possibility that variability in analytical results might be due to internal inhomogeneity of the gold distribution within the sample. The gold-particle-size range and grade in this sand were established by analysis of sieved fractions. The effective and maximum significant gold particle size determined from multiple analyses of the sieved fractions were compared to the effective gold particle size estimated from the distribution of analytic data from a number of unsieved splits. Adequate sample size was determined from figure 3 by using the various estimates of effective and maximum significant gold particle size, and the different sample sizes thus indicated were evaluated by comparing the results of analysis of samples of different sizes.

Initially, a split weighing about 5,000 g was sieved and the size fractions analyzed for gold, using a combination of wet chemical and atomic-absorption techniques (Lakin and Nakagawa, 1965). Table 2 and figure 7 summarize these analytic data, which show the gold to range in size from less than 0.044 to 0.354 mm (millimeter). The size frequency curve of this distribution indicates a maximum significant gold particle size of about 0.27 mm (fig. 7); particles larger than this constitute less than 5 percent of the total gold. Gold grains from the deposit were examined under the microscope and found to be flakes whose thickness is about one-tenth of the diameter. The average gold content of all analyzed splits of this sample is 0.38 ppm. The intersection of this grade in figure 3 with the maximum significant diameter indicates that about 1,500 g should constitute an adequately representative sample. In con-

TABLE 2.—*Occurrence of gold in size fractions of a 5,150-g beach sand sample*

Size class (mm)	Weight of gold in size class (μ g)	Percent of total gold
0.354-0.500	<0.4	0.0
0.250-0.354	138	7.6
0.177-0.250	195	10.7
0.124-0.177	327	18.0
0.088-0.124	680	37.5
0.062-0.088	340	18.7
0.044-0.062	126	6.9
<0.044	8.6	.5
Total	1815	99.9

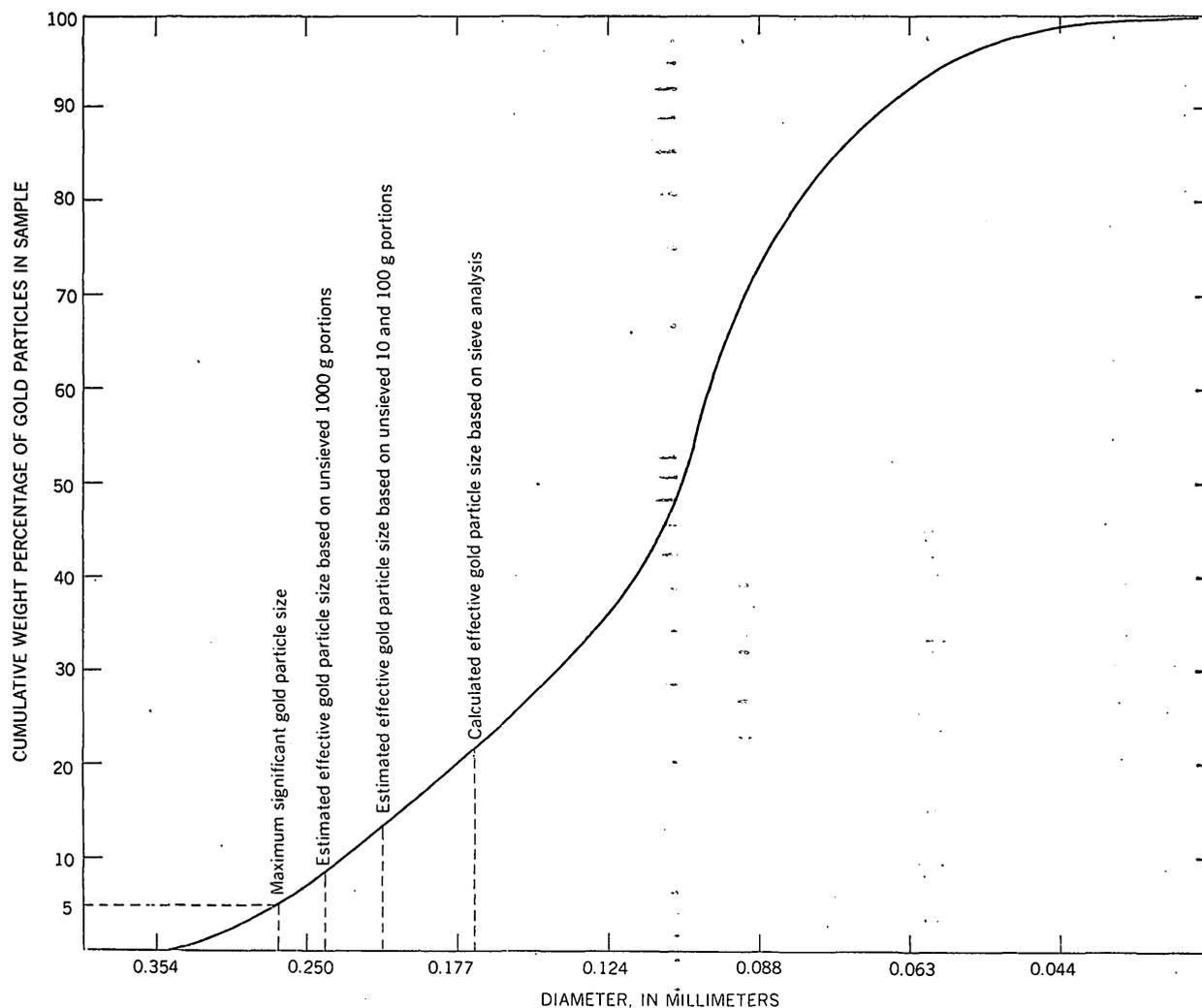


FIGURE 7.—Cumulative curve of gold grain-size distribution in a sample of beach sand. Shown are the various measures of particle size for a deposit in which gold grain-size is variable, including the maximum significant size (0.27 mm, equal to the coarsest 5th percentile), the effective particle size as estimated from the distribution of analytical data from unsieved 1,000-g portions (0.24 mm), from 100-g portions (0.21 mm), from 10-g portions (0.21 mm) and as calculated from the analyses of sieved fractions (0.17 mm).

trast, the effective grain diameter, calculated by Gy's equation in the foregoing section, is 0.17 mm (fig. 7). The application of this size to figure 3 indicates that a sample of about 360 g would provide adequate representation.

In addition to being calculated from the analysis of size fractions, the effective gold-particle diameter was estimated from the distribution of analytical data for a number of unsieved splits. This method, described in the preceding section, should be useful in estimating particle size where sieve analyses are not available. Three series of unsieved splits, weighing about 10 g, 100 g, and 1,000 g per split, were analyzed.

The analytic results from ninety-six 10-g splits are shown in figure 8. The relative standard deviation of the

analytical values is 1.69 (table 3), and 49 of the splits contained no gold particles coarse enough to be detected. This distribution of data suggests (table 1) that the number of particles per split is less than one. More precisely, the value of the relative standard deviation indicates (see fig. 1, value extrapolated to values of X less than 1.0) an average of effectively 0.36 gold particles per 10-split or 36 particles per kilogram of sample. The effective size of these particles, as found by projecting this number in figure 2 against the average grade of 0.52 ppm for the 96 splits, is approximately 0.21 mm. Figure 3 indicates that, for gold of this size from a deposit having a grade of 0.38 ppm (the average of all analyzed splits of the sample), a 750-g sample would suffice.

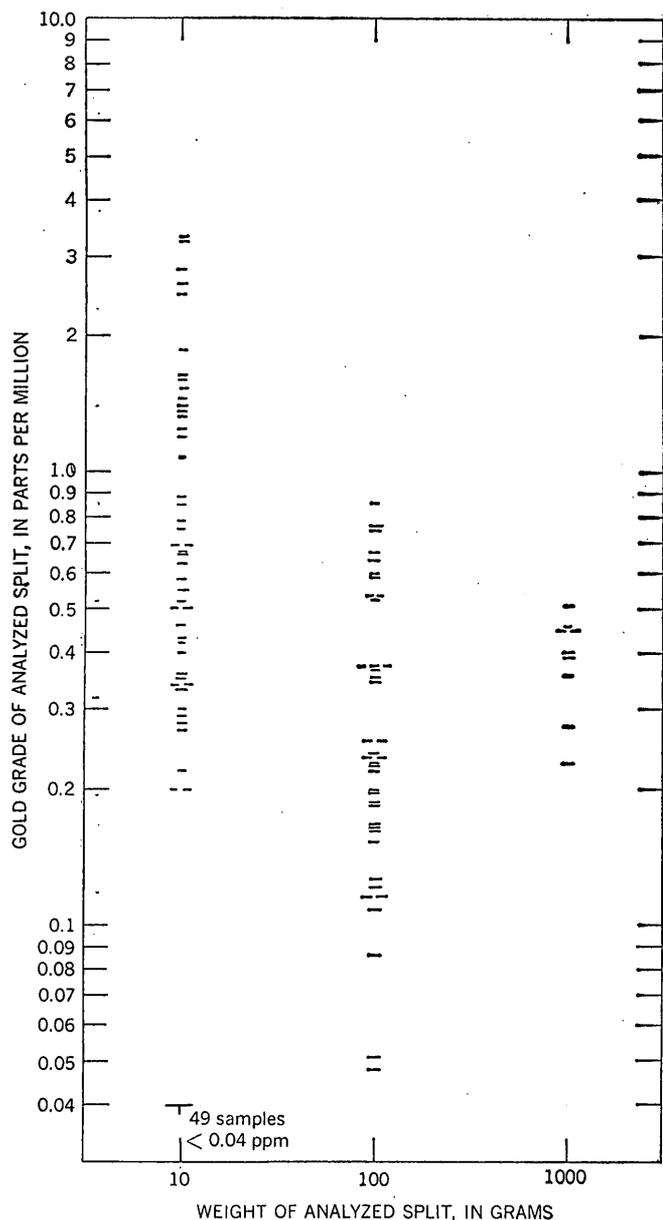


FIGURE 8.—Distribution of analytical values for three sample sizes. The values shown are for ninety-six 10-g samples, forty 100-g samples, and nine 1,000-g samples that were split from an 80-pound sample of beach sand.

The analytical results from forty 100-g splits and nine 1,000-g splits are also shown in figure 8. The relative standard deviations are 0.69 for the 100-g samples and 0.23 for the 1,000-g samples (table 3). These values indicate (fig. 1) that the 100-g splits contained effectively 2.1 gold particles per split and that the 1,000-g splits contained effectively 19 particles per split. By applying these values to figure 2, the effective gold particle size is estimated to be 0.21 mm for the 100-g splits and 0.24

mm for the 1,000-g splits. By using these sizes in figure 3, it can be seen that adequate sample sizes of 750 g and 1,100 g are indicated by the analytical results of the 100-g splits and 1,000-g splits (table 3).

TABLE 3.—Measures of gold particle size for splits of a large sample, adequate sample sizes predicted from these data, and statistical parameters by which these were calculated

	10-g splits	100-g splits	1,000-g splits	5,150-g sieved split
Number of splits	96	40	9	1
Mean gold grade, in parts per million ¹	0.52	0.32	0.39	0.35
Standard deviation, in parts per million	0.88	0.22	0.09	-----
Relative standard deviation	1.69	0.69	0.23	-----
Effective number of gold particles per split	0.36	2.1	19	-----
Effective gold particle diameter, in millimeters (assuming flake shape)	0.21	0.21	0.24	0.17
Maximum significant gold particle diameter, in millimeters	-----	-----	-----	0.27
Adequate sample size, in grams (sample size expected to contain effectively 20 particles)	750	750	1,100	* 360, * 1,500

¹ The mean gold grade of the total 14 kg of analyzed sample is 0.38 ppm. This was the figure used, in combination with the measure of gold particle diameter, to determine adequate sample size from figure 3.

² Based on effective gold particle diameter.

³ Based on maximum significant gold particle diameter.

A comparison of the adequate sample sizes obtained by using the various estimates of effective particle size shows a significant difference between the value, 360 g, obtained from analysis of sieved fractions, and the values, 750 to 1,100 g, obtained from analysis of unsieved splits. In contrast, the adequate sample size given by using the maximum significant gold particle size obtained from the analysis of sieved fractions is 1,500 g, a figure greater than those given by analyses of unsieved splits.

The reason for the discrepancy between the effective gold particle size estimated from the analysis of sieved fractions and the effective sizes estimated from analyses of unsieved splits is uncertain. Among the possible reasons are imperfection in the splitting of samples and analytical error. A small part of the discrepancy could be due to the fact that the splits were taken from a sample of finite size rather than of infinite size (Deming, 1950, p. 113). Whatever the reason, the safety margin inherent in using the maximum significant gold particle size in calculating adequate sample size is evident.

MATHEMATICAL ANALYSIS

The minimum sample size considered adequate for gold analysis may be defined in terms suitable for statistical analysis as that sample size which allows one to have a certain confidence that the true gold content of the deposit is within a certain acceptable range of values. The confidence may be defined in percentage units as $c=100-\alpha$, where α , the level of significance as de-

fined in statistical usage (Dixon and Massey, 1957, p. 89-91), is the probability that the true gold content of the deposit actually lies outside the range of values. The range of values is the confidence interval, and the limits of the range of values are the confidence limits (Dixon and Massey, 1957, p. 79-80).

The minimum adequate sample size may be defined mathematically as that sample size for which

$$Pr[L_c < P < U_c] = c \quad (1)$$

where Pr is a notation meaning "the probability that . . .", P is the true mass proportion of gold in the deposit, L_c is the lower c percent confidence limit, and U_c is the upper c percent confidence limit. L_c and U_c are in the same units as P . A commonly used value for c is 95, in which case L_c and U_c are the lower and upper 95 percent confidence limits. In general, L_c will be smaller than P_o , the observed mass proportion of gold in the sample as determined by chemical analysis, and U_c will be larger than P_o .

It is advantageous for the present purpose to modify equation (1) to

$$Pr[P_o + E_c^- P_o < P < P_o + E_c^+ P_o] = c \quad (2)$$

where E_c^- and E_c^+ may be termed the negative and positive relative errors at c percent confidence. The relative errors are measures of the probable extent of error in the estimation of P by P_o . They are called relative because they are dimensionless numbers that measure the error relative to P_o .

The minimum percent confidence and the maximum width of confidence interval that are considered appropriate for gold analyses must be decided arbitrarily. These decisions will determine the minimum adequate sample size. We will require here that we be 95 percent confident that P is in the interval $P_o \pm$ approximately $0.5 P_o$. In other words, we will require that the relative errors at 95-percent confidence be equal to approximately -0.5 and $+0.5$. It should be noted that relative errors of ± 0.5 at 95-percent confidence are approximately equivalent in precision to relative errors of ± 0.25 at 68 percent confidence. For studies of reconnaissance nature, a lower precision might suffice; on the other hand, certain very detailed studies might require a higher precision.

The statistical analysis of the problem of adequate sample size may be greatly simplified by assuming that (1) the gold particles are of uniform mass, (2) that the other particles are also of uniform mass, although not necessarily of the same mass as the gold particles, and (3) that the mass proportion of gold in the sample

is less than 0.01. If these assumptions are true, the mass percentage of gold is proportional to the percentage of gold by number of grains. Specifically, the mass percentage of gold is equal to the percentage by number of grains multiplied by the gold particle mass and divided by the particle mass of the other particles (Prigogine, 1961, p. 12, eq. 4a). Then, for the same sample size for which equation (2) was true, it also is true that

$$Pr [p_o + E_c^- p_o < p < p_o + E_c^+ p_o] = c \quad (3)$$

where p is the proportion of gold in the deposit in terms of numbers of particles, p_o is the observed proportion of gold in the sample in terms of numbers of particles, and the relative errors are the same as those in equation (2).

Equations giving the relation between sample size and the relative errors, E_c^- and E_c^+ , in equations (2) and (3) may be derived from the binomial distribution. The population may be considered to consist of gold particles and particles that are not gold, in which gold particles form a proportion, p , of the population. Strictly speaking, the statistical population is not the deposit itself but consists of all the possible samples of a given size that could be taken from the deposit. The proportion of gold particles in a sample, p_o , is equal to X/N , where X is the number of gold particles in the sample and N is the number of all the particles in the sample. In random samples from this type of population, the best estimate of p is p_o and the sampling distribution of p_o is binomial (Dixon and Massey, 1957, p. 288).

The problem of collecting a truly random sample from a finely granular deposit is difficult. Grains cannot be selected one by one randomly from the entire deposit, nor is it possible to pass the entire deposit through a sample splitter to obtain a random sample. Rather, all the grains in a small part of the deposit must be collected. Samples collected in this way will give a binomial sampling distribution of p_o only if the gold grains are randomly distributed through the deposit. If systematic trends in gold content are present and not taken into account by the sampling plan, the sampling distribution of p_o may show greater variability than does the binomial distribution. The effects of non-random distribution of gold particles can be minimized by a proper sampling plan, but such procedures are beyond the scope of this paper. It is simply assumed here that the sample is a random one from a binomial population.

If the sampling distribution of p_o is binomial and if $Np > 5$ and $N(1-p) > 5$, the c percent confidence limits for estimating p are

$$\frac{N}{N+Z_{1-1/2\alpha}^2} \left[p_o + \frac{Z_{1-1/2\alpha}^2}{2N} \pm Z_{1-1/2\alpha} \sqrt{\frac{p_o(1-p_o)}{N} + \frac{Z_{1-1/2\alpha}^2}{4N^2}} \right] \quad (4)$$

where $Z_{1-1/2\alpha}$ is read from a table of the cumulative normal distribution (Dixon and Massey, 1957, p. 229).

The very large values of N and the very low values of p_o expected in samples from detrital gold-bearing deposits allow simplifications to be made in formula (4). The simplifications are valid for commonly used values of α . Specifically, they are valid when $Z_{1-1/2\alpha}$ is at least as large as 2.57, or when α is as small as 0.01.

If $N > 10^3$, corresponding to a sample weight of about 0.7 g of medium-grained quartz sand, the factor $N/N+Z_{1-1/2\alpha}^2$ in formula (4) is approximately equal to 1 and the factor $Z_{1-1/2\alpha}^2/4N^2$ is approximately equal to zero. Then, formula (4) may be simplified to

$$p_o + \frac{Z_{1-1/2\alpha}^2}{2N} \pm Z_{1-1/2\alpha} \sqrt{\frac{p_o(1-p_o)}{N}} \quad (5)$$

If $p_o < 10^{-3}$, as is true in all but extremely rich gold deposits, the factor $1-p_o$ in formulas (4) and (5) is approximately equal to 1, and the formula for the c percent confidence limits for estimating p may be further simplified to

$$p_o + \frac{Z_{1-1/2\alpha}^2}{2N} \pm Z_{1-1/2\alpha} \sqrt{\frac{p_o}{N}} \quad (6)$$

Formula (6) may be equated to the terms $p_o + E_c^- p_o$ and $p_o + E_c^+ p_o$ in equation (3). Solving for E_c^- and E_c^+ , it is found that

$$E_c^- = \frac{1}{p_o} \left[\frac{Z_{1-1/2\alpha}^2}{2N} - Z_{1-1/2\alpha} \sqrt{\frac{p_o}{N}} \right] \quad (7)$$

$$E_c^+ = \frac{1}{p_o} \left[\frac{Z_{1-1/2\alpha}^2}{2N} + Z_{1-1/2\alpha} \sqrt{\frac{p_o}{N}} \right] \quad (8)$$

Substituting X/N for p_o in equations (7) and (8) and simplifying, it is found that

$$E_c^- = X^{-1/2} \left[\frac{Z_{1-1/2\alpha}^2}{2} X^{-1/2} - Z_{1-1/2\alpha} \right] \quad (9)$$

$$E_c^+ = X^{-1/2} \left[\frac{Z_{1-1/2\alpha}^2}{2} X^{-1/2} + Z_{1-1/2\alpha} \right] \quad (10)$$

Equations (9) and (10) indicate that, in the range of N , p_o , and α considered here, the expected relative errors at a given percent confidence are functions of only one variable, the number of gold particles in the sample. In the problem of determining adequate sample size, the values of c , E_c^- , and E_c^+ are arbitrarily set, and equations (9) and (10) can be used to determine the value that X should have. The minimum adequate sample size, then, is the weight of sample necessary for the expected number of gold particles to equal X . Before a sample from a gold deposit of only roughly known gold particle size and grade is analyzed, the expected number of gold particles in the sample can be predicted only roughly. After the sample is analyzed and the particle size of its gold determined, the value of X can be determined from figure 2. Then, the values of E_c^- and E_c^+ actually resulting from the analysis of that particular sample can be determined by equations (9) and (10).

For the purpose of this study, we have defined the minimum sample size as that sample size for which E_{95}^- and E_{95}^+ are equal to approximately -0.5 and $+0.5$. For 95 percent confidence, $\alpha = 0.05$, $Z_{1-1/2\alpha} = 1.960$, and from equations (9) and (10),

$$E_{95}^- = X^{-1/2}(1.921X^{-1/2} - 1.960) \quad (11)$$

and

$$E_{95}^+ = X^{-1/2}(1.921X^{-1/2} + 1.960). \quad (12)$$

The values of E_{95}^- and E_{95}^+ are not precisely equal, but for $X = 20$, E_{95}^+ is slightly greater than 0.5, being equal to 0.54, and E_{95}^- is smaller in absolute value than 0.5, being equal to 0.34. Therefore, we will accept a sample containing 20 gold particles as the minimum sample size adequate for gold analysis. If a lower or higher degree of precision is required, the minimum sample size will contain fewer or more than 20 gold particles.

Figure 1, showing values of the relative errors at 68 and 95 percent confidence and for a large range of X , can be used by those who wish to define adequate sample size for other values of percent confidence and relative error (fig. 4). The figure can also be used to evaluate the reproducibility of a gold analysis after it is obtained assuming that analytical errors are absent and that the gold particles are of known uniform mass. It should be noted that, although the relative errors are drawn as continuous functions of X in figure 1, X may have integral values only.

In equations (9) and (10), when X is greater than 1,000 and c is 68 percent (or $Z_{1-1/2\alpha} = 1$), the absolute values of E_{68}^+ and E_{68}^- are approximately equal to $X^{-1/2}$. In comparison, the relative standard deviation or coefficient of variation of X in a binomial population

having a low value of p is equal to $(Np)^{-1/2}$, where Np is equal to the expected value of X (Deming, 1950, p. 114-119). It may be shown that the relative standard deviation of X is equal to the relative standard deviations of p_0 and P_0 in the model considered here, and that the equations of de Magnée (1956) and Prigogine (1961, p. 18, eq 22) for the relative standard deviation of P_0 are equivalent to Deming's equation for the relative standard deviation of X . The relative standard deviation, s_r , is plotted in figure 1.

In the range of N and p considered here, the Poisson distribution is a good approximation of the binomial distribution and can be used to define relations between X , E_c^- , and E_c^+ essentially the same as those shown in figure 1 (Ricker, 1937). The Poisson distribution may also be used to define the relation between the relative error and the expected number of gold particles, which may be called λ and is equal to Np . Given a value of λ , the proportion of all possible samples containing a given number of gold particles, X , can be determined from the equation of the Poisson distribution. The deviation of X from Np may be defined, as in the discussion based on the binomial distribution, in terms of a relative error, E , such that

$$E = \frac{X - \lambda}{\lambda} \quad (13)$$

Figure 5, derived from a table of the Poisson distribution (Dixon and Massey, 1957, p. 435), shows the probability that the relative error, E , will be less than or equal to a given value for a given value of Np , or λ . This probability is, by definition, the proportion of all possible samples in which E is less than or equal to the given value. It should be noted that, although the relative errors are drawn as continuous curves in figure 5, they have real values only at integral values of X .

CONCLUSIONS

To ensure adequate representation, a field sample should be sufficiently large to contain at least 20 gold particles. The number of gold particles per unit weight of sample depends on the grade and the grain size of the gold. Figure 3 shows the sample sizes that can be expected to contain 20 particles for different combinations of these two parameters. Smaller particle-per-sample ratios may suffice for certain reconnaissance studies, but lack the margin for error inherent in the choice of 20 particles per sample. Figure 4 may be used to establish sample-size requirements for other particle-per-sample ratios and degrees of precision required of the analyses. Preliminary analyses of the material may be necessary to establish the range of gold particle size and grade that can be expected.

The charts (figs. 2, 3, 4) specifically cover the particle size and grades that may be expected for detrital gold. They readily may be expanded to cover other fields of grain size or grade. The charts also may be used to establish sample-size requirements for other heavy metals such as platinum, silver, or mercury, and for other heavy minerals (fig. 9). In these cases, it is only necessary to change the grain size-mass relationships according to the density and grain shape of the material being studied. Grain size-mass relationships for minerals other than those shown in figure 9 could be developed. To establish adequate sample sizes for reliable analysis of materials other than gold, however, it is necessary that the same assumptions be made that were made in deriving the relation of analytical precision to number gold particles in a sample. Within these limitations, the methods presented here apply to any kind of analysis for particulate trace elements.

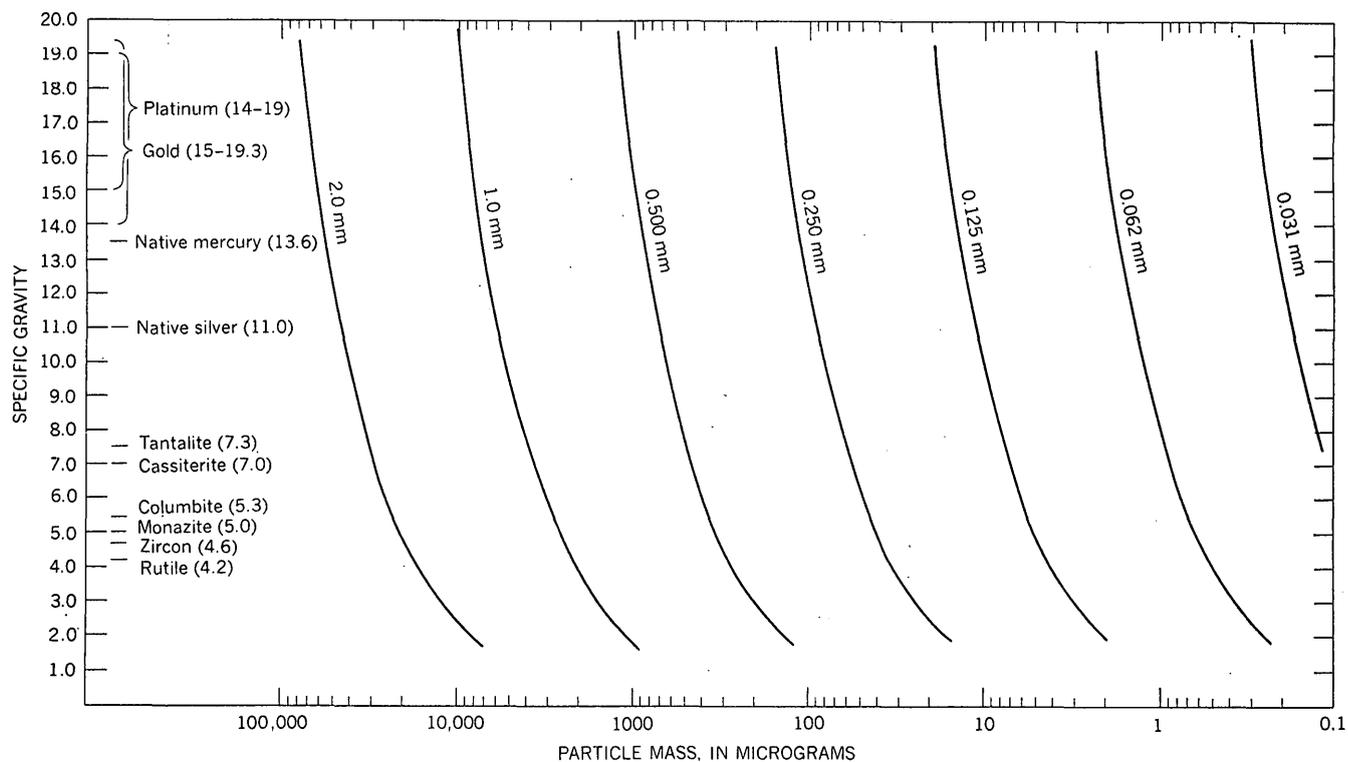


FIGURE 9.—Relationship between particle mass and grain size (diameters of spheres) of different particulate heavy metals and minerals as a function of specific gravity. The specific gravity of heavy metals that are likely to occur as discrete particles is shown at the left of the figure. The different relationships can be applied to figures 3 and 6 to determine adequate sample size and preconcentration requirements for minerals of any specific gravity, provided the assumptions made in relating precision of gold analyses to number of gold particles per sample are also true for deposits of these other minerals. If the analysis is for a metal component of a particulate mineral (for example, tin in cassiterite), the corresponding grades of the mineral must be calculated from the analytical data before application to figures 3 and 6.

REFERENCES CITED

- Becker, R. M., 1964a, Sampling to n items per sample, Pt. 1 of Some generalized probability distributions with special reference to the mineral industries: U.S. Bur. Mines Rept. Inv. 6329, 53 p.
- 1964b, Sampling to λ amount of items per sample, Pt. 2 of Some generalized probability distributions with special reference to the mineral industries: U.S. Bur. Mines Rept. Inv. 6552, 101 p.
- 1965a, Computer programs of distribution moments, Pt. 3 of Some generalized probability distributions with special reference to the mineral industries: U.S. Bur. Mines Rept. Inv. 6598, 79 p.
- 1965b, Experimental confirmation, Pt. 4 of Some generalized probability distributions with special reference to the mineral industries: U.S. Bur. Mines Rept. Inv. 6627, 57 p.
- 1966, Theoretical confirmation and applications, Pt. 5 of Some generalized probability distributions with special reference to the mineral industries: U.S. Bur. Mines Rept. Inv. 6768, 60 p.
- Clifton, H. E., 1967, Sample size preconcentration requirements for meaningful analysis of gold: U.S. Geol. Survey open-file report, July 13, 1967, 1 chart.
- Clifton, H. E., Hubert, Arthur, and Phillips, R. L., 1967, Marine sediment sample preparation for analysis for low concentrations of detrital gold: U.S. Geol. Survey Circ. 545, 11 p.
- Deming, W. E., 1950, Some theory of sampling: New York, John Wiley and Sons, Inc., 602 p.
- Dixon, W. J., and Massey, F. J., 1957, Introduction to statistical analysis [2d ed.]: New York, McGraw-Hill Book Co., Inc., 488 p.
- Gy, Pierre, 1954, Erreur commise dans le prélèvement d'un échantillon sur un lot de minerai [Errors committed in taking a sample from a lot of ore]: Revue de l'Industrie Minérale, v. 35, p. 311-345.
- 1956, Poids à donner à un échantillon. Abaques d'échantillonnage [Weight to give to a sample. Nomograph of sampling]: Revue de l'Industrie Minérale, v. 38, no. 636, p. 53-99.
- 1967, Théorie Générale [General theory], v. 1 of L'échantillonnage des minéraux en vrac [The sampling of minerals in bulk]: Bur. Recherches Géol. Minières Mem., no. 56, 186 p.
- Krumbein, W. C., and Graybill, F. A., 1965, An introduction to statistical models in geology: New York, McGraw-Hill Book Co., Inc., 475 p.
- Lakin, H. W., and Nakagawa, H. M., 1965, A spectrophotometric method for the determination of traces of gold in geologic materials, in Geological Survey research, 1965: U.S. Geol. Survey Prof. Paper 525-C, p. C168-C171.
- de Magnée, M., 1956, in Gy, Pierre, Poids à donner à un échantillon. Abaques d'échantillonnage; Discussion sous la présidence de M. Testut [Weight to give to a sample. Nomograph of sampling. Discussion under the chairmanship of Mr. Testut]: Revue de l'Industrie Minérale, v. 38, no. 636, p. 94-96.
- Miesch, A. T., 1967a, Chart showing number of particles of metal expected per 5-pound sample for various levels of grade and average particle size (regardless of the spatial distribution of particles): U.S. Geol. Survey open-file report, Jan. 9, 1967, 1 p., 1 chart.
- 1967b, Theory of error in geochemical data: U.S. Geol. Survey Prof. Paper 574-A, p. A1-A17.
- Ottley, D. J., 1966, Gy's sampling slide rule: World Mining, v. 19, no. 9, p. 40-44.
- Prigogine, A., 1961, Echantillonnage et analyse des minerais hétérogènes à faible teneur [Sampling and analysis of heterogeneous minerals of a weak grade]: Acad. Royale Sci. Outre-Mer, Cl. Sci. Tech. Mém., n.s. v. 15, no. 1, 180 p.
- Ricker, W. G., 1937, The concept of confidence or fiducial limits applied to the Poisson frequency distribution: Jour. Am. Statistical Assoc., v. 32, p. 349-356.
- VanSickle, G. H., and Lakin, H. W., 1968, An atomic absorption method for the determination of gold in large samples of geologic material: U.S. Geol. Survey Circ. 561, 4 p.