

EVALUATION OF PIPET AND X-RAY PROCEDURES FOR DETERMINING PARTICLE-SIZE DISTRIBUTIONS OF SEDIMENT



REPORT KK

A contribution of the
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Corps of Engineers	**	U.S. Geological Survey
Forest Service	**	Bureau of Reclamation
Federal Highway Administration	**	Agricultural Research Service
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By ROLLIN HOTCHKISS

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CONVERSION FACTORS AND ABBREVIATIONS

	Multiply	By	To obtain
	micrometer (μm)	3.937×10^{-5}	inch
	millimeter (mm)	3.937×10^{-2}	inch
	centimeter (cm)	3.937×10^{-1}	inch
	cubic centimeter (cm^3)	6.102×10^{-2}	cubic inch
	gram (g)	3.527×10^{-2}	ounce, avoirdupois

Temperature is given in degrees Celsius ($^{\circ}\text{C}$), which can be converted to degrees Fahrenheit ($^{\circ}\text{F}$) by use of the following equation:

$$F = 1.8(^{\circ}\text{C}) + 32$$

Suspended-sediment concentration is expressed in this report as milligrams per liter (mg/L) and is computed as 1 million times the ratio of the dry weight of sediment in grams to the volume of the mixture in cubic centimeters.

Other abbreviated units used in this report:

MeV	million electronvolts
V	volts

EVALUATION OF PIPET AND X-RAY PROCEDURES FOR DETERMINING PARTICLE-SIZE DISTRIBUTIONS OF SEDIMENT

By Rollin Hotchkiss ¹

ABSTRACT

Indirect measurements of sediment particle sizes in the subsieve range are commonly made by procedures based on the sedimentation method, such as the pipet procedure or the X-ray procedure. Compared to the pipet procedure, the X-ray procedure requires less training and testing time and produces more consistent results. The resulting particle-size distributions determined by the X-ray procedure are consistently finer than those produced by the pipet procedure. It is not known if this difference is due to sediment chemistry or if it is due to errors in the procedures themselves.

Available methods for comparing X-ray and pipet results require either the assumption of a parent statistical distribution or multiple tests from the same parent sample. Neither condition is desirable: the assumption of a parent statistical distribution is not fully justified, and multiple tests require time. Error limits based on existing tests can be established for each procedure. These error limits can then be compared to provide the basis for judging the acceptability of X-ray results. Specific steps are recommended in this report to achieve a standard procedure for comparing pipet and X-ray analyses.

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INTRODUCTION

The pipet and X-ray procedures are commonly used for indirect measurement of the size of sediment particles in the subsieve range (less than $62\ \mu\text{m}$). Both procedures are based on the sedimentation method for determining the fall diameter of sediment particles. In this method, the sediment sample is diluted with fluid, and the sediment-fluid mixture is agitated. Under carefully controlled conditions, the time required for a particle to settle a given distance is used to calculate the equivalent diameter of a spherical particle falling at the same velocity.

The pipet procedure (Guy, 1977) involves the withdrawal of sediment-fluid samples at a fixed depth in an open-topped tube at a series of specified settling times (fig. 1). Smaller sediment particles are expected to take longer to settle to the fixed depth. After the concentration is measured for each sample, a particle-size distribution curve that shows the relation between equivalent spherical diameter (fall diameter) and percentage of finer particles by weight is plotted. The curve is based on the assumptions that (1) the specific gravity of the sediment particles is known and (2) particle settling obeys Stokes Law (laminar conditions prevail).

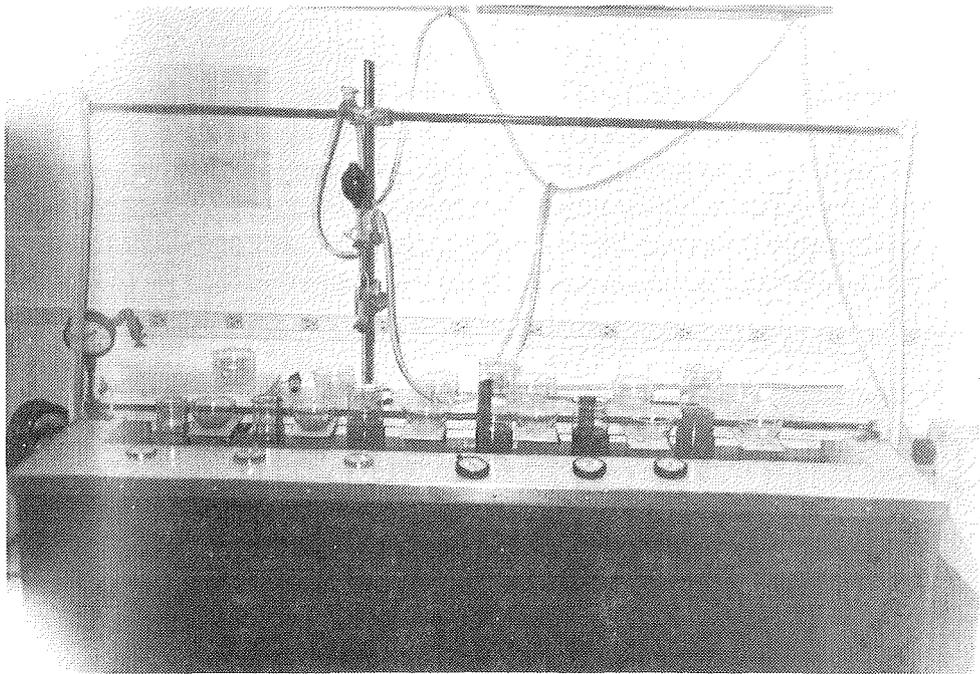


Figure 1. Pipet apparatus (photo furnished by W. J. Matthes, U.S. Geological Survey, Iowa City, Iowa).

In the X-ray procedure (Micromeritics, 1982), a finely collimated X-ray beam passes through a sediment-fluid suspension (fig. 2) to measure the transmittance of the suspension relative to the clear suspending fluid. The relative transmittance is a function of the weight concentration

of the solids in suspension. The Sedigraph, manufactured by Micromeritics¹, is a commercially available apparatus for analysis of fine-particle distribution by use of the X-ray procedure. The Sedigraph automatically plots the resulting particle-size distribution.

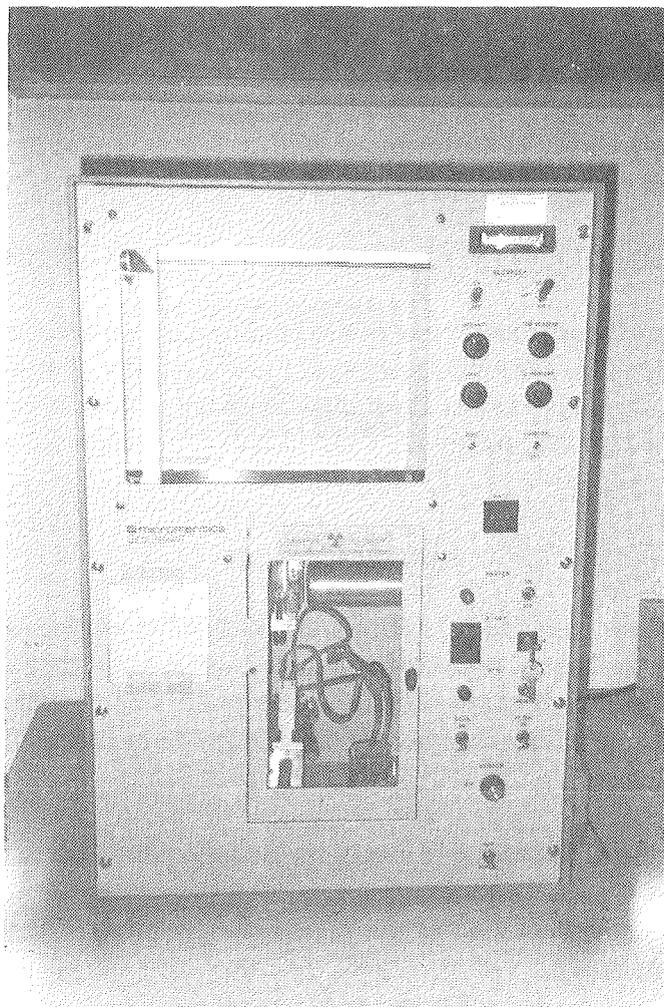


Figure 2. Apparatus used in X-ray procedure (photo furnished by W. J. Matthes, U.S. Geological Survey, Iowa City, Iowa).

Compared to the pipet procedure, training in the X-ray procedure requires less time, and analysis time required for a determination is decreased by 50 percent; results from the two procedures agree reasonably well (Lara and Matthes, 1986). It has also been suggested that, because X-ray analysis takes less time than the pipet analysis, all samples collected by a particular agency could be sent to one laboratory, thus reducing variability in data that might otherwise be introduced by several operators working with different machines.

¹Any use of trade, product, or firm names in this publications is for descriptive purposes only and does not imply endorsement by the U.S. GEOLOGICAL SURVEY.

Test results show the X-ray procedure consistently produces a finer particle-size distribution than the pipet procedure (Lara and Matthes, 1986; Weaver and Grobler, 1981; Schiebe and others, 1983). Because the effect of sediment chemistry on X-ray-beam attenuation has not been adequately investigated, it is possible that the X-ray procedure may produce different distribution curves for samples with identical particle-size distributions but different chemical compositions (J.V. Skinner, U.S. Geological Survey, oral commun., 1983).

The purpose of this report is to present information that could be useful for further comparisons of the X-ray and pipet procedures and to summarize the available data on reproducibility and comparability of the results of both procedures. A summary of statistical tools that could be used for the comparisons is also given.

EVALUATION OF PIPET AND X-RAY PROCEDURES

This evaluation includes (1) a review of the literature on potential errors inherent in the pipet and X-ray procedures, (2) a brief discussion of the availability of standard fine-particle-size reference samples, (3) a discussion of statistical methods that can be used to compare the pipet and X-ray results for the same samples, and (4) a comparison of some of the results available from both procedures.

Literature Review

The literature review included published and unpublished works, many of which concern potential sources of error in the procedures. Some sources of error in particle-size determinations are common to both procedures because both are based on the sedimentation method. Other sources of error, however, are unique to either the pipet or the X-ray procedure. Discussion follows in each of these categories.

Potential Sources of Error in the Sedimentation Method

The basis for the sedimentation method of particle-size analysis is the Stokes equation, which, in expanded form, is

$$V_s = f(g, d_s, \nu, \rho, c, v, w, \rho_s),$$

where V_s is particle settling velocity,
 g is gravitational acceleration,
 d_s is particle size,
 ν is fluid (kinematic) viscosity
 ρ is density
 c is sediment concentration,
 v is electrical charge on sediment particles and dispersants,
 w represents wall effects, and
 ρ_s is density of sediment.

Except for gravitational acceleration, each of these variables can be a source of error when either the pipet or the X-ray procedure is used. Adequate dispersion of the samples is assumed.

Particle size

Both the pipet and X-ray procedures are used for analysis of material that passes the 62 μm sieve. Stokes law is valid for particle diameters ranging from 1 or 2 μm to 50 μm . Brownian motion affects smaller particles, and larger particles do not settle in a laminar manner. Brownian motion is defined as the movement of very small particles due to the random impact of surrounding water molecules. Allen and Baudet (1977) showed that sedimentation methods are not accurate for particles smaller than 1 to 2 μm because of Brownian motion. Chung and Hogg (1985) quantified the errors and concluded that:

1. errors are greatest when the sample contains particles with a wide range of sizes;
2. errors are greater in short settling depths, such as in the X-ray procedure, than in long settling depths, such as in the pipet procedure; and
3. because of longer settling depths, errors in the pipet procedure are negligible in the 1- to 2- μm range.

Chung and Hogg (1985) showed that the X-ray procedure underpredicted the particle-size distribution curve by about 5 percent for 0.7- μm -diameter kaolin particles.

Micromeritics (1982) recommends use of the Sedigraph 5000 for particles in the 0.2 to 50 μm size range but point out that Brownian motion effects are most significant for low-density, uniform particles smaller than 1 μm . The American Institute of Chemical Engineers (1980) recommends the use of an X-ray procedure for particles as small as 0.1 μm . Unless the sample consists of a significant percentage of particles finer than 0.5 μm , they suggest that no adjustment is necessary. The American Society of Agronomy standards for particle size analyses maintain that sedimentation methods not be used for particles smaller than 2 μm . They feel Brownian motion is a major factor for smaller, clay sized, particles.

No minimum particle size is recommended for the USGS pipet procedure (Guy, 1977), but the calculation sheet lists the smallest diameter as 2 μm .

Fluid viscosity and density

Fluid viscosity and density are temperature dependent; however, significant errors in the particle-size distribution result only if suspending-fluid temperatures vary by 20 $^{\circ}\text{C}$ or more during different analyses.

Sediment concentration

Stokes Law is based on the assumption that each sediment particle settles independently. If sediment concentration is too high, particle interaction hinders or slows settling.

According to the literature, the concentration at which hindered settling begins varies from 0.1 to 3 percent by volume (2,600-80,000 mg/L) (Kaye, 1981) at an assumed specific gravity of

2.65; however, hindering is generally considered insignificant at a concentration of less than about 2 percent by volume (50,000 mg/L) (Weaver and Grobler, 1981; Olivier and others, 1970-71; Stein, 1985; Allen, 1981; Society for Analytical Chemistry, 1968; Orr and Dallavalle, 1959). A 1943 inter-agency study generally agrees that, for the pipet, hindered settling is not significant at volume concentrations of 1 to 2 percent. Concentrations of 0.08 to 0.2 percent by volume (2,100-5,000 mg/L) are recommended for analysis by the pipet procedure (Guy, 1977), whereas concentrations of 0.88 to 1.84 percent by volume (23,000-49,000 mg/L) are recommended for analysis by the X-ray procedure (Micromeritics, 1982).

Experiments with the X-ray procedure are less conclusive. Kaye (1981) states that a 0.5- to 3-percent concentration by volume definitely produces "significant interfine particle fluid dynamic interaction" but gives no supporting experimental data. After several Sedigraph analyses of a bottom sediment from the Rio Puerco River near Bernardo, New Mexico, Lara and Matthes (1986) concluded that "sample concentration may vary through a wide range without affecting the results of the analysis." Sample sediment concentrations ranged from a higher-than-recommended value to a low, unspecified value.

Welch and others (1979) compared results from the X-ray procedure for a concentration of 1.80 percent by volume to results from samples having higher and lower concentrations. They found concentrations of 3.7 and 5.6 percent by volume (higher than recommended) produced progressively finer curves that deviated significantly from those run at 1.80 percent. Weaver and Grobler (1981), however, showed that the X-ray procedure produced "similar" curves for volume concentrations of 2, 3, and 5 percent. The finest curve resulted from a 5-percent volume concentration. They decided to use 1.5 percent as an X-ray procedure standard for comparison to pipet analyses. Finally, Stein (1985) reports that X-ray analyses of samples having a concentration of 0.8 percent by volume produce consistent results but that errors occur for "higher" concentrations.

Electrical-charge effects

The effects of electrical charges on sediment particles and in the dispersant have not been studied extensively. Davies and others (1976) state that "the charge density on the solid surface exposed to bulk liquid is probably the dominant factor in determining hindrance to sedimentation," but they provide no experimental evidence. Sansone and Civic (1975) demonstrated the dependence of particle-size distribution of standard glass beads on the specific conductance of the media fluid. They concluded that their experiments showed "the necessity of ensuring that electrical forces are minimized when using liquid sedimentation."

Wall effects

A sediment particle settling very close to a wall may be hindered by the fluid-wall-particle interaction. A typical pipet cylinder is approximately 30 to 41 mm in diameter. The interior of a Sedigraph sample cell is a cube approximately 13 mm wide, 35 mm high, and 5.3 mm thick (Micromeritics, undated). Even though the smallest Sedigraph cell dimension is approximately 5.3 mm, Weaver and Grobler (1981) report that wall effects are negligible.

Density of sediment sample

Rarely, if ever, are fine-sediment samples homogeneous. They usually consist of a mixture of different minerals and organic matter. Organic matter is routinely removed before analysis by pipet or X-ray procedures (Guy, 1977; Welch and others, 1979), and a specific gravity of 2.65 is usually assumed for the remaining sediment particles. C. Bernhardt (Research Institute of Mineral Processing of the Academy of Sciences of the GDR, Freiburg, written commun., ca. 1984), in a study of heterogeneous powders, concluded that differences in density typically found within the same powder sample caused about a 1-percent error in the particle-size distribution. Differences in the mass absorption coefficient associated with the different densities, however, could result in a 10-percent error (see "Potential Sources of Error in the X-ray Procedure"). Grindrod (1968) tested powders with a specific-gravity range of 3.15 to 2.3 and found that density affected the indicated diameter by as much as a 20 percent for the coarse fraction (50-70 μm) of the sample.

Potential Sources of Error in the Pipet Procedure

The pipet procedure for particle-size analysis can produce errors as a result of disturbance of the sample during withdrawal, withdrawal of a sample from too large or too small a range of depth, and insufficient sample volume for analysis.

Disturbance of the sample during withdrawal

Irani and Callis (1963), describing the pipet procedure, stated that "The continuous removal of sample from the suspension considerably disturbs the sedimentation medium and falsifies one of the assumptions in Stokes equation, namely, that sedimentation is proceeding under steady-state conditions." They do not attempt to quantify resulting errors. They compared the particle-size distributions of a flour sample determined by use of pipet, sedimentation balance, and microscopy and concluded that "the Andreasen pipet data deviated from others for the finer flour sample," presumably because disturbance of the suspension occurred during sample withdrawal. The median diameter of the "finer" sample was 10 μm .

Kalita and others (1985) likewise reported that the pipet disturbs the suspension and causes undesirable mixing. Again, no error estimates are given. Stockham and Fochtman (1977), on the other hand, reported that the sampling tube interferes with the settling of the particles, especially in the region directly below the tube; no error estimates are provided.

Withdrawal technique

The withdrawal technique is often cited as a drawback to the pipet method. Dallavalle (1948) examined the withdrawal zone at the pipet tip in detail and concluded that the sampled zone generally extends about 1 cm above the tip and 3 cm below it. The pipet sample, therefore, can include particles that have settled below the tip and are coarser than particles at the level of the tip. For this reason, Orr and Dallavalle (1959) recommend that samples be withdrawn slowly and carefully for very fine particles. Allen (1981), however, states withdrawal time should always be the same. If the withdrawal time is too short, the sample will be withdrawn from outside the intended sampling zone; if too long, fine particles from above will enter the sampling zone during

withdrawal. The USGS (Guy, 1977) currently recommends an 8- to 12-second withdrawal time. The withdrawal technique was identified by Schiebe and others (1983) as a possible explanation for differences between pipet and X-ray results.

Insufficient sample for analysis

Guy (1977) states that 1 to 5 g of sediment is necessary for a pipet analysis. Pipet-analysis accuracy decreases with sample size because of mechanical limitations of the equipment. Welch and others (1979) state that neither the pipet nor the X-ray procedure is well suited to the analysis of suspended sediment because the minimum quantities of sediment (0.5 g for X-ray, 1.0 g for pipet) are often not present in collected samples.

The Society for Analytical Chemistry (1968) recognized the limitations of the pipet and said that "no excessive claims are now made for the precision of the pipet method; as an example, B.5.3406 [British Standard] is satisfied if duplicate estimates of cumulative proportions by weight do not differ by more than 4 percent." The Society concluded that "A large group of workers in size analysis has accepted the [pipet] method uncritically as a standard method, without adequate recognition of possible errors. On the other hand, some workers have stated that it is so prone to error as to render it inapplicable as a standard method. There seems to be a case for suspending judgment until more evidence is available on its accuracy and reproducibility."

Potential Sources of Error in the X-ray Procedure

Use of the X-ray procedure for particle-size analysis can result in errors due to sediment chemistry, differences in sample density, heat input from the X-ray, and incorrect determination of settling rate.

X-ray attenuation

Sample concentration is determined by X-ray attenuation. A clear suspending fluid is tested first. A well mixed sample is then tested, and the machine is set at 100 percent finer. No calibration is required because concentration is determined from the relative difference in attenuation between the clear suspending fluid and the fluid containing sediment.

Micromeritics (1982) states that an X-ray attenuation of 40 to 60 percent produces good results. Allen (1981) and Allen and Baudet (1977), however, suggest that this requirement leads to inaccurate results. In comparison tests with the X-ray (Sedigraph), pipet, and centrifuge procedures on kaolinite, Allen and Baudet found that "The Sedigraph gives far too fine an analysis in every case, and this is to be expected since the volume concentration required for an X-ray attenuation technique with a material such as kaolinite, which is semitransparent to X-rays, is so high that particle-to-particle interaction takes place."

According to Skinner, (U.S. Geological Survey, oral communs., 1983 and 1985) chemical effects on X-ray attenuation are pronounced between an X-ray energy level of 0.01 and 0.05 Mev. The X-ray energy level of the Sedigraph is 0.01 Mev.

Sediment density

Sediment density is closely related to X-ray attenuation. As stated previously, sediment particles of different densities typically have different mass absorption coefficients (C. Bernhardt, Research Institute of Mineral Processing of the Academy of Sciences of the GDR, Freiburg, written commun., ca. 1984). Although differences in density can result in a 1-percent error in a particle-size distribution, attendant differences in mass absorption coefficients can produce a 10-percent error.

Energy-source stability

The Sedigraph X-ray system generates 13,000 V. Allen (1981) questioned, without factual basis, the stability of the power source. Olivier and others (1970-71), specify a ± 5 -V source stability, which represents a potential error of less than 0.1 percent.

Heat input by X-ray

During a 100-minute analysis (15 minutes is required to define the particle-size distribution to 2 μm), the X-ray beam will raise the temperature of the sample 1.2×10^{-4} °C. This temperature increase introduces an error of the same percentage magnitude (0.01 percent) in the particle-size distribution (Olivier and others, 1970-71).

Determination of settling rate

The X-ray procedure decreases analytical time because the sample cell is continuously lowered with respect to the X-ray beam. The movement of the sample cell results in continuously decreasing sediment settling depths and thus reduces the total time required for the analysis. The pipet procedure requires 9 hours for a 2- μm determination, whereas the X-ray procedure requires only 15 minutes. The rate at which the cell moves during the X-ray procedure is computed by the operator and is a function of particle and fluid densities, fluid viscosity, and the maximum particle diameter in the sample (Micromeritics, 1982). If the rate is incorrectly determined, the particle-size distribution also will be incorrect. If the mistake is discovered after the analysis, however, the particle-size distribution can be corrected (Rootare, 1980).

Applications of the X-ray Procedure by Commercial Firms

Fine natural sediments--given the variations in their particle size, shape, density, and chemical and electrical properties--are difficult to analyze by any procedure. The X-ray procedure, however, has been accepted by many commercial firms.

Bunville (1984) says "perhaps the most widely used instruments for particle size analysis based on gravitational sedimentation are the Micromeritics Sedigraph 5000D and Sedigraph L." Although originally designed for clay minerals, the Sedigraph has been successfully used in analyzing pigments, minerals, and coatings, and in the photographic, metal powders, and ceramic industries. Micromeritics (1982) lists 57 different materials analyzed by the Sedigraph 5000 and typical particle-size distributions for 102 different materials, including a distribution for river sediment.

Summary of Findings

The following findings have been inferred from the literature:

1. Particle-size range.--A range of 2 to 50 μm is the optimum range for analysis. Although distributions from the X-ray procedure can include particles that are 0.2 μm or smaller, diameters smaller than 1 to 2 μm do not obey Stokes law and can be affected by Brownian motion.
2. Concentration.--The typical pipet concentration of 2,000 to 5,000 mg/L should not introduce hindered-settling. The X-ray procedure should be used at the smallest concentration that provides between 40 and 60 percent attenuation of the beam. Hindered settling is probably not a major factor as long as the concentration is less than 2 percent by volume.
3. Pipet analysis.--Because withdrawal time can affect particle-size distributions, use of a standard withdrawal time among laboratories is warranted.
4. Relation of sediment chemistry to X-ray determinations.--Sediment chemistry can apparently alter results from the X-ray procedure. Until additional information is available, routine comparative tests may be necessary to determine what types of sediment samples are chemically sensitive.

Availability of Standard Fine-Particle-Size Reference Samples

It is difficult to determine the accuracy of the pipet and X-ray procedures for natural river sediments because the true particle-size distribution is not known. Some standard particle-size reference samples of Polystyrene spheres are available from the National Bureau of Standards (Office of Standard Reference Materials, 3311 Chemistry Building, Gaithersburg, MD 20899, Ph 301 975 6776). Sizes are available of about 0.3, 0.9, and 10 μm at a cost of \$200-500 per 5 mL sample in 1994. Wilson (1980) discussed the certification of five natural quartz particle-size reference samples covering the range of 0.35 to 650 μm . The particle-size distributions for the four smallest diameter samples were "certified" by use of the pipet. Comparisons were made with results from the X-ray procedure (see the "Single-Run Comparisons" section).

Statistical Representations of Test Data

The purpose of this section is to describe common probability-distribution functions and statistical tests used to analyze particle-size results and to apply some of the test to available data.

Probability Distributions

Plotted particle-size distribution curves commonly resemble cumulative probability-distribution functions. Because of this similarity, several distributions have been compared to particle-size results. The lognormal distribution function is generally recommended for use with

sediments because the random variable can range from minus to plus infinity, it has successfully described many different test results, or results of different methods, and it provides a consistent basis for comparing and describing particle-size data. A recent distribution called the log-hyperbolic distribution (Durst and Macagno, 1986) is not recommended for use because of its difficult-to-read format.

The lognormal distribution is applicable to particle-size data because the lognormal distribution is bounded on the left by zero. It is formed by taking the logarithms of observed data; the resulting random variables are normally distributed and are therefore described by the logarithmic mean and standard deviation. In practice, nontransformed data are plotted on lognormal probability paper. Data from a lognormal distribution may plot as a straight line on such paper. The mean and the standard deviation can then be estimated by

$$d_g = \sqrt{d_{16} \times d_{84}} \quad \text{and} \quad s_g = \sqrt{\frac{d_{84}}{d_{16}}}$$

where d_g is geometric mean,

s_g is geometric standard deviation,
 d_{84} is the particle diameter for which exactly 84 percent of the sample is smaller, and
 d_{16} is the particle diameter for which exactly 16 percent of the sample is smaller.

Goodness-of-Fit Tests

The decision on whether or not data on lognormal probability paper plot "as a straight line" is sometimes difficult. Statistical tests corresponding to a visual judgment are discussed in this section.

Goodness-of-fit tests compare the differences between observed values and expected values, (those that fit an assumed distribution). Each observed value is derived from the experimental data, whereas the expected value is derived from the distribution postulated to fit the data. A threshold test statistic is selected on the basis of an acceptable probability of rejecting a valid distribution. If the computed differences are less than the threshold test statistic, the distribution is accepted as adequately representing the data. If not, then the distribution is rejected.

The chi-square test, the Kolmogorov-Smirnov correlation, and the Shapiro-Wick test are commonly used to determine goodness-of-fit (Haan, 1977; Loucks and others, 1981). The chi-square test is the least discriminating of these tests because it is the most likely to indicate that a given distribution adequately describes a data set. This lack of discrimination means that the probability of incorrectly accepting the distribution is highest with the chi-square test. Unfortunately, only the chi-square test can be used on the results of a single particle-size-distribution analysis. The other methods are based on multiple analyses of the same sample.

The results of 10 pipet analyses and 9 X-ray analyses of a sample from the Los Padres Reservoir near Carmel Valley, California, are listed in table 1. The size distributions as determined by the pipet and sedigraph are shown on figure 3. The chi-square goodness-of-fit test was applied to the data in table 1 to test the hypothesis that a lognormal distribution with a composite pipet

sample mean and standard deviation describes the size distribution data from both methods. The hypothesis cannot be rejected at a 90 percent significance level indicating there is no good reason to assume the same lognormal distribution does not fit both sets of data. In other words there is no good reason to assume the lines on figure 3 are not straight and that results from both test are from the same distribution.

Confidence Intervals

Confidence intervals allow the following kind of statement to be made: "In these pipet analyses, the probability that the interval from 70 to 90 percent finer contains the population d_{g4} is 90 percent." A confidence interval is a band about the data. The interval cannot be computed from a single particle-size-distribution test; multiple tests of the same sample are required. Confidence intervals can be used as an alternative to goodness-of-fit tests for comparison of different sizing methods. For example, if confidence limits from pipet and X-ray procedure tests of the same sample overlap, then it might be said that there is no good basis for assuming the methods produce different results.

Table 1. Results of replicate analyses of sample from Los Padres Reservoir, near Carmel Valley, California

[U, upper bound at 90-percent confidence limit; L, lower bound at 90-percent confidence limit]

Size	Percentage of finer particles, by weight, than indicated size, in micrometers					
	31	16	8	4	2	1
Pipet procedure						
Test statistic						
Mean (10 tests)	87.8	58.8	35.1	23.4	17.2	7.0
Standard deviation	2.84	2.49	6.30	8.07	7.40	.93
Upper bound	89.5	60.2	38.8	28.1	21.5	7.5
Lower bound	86.2	57.4	31.5	18.7	12.9	6.5
X-ray procedure						
Mean (9 tests)	93.2	68.1	41.6	23.6	13.3	6.8
Standard deviation	1.94	2.70	2.63	2.47	1.73	1.39
Upper bound	94.4	69.8	43.2	25.1	14.4	7.7
Lower bound	92.0	66.4	40.0	22.1	12.2	5.9

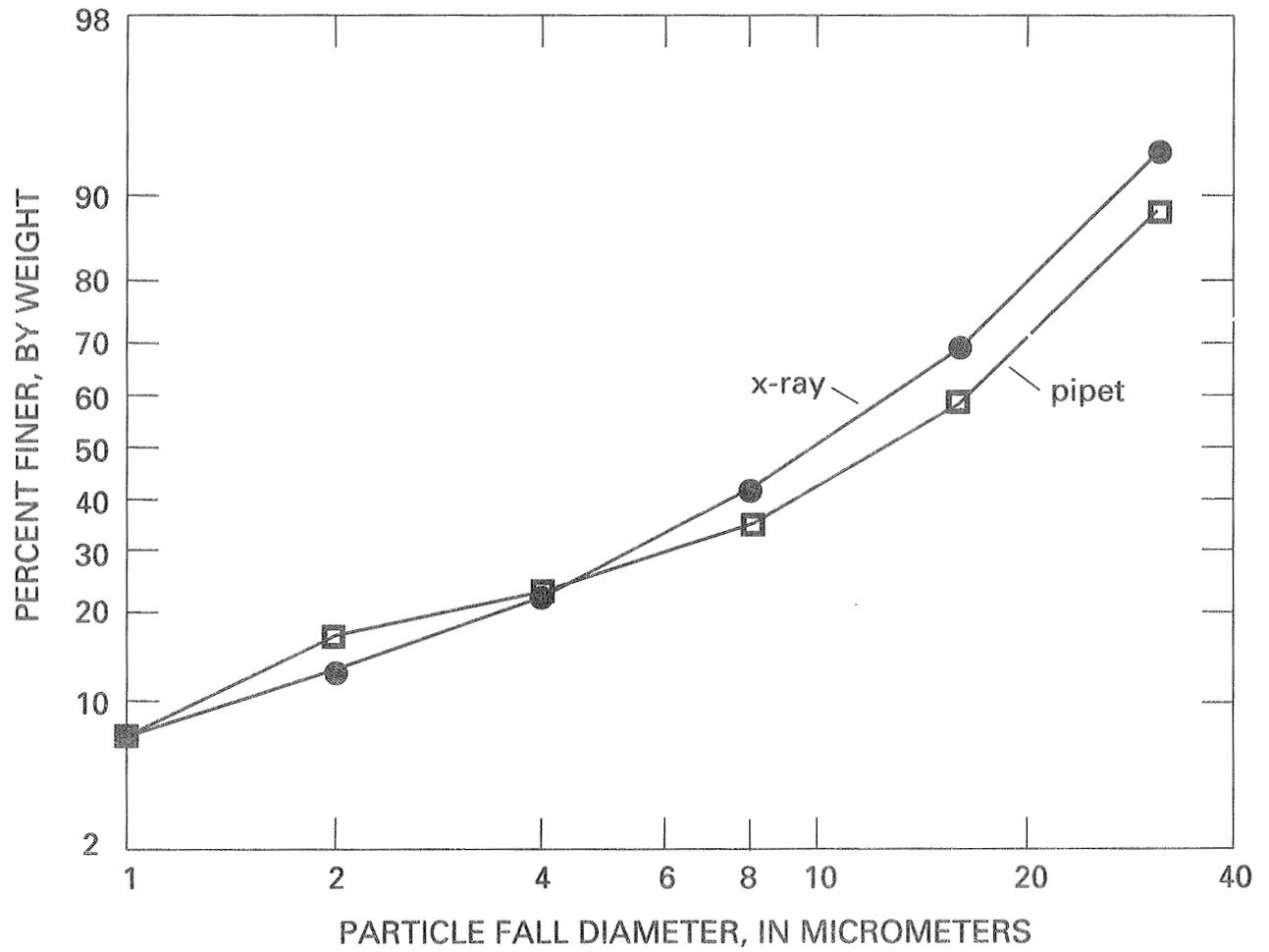


Figure 3. Particle-size distributions used for example chi-square test.

For example, the 90-percent confidence limits for the pipet and the X-ray data were computed and the results checked for an overlap in the results. The 90-percent confidence limits were computed as follows:

- a. The lower and upper bounds are computed from:

$$B = \bar{x} \pm t \frac{s}{\sqrt{n}}$$

where

- B is the upper or lower bound
 \bar{x} is the arithmetic mean of n percent-finer values at each of the breakpoints,
s is standard deviation of n breakpoint percent-finer values, and
t is the t-distribution statistic for a given confidence level.

- b. Calculate the t-statistics for pipet and X-ray data.

If a 90-percent confidence level is desired, the t value must be determined at a 0.95 level to allow for values either larger or smaller than the stated limits. The n value for determining t is the number of repeats minus 1. Or;

Pipet, $t_{0.95, 9} = 1.83$ (from Haan, 1977).
X-ray, $t_{0.95, 8} = 1.86$.

- c. Calculate the upper (U) and lower (L) bounds at 90 percent confidence from the data in table 1 using the equation. These values are also shown on table 1.

A plot of the confidence intervals and computed bandwidths are shown in figure 4. For this sample, the X-ray 90-percent confidence limits lie within the pipet confidence limits up to about 10 μm .

Hypothesis Testing

Hypothesis tests can be used to test for significant differences between statistical means from different methods or to derive error estimates from just one method. Like confidence intervals, they require multiple tests on the same sample. A typical hypothesis might be, "the mean d_{50} from the X-ray procedure is the same as the mean d_{50} from the pipet procedure." The hypothesis could be tested for each percent finer value and it may be proven false for some sizes. In contrast, goodness-of-fit tests compare the entire measured range of test data to a hypothesized probability distribution.

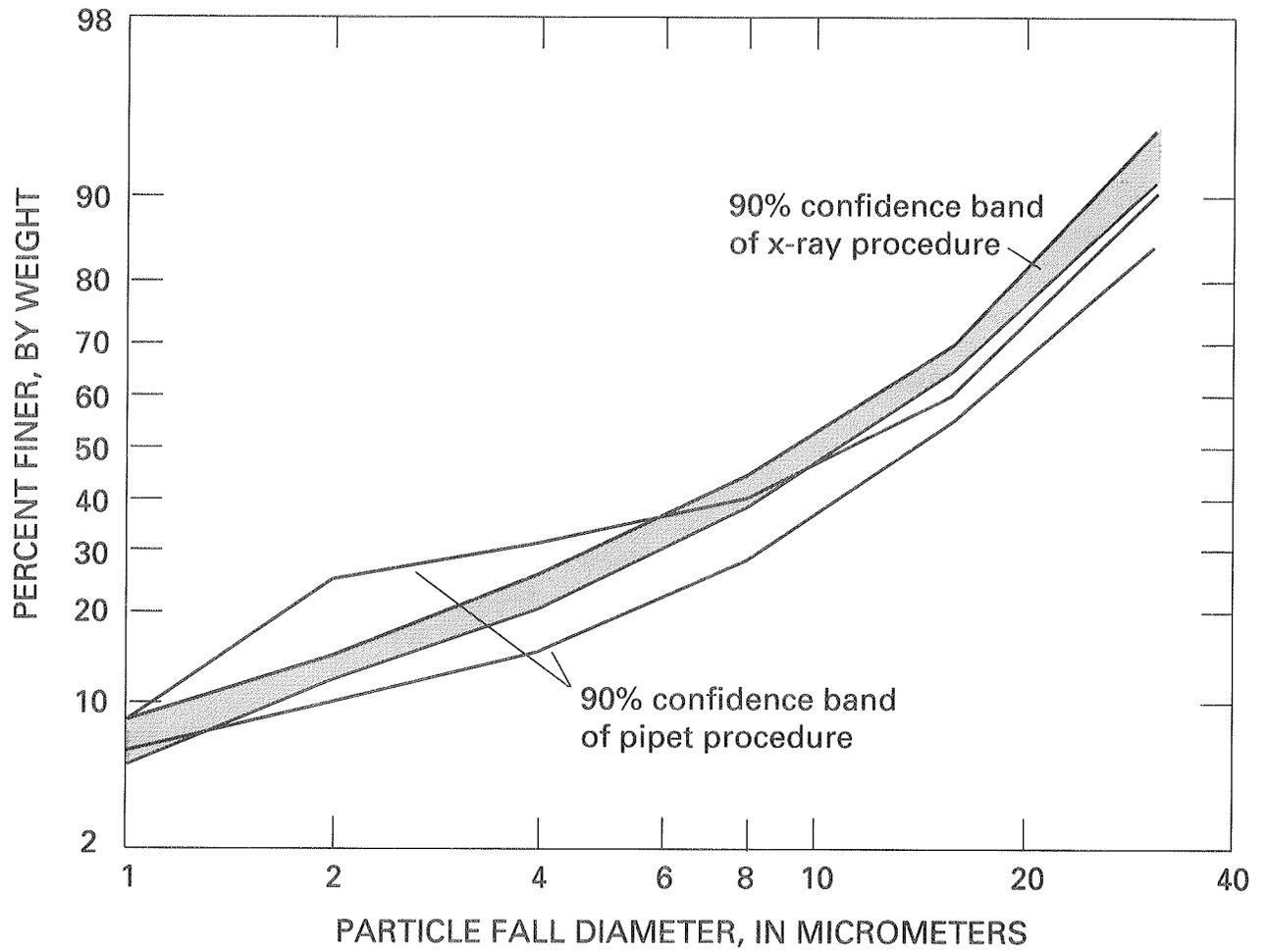


Figure 4. Standard deviations of test results on a sample from Los Padres Reservoir, California.

From the foregoing discussion, it is evident that statistical tests of particle-size analyses are limited by the following:

1. Single-run results.--Only the chi-square goodness-of-fit test can be applied to single-run results. The chi-square test is the least powerful of the common goodness-of-fit tests.
2. Analysis of a subset of a larger sized sample.--Often, the samples analyzed by means of the pipet or X-ray procedure are only the subsieve portions of larger samples. The exclusion of the rest of the sample raises some pertinent questions: Is the larger sized sample from the same distribution? Would the complete size-range analysis plot as a "straight" line on lognormal paper? Would the analytical results be continuous at the upper boundary of the subsieve sample and the lower boundary of the sieved sample?

Comparisons of Pipet and X-ray Determinations

In the appendix is a summary of results of 181 particle-size analyses from a variety of laboratories.

Single-Run Comparisons

Of the 181 analyses, 98 compare results from pipet and X-ray analyses of tests of the same parent sample. Of the 98 comparisons, all but ten show that the particle-size distribution from X-ray analysis is finer than that from the pipet analysis. The difference in the results increase with particle size. Because samples were analyzed only once, the only applicable statistical comparison test is the chi-square goodness-of-fit test.

Particle size analyses by Weaver and Grobler (1981) and by Wilson (1980) indicate that the X-ray analyses yield finer particle sizes than the pipet analyses. Weaver and Grobler, in discussing the differences, conclude that the X-ray procedure gave a true reflection of the particle-size distribution. On the basis of a microscopic examination, they conclude that the pipet procedure overestimated particle diameter for the larger particles in the sample. Wilson does not discuss differences in his test results.

Schiebe and others (1983) summarize pipet analyses done at the U.S. Department of Agriculture Sedimentation Laboratory at Oxford, Mississippi, and X-ray tests done at the Agricultural Research Service laboratory in Chickasha, Oklahoma. (See Schiebe and others, 1983, for typical plots.) In all 15 tests the X-ray results indicate finer particle sizes than do the pipet results. No reason for the differences was identified.

Repeat-Run Comparisons

Several pipet and X-ray tests were repeated to determine variability. The most exhaustive tests were done by O. G. Lara and W. J. Matthes (U.S. Geological Survey, written commun., undated). Some results are from interlaboratory pipet tests done at 10 USGS laboratories around the country. The average standard deviations for two analyses of each of three samples are listed in table 2. Standard deviations from replicate pipet and X-ray analyses of seven other samples are listed in table 3 (results are from a single laboratory).

Table 2. Standard deviations of percentage of finer particles from pipet analyses repeated once for three samples

[μm , micrometer. Data from O. G. Lara and W. J. Matthes, U.S. Geological Survey, written commun., undated]

Type of analysis	Standard deviation (%) at indicated particle diameter (μm)					
	2	4	8	16	31	63
Interlaboratory	5.4	4.8	3.0	2.0	3.4	0.7
Single laboratory	1.5	1.1	1.4	1.9	1.1	0

Table 3. Standard deviations of percentage of finer particles for seven samples at a single laboratory

[μm , micrometer. Data from O. G. Lara and W. J. Matthes, U.S. Geological Survey, written commun., undated]

Type of analysis	Standard deviation (%) at indicated particle diameter (μm)					
	1	2	4	8	16	32
Pipet	1.5	4.3	3.6	2.8	1.7	1.5
X-ray	1.9	1.6	1.3	1.4	1.3	1.6

Average standard deviations from pipet analyses of 12 samples are listed in table 4. Each sample was analyzed four or five times.

Table 4. Standard deviations of percentage of finer particles from pipet analyses of 12 different samples at one laboratory

[μm , micrometer. Data from O. G. Lara and W. J. Matthes, U.S. Geological Survey, written commun., undated]

Standard deviation (%) at indicated particle diameter (μm)					
2	4	8	16	31	63
0.8	0.3	0.4	0.6	0.7	0

In table 5, standard deviations are reported for results of (1) four repeat runs of one sample by the X-ray procedure, and (2) five samples, each analyzed four times by means of the pipet and X-ray procedures (Welch and others, 1979).

The standard deviations in tables 2 through 5 are not consistent. Lara and Matthes (U.S. Geological Survey, written commun., undated) report smaller standard deviations for the X-ray analyses than for the pipet analyses, whereas Welch and others (1979) report the opposite. The pipet standard deviations in table 4 are very small. The work by Lara and Matthes is considered by the author to be the best documented and most complete data available. These data strongly influence the conclusions of this report.

Table 5. Standard deviations at percentage of finer particles from pipet and X-ray analyses

[μm , micrometer. Data from Welch and others, 1979]

Type of analysis	Standard deviation (%) at indicated breakpoint diameter (μm)					
	2	4	8	16	31	63
Four runs, one sample:						
X-ray	1.3	1.9	0.8	2.9	1.0	0.5
Four runs, five samples:						
Pipet	0.5	0.3	0.4	0.5	0.7	--
X-ray	1.0	0.7	0.7	0.8	0.7	--

Effects of Sediment Concentration

Of the 181 analyses, 12 are for X-ray analyses of the same sample at different concentrations. Of these 12 analyses, only three show changes in the percent finer values with decreasing concentration and these changes are slight. This means that the highest initial concentration did not produce hindered settling.

Tests by Lara and Matthes (1986) also indicate that the initial concentrations of samples analyzed by means of the X-ray procedure can vary widely without affecting the results. Weaver and Grobler (1981) started an analysis with a much higher concentration than is recommended. As the sample was diluted and rerun, hindered settling decreased until the results stabilized at about 2 percent concentration by volume. This stabilization point is comparable to that determined by Lara and Matthes.

Finally, Welch and others (1979) compared results from the X-ray procedure at different concentrations to results from the pipet procedure at a standard concentration. They concluded that results of the X-ray procedure best agree with the pipet when an initial concentration of about 1 percent by volume is used.

CONCLUSIONS AND SUGGESTIONS FOR ADDITIONAL RESEARCH

Based on the data contained herein and a review of available literature the following conclusions and suggestions for additional research are offered.

Dispersants.--Tests on dispersants indicate that standard dispersant procedures for routine pipet and X-ray analyses are adequate and need no modification; however, microscopic examinations of dispersed samples are recommended to improve documentation of their conclusions.

Effects of sediment concentration and chemistry on results of X-ray analyses.--

Comparative tests between the pipet and X-ray procedures show that the X-ray procedure commonly produces a finer particle-size distribution curve than the pipet procedure. A reason for this discrepancy seems to be that the X-ray procedure requires a sediment concentration large enough to cause a 40- to 60-percent reduction in X-ray intensity, and this large concentration may produce hindered settling. Hindered settling biases particle-size curves toward overestimation for the smaller particle sizes.

The following program is recommended to further evaluate the effects of sediment concentration and chemistry on the results of X-ray analysis:

1. Ongoing documentation.--The X-ray procedure is already being used routinely by several laboratories. A effort should be made to document the following for each test:
 - a. concentration by volume or weight (mg/L) used in each test
 - b. mineralogical description of sample (clay, silt, etc.)
 - c. predominant color of sample
 - d. X-ray intensity recorded at the 100-percent line
2. Concentration and chemistry testing.--Systematic tests should be done to document effects of concentration and sediment chemistry. To test for concentration, the following should be done:
 - a. Obtain standard particle-size reference samples. Special effort should be made to obtain the natural quartz samples described in Wilson (1980).
 - b. Standard samples should be tested at different concentrations. This would define the concentrations at which deviations (biases) from a "true" particle-size distribution occur.
3. Effects of particle-size distribution.--To test the effects of sediment chemistry (and concentration) on particle-size distribution, the following should be done:
 - a. Natural samples should be obtained from several sources, with an emphasis on mineralogical variety.
 - b. Samples should be tested on Sedigraph 5000 and the Sedigraph 5500L machines.

As described in the literature review, the Sedigraph 5500L is well suited to analyze sediments with low X-ray absorption coefficients. It may be possible to identify chemically sensitive sediments by comparing results from the two machines. Discrepancies may indicate a chemical sensitivity to X-rays and provide guidelines for identifying sediments that are not appropriate for analysis on the Sedigraph 5000.

Precision and bias of pipet analyses.--The precision and bias of the pipet are not well established. Interlaboratory pipet analyses that have already been done are described in the section "Comparison of Pipet and X-ray Determinations." More tests should be done to improve definition of expected deviations. Interlaboratory pipet analyses could be used to establish the expected precision and bias of the pipet. Interlaboratory tests should be used because pipet analyses are done at several locations, and interlaboratory-test results would reflect the expected variations.

Comparison of pipet and X-ray analyses.--Many tests have compared results of pipet and X-ray analyses. Differences are relatively small but are consistent. It is suggested that the standard deviations in table 2 from the inter-laboratory test be considered as a measure of pipet accuracy, and that the standard deviations from the single laboratory X-ray tests in table 3 be used as a measure of X-ray accuracy. These respective band widths may then be superimposed on comparison tests to determine regions of overlapping and acceptance.

Analysis of the entire size range of a sample.--Discrepancies between the pipet and X-ray procedures are largest for large particle diameters. At diameters between 30 and 50 μm , the expected deviation bandwidths will probably not overlap (fig. 4). Often, the pipet and X-ray procedures are used to analyze only part of a collected sample, the larger material being analyzed by sieving.

Canadian investigators have identified a "silt-sand overlap problem" with samples analyzed by use of the X-ray procedure. Presumably, a particle-size distribution curve should be continuous throughout all size ranges. There is a need to do the following:

1. Contact Canadian researchers to investigate this "silt-sand overlap."
2. When possible, plot a continuous distribution curve for the entire range of sediment sizes. Lognormal probability paper is especially useful for plotting because the fraction of the sample analyzed by the pipet or X-ray procedure may be a very small fraction by weight of the entire sample.

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APPENDIX 1

Table 6. Summary of available test results on pipet and X-ray particle-size analyses

[USDA, U.S. Department of Agriculture; USGS, U.S. Geological Survey]

Data sheets	Description
1-16	Pipet tests on dispersants—USDA.
17-49	Pipet/X-ray comparisons—USDA. Includes repeat X-ray runs when sample remained idle for different periods between tests.
50-52	X-ray tests on dispersants—USDA.
53-54	X-ray tests on sample at rest for days between tests—USDA.
55-62, 66	Pipet/X-ray comparisons—USDA.
63-65	Pipet/X-ray comparisons at different concentrations—USDA.
67-75	X-ray tests—USDA. Pipet comparisons not available.
76-79	Four repeat runs of pipet and X-ray on made-up sample.
80-84	Pipet tests: two per sample. X-ray runs were done, but results are not available.
85-92	Pipet/X-ray comparisons (including some with no dispersant).
93-105	Pipet/X-ray comparisons—USDA. Also shows standard deviations of repeat pipet runs based on 4-5 analyses.
106-108	Pipet data—USGS. Results of comparative tests on three different samples. Comparative test results are compared to those in Open-File Report 79-1590 (Delaney and Schroder, 1979), which discusses analysis of the same samples at only one location. Values not yet plotted. A data sheet could also be prepared for each of 10 labs in the comparative test.
109-124	Pipet/X-ray comparisons from William W. Emmett. Data sheets not yet filled out. An additional 26 X-ray tests were done.
125-127	X-ray tests—variety of concentrations.
128-130	X-ray tests—variety of concentrations.
131-140	X-ray tests—effect of interchanging cells.
141-149	Pipet/X-ray comparisons from O. G. Lara and W. J. Matthes (U.S. Geological Survey, undated). Each data sheet includes mean and standard deviation for from 7 to 28 replicate runs. Data sheets could be made for each sample if desired. X-ray corrections are included.
150-151	Pipet/X-ray comparison of two USGS tests distributed by Vick Janzer.
152-158	Tests by Weaver and Grobler, 1981.
152	X-ray procedure repeat runs at different concentrations.

Table 6. Summary of available test results on pipet and X-ray particle-size analyses—Continued

Data sheets	Description
153-156	X-ray procedure: reproducibility of unspecified number of runs. No standard deviation listed. Standard glass beads, silt/clay and made-up clay samples.
157	X-ray comparison for "small" and "large" test cell.
158	Pipet/X-ray comparison of natural A clay.
159-161	Test by Welch and others, 1979.
159	Reproducibility, pipet and X-ray. Five samples repeated four times. Standard deviations averaged for all five samples.
160-161	Pipet/X-ray comparison at five different Sedigraph concentrations, 11,500 to 137,700 mg/L (0.46 percent to 5.52 percent by volume).
162-166	Pipet/X-ray tests by Wilson, 1980.
166	Pipet/X-ray comparison on natural quartz standard sample.
167-181	Pipet/X-ray comparison from Schiebe and others (1983) on Clay Lake cores.

Table 7. Test results, by category

Category	Data sheets
Dispersants	1-16, 50-52, 85-92
Single pipet/X-ray comparisons	17-49, 55-62, 66, 85-105, 109-124, 150-151, 158, 166-181
Repeat-run tests	106-108, 141-149, 93-105, 167-181
X-ray concentration	63-65, 125-130, 152, 160-161
X-ray tests—no pipet run	67-75
Pipet tests—no X-ray run	80-84
X-ray tests—cell size	131-140, 157
X-ray tests—lapse time between repeat runs	53-54