Designation: D 3975 – 93 (Reapproved 1999)

Standard Practice for Development and Use (Preparation) of Samples for Collaborative Testing of Methods for Analysis of Sediments[1]

This standard is issued under the fixed designation D 3975; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice establishes uniform general procedures for the development, (preparation) and use of samples in the collaborative testing of methods for chemical analysis of sediments and similar materials.

1.2 The principles of this practice are applicable to aqueous samples with suitable technical modifications.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 596 Practice for Reporting Results of Analysis of Water[2]

D 1129 Terminology Relating to Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]

D 3670 Practice for Determination of Precision and Bias of Methods of Committee D-22[3]

D 3976 Practice for Preparation of Sediment Samples for Chemical Analysis[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

3. Terminology

3.1 *Definitions*—For definition of terms used in this practice, refer to Terminology D 1129.

4. Summary of Practice

4.1 Test samples of adequately defined composition and homogeneity are required for evaluating the precision and bias of test methods. These samples should be typical in all respects to the sample for which the test method is applicable. Samples with three levels of concentration of the measurand are recommended to evaluate the linearity of the test method. Acceptable test materials, in order of preference are: three samples of different compositions; mixtures of two samples to obtain the desired concentration levels; samples prepared by dilution of a single sample.

4.2 In the absence of samples of known composition, the use of the spiking technique, in which standard additions of known constituents are made by established techniques, will be acceptable for evaluating the linearity and the bias of test methods. In such a case, the bias statement will consist of the accuracy of recovery of the spike.

4.3 Comparison of a candidate test method with a standard test method of known precision and bias will constitute an acceptable technique for evaluation of precision and bias. In such comparative measurements, any convenient test samples may be used, provided they are shown to be stable during the time required to make the intercomparison, and that the measurement sequences are chosen to minimize or eliminate errors due to sample instability.

5. Significance and Use

5.1 The objective of this practice is to provide guidelines for the preparation of samples for use in collaborative tests, to evaluate methods during their development, and for the evaluation of the precision and bias of proposed test methods.

5.2 Statements of the precision and bias are a mandatory part of ASTM test methods. Such an evaluation is necessary to provide guidance to the user as to the reliability of measurements that can be expected by its use. The statements are developed on the basis of user experience (ordinarily collaborative tests) with the test method.

5.3 The availability of test samples is a key requirement for collaborative evaluation of test methods.

6. Rationale

6.1 The use of materials of demonstrated adequate homogeneity and known composition enable evaluation of the precision and bias of a test method. Materials of known composition are required to identify biases. Consensus values obtained as the result of collaborative testing are not adequate to permit quantitative evaluation of biases, although they may show that such exist.

6.2 Materials of adequate homogeneity but uncertain composition may be used to determine the precision of a given test

[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.07 on SedimentsCurrent edition approved Sept. 15, 1993. Published December 1993. Originally published as D 3975 – 80. Last previous edition D 3975 – 88.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.03.

[4] *Annual Book of ASTM Standards*, Vol 11.02.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

method. Both single-laboratory precision or between operator-laboratory precision can be evaluated.

6.3 Samples at only one compositional level can provide information for performance statements for only the concentration level of the test sample. Accordingly, other evidence is required to evaluate such factors as linearity and sensitivity.

6.4 A series of samples, spanning the useful concentration range of the test method, are required to evaluate the relation of the precision and bias to the concentration level measured.

7. Requirements for Test Samples

7.1 The collaborative testing of proposed analytical procedures ideally requires samples identical to, or closely resembling the materials for which the test method is designed to analyze. Because this is not always possible, subrogate materials must often be used. Acceptable kinds of samples may be classified as:

7.1.1 *Authentic*—Samples identical in all respects to typical test specimens.

7.1.2 *Synthetic*—Samples synthesized to be equivalent to typical test samples. Spiked samples are a special class of synthetic samples.

7.1.3 *Simulative*—Samples that do not resemble typical samples but that possess some parameter of concern of the test method.

7.2 As one proceeds down the list, the ability of the material to test the analytical method becomes more controversial.

7.3 Test samples must have stable compositions during the test period.

7.4 Test samples must be sufficiently homogeneous to evaluate the test method. The degree of homogeneity is related to the size of sample analyzed. Hence the minimum size of sample meeting a specified homogeneity must be stated, and this must be equal to or smaller than the size of sample specified in the test method.

7.5 The sample must be available in sufficient quantity both for the requirements of the collaborative test and to permit further examination to resolve any operational questions. Preferably, an additional amount should be available for possible examination by other techniques. A desirable objective would be the establishment of sample banks for future use in: (*a*) testing refinement of the method and (*b*) testing other methodologies.

7.6 The uncertainties in homogeneity or composition, or both, of test samples should not exceed one third of the measurement uncertainties they are expected to evaluate. When this specification is met, sample uncertainties make a negligible contribution to the variance of the test results. While replicate samples may be used in practical analysis to average out sample variations, this is usually not feasible in the case of collaborative test samples, hence homogeneity should be attained, as far as possible.

8. Preparation of Test Samples

8.1 Authentic test samples may be procured from natural sources or from suppliers of such materials. The specifications for such materials must be established on the basis of the requirements for matrix composition, composition levels, and sample size-homogeneity considerations of the particular test method. Ordinarily, such materials will need to be disaggregated, sieved, and blended to obtain requisite homogeneity. Pulverizing samples is not recommended because the resulting changes in particle size distribution essentially preclude the use of the original size distribution or surface area for normalizing analytical results. Much of the sample to sample concentration variability, commonly observed in natural sediments, results from differences in the particle size distribution. Samples may need preliminary drying (preferably freeze-drying) and the drying procedure necessary to obtain constant weight should be established. Practice D 3976 provides guidance in this respect.

8.2 Synthetic test samples are prepared to be equivalent to typical analytical samples as far as practicable. Materials required to prepare the test samples include those to simulate the matrix and the parameter(s) of the test method. The extent to which these simulate a typical sample will determine the reliability of its use as a test material. Homogeneity of mixing of synthetic samples must always be verified.

8.3 Spiked samples consist of those in which the substance to be measured is added to an authentic or synthetic test sample, which may or may not already count measurable levels of the constituent added. The spike may be a pure substance or a mixture or solution containing a known amount of the substance that is added quantitatively to the dried sediment. The spiking procedure must be developed in accordance with the requirements of the specific situation. Matrix considerations are always of concern in that the added material may not behave as it would in the case of natural occurrence. Thorough mixing of the spiked sample is very important, although less critical if the entire sample is used in the subsequent measurement.

8.4 Samples that only possess some parameter of interest, hence classified as "simulative," should be used only when it is not feasible to obtain "authentic" or "synthetic" samples. The use of several simulative samples of differing matrices is recommended to minimize dependence of the test results on matrix effects.

9. Test Levels

9.1 The test specimens used in a collaborative test should span the concentration range for which the test method is expected to be valid. Three levels—a high, intermediate, and low level—are recommended. This requirement can be met by the use of several test samples, by a dilution technique involving a single sample, by mixing of two samples, or by the spiking technique.

9.2 Two samples of differing concentration but with similar matrices may be quantitatively mixed to provide several test levels. Samples must be thoroughly blended to obtain the required homogeneity. In the absence of this, test samples may be individually prepared and analyzed in their entirety. The expression used to calculate the composition of a blend of two samples, *A* and *B*, is as follows:

$$\alpha_{A+B} = \alpha_A W_A + \alpha_B W_B / W_A + W_B$$

where:

α_A = weight percent (or ppm) of constituent *a* in sample *A*,

α_B = weight percent (or ppm) or constituent *a* in sample *B*,
α_{A+B} = weight percent (or ppm) of constituent *a* in mixture,
W_A = weight of sample *A* in mixture, and
W_B = weight of sample *B* in mixture.

Note that α_A and α_B must be substantially different to provide a range of concentrations in the mixture. This technique is best utilized when *A* and *B*, respectively represent typical high- and low-level compositions. One mixture, *A* + *B*, will provide the desired intermediate level.

9.3 A sample containing the desired high-level concentration of constituent *a* may be diluted with a second sample containing an insignificant concentration of *a* to obtain samples with several test levels. The matrix composition of the diluent should be similar to that of the test sample. The composition of the mixture is calculated from the following:

$$\alpha_{A+D} = \alpha_A\, W_A/W_A + W_D$$

where:
W_D = weight of diluent sample mixed with W_A.

The same considerations for homogeneity apply as discussed in 9.2.

9.4 The spiking technique may be used to prepare samples of any concentration higher than that of the base matrix. The spike, in suitable form, is added to the base matrix and the resulting concentration is calculated as follows:

$$\alpha_{Sa} = \alpha_A W_A + 100 S_a/W_A + W_s$$

where:
S_a = absolute weight of *a* added in the spiking operation,
α_{Sa} = weight percent of constituent *a* in spiked sample, and
W_S = total weight of spiking material added.

It may be necessary to calculate S_a from the expression

$$S_a = \alpha_{Sa}\, W_s/100$$

The same considerations for homogeneity apply as in the case of 9.2.

Recommended levels, S_n, are as follows:

S_1 = $\alpha\, W_A$
S_2 = $4\,\alpha\, W_A$
S_3 = $9\,\alpha\, W_A$
S_4 = $49\,\alpha\, W_A$
S_5 = $99\,\alpha\, W_A$

Ordinarily, three levels are used, namely: S_1, S_2, and S_3; or, S_1, S_4, and S_5.

9.5 The evaluation of the bias of a test method is ordinarily based on comparison of the "true" value with the measured value. The recovery of a spike may also be used to evaluate bias.

10. Verification of Composition of Test Samples

10.1 The adequacy of the test samples can never be assumed and must always be verified before they may be used in a collaborative study. This should be done by a single laboratory of high competence, using a precise technique, so that measurement uncertainty is limited to within-laboratory variability. However, the collaborative exercise must be designed to detect any contribution due to variability of the sample.

10.2 The homogeneity of a test sample may be verified by measurement of an adequate number of subsamples of specified size, using a test method of known requisite precision.

10.3 The test method used for establishing the composition of a test sample must be one of known and adequate accuracy. This normally means a standard method of test or its equivalent. In the absence of a standard method of test, at least two independent test methods of known adequate precision and believed to be bias-free should be used and the agreement of the results will constitute evidence of accuracy of the reported value. It is recommended to use standard reference materials as controls in each of the above described analytical situations, as far as they are available.

11. Comparison Technique

11.1 The problems of an adequate test sample may be circumvented by intercomparing a candidate test method with a standard method of test, using any conveniently available test material. A standard method of test must be available, which is often not the case, and furthermore the laboratories making the comparison must be expert in its utilization. Furthermore, the intercomparison must be made according to a statistically valid plan.

12. Collaborative Test

12.1 *Planning the Collaborative Test*:

12.1.1 Because of the technical diversity of test methods and practices within the scope of responsibility of Committee D-19, it is not possible to establish a single rigid protocol for collaborative testing. Accordingly, the responsibility for planning and conducting an adequate collaborative test is delegated to the corresponding task group. All aspects including initial planning, conducting the test program, and analyzing and interpreting the test results shall be consistent with following guidelines:

ASTM Special Technical Publication 335;[6] Practice E 691; Practice D 2777; Practice D 596, Practice D 3670.

12.1.2 A written protocol, describing the proposed experimental design and statistical analysis, must be submitted to the results advisor of Committee D-19 or the advisor's designee, for approval. This must include full details of the test samples proposed for use, that must also be approved by the results advisor.

12.1.3 The collaborative test plan shall include specific instructions with respect to the test sample as to sample preservation and any required pretreatment such as drying, for example. See Table 1

12.2 *Conducting the Collaborative Test*:

12.2.1 The task group shall have the overall responsibility for developing test methods, including the preparation of appropriate test samples. In consequence of the expertise of the task group in the measurement area involved, it will direct and coordinate all aspects of the collaborative test.

12.2.2 The task group shall verify in its review of a test method that it is ready for collaborative test before such an exercise is attempted. This ordinarily means that the test

[6] This publication is out of print, but is still available in many libraries and on microfilm.

Title of Method__________ ASTM No.____
(if applicable)

Synopsis of Method: ________________

Determinant	Low Level	Intermediate Level	High Level
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____

Sample Size Per Determination ____
Number of Determinations ____
Number of Participants ____
Type of Test: Round Robin ____ Collaborative ____
Evaluation

Sample Type(s) ________________
Homogeneity Requirement ________________
Container/Storage Recommendations ________________
Other Information ________________

Information Furnished By: Name ________________
Date ________________

Additional Information on Continuation Sheet(s) Yes____ No____

FIG. 1 Collaborative Test Sample Requirement

method has been given a ruggedness test to identify critical variables. Only after a test method has been tried, proven, and reduced to unequivocal language should a collaborative test be attempted to determine its bias or precision, or both.

12.2.3 The instructions for collaborative testing must require preliminary work by potential collaborators to familiarize them with the procedure, prior to the test measurements. This is necessary to ensure that the collaborative tests are made by peer groups and that a "learning experience" is not included in the statistics of the collaborative test. The task group may also develop procedures and conduct preliminary tests to qualify prospective collaborators, and this approach is strongly recommended.

12.2.4 The task group has the responsibility to review and statistically evaluate the test data including sample stability and homogeneity and to prepare the statements of precision and bias, on the basis of established procedures.

12.2.5 Statements of the precision or bias of a test method, or both, must indicate the type of test sample upon which the information is based.

12.2.6 All other aspects of the collaborative test, including reporting of results shall be in conformance with guidelines and procedures established by Committee D-19.

13. Keywords

13.1 analysis; collaborative testing; development; preparation; use; methods; sediment samples; Geomorphology; and Open-Channel Flow.