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Chapter A6

QUALITY ASSURANCE PRACTICES FOR THE CHEMICAL AND BIOLOGICAL ANALYSES OF WATER AND FLUVIAL SEDIMENTS

By Linda C. Friedman and David E. Erdmann

Book 5

Laboratory Analysis

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PREFACE

This manual is one of a series of manuals on techniques used by the U.S. Geological Survey for planning and conducting water-resources investigations. The material is arranged under major subject headings called books and is further subdivided into sections and chapters. Book 5 is on laboratory analyses; section A is on water. The unit of publication, the chapter, is limited to a narrow field of subject matter. "Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments" is the sixth chapter under Section A of Book 5. The chapter number includes the letter of the section.

This chapter was prepared with the assistance of many Geological Survey chemists and hydrologists as a means of documenting and making available the practices used by the Geological Survey to assure the quality of water-quality data produced by the collection and analysis of water, fluvial sediments, and aquatic organisms. Documentation of practices associated with certain specific instruments, such as inductively-coupled plasma spectrometers, mass spectrometers, and alpha counters is not yet complete. It is intended that, when completed, they and other practices will be incorporated in a supplement to or in a new addition of this chapter.

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The editors are also grateful to the Literary Executor of the late Sir Ronald A. Fisher, F. R. S., to Dr. Frank Yates, F. R. S., and to Longman Group Ltd., London, for permission to reprint table III "Distribution of t" from their book "Statistical Tables for Biological, Agricultural and Medical Research," (sixth edition, 1974).

Reference to trade names, commercial products, manufacturers, and distributors in this manual does not constitute endorsement by the Geological Survey nor recommendation for use.

TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS OF THE U.S. GEOLOGICAL SURVEY

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The manuals published to date are listed below and may be ordered by mail from the **Eastern Distribution Branch, Text Products Section, U.S. Geological Survey, 604 South Pickett St., Alexandria, Va. 22304** (an authorized agent of the Superintendent of Documents, Government Printing Office).

Prepayment is required. Remittances should be sent by check or money order payable to U.S. Geological Survey. Prices are not included in the listing below as they are subject to change. **Current prices can be obtained by calling the USGS Branch of Distribution, phone (703) 756-6141.** Prices include cost of domestic surface transportation. For transmittal outside the U.S.A. (except to Canada and Mexico) a surcharge of 25 percent of the net bill should be included to cover surface transportation.

When ordering any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations."

TWI 1–D1. Water temperature—influential factors, field measurement, and data presentation, by H. H. Stevens, Jr., J. F. Ficke, and G. F. Smoot, 1975, 65 pages.

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TWI 5–A3. Methods for analysis of organic substances in water, by D. F. Goerlitz and Eugene Brown, 1972, 40 pages.

TWI 5–A4. Methods for collection and analysis of aquatic biological and microbiological samples, edited by P. E. Greeson, T. A. Ehlke, G. A. Irwin, B. W. Lium, and K. V. Slack, 1977, 332 pages.

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QUALITY ASSURANCE PRACTICES FOR THE CHEMICAL AND BIOLOGICAL ANALYSES OF WATER AND FLUVIAL SEDIMENTS

Linda C. Friedman and David E. Erdmann

Abstract

This chapter contains practices used by the U.S.Geological Survey to assure the quality of analytical data for water, fluvial sediment, and aquatic organisms.

These practices are directed primarily toward personnel making water quality measurements. Some detail specific quality control techniques, others document quality assurance procedures being used by the Central Laboratories System of the U.S. Geological Survey, and still others describe various statistical techniques and give examples of their use in evaluating and assuring the quality of analytical data.

The practices are arranged into eight sections:

Analytical Methods Development Procedures
Standard Quantitative Analysis Techniques
Instrumental Techniques
Reference Material
Laboratory Quality Control
Quality Assurance Monitoring
Documentation, Summary, and Evaluation of Data
Materials Evaluation

Each section is preceded by a brief description of the material covered. Similarly within each section, each practice is preceded by a description of its application or scope.

Introduction

The Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient utilization of the Nation's natural resources—including water as a resource as well as water involved in the use and development of other resources. As one of several Interior agencies, the Geological Survey's primary function in relation to water is to assess its availability and utility as a national resource for all uses. The Geological Survey's responsibility for water appraisal includes assessments of the location, quantity, availability, and quality of water.

As part of its mission, the Geological Survey is responsible for producing a large part of the Nation's water-quality data. These data are gathered through the collection and chemical, biological, and physical analyses of water, water plus suspended sediments, and bottom materials, and are produced not only by the laboratories and field units of the Geological Survey, but also by other organizations in cooperation with or through contract with the Geological Survey.

This manual is one of a series prepared to document and make available data collection and analysis procedures used by the Geological Survey. The series describes procedures for planning and executing specialized work in water-resources investigations. The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. For convenience the chapters on methods for water-quality analysis are grouped into the following categories:

Inorganic substances
Minor elements by emission spectroscopy
Organic substances
Aquatic biological and microbiological samples
Radioactive substances
Quality assurance practices

Interpretation and utilization of analytical data are affected strongly by the data's reliability. This chapter contains specific practices to be used in assuring, documenting, and evaluating the quality of water-quality data produced or used by the Geological Survey. As additional quality assurance practices are completed, they will be incorporated in a supplement to or in a new edition of this chapter and will be available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

Purpose

Analytical data must be comparable no matter when and where the analyses were made and what methodology and specialized techniques were followed. In an era of rapidly changing technology for the study of water-quality characteristics, the difficulty of looking at long-term characteristics of the nation's waters is compounded by the problem of knowing whether data produced today by laboratory A using method X will have the same precision and bias as data produced 10 years in the future by laboratory B using method Y. The purpose of this chapter is to record and disseminate practices used by the Geological Survey to control and assure the quality of analytical data so that the data will be of known accuracy and can be compared.

Scope

This chapter includes techniques and procedures found applicable to the quality control and quality assurance of water and fluvial sediment data. Practices are directed primarily towards personnel making water quality measurements and detail procedures which are necessary to evaluate and assure the quality of analytical data. Practices are grouped in eight sections:

"Analytical Methods Development," includes procedures for determining the precision and bias of analytical methods and a procedure to be used in considering whether a new method is to be preferred over an established one. Statistical concepts and formulas are presented.

"Standard Quantitative Analysis Techniques," includes basic techniques, necessary to anyone in an analytical laboratory. It supplements, not substitutes for, techniques described in basic texts on quantitative analysis.

"Instrumental Techniques," describes quality control measures for instruments currently in use in water-analysis laboratories. Special emphasis is placed on operation and calibration of these instruments.

"Reference Material," presents methods for preparing ampouled concentrate and natural water matrix reference materials. Statistical techniques used in the Geological Survey's Standard Reference Water Samples program are also described.

"Laboratory Quality Control," describes procedures necessary for specific analytical techniques and determinations. Methods for the preparation and use of quality control charts are also given.

"Quality Assurance Monitoring," describes procedures which can be used by someone "outside" the laboratory or by the heads of large laboratories to assure analytical quality.

"Documentation, Summary, and Evaluation of Data," describes records to be kept and presents various tabular, graphical, and statistical examples of data summarization and evaluation. A program for laboratory evaluation is also described.

"Materials Evaluation," describes procedures to assure that materials are of adequate and uniform or known quality. Included is information on determining how many and which items from a large lot need to be tested.

This chapter should be used as a supplement to the analytical methods chapters, (Book 5, Chapters A1 through A5) of this series. In using the practices contained herein to develop a specific data quality assurance plan for a specific water-quality program, many readers also may find the general guidelines published by the National Oceanic and Atmospheric Administration (Farland, 1980) to be useful. Although many basic quantitative techniques are included, this chapter is not meant to be a replacement for standard quantitative analysis texts.

Definitions

Accuracy. A measure of the degree of conformity of the mean value obtained by using a specific method or procedure with the true value. The concept of accuracy includes both bias (systematic error) and precision (random error).

Average deviation. A number which represents the dispersion of values around their mean, calculated as the mean or average of the absolute deviations of all values from the mean.

Bias. A persistent positive or negative deviation of the mean value obtained by using a specific method or procedure from the true value. In practice, expressed as the difference between the accepted true value and the mean value obtained by repetitive testing of a homogeneous sample.

Degrees of freedom. The number of independent values used to calculate a statistic.

Mean. The arithmetic average.

Percent relative standard deviation. The relative standard deviation multiplied by 100 percent.

Precision. The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value.

Quality assurance. A term used to describe programs and the sets of procedures, including (but not limited to) quality control procedures, which are necessary to assure data reliability. In this manual, the term includes both practices employed by sources outside of an analytical laboratory and practices used by the head of a large laboratory to assure the quality of laboratory data.

Quality control. A term used to describe the routine procedures used to regulate measurements and produce data of satisfactory quality.

Relative standard deviation. The sample standard deviation expressed as a fraction of the sample mean. Although the synomous term "coefficient of variation" is more usually found in statistics books, this manual follows the recommendation of the journal, "Analytical Chemistry" that "relative standard deviation is preferred over 'coefficient of variation' " (American Chemical Society, 1981).

Standard deviation. A number which represents the dispersion of values around their mean calculated as the square root of the variance.

Variance. A number which represents the dispersion of values around the mean value, calculated by dividing the sum of squares of deviations from the mean by the appropriate degrees of freedom.

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Analytical Methods Development Procedures

An analytical procedure should provide adequate documentation of its accuracy. Development of a new analytical method requires that sufficient data be collected so that a decision can be made whether to accept the method for general use, to limit its use, or to reject it. Proper documentation of all data is necessary. If an accepted analytical procedure already exists for determining a certain constituent, a comparison of results between the accepted and the proposed method must be provided

Single Operator Precision

1. Application or scope

1.1 This practice details procedures for obtaining a statement of single operator precision. It describes how the analytical standard deviation for each sample is computed, details criteria for rejecting outliers, and indicates how precision statements should be expressed depending on whether the precision is linear, constant, or curvilinear with respect to concentration.

1.2 All analytical procedures must include a single operator precision statement. The raw analytical data and the single operator precision statement should accompany the research report.

1.3 Precision statements should be developed for the analysis of the constituent in both distilled and natural water or sediment. Data should cover the analytical range of the method.

2. Practice

2.1 Determination of standard deviation

2.1.1 Analyze each sample a minimum of 10 times on two or more different days.

2.1.2 Compute the standard deviation:

$$s=\sqrt{\frac{\Sigma(x_i-\bar{x})^2}{n-1}} \text{ or } s=\sqrt{\frac{\Sigma x_i^2-(\Sigma x_i)^2/n}{n-1}} \qquad (1)$$

where

s = standard deviation of analysis of each sample,

x_i = each individual value,

$\bar{x}$ = arithmetic mean (average) of all values, and

n = number of values.

2.2 Rejection of outliers

2.2.1 Several tests are available for rejecting values which appear to be outliers. (Any value which is the result of a known deviation from the procedure should also be rejected). If values are rejected, the test used should be stated in the report, and the standard deviation should be recomputed before calculating the single operator precision.

2.2.2 The method for rejecting outliers used most commonly in the National Water Quality Laboratories of the U.S. Geological Survey is based on the T value (Grubbs test) as described in the American Society for Testing and Materials (ASTM) Standard E–178–80 (1980). Compute:

$$T=\frac{x_n-\bar{x},}{s} \qquad (2)$$

where

T = T value for probable outlier,

x_n = concentration of probable outlier,

$\bar{x}$ = arithmetic mean (average) of all values, and

s = standard deviation of all values.

Any computed T greater than the critical values for T found in table A1 in the appendix indicates that the outlier (x_n) may be rejected.

2.2.3 Dixon's test is recommended in the Statistical Manual of the Association of Official Analytical Chemists (Youden, 1975, and Steiner, 1975). It may be applied by ranking the data and computing:

for x_n	or	for x_1	
$\frac{x_n-x_{n-1}}{x_n-x_1}$		$\frac{x_2-x_1}{x_n-x_1}$	for $n<8$
$\frac{x_n-x_{n-1}}{x_n-x_2}$		$\frac{x_2-x_1}{x_{n-1}-x_1}$	for $8 \leq n \leq 10$
$\frac{x_n-x_{n-2}}{x_n-x_2}$		$\frac{x_3-x_1}{x_{n-1}-x_1}$	for $11 \leq n \leq 13$
$\frac{x_n-x_{n-2}}{x_n-x_3}$		$\frac{x_2-x_1}{x_{n-2}-x_1}$	for $13 \leq n \leq 25$

where

x_1 = the smallest result, and

x_n = the largest result.

Any value greater than that found in table A2 in the appendix indicates that the x_n or x_1 may be rejected.

2.2.4 If several outliers are to be tested, the above tests are not recommended for repeated rejection (ASTM method E-178, 1980). If suspected outliers are either all high or all low, the sample coefficient of skewness should be used; if the suspected outliers are both high and low, the sample coefficient of kurtosis should be used:

$$\sqrt{b_1}=\sqrt{n}\sum_{i=1}^{n}(x_i-\bar{x})^3/(n-1)^{3/2}s^3$$

$$=\sqrt{n}\sum_{i=1}^{n}(x_i-\bar{x})^3/[\Sigma(x_i-\bar{x})^2]^{3/2} \qquad (3)$$

where

$\sqrt{b_1}$ = the coefficient of skewness, and other symbols are as previously defined, and

$$b_2=n\sum_{i=1}^{n}(x_i-\bar{x})^4/(n-1)^2s^4$$

$$=n\sum_{i=1}^{n}(x_i-\bar{x})^4/[\Sigma(x_i-\bar{x})^2]^2 \qquad (4)$$

where

b_2 = the coefficient of kurtosis, and other symbols are as previously defined.

If $\sqrt{b_1}$ or b_2 exceed the values given in tables A3 and A4 in the appendix, then the observation farthest from the mean should be rejected and the procedure repeated.

2.3 Determination of precision

2.3.1 Analyze samples at several concentration levels to acquire data which cover the analytical range of the method. Analyze at least three samples which contain concentrations which are approximately 10, 50, and 80 percent of the analytical range.

2.3.2 If precision varies linearly with concentration level (determined by plotting the means versus the standard deviation), a regression line can be determined (NOTE 1):

$$S_o=a+bx \qquad (5)$$

where

S_o = overall single-operator precision, throughout the range,

x = concentration of the constituent,

a = intercept of line with the y axis (NOTE 2), and

b = the slope of the line.

NOTE 1. Concentrations should be evenly spaced throughout the range to avoid distortion. Avoid having one or two points at one end of the range and all other points near the other end of the range (fig. 1).

NOTE 2. A negative intercept implies that the standard deviation is negative when the concentration is zero and, therefore, should be viewed with some suspicion. However, the line should not arbitrarily be discounted as being invalid. It should be recognized that the line is an estimate of the standard deviation, that there is a standard error associated with this estimate, and that concentrations near zero may not have been available for use in developing the line. The line is simply assumed to be the best representation of the standard deviation based on all available data. The concentration for which the line is applicable must always be reported.

2.3.2 If linear precision is reported, the correlation coefficient should also be reported since it will give an idea of how "good" the line is (NOTE 3):

$$r=b\,\frac{s_x}{s_s} \qquad (6)$$

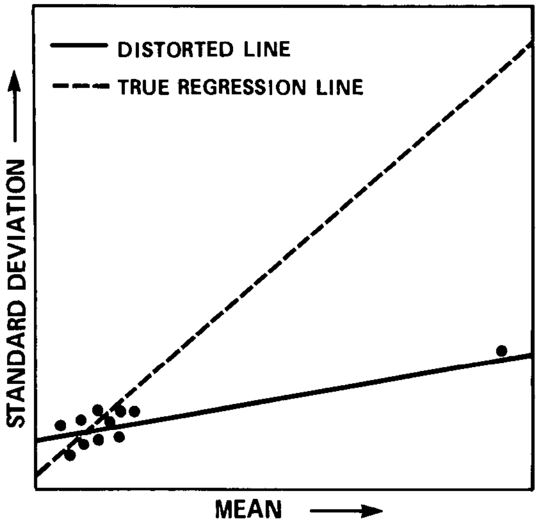

Figure 1.—Distortion of regression line by unequal distribution of values; true regression line would have been drawn if concentrations had been equally spaced throughout the analytical range.

where

r = the correlation coefficient,
b = the slope of the line,
s_s = the standard deviation of the individual standard deviations (obtained for the analysis of each sample).

NOTE 3. A correlation coefficient near one is an indication that there is a good fit of the points to the line. A correlation coefficient near zero is an indication that either there is a poor fit of the points or that the precision is constant and the line is horizontal over the concentration range tested. Table A-30a in Dixon and Massey (1969) can be used to statistically test the hypothesis that the correlation coefficient is equal to zero. If the precision does appear constant, proceed to step 2.3.3 instead of determining the regression line.

2.3.3 If the precision appears constant over the range of the method, then the precision may be expressed by the following formula (ASTM, D–2777–77, 1980):

$$S_o = \sqrt{\frac{(n_1 \times s_1^2) + (n_2 \times s_2^2) + \ldots . (n_n \times s_n^2)}{n_1 + n_2 + \ldots . n_n}} \qquad (7)$$

where

S_o=The single-operator standard deviation over the method range,
s_n=the standard deviation of the nth sample,
n_1=the number of values for the 1st sample, and
n_n=the number of values for the nth sample.

2.3.4 When precision varies curvilinearly with concentration, the curve should be presented. If possible, an equation should also be computed (for example, $S_o = a + bx + cx^2$, where S_o is the single operator precision, x is the concentration of the constituent, a is the intercept of the line with the y-axis, and b and c are coefficients for the first and second order terms, respectively.)

2.3.5 Precision may also be expressed in terms of percent relative standard deviation:

$$R.D. = \frac{s}{\bar{x}} \times 100 \text{ percent} \qquad (8)$$

where

$R.D.$ = the relative standard deviation in percent,
x = the mean concentration of a sample, and
s = the standard deviation for the mean of that sample.

2.3.6 In addition to the precision statement, the range for which the precision is applicable should also be reported.

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Bias

1. Application or scope

1.1 This practice presents guidelines for developing a bias statement.

1.2 All analytical procedures should include a statement of bias. The bias statement and supporting raw analytical data should accompany the methods development research report.

1.3 Bias statements are developed by using either a standard reference material or an accepted method. The reference type must always be specified in the bias statement.

2. Practice

2.1 Determination of bias

2.1.1 Analyze known reference materials (such as ones certified by the National Bureau of Standards) and compare the determined values to the known values.

2.1.2 Alternatively, if an accepted method (or methods) exists for the determination, analyze 25 to 50 samples by both the proposed and the accepted method and compare resulting values.

2.1.3 In addition to or instead of the above procedures (if neither of them is practical), add known amounts of a standard to distilled and natural waters. Compare the determined values to the concentrations added.

2.2 Expression of bias

2.2.1 Express bias as a percent:

$$\text{Bias} = \frac{x_{exp} - x_{acc}}{x_{acc}} \times 100 \text{ percent} \qquad (9)$$

where

x_{exp} = the experimental value, and

x_{acc} = the accepted value.

2.2.2 Bias may be expressed in terms of concentration rather than percent. The words "positive" or "negative" must prefix the concentration value.

2.2.3 As noted in the practice, "Acceptance or rejection of a new method," a *t*-test may be used to test for the significance of the bias.

Selected Reference

American Society for Testing and Materials, 1980: D-2777-77, Determination of precision and bias of methods of committee D-19 on water, *in* Annual Book of ASTM Standards, Part 31, Water: Philadelphia, American Society for Testing and Materials, p. 16–28.

Chemical Interferences

1. Application or scope

1.1 This practice gives general guidelines for investigating nonspecificity of a method.

1.2 Documentation of the development of an analytical procedure should include data relating to suspected interfering substances.

2. Practice

2.1 Addition of interfering substance to standards and samples

2.1.1 Spike standards and samples with a minimum of three different concentrations of the suspected interfering substance. Initial concentrations of the spike should cover the range in which the suspected substance is expected to occur in nature (or from environmental pollution), or that may result if the sediment in a sample is digested as in a "total" or "bottom material" analysis.

2.1.2 Calculate the percent recovery of the consitituent being analyzed:

$$\text{Recovery} = \frac{x_{exp}}{x_{acc}} \times 100\,\text{percent} \tag{10}$$

where

x_{exp} = the experimental value, and

x_{acc} = the accepted value.

2.1.3 If an interfering substance causes an interference at a particular concentration, but not at another concentration, repeat steps 2.1.1 and 2.1.2 using a narrower concentration range of interfering substance. (For example, if the high concentration is observed to cause an interference, but the medium concentration does not, use three additional spikes of concentrations between the medium and high).

2.1.4 Repeat the process until the concentration at which the added substance interferes is determined.

2.1.5 If no interference is noted, state: "_________causes no interference at concentrations less than (maximum concentration tested)."

2.1.6 If interference is noted, state: "_________at_________concentration interferes." State whether the observed interference was positive or negative and give any other information that might be helpful to an analyst or user of the data.

2.2 Addition of interfering substance to a series of standards

2.2.1 Add the interfering substance to five to ten standards covering the analytical range of the method. Use a concentration level that is known to cause interference.

2.2.2 Analyze the standards to determine the pattern of interference over the range of concentrations of the constituent being determined.

2.2.3 Prepare a concise statement as in 2.1.5 above giving the results. Indicate whether the interference increases linearly with increasing concentration, decreases with increasing concentration, or shows some other relationship to the concentration of the constituent being analyzed.

Intralaboratory Precision And Bias

1. Application or scope

1.1 This practice gives general guidelines for developing intralaboratory bias and precision statements.

1.2 After preliminary methods development work is completed (often in a research laboratory), test the method on actual samples in an operating laboratory. Data should be quickly developed which cover the range of the method in a variety of natural matrices.

1.3 If interlaboratory data are unavailable, intralaboratory precision and bias statements should be included in the published procedure.

2. Practice

2.1 Analysis by two methods to determine bias

2.1.1 Analyze all samples for which the determination in question has been requested by both the accepted procedure and the new procedure until sufficient analyses are obtained to cover the applicable concentration range. Perform the paired analysis of all samples received by the laboratory during a minimum period of 1 week. Continue analyses until a minimum of 30 samples are analyzed (NOTE 1). If at the end of a month the range of the method has not been sufficiently covered, dilute or add spikes to samples to obtain concentrations distributed throughout the analytical range.

NOTE 1. Requirements for analyses of all samples received during a minimum of 1 week and for analyses of at least 30 samples have been placed in the attempt to obtain data from a variety of matrices. However, if all samples are known to come from one site or one area of the country, these minimums should be exceeded.

2.1.2 If possible, analyze samples by both methods at the same time (in parallel).

2.1.3 If parallel determinations of the constituent by the two methods are not possible, randomize both the order in which the samples are analyzed and the method by which they are first analyzed. Consult a random numbers table (available in most statistics books) to achieve randomization.

2.1.4 Calculate the bias of the new method with respect to the accepted method (see practices "Bias" and "Acceptance or rejection of a new method").

2.2 Analysis of spikes to determine bias

2.2.1 If an accepted method does not exist, use the new method to analyze all samples for which the determination in question has been requested and for which sufficient water has been provided so that a second portion of the sample may be spiked and analyzed. Analyze a minimum of 30 samples.

2.2.2 Spike all samples (for which enough water has been provided) with a known concentration of standard. Add a sufficient amount of standard to samples which have original values in the low portion of the analytical range to approximately double the concentration. Do not spike samples to concentration levels which are outside of the analytical range. If the sample requires dilution in order to be analyzed, spike the samples so that the resulting concentration requires the same dilution.

2.2.3 Subtract the original concentration of the sample from the concentration determined after spiking and determine the bias or percent recovery (see practices "Bias" and "Acceptance or rejection of a new method").

2.3 Analysis of samples to determine precision

2.3.1 Analyze each sample which has sufficient volume and for which the determination in question has been requested, on a minimum of four different days. Randomize the order in which the samples are analyzed (using a random numbers table).

2.3.2 If possible, three analysts should analyze the samples, each performing the analysis in duplicate.

2.3.3 Continue analysis until either the range of the method or the naturally occurring range of the constituent has been covered.

2.3.4 Calculate the precision (see practice "Single operator precision").

Interlaboratory Precision

1. Application or scope

1.1 This practice provides a guideline for developing an interlaboratory precision statement. Such a statement should be developed for each method and included in the published procedure.

1.2 Statistics from interlaboratory tests will aid the user of analytical data in comparing analyses from two or more laboratories. If it is not practical to develop the interlaboratory precision statement prior to publication of the method (for example, not enough laboratories are willing or able to participate) a statement of intralaboratory or single operator precision should be used and the method updated once interlaboratory data are available.

1.3 Interlaboratory test data normally include both random and systematic errors of each laboratory. These systematic errors are not "inherent" to the method, but rather are ones introduced, inadvertently, by participating laboratories. Thus, a slight difference in a reagent or an oven temperature (both systematic errors) will become incorporated in the measurement of interlaboratory precision. As Youden points out, "Differences in systematic errors are the major source of disagreement among laboratories." (Youden, 1960).

2. Practice

2.1 Reference samples

2.1.1 Prepare and distribute reference samples containing either concentrated or working level concentrations of constituent(s) in question. Use a natural or distilled water matrix or both (NOTE 1).

NOTE 1. Ideally, precision statements should be developed using both natural and distilled water matrices.

2.1.2 Reference samples should cover the concentration range of the method. A minimum of three samples representing approximately 10, 50, and 80 percent of the analytical range should be distributed.

2.1.3 See the section "Reference Material," for further information on reference material preparation.

2.2 Experimental design

2.2.1 Calculate the required number of replicate analyses to be made on each sample by each analyst, using the formula (ASTM, D-2777-77, 1980):

$$rep > 1 + \frac{30}{p} \qquad (11)$$

where

rep = number of replicates required, and

p = product of variables (operators, laboratories, concentration levels, and so forth).

For example, if two operators in each of six laboratories are to analyze samples at four concentration levels, the number of replicates required is calculated:

$$rep > 1 + \frac{30}{(2)(6)(4)}, \text{ or}$$

$$rep > 1 + 0.25.$$

In this case, two replicates are required.

2.2.2 Although overall interlaboratory precision can be determined without replicates, there is no way to the separate the components of laboratory systematic error from random error without replicates.

2.2.3 A minimum of six operators and three laboratories is required (ASTM, D-2777-77, 1980); more laboratories are desirable.

2.2.4 The number of analysts should be spread evenly among participating, laboratories, if possible. For example, 1 analyst in each of 10 laboratories or 2 analysts in each of 5 laboratories is preferable to 1 analyst in 6 laboratories plus 2 analysts in 2 laboratories.

2.2.5 A copy of the analytical method to be used should be provided to each laboratory. Each laboratory should be instructed to follow the written method exactly (a similar method they are using must not be substituted) and should be requested to submit results from each of the required replicates (results should not be averaged prior to submission). Each laboratory should be given the opportunity to "practice" the method on a sample containing a "known" concentration of the constituent being determined before analyzing the "unknown" reference samples.

2.3 Data Analysis

2.3.1 Reject a laboratory's data if it is so high or so low that a large systematic error, specific to the laboratory, is evident. As recommended by Youden (1975), in order to decide whether a laboratory's data should be rejected, first rank the data. Reject any laboratory determined to have less than a 5 percent chance of being within the limits specified in table A5 in the appendix.

For example, consider the data presented in table 1.

a. Rank the data for each sample, giving a "1" to the largest amount, a "2" to the second largest amount, and so forth, (table 2). Assign equal ranks to equal values.

Table 1.—Example: Data from five laboratories for analysis of four samples

Laboratory	Samples			
	1	2	3	4
1	1.5	3.1	8.1	15.0
2	1.6	3.0	8.3	14.8
3	1.4	3.2	8.1	15.0
4	1.4	3.3	8.2	14.9
5	1.8	3.5	8.7	15.7

Table 2.—Example: Ranking of data prior to rejection of "outlying" laboratories

Laboratory	Rank				Sum
	1	2	3	4	
1	3	4	4.5	2.5	14
2	2	5	2	5	14
3	4.5	3	4.5	2.5	14.5
4	4.5	2	3	4	13.5
5	1	1	1	1	4

b. Sum the ranks for each laboratory (table 2).

c. Consult table A5. For five laboratories and four materials, the upper and lower limits are 19 and 5, respectively. The sum of "4" for laboratory number 5 is below the lower limit. All data from laboratory number 5 should be rejected.

2.3.2 From the remaining raw data, reject individual outliers and calculate the standard deviation for each sample as specified in the practice, "Single operator precision":

$$s=\sqrt{\frac{\Sigma(x_i-\bar{x})^2}{n-1}}$$

$$\text{or } s=\sqrt{\frac{\Sigma x_i^2-(\Sigma x_i)^2/n}{n-1}} \qquad (12)$$

where

s = interlaboratory standard deviation for each sample,

x_i = value reported by each laboratory, and

n = number of laboratories.

2.3.3 If precision varies linearly with concentration level (determined by plotting the means versus the standard deviation), determine the regression line:

$$S_T=a+bx \qquad (13)$$

where

S_T = interlaboratory precision,

x = concentration of the constituent,

a = intercept of line with the y axis, and

b = the slope of the line.

2.3.4 If precision appears constant over the range of the method, calculate the overall precision (ASTM, D-2777-77, 1980):

$$S_T=\sqrt{\frac{(n_1\times s_1^2)+(n_2\times s_2^2)+\ldots(n_n\times s_n^2)}{n_1+n_2+\ldots n_n}} \qquad (14)$$

where

S_T = interlaboratory precision,

s_1 = the standard deviation of the 1st sample,

s_n = the standard deviation of the nth sample,

n=the number of values for the 1st sample, and

n_n=the number of values for the nth sample.

2.3.5 If precision varies curvilinearly with the concentration level, present the plot. If possible, also include an equation for the curve.

2.3.6 The precision values may also be expressed in terms of percent relative standard deviation.

$$R.D. = \frac{s}{\bar{x}} \times 100 \text{ percent} \qquad (15)$$

where

$R.D.$ = the relative standard deviation in percent,

$\bar{x}$=the mean concentration of a sample, and

s=the standard deviation of the mean of the sample.

2.3.7 Report, in addition to the precision statement, the number of analysts and (or) laboratories participating in the interlaboratory "round robin" and the range for which the precision statement is applicable.

2.3.8 Report whether the analyses were made using a natural or distilled water matrix. Report two statements if both natural and distilled water matrices were used and the precision is different.

2.4 Single operator precision

2.4.1 Single operator precision can be developed by using analysis of variance techniques on duplicate interlaboratory analyses and separating the within-lab variance (single operator precision) and between-lab variance (Steiner, 1975).

2.4.2 Alternatively, operator precision and laboratory biases may be separated by using a series of paired concentration samples (Youden, 1975).

References

American Society for Testing and Materials, 1980, D-2777-77, Determination of precision and bias of methods of committee D-19 on water, *in* Annual Book of ASTM Standards, Part 31, Water: Philadelphia, American Society for Testing and Materials, p. 16–28.

Steiner, E. H., 1975, Planning and analysis of results of collaborative tests, *in* Statistical Manual of the Association of Official Analytical Chemists: Washington, D.C., Association of Official Analytical Chemists, p. 1–61.

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Acceptance Or Rejection of A New Method

1. **Application or scope**

1.1 This practice describes tests to use and factors to consider in deciding whether to accept, reject, or limit the use of a new method.

1.2 The decision must be based on all available data. In particular, both the precision and bias statements must be considered and compared to those of the accepted method.

2. **Practice**

2.1 Test for significant bias of a method

2.1.1 A *t*-test may be used to compare the determined mean concentration with the "known" concentration of a reference material (Youden, 1975, p. 36). (See practice "Methods used for data evaluation: *t*-test," in section "Documentation, summary, and evaluation of data.")

2.1.2 Alternatively, a *t*-test may be used to compare the mean concentration obtained using a new method with the concentration obtained from repeated analysis of the same sample by an approved method.

2.2 Test for significantly smaller variance

2.2.1 An *F*-test may be used to test whether a newly developed method shows better precision (has a smaller variance) than an accepted method (Youden, 1975, p. 38).

2.2.2 Calculate:

$$F=\frac{s^2_{acc}}{s^2_{new}} \qquad (16)$$

where

s_{acc}=standard deviation obtained using the accepted method,

s_{new}=standard deviation obtained using the new method, and

F=calculated F statistic (NOTE 1).

NOTE 1. The F value will be associated with (n_A-1, n_N-1) degrees of freedom where n_A = the number of determinations by the accepted method and n_N = the number of determinations by the new method.

2.2.3 Compare the computed F value with the F value from table A6 in the appendix (using the appropriate degrees of freedom.) If the calculated value is greater than that in the table, then the variance of the accepted method is greater than that of the new method.

2.3 Better precision, less bias

2.3.1 If the new method shows better precision and less bias than the accepted method, select the new method as the preferred method (assuming that interference problems are no greater than found in the accepted method).

2.4 Better precision and greater bias or worse precision and less bias

2.4.1 As Youden (1961) indicates, when a new method shows better precision, but also greater bias than the accepted method, or vice versa, the decision of whether to accept the new method may not be immediately obvious.

2.4.2 For example, table 3 lists results for two methods which were used to repeatedly

Table 3.—Example: Analytical results of two methods [Accepted "true" sample concentration=30 mg/L]

Method	Analytical results (mg/L) 1	2	3	4	5	6	7	Mean (mg/L)	Standard deviation (mg/L)	Bias (mg/L)
New method	40	35	45	42	38	50	30	40.0	± 6 .56	+ 10.0
Accepted method	30	20	40	52	8	50	10	30.0	± 18.11	0.0

analyze a sample containing 30 mg/L of a certain constituent. As the standard deviation and bias figures for each method indicate, the new method has better precision than the accepted method, but shows a positive bias.

As can be readily seen from figure 2, a single value obtained by the new method can be expected to be closer to the accepted "true" value than can a single value obtained by the accepted method because 95 percent of the values can be expected to fall within approximately ± 2 (2.447 for 7 values) standard deviations of the mean: 95 percent of the values are within 16.1 mg/L of the true value for the new method, while 95 percent of the values are within 44.3 mg/L of the true value for accepted method. Thus, in this case the new method appears preferable to the accepted method (NOTE 2).

NOTE 2. If the bias of the new method were +50 mg/L instead of only 10 mg/L, a single value from the new method would be less likely than a single value from the accepted method to be near the true value, and the accepted method would be preferable to the new method.

2.5 Same precision, same bias

2.5.1 In deciding whether to accept or reject a new method, consider whether the new method would increase productivity and (or) lower the cost of analyses, limit interfering substances, or eliminate a toxic reagent in the method.

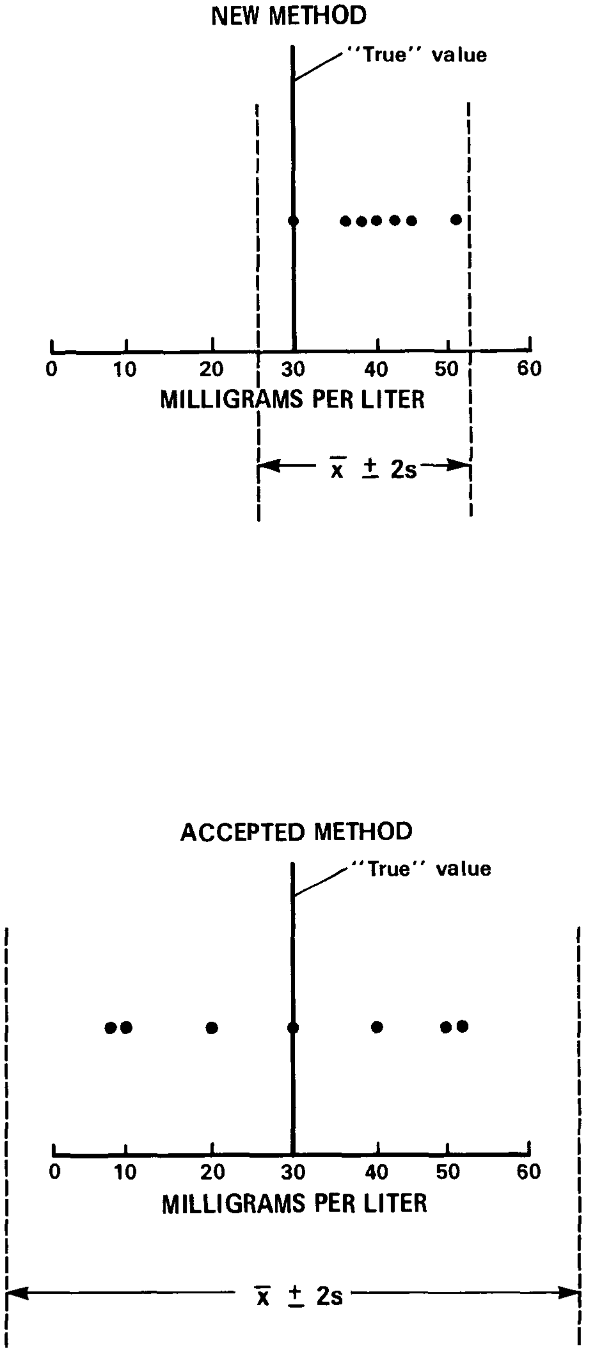

Figure 2.—Bias and precision, results of new and accepted analytical methods.

Selected References

American Society for Testing and Materials, 1980, D-2777-77, Determination of precision and bias of methods of committee D-19 on water, *in* Annual Book of ASTM Standards, Part 31, Water: Philadelphia, American Society for Testing and Materials, p. 16–28.

Dixon, W. J., and Massey, F. J., 1969, Introduction to statistical analyses (3d ed.): New York, McGraw-Hill, p. 109–112, 470–471.

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Youden, W. J., 1975, Statistical techniques for collaborative tests, *in* Statistical Manual of the Association of Official Analytical Chemists: Washington, D.C., Association of Official Analytical Chemists, p. 36–39.