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Techniques of Water-Resources Investigations
of the United States Geological Survey

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."

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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 devia-

tion 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:

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

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:

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

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

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):

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

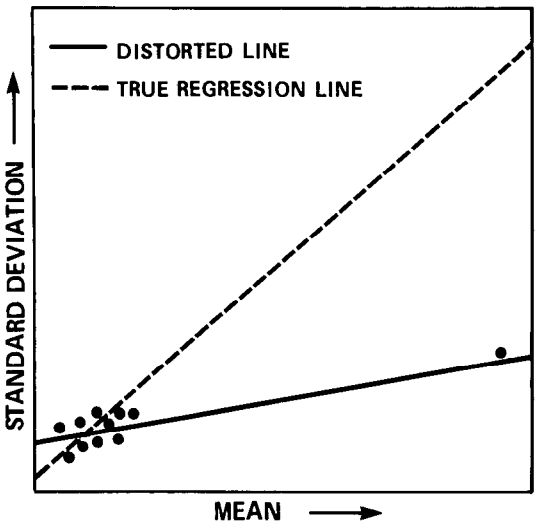

Figure 1.—Distortion of regression line by unequal distribution of values; true regression line would have been drawn if concentrations had been equally spaced throughout the analytical range.

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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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. 30–31.

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:

$$\text{Recovery} = \frac{x_{exp}}{x_{acc}} \times 100 \text{ percent} \qquad (10)$$

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.

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

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.

Youden, W. J., 1960, The sample, the procedure, and the laboratory: Analytical Chemistry, v. 32, no. 13, p. 23A–37A

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. 69–88.

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)							Mean (mg/L)	Standard deviation (mg/L)	Bias (mg/L)
	1	2	3	4	5	6	7			
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.

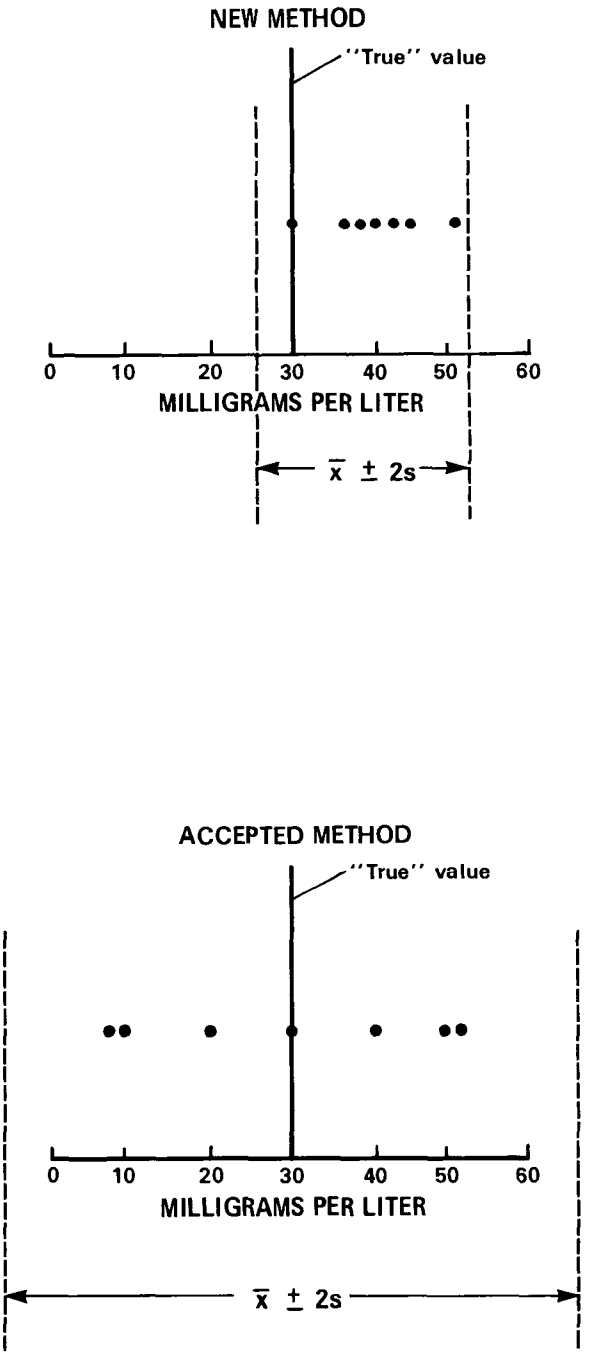

Figure 2.—Bias and precision, results of new and accepted analytical methods.

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.

Youden, W. J., 1961, How to evaluate accuracy: Materials Research and Standards, April 1961, American Society for Testing and Materials, p. 361–268—361–271.

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.

Standard Quantitative Analysis Techniques

The production of quantitative analyses requires the use of standard quantitative analysis techniques. Some of the more common techniques are included in this section. Familiarity with them is mandatory for anyone working in an analytical laboratory.

Cleaning Glassware

1. Application or scope

1.1 This practice details some basic procedures to be followed in cleaning laboratory glassware.

1.2 The type and amount of cleaning which is necessary depends on the analysis to be done and on the contaminant present in the vessel to be cleaned.

2. Practice

2.1 Washing

2.1.1 Remove wax or grease pencil markings by hand (usually with the aid of acetone).

2.1.2 Wash glassware either by hand or in a specially designed automatic washer which has a distilled rinse capability (laboratory washer). Glassware will be suitable for use in making analysis of most inorganic constituents which have concentrations reported in the milligram per liter range (such as calcium or sulfate).

2.1.3 Use phosphate-free detergent for glassware used for phosphorus determinations.

2.1.4 If washing by hand, chromic acid cleaning solution may be used (NOTE 1 and 2). Follow the wash by rinsing with tap water and at least four distilled water rinses.

NOTE 1. The cleaning solution may be prepared by adding 1 liter concentrated H_2SO_4 to 35 mL saturated sodium dichromate solution.

NOTE 2. Because of safety hazards associated with chromic acid cleaning solutions, its use is discouraged unless absolutely necessary. Substitutes are now available which can be used; for example, Lab Safety Supply Co. (1980) advertises "Nochromix" as a substitute solution.

2.1.5 Do not use strong caustic solution on volumetric glassware.

2.1.6 Do not soak spectrometer absorption cells in caustic or in strong cleaning solution and never use abrasive material on them.

2.1.7 For glassware to be used in the determination of organic constituents, rinse, after washing, with an organic solvent such as acetone, or follow the wash by baking at 350°C for at least 8 hours.

2.1.8 Wash glassware used for trace-metal analysis with 1:1 nitric acid-water solution. Follow the wash by at least four deionized-water rinses.

2.1.9 Acetone or a warm sodium hydroxide solution followed by an acid rinse may be used to eliminate grease.

2.1.10 Glassware to be used in bacteriological analysis should be rinsed at least three times with distilled water which has not come in contact with copper tubing or other toxic material (glass or stainless steel plumbing is acceptable).

2.1.11 Clean glassware until the surface drains uniformly, in a thin film. Droplets, instead of a thin film, indicate glassware is not completely clean and must be rewashed.

2.2 Drying

2.2.1 If air drying or oven drying, be sure glassware does not become contaminated from the air.

2.2.2 If drying on a rack, be careful the glassware does not become contaminated from the rack (as from metal or a paint chip).

2.2.3 Sterilize glassware to be used in

bacteriological analysis for 1 hour at 170°C. Heat glassware in metal containers for 2 hours at 170°C (American Public Health Association and others, 1976).

Selected References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed.): Washington, D.C., American Public Health Association, p. 885.

Bordner, Robert, Winter, John, and Scarpino, Pasquale, 1978, Microbiological methods for monitoring the environment, water and wastes: U.S. Environmental Protection Agency EPA–600/8–78–017, Cincinnati, p. 36.

Lab Safety Supply Co., 1980, Safe handling of toxic and hazardous chemicals: 1981 Catalog, Janesville, Wis., Lab Safety Supply Co., p. 93.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 4–5—4–9.

Correction for Color Interference

1. Application or scope

1.1 This practice describes corrective actions to be taken when color interferes with an analysis. The natural color in many water samples shows an appreciable absorbance at the wavelengths used in a number of colorimetric determinations; if the absorbance changes the apparent concentration of the constituent being determined, it must be compensated for or eliminated.

1.2 Also see practice "Standard-addition technique."

2. Practice

2.1 Highly sensitive analytical method

2.1.1 If the absorbance due to the constituent sought exceeds the absorbance due to natural color by a factor of at least 50, no compensation for natural color is required for most analyses (NOTE 1).

NOTE 1. If the factor is 50, the error introduced is 2 percent.

2.1.2 If the sensitivity of the method is sufficient (Skougstad and others, 1979) so that the color interference can be eliminated by diluting the sample and an accurate concentration value still can be obtained, dilute the sample and proceed with the analysis (NOTE 2).

NOTE 2. The sensitivity of the method for the constituent being determined must be known and must be high relative to the interference.

2.2 Preparation of a color "blank"

2.2.1 If the sensitivity of the method relative to the interference is not known or if there is any doubt as to the effect of color on the absorbance of the element sought, use two equal volumes of the sample.

2.2.2 To one volume of sample, add all reagents. To the other volume of sample, add all reagents except the indicator reagent; instead add a volume of indicator solvent which is equal to the volume of indicator reagent normally added.

2.2.3 Measure the absorbance of both samples.

2.2.4 Calculate the difference between the absorbances to obtain a corrected absorbance. Use this corrected absorbance in determining the concentration of the constituent (NOTE 3).

NOTE 3. This procedure will work for most waters. However, if the indicator reagent reacts with or affects the natural color or turbidity in the water sample, this method should not be used. Filtration of excessively turbid samples may be required prior to analysis.

2.3 Bleaching or adsorption

2.3.1 If the above procedure proves inadequate, try a bleaching procedure (such as hydrogen peroxide) or adsorption procedure (such as activated carbon) provided these procedures do not change the chemical equilibrium or contaminate the sample.

2.3.2 Be extremely careful, since it is relatively easy to contaminate the sample by either adding or removing constituents from the water sample (NOTE 4).

NOTE 4. Because of the problems associated with the removal of color, it is usually preferable to use an alternative, noncolorimetric procedure to make the analysis.

2.3.3 Consult an applicable reference before trying either bleaching or adsorption.

Reference

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Gravimetry

1. Application or scope

1.1 This describes some of the basic principles and techniques to be followed in making gravimetric analyses.

1.2 Operating procedures for analytical balances, discussed in the practice "Analytical balances," in the section "Instrumental Techniques," must be followed.

2. Practice

2.1 Requirements

2.1.1 Use desiccators of sufficient size and limit the number of samples placed in them so that samples will have achieved room temperature at the end of the specified drying period.

2.1.2 Use a desiccant which conforms to that specified in the applicable procedure. Replace or regenerate before its drying power has diminished (NOTE 1).

NOTE 1. Many desiccants contain a moisture absorption indicator to indicate need for regeneration or replacement.

2.1.3 Maintain temperature of drying ovens within the specified limits of the required drying temperature.

2.1.4 An analytical balance is an essential part of every gravimetric procedure. The type commonly used for this purpose is a single-pan, direct-reading balance which is capable of determining the mass of an object to 0.1 mg. Be certain that it receives regular maintenance and is properly calibrated with Class S weights.

2.2 Measurement procedures

2.2.1 Prepare sample solutions as directed in the method used. If a determination involves precipitation, it is of importance that conditions be carefully controlled as directed in the analytical procedure in order to optimize the purity and percent recovery of the precipitate.

2.2.2 The validity of a gravimetric procedure does not depend on standard solutions; however, carefully prepare reagents, if any, as specified in the analytical procedure.

2.2.3 In any direct gravimetric analysis, separate the constituent being determined from the other constituents of the sample, either in the form of the constituent itself or as a compound of known, definite composition. In the latter case, calculate the weight of the constituent from its theoretical percent of the compound.

2.2.4 In any indirect gravimetric analysis, determine the weight of the residue remaining after the volatilization of the constituent. Determine the amount of the constituent sought from the loss in weight.

2.2.5 Follow the appropriate concentration range specified in the analytical method. If the concentration of a constituent falls outside of this range, use a smaller sample volume, dilute the sample, or use an alternate approved method. If the working range of the method is exceeded, the procedure must be repeated because the amount of residue will be so great that it is very likely that water will be entrapped and not completely driven off during the drying period.

2.2.6 Regulate the temperature of the drying oven, the drying time, and the cooling time in the desiccator.

2.2.7 Never weigh chemicals directly on the balance pan. Use a weighing paper or other container.

2.3 Calculations

2.3.1 The calculations for gravimetric analyses are relatively simple. For determinations of dissolved and suspended solids, convert the weight of the residue per volume of sample evaporated to weight of residue per liter.

2.3.2 For procedures involving compound formation and precipitation, a factor must be applied to convert the weight of the precipitate to the weight of the constituent sought.

2.3.3 Consult the appropriate method for specific directions.

Selected References

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, Stanley, 1969, Quantitative chemical analysis (4th ed.): Toronto, Macmillian, p. 565.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 551–578.

Reagents and Gases

1. Application or scope

1.1 This practice lists the grades of chemicals and gases used in analytical work, gives general guidelines for their use, and describes quantitative practices which must be followed in preparation of all standard solutions.

2. Practice

2.1 Purity

2.1.1 As noted in Skougstad and others (1979), "Unless indicated to the contrary, all chemicals specified for use in the analytical procedures shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Those chemicals not listed by this organization may be tested as indicated by Rosin (1955). Chemicals used for primary standards may be obtained from the U.S. National Bureau of Standards or from manufacturers marketing chemicals of comparable purity."

2.1.2 The grade of purity of chemicals and solvents and of gases are listed in table 4 and table 5, respectively. Table 6 is a general guideline which may be followed in determining the purity needed (NOTE 1).

NOTE 1. The specific purity needed will depend on the instrument, analytical method, and so forth. Use only chemicals that are within the allowable date of use.

2.2 Dilution water

2.2.1 Demineralized water is the most commonly used reagent in the laboratory. For inorganic analysis, prepare demineralized water either by distillation, by use of mixed cation-anion exchange resins, or by reverse osmosis. A combination of the above procedures may be necessary, especially if the distillation is carried out in a metal still, to produce water of adequate purity. The specific conductance of the demineralized water should not exceed 1.5 μmho/cm at 25°C.

2.2.2 Prepare carbon dioxide-free water by boiling and cooling demineralized water immediately before use. Its pH should be between 6.2 and 7.2.

2.2.3 Prepare ammonia-free water by passing distilled water through a mixed-bed ion-exchange resin or through a cation-bed in the hydrogen ion form.

2.2.4 Use water from an all-glass or glass-lined still for organic determinations. It may be necessary to redistill from alkaline permanganate solution in order to obtain a water with low organic residual.

2.2.5 Use water which is free from traces of dissolved metals, nutrients, residual chlorine and other bactericidal compounds for bacteriological analyses.

2.3 Measurement accuracy

2.3.1. Weigh materials to the precision required by the method. As noted in Book 5, Chapter A1 of Techniques for Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979), "a mass designated as 4.532 g must be weighed accurately to +0.0005 g, whereas a mass designated as 4.5 g must be weighed accurately to +0.05 g."

2.3.2 Use borosilicate glass for volumetric glassware.

2.3.3 Select volumetric glassware which will give the accuracy required by the method. Again as noted in Skougstad and others (1979), " 'add 2.00 mL of reagent' shows that a volumetric pipet must be used for the addition, but 'add 2 mL' or 'add 1.5 mL' shows that a serological pipet may be used; 'dilute to 1,000 mL' shows that a volumetric flask is essential, but 'dilute to 1 liter' permits the use of a graduated cylinder."

2.3.4 Volumetric glassware is calibrated either to deliver (marked TD) or to contain (marked TC). Know which is being used. Almost all volumetric pipets are calibrated to deliver. Allow a pipet marked TD to drain freely for the time stated on its side (for example, 25 s). Then hold the tip against the inner wall of the vessel into which it is draining, being careful not to touch the liquid already in the container. Some liquid always should remain in the tip of the pipet.

Table 4.—Grades of chemicals and solvents

Grade	Abbreviation	Description
Ultra pure	Ultrex, Nanograde, and so forth.[1/]	Ultrahigh-purity materials. Certificate showing actual concentration of impurities furnished.
Primary standard	PS	Exceptional purity for standardization and preparing standards.
Spectroquality	--	Specially purified to provide insignificant background in absorption and emission spectroscopy.
Analytical reagent	AR	High purity for laboratory use. Lot analysis usually on label of container.
American Chemical Society	ACS	Meets specifications published by the American Chemical Society.
Chemically pure	CP	Suitable for most routine use. Lot analysis not specified on label.
National Formulary	NF	Meets specifications of the National Formulary.
United States Pharamacopeia	USP	Meets specifications of the United States Pharmacopeia.
Food Chemicals Codex	FCC	Meets specification of Food Chemicals Codex.
Purified	PURI	Higher quality than technical but no official standards. Used principally for bulk applications.
Practical	PRACT	Sufficiently high quality for most organic synthesis.
Technical	TECH	Suitable for most general industrial uses.

[1/] These and other trademarks are used by chemical companies to designate their highest purity solvents.

2.3.5 Note also that, as indicated in Skougstad and others (1979), "although the glassware is calibrated to deliver a specific volume at 20°C, the error in measurement incurred by pipetting samples at room temperature is insignificant for water analysis. One gram of pure water is contained in 1.002 mL at 20°C and in 1.007 mL at 38°C; the maximum error in volume that will result from those temperature differences is only 0.5 percent. Brine samples should be brought to as near 20°C as possible before making dilutions for analysis."

2.3.6 For highly precise work or when volumetric glassware has been frequently used

Table 5.—Typical grades of gases

Grade	Description	Application
Research	99.995-99.999 percent pure; highest level of purity obtainable; certificate of impurities available.	Research and development.
Ultrahigh purity	99.99-99.999 percent pure; certificate of impurities available.	Gas chromatographic and spectrophotometric.
High purity	99.99-99.999 percent pure; certificate of impurities available.	Gas chromatographic and spectrophotometric.
Zero	Low total hydrocarbon content; certificate of impurities available.	Reference gases for hydrocarbon analyses.
Commercial, industrial, or technical	93-99 percent pure; no certification.	Welding, atomic absorption, normal commercial and laboratory uses.

Table 6.—General useage guide for chemicals, solvents, and gases

Chemical process	Grade of purity
Inorganic standards	PS, AR, ACS
Organic standards	Ultra Pure, PS
Gas chromatography, carrier gas	Carrier, Zero
Atomic absorption, fuel gases	Zero, Commercial
Extractions and separations	AR,ACS
Definitive reactions	AR, ACS
Additive chemicals	AR, ACS, CP
Biological nutrients and media	USP, NF
Cleaning solutions	PURI, TECH
Organic synthesis	PURI, PRACT

to measure strong alkaline solutions, the glassware should be calibrated. Directions for calibration are found in standard quantitative texts and in the U.S. National Bureau of Standards Circular 602 (1959).

2.4 Storage

2.4.1 Store reagents and stock standard solutions according to the manufacturer's directions. If sensitive to light, keep in a dark bottle. If sensitive to heat, store in a refrigerator. Include the expected shelf-life of the reagent on the label.

2.4.2 Store most neutral and acid solutions in borosilicate glass containers (NOTE 1). Plastic containers may be substituted only if they will not absorb or contaminate the constituent of interest.

NOTE 1. Volumetric glassware should not be used to store solutions.

2.4.3 Use polyethylene or Teflon containers to store alkaline solutions and solutions containing boron or silica.

2.4.4 Store all reagent solutions used for organic analyses in glass containers.

2.4.5 Discard chemicals and solutions if there is any possibility of contamination or deterioration or if the date for safe use has expired. Unless the analytical procedure states specifically that a change in color of a reagent does not affect its usefulness, discard immediately if any change in color or concentration is noticed. If a time limit is specified in an analytical method for a reagent or standard, do not exceed it.

References

Rosin, Joseph, 1955, Reagent chemicals and standards: New York, D. Van Nostrand, 561 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 13–14.

U.S. National Bureau of Standards, 1959, Testing of glass volumetric apparatus: Circular 602, 21 p.

Standard-Addition Technique

1. Application or scope

1.1 This practice can be used to compensate for known or suspected matrix effects or analytical interferences. However, this method can be used only if the measured absorbance is linear with respect to concentration and if the observable interference is independent of the concentration of constituent being analyzed (NOTE 1).

NOTE 1. In general, the slope of the plotted line should be similar to the slope of the corresponding aqueous standard curve.

1.2 Since both samples and standards are affected equally, it is not necessary to prepare matrix water comparable to the unknown sample in order to correct the analyses.

2. Practice

2.1 Preliminary analysis and preparation

2.1.1 Make a preliminary analysis for the constituent in question.

2.1.2 Prepare a blank and three standards containing different amounts of the constituent to be analyzed (NOTE 2).

NOTE 2. Volume of blank and standards must be the same.

2.1.3 Select volumes of sample and highest standard such that, when mixed together, the resulting concentration will not exceed the analytical range specified in the method.

2.1.4 Add equal volumes of sample to the blank and three standards.

2.2 Determination of concentration

2.2.1 Measure the absorbance of the constituent being analyzed in the spiked (with sample) blank and standards.

2.2.2 Plot the absorbances on the vertical axis and the known concentrations of the constituent prior to the addition of the sample on the horizontal axis. Continue the horizontal axis to the left of the vertical axis, scaling it backwards from the zero (blank) concentration (see fig. 3).

2.2.3 Draw a line through the plotted points and extrapolate back to zero absorbance.

2.2.4 Record the concentration at the intercept as the concentration of the constituent in the sample. Retain all records.

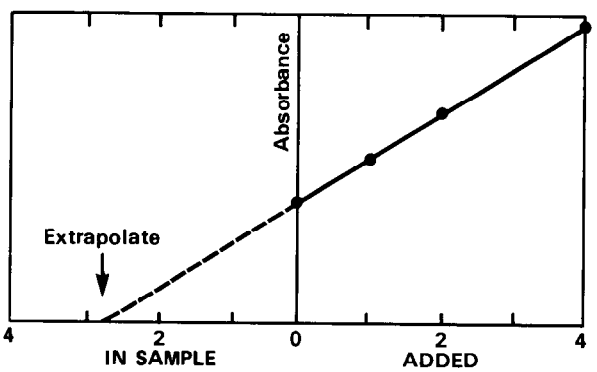

Figure 3.—Example of standard-addition method (from Skougstad and others, 1979).

Selected References

Klein, Robert, Jr., and Hach, Clifford, 1977, Standard additions, uses and limitations in spectrophotometric analysis: American Laboratory, v. 9, no. 7, p. 21–27.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the analysis of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 32.

U.S. Environmental Protection Agency, 1979, Methods for chemical analyses of water and wastes: U.S. Environmental Protection Agency EPA–600/4–79–020, Cincinnati, p. Metals 12—Metals 13.

Youden, W. J., 1960, The sample, the procedure, and the laboratory: Analytical Chemistry, v. 32, no. 13, p. 23A-37A.

Titrimetry

1. Application or scope

1.1 This practice describes some of the basic principles and standard techniques necessary for reliable titrimetric analyses.

1.2 The basic equipment employed in titrimetric procedures consists of pipets, burets, and other glassware. The appropriate glassware specifications and cleaning procedures must be rigorously observed.

1.3 If pH meters or spectrophotometers, are used to detect the titrimetric end point, operating procedures discussed in the section on instrumental quality control should be followed. If automated instruments are used, the manufacturer's manual should be consulted for operating instructions. An instrument of this type may be used only if its accuracy is equal to or superior to that obtained by manual procedures.

2. Practice

2.1 Requirements

2.1.1 To be suitable as a basis for a titrimetric determination, the chemical reaction involved must proceed rapidly to completion with no side reactions. In addition, other substances present in the sample should not react or interfere with the desired reaction, and the end point should be readily detectable by visual or instrumental means.

2.1.2 The end point does not as a rule coincide exactly with the equivalence point. The difference between the amount of titrant corresponding to the end point and that corresponding to the equivalence point represents the titration error. This difference should be as small as possible for a given procedure, and care should be taken to titrate every sample to the same end point.

2.1.3 Ideally, the standard solution used in titrimetry should be simple to prepare and be stable for a comparatively long time to avoid the need for frequent restandardization. Quite commonly, the standard is prepared at a concentration very close to that desired and then standardized by titrating an accurately measured amount of a primary standard. The primary standard must be of high purity, stable, and easily dried and weighed. Primary standards are available on specification from most chemical supply houses and often from the National Bureau of Standards.

2.2 Standardization

2.2.1 Standardize titrant solutions according to the procedures listed in the analytical methods in order to determine their exact normalities. Store and preserve properly. Restandardize as specified in the procedure or whenever there is reason to believe that the concentration has changed.

2.2.2 Include a primary standard solution with each set of samples or at weekly intervals, whichever is less frequent, to ensure that the titrant has not changed or become contaminated. Keep a written record of the original standardization value and also of the values obtained for subsequent restandardizations.

2.3 Measurement procedure

2.3.1 Observe the appropriate concentration range specified in the method. If the concentration of a constituent falls outside this range, adjust the concentration by dilution or use an alternative method.

2.3.2 For visual and spectrophotometric titrations, titrate a solution consisting of demineralized water plus all necessary reagents to the end point to determine the blank correction.

2.4 Calculations

2.4.1 Subtract the volume of standard solution required for the titration of the blank from all sample titration volumes to determine the actual volume of standard solution involved in the reaction.

2.4.2 After the normality of a standard solution has been determined, each unit volume can be equated to a known amount of sample constituent. Determine the concentration of the constituent by considering this factor in addition to the volume of sample, the volume of titrant required, and the blank titration volume.

Consult each method for more specific calculation directions.

Selected References

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, Stanley, 1969, Quantitative Chemical Analysis (4th ed.): Toronto, Macmillian, p. 681.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the analysis of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 579–580.

Instrumental Techniques

The proper use of analytical instruments is important in the production of reliable analytical values. The following practices confront this problem with special emphasis on the operation and calibration of instruments normally encountered in a water-analysis laboratory. Laboratories that analyze samples for the U.S. Geological Survey are expected to follow the detailed recommended procedures for the operation and calibration of instruments.

Instrument Maintenance

1. Application or scope

1.1 This practice is applicable to field equipment as well as to laboratory instruments.

1.2 In order to obtain valid responses, instruments must be checked on a regular basis. Where instrument maintenance schemes have not been established, 25 percent or more of the measuring equipment is often found to give erroneous answers (Juran and Gryna, 1976).

2. Practice

2.1 Identification number

2.1.1 Assign a number to each instrument. Although numbers used for inventory control (U.S. Geological Survey "W" numbers) may be used, a separate series for each type of instrument may be easier to use (for example, pH meter 001, 002, and so forth).

2.1.2 Number each instrument with a permanent marking.

2.2 Record card

2.2.1 Prepare a record card for each instrument. Record the type of instument, the model number, and its assigned number at the top of the card.

2.2.2 Indicate on the card the calibration limits of the instrument, the frequency with which the instrument should be checked, and the tests which should be made.

2.2.3 Indicate to whom the instrument is assigned and the date. Change this information whenever necessary (but keep a record).

2.2.4 Keep a record of the dates on which the instrument was checked. Include the name of the person who checked it, whether any changes were necessary, and so forth.

2.3 Frequency of maintenance check

2.3.1 Consider the amount of usage usual for a type of instrument (for example, atomic absorption spectrometers) and estimate the rate of instrument deteriortion.

2.3.2 Establish the necessary checking frequency for each type of instrument. This frequency may be based on units of time (for example, check every week) or may be based on use (for example, check every 200 samples).

2.3.3 Establish a maintenance schedule for each instrument and provide a way to keep track of it. For example, mark on a calendar (a couple of months in advance) the identification number of each instrument to be checked. Alternatively, mark the date of the next check on the instrument record card and maintain cards in a file, in order, by date. This frequency record file can be kept by a section leader for instruments in his section, or by an assigned person in a laboratory, district, or field office.

2.4 Record of findings

2.4.1 Record on the card the types of errors found and repairs needed.

2.4.2 Establish when the instrument last needed to be repaired. Determine the rates of repair or instrument change.

2.5 Analysis of record

2.5.1 Review records periodically. Be sure the schedule for maintenance checking is being adhered to.

2.5.2 If a particular model of instrument shows repeated problems, consider recommending a different model. If a particular type of

instrument shows repeated problems, increase the frequency of maintenance.

2.5.3 If no changes or problems are recorded, decrease the frequency of maintenance checks.

Selected References

Juran, J. M., 1974, Measurement, *in* Juran, J. M. and others, eds., Quality control handbook (3d ed): New York, McGraw-Hill, p. 13–15—13–18.

Juran, J. M., and Gryna, F. M., Jr., 1976, Quality planning and analysis: New York, McGraw-Hill, p. 393–398.

Analytical Balances

1. Application or scope

1.1 This practice details general procedures to be followed in using an analytical balance to prepare standards and reagents and to make gravimetric analyses.

1.2 The practice "Gravimetry," in the section "Standard Quantitative Analysis Techniques" should also be consulted.

2. Practice

2.1 Basic operational procedures

2.1.1 Mount and level the analytical balance on a heavy shock-proof table, located away from laboratory traffic, and protected from sudden drafts and humidity and temperature changes.

2.1.2 Clean up any material spilled in the balance case immediately.

2.1.3 Use ivory-tipped forceps or platinum-tipped tongs to handle objects to be weighed. Never use bare hands.

2.1.4 When not in use, raise the beam from the knife edges, return the weights to the beam, remove objects from the pan, and shut the side doors.

2.2 Calibration procedure

2.2.1 Check the calibration of a balance at least every 3 months using Class S weights.

2.2.2 If recalibration is necessary, consult and follow the manufacturer's instructions.

2.3 Measurement procedure

2.3.1 Set the meter to read zero when the balance is empty.

2.3.2 Set the object to be weighed on the balance pan using a pair of forceps or tongs, that have tips softer than brass (for example, ivory-tipped forceps, plastic-covered tongs, platinum-tipped tongs).

2.3.3 Add weights, generally starting with the largest, until balance is achieved. Consult the manufacturer's instructions for specific instructions.

Selected References

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the analysis of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 551.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–1—3–15.

Atomic Absorption Spectrometers

1. Application or scope

1.1 This practice details procedures to be followed in using atomic absorption spectrometers.

1.2 Although all atomic absorption spectrometers must undergo similar operational optimization, calibration, and standardization procedures, some variation in instrumental quality control may be necessary since commercially available instruments vary somewhat with regard to features such as read-out devices, burners, background correction, and curvature correction devices. The analytical requirements of a laboratory dictate the instrument and optional features to be utilized.

2. Practice

2.1 Basic operational procedures

2.1.1 Set controls such as gain, slit width, flame type, and wavelength in accordance with either the manufacturer's manual or journal literature.

2.1.2 Commercial grade gases are adequate. If compressed air is to be used for an air-acetylene flame, provide a filter to remove water and oil.

2.1.3 Select the lamp to be used, adjust the lamp current, and allow the lamp to electronically stabilize as recommended in the manufacturer's manual. Aline the lamp by adjusting the vertical and horizontal lamp controls until maximum absorbance is achieved (NOTE 1).

NOTE 1. Hollow-cathode or electrodeless discharge lamps are usually used as the line source in atomic absorption spectrometry. Multielement hollowcathode lamps are available which contain from two to six elements. These lamps are less expensive than buying several single-element lamps; however, the useful life is usually shorter and sensitivity less. Furthermore, the utility of the lamp decreases considerably after one of the elements has completely vaporized from the cathode. The use of a multielement lamp, therefore, is often a bad trade off unless the several elements contained in the lamp are determined only infrequently.

2.1.4 When the burner head is correctly alined, the slot in the burner head is parallel to and slightly below the source beam. To adjust the burner head, raise it until it intercepts the light beam from the source, as indicated by an increase of absorbance on the display; then lower it slowly until the display again reads zero. Ignite the appropriate gases as described in the operator's manual, zero the instrument, and select a standard solution for the element of interest which gives an absorbance of from 0.2 to 0.6 absorbance units. While aspirating the standard, sequentially adjust the vertical, horizontal, and rotational positions to achieve maximum absorbance. Adjust the vertical height prior to determining different elements. Usually the rotational and horizontal positions need to be realined only when changing burner heads.

2.1.5 If it is necessary to adjust the nebulizer, aspirate a standard solution containing an element that has a wavelength above 250 nm and requires an oxidizing air-acetylene flame. Recommended elements are copper, magnesium, nickel (341.5 nm), and lead (283.3 nm). Change the aspiration rate slowly until maximum absorbance is reached.

2.1.6 Background correction devices, available for most atomic absorption instruments, must be used whenever there may be interfering substances such as gaseous molecular particles, smoke, or salt particles present in the source-light path. Always use background correction when elements are determined by heated-vaporization techniques utilizing equipment such as a graphite furnace.

2.1.7 Adjust the wavelength by setting the monochromator reading to the recommended wavelength for a particular element and then slowly changing the monochromator fine adjustment until maximum light passage is obtained. It is usually easier to optimize the monochromator setting if a slightly narrower than recommended slit width is used during this adjustment. The slit width must be returned

to the recommended setting after the wavelength setting has been optimized.

2.2 Calibration procedure

2.2.1 After the alinement procedures have been completed and the operating parameters adjusted according to instructions in an instrument manufacturer's manual or to literature procedures, turn on fuel and support gases and adjust to recommended flow rates. Ignite the burner and aspirate water until thermal equilibrium is reached.

2.2.2 Adjust the electronics of the instrument to read zero absorbance while aspirating a blank solution that contains all reagents, except for the elements of interest, in the same proportion as the calibration standards. Continue the aspiration until a stable signal is obtained.

2.2.3 Aspirate a standard solution containing the analyte at a concentration that will give an absorbance of between 0.2 and 0.6 and that will be within the linear absorbance range for the test element. Determine if adequate sensitivity has been obtained by reference to the manufacturer's manual. Keep a record of the sensitivity of each element for a particular intrument in order to detect deficiencies in the instrument or operating conditions.

2.2.4 The appropriate concentration ranges for each parameter are specified in Book 5, Chapter A1 of the series, Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979). Use a minimum of five standards, equally spaced over the concentration range. The blank, standards, and sample solutions all must contain the same concentration of added reagents.

2.2.5 When calibrating these instruments in the concentration mode, follow manufacturer's instructions. If less than five standards are employed in this procedure, use the remaining standards to confirm the validity of the calibration.

2.2.6 Reaspirate the five standards in random order to determine if the readings have remained constant. If there is a question about the stability of the operating parameters, the following procedure can be applied. Zero the instrument while aspirating a blank solution. Aspirate a standard solution having an absorbance of between 0.2 and 0.6 and record the reading. Repeat the process of alternately aspirating the blank and standard solution until a total of six readings have been obtained for the standard solution. The standard deviation obtained from these six measurements should not exceed 1 percent of the average reading of the standard solution. if the repeatability is less consistent, determine the source of variability before analyzing samples. If the solids content of the standard solution is too high, make an appropriate dilution to prevent either clogging of the burner or an erratic flame.

2.2.7 Each time an instrument is calibrated, keep a written record of the absorbance readings or, in cases where the direct concentration mode is used, the scale expansion of the instrument for each set of standards. A significant change ($\geq$10 percent) from previous results immediately indicates that a problem exists with the operational settings, the performance of the atomic absorption spectrometer, or the accuracy of the standard solutions. Corrective action must be taken before analyzing samples. Furthermore, an analyst must also be aware of subtle, but consistent changes in absorbance or expansion readings that may be indicative of such things as the gradual deterioration of the standard solutions, a dirty nebulizer system, a clogged burner, an instrument-part malfunction, or the initial stage of a lamp failure.

2.3 Measurement procedure

2.3.1 Prepare the sample solutions as directed in the appropriate analytical procedure. After calibration of the instrument, aspirate the sample solutions until a stable reading is obtained and recorded. If the concentration of a constituent in a sample falls outside of the analytical range, adjust the concentration dilution or use an alternative method.

2.3.2 Aspirate demineralized water or other sample solvent between each sample.

2.3.3 After every seventh sample, check the operating conditions of the instrument by aspirating a blank and, in random order, one of the calibration standards. If the reading of the calibration standard differs from the original calibration results by more than 2 percent or if baseline drift is indicated, take corrective measures immediately.

2.3.4 It is usually unnecessary to match the dissolved solids content of the standards

and samples unless the dissolved solids concentration of the samples exceeds 1 percent. If matrix effects are severe, dilute the sample, use a chelation-extraction technique, or use the standard-addition technique.

2.3.5 When a sample is to be analyzed by the method of standard additions, take four equal aliquots of sample. Add to three of these aliquots known amounts of analyte equal to one, two, and three times the approximate concentration of the sample. Dilute all four solutions to the same volume. Aspirate with solvent and adjust the absorbance read-out to zero. Aspirate, in random order, the above standard-addition solutions. If necessary, subtract any nonatomic absorbance from the absorbance readings. Prepare a calibration graph by plotting the absorbance against the added concentration. Extrapolate the resulting straight line through zero absorbance. The intercept on the absorbance axis gives the concentration of the constituent in the original sample. The standard-addition technique must show linear relationship between absorbance and concentration in order to be valid.

2.3.6 Atomic absorption procedures involving the use of flameless and electrothermal-vaporization techniques have become increasingly popular. The operation and calibration steps closely parallel those for flame determination although a recorder, if employed as a read-out device, must have a full-scale response time of 0.5 seconds or less. The matrix effects for electrothermal-vaporization techniques are much more severe, and the method of standard additions must be used routinely. Background correction must also be employed for electrothermal-vaporization procedures.

2.4 Read-out and graphical techniques

2.4.1 If Beer's law is followed or if a nonlinear curve can be electronically corrected by the atomic absorption spectrometer, obtain concentration readings directly from the instrument.

2.4.2 Alternatively determine the constituent concentration from a plot of the average absorbances obtained for the standard solutions versus their respective concentrations.

2.4.3 If the analytical curve is nonlinear and uncorrected, use the calibration values to obtain, by regression analysis, a parabolic equation, $y = a_0 + a_1x + a_2x^2$, where y = absorbance and x = concentration. Obtain the constituent concentrations for the sample solutions by the direct substitutiion of absorbance values into the equation, or use the derived parabolic equation to construct a graph of absorbances of standards versus their respective concentrations and use the graph to obtain the concentration values of the sample solutions.

2.4.4 If the analytical curve is linear at low concentrations and becomes curved as the concentration increases, plot the linear portion of the curve immediately and use the calibration values from the nonlinear portion of the curve to calculate the parabolic equation. This equation, of course, applies only to the nonlinear portion of the curve.

Selected References

American Society for Testing and Materials, 1980, 1980 Annual book of ASTM standards, Part 31, water: Philadelphia, American Society for Testing and Materials, 1404 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Slavin, Walter, 1968, Atomic absorption spectroscopy: New York, Interscience Publishers, p. 72

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–1—3–15.

Automated Analyzers

1. Application or scope

1.1 This practice details procedures to be followed in using automated wet-chemical analyzers.

1.2 The most commonly used automated analyzer system is the Technicon AutoAnalyzer which generally includes a sampler, proportioning pump, cartridge manifold, heating bath (if necessary), colorimeter or ion-selective electrode module, voltage stabilizer, recorder, and possibly a printer.

1.3 Other automated systems (for instance, discrete or batch analyzers) or modular components compatible with AutoAnalyzer modules may be substituted, but their precision and accuracy must be at least equivalent.

1.4 AutoAnalyzer modules, on occasion, have been used to automate instruments such as atomic absorption spectrometers. It is imperative that the applicable precautions, such as changing pump tubes routinely, which are recommended for the complete system, also be practiced when modules are used in this manner. Some automated atomic absorption procedures are designed to handle water-suspended sediment mixtures. A sampler with a stirring attachment is required in these situations.

2. Practice

2.1 Basic operational procedure

2.1.1 The platen pressure for the proportioning pump is adjusted at the factory and remains quite consistent if the platen is not used on different pumps. However, adjust the platen according to the manufacturer's instructions if the pump tubes wear rapidly because the platen pressure is too low (NOTE 1).

NOTE 1. There are many causes for erratic flow; improperly adjusted platen pressure is one of the less frequent causes.

2.1.2 The material of the pump tubes must be compatible with the solution being pumped. Inspect them frequently, and determine a routine replacement schedule based on the amount and frequency of use.

2.1.3 The Technicon "colorimeter" is a two-photocell filter photoelectric colorimeter. The procedures described in the practice, "Colorimetric spectrometers" are generally applicable to its operation.

2.1.4 The two most common flow-cell lengths are 15 mm and 50 mm; the length to be used is determined primarily by the sensitivity of the procedure. The flow cell is removed from the instrument infrequently; therefore, the opportunity for handling-contamination is reduced. When it is necessary to handle the cell, handle carefully and do not scratch it.

2.1.5 Handle the light source with care. Keep the light filters used in the instrument scrupulously clean.

2.1.6 Check and optimize the optical alinement periodically and follow the manufacturer's instructions, whenever a light source is replaced.

2.1.7 Replace the filter photometer with an ion-selective electrode module for electrometric determinations. Determinations are usually performed at temperatures exceeding 25°C and thermal stability as well as electronic stability is very important. Handle the ion-selective electrodes according to the manufacturer's instructions.

2.1.8 Set the indicator control on the filter photometer first to zero and then to full scale. The recorder should read zero and 100, respectively. If it does not, adjust the appropriate set screws on the photometer until the desired recorder readings are obtained.

2.1.9 Similar controls are also present in the ion-selective electrode module. In addition, another control switch contains four positions, two of which are labeled "Cal 1" and "Cal 2." Adjust these positions to give recorder readings of zero and 50, respectively. Adjustments are also available on the ion-selective electrode module to correct these readings, if necessary.

2.1.10 If results appear inconsistent or noisy, check to see if the following problems exist:

- Dirty transmission line
- Inadequate warm-up time
- Erratic bubble patterns
- Improper sample-to-wash ratio
- Worn pump tubing
- Improper sampling rate
- Improperly functioning air-bar
- Improper cooling of the flow cell.

Correct any of the above factors which are present. A properly operating system will contain evenly spaced sample segments which flow with little or no surging through the system.

2.2 Calibration procedure

2.2.1 Allow the instrument to electronically stabilize, and set the operating parameters as specified for the analytical method. Specified parameters should include sampling rate, sample-to-wash ratio, flow-cell length, heating bath temperature, filters, and wavelength. The size and type of pump tubing and the manifold arrangement are to be considered an integral part of the methodology for a particular determination.

2.2.2 Pumping all reagents through the system, but using wash solution (usually demineralized water) in the sample line, adjust the baseline on the recorder to read zero. Adjust the printer to read zero also.

2.2.3 After the baseline has stabilized with wash solution in the sample line, proceed with calibration and with analysis of samples. Beginning with the highest standard, place a minimum of five standards, equally spaced over the analytical range, in the first positions of the first sample tray.

2.2.4 Place individual standards of differing concentrations or a blank solution in every eighth position of this and subsequent sample trays, filling the remainder of each tray with unknown samples.

2.2.5 When the peak from the highest standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale. Adjust the printer to read the correct concentration value.

2.2.6 If the STD CAL setting and instrument noise are consistent with previous, acceptable determinations, proceed with the analysis. If a problem exists, locate and correct it; then recalibrate and continue.

2.2.7 Whenever an instrument is calibrated, keep a written record of the STD CAL setting for each set of standards. A significant change ($\geq$ 10 percent) from previously documented results immediately indicates that a problem exists with the operational settings, the performance of the system, or the accuracy of the standard solutions. Take corrective action before analysis of samples begins. Be aware that subtle but consistent changes in STD CAL settings may be indicative of such things as the gradual deterioration of standard solutions, an instrument part malfunction, or the initial stage of a lamp failure.

2.3 Measurement procedure

2.3.1 Appropriate analytical ranges for each parameter are specified in Skougstad and others (1979) and must be closely followed. If the concentration of a constituent falls outside of the recommended range, adjust the concentration by dilution, or use an alternative analytical method.

2.3.2 If the calibration standards which are in every "eighth" position differ from the original calibration results by more than 2 percent, or if baseline drift is indicated, take corrective measures immediately.

2.3.3 The information concerning colored waters in the practices "Correction for color interference" and "Colorimetric spectrometers," is generally applicable to automated, colorimetric procedures. Attempt to compensate for color by passing an additional stream containing the sample and all reagents, except for the indicator reagent, through the reference channel of the photometer. The points at which reagent solutions are added and the mixing schemes have to be identical for the two streams, and the sample solution must be phased to arrive at both cells at the same time. In applicable cases, the absorbance due to sample color will be subtracted.

2.3.4 Alternatively, use a bleaching or adsorption procedure to remove the color before the sample is placed on the sampler turntable. Be sure that the chemistry of the constituent being determined is not affected and be careful to avoid contamination and the problems associated with adsorption.

2.3.5 If excess turbidity is present, remove it by passing the sample through a 0.45-

μm filter or use an alternative procedure (NOTE 2).

NOTE 2. The sample also may be centrifuged, often after using a flocculating agent such as acidified sodium chloride, to remove turbidity. However, as noted in Skougstad and others (1979, p. 294), "Centrifuging is often useful, but it is less efficient than membrane filters for fine particles."

2.4 Read-out and graphical techniques

2.4.1 If the AutoAnalyzer procedure follows Beer's law, use the printer concentration directly.

2.4.2 If a printer is unavailable, plot standard concentration versus recorder readings and determine the concentrations of the samples from the graph.

2.4.3 If the analytical curve is nonlinear, use the calibration values to obtain, by regression analysis, a parabolic equation $y = a_0 + a_1x + a_2x^2$ where y = recorder reading and x = concentration. Sufficient standards must be used in the nonlinear portion of the curve to properly define it. Obtain the constituent concentrations by direct substitution of recorder readings into the equation, or use the derived parabolic equation to construct a graph of recorder values of standards versus their respective concentrations and use the graph to obtain the concentration values of the sample solutions.

2.4.4 If the analytical curve is linear at low concentrations and becomes curved as the concentration increases, plot the linear portion of the curve immediately and use the calibration values from the nonlinear part of the curve to calculate the parabolic equation. This equation, of course, applies only to to the nonlinear portion of the curve.

Reference

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Colorimetric Spectrometers

1. Application or scope

1.1 This practice details procedures to be followed in the calibration and operation of spectrometers.

1.2 A spectrophotometer consists essentially of a radiant-energy source; a device, such as a prism or grating with a selection slit, for isolation of relatively monochromatic radiant energy; one or more absorption cells to hold the sample, standards, and blank; and a photodetector to measure the radiant energy passed through the solution. Commercially available spectrophotometers vary with regard to such features as spectral bandpass, type and quality of monochromators, read-out devices, and availability of optional equipment.

1.3 A filter photometer uses a filter in place of a prism or grating. The resulting light is not as monochromatic; in addition, this instrument lacks the versatility of a spectrophotometer. However, in spite of these drawbacks, the recent trend towards automated procedures has increased the popularity of the filter photometer because it is well suited to individual determinations.

1.4 The addition of a semiautomated device to aspirate the samples directly into the cell, and then to a waste line after a reading has been obtained, is a very desirable feature if a large number of samples is being analyzed, because it is faster and eliminates most of the problems involved with cell handling and placement.

2. Practice

2.1 Basic operational procedures

2.1.1 The light source usually used in the visible region is a tungsten filament incandescent bulb. Align the bulb according to the manufacturer's manual whenever it is replaced or disturbed. Be careful not to touch the glass part of the lamp because serious deterioration of an instrument's performance may result.

2.1.2 Check the alinement of the cell holder periodically. If it is removed or disturbed, realine the cell holder according to the manufacturer's instructions.

2.1.3 When handling a cell, protect it from scratches and never permit it to rub against another cell or against other hard surfaces.

2.1.4 Avoid using abrasive, corrosive, or stain-producing cleaning agents in or on a cell.

2.1.5 Do not handle the part of the cell through which the light beam will pass.

2.1.6 Always rinse the cell with several portions of the solution before taking a measurement.

2.1.7 Wipe the outside of the cell with clean lens paper to eliminate any liquid drops or smudges. Inspect to ensure that no lint remains on the outside or that no small air bubbles cling to the inner surface of the cell.

2.1.8 If two cells are used simultaneously, always use one for the blank solution and the other for the various samples.

2.1.9 Carefully place the cells in the sample holder to avoid scratches. Position cells with identifying lines or marks as specified in the manufacturer's manual.

2.1.10 For maximum precision and accuracy, standardize and measure with matched cells. The placement of cells in a correct (exactly at right angles to the beam), reproducible manner cannot be overemphasized.

2.1.11 Check the wavelength calibration at least every 6 months. Many high quality standards having very sharp absorption or emission peaks that are isolated from nearby peaks can be used. Some of the more practical methods for calibration in the visible region involve the use of one of the following materials: holmium oxide glass, holmium oxide solution, mercury lamp, or deuterium lamp. Consult the manufacturer's manual for specific directions.

2.2 Calibration procedures

2.2.1 After the alinement procedures have been completed, allow the instrument to electronically stabilize and then set the

wavelength, slit width, if variable, and other operating parameters as specified in either the Techniques of Water-Resources Investigations (TWRI), Book 5, Chapters A1 and A3, or in the operator's manual.

2.2.2 If information on the optimum slit width for a particular determination is unavailable, it must be determined. This depends on the spectral characteristics of the sample and the dispersion of light in the spectrophotometer. Use the narrowest slit width that will give an acceptable signal-to-noise ratio. Block the source light from the photodetector and set the percent transmittance reading to 0.00. Insert a blank, consisting of demineralized water and reagents added in the same volume and manner as for standards and samples into the light path and set the percent transmittance to 100.0 (equivalent to an absorbance of 0.000). Refer to the manufacturer's manual for a complete description of the calibration procedures for the absorbance and concentration modes. Do not use the concentration mode if the calibration curve is not linear over the operating range. When reading concentration directly, do not measure absorbances of solutions that exceed the working range of the procedure.

2.2.3 The appropriate concentration ranges for each parameter are specified in the TWRI, Book 5, Chapters A1 and A3 or in other analytical methods manuals and technical journals. Use a minimum of four standards, equally spaced over the concentration range, to calibrate a visible-range spectrophotometer in the absorbance mode. The blank, standards, and sample solutions all must contain the same concentration of added reagents.

2.2.4 Follow the manufacturer's instructions when calibrating an instrument in the concentration mode. If less than four standards are employed in this procedure, use the remaining standards to confirm the validity of the calibration.

2.2.5 Recheck the 0.00 and 100.0 percent transmittance points, and if they and the readings for the standards are satisfactory, the instrument is correctly calibrated. If not, repeat the above procedure. If a problem still exists, locate and correct it before proceeding further.

2.2.6 Whenever an instrument is calibrated for a determination, keep a written record of the slit width, if applicable, and absorbance readings (percent transmittance readings should be used only if this is the only measurement scale available) for each set of standards. A significant change (≥ 10 percent) from previously documented results, immediately indicates that a problem exists with the operational settings, the performance of the spectrophotometer, or the accuracy of the standard solutions. Take immediate, corrective action. Be aware that subtle, but consistent changes in absorbance readings may be indicative of such things as the gradual deterioration of standard solutions, an instrument-part malfunction, or the initial stage of lamp failure.

2.2.7 The rate of development and the stability of the color formed in spectrophotometric procedures for water analysis vary considerably. Most procedures specify the time required for color development. The recommended time interval must be closely followed for both standards and samples.

2.3 Measurement procedure

2.3.1 Prepare sample solutions as directed in the analytical procedure. If the working range of the method is exceeded, dilute the sample or use an alternative procedure.

2.3.2 After every 10th sample, check the stability of the spectrophotometer by measuring a blank, and in random order, one of the calibration standards. If the reading of the calibration standard differs from the original calibration value by more than 2 percent, or if drift is indicated, take corrective measures before proceeding with the analysis. If the color complex is unstable, sufficient standards must be prepared in the order in which they will be read, so that a standard can be inserted after every tenth sample.

2.3.3 The natural color in many water samples shows an appreciable absorbance at the wavelengths used in a number of determinations; this effect requires either compensation or elimination. In some cases, a procedure has such high sensitivity that the absorbance of the constituent sought will exceed the absorbance of the natural color by a very large factor. If this factor is as high as 50 for a particular determination, the error introduced by the natural color will be only 2 percent and, in routine work, no compensation will be required. Simi-

larly, if the sensitivity of a procedure is sufficiently high, it is often possible to minimize the color absorbance by diluting the sample while still obtaining an accurate concentration value for the constituent. This technique requires a knowledge of the relative sensitivity for the constituent sought.

2.3.4 If the relative sensitivity is not known or if there is any doubt as to the effect of color on the absorbance of the element sought, attempt should be made to remove or compensate for the color present by using the following procedure. Take the same volume of sample water as was used for the test sample with one exception: do not add the indicator reagent. Instead, add an equal volume of indicator solvent, usually dilution water. Measure the absorbances of these two samples. The corrected absorbance, which is used to obtain concentration values, is the difference between the absorbance of the test sample with indicator reagent and the natural-color corrections. This method fails when the indicator reagent reacts with or affects the natural color or turbidity in the water sample. The latter qualification relates more to turbidity than color, and filtration of an excessively turbid sample through a 0.45 μm filter may be required.

2.3.5 If (such as with very highly colored waters), the above procedure is not applicable, procedures involving bleaching or adsorption can sometimes be used to advantage. These techniques must be applied with great care, however, because it is relatively easy to contaminate or change the sample by either adding or removing constituents from the water sample.

2.4 Read-out and graphical techniques

2.4.1 If Beer's law is followed, the concentration readings can be obtained directly from the instrument, if it has concentration mode capabilities.

2.4.2 Alternatively, the constituent concentration can be determined from a plot of absorbances obtained for the standard solutions versus their respective concentrations.

2.4.3 If the analytical curve is nonlinear, the calibration values of the standards must be used to obtain, by regression analysis, the parabolic equation $y = a_0 + a_1x + a_2x^2$ where y = absorbance and x = concentration. Sufficient standards must be used to properly define the equation. Obtain constituent concentrations by direct substitution of absorbance values into the above equation, or use the derived parabolic equation to construct a graph of the absorbances of standards versus their respective concentrations, and use the graph to obtain the concentration values of the samples.

2.4.4 If the analytical curve is linear at lower concentrations and becomes curved as the concentration increases, plot the linear portion of the curve immediately and use the calibration values from the nonlinear part of the curve to calculate the parabolic equation. This equation, of course, applies only to the curved portion.

2.4.5 If the scale of the spectrophotometer does not read directly in absorbance, it is most convenient to plot concentration against percent transmittance on semilogarithmic paper, using the logarithmic scale for the percent transmittance values.

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Reilley, C. N., and Sawyer, D. T., 1961, Experiments for instrumental methods: New York, McGraw-Hill, p. 105.

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U.S. Environmental Protection Agency, 1969, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–1 - 3–15.

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Conductivity Meters

1. Application or scope

1.1 This practice details procedures to follow in using conductivity meters. Conductivity meters are of relatively uncomplicated design and produce excellent results with simple quality control measures.

1.2 Conductivity meters consist essentially of a source of alternating current, a wheatstone bridge, a null indicator, and a conductivity cell. Conductivity cells usually consist of two thin plates of platinized metal, rigidly supported with a very precise parallel spacing. Pure platinum electrodes and circular carbon rings imbedded in an epoxy-type plastic cell are also used.

2. Practice

2.1 Basic operational procedure

2.1.1 At regular intervals, visually check the cell to insure that the platinized electrode surfaces are in good condition, that the electrodes are not bent, distorted, or fouled, and that the lead wires are properly separated and shielded to prevent electrolytic and capacitive current.

2.1.2 Clean and replatinize electrodes whenever the readings become erratic or inspection shows that any platinum black has flaked off. New electrodes must also undergo these cleaning and platinizing steps.

2.2 Calibration procedure

2.2.1 Allow the conductance instrument to electronically stabilize.

2.2.2 Prepare the KCl standard with care (NOTE 1). Compare the conductivity of a newly prepared standard with a previously prepared standard in order to ensure that the standard is correct.

NOTE 1. To prepare a 0.00702*N* potassium chloride solution, dissolve 0.5234 g KCl, dried at 180°C for 1 hour, in demineralized water and dilute to 1,000 mL (Skougstad and others, 1979); this solution has a specific conductance of 1,000 μmho/cm at 25°C. For potassium chloride solutions which will have other specific conductances, see Standard Methods (American Public Health Association and others, 1976).

2.2.3 Carefully measure the temperature of the standard solution (NOTE 2).

NOTE 2. Temperature significantly affects conductance measurements since conductance increases about 2 percent per degree Celsius. In the U.S. Geological Survey, specific conductance measurements are routinely reported at 25°C.

2.2.4 For direct-reading instruments with temperature compensation, measure the temperature of a 1,000 μmho/cm KCl standard, set the temperature control, and adjust the instrument to read 1,000. If another scale is used, check the calibration with another standard which is known to be in the range of the new scale.

2.2.5 For direct-reading instruments that are not temperature compensated, calibrate the instrument to read the conductance value of the KCl standard solution at the measured temperature by preparing a table of the conductivity of 0.00702*N* KCl versus temperature. If another scale is used, check the calibration with another standard which is known to be in the range of the selected scale.

2.2.6 For resistance measurements made using a wheatstone bridge, determine the cell constant of a particular cell according to directions in the methods manual. Inasmuch as the cell constant can change, it is necessary to recalculate this constant periodically. The resistance of sample solutions, and consequently their specific conductance, may be determined at 25.0°C by using a 25°C bath or by allowing samples to stabilize in a constant-temperature room (Skougstad and others, 1979). However, usually it is easier to determine experimentally the resistance of a standard KCl solution at 0.1°C intervals and make a correction to obtain the corresponding conductance at 25.0°C.

2.3 Measurement procedure

2.3.1 Carefully and thoroughly rinse the cell between each sample.

2.3.2 Record the temperature of each sample solution to the nearest 0.1°C.

2.3.3 Record the reading on the meter.

2.3.4 If the conductance meter is functioning properly, it is not necessary to check the standardization more than twice a day.

2.4 *Read-out and graphical techniques*

2.4.1 For a direct-reading instrument with temperature compensation, record the specific conductance directly from the meter with the temperature compensator adjusted to the observed temperature of the sample solution.

2.4.2 For a direct-reading instrument which is not temperature compensated, obtain the reading at a certain temperature x and multiply it by the ratio of the specific conductance of KCl solution at 25.0°C to that of the same solution at temperature x. This ratio is obtained from the table which is prepared as discussed in 2.2.5. If the resistance of the sample is measured by a wheatstone bridge, determine the specific conductance of the sample by dividing the resistance of the KCl standard solution at temperature x by the resistance of the sample solution at temperature x and multiplying by 1,000.

References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed.): Washington, D.C., American Public Health Association, 1193 p.

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Gas Chromatographs

1. Application or scope

1.1 This practice details procedures to be followed in using gas chromatographs to analyze water samples, and particularly to determine pesticides.

1.2 Although all gas chromatographs require similar operational optimization and calibration procedures, some variation in instrumental quality control may be necessary since commercially available instruments vary somewhat and since different columns and detectors must be used depending on analytical methodology.

2. Practice

2.1 Basic operational procedure

2.1.1 Unless there is sufficient reason for an exception, use column tubes of glass or Teflon. Copper and stainless steel may cause decomposition of certain compounds in the column (Sherma, 1979).

2.1.2 Use columns of either 2 mm or 4 mm ID for pesticide (NOTE 1). For electron-capture detectors, columns of about 2 mm are usually preferred (Goerlitz and Brown, 1972).

NOTE 1. Sample injection volumes should not exceed 10 μL for the 2 mm and 80 μL for the 4 mm ID columns.

2.1.3 Acid-wash each new column with dilute HCl, rinse thoroughly with distilled water, methanol, and hexane, and treat with Glass Treat or similar silylating reagent. Allow to dry completely.

2.1.4 When packing a column, use vibration and pressure and (or) vacuum to settle the material and small plugs of "silanized" glass wool to hold the packing in place. Sherma (1979) recommends hand vibration for high quality columns.

2.1.5 After installing the column in the gas chromatograph, but before connecting to the detector, condition it as follows (Goerlitz and Brown, 1972):

2.1.5a Purge the columns for 30 minutes with inert carrier gas.

2.1.5b Turn off carrier gas flow and heat columns to 250°C for 2 hours (NOTE 2).

NOTE 2. Do not exceed the manufacturer's maximum usable temperature during the conditioning procedure.

2.1.5c Reduce the temperature to 210°C and allow it to equilibrate for 30 minutes.

2.1.5d Turn on carrier gas to about 30 mL/mm and continue heating at 210°C for about 12 hours (NOTE 3).

NOTE 3. Between 24 and 72 hours may be required for fluorinated or other high-bleed liquids, especially when using the electron-capture detector.

2.1.6 Tightly cap columns not in use and recondition them before reuse if they have been out of the instrument for more than a few days.

2.1.7 After conditioning, inject an appropriate solution (see 2.1.7a for pesticides), calculate the theoretical plate value, and compare to published results to determine performance, retention-time characteristics, and efficiency of each column. Use the following formula (NOTE 4):

$$n = 16\left(\frac{tr}{\Delta t}\right)^2 \qquad (17)$$

where

n = number of theoretical plates,
tr = uncorrected retention time of peak, and
Δt = peak retention width (length of baseline cut by the two tangents of the peak at the half-height point).

NOTE 4. Within the Geological Survey Central Laboratory System, calculations are being performed by a computer program using the chromatographic peak data and the formula:

$$p = \left(\frac{tr}{w_i}\right)^2 5.54 \qquad (18)$$

where

p = number of theoretical plates,
tr = uncorrected retention time, and
w_i = peak width at half height.

2.1.7a Inject a solution of DDE, dieldrin, and DDT to test for organochlorine insecticides; inject parathion to test for organophosphorus insecticides, and inject 2,4,5–T to test for chlorinated phenoxy acid herbicides (NOTE 5).

NOTE 5. Using the computer program indicated in NOTE 4, the plate numbers for more pesticides can be easily calculated.

2.1.7b For example, if p,p'–DDT is used as a standard, a 1.8-m column should have an efficiency of more than 1,500 theoretical plates in order to be acceptable for pesticide analysis. A column must be replaced as soon as deterioration is observed as indicated by changes in elution pattern, relative retention time, relative proportion of peaks, and peak geometry.

2.1.8 Calculate the resolution:

$$R = \frac{2d}{W_1 W_2} \tag{19}$$

where

R = resolution
d = the distance between the apex of each peak, and
W_1 and W_2 = width of baselines at the point where tangents to each peak intersect.

At least one of the columns to be used should give an R value of at least 1.0 for the compound of interest. Separation of p,p'–DDE and dieldrin on the mixed phase column, for example, should give a resolution of at least 1.0.

2.1.9 Check resolution and theoretical plate values at least monthly. Record data in a notebook. Include identification number of the column, material in it, mesh size, percent coating, and date prepared. Include a sample chromatograph in the book to which graphs from subsequent analyses can be compared to detect gradual decomposition of the column.

2.1.10 Identify each column by attaching a metal tag with an assigned number, material in it, mesh size, percent coating and date prepared.

2.1.11 Precise column temperature control (±0.5°C) is mandatory if reproducible analyses are to be obtained. The column-oven temperature is generally set between 175° to 200°C. To monitor the temperature, insert a mercury thermometer through an unused injection port or insert the stem of a precalibrated dial thermometer through the oven door.

2.1.12 Column temperature may be checked by computing the relative retention ratio for two pesticides (for example p,p'–DDT compared to aldrin) as specified in Sherma, 1979, p. 108.

2.1.13 The inlet temperature is usually maintained at 25° to 50°C above the maximum column-oven temperature. Change the septum at the end of each day; avoid handling the septum with the fingers.

2.1.14 The quality of compressed gas needed depends on the type of detector. Use only the grade of gas recommended by the vendor for the particular instrument being used. "Specialty" grade, or equivalent, is generally specified for electron-capture detectors.

2.1.15 Change gas cylinders when tank pressure reaches 200 lb/in^2 to avoid potential fouling of system and detector. Replace gas cylinders immediately if the gas produces excessive baseline noise or poor sensitivity.

2.1.16 Gas cylinders should be equipped with dual stage regulators. The gas chromatograph must be equipped with accurate needle-valve gas-flow controls. If these controls were not previously calibrated, this can be accomplished by using a soap-bubble flow meter and a stopwatch. The optimum flow rates of gases used with various detectors can be found either in the manufacturer's manual or in the procedure for a particular determination. Shut off purge gas and gas to columns not in use (but going to the same detector) when measuring the flow rate of the column.

2.1.17 Choose a detector suited to the compounds being determined and the sensitivity desired. For example, the electron-capture detector is extremely sensitive to electronegative functional groups and therefore to constituents such as: halogens, conjugated carbonyls, nitrates, nitrites, and organometals. The selective sensitivity to halides makes this detector of particular value for the determination of

many pesticides. Although the sensitivity of the microcoulometric detector is not outstanding, it is specific for halogen-, sulfur-, or nitrogen-containing compounds. Other commonly used detectors include the flame-ionization, flame-photometric, electrolytic-conductivity, and alkali-flame detectors. The detector temperature is generally maintained at between 25° to 50°C above the maximum column-oven temperature.

2.1.18 Check the condition of nickel-63 detectors at least monthly, and more often if noise, low response, nonlinearity, or other symptoms indicate the possibility of a dirty detector. Use an electrometer amplifier to give a detector profile as shown in the instrument manuals. Usually when a poor profile is recorded, the detector is not usable and must be returned to manufacturer for cleaning and replacement or cleaning of the source, gaskets and electrodes. Spare detectors are necessary to eliminate lost time while a detector is being cleaned and repaired.

2.1.19 Help prevent detector contamination from a carrier gas containing grease or water vapor by using a molecular sieve filter drier; check or regenerate the trap at least monthly. If a detector becomes contaminated from this or other sources, follow the manufacturer's cleaning instructions.

2.1.20 A recorder with an adequate input voltage range and pen response is used to record the chromatogram. In addition, the actual peak area values must be determined by a digital integrator when peak separation warrants, or by a compensatory polar planimeter reading to the nearest 0.01 in^2 if a digital integrator is not suitable because of a lack of peak separation (NOTE 6).

NOTE 6. Baseline noise should be less than 1 percent of full scale. Proper adjustment of the recorder gain control is important. If gain is lowered too much, to compensate for excessive baseline noise, peaks are jagged or flat instead of pointed.

2.1.21 Because of the stabilization time needed for the proper operation of a gas chromatograph, it is common practice to keep the instrument turned "on" continuously. When not actually in use, keep a low carrier flow (about 25 mL/min) through the column and a purge of 25 to 30 mL through the detector.

2.2 Calibration procedure

2.2.1 The calibration procedures are performed after the gas chromatograph has stabilized, thermally and electronically, and with the operating conditions adjusted as specified. Use a precision, gas-tight microliter syringe that can be accurately filled, that will deliver reproducible injections, and that may be easily cleaned.

2.2.2 Flush the syringe several times with the standard to be inserted, then overfill the syringe, withdraw it from the sample container, check it visually for bubbles, and discharge the excess solution.

2.2.3 Immediately and smoothly inject the standard. The volume injected is measured by reading the syringe both before and after injection.

2.2.4 To determine linear response for each pesticide of interest, use a suite of four to six standards, spaced at equal logarithmic intervals of the concentration range. The concentration of the pesticide in the series of standard solutions should be such to calibrate either the full range of linear detector response or the range of anticipated concentration in the sample, whichever is less.

2.2.5 Pesticide standards may be obtained from reliable sources such as gas chromatography specialty houses or from the instrument manufacturer. In some cases, additional purification may be necessary. They should be refrigerated or stored in a desiccator during prolonged storage. At least two separate sources should be used.

2.2.6 Inject a standard of a given concentration until at least three peaks have the same reading (within 5 percent) at the same attenuation.

2.2.7 If a linearized detector is part of the operating instrument, the following alternative calibration procedure may be used: Inject four calibration standards. The first is one order of magnitude above the detection limit for the pesticide of interest, the second is twice the concentration of the first; the third is between three and four times the concentration of the first, and the fourth standard is either two or three orders of magnitude greater than the first standard or is equal to the highest anticipated concentration of pesticide, whichever is less. If

the average reading of the most concentrated standard does not deviate from linearity by more than 5 percent, the calibration curve is acceptable and the linearized detector can be adjusted to give a straight line response over the entire calibration range.

2.2.8 Use one of the above calibration procedures semiannually or when response factors have changed by more than 10 percent, when a new column has been installed, or when any other major changes have been made in the system. Record all data, including date of calibration, in a notebook.

2.2.9 In addition, include at least two sets of two standards each in each day's determination. Use concentrations at the first and second order of magnitude above the detection limit.

2.2.10 Analyze one set of standards before any samples are analyzed to verify proper operation of the instrument. Operating conditions are satisfactory if a line drawn between the read-out values for these two standards is parallel to the original calibration curve and if these values do not differ by more than 10 percent from the values for the same concentrations on the original calibration curve.

2.2.11 The values obtained from these two standards are used as a basis for determining the concentrations of the samples analyzed on that particular day. The second and any subsequent sets of standards will be introduced later for a continued check of operating conditions. Inject a second set of standards if more than 2 hours have elapsed since the start of the run, if instrument conditions are changed, or if the analyst suspects (because of very concentrated or dirty samples) any change in instrument response. If the results from the standards indicate that a problem exists, prepare fresh standards and repeat the procedure. If this does not solve the problem, the difficulty exists in the instrument and must be located and corrected before proceeding.

2.2.12 Record all information pertinent to the analysis of standards or samples, such as analysis date and time, column description, operating conditions, sample number, and type of pesticide, directly on the recorder chart.

2.3 Measurement procedure

2.3.1 After calibration has been completed, the analysis of water samples may begin. Prepare sample solutions as directed in the analytical procedure.

2.3.2 If the concentration of the prepared sample does not fall within the working range of the procedure, either concentrate or dilute the sample extract or use an alternative analytical method.

2.3.3 Fill the syringe and inject the sample as described in steps 2.2.2 and 2.2.3 above.

2.3.4 After a sample extract has been injected, do not make any subsequent injections until the last compound has been eluted and the baseline has returned to normal.

2.3.5 Before every set of samples, inject a reagent blank. If baseline drift is indicated, take corrective measures before proceeding with the analysis.

2.4 Read-out and graphical techniques

2.4.1 Compare the relative retention times (the ratio of the retention time of an unknown to that of a selected standard on two or more columns) to qualitatively identify constituents. For pesticides use as the standard: aldrin for chlorinated hydrocarbon insecticides, parathion for organophosphorus insecticides, and the methyl ester of 2,4-D for chlorinated phenoxy acid herbicides.

2.4.2 A digital integrator or data system (such as the Hewlett Packard 3352) is the most accurate device for measuring chromatographic peaks and must be used whenever conditions permit. For the first calibration procedure (described in the earlier subsection on "Calibration Procedure," involving the use of four to six standards) derive a least squares equation ($y = mx + b$) from the observed values of concentrations and peak areas of the standards. Use the response factor, m, thus obtained to calculate the concentrations of the sample solutions.

2.4.3 The measurement of peaks is often complicated by the different manners in which they appear. They may appear as (a) a single peak or two or more completely separated, discrete peaks, (b) two or more discrete peaks not completely separated, (c) a small peak or shoulder on the leading or trailing edge of a relatively large peak, or (d) two or more peaks perfectly overlapping each other. Generally, the digital integrator can be used with satisfactory results for cases (a) and (b).

2.4.4 It is very difficult to isolate a shoul-

der from a larger peak in a reproducible manner. In this situation, construct a line drawn to conform with the shape of the larger peak, then measure both the area of the shoulder and the area of the larger peak with a planimeter. Average at least two independent measurements to obtain the peak area of each portion. The area under the larger peak is usually quite accurate, that of the shoulder is not. Similarly, components eluting at nearly the same time to form a single peak are easily misinterpreted. Preferably, in either of the above situations where the peak separation is poor, make changes in order to isolate compounds for quantitative determination. For example, use a different type column, different type detector, or thin-layer chromatography.

2.4.5 Because a column may not separate all pesticides present in a water sample, corroborate each pesticide detected by at least one other technique (for example, different type column or different type detector). For example, all water samples and sediments containing pesticides must be analyzed by electron-capture gas chromatography using two different types of columns for confirmation. Because lack of peak resolution increases the apparent concentration, the lower concentration from two determinations is more likely to be correct and, in general, should be reported. If peak resolution seems poor for both determinations and (or) if differences in the two results seem large, further corroboration should be used.

2.4.6 The presence of pesticides at concentrations greater than 1.0 μg/L in water or 10.0 μg/kg in sediment samples must be confirmed by conductivity gas chromatography; report the electron-capture values since conductivity detectors are inherently less sensitive and pesticide concentrations are commonly near their detection limits. The quantitative results between the specific-element and the electron-capture detectors should, however, agree within 20 percent. If the pesticide concentration is greater than 2.0 μg/L in water or 20 μg/kg in sediment, the pesticide must be confirmed by gas-chromatography–mass spectrometry.

Selected References

American Society for Testing and Materials, 1975, Annual book of ASTM standards, Part 42: Philadelphia, American Society Testing Materials, p. 174.

Budde, W. L., and Eichelberger, J. W., 1979, An EPA manual for organic analyses using gas chromatography/mass spectrometry: U.S. Environmental Protection Agency EPA–600/8–79–006, Cincinnati, 142 p.

Goerlitz, D. F., and Brown, E., Methods for analysis of organic substances in water: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3, 40 p.

Goerlitz, D. F., and Lamar, W. L., 1967, Determination of pheonoxy acid herbicides in water by electron-capture and microcoulometric gas chromatography: U.S. Geological Survey Water-Supply Paper 1817–C, 21 p.

Sherma, Joseph, 1979, Manual of analytical quality control for pesticides and related compounds in human and environmental media: U.S. Environmental Protection Agency EPA–600/1–79–008, Research Triangle Park, North Carolina, 401 p.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 8–1 - 8–10.

U.S. Office of the Federal Register, 1979, Guidelines establishing test procedures for the analysis of pollutants; proposed regulations: Federal Register, v. 44, no. 233, p. 69464–69575.

Potentiometers

1. Application and scope

1.1 This practice details procedures to be followed in using potentiometric meters. The design and operation of the meters are quite uncomplicated and most of the problems with this type of instrumentation are associated with the electrodes.

1.2 Ion-selective electrode procedures employ a potentiometer in conjunction with a reference electrode and an ion-selective electrode that is responsive to the ion of interest (NOTE 1).

NOTE 1. In the last few years, some ion-selective electrode determinations have been automated. The care of the involved electrodes is identical to that for manual procedures, although the manufacturer's manual should be consulted for additional information on the operation of the potentiometer.

2. Practice

2.1 Basic operational procedure

2.1.1 Electrodes must be conditioned according to the manufacturer's directions before they are ready for initial use. Ion-selective electrodes tend to deteriorate with use. Periodically replace or, if possible, recondition them.

2.1.2 If erratic, incorrect, or nonlinear readings are observed, check the electrode to see if it is cracked or scratched. Check also to see if the electrode is sufficiently filled, if there is a break in the shielding of the electrode leads, or if there is poor connection between the electrodes and the meter.

2.1.3 Store the electrodes carefully, following the manufacturer's instructions (NOTE 2).

NOTE 2. A glass pH electrode must be soaked for several hours if allowed to dry out until stable readings can be obtained.

2.1.4 Many potentiometers have a standby mode which maintains the electronics of the instrument in a "ready" condition and requires a change from the measuring mode into the standby mode before removing the electrodes from solution. Check the manufacturer's manual to see if this change must be made and (or) what other requirements are necessary.

2.2 Calibration

2.2.1 Begin the calibration procedure only after the potentiometer has electronically stabilized.

2.2.2 To calibrate a potentiometer to determine pH, immerse the electrodes in a buffer solution (usually pH 7.00), measure the temperature of the buffer solution, adjust the temperature control and use the standardization control to give the correct reading on the meter. Check the millivolt scale while the electrode is in the pH 7.00 buffer; if the reading is not 0 ± 10 mV, replace the electrode.

2.2.2a As noted in Skougstad and others (1979), at least three buffer solutions (pH 4.00, 7.00, and 9.00) must be available to standardize the pH instrument. Provide additional standard buffer solutions, if needed, to cover the pH range of the samples. If the electrodes are functioning correctly, a reasonably correct value ($\leq$ 0.1 pH unit) should then be obtained when the electrodes are rinsed and immersed in the second buffer solution. Some meters contain a slope adjustment feature to compensate for small amounts of asymmetric behavior in the glass electrode. The manufacturer's manual describes the function and operation of this feature. If the second buffer reading differs by more than 0.1 pH unit from the known value, the cause of this excessive deviation should be located and corrected before proceeding.

2.2.2b Prepare buffer solutions every 3 months or whenever a visible change occurs, since some of the buffer solutions deteriorate with age (NOTE 3). Discard the buffer solutions used for standardization and never mix with unused portions.

NOTE 3. Prepared buffer solutions or buffer concentrates are available from instrument and chemical manufacturers.

2.2.3 To calibrate the potentiometer for ion-selective electrode procedures other than

pH, prepare and use three standards covering the concentration range, as specified in the appropriate analytical method.

2.2.3a To calibrate the instrument, set the temperature of the meter to that of the standard solutions.

2.2.3b Both "mV" and "log" scales can be used to measure concentrations. For the "mV" scale, sequentially place the electrodes in each of the three standards, and record the readings. Plot the values as described in paragraph 2.4.2; if they are satisfactory, the instrument is ready to begin analysis. If not, correct the problem before proceeding.

2.2.3c For the "log" scale, place the electrodes in the first standard and use the standardization control to set the correct concentration on the "log" scale. Then measure the concentration of the second standard, reading the concentration directly. If the reading deviates only slightly from the actual concentration, use the slope correction to correct this value. Check the third standard. If it reads correctly, the instrument is properly calibrated; if not, correct the problem before proceeding.

2.2.4 Scale expansion features are available on many meters. If the concentration range of interest is relatively narrow, expand the scale.

2.2.5 If the meter and electrodes are functioning normally, it is not necessary to check the standardization more than twice a day. This applies to measurements made in the laboratory and does not apply to field measurements where more frequent standardization checks are usually necessary.

2.3 Measurement procedures

2.3.1 The temperature of the samples to be analyzed should not differ by more than 5°C from the temperature of the pH buffers or the standard solutions.

2.3.2 Measure the temperature of the sample and set the temperature control.

2.3.3 If there is a significant difference between sample and electrode temperatures, allow the electrodes to reach the sample temperature before making an analysis. If this occurs, use a fresh portion of sample for the measurement after temperature equilibration has been reached.

2.3.4 After the meter has been calibrated and the temperature control adjusted, thoroughly rinse the electrodes, immerse them in a sample, and record the observed value.

2.3.5 Rinse the electrodes well between samples and take adequate time to obtain accurate measurements (NOTE 4).

NOTE 4. Response of the pH glass electrode becomes much slower as solutions become more weakly buffered. This problem is magnified if a weakly buffered sample follows a strongly buffered sample as is usually the situation for the first sample following standardization. This "memory effect" varies from one brand of electrode to another; consequently, electrodes should be selected which minimize this problem.

2.3.6 Use a minimum of aeration or agitation when determining the pH (Skougstad and others, 1979). If sample is to be agitated, agitate at the same rate when standardizing the meter with the buffers.

2.3.7 Operating and measurement conditions for other ion-selective procedures are detailed in the analytical procedures. The response time of electrodes increases as the concentration for the ion of interest decreases. Allow adequate time for equilibrium to be achieved to obtain an accurate reading for the samples.

2.3.8 Check the stability of the ion-selective electrode instrument by measuring, in random order, one of the calibration standards after every tenth sample. If drift is indicated, restandardize the instrument before continuing with the analysis.

2.4 Read-out and graphical techniques

2.4.1 The pH results are read directly in pH units. If a recorder is used, follow the manufacturer's instructions.

2.4.2 The output from other ion-selective electrode procedures is read either on the "mV" or "log" scales. For the "mV" mode, plot a graph of the potential in microvolts versus concentration on semilong paper with the concentrations plotted on the logarithmic axis. Obtain the concentrations of the ions of interest from this graph.

Selected References

Reilley, C. N., and Sawyer, D. T., 1961, Experiments for instrumental methods: New York, McGraw-Hill, p. 11.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–1—3–15.

Reference Material

The use of reference material is an integral part of any quality assurance program. For water analyses, two types are primarily prepared: ampouled concentrates and natural waters.

In the Central Laboratories System of the U.S. Geological Survey, ampouled concentrates are obtained from the U.S. Environmental Protection Agency, the National Bureau of Standards, and commercial sources, or are prepared by a Geological Survey quality assurance project which is independent of the analytical laboratories. Ampouled concentrates can easily be used to develop precision and bias data for methods-development and methods-comparison studies.

Reference samples with working level concentrations in natural water are also prepared by the independent quality assurance project. These samples are easily introduced into the laboratory as blind samples since they need no dilution. The Standard Reference Water Sample (SRWS) program has, since 1962, distributed reference materials semiannually, and has involved an increasing number of participating laboratories. In April 1978, for example, a set of reference samples for 41 constituents was distributed to 8 U.S. Geological Survey laboratories, to 50 other laboratories in the continental United States, and to 6 laboratories in Puerto Rico, Brazil, and Saudi Arabia.

Preparation of Ampouled Concentrates

1. Application or scope

1.1 This practice details procedures to be followed in preparing ampouled reference material.

1.2 Most constituents can be prepared as ampouled concentrates and later quantitatively diluted with either distilled or natural water to provide a variety of matrices and concentrations. The concentrates can also be used to perform standard-additions analysis.

2. Practice

2.1 Materials and equipment

2.1.1 Ampoules, prescored to break at a non-painted part of the ampoules, such as Wheaton 176780 or equivalent.

2.1.2 Ampoule washer, Cozzoli or equivalent (NOTE 1).

NOTE 1. If an organic solvent wash is required, ampoule washer must be explosion proof.

2.1.3 Automatic ampouling equipment, Cozzoli or equivalent (NOTE 2).

NOTE 2. Ampoules may also be washed and filled by hand.

2.1.4 Oven, 105°C.

2.2 Procedure

2.2.1 Dissolve carefully weighed primary standard(s), or equivalent quality chemicals, in demineralized water or other solvent, and dilute to obtain a concentrated solution which, when further diluted, will yield the desired "working-level" concentration (NOTE 3). Acidify or chemically preserve the solution, if necessary.

NOTE 3. Ordinarily, the concentration of each constituent is prepared so that an aliquot of the ampouled concentrated solution can be diluted to 1 liter to yield working level concentrations. For example: dissolve x grams of iron wire which has been cleaned in diluted HCl, rinsed and dried. Dilute to 10,000 mL with demineralized water. Ampoule 15 mL of solution. Withdraw 10 mL of ampouled solution and dilute to 1,000 mL with demineralized water, for a final concentration of y µg/L.

2.2.2 Determine the concentration of each constituent to assure that the concentrate was correctly prepared.

2.2.3 Wash all ampoules with tap water and demineralized water using ampoule washer. If organic concentrates are being prepared, also wash with an organic solvent.

2.2.4 Dry ampoules at 105°C for 1 hour (NOTE 4).

NOTE 4. If organic solvent was used, air-dry ampoules before drying in an oven.

2.2.5 If automated equipment is used to fill the ampoules, adjust settings according to manufacturer's instructions. Make test run(s) to assure that dispensing and sealing alignments are properly set.

2.2.6 Fill and seal ampoules.

2.2.7 Label ampoules, including date of preparation.

2.2.8 Analyze sufficient samples, randomly selected, to assure that correct concentration is obtained (NOTE 5).

NOTE 5. Refer to the section, "Materials Evaluation," to determine the number of ampoules to be analyzed and use a random numbers table (available in most statistic books) to select which ampoules should be analyzed.

Preparation of Natural Water Reference Material

1. Application or scope

1.1 This practice gives general procedures to be followed in preparing reference materials with working level concentrations of stable constituents in natural water matrices.

1.2 Reference materials for major inorganic constituents and trace metals should be prepared so that they will be stable from 5 to 10 years. Reference materials for nutrient and pesticide constituents are expected to be stable for 4 to 12 months.

1.3 In the U.S. Geological Survey, reference materials in natural water are prepared at least semiannually for use in the Standard Reference Water Sample (SRWS) program (NOTE 1).

NOTE 1. In 1980, it is expected that each SRWS set will consist of a major constituent sample, a trace-metal sample, a nutrient sample, an insecticide sample, and a herbicide sample.

2. Practice

2.1 Materials and equipment

2.1.1 Autoclave.

2.1.2 Bag, paper, rated for 12 lb load.

2.1.3 Bag, polyethylene.

2.1.4 Bands, opaque white cellulose.

2.1.5 Bottles, 1-liter Teflon for major inorganic constituents and trace metal samples; 500-mL polyethylene for nutrient samples; 1-liter glass, for organic samples.

2.1.6 Filter, 0.45-μm, in-line, Acroflow II cartridge single pen-end, epoxy coated top and bottom, Model 12611, Gelman Institute Co., or equivalent.

2.1.7 Sterilizer, ultraviolet, flow-through with flow-rate capacity of 6 liters per minute.

2.1.8 Hood, equipped with ultraviolet light.

2.1.9 Oven.

2.1.10 Stirrer, polyethylene or Teflon coated for inorganic samples; stainless steel for organic samples.

2.1.11 Tank, of sufficient size for entire sample; 300-gallon (1,140-liter) polyethylene for major inorganic constituent and trace metal samples; 55-gallon (210-liter) polyethylene for nutrient sample; 55-gallon (210-liter) stainless steel for organic sample.

2.2 Procedure

2.2.1 Collect sample at specified site (NOTE 2).

NOTE 2. For SRWS sample collection, site will be specified by the SRWS project chief. Collect a minimum of 750 gallons to prepare samples to be analyzed for major inorganic constitutents, trace metals, and nutrients.

2.2.2 Allow samples to come to room temperature.

2.2.3 Filter 300 gallons (each) for major inorganic and trace metal samples or 55 gallons (each) for nutrient and organic samples through 0.45 micrometer filter into appropriate mixing tank (NOTE 3). For organic samples, use a stainless steel filter and refrigerate water after filtration.

NOTE 3. Minimum movement of water during temperature equilibration will aid filtration.

2.2.4 Add 1.5 g thymol to solution for major inorganic constituents. Add 1.5 g thymol and 2,100 mL of concentrated nitric acid to solution for trace metals. Add 10 g $HgCl_2$ + 93 g NaCl to solution for nutrients.

2.2.5 Prepare any desired spiking solutions individually in deionized water or acetone for inorganic or organic samples, respectively. Then slowly add, with stirring, to solution in tank.

2.2.6 Return solution for organic reference material to refrigerator until ready to bottle. Stir solution for nutrient samples overnight. Stir solutions for major inorganic constituents and trace-metal reference materials several times a day for 2 to 3 days.

2.2.7 Clean bottles.

2.2.7a For major inorganic constituent and trace metal samples, clean at least 800 1-liter Teflon bottles. Clean the outside thoroughly. Add 15 mL of concentrated HNO_3 (sp gr 1.41) to each bottle, fill with demineralized water and allow to stand for 24 hours. Soak caps in dilute HNO_3. Rinse bottles and caps three times with demineralized water. Package two bottles per brown bag and fold top of bag and staple. Put 20 or more caps in an autoclavable plastic bag. Sterilize bottles with dry heat at 160°C for 3 hours and sterilize caps in autoclave (NOTE 4).

NOTE 4. Dry sterilization will shrink caps.

2.2.7b For organic samples, clean at least 200 1-liter glass bottles. Clean the bottles thoroughly and rinse bottles and caps three times with demineralized water. Heat bottles at 350°C for 12 hours and tightly cap.

2.2.8 Bottle the sample as soon as all bottles for a particular reference material are sterilized (NOTE 5).

NOTE 5. Teflon bottles will remain sterile in the bags for 4 to 5 days.

2.2.9 For major constituent and trace metal samples, pass the water through an in-line, 0.45 micrometer filter and ultraviolet sterilizer at a flow rate of less than 6 liters per minute. Package in Teflon bottles in a hood equipped with ultraviolet light, putting on caps and tightening them while in the hood. Do not refilter organic samples and do not use ultraviolet light for either nutrient or organic samples.

2.2.10 Place a cellulose band around Teflon caps.

2.2.11 Label each bottle "Standard Reference Water Sample No._____."

2.2.12 Store all nutrient or organic samples at 4°C.

Selected References

Schroder, L. J., Fishman, M. J., Friedman, L. C., and Darlington, G. W., 1980, The use of standard reference samples by the U.S. Geological Survey: U.S. Geological Survey Open-File Report 80–738, 11 p.

Skougstad, M. W., and Fishman, M. J., 1975, Standard reference water samples: Proceedings of the AWWA Water Quality Technology Conference, December 1974, p. XIX–1–XIX–6.

Development of Statistical Data for Standard Reference Water Samples

1. Application or scope

1.1 This practice describes how the interlaboratory statistics for the Standard Reference Water Sample (SRWS) program are developed. Most of the computations are handled by a computer program.

1.2 The mean, average deviation, standard deviation, range, 95 percent confidence interval of the mean, and the percent deviation of each value from the mean are calculated for each constituent. The mean and standard deviation for each method are also computed for each constituent.

1.3 Inasmuch as the validity of the most probable concentration of each constituent is dependent upon the competence of the laboratories (as well as the number of laboratories analyzing the sample), the most probable means and standard deviations are refined by eliminating laboratories with inferior overall ratings.

2. Practice

2.1 Reported statistics

2.1.1 Values are rounded to conform with Geological Survey reporting policy.

2.1.2 The mean, average deviation, standard deviation, and total range are calculated for each determination. "Less than" values are not included. Outlying values are rejected using the *T* test described in the practice "Single operator precision" in section "Analytical Methods Development Procedures" (*T* values are listed in table A1).

2.1.3 The 95 percent confidence interval about the mean is calculated:

$$CI = \bar{x} \pm \frac{ts}{\sqrt{n}} \qquad (20)$$

where

CI = the confidence interval

$\bar{x}$ = mean of all unrejected values,

s = standard deviation,

n = number of values, and

t = value from Student t table at the 95 percent level for the (n-1) degrees of freedom.

2.1.4 The percent deviation of each value from the mean is calculated:

$$\frac{\bar{x} - x_i}{\bar{x}} \times 100 \text{ percent} \qquad (21)$$

where

$\bar{x}$ = the mean of all unrejected values from all laboratories, and

x_i = value from one laboratory.

2.1.5 Histograms are plotted showing each laboratory's result (figure 4). Because the computer program is designed to show differences in the significant figures appropriate to the determination and to depict only 25 columns, values which are very different from the mean may not be shown in the computerized plot.

2.1.6 The mean and standard deviation for each method in which there are three or more unrejected values are also calculated (NOTE 1).

NOTE 1. After a sufficient number of reference materials have been distributed for a constituent, these data are also used to develop precision statements for the analytical methods. Usually this precision is reported as a regression line and (or) as the relative percent standard deviation (coefficient of variation). See practice "Interlaboratory precision" in section "Analytical Methods Development Procedures." Also see individual precision statements in Skougstad and others, 1979.

2.2 Development of most probable value for reference material.

2.2.1 All laboratories are confidentially rated on a scale ranging from 0–4 that is based upon the number of standard deviations from the most probable mean as follows:

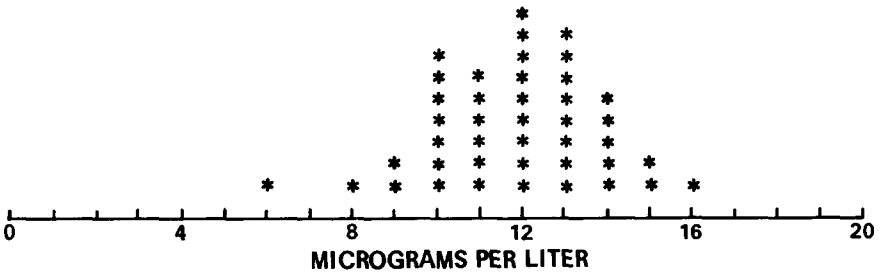

Figure 4.—Standard Reference Water Sample 65 histogram for cadmium. Each * equals a value from one laboratory.

Number of deviations from mean	*Rating number*
0–0.50	4
0.51–1.00	3
1.01–1.50	2
1.51–2.00	1
>2.00	0

2.2.2 All laboratories with an overall rating of less than 2.5 are eliminated, and the means and standard deviations are recomputed to determine the most probable concentration for each constituent.

Selected References

Schroder, L. J., Fishman, M. J., Friedman, L. C., and Darlington, G. W., 1980, The use of standard reference water samples by the U.S. Geological Survey: U.S. Geological Survey Open-File Report 80–738, 11 p.

Skougstad, M. W., and Fishman, M. J., 1975, Standard reference water samples: Proceedings, AWWA Water Quality Technology Conference, December, 1974, American Water Works Association, p. XIX–1–XIX–6.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Laboratory Quality Control

Fundamental to the quality assurance of analytical data are quality control procedures in the laboratory. The practices which follow are interrelated with practices in other sections in this manual, particularly with the sections on "Standard Quantitative Techniques" and on "Instrumental Techniques." Each analyst must be familiar with and participate in the laboratory's quality control program.

Biological Quality Control

Analysis of Aquatic Organisms (benthic invertebrates, phytoplankton, and periphyton)

1. Application or scope

1.1 This practice specifies some general factors which are necessary for qualitative and quantitative measurements of aquatic biological samples. Specifically, this practice applies to taxonomic identification and determination of biomass of benthic invertebrates, phytoplankton, and periphyton.

1.2 Refer to applicable methods in Book 5, Chapter A4, of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Greeson and others, 1977) and in the supplement to chapter A4 (Greeson, 1979). Also refer to other practices in this manual such as the practice, "Required documentation and review of data" and the practice, "Gravimetry."

2. Practice

2.1 Collection and preservation

2.1.1 In general, collect samples from downstream to upstream. When using a sieving device to collect benthic invertebrates, for example, stand in the downstream side and take samples in an upstream or a lateral direction (Tracor Jitco, Inc., 1978).

2.1.2 Collect samples at a depth appropriate to the object of the study; in order to lessen the chance of collecting terrestrial insects, collect samples from below the surface. To collect periphyton, be sure substrates are submerged (NOTE 1).

NOTE 1. Because of the amount of time needed to collect a periphyton sample and because of possible fluctuations in water levels, possibility of vandalism, and so forth, it is recommended that four replicate substrates be taken and duplicate samplers used (Tracor Jitco, Inc., 1978).

2.1.3 Prepare and use a formaldehyde-cupric sulfate solution or Lugol's solution to preserve phytoplankton and periphyton samples which are collected for taxonomic identification. Use ethyl alcohol or isopropyl alcohol to preserve benthic invertebrate samples collected for taxonomic identification; do not use formaldehyde (Greeson and others, 1977). If possible, freeze samples collected for the determination of biomass instead of using a chemical preservative (NOTE 2).

NOTE 2. All samples collected for a particular determination as part of a specific study should be preserved in a similar fashion and the method of preservation should be clearly documented.

2.1.4 In preserving benthic invertebrates, fill containers almost to the top (half of volume in container should be preservative) to avoid damage to specimens during transport. If unsorted samples are to be stored for more than a few weeks, drain preservative and replace with fresh preservative after a week (Greeson and others, 1977).

2.1.5 Label container with pertinent information including date, time, location, volume or area of sample, name of collector, preservative, and mesh or sieve size. If a sample is

sorted into categories (either in the field or in the laboratory), include the total number of containers per sample and the name of the sorter on the label; keep the sample together as a unit.

2.2 Calibration and measurement

2.2.1 Calibrate new microscopes or a microscope which has not been used for several months using an optical reticle and stage micrometer.

2.2.2 After every use, clean optics and stage of microscope with lens paper.

2.2.3 Check temperature of oven prior to each use to make sure it is correct (NOTE 3).

NOTE 3. The setting on the outside may be incorrect and not reflect the actual temperature in the oven. The thermometer, rather than the setting, must be read.

2.2.4 Carefully maintain records of dilution or concentration, if either is necessary, and apply the appropriate dilution or concentration factor in reporting analyses. When concentrating a phytoplankton sample, be careful that it has settled sufficiently before siphoning the supernatant liquid since different shapes and sizes of particles will have different sedimentation rates (Tracor Jitco, Inc., 1978); in general, allow the sample to sit undisturbed for 4 hours per centimenter of depth before siphoning the supernatant liquid (Greeson and others, 1977).

2.2.5 For sorting benthic invertebrates, consider use of the optional procedures (density separation, differential staining, and (or) subsampling) specified in the analytical procedure (see Greeson and others, 1977).

2.2.6 For phytoplankton or periphyton, use the magnification specified in the analytical procedure. Count, in randomly chosen fields, the minimum number of organisms or minimum number of fields specified in the procedure. In counting, enumerate all forms wholly within the grid boundaries and all forms which intersect two adjacent grid borders, but not those intersecting the opposite two borders (see Greeson and others, 1977, and Greeson, 1979).

2.2.7 Be sure taxonomic references are adequate and are readily available to each analyst. Consult references if taxonomy identification is uncertain.

2.2.8 Develop and maintain an "in-house" reference specimen collection.

2.2.9 Consult with outside taxonomic experts on unusual specimens to confirm or provide identification.

2.3 Calibration checks

2.3.1 Using an optical reticle and stage micrometer, recalibrate each microscope at least semiannually. Record the date of calibration in a notebook kept near the microscope.

2.3.2 Check calibration of oven thermometer with a U.S. National Bureau of Standards certified themometer at least every 3 months. Record date checked in a notebook kept near the oven.

2.3.3 Check calibration of analytical balance at least every 3 months using Class S weights. Record date of calibration check in a notebook kept near the balance. If recalibration is necessary, consult the manufacturer's directions.

2.3.4 For taxonomic identification, have every 20th slide checked by another analyst. Preferably, the analyst should be from another laboratory.

Selected References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed): Washington, D.C., American Public Health Association, 1193 p.

Greeson, P. E., ed., 1979, A supplement to—Methods for collection and analysis of aquatic biological and microbiological samples: (U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A4): U.S. Geological Survey Open-File Report 79–1279, 92 p.

Greeson, P. E., Ehlke, T. A., Irwin, G. A., Lium, B. W., and Slack, K. V., eds., 1977, Methods for collection and analysis of aquatic biological and microbiological samples: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A4, 332 p.

Tracor Jitco, Inc., 1978, Quality assurance guidelines for biological testing: U.S. Environmental Protection Agency EPA–600/4–78–043, Las Vegas, 474 p.

Bacteriological Analysis

1. Application or scope

1.1 This practice applies to the measurement of bacteria in water (for example, the measurement of total or fecal coliform bacteria).

1.2 Refer to applicable methods in Book 5, Chapter A4 of Techniques of Water-Resources

Investigations of the U.S. Geological Survey (Greeson and others, 1977) and in the supplement to chapter A4 (Greeson, 1979).

2. Practice

2.1 Preparation of reagents

2.1.1 Use demineralized water free from traces of dissolved metals, nutrients, residual chlorine, and other bactericidal compounds. Test demineralized water semiannually to determine if it contains substances which are toxic to bacteria or which will stimulate the growth of bacteria (NOTE 1). Record dates and results of the tests.

NOTE 1. The test procedure and specifications are described in Standard Methods (American Public Health Association and others, 1976) and in the U.S. Environmental Protection Agency EPA–600/8–78–077 (Bordner and Winter, 1978). As noted in the latter publication, the test is ". . . a complex method that requires skill and experience, (and) is very sensitive to toxicants . . ."

2.1.2 Follow directions specified in the analytical method for the preparation of all reagents. Record date of preparation in notebook and on container.

2.1.3 Follow storage requirements, including refrigerating or storing in dark, specified in the method. Do not exceed maximum allowable storage times.

2.1.4 Keep a record of each bottle of media including its lot number, date of receipt, date of opening bottle, and date of expiration (NOTE 2).

NOTE 2. The U.S. Environmental Protection Agency recommends that, as a general guideline, "storage of unopened bottles of cultural media (be limited) to 2 years" (Bordner and Winter, 1978).

2.1.5 When preparing a new batch of media, indicate in notebook the number of tubes or plates prepared, date of preparation, bottle lot number, and name of preparer. Be extremely careful not to overheat media. Test 5 percent of noninhibitory media by overnight incubation at 35°C. Discard the entire batch if two out of five plates show contamination (McClelland and others, 1978).

2.1.6 Check each set of washed glassware for acid or alkaline residue by adding a few drops of a 0.04 percent solution of bromothymol blue indicator to a few pieces, randomly chosen from the set (Bordner and Winter, 1978). The indicator will show a yellow color at pH less than 6.2 and blue at pH greater than 7.6 (Dean, 1973).

2.2 Calibration and measurement

2.2.1 Temperature is critical to bacteriological tests. At least quarterly, check calibration of thermometer(s) against a U.S. National Bureau of Standards certified thermometer. Record the date checked.

2.2.2 Follow sterilization procedures specified in the method. Once a week or with every batch, whichever is less frequent, include in autoclave load a sterilization indicator (such as a Diack control ampoule or Sterilometer tape). Place indicator in center of load. Record date and result of indicator test. If sterilization is shown to be incomplete, locate problem and correct.

2.2.3 When in use, daily check the temperature of all water baths and incubators upon first opening. Temperature must be within limits specified in the method. Record daily temperature.

2.2.4 As noted in Greeson and others (1977), when determining total coliform bacteria by the most probable number method (B–0035–77), check broth in inverted tubes for air bubbles before use. Discard any tubes which contain a bubble.

2.2.5 Prior to use, check each batch of medium by inoculating two tubes or plates with pure cultures of organisms which will produce positive or negative reactions (Bordner and Winter, 1978). See table 7 for organisms which can be used.

2.2.6 Weekly or the day before use, whichever is less frequent, check phosphate buffer dilution water for sterility. Follow method B–0030–77, Total Coliform Bacteria (Membrane Filter Method) from Greeson and others (1977), after selecting three bottles of buffer at random and filtering. Record all information, including date, in notebook. If any plate shows a count greater than 2 colonies/mL, resterilize all buffer water prepared on same date (McClellend and others, 1978).

2.3 Calibration checks

2.3.1 Monthly, test a pure culture known to give positive results. Record data in notebook.

Table 7.—Cultures for use in testing media[a]

Medium	Control cultures	Expected results
M-Endo MF broth or agar	*Escherichia coli*	Golden green metallic sheen.
	Enterobacter aerogenes	Do.
	Achromobacter species	Red colonies.
	Pseudomonas species	Do.
	Salmonella species	Red colonies if medium is overheated.
M-FC broth or agar	*Escherichia coli*	Blue colonies.
	Klebsiella pneumoniae	Do.
	Enterobacter aerogenes	No growth.
Brilliant green bile lactose broth	*Escherichia coli*	Growth with gas.
	Enterobacter aerogenes	Do.
	Citrobacter freundii	Do.
	Staphylococcus aureus	No growth.
Lauryl tryptose broth	*Escherichia coli*	Growth with gas.
	Enterobacter aerogenes	Do.
	Salmonella typhimurium	Marked to complete inhibition.
	Staphylococcus aureus	Do.
Levine's eosin methylene blue agar	*Escherichia coli*	Nucleated black colonies with golden green metallic sheen.
	Enterobacter aerogenes	Pink colonies with dark centers.
	Citrobacter freundii	Colorless colonies.
	Salomnella species	Do.
	Klebsiella species	Large brown mucoid colonies.
Xylose lysine Desoxycholate agar (XLD)	*Salmonella species*	Red colonies, to red with black centers.
	Klebsiella species	Yellow colonies.
	Escherichia coli	Do.
	Enterobacter aerogenes	Do.
Bismuth sulfite agar	*Salmonella typhosa*	Black colony with black or brownish-black zone, with or without sheen.
	Other Salmonella species	Raised green colonies.
	Coliforms	Green colonies.
Brilliant green agar	*Salmonella species*	Pink-white opaque colonies surrounded by brilliant red zone.
	Escherichia coli	Inhibition or yellow green colonies.
	Proteus vulgaris	Marked to complete inhibition or red colonies.
KF streptococcus agar	*Streptococcus faecalis*	Pink to red colonies.
	Streptococcus pyogenes	No growth.
	Straphylococcus aureus	Do.
	Escherichia coli	Do.
PSE agar	*Streptococcus faecalis*	Black colonies.
	Escherichia coli	No growth.
	Straphylococcus aureus	Do.

[a] Table is modified from Bordner, Robert, and Winter, John, 1978, Microbiological methods for monitoring the environment, water and wastes: U.S. Environmental Protection Agency EPA-600/8-78-017, Cincinnati, p. 220-221.

2.3.2 Carry along a blank with each set of analyses. Blank should not show contamination.

2.3.3 Run every 20th sample in duplicate.

2.3.4 Confirm every 10th sample by having another analyst count colonies.

2.3.5 Record data from blank, duplicates, and recounts in a notebook, along with a date of analysis and identification of samples analyzed.

2.3.6 Prepare and use quality control chart (see practice "Quality control charts").

2.3.7 Within 24 hours of membrane filtering, confirm coliform colonies by using method B–0045–77, and confirm fecal streptococcal bacteria by using method B–0060–77 (Greeson and others, 1977).

Selected References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed): Washington, D.C, American Public Health Association, 1193 p.

Bordner, Robert, and Winter, John, eds., 1978, Microbiological methods for monitoring the environment, water and wastes: U.S. Environmental Protection Agency EPA–600/8–78–017, Cincinnati, 337 p.

Dean, J. A., ed., 1973, Lange's handbook of chemistry (11th ed.): New York, McGraw Hill, p. 5–80.

Greeson, P. E., ed., 1979, A supplement to—Methods for collection and analyses of aquatic biological and microbiological samples (U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A4): U.S. Geological Survey Open-File Report 79–1279, 92 p.

Greeson, P. E., Ehlke, T. A., Irwin, G. A., Lium, B. W., and Slack, K. V., eds., 1977, Methods for collection and analysis of aquatic biological and microbiological samples: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A4, 332 p.

McClelland, N. J., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. L., 1978, *in* Inhorn, S. L., ed., 1978, Quality assurance practices for health laboratories: Washington, D. C., American Public Health Association, p. 1175–1182.

Prier, J. E., Bartula, J. T., Friedman, Herman, 1975, Quality control in microbiology: Baltimore, University Park Press, 188 p.

Tracor Jitco, Inc., 1978, Quality assurance guidelines for biological testing: U.S. Environmental Protection Agency EPA–600/4–78–043, Las Vegas, 474 p.

U.S. Environmental Protection Agency, 1977, Manual for the interim certification of laboratories involved in analyzing public drinking water supplies: U.S. Environmental Protection Agency EPA–600/8–78–008, Washington, D.C., 92 p.

Inorganic Quality Control

Atomic Absorption Analysis

1. Application or scope

1.1 This practice applies to the determination of constituents by atomic absorption spectrometry.

1.2 The practice "Atomic absorption spectrometers," in the section "Instrumental Techniques" and the applicable analytical procedures in Book 5, Chapter A1 of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979) should be referred to.

2. Practice

2.1 Preparation of standards, blanks, and reagents

2.1.1 Prepare a stock solution and intermediate standards as specified in the analytical procedure. Intermediate standards should be prepared bimonthly (and dated) or at time intervals specified in the analytical procedure.

2.1.2 Prepare reagents, if any, as specified in the analytical procedure. If reagents deteriorate with age, prepare fresh daily or at time intervals specified in the method.

2.1.3 Prepare working standards and reagent blank, if any. Add all reagents which will be added to the samples. Extract standards and blanks if samples will be extracted. A minimum of five standards, equally spaced over the analytical range, should be prepared. In general, prepare working-level standards fresh each day.

2.2. Calibration and measurement

2.2.1 Adjust lamp current and aline lamp.

2.2.2 Adjust wavelength as specified in the analytical procedure and set the gain and slit width.

2.2.3 Adjust compressed gas regulators to achieve correct type of flame.

2.2.4 Aline burner.

2.2.5 Adjust nebulizer if necessary.

2.2.6 If the system has been automated with a sampler and pump, check pump tubing to make sure it is in good condition.

2.2.7 Aspirate a blank and adjust electronics, including recorder or digital read-out to read zero.

2.2.8 Aspirate a standard known to give a 0.2 to 0.6 absorbance and known to be within the linear portion of the analytical range. Keep a record of the sensitivity of each element for each instrument. A significant change ($\geq$10 percent) from previous results indicates that a problem exists which must be corrected.

2.2.9 Determine the concentration of the five standards, aspirating the solvent between each sample. If a direct-concentration read-out is used, the instrument is set with one standard, usually the highest, and the concentration in the other standards determined; concentrations must agree with their theoretical concentration or analyses discontinued until it is determined why they do not and until corrections are made.

2.2.10 Aspirate samples with solvent aspirated between each sample (NOTE 1).

NOTE 1. Demineralized water (or solvent such as methyl isobutyl ketone) is not to be considered the reagent blank unless no reagents have been added to standards and samples.

2.2.11 If concentrations of samples are outside of those specified as the range in the analytical procedure, dilute or run by an alternative procedure.

2.2.12 Use a standard addition technique when interferences cannot be avoided or are unknown. Use standard additions for all flameless and electrothermal-vaporization methods.

2.3 Calibration checks

2.3.1 Insert, in random order, a standard or reagent blank at every seventh or eighth sample or as specified in the method.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is noticeable baseline drift, recalibrate the instrument and reanalyze all samples that were analyzed after the last acceptable calibration check.

2.3.3 Use a standard reference material as the first sample to be analyzed and as every twentieth sample thereafter. The value for the reference material should fall within 1.5 standard deviation of the theoretical value. If it does not, the reason for the discrepancy must be determined and corrected and the concentration of all samples from the last "good" reference value should be reanalyzed.

2.3.4 Record reference sample values in a notebook, preferably kept near the instrument, along with the date of analysis. Also record the laboratory-assigned log-in numbers of all samples included in the set analyzed.

2.3.5 Plot values on a quality control chart as outlined in the practice "Quality control charts." If a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Reference

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Automated Colorimetric or Potentiometric Analysis

1. Application or scope

1.1 This practice applies to analyses, using the Technicon AutoAnalyzer, of samples in which the constituent of interest forms a unique colored complex with the reagent used.

1.2 This practice is also applicable to automated potentiometric analyses (such as fluoride). If specific conductance or pH are to be measured, refer to the practice "Inorganic quality control: automated measurements of specific conductance and pH."

1.3 Refer also to the practice "Automated analyzers" in the section "Instrumental Techniques," and the applicable analytical procedures in Book 5, Chapter A1 of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979).

2. Practice

2.1 Preparation of standards, blanks, and reagents

2.1.1 Prepare a stock solution and intermediate standards as specified in the analytical method. Intermediate standards should be prepared at least bimonthly (and dated), or at time intervals specified in the analytical method.

2.1.2 Prepare reagents, if any, as specified in the analytical method. Prepare fresh daily, or at time intervals specified in the method, all reagents which deteriorate with age.

2.1.3 Prepare a minimum of five working-level standards, spaced evenly over the analytical range. If there is evidence of instability, working-level standards should be prepared fresh daily, or at time intervals specified in the method.

2.2 Calibration and measurement

2.2.1 Set up the manifold as specified in the appropriate analytical procedure. Select proper flow-cell length, sampling rate, sample-to-wash ratio, and heating bath temperature (if a heating bath is part of the manifold) as specified in the analytical procedure.

2.2.2 Check manifold tubing and glassware to make sure that they are clean and free of leaks, and that pump tubes are taut. Replace limp tubing.

2.2.3 Set wavelength, with the appropriate filter, as specified in the analytical procedure and allow colorimeter or potentiometer to warm up and stabilize (NOTE 1).

NOTE 1. Stabilization usually will take 20 to 60 minutes.

2.2.4 Set indicator control to zero and see if recorder reads zero; then set indicator control to full and see if recorder reads 100. For ion-selective electrodes (for example, for fluoride), set control to "Cal 1" and see if recorder reads zero; then set control to "Cal 2" and see if recorder reads 50. Adjust recorder if it does not give correct response (see practice "Automated analyzers").

2.2.5 With all reagents being pumped, with wash solution in the sample line, and after the chart recorder shows a stable reading indicating that the system has reached equilibrium, set the baseline of the recorder to read zero

or to a positive value if specified in the analytical method; the printer should give a reading similar to that of the recorder.

2.2.6 If the AutoAnalyzer is linked to and controlled by a computer system, activate the interface connection which links the colorimeter to the computer system. Follow any special instructions related to the computer (such as initially setting the colorimeter at full scale and then at normal operating conditions) (NOTE 2).

NOTE 2. Once control is turned over to the computer system, only minor adjustments may be made to Technicon equipment without restarting the entire analysis. No adjustment may be made without supervisor's knowledge.

2.2.7 Rinse the sample cups (NOTE 3).

NOTE 3. Keep sample cups sealed until ready to use and rinse immediately before use. If chloride is to be determined, avoid contamination of the cups with perspiration from hands; thin gloves are recommended.

2.2.8 Place a complete set of standards (minimum five) in the sampler.

2.2.9 For routine use of the Technicon AutoAnalyzer, place standards in descending order, beginning with the highest standard and ending with a blank (NOTE 4).

NOTE 4. The following scheme has been found to be helpful in setting up the first sample tray: highest standard, blank, highest standard, blank, all standards in decreasing order of concentration, two blanks. This scheme enables the analyst to adjust instrumental controls and to check that adjustment, and to rezero the printer and (or) recorder using the last blank.

2.2.9a If the AutoAnalyzer is linked to and controlled by a computer system, set up the tray as follows: three high standards, two blanks, all of the standards in ascending order, and two blanks (NOTE 5).

NOTE 5. Be sure that the computerized tray pattern correctly identifies the standards, blanks, and samples.

2.2.10 As the first standard is read, adjust the "STD CAL" control on the colorimeter so that the flat portion of the peak reads full scale. When the peak is at maximum, press the start print button on the printer.

2.2.11 Use subsequent high standards to check the adjustment and "fine tune" the system.

2.2.12 Keep a record of the STD CAL setting for each constituent for each instrument. A significant change ($\geq$10 percent) from previous results indicates that a problem exists which must be determined and corrected before proceeding (NOTE 6).

NOTE 6. This problem may be instrumental or it may be chemical (for example, a reagent has deteriorated or standards have been incorrectly prepared.)

2.2.13 Record and compare the results for the rest of the set of standards (that is for all of the standards except the initial one(s) used to adjust the STD CAL control) with those obtained previously. If they differ significantly (over 5 percent), a problem exists which must be determined and corrected before proceeding (NOTE 7).

NOTE 7. If a computerized system is used, the computer will make any curve corrections and will print out the calculated concentration of the standards; in this case, check to see if the concentration is within 5 percent of the theoretical value (rather than comparing previous results). The computer will also print a "CD" (correlation coefficient of the determination or r^2) value; if this value is not 0.99 or greater, a problem exists which must be determined and corrected before proceeding.

2.2.14 Analyze samples. If concentrations are outside those specified as the range in the analytical method, dilute or determine by an alternative procedure. If a computerized system is used, dilute to the amount specified by the computer and place the dilution in the tray at the location specified by the computer.

2.2.15 If interferences cannot be avoided, use a standard addition technique or select an alternative procedure.

2.2.16 If color is an interference, it may be possible to compensate for it by subtracting the concentration obtained when all reagents except the indicator reagent are used, or by using a bleaching or adsorption procedure. (See the section on "Instrumental Techniques.")

2.3 Calibration checks

2.3.1 Insert in random order a standard or reagent blank at every seventh or eighth sample or as specified in the analytical method.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is noticeable baseline drift, recalibrate the instru-

ment and reanalyze all samples analyzed after the last acceptable calibration check.

2.3.3 Use a standard reference material as the first sample to be analyzed and as every twentieth sample thereafter. The reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, determine the reason for the discrepancy, make necessary corrections, and remeasure the concentration of all samples from the last "good" reference value.

2.3.4 Record determined reference sample values, along with the expected value and date of analysis. Also record the laboratory-assigned log-in numbers of all samples run in the set.

2.3.5 Plot values on a quality control chart as outlined in the practice "Quality control charts." If a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Reference

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Automated Measurement of Specific Conductance and pH

1. Application or scope

1.1 This practice applies to automated measurements of specific conductance and pH. The pH system uses a Technicon printer and recorder while the conductivity system employs a specially designed printer used in conjunction with a conductivity bridge. Both use a "flow-through" cell.

1.2 Refer to practices "Potentiometers," "Conductivity meters," and "Automated wet-chemical analyzers" in the section "Instrumental Techniques." Refer also to analytical methods I–1586–78 and I–1780–78 ("pH, electrometric, glass electrode" and "Specific conductance, electrometric, wheatstone bridge") in Skougstad and others (1979).

2. Practice

2.1 Preparation of standards and buffers

2.1.1 Prepare a minimum of three standards for specific conductance: 0.00702 *N* KCl (1,000 μmho/cm at 25°C), 0.02 *N* KCl (2,767 μmho/cm at 25°C), and 0.1 *N* KCl (12,900 μmho/cm at 25°C). See method I–1780–78 and also see Standard Methods (American Public Health Association and others, 1975).

2.1.2 Check the new KCl solutions against previous KCl standard solutions. If conductances of new and old solutions are different, check both solutions against a third solution (prepared by another analyst).

2.1.3 Prepare a minimum of three buffer solutions as specified in method I–1586–78. Date the solutions and prepare fresh every 3 months or when noticeable discoloration or deterioration of a buffer occurs (NOTE 1).

NOTE 1. Prepared buffer solutions or buffer concentrates are available from chemical and instrumental suppliers.

2.2 Calibration and measurement

2.2.1 Set up the manifold, check tubing, and glassware to make sure that they are clean and free of leaks and that pump tubes are taut. Replace limp tubing.

2.2.2 With wash solution being pumped through the sample line, allow the instruments to warm up and stabilize (usually 60 minutes).

2.2.3 In order to adjust the recorder and printer for pH, and the printer and bridge for conductance, to calibrate the system, and to check the accuracy of the determination, set up the first sample tray in the following manner: 1,000-μmho conductance standard, 1,000-μmho conductance standard, 12,900-μmho conductance standard, blank, 2,767-μmho conductance standard, 12,900-μmho conductance standard, blank, 2,767-μmho conductance standard, pH 4 buffer, pH 4 buffer, pH 7 buffer, blank, pH 9 buffer, blank, 3 reference materials, and samples.

2.2.4 Turn on the conductance system printer and start up the sampler. When the sampler is turned on, press the reset button on the printer. Watch the timer; when it reads 45 seconds, press the reset button on the printer again. Then press the event counter reset button to set the counter.

2.2.5 Calibrate the conductance system by adjusting the printer to read 1,000 with the temperature control knob on the conductivity bridge (after the first 1,000-μmho standard triggers the conductivity printer, wait 5 seconds and press the start-print button on the pH printer.) Adjust the printer to read 12,900 with the "span" control knob on the conductivity printer. Finally, adjust the printer to read 2,767 with the "offset" control knob on the conductivity printer.

2.2.6 Calibrate the pH system with the various standards. For the pH 4 standard, use the baseline control on the potentiometer; for the pH 7 standard, use the STD CAL control on the potentiometer.

2.2.7 If, at any time, the system cannot be calibrated following the procedures outlined above, do not proceed further. The problem may be instrumental and (or) chemical; determine its cause, correct it, and start again.

2.3 Calibration checks

2.3.1 Analyze a blank, 1,000-μmho conductance standard, and two pH buffers after every 20 samples.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is a noticeable baseline drift, recalibrate the instrument and reanalyze all samples that were analyzed after the last acceptable calibration check.

2.3.3 As indicated in paragraph 2.2.3, use three reference materials as the first three samples to be analyzed. Also use at least one reference material either as every 20th sample or immediately after the required standards in paragraph 2.3.1 (that is, either before or after the standards).

2.3.4 The reference material values should fall within 1.5 standard deviations of the theoretical value. If they do not, determine the reason for the discrepancy, make necessary corrections, and remeasure the concentration of all samples since the last "good" reference value.

2.3.5 Record reference sample values, along with the expected value and date of analysis. Also record the laboratory-assigned log-in numbers of all samples run in the set.

2.3.6 Plot values on a quality control chart as outlined in the practice "Quality control charts." If a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct it before continuing.

2.3.7 At the end of each day's analyses, remeasure the specific conductance and pH of every 30th (nonreference) samples.

2.3.8 Record duplicate sample values along with their lab identification number and date of analysis.

2.3.9 Plot duplicate values on a quality control chart as outlined in the practice "Quality control charts." If differences are greater than warning limits, determine and correct the problem before continuing to make analyses. If differences are greater than control limits, reanalyze the appropriate portion, or all, of the samples.

References

American Public Health Association and others, 1975, Standard methods for the examination of water and wastewater (14th ed.): Washington D.C., American Public Health Association, 1193 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Colorimetric Analysis

1. Application

1.1 This practice applies to the analysis of samples in which a spectrometer is used to measure a unique colored complex formed between the constituent of interest and an appropriate reagent.

1.2 The practice "Inorganic quality control: automated colorimetric or potentiometric analysis," should be used instead of this one if the colored complexes are to be measured using the Technicon AutoAnalyzer.

1.3 Refer also to the practice "Colorimetric spectrometers," in the section "Instrumental Techniques" and the applicable methods in Book 5, Chapter A1, of Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979).

2. Practice

2.1 Preparation of standards, blanks and reagents

2.1.1 Prepare a stock solution and intermediate standards as specified in the analytical method. Intermediate standards should be prepared bimonthly (and dated) or at time intervals specified in the analytical method.

2.1.2 Prepare reagents, if any, as specified in the analytical method. If reagents deteriorate with age, prepare fresh daily, or at time intervals specified in the method.

2.1.3 Prepare working standards and reagent blank, if any. Add all reagents which will be added to the sample. Prepare a minimum of four standards, evenly spaced over the analytical range. If there is any evidence of instability, prepare all working-level standards fresh daily, or at time intervals specified in the method.

2.2 Calibration and measurement

2.2.1 Check light source and cell holder alignment as necessary (see practice "Colorimetric spectrometers" in section "Instrumental Techniques").

2.2.2 Check wavelength calibration every six months (see practice "Colorimetric spectrometers," in section "Instrumental Techniques").

2.2.3 Set wavelength as specified in the method.

2.2.4 Transfer the reagent blank to the cell and set spectrometer to zero absorbance. Record slit width.

2.2.5 Transfer standards to cells and record absorbance.

2.2.6 Keep a record of slit width and absorbance of each element for each instrument. A significant change ($\geq$10 percent) from previous results indicates that a problem exists which must be corrected. This problem may be instrumental (for example, the cell holder is out of alinement) or chemical (for example, a reagent has deteriorated or standards have been incorrectly prepared).

2.2.7 Analyze samples. If concentrations are outside those specified as the analytical range in the procedure, dilute or run by an alternative procedure.

2.2.8 If interferences cannot be avoided, use a standard addition technique or select an alternative procedure.

2.2.9 If color is an interference, it may be possible to compensate for it by using a sample containing all reagents except the indicator reagent or by using a bleaching or adsorption procedure (see section, "Instrumental Techniques").

2.3 Calibration checks

2.3.1 Read a blank and, if the color complex is stable, read in random order a standard after every 10th sample. If the color complex is unstable, sufficient standards must be prepared in the order in which they will be read, so that a standard can be inserted after every 10th sample.

2.3.2 If there is a difference of over 2 percent from the initial readings or if there is noticeable baseline drift, recalibrate the instrument and reanalyze all samples analyzed since the last acceptable calibration check.

2.3.3 For chemical oxygen demand and cyanide, analyze every 10th sample, in duplicate.

2.3.4 When determining boron, bromide, iodide and vanadium, repeat the analysis of every 10th sample either by diluting and using half the original concentration or by spiking with a standard to give double the original concentration.

2.3.5 Record the values in a notebook, along with date of analyses and the laboratory-assigned log-in numbers of all samples run in the set.

2.3.6 Plot values on a quality control chart as outlined in the practice "Quality control charts." If values exceed control limits or if a bias appears to be developing in the results, correct the problem before continuing.

Selected References

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. C., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., Quality assurance practices for health laboratories: Washington, D. C., American Public Health Association, p. 1145–1188.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

U.S. Environmental Protection Agency, 1979, Handbook of analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, 104 p.

Determination of Color or Turbidity

1. Application

1.1 This practice applies to the measurement of color and turbidity.

1.2 Refer also to methods I–1250–78, "Color, electrometric, visual comparision," and I–3860–78, "Turbidity, nephlometric," in Skougstad and others (1979).

2. Practice

2.1 Preparation of standards

2.1.1 Prepare turbidity suspensions as specified in method I–3860–78. The working-level concentration (40 NTU) must be prepared fresh weekly (NOTE 1).

NOTE 1. Sealed suspensions are also available, usually from the instrument manufacturer.

2.2 Calibration and measurement

2.2.1 Measure color in color comparator and turbidity in turbidimeter. Be careful not to entrap bubbles in the glass tubes.

2.2.2 Follow the manufacturer's operating instructions in calibrating the turbidimeter. Prepare a calibration graph for each range of the instrument (unless a precalibrated scale is supplied) as specified in method I–3860–78.

2.3 Calibration checks

2.3.1 At the end of every set of samples, rerun every tenth sample. If possible, use a fresh portion of the sample.

2.3.2 Record duplicate values in a notebook along with the date of analysis and the laboratory-assigned log-in numbers of all samples in the set.

2.3.3 Plot control charts (see practice "Quality control charts").

Selected References

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. L., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., 1978, Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Determination of pH

1. Application or scope

1.1 This practice applies to field and non-automated laboratory measurements of pH.

1.2 Refer also to the practice "Potentiometers," in the section "Instrumental Techniques," to method I–1586–78, "pH, electrometric, glass electrode" in Skougstad and others (1979), and to Water-Supply Paper 1535-H (Barnes, 1964).

2. Practice

2.1 Preparation of buffers

2.1.1 Prepare a minimum of three buffer solutions as specified in method I–1586–78 (NOTE 1).

NOTE 1. Prepared buffer solutions or buffer concentrates are available from instrument and chemical manufacturers.

2.1.2 Date all buffer solutions and prepare fresh every 3 months or when noticeable discoloration or deterioration occurs.

2.2 Calibration and measurement

2.2.1 Check electrodes visually for scratches or cracks and to see if they are filled sufficiently. Check connections between electrodes and meter.

2.2.2 Insert the electrodes in a pH 7.00 buffer.

2.2.3 Measure the temperature and adjust the temperature control.

2.2.4 Adjust the meter reading to give the correct pH value. Check the millivolt scale to be sure the electrode gives a reading that is 0 ± 10 mV.

2.2.5 After rinsing the electrodes thoroughly, insert them in a second buffer. If the reading is over 0.1 pH unit from its theoretical value, adjust the "slope adjustment," if the meter is equipped with one. If the slope adjustment is changed, always go back and recheck the first reading.

2.2.6 If it is known that the pH values of all samples will fall between the two buffers,

the use of a third buffer is unnecessary. In most cases, however, the third buffer should also be used in calibration. All three buffers should read correctly if meter and electrodes are in good condition.

2.2.7 Rinse the electrodes thoroughly between samples and between buffers (NOTE 2).

NOTE 2. It is relatively easy to contaminate a sample or a buffer of high pH with a low pH buffer. A pH of 9 indicates 10^{-9} hydrogen ions while a pH of 4 indicates 10^{-4} hydrogen ions (or 100,000 times the pH 9 hydrogen ion concentration). Electrodes should be rinsed using portions of the solution to be measured; particular care should be used in rinsing before measuring a sample which has a specific conductance of less than 50 μmho.

2.2.8 Be sure to calibrate the meter under the same agitation conditions that samples are to be read.

2.2.9 Measure the temperature of each sample. The sample temperature must not differ from that of the buffer by more than 5°C.

2.2.10 Begin pH measurements (NOTE 3).

NOTE 3. In measuring the pH of ground water, the well must be pumped until readings are stable. Similarly, care must be taken to achieve stable readings in measuring the pH of samples that have a specific conductance less than 50 μmho (such as precipitation samples).

2.3. Calibration checks

2.3.1 Check the calibration of the instrument at least every 3 hours with buffer solutions (NOTE 4). Record the readings in a notebook. Include the date and time of initial calibration and of the calibration checks.

NOTE 4. In the case of most field work, meter should be recalibrated with every site change.

2.3.2 If there has been a noticeable (>.02 pH units) shift in the readings for the buffers, recalibrate the instrument and measure the pH of all samples back to where the shift occurred (Wood, 1976).

2.3.3 Use a reference material as the first sample to be analyzed and as every 30th sample thereafter. The reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, the reason for the discrepancy should be determined and corrected and the pH of all samples from the last "good" reference value should be remeasured.

2.3.4 Record reference sample values, along with the expected value. Also record the laboratory-assigned log-in numbers (or sample identification numbers for measurements made in the field) of all samples analyzed.

2.3.5 At the end of each set of measurements, recheck the pH of every 20th sample. If the set consists of less than 20th analyses, recheck the pH of the first nonreference sample at the end of the set.

2.3.6 Record the duplicate values, in a notebook, along with the date of analysis and all laboratory-assigned log-in numbers of samples run in the set.

2.3.7 Plot values on quality control charts as outlined in the practice "Quality control charts." If values exceed control limits or if a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Selected References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535-H, 17 p.

McClelland, N. J., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris F. L., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

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U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–3—3–4.

Wood, W. W., 1976, Guidelines for collection and field analysis of ground water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 1, Chapter D2, 24 p.

Determination of Solids Concentration

1. Application

1.1 This practice applies to the gravimetric determination of dissolved, suspended, total, and volatile solids concentration.

1.2 Refer to practices "Gravimetry," and "Analytical balances," in the sections on "Standard Quantitative Analysis Techniques," and "Instrumental Techniques," respectively, and to the applicable analytical methods in book 5, chapter A1 of Techniques of Water Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979).

2. Practice

2.1 Calibration and measurement

2.1.1 Check desiccators to see if they have a good seal and if desiccant in them is still effective. Regrease top of desiccator and regenerate or replace desiccant as necessary.

2.1.2 Check temperature of oven to see if it is correct (NOTE 1).

NOTE 1. The setting on the outside may be incorrect and not reflect the actual temperature. The thermometer must be read.

2.1.3 Proceed with the determination following directions specified in the analytical method.

2.2 Calibration checks

2.2.1 Check calibration of oven thermometer with a U.S. National Bureau of Standards certified thermometer at least once a year. Record date checked in a notebook kept near the oven.

2.2.2 Check calibration of analytical balance at least every 3 months using class S weights. Record date of calibration check in a notebook. If recalibration is necessary, consult the manufacturer's directions.

2.2.3 For dissolved solids, analyze 1 reference sample for every 50 samples or 1 in every set if fewer than 50 samples are run.

2.2.4 Analyze every 20th sample, in duplicate (NOTE 2).

NOTE 2. If the amount of water in a sample selected to be analyzed in duplicate is not sufficient for a second analysis, analyze in duplicate the first sample (after the 20th sample) for which there is enough water.

2.2.5 Record the determined and theoretical values or the duplicate values in a notebook. Also record the date of analysis and the laboratory-assigned log-in numbers of all samples which were analyzed.

2.2.6 Plot values on a control chart (see practice "Quality control charts"). If values exceed control limits or if a bias appears to be developing in the results, correct it before continuing.

Selected References

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. C., 1978, Water and wastewater analysis, *in* Inhorn, S. L., ed., Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1., 626 p.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, 104 p.

Determination of Specific Conductance

1. Application or scope

1.1 This practice applies to field and non-automated laboratory measurements of specific conductance.

1.2 Refer to the practice "Conductivity meters," in the section "Instrumental Techniques," and to method I–1780–78, "Specific conductance, electrometric, wheatstone bridge," in Skougstad and others (1979).

2. Practice

2.1 Preparation of standard

2.1.1 Prepare a 0.00702 *N* KCl solution as specified in method I–1780–78. This solution has a conductance 1,000 μmho/cm at 25°C.

2.1.2 Check the specific conductance of each new KCl solution against a previous KCl standard solution. If the specific conductances of the two solutions are different, check both solutions against a third solution prepared by another analyst.

2.2. Calibration and measurement

2.2.1 Visually inspect the electrodes. Platinized electrodes require replatinization every few months. Replatinize electrodes when

platinum black has noticeably flaked off or when readings become erratic; consult method I–1780–78 for directions.

2.2.2 Measure the temperature of the 0.00702 *N* KCl solution to the nearest 0.1°C, and record the temperature. Adjust temperature control knob if applicable.

2.2.3 If the meter is temperature-compensated, adjust it to read 1,000 μmho. If a table of conductance or resistance versus temperature has been prepared, check the meter reading against the value in the table.

2.2.4 Rinse the cell thoroughly with distilled water and then rinse and fill with the first sample (NOTE 1).

NOTE 1. In reading standard KCl solution or samples, care must be taken that air bubbles are not entrapped in the cell.

2.2.5 Measure the conductance (or resistance) of each sample as directed in method I–1780–78 (NOTE 2). Be careful to record or compensate for the temperature of each sample.

NOTE 2. In measuring ground waters, be sure wells are pumped until readings are stable.

2.2.6 Thoroughly rinse the cell with each sample before filling the cell and measuring the conductivity.

2.2.7 If, using different cells, more than one cell constant is used or if instrumental scale changes are available and used, other KCl standard solutions should also be used. See Standard Methods (American Public Health Association and others, 1976) for KCl solutions which have a specific conductance of from 14.94 to 111,900 μmho.

2.3. Calibration checks

2.3.1 Check the calibration of the instrument at least every 3 hours with standard KCl solution (NOTE 3). Record the reading in a notebook. Include the date and time of initial calibration and of the calibration check.

NOTE 3. For field work, recalibrate the meter at each location.

2.3.2 If there has been a noticeable shift in the measurement value of the standard KCl solution, recalibrate the instrument and remeasure the conductivity of all samples back to where the shift occurred.

2.3.3 Use a reference material as the first sample to be analyzed and as every 30th sample thereafter. The reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, the reason for the discrepancy should be determined and corrected, and the specific conductance of all samples from the last "good" reference value reading should be remeasured.

2.3.4 Record reference sample values, along with the expected value. Also record the laboratory-assigned log-in numbers of all samples analyzed in the set.

2.3.5 At the end of each set of conductivity measurements, recheck the specific conductance of every twentieth sample. If the set consists of less than 20 samples, recheck the specific conductance of the first non-reference sample at the end of the set. Record values in a notebook.

2.3.6 Plot reference sample and duplicate results on quality control charts as outlined in the practice, "Quality control charts." If values exceed warning limits or if a bias appears to be developing in the results (for example, all reference sample results are greater than the theoretical), correct for it before continuing.

Selected References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed.): Washington, D.C., American Public Health Association, 1193 p.

McClelland, N. I., Delfino, J. J., Greenberg, A. E., McDonald, D. B., and Morris, R. C., 1978, Water and wastewater analysis, *in* Inhorn, S. L, ed., Quality assurance practices for health laboratories: Washington D.C., American Public Health Association, p. 1145–1188.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

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Wood, W. W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 1, Chapter D2, 24 p.

Electrometric Titration (alkalinity and acidity)

1. Application

1.1 This practice applies to measurements of alkalinity (as $CaCO_3$) and acidity.

1.2 Refer to the practices "Titrimetry," and "Potentiometry," in the sections "Standard Quantitative Analysis Techniques" and "Instrumental Techniques," respectively, and to methods I–1020–78, "Acidity, Electrometric Titration"; I–2030–78, "Alkalinity, Electrometric Titration, Automated"; and I–1568–78, pH, "Electrometric, Glass Electrode," in Skougstad and others (1979).

1.3 For determination of carbonate species concentration, refer to Water-Supply Paper 1535-H (Barnes, 1964).

2. Practice

2.1 Preparation of titrant and buffers

2.1.1 Prepare primary standard as specified in method I–1020–78 or I–2030–78, using potassium hydrogen phthalate for acidity and sodium carbonate for alkalinity.

2.1.2 Prepare standard base (NaOH) or acid (H_2SO_4) solutions as specified in the method. Either standardize to the exact specified normality or determine the normality and use the appropriate factor in subsequent calculations.

2.1.3 Prepare a minimum of three buffer solutions for pH meter calibration. Date all buffer solutions and prepare fresh every 3 months or when noticeable discoloration or deterioration of the buffer occurs (NOTE 1).

NOTE 1. Premixed buffer solutions and buffer concentrates are available from instrument and chemical manufacturers.

2.2. Calibration and measurement

2.2.1 Check electrodes visually for scratches or cracks and to see if they are filled sufficiently. Check connection between electrode and meter.

2.2.2 Standardize the potentiometer using the three buffer solutions.

2.2.3 Titrate the samples with the standard solution to the end point specified in the analytical method.

2.3 Calibration checks

2.3.1 Titrate a primary standard biweekly or in every set, whichever is less frequent.

2.3.2 Calculate and record the normality of the titrant and the date on which the primary standard was analyzed.

2.3.3 If the normality is found to have changed slightly, either restandardize the titrant or adjust the factor used in the calculation of concentrations to reflect the new normality.

2.3.4 For alkalinity, use a reference material as the first sample to be analyzed and as every 20th sample thereafter. The value for the reference material should fall within 1.5 standard deviations of the theoretical value. If it does not, the reason for the discrepancy should be determined and corrected and the concentration of all samples from the last "good" reference value should be remeasured.

2.3.5 For acidity, repeat the analysis of every 10th sample using double the original volume.

2.3.6 Record values, along with the date of analysis. Also record the laboratory-assigned log-in number of all samples analyzed in the set.

2.3.7 Plot the values on a control chart as outlined in the practice "Quality control charts." If values exceed control limits or if a bias appears to be developing in the results, isolate and correct the problem before continuing.

References

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535, 17 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Organic Quality Control

Gas Chromatographic Analysis

1. Application or scope

1.1 This practice applies to measurement by gas chromatography of chlorinated phenoxy acid herbicides, organochlorine insecticides, and organophosphorus insecticides.

1.2 The practice "Gas chromatographs," in the section on "Instrumental Techniques," and the applicable analytical method in Book 5, Chapter A3, of this series should be referred to.

2. Practice

2.1 Preparation of standards, blanks, and reagents

2.1.1 Initially, obtain pesticide standards of the highest available purity from at least two sources. A source for most standards is the U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina (see Watts, 1980).

2.1.2 Preferably, use standards with a purity guaranteed by the supplier and (or) checked in the laboratory. In all other cases, analyze standards from both sources; if results are not equivalent, obtain a standard from another source.

2.1.3 Use distilled water from an all-glass still. In order to obtain water with a low organic background, it may also be necessary to redistill from alkaline permanganate solution or to double extract with an appropriate solvent, such as benzene, followed by boiling to remove residual solvent.

2.1.4 Use "pesticide quality" or "distilled in glass" solvents. Test each lot by concentrating to as great a concentration factor as will ever be used, injecting into the gas chromatograph, and recording detector response for 20 to 30 minutes. There should be no extraneous peaks greater than 10 picograms of heptachlor epoxide on electron capture detectors or 50 picograms of diazinon with a flame photometric detector when the solvent is used as a reagent blank. If potentially interfering peaks are noticeable, redistill the solvent over sodium-lead amalgam or other suitable agent to remove interferences (NOTE 1).

NOTE 1. Some solvents need to be subjected to procedural treatment (such as esterification) to determine if derivatizable interferences exist.

2.1.5 Check all adsorbents and reagents prior to use to insure non-interference with the chromatographic procedure. The tests employed to determine suitability would include the most rigorous test at the lowest detection limit that will be reported by use of the procedure (NOTE 2).

NOTE 2. For example, concentrate hexane by at least a factor of 75 and inject 5 microliters into a gas chromatograph, both before and after cleanup with alumina. There should be no extraneous peaks greater than those indicated above and the width of the solvent peak must not exceed 60 seconds prior to cleanup or 30 seconds after cleanup. If these requirements are not met, redistill the solvent and prepare a different batch of alumina.

2.1.6 Using a microbalance, accurate to at least .001 mg, prepare stock solutions of pesticide standards by accurately weighing between 2.000 and 10.000 mg of appropriate standard. Quantitatively transfer the compound to a 25.0 mL glass-stoppered volumetric flask; dissolve in benzene or other appropriate solvent and dilute to 25.0 mL with the solvent (NOTE 3).

NOTE 3. Benzene is usually the preferred solvent since it is relatively nonvolatile, and the stock solutions can be stored under refrigeration for long periods (Goerlitz and Brown, 1972).

2.1.7 If the purity of the standard is less than 100 percent, apply an appropriate correction factor. For example, if 5.000 mg of a standard which is only 90 percent pure is weighed and diluted to 25.0 mL, the weight of pure material is $5.000 \times 0.90 = 4.500$ mg in the 25.0 mL.

2.1.8 Have concentration calculations checked by another person.

2.1.9 Record all data used in stock solution preparation in a notebook. Include weight, volume, solvent, source of standard, purity, date prepared, and name of analyst who prepared the solution. Stock solutions from both sources (see paragraph 2.1.2, above) must be prepared, preferably by different analysts.

2.1.10 Store stock solutions in the dark, under refrigeration (-15 to -18°C). In general, prepare organophosphorus insecticide stock solutions fresh at least every 4 months and prepare organochlorine insecticide stock solutions fresh at least every 6 months (NOTE 4). Prepare sooner if there is an obvious change, such as a major shift in response factor and the shift is determined not to be due to other causes (such as column failure).

NOTE 4. Specific compounds may not need stock solution prepared this frequently, but, if they are not, it must be documented that they are stable for longer periods. For example, some organophosphorus insecticides may be stable for 6 months and some organochlorine insecticides may be stable for 1 year.

2.1.11 Allow stock solutions to warm to room temperature. Partially fill 100 mL volumetric flasks with appropriate solvent, as specified in the analytical methods, and prepare a minimum of six concentrations of working standards from both original sources using micropipets to transfer stock solutions to flasks and diluting to volume with solvent (NOTE 5).

NOTE 5. Working standards are usually mixtures of several compounds. A DDT standard should be prepared in which DDD and DDE are not mixed since the appearance of these degradation products in a DDT standard solution can be used to monitor for on-column breakdown (Sherma, 1979, p. 66).

2.1.12 Store working solutions in an explosion-proof refrigerator (approximately 5°C) during the night and weekends. Warm to room temperature before each use. Prepare new organochlorine working standards monthly and new organophosphate working standards every 2 weeks. Record all data from preparation, including date, in notebook.

2.2 Calibration and measurement

2.2.1 Extract samples a minimum of three times using the solvent and following the procedure specified in the analytical method (NOTE 6).

NOTE 6. If emulsions form, small amounts of distilled water or acetone may be added to water extractions and small amounts of anhydrous sodium sulfate to sediment plus water mixture in order to break the emulsions.

2.2.2 Simultaneously with the extraction of samples, extract a blank.

2.2.3 Concentrate the extracts as specified in the analytical method (for example, using a Kuderna-Danish evaporator). Do not allow complete evaporation of solvent.

2.2.4 Follow cleanup procedures specified in the method. Generally this involves using at least one microcolumn containing an absorbent (for example, alumina or Florisil), washing with solvent, and concentrating the sample. In some cases, more than one clean-up column will be necessary.

2.2.5 Check tank pressure daily to see if it is sufficient for the days work. Check carrier-gas trap monthly.

2.2.6 Check flow rates daily to see if they are set to those specified in analytical method or instrument manual.

2.2.7 Check oven, inlet, and detector temperatures daily to see if they are set to those specified in the analytical method or instrument manual and if they are remaining stable.

2.2.8 Check septum, "O" rings, and glass injection inserts daily to see if they appear in good condition.

2.2.9 Check recorder daily to see if the gain and speed controls are set properly and if ink supply and paper are sufficient. Clean recorder slide wire monthly.

2.2.10 Check nickel-63 detector monthly using an electrometer to obtain detector profile as specified in the instrument manual. If a poor profile is noted, detector must be cleaned or repaired; installation of a spare detector is recommended to avoid loss of analytical time.

2.2.11 Calibrate the instrument with a series of four to six standards semiannually or when response factors have changed by more than 10 percent, a new column has been installed, or any other major changes have been made in the system. Prepare standard curve as

indicated in the practice "Gas chromatographs," in the section "Instrumental Techniques," and in the method "Pesticides-gas chromatographic analysis," in Goerlitz and Brown, 1972.

2.2.12 Analyze one set of two standards before any samples are analyzed. If a line drawn between the read-out values for these two standards does not parallel the original calibration line or if concentration values differ by more than 10 percent from the values for the same concentrations on the original calibration line, do not proceed with analysis until the problem has been isolated and corrected.

2.2.13 Inject a reagent blank.

2.2.14 At least twice a week, inject a p,p'-DDT standard at a concentration known to give about 50 percent full scale deflection. The standard should be free of p,p'-DDD and p,p'-DDE. Appearance of either of these degradation products indicates on-column breakdown.

2.2.15 Weekly inject an endrin standard at a concentration known to give about 50 percent full scale deflection. Appearance of additional peaks indicates on-column breakdown.

2.2.16 Proceed with the analysis. Inject sample extracts. Allow sufficient time between samples for the last compound to be eluted and for the baseline to return to normal (NOTE 7).

NOTE 7. When injecting standards, blanks, or samples, flush the syringe several times with the standard to be injected, overfill the syringe, withdraw it from the sample container, check it visually for bubbles, discharge the excess solution, and immediately and smoothly inject the extracts.

2.2.17 Analyze all samples, blanks, and standards using a minimum of two different columns. Because a column may not separate all pesticides present, report the lower value obtained.

2.2.18 Confirm the presence of pesticides in concentrations greater than 1.0 μg/L in water or 10.0 μg/kg in sediment by conductivity gas chromatography. Confirm the presence of pesticides in concentrations greater than 2.0 μg/L in water or 20 μg/kg in sediment by gas chromatography-mass spectrometry (unless definite foreknowledge of the presence of a specific compound obviates this need, as in the weekly monitoring of a pesticide known and confirmed to be in a steam).

2.3 Calibration checks

2.3.1 As noted in 2.2.12, analyze one set of two standards before any samples. If instrument conditions change or if the analyst suspects (possibly because of dirty or very concentrated samples) that there may be a problem, inject another set of standards.

2.3.2 If results indicate a problem exists (for example, concentration values differ more than 10 percent from initial values) remake the standards and reinject them. If this does not solve the problem, it must be isolated and corrected and all samples from the last set of standards must be reanalyzed.

2.3.3 Analyze a reagent blank after every set of standards. If baseline drift is indicated, take corrective measure before proceeding with the analysis.

2.3.4 Inject a reference material, if available, as every 20th sample.

2.3.5 If reference material is unavailable, spike extracts of every 20th sample with mixed standard(s) of constituents of interest. If reference material is available but includes very few of the constituents to be analyzed, alternate reference material and spikes on every 20 samples.

2.3.6 Analyze at least one reference material or spike per week.

2.3.7 Spike a natural water sample (tap water is acceptable if nothing else is available) with a suitable reference material or with standards prepared in an acetone matrix. Carry out a complete analysis (including extraction and cleanup) of the spiked and unspiked sample at least once every 30th sample or every 2 weeks, whichever occurs first.

2.3.8 If bottom materials are being analyzed, reanalyze at least one bottom material a week.

2.3.9 Record all values in a notebook. Include expected reference sample concentration, concentration of spike, and date of analysis. Also record the laboratory-assigned log-in numbers of "duplicates" and of all samples run between reference materials or spikes.

2.3.10 Plot values on a quality control chart as outlined in the practices, "Quality control charts." If a bias is noticeable or if the anal-

ysis is out of control, determine the reason and correct before continuing analyses. If a constant bias is known to be inherent in the methodology, adjust all concentrations in order to eliminate the bias and indicate the correction with the results.

Selected References

Goerlitz, D. F., and Brown, Eugene, 1972, Methods for analysis of organic substances in water: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A3, p. 24–40.

Sherma, Joseph, 1979, Manual of analytical quality control for pesticides and related compounds in human and environmental samples: U.S. Environmental Protection Agency EPA–600/1–79–008, Research Triangle Park, North Carolina, 401 p.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 8–1—8–10.

Watts, R. R., 1980, Analytical reference standards and supplemental data for pesticides and other selected organic compounds: U.S. Environmental Protection Agency EPA–600/2–81–011, Research Triangle Park, North Carolina, 182 p.

Quality Control Charts

1. Application or scope

1.1 This practice describes the construction and use of several types of control charts. Control charts indicate trends and variability in analyses which may not be readily apparent from an examination of tabulated results (NOTE 1). They can be effectively used to monitor analytical results in order to determine if bias is developing or if precision is less than expected. When used to monitor the quality of results produced by a particular analyst, control charts can be a helpful training and supervisory tool.

NOTE 1. The scale of the abscissa is in increments of time. The date of analysis will probably be the most useful unit to plot, although other time units can be used.

1.2 If standard reference materials are available for a constituent in sufficient quantity to be analyzed routinely, quality control charts can be constructed from the resulting analytical data. In many cases, large quantities of stable "reference samples" may be prepared by a section head or analyst by adding constituents of interest to either demineralized or ambient water. Results from repeated analyses of spiked (with constituent of interest) or unspiked samples can also be used for control charts.

1.3 Results which fall outside of the established "warning limits" indicate that there may be a problem and should be investigated. Results which fall outside of the "control limits" require that analyses cease being made until the reason for lack of control is determined and corrections are made (NOTE 2).

NOTE 2. Warning limits for the charts in this practice are set at either 1.5 or 2 times and control limits at 3 times the standard deviation of the statistic used. If only normal random errors are present, approximately 86.6 percent of the values should be within 1.5 standard deviations, 95.5 percent should be within 2 standard deviations, and 99.7 percent of the values should be within 3 standard deviations. In general, there should be less than a 0.3 percent chance of deciding on lack of control when there is control.

1.4 Many of the charts described in this practice use average values; their use is desirable because "averages are more sensitive to change than are individuals" (Becking and Gryna, 1974). Such charts are useful if a fixed number of analyses are made on a reference sample in a given time period or for a given number of samples (NOTE 3).

NOTE 3. They can be used, for example, if three analyses of a reference material are always made per day or if one reference material analysis is made for each 20 samples and the results plotted after every 80 samples.

1.5 Other charts described in this practice use individual values and, although less sensitive, have the advantage of being able to be plotted as soon as an analysis is made. Such charts can be particularly useful when it is considered more desirable to make a single analysis of several reference materials containing different concentration levels of a particular constituent than to make several analyses of one reference material (and when time, money, and so forth, prohibit multiple analyses of several reference materials of different concentrations.)

1.6 A value outside of the control limits of a mean concentration chart suggests that there may be an overall change in the method (such as might result from a shift in alinement of the light source in a spectrometer). A value outside of the control limits of a standard deviation or range chart tends to indicate an increased variability in analyses (such as might result from dirty or limp tubing in an analysis using a Technicon AutoAnalyzer). Thus, using both types of charts increases the probability of spotting problems soon after they occur.

1.7 To determine what type of chart to use, consider whether average or individual values are to be plotted, whether the results to be plotted reflect analyses of reference materials or of ambient waters, whether the concentration or range is the parameter of interest, and so forth. Go to 2.1 and (or) 2.4 if values to be

plotted are from analysis of a reference material for a specified, fixed number of times per time period or per number of samples; go to 2.2 if values to be plotted are from individual measurements of up to three reference materials; go to 2.3 if values to be plotted are from a variety of reference materials which have a variety of most probable values and associated standard deviations; go to 2.1 and (or) 2.5 if values to be plotted are from replicate analyses of ambient samples; go to 2.6 if values to be plotted are from spiked samples and are to be used in looking at bias; and go to 2.7 if values to be plotted are from diluted samples and are to be used in looking at bias.

2. Practice

2.1 Mean concentration control chart:

2.1.1 Set up and use this chart if an ambient sample or a reference material is being analyzed a fixed number of times per time period or per given number of samples (for example, the reference sample is analyzed twice a day or twice for each set of 30 samples) (NOTE 4).

NOTE 4. Because there must be sufficient quantity of a stable sample available to be analyzed over a long time period, this chart will usually be more appropriate for use with a reference material.

2.1.2 Decide on the number of times the sample will be analyzed in an analytical sequence or per day (or other convenient numerical or time division).

2.1.3 Indicate concentration along the vertical axis and the date of analysis along the horizontal axis (fig. 5).

2.1.4 If repeated analyses are being made of a reference material, draw a horizontal line to indicate the theoretical (most-probable) concentration. If repeated analyses are being made of an actual sample or of a material prepared (usually by use of "spikes") for the constituent of interest (and the concentration is unknown), calculate:

$$\bar{\bar{x}} = \frac{\Sigma \bar{x}}{N} = \frac{\Sigma(\Sigma x_i/n)}{N} \qquad (22)$$

where

$\bar{\bar{x}}$ = the average of the means of the sets of results,

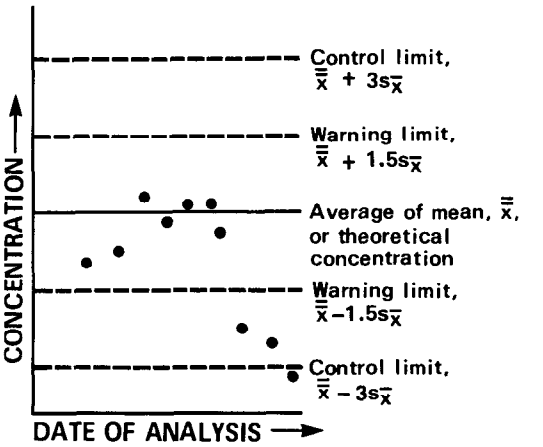

Figure 5.—Concentration control chart: plot of mean values.

$\bar{x}$ = the mean of each set of results,

N = the number of sets of results (NOTE 5),

x_i = the individual results of a set of analyses, and

n = the number of results in a set of analyses.

NOTE 5. In order to have a fairly reliable $\bar{\bar{x}}$, use a relatively large number of sets of results (20 to 30) and keep in mind that it may be necessary to later revise the value for $\bar{\bar{x}}$.

2.1.5 Estimate the standard error of the mean as follows:

2.1.5a If analyses are being made of a reference material and the value for the standard deviation (based on data from the original analyses of the material) which is supplied with the material is based on at least 20 analyses, calculate an estimate of the standard error of the mean (NOTE 6):

$$s_{\bar{x}} = \frac{s}{\sqrt{n}} \qquad (23)$$

where

$s_{\bar{x}}$ = the standard error of the mean,

s = the standard deviation, and

n = the number of results in a set of analyses.

NOTE 6. Since the standard deviation for results of analyses made on the reference material was based on a limited number of analyses, keep in mind that the upper and lower control limits may have to be revised after more analyses are made.

2.1.5b If the standard deviation for analysis is unknown or is likely to be unreliable (if, for instance it was based on only three or four results), calculate the standard deviation for each set of analyses and determine:

$$\bar{s}=\frac{\Sigma s_i}{N} \tag{24}$$

where

$\bar{s}$ = the average of the standard deviations of the sets of analyses,
s_i = the individual standard deviation of each set of analyses, and
N = the number of sets of results (see NOTE 5).

Then calculate an estimate of the standard error of the mean.

$$s_{\bar{x}}=\frac{s}{\sqrt{n}}=\frac{\bar{s}/c_2}{\sqrt{n}} \tag{25}$$

where

$s_{\bar{x}}$ = the standard error of the mean,
s = the standard deviation,
n = the number of results in each set of analyses,
$\bar{s}$ = the average of the standard deviations of the set of results, and
c_2 = factor from table A7 in the appendix.

2.1.5c Alternatively to calculating the standard deviations for each set of results, calculate the range:

$$R=x_H-x_L \tag{26}$$

where

R = the range for a set of results,
x_H = the highest concentration in a set of results, and
x_L = the lowest concentration in a set of results.

Calculate the average range:

$$\bar{R}=\frac{\Sigma R_i}{N} \tag{27}$$

where

$\bar{R}$ = the average range of the sets of results,
R_i = the individual range of each set of results, and
N = the number of sets of results (see NOTE 5).

Calculate an estimate of the standard error of the mean:

$$s_{\bar{x}}=\frac{\bar{R}/d_2}{\sqrt{n}} \tag{28}$$

where

$s_{\bar{x}}$ = the standard error of the mean,
$\bar{R}$ = average range of the sets of results,
n = the number of results in each set of analyses, and
d_2 = factor from table A8 in the appendix (NOTE 7).

NOTE 7. The control limits can be determined more directly by multiplying $\bar{R}$ by the factor A_2 also found in table A8. $A_2=3/d_2\sqrt{n}$(Grant and Leavenworth, 1974) and is, for example, 1.88, 1.02, and 0.73 for sets of 2, 3, and 4, respectively.

2.1.6 Draw short-dashed horizontal lines at ± 1.5 times the standard error of the mean and long-dashed lines at ± 3 times the standard error of the mean to mark warning and control limits, respectively (fig. 5).

2.1.7 After each set of analyses, plot the mean concentration. Use different symbols for values obtained by different analysts, if desired, in order to monitor the "quality control" of the analyst as well as that for the constituent.

2.1.8 If a bias appears to be developing (for example, all values are positive), or if several analyses are beyond the warning limits (even if some are positive and some are negative), investigate the analytical technique used and make necessary corrections. (See step 2.6.8 for more information on deciding on bias.) If an analysis is beyond the control limit, discontinue making analyses until the reason for lack of control has been determined and corrected.

2.2 Concentration control chart, using individual results

2.2.1 Set up and use this chart if reference materials are analyzed and individual results are to be plotted. Use, for example, if several different reference materials are analyzed each day (NOTE 8).

NOTE 8. It is desirable to use reference materials containing concentrations of the constituent to be analyzed in both the high and low areas of the analytical range. In order avoid confusion, it is recommended that the chart be limited to a maximum of three reference materials per constituent.

2.2.2 Indicate concentration along the vertical axis and the date of analysis along the horizontal axis (fig. 6).

2.2.3 Draw horizontal line(s) to indicate the theoretical (most-probable) concentrations of reference material(s). Draw short-dashed horizontal lines at ± 1.5 standard deviations from the theoretical concentration and long-dashed horizontal lines at ± 3 standard deviations to mark warning and control limits respectively.

2.2.4 Plot each analysis of a reference sample, immediately. Use a different symbol or different color for different reference samples. A different symbol or color can also be used for different analysts and the "quality control" of the analyst watched as well as monitoring each constituent.

2.2.5 If a bias appears to be developing (for example, all values are positive), or if several analyses are beyond the warning limits (even if some are positive and some negative), investigate the analytical technique used and make necessary corrections. (See step 2.6.8 for more information on deciding on bias.) If an analysis is beyond the control limit, discontinue making analyses until the reason for lack of control has been determined and corrected.

2.3 Standard deviation increment control chart

2.3.1 Set up and use this control chart if several different reference samples having different theoretical (most-probable) concentrations and standard deviations are to be used. Use this chart if a number of "reference materials" containing different concentrations of the constituent of interest are available (prepared, perhaps, by mixing different reference materials or by spiking deionized water) and if an estimate of the standard deviation can be made using the equations developed for interlaboratory or intralaboratory precision (see section "Analytical Methods Development Procedures").

2.3.2 Indicate number of standard deviations along the vertical axis and the date along the horizontal axis (fig. 7). Draw a horizontal line at 0 and draw short-dashed horizontal lines at ± 1.5 for warning limits and long-dashed horizontal lines at ± 3 for control limits.

2.3.3 Immediately following the analysis of a reference sample determine the sign (posi-

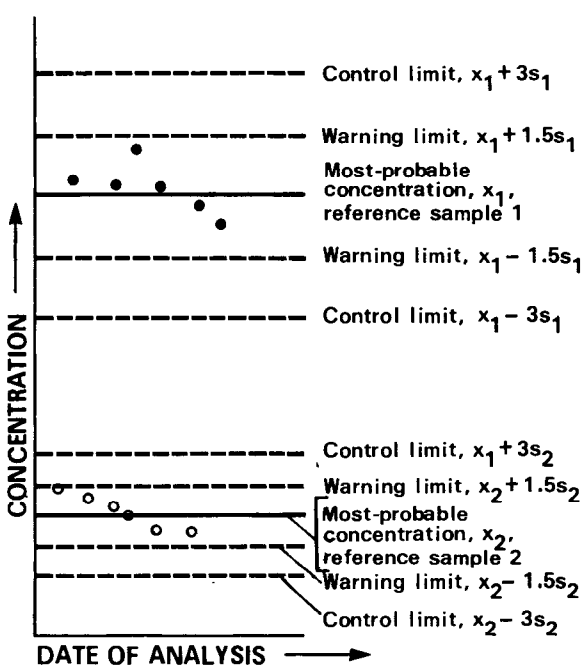

Figure 6.—Concentration control chart: plot of individual values.

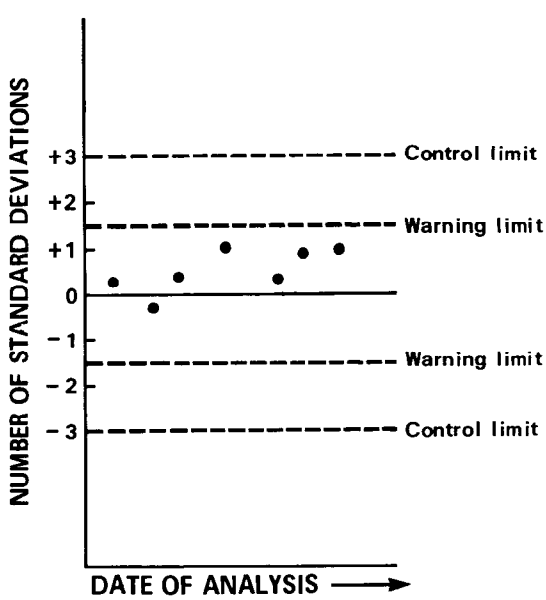

Figure 7.—Standard deviation increment control chart.

tive or negative) and number of standard deviations which the analyzed concentration is from the theoretical concentration:

$$V = \frac{x_a - x_t}{s_t} \qquad (29)$$

where

V = the value to be plotted,
x_a = the analyzed concentration,
x_t = the theoretical concentration, and
s_t = the theoretical standard deviation.

2.3.4 Plot the value.

2.3.5 If a bias appears to be developing (for example, all values are positive or negative) or if several analyses are beyond the warning limits (even if some are positive and some are negative), investigate the analytical technique used and make corrections. If an analysis is beyond the control limit, discontinue analysis until reason for lack of control has been determined and corrected.

2.4 Standard deviation or range control chart, using reference materials

2.4.1 Set up and use this control chart if a reference material is being analyzed a fixed number of times per time period or per number of samples. Use in conjunction with a mean concentration control chart (see paragraph 2.1).

2.4.2 Decide on the number of times the sample will be analyzed in an analytical series or per day (or other convenient numerical or time division).

2.4.3 Indicate increments of concentration along the vertical axis and the date along the horizontal axis (figs. 8 and 9).

2.4.4 Calculate the standard deviation or range for each set of analyses. Then calculate the average of the standard deviations of the set of results, $\bar{s} = \Sigma s_i/N$ (see 2.1.5b above) or calculate the average range, $\bar{R} = \Sigma R_i/N$ (see 2.1.5c above) (NOTE 9).

NOTE 9. Although for the mean concentration control chart, the standard deviation or range for each set of analyses will need to be calculated only when initially setting up the control chart, for this control chart (the standard deviation or range control chart) either the standard deviation or range must be calculated for each successive set of analyses. Because it is easier to calculate the range for each set than it is to calculate the standard deviation, it is recommended that the range control chart be used. As is pointed out in Grant and Leavenworth (1974, p. 89), the $\bar{R}$ control chart is also preferable, because it is easier to understand "range" than it is to understand "standard deviation."

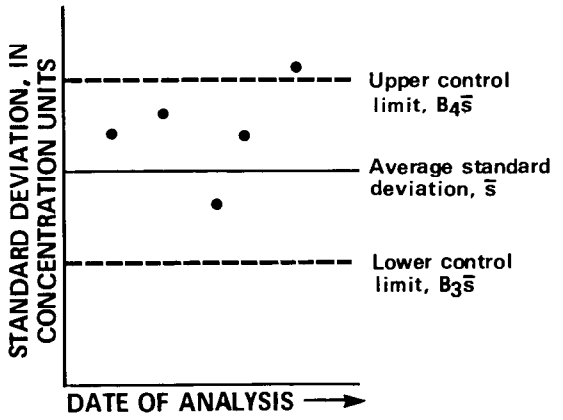

Figure 8.—Standard deviation control chart for replicate analyses.

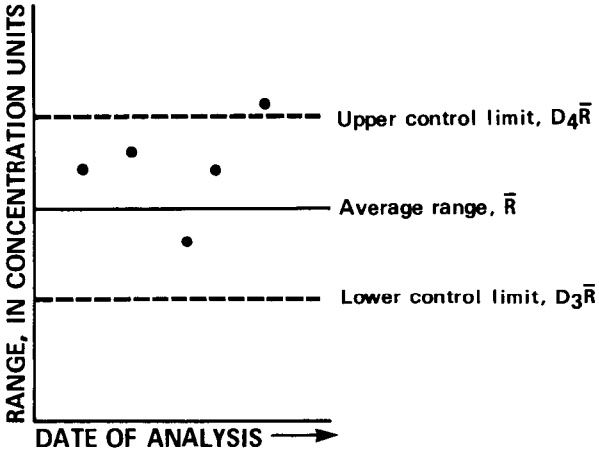

Figure 9.—Range control chart for replicate analyses.

2.4.5 Calculate and draw lines for control limits for the standard deviation or for the range:

Upper control limit = $B_4\bar{s}$
Lower control limit = $B_3\bar{s}$
Upper control limit = D_4R
Lower control limit = D_3R

where values for B_4 and B_3 are from table A9 and values for D_4 and D_3 are from table A10 (NOTE 10).

NOTE 10. For samples analyzed in duplicate, lower control limits are zero, and D_4 = 3.267 (fig. 10). A warning limit set to include 95 percent of the values can be drawn at 2.456 (Youden, 1975).

2.4.6 Immediately after analyzing a set of samples, calculate the range (or standard deviation) and plot on the control chart.

2.4.7 If a determined value is outside the upper control limit, discontinue further analyses until the reason for the lack of control has been determined and corrected. Values falling below the lower control limit suggest that the initial $\bar{s}$ or $\bar{R}$ is in error and that a smaller value could be used.

2.5 Range control chart, using duplicate or replicate analyses of actual samples.

2.5.1 Set up and use this control chart if a proportion of all analyses made are being repeated. Use to supplement charts prepared with reference samples in order to get an idea of the quality of analytical results for actual samples (since the actual samples have much more varied composition than is possible for a few reference materials) or use when a reference material is not available for the constituent of interest (if, for example, the constituent is not sufficiently stable for a reference material to be prepared).

2.5.2 After considering the analytical method, number of samples routinely run for the constituent, and so forth, determine both how many times a sample will be analyzed (often duplicate analyses will be specified) and the frequency of samples to be reanalyzed. (Analyze every 10th sample in duplicate, for example.)

2.5.3 Indicate increments of concentration along the vertical axis and the date along the horizontal axis.

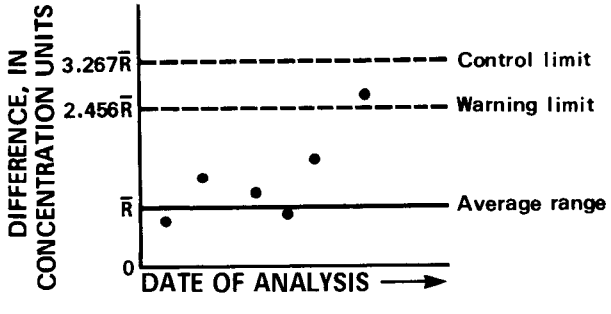

Figure 10.—Range control chart for duplicate analyses.

2.5.4 If the difference in concentrations of duplicate analyses (or the deviation of replicate analyses) is known or has been determined to be constant throughout the analytical range, follow the procedure outlined in paragraph 2.4 above to set up a control chart similar to figure 10. (Probably temperature measurements would fall into this category.)

2.5.5 If the differences in analytical results are known or suspected to vary with concentration (which is likely to be the case in environmental analyses), but the naturally occurring concentration range of the constituent is very narrow, it may be possible to consider the differences constant throughout the range and follow the procedure outlined in paragraph 2.4.

2.5.6 In most cases where the differences vary with concentration, it will be necessary to determine the appropriate regression model (NOTE 11).

NOTE 11. It may also be possible to set up several different concentration ranges and apply the appropriate factor for each range (see EPA, 1979). However, this will often cause interpretation problems in "border-line" cases. Thus, if 0.5 µg/L difference is allowed for concentrations less than 5 µg/L and 1.5 µg/L difference is allowed for concentrations between 5 and 10 µg/L, the limit of 1.5 µg/L might be considered suspect for a value of exactly 5 µg/L.

2.5.6a After a sufficient number of duplicate or replicate analyses have been made throughout the concentration range, plot the difference or range for each set on the vertical axis and the mean concentration for each set on the horizontal axis (fig. 11).

2.5.6b Apply appropriate factors to determine limits. For duplicates, apply 2.456 for warning limits and 3.267 for control limits (see fig. 11).

2.5.6c Set up a control chart by indicating proportion of "theoretical" difference along the vertical axis and the date along the horizontal axis (fig. 12). Draw a horizontal line at 1.0 (which would indicate the observed difference and difference determined from the regression model are the same). Draw a short-dashed horizontal warning line at 2.456 (for duplicates) and a long-dashed horizontal control line at 3.267 (for duplicates), or at appropriate values if more than two analyses will be made on the sample.

2.5.6d Each time "duplicate" (or replicate)

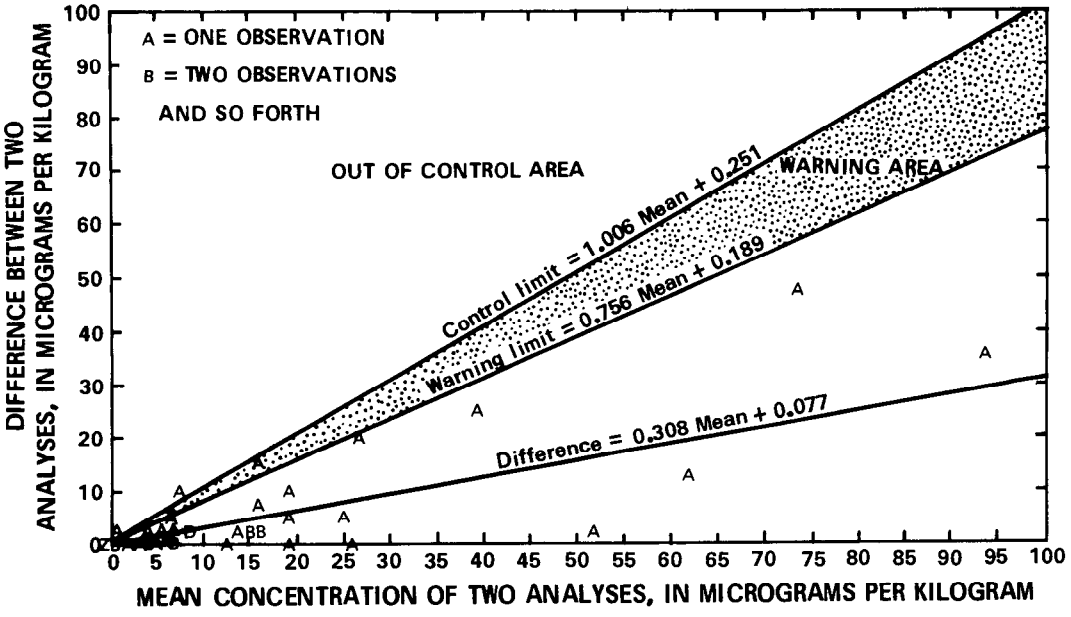

Figure 11.—Tentative model for duplicate analyses of polychlorinated biphenyls, total in bottom material.

analyses are made, determine the mean concentration:

$$\bar{x}=\frac{x_1+x_2}{2} \qquad (30)$$

where

$\bar{x}$ = the mean concentration of constituent of interest,

x_1 = the concentration of constituent of interest found in sample 1, and

x_2 = the concentration of constituent of interest found in sample 2.

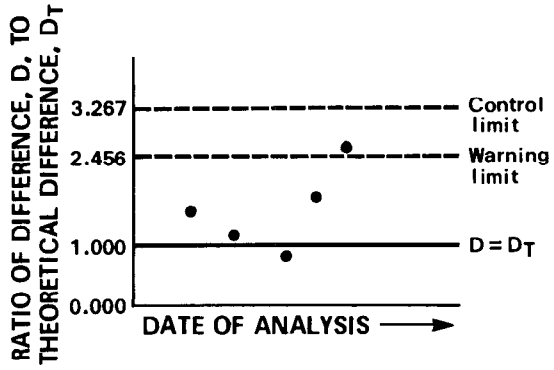

Figure 12.—Control chart for difference in duplicate analyses, for cases in which the difference between analyses varies with mean concentration.

2.5.6e Using the appropriate regression model, calculate the most-probable difference, D_t.

2.5.6f Calculate the difference between the "duplicate" analyses:

$$D=|x_1-x_2| \qquad (31)$$

where

D = the difference between duplicate analyses, and

x_1 and x_2 are as previously defined.

2.5.6g Determine the value to be plotted:

$$V=\frac{D}{D_t} \qquad (32)$$

where

V = the value to be plotted, the proportion of the theoretical difference,

D = the difference between duplicate analyses, and

D_t = the theoretical (most-probable) difference.

2.5.6h Plot the value after each set of analyses. If several values are outside of the warning limits, investigate the analytical technique used and make corrections. If an analysis

is beyond the control limit, discontinue analyses until the reason for lack of control has been determined and corrected (NOTE 12).

NOTE 12. If values are consistently less than "one," the regression model may be in error and allow differences which are "too large."

2.6 Bias control charts, using spikes

2.6.1 Set up and use this control chart if samples are to be analyzed both with and without a spike (known amount of constituent of interest).

2.6.2 Determine the frequency of samples to be spiked (for example, every 20th sample in an analytical series) depending on the method, instrument, number of samples analyzed per day, and so forth.

2.6.3 Analyze samples prior to spiking.

2.6.4 For a sample in which the original concentration is in the low portion of the range, add a spike which is sufficient to double the concentration. For a sample in which the original concentration is relatively high, add a spike small enough to ensure that the final concentration is not near the top of or outside of the analytical range. If it has been determined that the original concentration of the sample requires that a one-half dilution be made in order to be analyzed, add a spike such that the resulting concentration will also require a one-half dilution (NOTE 13).

NOTE 13. In quality control monitoring, usually only one spike concentration is added for a sample. This should not be confused with the method of standard additions in which multiple spikes of several concentrations are added.

2.6.5 Prepare a control chart. Indicate concentration (both "+" and "−") along the vertical axis and the date along the horizontal axis (fig. 13). Draw a solid horizontal line at "0" difference.

2.6.6 After the analyses, plot the difference between the known and determined concentrations of the spike (NOTE 14).

NOTE 14. Always subtract the known concentration from the determined concentration of the spike.

2.6.7 Use the binomial distribution to determine criteria for assuming positive or negative bias (NOTE 15). For a risk of about 1 percent of assuming bias where there is none (compared to a 0.3 percent risk for a 3 standard deviation limit), check to see if 7 out of 7 successive positive or negative points, 10 out of 11, 12 out of 14, 14 out of 17, or 16 out of 20 successive positive or negative points are either positive or negative (Grant and Leavenworth, 1974, p. 97–98). Similarly check for 19 out of 25, and 22 out of 30 positive or negative successive points. If the number of points on one side of the zero line meet or exceed these criteria, investigate (and correct if necessary) the reason for the possible bias before continuing with the analysis (NOTE 16).

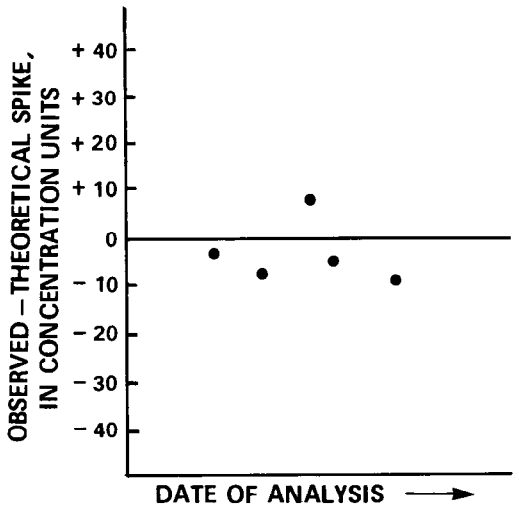

Figure 13.—Control chart for bias, based on recovery of spike.

NOTE 15. Use the formula:

$$P(x)=2\left\{\sum_{i=x}^{N}\frac{N!}{i!(N-i)!}(\tfrac{1}{2})^{i}(\tfrac{1}{2})^{N-i}\right\} \qquad (33)$$

where

$P(x)$ = the probability of having x or more points on the same side of the zero line,

N = the number of successive points, and

i = the number of points on the same side of the zero line.

The 2 is used to multiply the sum because a run of points above or below the line must be considered. See Grant and Leavenworth (1974, p. 235–236) for further explanation.

NOTE 16. The bias of results from a single sample could be due to factors such as an unsuspected matrix interference or glassware contamination. Note also that any inherent bias in an analytical method should have been determined during the development of the method and applied when reporting results.

2.7 Bias control chart, using diluted replicates

2.7.1 Set up and use this control chart instead of the spike recovery control chart if the use of spikes is undesirable for some reason (for example, the pure constituent is difficult to obtain) (NOTE 17).

NOTE 17. The bias must be constant over the analytical range.

2.7.2 Determine the number and (or) intervals of samples to be run as a dilution depending on the method, instrument, number of samples analyzed per day, etc. For example, a dilution of every 10th sample might be made and analyzed.

2.7.3 Determine an estimate of the bias for a sample using the following example as a guide: Consider a sample which contains a "true" concentration of 440 mg/L of a constituent. Analysis of the sample yields a result of 500 mg/L (a positive 60 mg/L bias) and a repeat analysis still gives 500 mg/L. However, when a one-half dilution is made, rather than finding the expected concentration of 250 mg/L, the concentration is found to be 280 mg/L (220 mg/L + 60 mg/L). The amount of the bias may be estimated by plotting the results (fig. 14). Rather than going through the origin, the line will intercept the y-axis at a point equal to the "bias concentration."

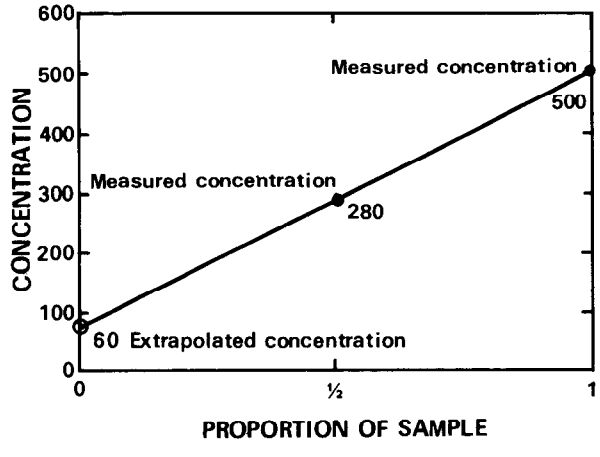

Figure 14.—Determination of bias using a diluted duplicate sample.

2.7.4 Indicate concentration (both "+" and "−") along the vertical axis and the date along the horizontal axis (see fig. 13).

2.7.5 After the analyses, plot the estimated bias for the sample.

2.7.6 Proceed as in step 2.6.8 to determine whether there is reason to assume a positive or negative analytical bias.

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Quality Control Duties and Responsibilities of Section Leader

1. Application or scope

1.1 This practice describes quality control responsibilities of the section leader or, in small laboratories, of the laboratory chief. In general, it also applies to field operations. Although many of the duties may be delegated, the responsibility may not.

1.2 Refer also to the quality control and quality assurance practices outlined in this manual, and to the appropriate analytical methods.

2. Practice

2.1 Methods

2.1.1 Be familiar with all methods and equipment in use.

2.1.2 Be sure each analyst has a written copy of methods to be used.

2.1.3 Know which methods should be used and when.

2.1.4 Be aware of samples that require special handling or analysis and ensure that they are analyzed by the correct procedure.

2.1.5 If a sample requires a slight method modification, approve, have recorded, and initial the results. Be sure that the effect of a modification has been tested and recorded.

2.1.6 Do not allow major methodology changes in the section, unless there has been formal documentation of data and approval has been obtained.

2.1.7 Be sure any required qualitative or quantitative confirmation of analysis (such as in gas chromatography) is made.

2.2 Training

2.2.1 Train or assign an experienced analyst to training new employees. If delegated, this duty is performed by one or at the most two senior analysts who have a formal, recognized function of training all new employees.

2.2.2 Until the quality of work of a new employee is at least equivalent to existing employees, do not allow new employee to work alone. Use quality control charts or other data review procedures to verify quality.

2.2.3 Be sure that training is sufficient before allowing new methods or new instruments to be used. Take advantage of training courses offered by instrument manufacturers.

2.2.4 Become familiar with each new method, instrument and technique; do not simply assign an analyst to learn about it.

2.3 Standard and reagent preparation

2.3.1 Be sure all standards and reagents are of correct quality grade.

2.3.2 Record lot number and "date-opened" of each standard and reagent.

2.3.3 Prepare (or assign an experienced analyst to prepare) stock standard solutions.

2.3.4 Check or have a different experienced analyst check all calculations relating to stock standard preparation.

2.3.5 Whenever possible, insure the correct preparation of stock standards by cross-checking. For example, a chloride standard of sodium chloride can be analyzed for sodium, and a new standard solution can be compared against an old standard solution.

2.3.6 Date all stock, intermediate, and working standards and reagents and record the dates in a notebook along with data pertaining to their preparation. Set up a system for monitoring the stability of standards. Discard all solutions immediately on reaching the expiration date specified in the method.

2.4 Instrumental

2.4.1 Be sure that required operational and calibration procedures are performed, that required checks are performed, and that all data are recorded in a notebook.

2.4.2 If an instrument is shared by more than one section, one section leader should be responsible for primary calibration check; be sure it is clear to which section the responsibility is assigned. For example, analytical balances

must be checked at least every 3 months using Class S weights and a record of this check kept; unless each section maintains its own balance, checking to ensure that this recalibration check is done would probably fall under the jurisdiction of the section most likely to use the balances.

2.4.3 Be sure any maintainence is promptly done and that any instrument not in proper working order is not used.

2.5 Analyst quality control

2.5.1 Be sure all required standards, blanks, reference materials, spikes, duplicates, and so forth, are analyzed.

2.5.2 Be sure all quality control information is recorded in a notebook, along with the date of analysis and all laboratory-assigned log-in numbers of samples that were analyzed.

2.5.3 Be sure required quality control charts are maintained.

2.5.4 At least weekly, check and initial all quality control data. Be sure that problems (such as bias or lack of control) are being caught and corrected.

2.5.5 Monitor quality of work of all analysts in section, especially of newer analysts. A quality control chart for each analyst or one in which all analyst's data are recorded is a good way to conduct this monitoring.

2.6 Investigation of quality control problem

2.6.1 If a quality control problem is noticed by the section leader or is reported by the laboratory's quality control staff, personally investigate to find the cause.

2.6.2 Ensure that corrective action is taken. In making any necessary changes, clearly explain to the analyst(s) why such changes are being made (NOTE 1).

NOTE 1. Often quality control problems continue, because the analyst is unaware that there is a problem, because an improper modification of a method has been made and has existed for so long that it is accepted by the analyst, or because analysts are convinced that if they report a problem, nothing will be done. Clear explanations often solve the problem.

Selected Reference

American Society for Quality Control, 1977, Guide for reducing quality costs: Milwaukee, American Society for Quality Control, p. 27–28.

Quality Assurance Monitoring

In this and the preceding section, the term "quality control" is used when considering the effort made within a laboratory or analytical section of a laboratory to control the quality of the analytical data produced. The phrase "quality assurance monitoring," on the other hand, is considered here not only to involve practices employed by an outside source to assure the quality of the laboratory, but also encompasses practices used by the heads of large laboratories to assure the quality of their laboratory.

Quality assurance efforts should constitute a minimum of about 15 percent of the workload for any determination. This percentage should approach 30 percent for rarely used methods or rarely determined constituents.

Analytical Data Review and Quality Assurance

1. Application or scope

1.1 This practice describes data quality assurance checks made by a computer to aid the quality assurance staff of the Central Laboratories System. Quality control techniques, largely developed prior to 1940 (Howard, 1933; Durum, 1978), plus results from several years of analyses made by the Central Laboratories were used to develop the computer program. All checks described in this practice may also be made by a reviewer using a simple, desk-top calculator.

1.2 The completed analytical report for each sample should be reviewed to determine the acceptability of the analytical data prior to its release outside of the laboratory. Although the quality assurance checks are a guide, the reviewer must judge whether there is a reason for the data to have "failed" a check. This practice details many possible reasons which must be considered for such "errors."

1.3 After receiving the analytical report, the requestor(s) of the analyses must review it. Because the requestor is expected to be familiar with the sampling site (which the analyst is unlikely to be), he may spot questionable values which were not apparent in the laboratory data review.

2. Practice

2.1 Computerized data review

2.1.1 A check is made to determine if bicarbonate, calcium, magnesium, potassium, silica, sodium, sulfate, specific conductance, or calculated solids have been reported as present in the sample. If any of them are reported as present, their corresponding values are checked; if any values have been reported as zero, a warning message so indicating is printed.

2.1.2 A check is made to determine if sodium and potassium are present in the analysis. If they are, the values are compared. If sodium is less than potassium and potassium is greater than 10, a warning message stating that sodium is less than (<) potassium is printed.

2.1.3 A check is made on the pH value and if it is less than 4.5, or greater than 9.0, a warning message is printed.

2.1.4 A check is made to see if calcium, magnesium, and sodium are in the analysis. If this minimum number of major cations plus specific conductance have been reported to be present, then the total milliequivalents of all cations is computed and used to calculate a total cation/0.01 conductance ratio. If the ratio falls outside the range of 0.92 to 1.24, a warning message is printed.

2.1.5 A check is made to see if bicarbonate, carbonate, chloride, and sulfate are in the analysis. If this minimum number of anions plus specific conductance are present, then the total milliequivalents of all major anions are computed and used to calculate a total anion/0.01 conductance ratio. If the ratio falls outside the range of 0.92 to 1.24, a warning message is printed.

2.1.6 A check is made to see if calculated dissolved solids and specific conductance have been reported for the sample. If they are, then a calculated solids/conductance ratio is computed. If the ratio is outside the range of 0.55 to 0.81, a warning message is printed.

2.1.7 A check is made to see if dissolved solids (residue on evaporation at 180°C) and specific conductance are in the analysis. If they are then a dissolved solids/conductance ratio is computed. If the ratio is outside the range 0.55 to 0.86, a warning message is printed.

2.1.8 A check is made to see if the dissolved solids (residue on evaporation at 180°C) and calculated solids are in the analysis. If they are, then a dissolved solids/calculated solids ratio is computed. If the ratio is outside the range 0.90 to 1.12 a warning message is printed.

2.1.9 A check is made to see if a percent difference can be computed using the sums of the milliequivalents of major cations and anions. If a check can be, it is computed and compared to the curve shown in figure 15. If the percent difference is in the rejection zone, a warning message is printed.

2.1.10 A check is made to compare selected dissolved and total (or total recoverable) constituent concentrations if they were reported (table 8). If the total or total recoverable concentration for a constituent is not equal to or greater than the dissolved concentration for that constituent (within specified limits), a warning message so indicating is printed.

2.1.11 A check is made of certain dissolved, suspended, and total solids concentrations (table 9). If a dissolved and (or) suspended concentration exceeds the total concentration, a warning message is printed.

2.1.12 A check is made to see if reported concentrations for any constituent listed in table 10 exceed the tabulated value. If the tabulated value is exceeded, a warning message is printed indicating that the value increases the milliequivalent sum.

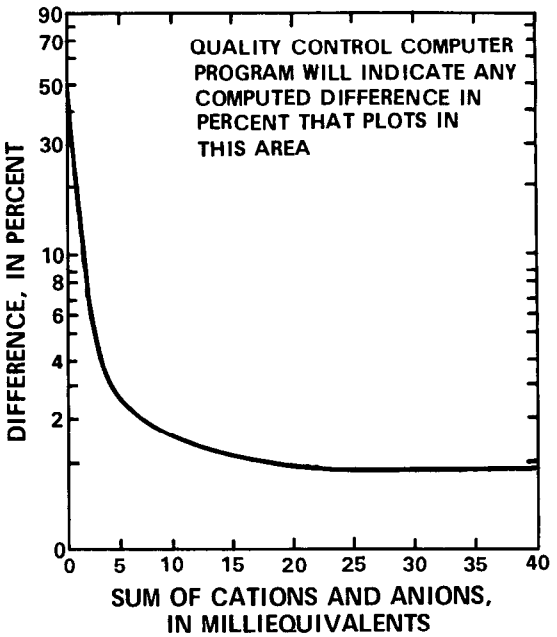

Figure 15.—Cation and anion percent difference curve.

2.2 Data review by laboratory quality assurance staff

2.2.1 In the Central Laboratories, each analytical report is accompanied by a sheet listing all applicable computer messages (fig. 16). The laboratory's quality assurance staff must review this information and examine each analytical report for anomalies.

2.2.2 Because extremely low values should be reported by the analyst as "less than" the appropriate detection level, the reviewer should be aware that a "zero" concentration usually indicates an error.

2.2.3 The reviewer should realize that, although "concentrations of potassium more than a few tens of milligrams per liter . . . are . . . unusual" (Hem, 1970) and that although the concentration of sodium in ambient water is usually greater than the concentration of potassium, neither of these relationships is always true. Similarly, the reviewer should be aware that, although the concentration of calcium is usually greater than magnesium, the two ions

may be nearly equal (as in waters from a dolomitic formation, for instance) or magnesium may be the predominent ion (in some brines, for instance).

2.2.4 When large percent differences between the milliequivalents of cations and milliequivalents of anions are observed, the reviewer must consider the following:

2.2.4a If not all the major ionic species have been determined, the sum of milliequivalent values may be in error.

2.2.4b If an analytical determination includes undissociated as well as dissociated species, the corresponding milliequivalent value may be "too large." Published dissociation constants may aid in evaluating the analysis.

2.2.4c In acidic samples, the calculations of milliequivalents of hydrogen ion from the pH may be in error because of the effect of other ions on hydrogen ion activity.

2.2.4d Because alkalinity (and acidity) are determined by titration, weak-acid radicals other than carbonate species (such as phosphate or borate) may be included twice in the summation of anion milliequivalents (once as part of the titration and again as part of the specific constituent analysis).

2.2.5 When large differences between the calculated dissolved solids and the dissolved solids determined by residue on evaporation are observed, the reviewer must consider the following:

2.2.5a The residue may contain organic and inorganic materials which were not specifically determined in the analysis. The measured residue will appear high.

2.2.5b The residue may contain water of hydration (for example, if high in calcium sulfate). The measured residue will appear high.

2.2.5c Certain constituents may be volatilized in the determination of the residue; for example, waters which are high in magnesium chloride may show a loss of chloride, and waters high in nitrate may show a loss of nitrate. The measured residue will appear low.

2.2.5d Weak-acid radicals other than carbonate species (such as phosphate, borate, and silica) may be included in the alkalinity value and also specifically be determined. The calculated value will appear high.

2.2.6 When ratios of dissolved solids to specific conductance which fall outside of the allowable range are observed, the reviewer must consider the following:

2.2.6a Waters which are high in silica or saturated with respect to gypsum may give ratios as high as 1.0.

2.2.6b The dissolved solids/specific conductance ratios for very dilute waters, such as precipitation samples, or for waters which are high (over 30,000 mg/L) in dissolved solids show great variability and are not a useful check on the analysis.

2.2.7 The quality assurance staff must request redetermination of any constituent in which an error is suspected to have been made.

2.2.8 The quality assurance staff evaluates results from reanalyses and, if it is judged that an error (or errors) was made in analysis (or in transcribing results, and so forth), the new value(s) is entered into the data file and a revised analytical report is generated.

2.3. Review by requestor of analyses

2.3.1 After computer and laboratory quality assurance staff data review and approval of the analysis, the analytical report is released to the individuals who requested the analyses.

2.3.2 In the Central Laboratories, all samples are retained for two weeks after approval of the analysis by the laboratory quality assurance staff. During this time, the individuals responsible for requesting the analysis (district or project personnel) must review the analytical report.

2.3.3 Such individuals are expected to be familiar with the site where the sample was collected. Using this knowledge plus historical records, they determine whether any values appear "unreasonable."

2.3.4 If, during the 2-week limit, the "outside" reviewers feel that an error may have been made, they inform the laboratory's quality assurance staff and request that the laboratory reanalyze the sample (for a stable constituent). The quality assurance staff reports the value from reanalysis directly to the requesting reviewers.

Table 8.—Computerized comparison of dissolved and total or total recoverable constituents

WATSTORE code	Constituent	Computer check	WATSTORE code	Constituent
01105	Aluminum, total recoverable	>	01106	Aluminum, dissolved
01030	Chromium, dissolved	>	01030	Chromium, hexavalent
01045	Iron, total recoverable	>	01046	Iron, dissolved
01055	Manganese, total recoverable	>	01056	Manganese, dissolved
00625	Nitrogen, ammonia plus organic as N, total	>	00610	Nitrogen ammonia as N, total
00625	Nitrogen, ammonia plus organic as N, total	>	00623	Nitrogen, ammonia plus organic as N, dissolved
00625	Nitrogen, ammonia plus organic as N, total	>	00608	Nitrogen, ammonia as N, dissolved
00745	Sulfide, total	>	00746	Sulfide, dissolved
00680	Carbon, organic, total	>	00681	Carbon, organic, dissolved
00610	Nitrogen ammonia as N, total	>	00608	Nitrogen ammonia as N, dissolved
00666	Phosphorus as P, dissolved	>	00671	Phosphorus, orthophosphate as P, dissolved
00665	Phosphorus as P, total	>	00666	Phosphorus as P, dissolved
00665	Phosphorus as P, total	>	00671	Phosphorus, orthophosphate as P, dissolved
00665	Phosphorus as P, total	>	70507	Phosphorus, orthophosphate, as P, total
00500	Solids, residue at 105°-110°C, total	>	70300	Solids, residue at 180°C, dissolved
71900	Mercury, total	>	71890	Mercury, dissolved
00631	Nitrogen, nitrite plus nitrate as N, dissolved	>	00613	Nitrogen, nitrite as N, dissolved
01002	Arsenic, total	>	01000	Arsenic, dissolved
01007	Barium, total	>	01005	Barium, dissolved
01012	Beryllium, total	>	01010	Beryllium, dissolved
01027	Cadmium, total	>	01025	Cadmium, dissolved
00916	Calcium, total	>	00915	Calcium, dissolved
01034	Chromium, total	>	01030	Chromium, dissolved
01037	Cobalt, total	>	01035	Cobalt, dissolved
01042	Copper, total	>	01040	Copper, dissolved
01051	Lead, total	>	01049	Lead, dissolved
00927	Magnesium, total	>	00925	Magnesium, dissolved

Table 8.—Computerized comparison of dissolved and total or total recoverable constituents—Continued

WATSTORE code	Constituent	Computer check	WATSTORE code	Constituent
01062	Molybdenum, total	>	01060	Molybdenum, dissolved
01067	Nickel, total	>	01065	Nickel, dissolved
00623	Nitrogen, ammonia plus organic as N, dissolved	>	00608	Nitrogen, ammonia as N, dissolved
01022	Boron, total	>	01020	Boron, dissolved
00951	Fluoride, total	>	00950	Fluoride, dissolved
01132	Lithium, total	>	01130	Lithium, dissolved
00669	Phosphorus, hydrolyzable as P, total	>	00672	Phosphorus, hydrolyzable as P, dissolved
01147	Selenium, total	>	01145	Selenium, dissolved
01077	Silver, total	>	01075	Silver, dissolved
01082	Strontium, total	>	01080	Strontium, dissolved
01102	Tin, total	>	None	Tin, dissolved
01087	Vanadium, total	>	01085	Vanadium, dissolved
01092	Zinc, total	>	01090	Zinc, dissolved
70507	Phosphorus, orthophosphate as P, total	>	00671	Phosphorus, orthophosphate as P, dissolved
00615	Nitrogen, nitrite as N, total	>	00613	Nitrogen, nitrite as N, dissolved
00630	Nitrogen, nitrite plus nitrate as N, total	>	00613	Nitrogen, nitrite as N, dissolved
00630	Nitrogen, nitrite plus nitrate as N, total	>	00631	Nitrogen, nitrite plus nitrate as N, dissolved
00630	Nitrogen, nitrite plus nitrate as N, total	>	00615	Nitrogen, nitrite as N, total
01097	Antimony, total	>	01085	Antimony, dissolved

Table 9.—Comparison of solids

WATSTORE code	Constituent	Computer check	WATSTORE code	Constituent
00500	Solids, residue at 105-110°C, total	>	70299	Solids, residue at 105-110°C, suspended
00500	Solids, residue at 105-110°C, total	>	00530	Solids, residue at 105-110°C, suspended
00500	Solids, residue at 105-110°C, total	>	00510	Solids, nonvolatile, total
00500	Solids, residue at 105-110°C, total	>	00505	Solids, volatile on ignition, total
00530	Solids, residue at 105-110°C, suspended	>	00540	Solids, nonvolatile, suspended
00530	Solids, residue at 105-110°C, suspended	>	00535	Solids, volatile on ignition, suspended
70300	Solids, residue at 180°C, dissolved	>	00520	Solids, volatile on ignition, dissolved

Table 10.—Trace constituent concentrations which will contribute to milliequivalent

WATSTORE Code	Constituent	Concentration[a] (µg/L)
01106	Aluminum, dissolved	450
01046	Iron, dissolved	930
01130	Lithium, dissolved	350
01056	Manganese, dissolved	690
01090	Zinc, dissolved	1630
01005	Barium, dissolved	3400
01080	Strontium, dissolved	2200
01040	Copper, dissolved	1590
01049	Lead, dissolved	5180
01060	Molybdenum, dissolved	800

[a] These concentrations will yield a milliequivalent value which will contribute to the cation milliequivalent value.

QUALITY CONTROL INFORMATION FOR LAB ID # 334016 RECORD # 50510

**CATION/.01 CONDUCTANCE RATIO IS EITHER BELOW 0.92 OR ABOVE 1.24 - = 0.873

**CALCULATED SOLIDS/CONDUCTANCE RATIO IS EITHER BELOW 0.55 OR ABOVE 0.81 - - - - - - - - - - - - - - = 0.529

**THE PERCENT DIFFERENCE COMPUTED FOR THE ANALYSIS DOES NOT AGREE WITH THE CURVE VALUE = 0.690

Figure 16.—Example of computer-generated "error" messages.

References

Durum, W. H., 1978, Historical profile of quality of water laboratories and activities, 1879–1973: U.S. Geological Survey Open-File Report 78–432, 235 p.

Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water (2d ed.): U.S. Geological Survey Water-Supply Paper 1473, 363 p.

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial and Engineering Chemistry, v. 5, no. 1, p. 4–6.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 7–9.

Reference Material Submitted by Laboratory Management

1. Application or scope

1.1 This practice describes and documents the Central Laboratories System program in which the chief of each Central Laboratory ensures that reference materials which are unknown to any analyst or section head are submitted daily to the laboratory. Results from analyses of the reference materials are used to aid the laboratory chief in monitoring the quality control program of his laboratory and in assuring data quality.

1.2 The section "Reference material," should also be referred to.

2. Practice

2.1 Sample submission

2.1.1 A minimum of one reference material for major inorganic constituents (calcium, magnesium, sodium, potassium, chloride, fluoride, sulfate, silica, alkalinity, dissolved solids, and nitrite plus nitrate) are submitted every day.

2.1.2 A minimum of two reference materials for trace inorganic constituents (aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, and zinc) are submitted every week.

2.1.3 A minimum of one natural sample for gross alpha and beta radioactivity and for uranium are submitted every week.

2.1.4 Prior to their submission to the laboratory, the reference materials are rebottled in the type of sample bottles which are routinely received by the laboratory.

2.1.5 Each rebottled reference material is assigned a routine log-in number, and the log-in sheet accompanying the samples is coded to allow computer recognition of the reference material so that the results can be checked automatically as they are produced. Log-in sheets go directly to the automatic data processing (ADP) section and are not seen by the analyst.

2.2 Data processing

2.2.1 The most probable values and associated standard deviations for the reference material constituents are stored in a computerized file. The file is updated as new reference materials become available.

2.2.2 Upon completion of a set of analyses, the analyst submits the data for computer entry. The following morning, the laboratory's quality assurance staff receives a list of reference sample values which are greater than 1 standard deviation from the most probable value; values which are greater than 1.5 standard deviations from the most probable value are starred (fig. 17).

2.2.3 The quality assurance staff of the laboratory asks the section head to investigate analyses of reference material which showed significant (over 1.5 standard deviations) error.

2.2.4 During his investigation, the section head may require the analyst to perform the analysis again. (This would not be the case for obvious transcribing or data processing errors.) When the reference sample is reanalyzed, several samples throughout the analytical run must also be reanalyzed including samples near the beginning, the end, and on either side of the reference sample.

2.2.5 Once the area in which the error occurred has been defined, analyses thoughout the area are repeated and the data are corrected. The section head informs the quality control staff of the reason for the error, describes corrective measures to eliminate the problem, and indicates which samples were reanalyzed.

* * * * * * * * UNKNOWN STANDARD REFERENCE SAMPLE PROGRAM, BOTH GOOD AND BAD ARE REPORTED * * * * * * * *

LAB-ID	RECORD #	STANDARD REF. SAM.	PARAMETER NAME	LAB-CODE	REPORTED VALUE * 1.5 STAN. DEV. GOOD 1.0 S. DEV.	ACCEPTANCE INTERVAL MEAN +- 1 STAN. DEV. MEAN +- 1.5 STAN. DEV.		MEAN	STANDARD DEV.
293107	347	64	POTASSIUM DISSOLVED	54	8.10 GOOD	7.41 TO	9.13	8.27	0.86
						6.99 TO	9.55		
293115	366	63	MERCURY DISSOLVED	226	2.20*	3.98 TO	5.38	4.68	0.70
						3.63 TO	5.73		
394209	838	62	CHLORIDE DISSOLVED	15	8.50 GOOD	8.13 TO	9.39	8.76	0.63
						7.82 TO	9.70		
294209	838	62	SULFATE DISSOLVED	63	63.00 GOOD	55.34 TO	64.06	59.70	4.36
						55.16 TO	66.24		
298124	1843	63	COBALT DISSOLVED	18	17.00	12.68 TO	16.92	14.80	2.12
						11.61 TO	17.99		
298124	1843	63	COPPER DISSOLVED	22	85.00*	52.67 TO	71.32	62.00	9.32
						48.01 TO	75.99		
298124	1843	63	LEAD DISSOLVED	38	0.00	1.03 TO	8.77	4.90	3.87
						0.00 TO	10.70		
298124	1843	63	MANGANESE DISSOLVED	42	250.00 GOOD	228.50 TO	277.50	253.00	24.50
						216.25 TO	289.75		
298124	1843	63	NICKEL DISSOLVED	44	4.00	4.04 TO	10.76	7.40	3.36
						2.36 TO	12.44		
298124	1843	63	CADMIUM DISSOLVED	73	13.00 GOOD	11.77 TO	18.03	14.90	3.13
						10.20 TO	19.60		

Figure 17.—Example of computer messages for reference samples submitted by laboratory management.

Reference Material Submitted from Outside the Laboratory

1. Application or scope

1.1 This practice describes and documents the Central Laboratories System program in which reference materials that are unknown to anyone in the laboratory system are submitted by Geological Survey district personnel, along with their routine samples, to the laboratories. Data from analysis of the reference materials are used for quality assurance monitoring.

1.2 The section, "Reference material," should also be referred to.

2. Practice

2.1 Preparation and submission of samples

2.1.1 Inorganic reference materials are specially prepared by a quality assurance project which is independent of the production laboratory system. Usually two or more Standard Reference Water Samples (SRWS) are combined; for example, 60 percent of SRWS 10 is mixed with 40 percent of SRWS 12.

2.1.2 Samples are mailed to Geological Survey district offices. Only two quality assurance projects, both independent of the analytical laboratory, are aware of which WRD districts are involved and what the concentrations of the reference materials are; but even they do not know when the samples will be submitted.

2.1.3 District personnel are requested to submit samples on a weekly basis at times of their choosing. Field personnel know the composition but not the concentrations of the reference material.

2.1.4 The samples are provided with "unique" station identification numbers (downstream order numbers) which will allow computer recognition of the sample; in all other respects they appear identical to other samples submitted by the district. Thus, samples are "blind" to everyone in the laboratory.

2.2 Data processing

2.2.1 The expected analytical result and standard deviation is stored in the computer file under the station identification number assigned to the sample.

2.2.2 As in the case of the reference material submitted via the laboratory management, there is a 1-day response delay between analysis of the sample and receipt of the results by the laboratory's quality assurance staff. (This delay will be eliminated with the advent of "on-line" instruments; real-time reference sample monitoring will then be routine.)

2.2.3 The computer-generated report indicates how close the analysis is to the theoretical (most probable) value and specifically notes values which are significantly (over 1.5 standard deviations) in error. The laboratory is not informed which sample is the reference sample, but only informed of the Julian date (job) when the reference sample was submitted (fig. 18).

2.2.4 Section heads are required to respond, in writing, to any problems indicated by the results of reference sample analyses. They must describe what the problem was and the corrective action taken. The response is stored in the computer (fig. 19).

THE FOLLOWING PARAMETERS HAVE BEEN DETERMINED ON BLIND SAMPLES SUBMITTED TO YOUR CENTRAL LABORATORY BY DISTRICTS THAT YOU SERVE. FOR PARAMETER VALUES ≦ 1.5 STANDARD DEVIATIONS, NO RESPONSE IS NECESSARY. HOWEVER, FOR VALUES >1.5 A RESPONSE IS MANDATORY. THIS REPORT IS PREPARED TO ASSIST YOU IN TURNING OUT THE HIGHEST QUALITY WORK POSSIBLE.

LAB CODE	PARAMETER NAME	LAB SEC.	JOB SET	# STAN. DEV.	COMMENT	RESPONSE KEY (COLS. 1-8)	RECORD NO (COLS. 9-12)	LAB CODE (COLS. 13-16)	EXPLANATION OF PROBLEM (COLS. 17-80)
6	ARSENIC DISSOLVED	3	199	-0.19	LOOKS GOOD	-	-	-	-
69	SP. CONDUCTANCE LAB	2	206	0.86	LOOKS GOOD	-	-	-	-
63	SULFATE DISSOLVED	2	194	5.13	**OH OH**	77081142	100	63	RESPONSE REQUIRED
15	CHORIDE DISSOLVED	2	194	-2.26	**OH OH**	77081142	101	15	RESPONSE REQUIRED

Figure 18.—Example of computer-generated reference sample report.

RETRIEVAL OF LABORATORY RESPONSES FOR MONTH: MAR BEGIN RECORD: 45 END RECORD: 56 DATE OF REPORT (YEAR, MONTH, DAY): 780202

RECORD NO.	LAB #	SEC #	STANDARD DEV. ID	LAB CODE	DETERMINED VALUE	TRUE VALUE	# OF STAN. DEVIATIONS	CENTRAL LABORATORY LAB ID	CENTRAL LABORATORY REC. NO.	DATE OF ANALYSIS	DATE OF RESPONSE
45	3	3	04180300	59	110.00	121.00	2.47	46029	47337	770301	770311
**********	RESPONSE MESSAGE: SRS RECHECKS ALL SAMPLES IN RUN RECHECK										**********
46	2	3	03566403	67	150.00	194.00	2.34	59129	50222	770303	770331
**********	RESPONSE MESSAGE: OTHER REFERENCES OK										**********
47	2	4	05521800	10	140.00	76.00	1.80	49034	48166	770303	770331
**********	RESPONSE MESSAGE: SAMPLES RERUN - WITH INCREASED INCUBATION 40-48 HRS										**********
48	2	2	03566403	36	370.00	237.00	5.29	59129	50222	770303	770331
**********	RESPONSE MESSAGE: POSSIBLE CONTAMINATION OF SAMPLE CUP										**********
49	4	2	01245637	69	825.00	861.20	1.85	60055	59214	770304	770315
**********	RESPONSE MESSAGE: WRONG TEMP CORR - JOB 060 UPDATED WITH CORR VALUES										**********
50	2	3	03566403	226	2.40	4.29	2.91	59129	50222	770304	770331
**********	RESPONSE MESSAGE: OTHER REFERENCES OK - CURVES LOOK OK										**********
51	3	2	04180300	63	4500.00	450.00	268.48	46029	47337	770304	770309
**********	RESPONSE MESSAGE: KEY PUNCH ERROR										**********
52	4	3	03468499	226	2.60	0.86	7.97	56034	58805	770308	770706
**********	RESPONSE MESSAGE:CONTAMINATED BOD BTLS USED-ALL SAMPLES RERUN AND UPDATED 3/27/77										**********
53	4	3	03468499	110	11.00	14.60	1.59	56034	58805	770308	770518
**********	RESPONSE MESSAGE: STD CURVE CKD OK - JOB 056 LOOKS GOOD NO OBVIOUS ERRORS NOTED										**********
54	4	2	01245637	15	150.00	135.00	2.84	60055	59214	770315	770317
**********	RESPONSE MESSAGE: INHOUSE SRWS & ANALYSIS REF CKD OK - JOB 060 OK										**********
55	4	3	04207700	6	42.00	27.40	1.88	68009	60165	770323	
**********	RESPONSE MESSAGE:										**********
56	2	1	03374050	8	41.00	48.30	2.27	87112	57076	770330	770428
**********	RESPONSE MESSAGE: CURVE RERUN, VALUES 41, 40, 43 WERE REPORTED, OTHER ST. OK										**********

Figure 19.—Example of section responses to reference sample "errors."

Reference Material Submitted to Cooperator and Contractor Laboratories

1. Application or scope

1.1 This practice provides some guidelines for submitting reference samples to those laboratories that are analyzing samples for the Geological Survey under the terms of a cooperative agreement or contract. Specific quality assurance procedures depend on the type of analyses that are to be performed; because Geological Survey cooperator and contract programs vary, specific requirements should be included with each cooperation agreement or contract.

1.2 Analyses used by the Geological Survey or stored in the WATSTORE computer system should be of known precision and of acceptable accuracy. Analyses performed by cooperator and contractor laboratories must yield data comparable to the Central Laboratories.

1.3 Refer also to the section "Reference Material."

2. Practice

2.1 Prepared reference material

2.1.1 If reference materials are available for the constituent(s) of interest, submit at least 1 for every 25 samples analyzed (NOTE 1).

NOTE 1. At least three Standard Reference Water Samples must be submitted per year (see 2.1.4, below).

2.1.2 If in any month 10 or more samples are analyzed, submit a reference sample (even though less than 25 samples are analyzed).

2.1.3 If possible, submit samples in such a way that the receiving laboratory will not know they are reference materials. When a cooperating agency both collects and analyzes the sample, such "blind" submission is not possible; however, in no case is the analyzing laboratory or cooperative agency to be informed of concentration values prior to sample analyses.

2.1.4 Standard Reference Water Samples (SRWS) are usually prepared from natural water and are available, on a limited basis, for the following constituents: aluminum, antimony, arsenic, barium, beryllium, bicarbonate alkalinity, boron, cadmium, calcium, chloride, chromium, cobalt, copper, dissolved solids, fluoride, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, nitrate, nitrite, pH, phosphorus, potassium, selenium, silica, silver, sodium, specific conductance, strontium, sulfate, thallium, and zinc. Semiannually, samples are also available for ammonia, Kjeldahl nitrogen, orthophosphate, and dissolved phosphorus. The most probable concentration of each constituent and the standard deviation of the analysis is determined from interlaboratory analyses.

2.1.4a Each cooperating or contracting laboratory must analyze a minimum of three SRWS per year for each of the above-named constituents which it determines; two out of the three analyses needed to meet this minimum requirement may be obtained by participation in the program to analyze new SRWS. For inclusion in this program, contact:

Project Chief for Standard Reference
Water Sample Program
U.S. Geological Survey
Water Resources Division
Mail Stop 407, Box 25046
Denver Federal Center
Denver, CO 80225

2.1.4b In order to obtain more reference materials for continuing laboratory evaluation, contact:

Project Chief for Laboratory Evaluation
U.S. Geological Survey
Water Resources Division
Mail Stop 407, Box 25046
Denver Federal Center
Denver, CO 80225

2.1.5 Ampouled concentrates of many constituents, prepared in distilled water, are

available; however, Geological Survey district personnel are responsible for quantitatively preparing solutions from the concentrates. If solutions are prepared in a natural-water matrix, submit to the laboratory for analysis both the sample spiked with the concentrate and the unspiked sample. Ampoules should be used to monitor Kjeldahl nitrogen, ammonia, chemical oxygen demand, and carbon analyses.

2.1.5a In order to obtain ampoules, contact the Project Chief for Laboratory Evaluation.

2.1.5b Alternatively, obtain samples from:

U.S. Environmental Protection Agency
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Cincinnati, OH 45268

As more fully described in the January 1981 edition of the EPA Quality Assurance Newsletter, the following types of Quality Control samples are available, primarily as ampouled concentrates, for use to interested water analyses laboratories:

Antimony, thallium, and silver
Chlorine
Chlorophyll
Cyanide
Demand analyses
Haloethers
Herbicides
Linear alkylate sulfonate
Mercury
Mineral/physical analyses
Municipal digested sludge
Nitrate/fluoride
Nitrilotriacetic acid
Nutrients
Oil and grease
Pesticides
Pesticides, organochlorine
Pesticides, organophosphorus
Pesticides, urea-based
Petroleum hydrocarbons
Phenol
Phthalate esters
Polychlorinated biphenyls
Polychlorinated biphenyls in fish
Polychlorinated biphenyls in oils
Polychlorinated biphenyls in sediments
Purgeables, halogenated
Purgeables, nonhalogenated
Residues, nonfilterable, volatile, and total filterable
Sludge, municipal
Trace metals
Trihalomethanes
Turbidity
Volatile organics

2.1.6 Reference materials prepared in a natural-water matrix typical of water being analyzed by a laboratory may also be obtained. Matrix water for these samples is generally collected by the district and submitted to the Project Chief for Laboratory Evaluation. This bulk matrix water sample may be split and treated to yield several types of reference material samples which are then returned to the District. These may include: (1) filtered, untreated sample, (2) filtered, untreated sample with known amounts of major constituent additions, (3) filtered, acidified sample, and (4) filtered, acidified sample with known amounts of trace constituent additions.

2.1.6a Direct requests for the preparation of "matrix material samples" to the Project Chief for Laboratory Evaluation.

2.1.6b Submit matrix samples to at least two laboratories; participation by more than two laboratories is desirable. Submit at least four subsamples of any specific prepared sample (over a period of time) to each laboratory (NOTE 2).

NOTE 2. Sufficient water must be collected initially to allow for each participating laboratory to analyze the samples the minimum four times. Preferably, when collecting the water, a minimum of four samples of the natural water should be collected and submitted to each participating laboratory to provide "base level" data.

2.2 Spikes and dilutions: substitution for prepared reference material

2.2.1 For many constituents, prepared reference materials are difficult to obtain or are unavailable. Spiked or diluted samples may often be substituted.

2.2.2 Since these samples are being substituted for reference material (or used in conjunction with reference materials when supplies of the latter are limited), all of the requirements of the previous section also apply.

2.2.3 Because the analyses will yield more information on the quality of a laboratory's work, spiking with known concentrations of contituents to be determined is preferred over the dilution techniques.

2.2.4 For "spiked samples," spike every 25th sample collected (or 1 sample per month if between 10 and 25 samples are analyzed in a month) with a known amount of the constituent(s) to be determined. Submit both

spiked and unspiked portions to the laboratory. If possible, select or prepare concentrations of the material to be used as spikes so that the resulting concentration will remain in the analytical range of the method or will need the same dilution as the unspiked sample. Examination of other analyses from the same site, and determination of the specific conductance of the sample, will be helpful in making the dilution. Report concentrations determined in the original (unspiked) sample, the spiked sample, and report the calculated percent recoveries (bias).

2.2.4a If there is a possibility that spiking with more than one constituent may cause interference problems (such as coprecipitation) or if the cooperating agency collects its own samples, provide the material to be used for the spikes directly to the analyzing laboratory and supply directions for adding the material to the samples. In no case should the laboratory or cooperating agency be informed of the concentration of the spike prior to the analysis.

2.2.4b The Project Chief for Laboratory Evaluation can provide some material suitable for use as spikes.

2.2.4c Many organic compounds are available from the Environmental Protection Agency, Research Triangle Park, in 100 mg quantities (Watts, 1980). If obtained by the district directly, it will be the responsibility of the district to ensure that solutions to be used in spiking are quantitatively prepared (NOTE 3).

NOTE 3. CAUTION: Since many of these compounds are extremely hazardous, extreme care must be taken in their handling.

2.2.5 For "diluted samples," dilute every 25th sample (or 1 sample per month if between 10 and 25 samples are analyzed in a month). Use a one-half dilution (unless it is known that the diluted and undiluted samples will require different treatment to be in the analytical range) and submit both diluted and undiluted portions to the laboratory. If the cooperating agency collects its own samples, submit these dilution "replicates" in addition to the regular samples analyzed. Vary the dilution and do not inform the laboratory or cooperating agency of the dilutions. Obtain the reported concentrations determined in both diluted and undiluted samples. Estimate the bias, using the explanation for figure 14 in the practice, "Quality control charts" as a guide.

2.3 Split samples

2.3.1 Split every 30th sample into a minimum of 8 samples. Send equal numbers (at least four) to the cooperating laboratory and to a central laboratory.

2.3.2 In any month in which 10 or more samples are analyzed, submit the split subsamples to both the cooperating and central laboratory (even though less than 30 samples are done).

2.3.3 If possible, submit samples in such a way that the receiving laboratory will not know that they are splits of a given sample. (For example, disguise the name of the sample.) If the cooperating agency collects its own samples, submit the pair of "splits" to the laboratory in addition to the regular samples analyzed; be sure to also submit a simultaneous pair to a central laboratory (NOTE 4).

NOTE 4. If a cooperator agency collects its own samples, it may be advisable to occasionally dilute one of the "splits" in order to make the split more of an "unknown."

2.4 Other material

2.4.1 As indicated previously, 1 in every 25 samples analyzed should include a prepared reference material or a spiked or diluted sample. An additional 2 out of every 31 samples should be a split sample. This combination constitutes a quality assurance workload of approximately 10.5 percent. An additional 4.5 percent quality assurance workload is needed to achieve the required 15 percent total (NOTE 5).

NOTE 5. Although initially this "external" quality assurance should comprise 15 percent of the laboratory work, if a laboratory has an active quality control program and if results from the initial quality assurance analyses appear acceptable, the percentage may be decreased. The percentage, however, should never be less than 5 percent of the laboratory work.

2.4.2 Unless the District obtains and submits more reference materials, data must be obtained from each laboratory showing results from any other reference samples which are run (as part of a state program for example), spiked or duplicate samples run as part of a quality

control program, etc. Quality control charts should be obtained if available. This data must be sufficient to show that, when combined with data from district submitted samples, there is a total quality assurance–quality control workload of at least 15 percent (NOTE 6).

NOTE 6.. If less than 30 samples are analyzed for a constituent in a month, the percentage of district-submitted "split" samples must be increased, and if there is less than 25 samples analyzed for a constituent in a month, the percentage of district-submitted reference materials (on spiked or diluted substitutes) must be increased. If additional information is available, it is recommended that it be obtained; however, this additional information is required only if the quality assurance workload from the above-mentioned district-submitted samples is less than 15 percent.

References

U.S. Environmental Protection Agency, 1981, Quality assurance newsletter: U.S. Environmental Protection Agency, Cincinnati, v. 4, no. 1, p. 11–13.

Watts, R. R., 1980, Analytical reference standards and supplemental data for pesticides and other organic compounds: U.S. Environmental Protection Agency EPA–600/2–81–011, Research Triangle Park, North Carolina, 182 p.

Reference Material Use in Monitoring Field pH and Specific Conductance Measurements

1. Application or scope

1.1 This practice describes and documents the Geological Survey field proficiency testing program. Significant amounts of Geological Survey water-quality data are obtained by field measurements made by large numbers of personnel using a wide variety of instrumentation and equipment; the program described in this practice is used to document acceptability of data obtained by field measurements.

1.2 More specifically, this practice describes the use of reference sample test solutions for pH and specific conductance in the program.

2. Practice

2.1 Preliminary information required

2.1.1 Approximately 1 month prior to shipment of the test solutions, each district is requested to supply a list detailing the make, model, serial number, and location (if in a field or subdistrict office) of each pH and specific conductance meter in the district.

2.1.2 Each district also lists the names of the individual(s) assigned to each instrument for purposes of the test.

2.1.3 Every person performing pH or specific conductance measurements and every instrument in use must be included in the tabulation. This requirement may make it necessary to assign more than one person to an instrument or more than one pH and (or) specific conductance instrument to a person.

2.2 Reference material assignment

2.2.1 A number of different quality assurance pH and specific conductance test solutions are prepared under the direction of the Project Chief for Laboratory Evaluation. Each reference material is assigned to a specific instrument analyst combination so that, insofar as possible, each combination in any one field office is sent a set (pH and specific conductance) of reference materials which is unique.

2.2.2 Sample numbers are designed to identify the district, instrument-analyst combination, and the test sample type. Each sample number begins with two letters identifying the district. The third symbol in the sample number is coded P for a pH test sample or C for a specific conductance test sample. The next two symbols are the test sample sequence numbers assigned to each instrument analyst combination given on the inventory sheets submitted by the respective district. The sixth symbol is a letter A, B, or C, and so forth, to represent the first, second, third, or other sample assigned to each instrument. Thus, the six symbols comprising the sample number identify the district and sample type and provide a sequence number which, when used with a computerized cross-reference list, identifies the instrument make, model, and serial number, the analyst, and the theoretical value of each sample.

2.3 Measurement and data submission.

2.3.1 Prior to making measurement on any of the pH or specific conductance test solutions supplied for this effort, instruments should be calibrated in the usual manner. The section, "Instrumental Techniques," should be referred to for specific calibration procedures.

2.3.2 Data should be reported for all samples sent to a field office. If no data are reported for a sample, an unsatisfactory (U) rating will be listed in the final report for each district. Consequently, in case of absences, alternate analysts should be assigned and changes noted. Similarly if the test solution samples are used for meters other than those initially assigned, the meter identification model and serial number should also be corrected on the computer sheet listing.

2.3.3 Computer-generated listings of the analysts and meters and the corresponding test samples assigned to each combination are in-

cluded with each sample shipment for recording and reporting the analytical data. The data are analyzed and evaluated by a quality assurance project independent of district personnel (see practice "Evaluation of field reference material data," in the section "Review, Summary and Evaluation of Data" for further information).

Quality Assurance and Quality Control Personnel

1. Application or scope

1.1 All laboratory personnel have responsibility for the quality of the laboratory's analyses. In order to increase reliability of the laboratory's analytical data, the laboratory staff must include a portion of laboratory personnel that are involved solely in the effort to define and control the quality of analytical data.

1.2 Additionally, someone outside the laboratory system should monitor laboratory quality control

2. Practice

2.1 Laboratory chief and quality control staff

2.1.1 The responsibility for the quality of analytical result rests with the laboratory chief. If analytical results are produced in the field, the responsibility rests with the district chief, project chief, or equivalent.

2.1.2 In order to fulfill this responsibility, each laboratory chief should have on his staff at least one person involved in quality assurance/quality control activities. Such a person(s) should not be involved in making analyses. This person should be at an organizational level equivalent to a section chief and should report directly to the laboratory chief.

2.2 Section chiefs and analysts

2.2.1 The section chief has dual quality control and production functions. Although analyses deadlines must be met, the section chief is responsible for the quality of work in his section; the production of greater numbers of analyses is meaningless unless a high degree of quality control also is maintained. The practice "Quality control: section leader duties and responsibilities," in the section on "Laboratory Quality Control" should be referred to for specific requirements.

2.2.2 The analyst also has dual quality control and production functions. Although he may be under pressure to increase the number of analyses made, the analyst must be certain not to compromise the quality of the work. Specific quality control requirements are discussed in the section "Laboratory Quality Control."

2.2.3 Although not directly involved in producing the analytical result, personnel involved in logging in the sample, processing the data and so forth, have equivalent responsibilities.

2.3 Quality assurance overseer

2.3.1 Laboratory quality control should be monitored by someone from outside the laboratory. One person overseeing all quality assurance and possibly all quality control practices may suffice.

2.3.2 This person should be on the organizational level with the laboratory chief and should report to the same person as does the laboratory chief.

Documentation, Summary, and Evaluation of Data

All data relating to the analyses of water and fluvial sediments and to the quality assurance of the analyses must be carefully documented. Thorough records must be kept both by each laboratory doing work in cooperation with or through a contract with the Geological Survey and by the Geological Survey office responsible for the cooperation agreement or contract.

Periodic review of all laboratory records must be made including review of documentation of standard solution preparation, instrument calibration, and reference material analyses. Quality assurance data should be summarized and evaluated semiannually. The documentation, summary, and evaluation of data should ensure that data of a known and comparable quality is being produced.

Required Documentation and Review of Data

1. Application or scope

1.1 This practice describes records to be kept by field and laboratory personnel. These records must completely document all aspects of sample collection and analysis. Specific practices elsewhere in this chapter should also be referred to.

2. Practice

2.1 Field data

2.1.1 At the time a sample is collected, all information pertaining to its identification must be recorded in a "field notebook." All data also must be written on or submitted with the sample bottle. Such information should include, but is not limited to, the date and time of collection, complete site identification information (such as latitude, longitude, and depth of a well), the name of the person or persons collecting the sample, and important environmental facts and observations (such as weather conditions or apparent turbidity of river).

2.1.2 Data from field measurements (such as temperature, pH, specific conductance, and alkalinity) must also be recorded in the field notebook, along with information pertinent to instrument calibration. Results from such field measurements must be written on or submitted with the sample bottle.

2.1.3 If an automated monitor is in use at the sampling site, a comparison must be made between observed values and those recorded by the monitor. Discrepancies, such as differences in temperature, dissolved oxygen, or gage height, must be noted in both the field notebook and on the monitor's recorder output. Monitor intake systems should be carefully checked and, if necessary, cleaned. If debris (such as leaves) appears to have caused a problem, this fact should be recorded.

2.2 Laboratory data

2.2.1 All analytical methods must be carefully documented and available to the analyst. The analyst should record every deviation from routine procedure. For example, notes should be kept on any interferences and on modifications taken to eliminate them.

2.2.2 Records should be kept on the method used to analyze each sample and the expected precision of that method should be documented. (In the Geological Survey's Central Laboratories System, results are entered into the computer using "lab codes"; these codes

represent not only the constituent determined, but also the method used.)

2.2.3 Records should be kept on the preparation of all standards. All weights and volumes should be recorded. Records should include not only data related to the preparation of stock solutions, but also data on all intermediate and working standards. The dates of preparation and the name of the preparing analyst should be noted. Date of opening reagents and standards should be recorded on the bottle labels and, if critical, also in a notebook.

2.2.4 Instrument calibration procedures should be documented and readily available to the analyst. The analyst should retain records on instrument calibration, and may use recorder charts to do so (for example, on gas chromatographs.)

2.2.5 All analyses of reference materials should be recorded and kept. The identification of all samples run with individual reference samples should also be recorded.

2.2.6 Careful records must be kept by "cooperator" and "contract" laboratories and by the Geological Survey office responsible for the cooperation agreement or contract. The quality of the data must be comparable to that of the central laboratories, since these data may be entered into the WATSTORE computer system and must be able to be used without qualifications.

2.2.7 Regular review of all laboratory records must be scheduled and made. This includes review of documentation of standard solution preparation, instrument calibration, and reference material analyses.

2.2.8 Data review programs should provide for continual review and evaluation of laboratory performance for all laboratories.

Selected References

Farland, R. J., ed., 1980, Data quality assurance guidelines for marine programs: National Oceanic and Atmospheric Administration, p. 4–1—4–36.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 164.

Evaluation of Field Reference Material Data

1. Application or scope

1.1 This practice describes computerized data processing techniques that are used to process and analyze the voluminous amount of data produced in conjunction with efforts to evaluate measurements made in the field. (See practice "Reference material use in monitoring field pH and specific conductance" in section "Quality assurance monitoring.)"

2. Practice

2.1 Data evaluation

2.1.1 Measurement results for the reference materials are required to be submitted to the initiating quality assurance project, located at the National Water Quality Laboratory (NWQL), within approximately 30 days of the initial sample distribution dates. Data received at the NWQL within the required time frames are considered "on time," and are used to calculate the mean, average deviation, percent deviation from the mean, standard deviation, and total range values for each test solution. Outlying values are rejected using the *T* test described in the practice "Single operator precision" in the section "Analytical Methods Development Procedures." (*T* values are listed in table A1.) After deleting outlying observations, the mean of these remaining data is computed and taken to be the most probable value (MPV). The data calculations are made by computer. Each data set is then examined to determine how individual test sample analyses meet *a priori* evaluation criteria.

2.1.2 Initially, acceptance criteria (expressed as "maximum allowable deviation from the most probable value") were arbitrary: for pH, values with maximum deviations of 0.1 unit or less were satisfactory (S), values with deviations from 0.1 to 0.2 unit were marginal (M), and values with deviations greater than 0.2 unit were unsatisfactory (U); for specific conductance, values with deviations equal to or less than 4 percent were satisfactory (S), values with deviations from 4 to 5 percent were marginal (M), and values with deviations greater than 5 percent error were unsatisfactory (U). These criteria may be revised as more information from this program becomes available.

2.1.3 Each test sample is identified by a unique number which assigns the sample to a specific district, instrument and analyst. Individual results for each test sample are alphabetically listed by district and analyst on computer generated tabulations. The measured test value for each test sample and the corresponding MPV, obtained as described above, are given in the columns following the test sample number.

2.1.4 Values reported for each test sample are rated as satisfactory (S), marginal (M), unsatisfactory (U) or not rated (N). Comments explaining the assigned ratings are made when applicable.

2.1.5 Scatter diagrams (fig. 20) produced by using a Statistical Analysis System (SAS) computer program (Barr and others, 1976) have been used to illustrate the pH and specific conductance field measurement as reported for each district. The value and the number of measurements are indicated by the location of the plotted letters, A, B, C, and so forth, with an A indicating a single value reported for a field measurement, a B for two values, C for three, and so forth. The "most probable value" for each test solution is indicated by an appropriately plotted slash (/). A letter superimposed over the slash indicates the number of measurements reported that duplicate the most probable value.

2.1.6 Ideally, all points would be superimposed over the respective slash mark representing the most probable value for the respective test solution. An excessive vertical distance of the plotted letters from the respective "slash" value is readily evident and usually indicates

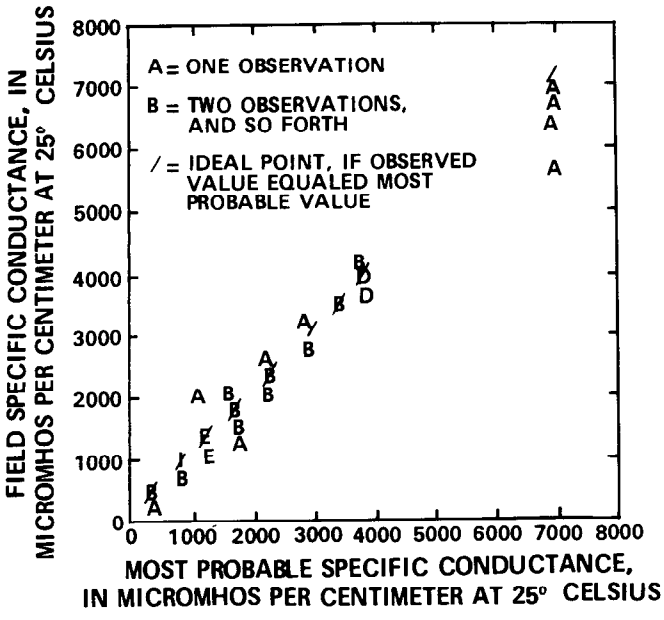

Figure 20.—Example of field laboratory evaluation graph. Produced by SAS (Barr and others, 1976) computer program.

unacceptable measurements or samples outside the range of the measuring instrument.

2.1.7 Most graphs include a statement at the bottom such as, "xx observations hidden." This statement refers to the fact that the computer plots an "MPV" (slash) for each measured and plotted test sample value (A, B, C, and so forth). Superimposed slashes are not recognizable and are called "hidden observations." Decimal point or sample identification errors will also result in excessive scatter of the plotted points and can generally be recognized.

2.2 Report preparation and distribution

2.2.1 All results, obtained within the required time frames, are compiled and tabulated. Overall results obtained within a Geological Survey region are then used to compute the relative performance ratings demonstrated by the districts in that region. These ratings are based on the percent of acceptable measurement submitted for the samples tested. Ratings obtained by each district are included in separate evaluation reports prepared for the respective testing period for each region.

2.2.2 If data from more than one round of testing have been obtained, such as during the second half of a testing year, presentation of all data may be useful. This summary can provide a convenient mechanism for identifying areas which have shown improvement or those in need of assistance. Whenever possible, specific problem areas are identified and ways are suggested to correct or reduce them.

2.2.3 After completion of a round of testing which has included all districts in all four regions, a summary report is prepared. These reports include both tabular and narrative evaluations of the results obtained by all districts and personnel participating during each complete round of testing. The combined efforts of all personnel involved provide the information necessary to effect the timely identification and correction of problems which may exist in the determination of field measured water quality data.

References

American Society for Testing and Materials, 1980, E178–75, Dealing with outlying observations, *in* Annual book of ASTM standards, Part 41: Philadelphia, American Society for Testing and Materials, p. 206–231.

Barr, A. J., Goodnight, J. H., Sall, J. P., Helwig, J. T., 1976, A user's guide to SAS 76: Raleigh, SAS Institute, 329 p.

Initial Evaluation of Cooperator and Contractor Laboratories

1. Application or scope

1.1 This practice describes procedures to follow in order to evaluate a laboratory.

1.2 Laboratory analytical data used by the Geological Survey are provided by numerous cooperator and contractor laboratories in addition to Geological Survey laboratories. The quality of all data must be comparable since data must be able to be used without qualifications.

2. Practice

2.1 The facility

2.1.1 In order to evaluate data to be provided by a cooperator or contractor laboratory, an initial assessment of the facility should be obtained from a visit to it. An 8-page form (fig. 21), has been designed to aid in this initial evaluation.

2.1.2 Prepare documentation on the laboratory's interior. Include information on bench space, safety standards, temperature regulation, air quality, hood space, and so forth.

2.1.3 Summarize education and experience of laboratory director and analysts.

2.1.4 Examine sample receipt and inventory (log-in) procedures, storage space (including refrigeration) and time of storage of samples (before and after analyses).

2.2 Analyses

2.2.1 Obtain a list of the number and type of determinations, both those which are routinely done by the laboratory and those which are planned as part of the contract or cooperation agreement.

2.2.2 Obtain a description of the instruments and analytical methods to be used and submit samples to test analytical proficiency prior to the award or initiation of the contract.

2.2.3 Update all information as changes occur.

2.3 Quality control

2.3.1 Examine quality control procedures.

2.3.2 Since experience has shown that some analyses will be in error and need to be remade when a properly functioning quality control program exists, obtain acceptability criteria and estimates of the percentages of analyses which are rerun.

2.3.3 Record the percentage of standards, blanks, spiked samples, laboratory duplicates, and unknown reference material which are analyzed for each constituent.

2.3.4 Obtain any quality control summaries which a laboratory may have. Also tabulate any data from analysis of proficiency testing samples or from analysis obtained in "round-robin" studies.

2.4 Quality assurance

2.4.1 Prepare or obtain a quality assurance plan for each laboratory, using the practice "Reference material submitted to cooperator and contractor laboratories" in section "Quality Assurance Monitoring," as a guide.

2.4.2 Prepare (or obtain from Geological Survey quality assurance project) a summary and evaluation of quality assurance data semiannually. Use examples outlined in this section as guides.

References

U.S. Environmental Protection Agency, 1978, Manual for the interim certification of laboratories involved in analyzing public drinking water supplies, criteria and procedures: U.S. Environmental Protection Agency EPA–600/8–78–008, Washington, D.C., 92 p.

Page 1 of 8

District _____ District liaison _____ Phone No. (FTS) _____

Laboratory name _____

Location _____

Director _____ Phone No. _____

Staff: Professionals _____ Technicians _____ Clerical _____

Computer _____ Other _____

(Organizational chart should be attached to this form, if available. Identify those sections and personnel routinely providing data for USGS.)

1. SAMPLE LOADS:

Approximate annual sample load for USGS and total analytical work for all agencies (USGS plus state, county, city, etc.) by category:

USGS: Major ions _____ Metals _____ Nutrients _____ Radiochemical _____

Total: _____ _____ _____ _____

USGS: Pesticides _____ Biological _____ Other[1/] _____

Total: _____ _____ _____

[1/] Identification of other _____

2. LABORATORY FACILITIES:

Approximate lab size _____ (ft^2) Linear bench space _____ (ft)

Hoods (number or linear feet) _____

Hoods (face velocity)	Adequate _____	Inadequate _____
Sinks	Adequate _____	Inadequate _____
Lighting	Adequate _____	Inadequate _____
Heating	Adequate _____	Inadequate _____

Figure 21.—Sample evaluation form for laboratories providing analytical data for the U.S. Geological Survey.

Cooling	Adequate _____	Inadequate _____
Humidity control	Adequate _____	Inadequate _____
Air quality-detectable fumes	Yes _____	No _____
Air quality-visible dust	Yes _____	No _____

Other _____

Apparent conformance to OSHA safety standards: _____

3. MAJOR LABORATORY EQUIPMENT:

Item	Model	No.	Age

Figure 21.—Continued

Major instrumentation:

Service contracts for: Most _____ Some _____ Few _____

Comments _____

Calibration procedures detailed: Most _____ Some _____ Few _____

Comments _____

Records kept:

Repairs Yes _____ No _____ Inspection Yes _____ No _____

Calibration Yes _____ No _____

4. CHEMICALS AND REAGENTS:

Date of receipt or preparation shown Yes _____ No _____

Analyst preparing reagents identified Yes _____ No _____

Proper storage:

Light-sensitive reagents Yes _____ No _____

Heat-sensitive reagents Yes _____ No _____

Flammable materials Yes _____ No _____

Carcinogenic compounds Yes _____ No _____

Other _____

5. SAMPLE COLLECTION:

Sampling for USGS analyses:

Personnel collecting samples: USGS _____ Cooperator _____

Other _____

Sample collection procedure reference(s) _____

_____

_____

Figure 21.—Continued

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Location indicated by (name, number, etc.) _____

_____

Sample identification includes:

Water type (surface water, ground water, etc.)	Yes _____	No _____
Analyses required	Yes _____	No _____
Name of collector	Yes _____	No _____
Date	Yes _____	No _____
Time	Yes _____	No _____
Treatment (filtered, raw, acidified, etc.)	Yes _____	No _____

Collection procedures (in brief) _____

_____

_____

_____

Preservation methods _____

_____

_____

_____

6. SAMPLE HANDLING:

Mode of shipment _____

Average elapsed time for shipment _____

Sample identification in laboratory: Program _____

Station location _____ Lab number _____

Other _____

Storage: Ambient _____ Refrigerated at _____ ^{o}C

_____

Figure 21.—Continued

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7. ANALYSES:

Generally begun within _____ days of receipt.

Average sample backlog (days, weeks, etc.) for following types of samples:

Major ions _____ Trace constituents _____ Nutrients _____

Pesticides _____ Biological _____ Other _____

Form of Analytical Data Report (letter, computer output, etc.)

_____

Analysts identified _____ Date of completion shown _____

Data review procedures (in brief) _____

_____

_____

_____

_____

_____

8. LABORATORY DATA RECORDS:

Raw data: Retention period _____ Form _____

Final data: Retention period _____ Form _____

Comments: _____

_____

_____

9. METHODS:

Analytical references available in laboratory Yes _____ No _____

Written procedures available at bench Yes _____ No _____

Figure 21.—Continued

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Source of methods other than USGS _____

_____

_____

_____

_____

_____

(Attach list of method references for each constituent.)

10. QUALITY CONTROL:

Summaries prepared:

Quarterly _____ Semiannually _____ Annually _____ Other _____

Obtained Yes _____ No _____

Analytical acceptability criteria obtained: Yes _____ No _____

Estimate percent of analyses passed on "first run": _____

Rerun criteria available to laboratory personnel: Yes _____ No _____

Obtained Yes _____ No _____

Approximate percent of total sample load: Standards _____ Blanks _____

Lab duplicates _____ Spiked standard additions _____

Blind reference samples _____ Other _____

_____

_____

Control charts:

Used Yes _____ No _____

Frequency Yes _____ No _____

Checked by (other analyst, lab chief, etc.) _____

Figure 21.—Continued

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11. QUALITY ASSURANCE PROGRAM PARTICIPATION:

Agency or organization (USGS, EPA, ASTM, etc.)	Sample type (major ions, nutrients, etc.)	Participation dates Initial	Last	Last performance Excellent	Average	Poor

Comments: _____

_____

_____

Report copies available: Yes _____ No _____

Obtained Yes _____ No _____

Laboratory certified by:

EPA Yes _____ No _____

State Yes _____ No _____

Other Yes _____ No _____

Copies of certificates available: Yes _____ No _____

Obtained Yes _____ No _____

Comments: _____

_____

_____

_____

Figure 21.—Continued

Page 8 of 8

12. SUMMARY:

General overall evaluation: _____

Suggestions for improvement: _____

Evaluator(s): _____ Date of visit: _____

Figure 21.—Continued

Methods for Data Summation and Evaluations: Tabular Presentations

1. Application or scope

1.1 This practice gives examples of tabular summaries and provides a guide for the type of information that should be included in a semiannual quality assurance report.

1.2 Often quality control and (or) quality assurance data are found in notebooks and charts throughout a laboratory as well as in laboratory computer files. Although, to be effective, laboratory quality control data must be examined as soon after an analysis as possible so that necessary corrections can be made, a periodic summary of quality control and quality assurance data will give the data user information on the quality of his data. Such a summary should be made at least semiannually.

1.3 In order to evaluate the quality of data so summarized, the precision and bias of the data should be calculated, reported, and compared to expected values when possible. As can be seen in the examples, the precision and bias can also be indicated in the tabular summation.

1.4 Quality control charts may also be included as visual summaries in the report and the precision and bias can be indicated graphically. The practice "Quality control charts" in the section "Laboratory Quality Control" and the practice "Methods for data evaluation: graphical presentation" in this section should be referred to.

1.5 Other practices in this section which describe techniques to evaluate the data should also be referred to.

2. Practice

2.1 Summary of data from analysis of reference materials

2.1.1 Present the value of the theoretical or most probable concentration along with the value or the mean value obtained by each laboratory. Indicate the total number of determinations used in the computations.

2.1.2 Tables 11 through 15 are examples of su uality control data summaries. Table 11 sum rizes 6 months of quality control data for flu le analyses made by the Geological Survey entral Laboratories on Standard Reference ater Samples (SRWS); table 12 summarize out 2 months of quality control data for nu nt analyses made by the Geological Survey entral Laboratories on solutions prepared m U.S. Environmental Protection Agenc PA) ampouled concentrates; table 13 summa s a year of Geological Survey Central Labora y radiochemical results obtained by analyz EPA "round- robin" samples; table 14 summa s data obtained in an evaluation of pH me rements made in the field; and table 15 sho a summary of results obtained by using SAS computer program (Barr and others, 76) to get a frequency distribution for the re s from the measurement of pH and specifi nductance.

2.2 mmary of data from replicate sample analys

2.2 Summarize results from analyses of sample hich are "split" by field personnel and submit to the laboratory as duplicates or replicate lso summarize results from individual sample alyzed two or more times by the laboratory

2.2 Tables 16 through 19 are summaries of resu from repeated analyses of samples. Table hows results from duplicates split by field p nnel and submitted to the laboratory and gi published (in Skougstad and others, 1979) p ision data; table 17 lists results from "duplic polychlorinated biphenyl analyses made the laboratory on bottom sediment sample able 18 gives the mean concentrations and pe nt relative standard deviation for replicate lyses made on samples and standards for rad -226; and table 19 lists results from replica radiochemical analyses submitted periodically to the laboratory by the laboratory.

Table 11.—Summary of standard reference water sample results for fluoride analyses

Constituent	Most probable values			Combined laboratory values			Laboratory 1			Laboratory 2			SRWS number
	Mean	Standard deviation	N[a]	Mean	Standard deviation	N[b]	Mean	Standard deviation	N[b]	Mean	Standard deviation	N[b]	
Fluoride, dissolved (mg/L)	.78	± .08	19	.77	± .10	44	.69	± .05	21	.84	± .06	23	55
	.80	± .06	25	.78	± .09	12	.72	± .08	6	.83	± .05	6	62
	.84	± .10	27	.84	± .14	73	.75	± .05	33	.92	± .13	40	60
	.92	± .07	17	.92	± .10	99	.83	± .06	44	.99	± .06	55	58
	1.03	± .14	19	.99	± .10	30	.89	± .05	13	1.06	± .05	17	54

[a] N = number of laboratories in interlaboratory test.
[b] N = number of determinations.

Table 12.—Summary of nutrient quality control data: 11/77–12/77

Determination	Theoretical value (mg/L)	Combined laboratory data				Laboratory 1				Laboratory 2			
		Mean (mg/L)	Relative deviation (percent)	Bias (percent)	No. of determinations	Mean (mg/L)	Relative deviation (percent)	Bias (percent)	No. of determinations	Mean (mg/L)	Relative deviation (percent)	Bias (percent)	No. of determinations
Nitrogen, ammonia dissolved	0.23	0.227	± 22	- 1	75	0.236	± 6	+ 3	28	0.221	± 28	- 4	47
	1.59	1.518	± 7	- 5	79	1.572	± 7	- 1	28	1.488	± 8	- 6	51
Nitrogen, ammonia plus organic, dissolved	0.41	0.371	± 19	- 10	96	0.420	± 8	+ 2	38	0.338	± 20	- 18	58
	3.51	3.297	± 6	- 6	98	3.468	± 3	- 1	38	3.189	± 5	- 9	60
Nitrogen, nitrite plus nitrate, dissolved	0.11	0.121	± 16	+ 10	75	0.119	± 10	+ 8	27	0.122	± 18	+ 11	48
	0.38	0.407	± 8	+ 7	80	0.380	± 3	0	27	0.421	± 7	+ 11	53
Phosphorus, dissolved	0.20	---	---	---	--	0.210	± 3	+ 5	42	---	---	---	--
	0.66	---	---	---	--	0.668	± 2	+ 1	44	---	---	---	--
Phosphorus, orthophosphate dissolved	0.052	0.050	± 20	- 4	49	0.050	± 7	- 4	27	0.050	± 28	- 4	22
	0.190	0.168	± 16	- 12	53	0.183	± 3	- 4	27	0.152	± 21	- 20	26

2.3 Data evaluation

2.3.1 The type of data evaluation will depend on the type of data. As examples of tabular presentation of data evaulation, note particularly table 12, in which the relative deviations were calculated for the two Geological Survey Central Laboratories (with the number of determinations reported) and the biases (with respect to the theoretical values) are indicated; table 13, in which both the standard and relative deviations are reported and biases on both the theoretical value and a multilaboratory determined value are tabulated; table 15, in which the frequency of "satisfactory," "unsatisfactory," "marginal," and "not determined" pH analyses is shown; and table 16, in which the "theoretical" relative deviation of the method has been used to calculate an artificial "acceptable range" using the means of the duplicates.

2.3.2 In order to determine the standard deviation and (or) the percent relative standard deviation (coefficient of variation) of the data, calculate:

Table 13.—Comparison of results of radiochemical analyses and most probable values

Determination	Theoretical value (pCi/L)	EPA "round-robin" results			Denver Central Laboratory					
		Mean (pCi/L)	Standard deviation (pCi/L)	Number of labs	Mean (pCi/L)	Standard deviation (pCi/L)	Number of analyses	Relative deviation (percent)	Bias (based on theoretical value) (percent)	Bias (based on multi-lab value) (percent)
Gross beta radioactivity, dissolved (as Sr-90)	12	16.3	6.0	59	12.2	4.0	4	27	+ 8	- 20
	15	15.9	3.6	42	16.3	.6	3	4	+ 9	+ 3
	49	51.2	9.5	65	52.3	1.5	3	3	+ 7	+ 2
Radium -226	3.5	----	---	--	3.12	.06	3	2	- 11	----
	5.1	----	---	--	4.80	.75	3	16	- 6	---
Strontium -89	14	14.9	4.3	28	16.7	.6	3	4	+ 19	+ 12
Strontium -90	10	9.2	2.2	28	9.3	.6	3	6	- 7	+ 1
Tritium	970	1008	197	52	1123	46	3	4	+ 16	+ 11
	980	1000	172	55	927	31	3	3	- 5	- 7
	1060	1098	219	50	1053	76.5	3	7	- 1	- 4
	1970	1988	258	50	2117	40.4	3	2	+ 7	+ 6

Table 14.—Comparison by WRD Region of field laboratory evaluation Round 1 pH data

Test sample	Central Region			Northeast Region			Southeast Region			Western Region			Combined data		
	Samples analyzed	MPV[1]	Standard deviation	Samples analyzed	MPV[1]	Standard deviation	Samples analyzed	MPV[1]	Standard deviation	Samples analyzed	MPV[1]	Standard Deviation	Samples Analyzed	MPV[1]	Standard deviation
P- 4	127	7.63	0.12	---	---	---	48	7.63	0.12	57	7.64	0.12	232	7.635	0.117
9	122	3.85	.08	86	3.88	0.08	49	3.87	.08	56	3.87	.06	313	3.861	.078
10	123	4.33	.09	89	4.32	.06	49	4.32	0.4	57	4.33	.06	318	4.315	.070
11	128	5.90	.07	89	5.90	.10	54	5.90	.06	54	5.89	.14	325	5.892	.065
12	123	7.45	.07	86	7.47	.09	52	7.46	.09	53	7.48	.09	314	7.458	.070
13	124	8.88	.17	100	8.89	.13	48	8.90	.15	54	8.95	.12	326	8.887	.132
14	---	---	---	---	---	---	3	3.00	.00	--	---	---	3	3.0 ± .02	2/
15	---	---	---	---	---	---	3	3.87	.15	--	---	---	3	4.0 ± .02	2/
16	---	---	---	---	---	---	2	5.05	.07	--	---	---	2	5.0 ± .02	2/
17	---	---	---	---	---	---	3	5.80	.00	--	---	---	3	5.8 ± .02	2/
18	---	---	---	---	---	---	3	7.37	.06	--	---	---	3	7.4 ± .05	2/
19	---	---	---	---	---	---	4	8.40	.02	--	---	---	4	8.4 ± .05	2/

1/ MPV = most probable value.
2/ Known Value at 25°C.

$$s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}} = \sqrt{\frac{\Sigma x_i^2 - (\Sigma x_i)^2/n}{n-1}} \quad (34)$$

$$R.D. = \frac{s}{\bar{x}} \times 100 \text{ percent} \quad (35)$$

where
s = standard deviation of a sample,
x_i = concentration reported for a constituent in the sample,
$\bar{x}$ = mean concentration,
n = number of analyses made for the constituent, and
$R.D.$ = relative standard deviation, in percent.

Table 15.—Example of computer produced table of frequency distribution of pH and specific conductance results

[Produced by SAS computer program (Barr and others, 1976)]

COMMENTS	PARAMETER		
FREQUENCY PERCENT ROW PCT COL PCT	C[1]	P[2]	TOTAL
M[3]	47	57	104
	4.98	6.04	11.02
	45.19	54.81	
	9.25	13.07	
N[4]	30	8	38
	3.18	0.85	4.03
	78.95	21.05	
	5.91	1.83	
S[5]	265	308	573
	28.07	32.63	60.70
	46.25	53.75	
	52.17	70.64	
U[6]	166	63	229
	17.58	6.67	24.25
	72.49	27.51	
	32.68	14.45	
TOTAL	508	436	944
	53.81	46.19	100.00

C[1] = specific conductance at 25°C

P[2] = pH

M[3] = marginal

N[4] = not determined

S[5] = satisfactory

U[6] = unsatisfactory

2.3.3 In order to determine the bias (percent error) calculate:

$$B = \frac{x_{exp} - x_{acc}}{x_{acc}} \times 100 \text{ percent} \qquad (36)$$

where

B = bias

x_{exp} = experimental value,

x_{acc} = accepted value.

References

Barr, A. J., Goodnight, J. H., Sall, J. P., and Helwig, J. T., 1976, A user's guide to SAS: Raleigh, SAS Institute, 329 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Table 16.—Results from duplicate analyses in which results are compared to ranges based on published precision data

Constituent	Published precision data (from Skougstad and others, 1979)			Duplicate Set No.1 Laboratory 1				Duplicate Set No. 2 Laboratory 2			
	For mean of (mg/L)	Relative deviation is (percent)	Based on data from (labs)	Sample A (mg/L)	Sample B (mg/L)	+1 std. dev. range (mg/L)	+2 std. dev. range (mg/L)	Sample C (mg/L)	Sample D (mg/L)	+1 std. dev. range (mg/L)	+2 std. dev. range (mg/L)
Calcium, dissolved	12.6	7	17	19	19	18-20	16-22	84	82	76-90	70-96
	110	8	23								
Magnesium, dissolved	22.0	5	20	10	9.5	9.2-10	8.8-11	39	39	32-46	26-52
	35.6	17	17								
Sodium, dissolved	3.44	9	26	1.4	1.7	1.4-1.7	1.3-1.8	4.7	4.6	4.0-4.7	3.6-5.1
Potassium, dissolved	0.8	14	15	.7	.7	.6-.8	.5-.9	2.4	2.4	2.1-2.7	1.9-2.9
	5.2	11	32								
Alkalinity as $CaCO_3$	96	8	19	75	77	70-82	64-88	180	180	164-196	148-212
	154	9	24								
Chloride, dissolved	1.7	16	7	.9	1.3	.9-1.3	.7-1.5	2.8	2.7	2.3-3.2	1.9-3.6
Fluoride, dissolved	0.78	12	3 (112 replicates)	.1	.0	.0-.1	.1	.9	.9	.8-1.0	.7-1.1
Sulfate, dissolved	13	13	7	6.3	6.9	5.7-7.5	4.9-8.3	190	190		
	68.7	4	3								
Silica, dissolved	17.4	7	5	13	14	13-14	12-15	22	22	20-24	19-25

Table 17.—Duplicate analyses of polychorinated biphenyls, total in bottom material

[1977 - 1979]

Mean (µg/kg)	Difference (µg/kg)	Mean (µg/kg)	Difference (µg/kg)
0.30	0.6	14.8	2.0
0.50	1.0	14.9	1.8
0.50	1.0	15.5	15.0
1.00	0.0	15.5	3.0
1.00	0.0	16.0	2.0
1.00	0.0	16.0	8.0
1.00	0.0	18.8	0.3
1.00	0.0	18.9	11.2
1.00	2.0	19.0	4.7
2.00	0.0	25.0	6.0
3.50	1.0	26.0	0.0
4.00	2.0	27.0	20.3
4.00	0.0	39.0	26.0
4.00	0.0	51.5	3.0
4.65	1.1	61.5	13.0
5.50	1.0	73.0	48.0
5.65	2.1	79.5	1.0
6.40	0.4	93.0	34.0
6.50	1.0	101.0	18.0
7.00	2.0	140.0	0.0
7.00	4.0	140.0	0.0
7.50	11.0	176.5	83.0
8.0	2.0	450.0	460.0
8.0	2.0	2250.	300.
8.0	2.0	4100.	200.
8.5	2.9	22500.	13000.
12.8	0.2	36000.	4000.
14.4	1.6	77500.	15000.

Table 18.—Radium-226 analyses of water by radon emanation method

Mean (pCi/L)	Relative deviation (percent)	Number of determinations
.036	58	4[c]
.008	36	5[c]
.124	27	5[d]
.221	13	5[d]
.522[a]	7	9[c]
.822	9	6[c]
1.415	9	7[c]
10.14[b]	5	5[e]
10.92	55	4[c]
12.85	5	6[f]
290	4	6[f]

[a] 0.50 pCi/L standard

[b] 10.0 pCi/L standard

[c] Different cell and different instrument used for each reading.

[d] Two of the five readings were made using the same cell. Instrument different in each case.

[e] All readings made using same cell; instruments different.

[f] Two of the five readings were made using the same cell.

Table 19.—Unknown replicates: gross alpha and beta radioactivity and uranium

Determination	Data submitted to laboratory										Mean	Standard deviation	Relative deviation (percent)
	6/11	6/17	6/22	6/30	7/7	7/14	7/19	7/26	8/3	8/9			
Gross alpha radioactivity dissolved (µg/L as U natural)	2.7	3.6	3.6	3.3	3.4	4.6	3.5	3.5	2.3	2.5	3.32	± 0.67	20
Gross beta radioactivity, dissolved (pCi/L as Cs-137)	3.2	2.8	3.5	3.2	3.3	2.7	2.8	3.1	5.9[a]	2.9	3.06	± .27	9
Uranium dissolved	2.4	1.7	1.9	2.1	2.2	2.4	2.3	3.0	2.1	2.3	2.24	± .35	16

[a] Outlier, not used in computation of standard deviation.

Methods for Data Evaluation: Graphical Presentations

1. Application or scope

1.1 This practice gives examples of types of graphs which may be used to evaluate quality assurance data. Such graphical presentations of quality assurance data may be effective aids to judging the quality of that data. Graphs may be used to estimate analytical precision, to compare results obtained by two analytical procedures, and to compare analyses from two or more laboratories.

1.2 Laboratory quality control charts, although meant to be plotted immediately after an analysis and used to indicate necessary corrections also can be used to look at the general precision and bias of a laboratory's data. The practice "Quality control charts" in the section "Laboratory Quality Control" should be referred to.

1.3 Other practices in this section which describe techniques to summarize and evaluate data should also be referred to.

2. Practice

2.1 Chart of analytical results from two samples.

2.1.1 In interlaboratory comparisons, analyses of two samples containing similar concentrations of the constituent being examined can be graphically compared and used to estimate laboratory bias (Youden, 1960, 1975, 1978) (NOTE 1). Concentration values for sample 1 are indicated along the x-axis and concentration values for sample 2 are indicated along the y-axis and the pair of values obtained from each laboratory is plotted on a graph (fig. 22). A vertical line is drawn at the mean concentration of sample 1 and a horizontal line is drawn at the mean concentration of sample 2 (NOTE 2).

NOTE 1. Similar concentrations are specified since both precision and bias may vary with concentration.

NOTE 2. It may be preferable to ignore points which are obviously separated from all other points when computing the mean concentrations (Youden, 1978).

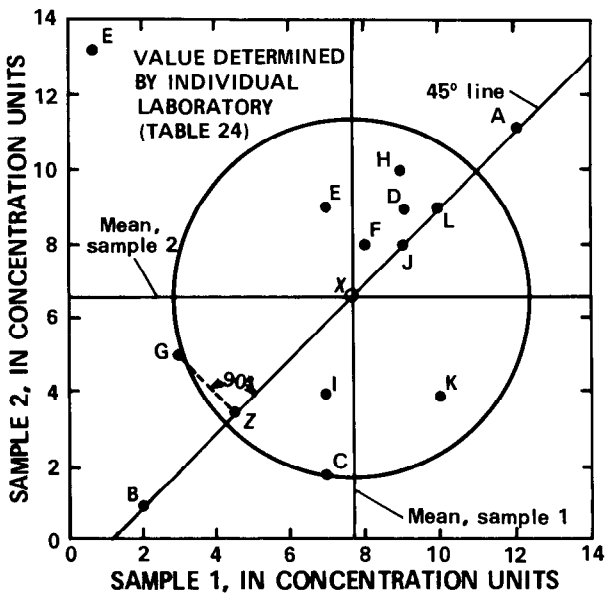

Figure 22.—Estimation of bias using two samples.

2.1.2 If systematic errors are not present, random errors will result in the points being equally distributed among the four quadrants (formed by the mean lines). On the other hand, in the hypothetical situation where only systematic errors are present, all values will be along a 45-degree line drawn though the intersection of the mean values. Generally, the data from all the participating laboratories will include both systematic and random errors and the majority of the data will be in the upper right or lower left-hand quadrants.

2.1.3 In order to estimate the standard deviation of a single result, first calculate the difference in the results submitted by each laboratory for samples 1 and 2. Then calculate the average difference and subtract it from each individual difference. The average of the absolute value of each individual difference minus the average difference, multiplied by $\sqrt{\pi/2}$ or .886 gives an estimate of the standard deviation (Youden, 1978).

2.1.4 If an estimate of the standard deviation is made, a circle whose radius is three times the estimated standard deviation should contain most of the points on the graph. Values outside of the circle indicate laboratory bias. A laboratory with a large, consistent bias will be represented by a point at one end of the 45-degree line (in the upper right quadrant for a positive bias or in the lower left quadrant for a negative bias).

2.1.5 If a numerical estimate of laboratory bias is desired, a perpendicular line can be drawn between each point and the 45-degree line. The difference between this intersection and the intersection of the two mean values divided by $\sqrt{2}$ will provide a numerical estimate of bias relative to the consensus values (Youden, 1960).

2.1.6 Illustrating this technique, data in table 20 are plotted in figure 22; points A to L represent the pairs of analytical results from the 12 laboratories. Point X represents the concentration values (of the consensus) for the two samples. Point Z is formed by the intersection of the 45-degree line (drawn through X) with a perpendicular line from point G. In order to estimate the standard deviation, the difference in results from each laboratory is calculated (12–11; 2–1; and so forth), and the average difference is determined to be 1.08. 1.08 is then subtracted from each difference, and the average of the absolute values of the results is calculated to be 1.79. Multiplying 1.79 by $\sqrt{\pi/2}$ gives 1.59, an estimate of the standard deviation, and 4.77 (3×1.59) gives the radius of the circle which should include most points; points A, B, and G all are outside the circle. The distance between point X and Z divided by $\sqrt{2}$ gives -3.2, an estimate of the overall bias of laboratory G with respect to the consensus values.

Table 20.—Example: Analytical results from 12 laboratories, tabulated prior to graphical evaluation

Laboratory	Sample 1 (concentration units)	Sample 2 (concentration units)
A	12	11
B	2	1
C	7	2
D	9	9
E	7	9
F	8	8
G	3	5
H	9	10
I	7	4
J	9	8
K	10	4
L	10	9

2.1.7 This graphical estimation of bias may be used to examine and evaluate data obtained by different analytical methods to determine which method is preferable. It may be used in the evaluation of data from laboratories; certainly if another set of samples was analyzed and the points representing laboratory A or B again were far away from the others and on the 45-degree line, there would be evidence of consistent, systematic laboratory error.

2.2 Quality-control type chart

2.2.1 If a variety of reference materials are analyzed over a period of time, a pictorial representation of bias and precision can be presented by using a quality control type of chart.

2.2.2 Figures 23 and 24 show results from analyses made by the laboratories on reference materials submitted as unknowns to the laboratories via field personnel. Although all values for the constituent plotted in figure 23 are less than two standard deviations from the theoretical (most-probable) value, a positive bias of results is clearly evident in the graph. Values for the constituent plotted in figure 24, on the other hand, show both a positive bias and a lack of precision. Charts showing the same type of "errors" for more than one laboratory indicate that there may be a problem with the analytical methodology itself.

2.2 Bar charts

2.3.1 A bar chart provides a simple means to graphically illustrate results. It can be used, for example, to compare results from laboratories participating in a "round-robin," or to show an increase or decrease in the percent of acceptable results produced by a laboratory (or Geological Survey district).

2.3.2 Figure 25 shows results from analysis of a standard reference water sample (see practice "Development of statistical data for standard reference water samples"); each point represents the values submitted by a laboratory, and points A, B, and C are in obvious disag-

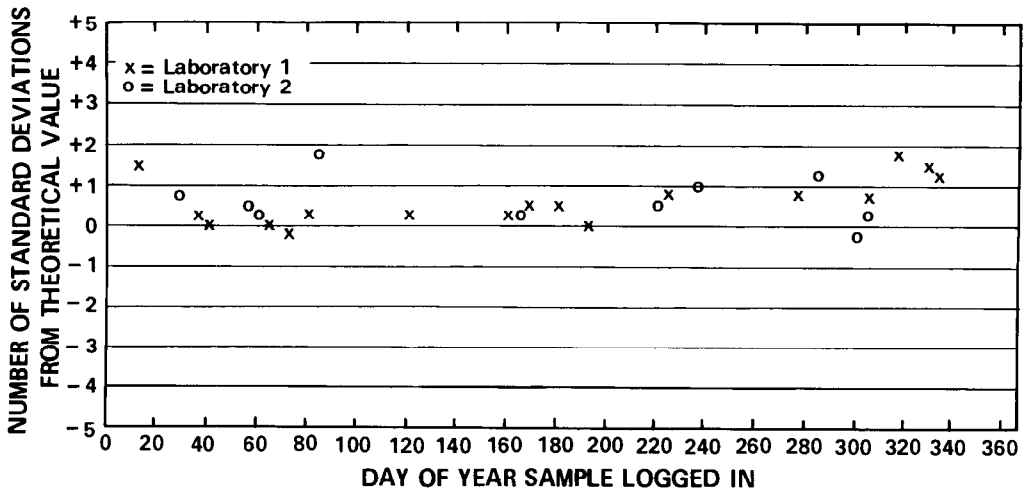

Figure 23.—Example of chart showing positive bias.

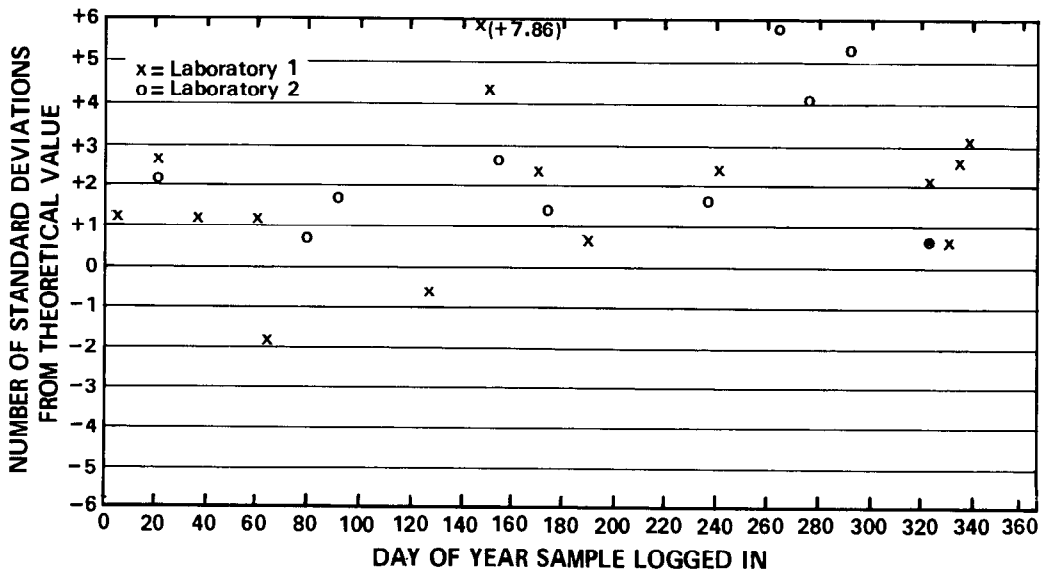

Figure 24.—Example of chart showing positive bias and lack of precision.

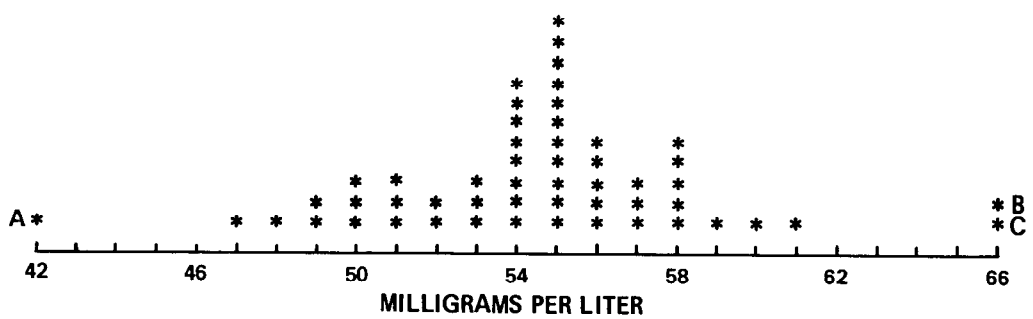

Figure 25.—Results from the analysis of magnesium in Standard Reference Water Sample 68. Each * equals a value from the laboratory; values marked A, B, and C are in obvious disagreement with the consensus.

reement with the consensus. Figure 26 demonstrates the use of a bar chart to show the percentage of correct results achieved by several different laboratories (or offices) after analyses of a round of reference materials and to show the percentage increase or decrease in correct results since the last round of analyses; this type of figure could be effectively used, for instance, to depict district results for the specific conductance field-monitoring program (see practice "Reference material use in monitoring field pH and specific conductance measurements" in section "Quality Assurance Monitoring").

2.4 Linear regression graph

2.4.1 If there is a linear relationship between two variables and if points representing the two variables are plotted on a graph, the relationship can be shown by drawing the line which best fits the points. This line can be written, $y = a + bx$, where y is the value which is observed for a given x value, a is the intercept of the line with the y-axis, and b is the slope of the line; it is often called a "least-squares" line since the sum of squares of vertical deviations of the points from it is smaller than the sum of squares of deviations from any other line. The line should not be extended beyond the limits supported by the data.

2.4.2 When a least squares equation is presented, it will be most useful if the correlation coefficient for the equation is also given so that anyone looking at the data will know how "valid" the stated relationship is. A correlation coefficient near 1 is an indication that there is a good fit of the points to the line, while a correlation coefficient near zero is an indication either of a poor fit of the points or of a relationship in which the y is constant for all x values and the line is horizontal.

2.4.3 Least-squares lines can be used, for instance, to show how the standard deviation of a method varies with the concentration of the constituent being tested, to show how differences between "duplicate" analyses vary with concentration, to compare results from two laboratories, to compare results obtained by two analytical procedures, or to compare results from field analyses with results from laboratory analyses. Figure 27, for example, shows a possible relationship between observed concentration differences and means for determination of polychlorinated biphenyls made on "duplicate" bottom sediment samples; in this case, more data needs to be collected.

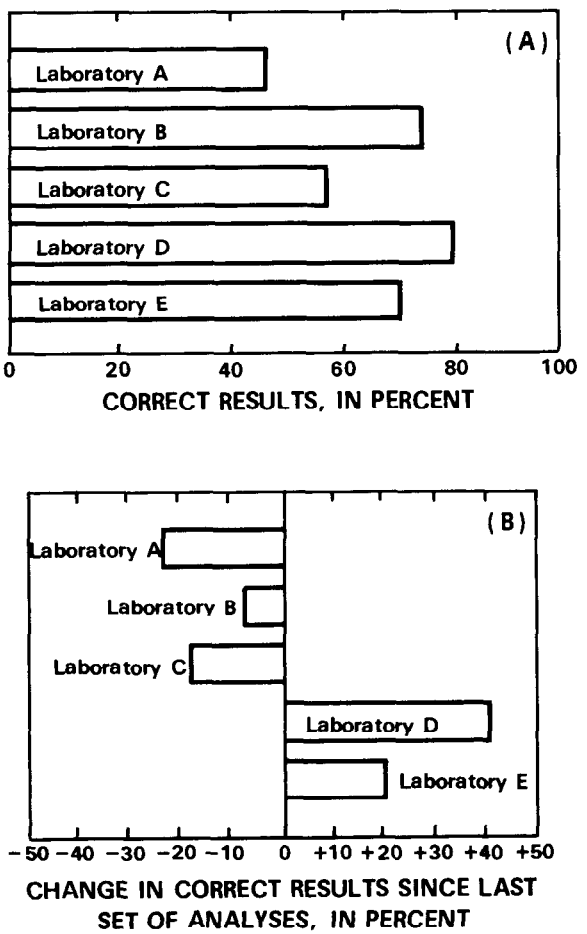

Figure 26.—Use of bar graph to depict (A) percentage of correct results achieved by five laboratories in an interlaboratory study and to show (B) the percent increase or decrease in correct results since last interlaboratory study.

References

Dixon, W. J., and Massey, F. J., Jr., 1969, Introduction to statistical analysis, (3d ed.): New York, McGraw-Hill, 638 p.

Draper, Norman, and Smith, Harry, 1966, Applied regression analysis: New York, John Wiley, 407 p.

Schmid, C. F., and Schmid, S. E., 1969, Handbook of graphic presentation, (2d ed.): New York, John Wiley, 308 p.

Youden, W. J., 1960, The sample, the procedure, and the laboratory: Analytical Chemistry, v. 32, no. 13, p. 23A–37A.

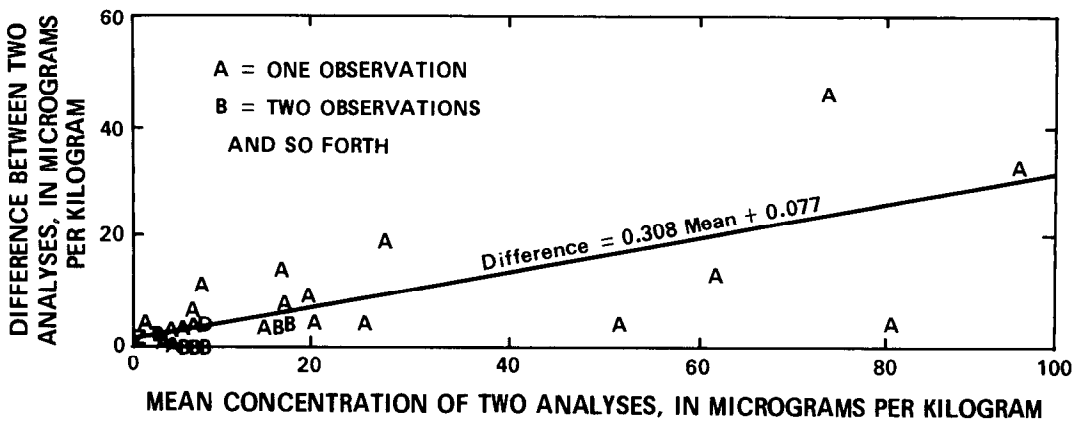

Figure 27.—Relationship between the concentration difference and mean for duplicate determinations of polychlorinated biphenyls in bottom material.

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. 10–11.

Youden, W. J., 1978, Graphical diagnosis of interlaboratory test results *in* Chemical Division Technical Supplement Interlaboratory Testing Techniques: Milwaukee, American Society for Quality Control, p. 12–16.

Methods Used for Data Evaluation: *t*-Test

1. Application or scope

1.1 This practice gives examples of tests which are based on use of the statistical parameter "*t*" (NOTE 1). Other examples of the use of "*t*" are available in most books on statistics.

NOTE 1. Often called "Student's *t*," the distribution of this parameter was discovered by W. S. Gosset (Fraser, 1958).

1.2 The *t*-test may be used to determine if two means are statistically different.

1.3 If data are paired, a paired *t*-test can be made on the differences. The paired *t*-test can be used, for example, to compare data from samples which have been split in the field and mailed to two laboratories. It cannot be used if the data are not really paired (for example, to compare daily temperature data for two different years).

2. Practice

2.1 *t*-test example

2.1.1 The interlaboratory mean for cadmium for Standard Reference Water Sample (SRWS) number 56 was determined to be 9.9 μg/L. Analyzing the reference sample six times over a period of several months, the Denver Central laboratory obtained a mean and standard deviation of 8.2±3.0 μg/L. The *t*-test may be used to decide if the mean value obtained by Denver is different from the SRWS mean.

2.1.2 The hypothesis to be tested (H_o) is: $\bar{X}_{DCL}=\bar{X}_{SRWS}$. The alternative hypothesis (H_a) is: $\bar{X}_{DCL}\neq\bar{X}_{SRWS}$. The *t* is calculated:

$$t=\frac{\bar{X}_{DCL}-\bar{X}_{SRWS}}{s/\sqrt{n}} \qquad (37)$$

where

t = the t statistic,

$\bar{X}_{SRWS}$ = the SRWS mean

$\bar{X}_{DCL}$ = the mean obtained by the Denver laboratory

s = the standard deviation found by the Denver Laboratory, and

n = the number of times the Denver Laboratory analyzed the sample.

In this case:

$$t=\frac{8.2-9.9}{3.0/\sqrt{6}}=-1.388$$

2.1.3 In order to determine whether the means are different, the calculated value for *t* is compared with the *t* value found in table A11 in the appendix. At the 95 percent level with 5 degrees of freedom, $t=2.571$ or $t=-2.571$ (NOTE 2). For the calculated *t* to be rejected requires that it be greater than 2.571 or less than -2.571. In this case, *t* is not rejected and there is a less than 5 percent chance that the means are different.

NOTE 2. The "degrees of freedom" is $n-1$ for the examples discussed.

2.2 Paired *t*-test

2.2.1 Data in table 21 represent results from samples which were split and analyzed for constituent A in two laboratories, B, and C.

2.2.2 In order to compare the two laboratories, the differences between the values are computed and a mean and standard deviation of the differences are determined (note that the original values themselves are not considered).

2.2.3 The hypothesis to be tested, H_o, is: $\bar{d}=0$. The alternative hypothesis of H_a is: $\bar{d}\neq 0$. (In other words the hypothesis is that there is no difference in the data). The *t* is calculated:

$$t=\frac{\bar{d}-0}{s/\sqrt{n}}=\frac{\bar{d}}{s/\sqrt{n}} \qquad (38)$$

Table 21.—Paired data tabulation

Laboratory B (mg/L of A)	Laboratory C (mg/L of A)	Difference (mg/L of A)
19	15	+ 4
7	5	+ 2
10	8	+ 2
4	2	+ 2
23	20	+ 3
20	18	+ 2
18	19	- 1
65	63	+ 2
27	25	+ 2
25	26	- 1
3	3	0
	Average difference, $\bar{d}$ =	1.545
	Standard deviation, s =	1.572

where

t = the t statistic,

d = the mean of the differences,

s = the standard deviation of the differences, and

n = the number of pairs.

In this case

$$t = \frac{1.545}{1.572/\sqrt{11}} = 3.260$$

3. From the table at the 95 percent level with 10 degrees of freedom, t=2.228. Since the calculated t is greater than that found in the table, the hypothesis is rejected. There is difference between the data from the two laboratories with a less than 5 percent chance that the difference is due to random causes.

Selected References

Dixon, W. J., and Massey, F. J., Jr., 1969, Introduction to statistical analysis: (3d ed.): New York, McGraw-Hill, 638 p.

Miller, Irwin, and Freund, J. E., 1977, Probability and statistics for engineers (2d ed.): Englewood Cliffs, New Jersey, Prentice-Hall, 529 p.

Methods Used for Data Evaluation: A Test of Laboratory Variance

1. Application or scope

1.1 This practice describes a technique for analysis of variance.

1.2 The technique can be used to compare data submitted by several laboratories. This practice gives an example of the technique's use and presents several tests which may be made on the data. Other examples and tests are available in most books on statistics.

2. Practice

2.1 Example of analysis of variance

2.1.1 Consider a Geological Survey district office which has contracts with three laboratories and must monitor their work to ensure that the data are comparable to that of a Geological Survey Central Laboratory. A reference material is specially prepared in a matrix which is typical of water which the contract laboratories are analyzing. A portion of the reference water is sent to each of the three contract laboratories and also to a Central Laboratory. Over a period of several months, each laboratory receives and analyzes five such portions, and the data indicated in table 22 are reported.

2.1.2 In order to compare each laboratory's data, the following values are calculated:

$$SS_x = \Sigma X^2 - \frac{(\Sigma X)^2}{n} \tag{39}$$

Table 22.—Example: Data tabulation for a given constituent, as reported by four laboratories

Lab 1 (mg/L)	Lab 2 (mg/L)	Lab 3 (mg/L)	Central Laboratory (mg/L)
8	7	8	8
9	6	10	9
7	5	11	10
8	8	9	8
8	7	9	9

$$SS_L = \frac{\Sigma L^2}{n/m} - \frac{(\Sigma X)^2}{n} \tag{40}$$

$$SS_w = SS_x - SS_L \tag{41}$$

where

X = each value,

L = the total of the values reported by each laboratory,

n = the number of values,

m = the number of laboratories,

SS_x = the total sum of squares,

SS_L = the between laboratory sum of squares, and

SS_w = the within laboratory sum of squares.

In this case

$$SS_x = (8^2+9^2+7^2 \ldots +9^2) - \frac{(8+9+7+\ldots 9)^2}{20}$$

$$= 1{,}382 - \frac{(164)^2}{20} = 37.2$$

$$SS_L = \frac{40^2+33^2+47^2+44^2}{20/4} - \frac{(164)^2}{20}$$

$$= 1{,}366.8 - \frac{(164)^2}{20} = 22$$

$$SS_w = 37.2 - 22 = 15.2$$

2.1.3 These data are arranged in table 23, in a format which is typical of an analysis of variance table. The total degrees of freedom are one less than the total number of values, the between-

Table 23.—Typical data tabulation for analysis of variance

Type of variance	Degrees of freedom	Sum of squares	Mean squares
Total	19	37.2	
Between labs	3	22	7.333
Within labs	16	15.2	.950

lab degrees of freedom are one less than the number of laboratories and the within-lab degrees of freedom are obtained by subtraction. The mean square values are calculated by dividing the sum of squares value by the appropriate number of degrees of freedom.

2.2 *F*-test

2.2.1 In order to test the hypothesis that the laboratory means are equal (or that there is no variance between the laboratory means), the *F*-test is used (NOTE 1).

NOTE 1. The statistical parameter *F* is based on the distribution of the ratios of two variances (Dixon and Massey, 1969).

2.2.2 The value for *F* is calculated:

$$F=\frac{BMS}{WMS} \tag{42}$$

where

F = the F statistic,

BMS = the between laboratory mean squares, and

WMS = the within laboratory mean square.

The *F* calculated for the example is

$$F=\frac{7.333}{.950}=7.72$$

2.2.3 The *F* so computed is compared to the tabular values for *F* in table A6. Locating the correct value in the table requires using a set of degrees of freedom values which correspond to the number of "between-lab" and "within-lab" degrees of freedom. A computed value greater than the tabular value means the hypothesis can be rejected.

2.2.4 At the 95th percentile with 3 and 16 degrees of freedom, the tabular *F* value is 3.24. Thus, the *F* calculated from the data in the example is greater than the tabular *F* values. The hypothesis is rejected: There is less than a 5 percent chance that the laboratory means are equal.

2.3 *q*-test

2.3.1 This test can be used to compare all the means (Dunn and Clark, 1974). It requires that the *F*-test must have shown a significant difference and also requires that the number of values used to compute each mean be equal (NOTE 2).

NOTE 2. This test was developed by Tukey and is based on the studentized range, *q*.

2.3.2 The number which would indicate significant difference between two means is calculated:

$$SD=q\sqrt{\frac{WMS}{n}} \tag{43}$$

where

SD = the significant difference,

q = the q statistic, taken from table A12 using the number of laboratories and using the degrees of freedom associated with the "within" mean square.

WMS = the "within" mean square, and

n = the number of values used to compute a laboratory

2.3.3 From table A12, the *q*-statistic at the 95 percent level is 4.05 for four laboratories and 16 degrees of freedom. The significant difference for the example is:

$$SD=4.05\sqrt{\frac{.950}{5}}=1.77$$

2.3.4 This calculated significant difference may be used to compare means of all laboratories. For ease in comparison, the laboratories are first ranked by their mean values (table 24).

2.3.5 A difference between two laboratory means which is greater than the calculated value indicates a significant difference. Thus, for the example, the mean of laboratory 2 is significantly different from the mean of laboratory 3 or the Central Laboratory (9.4–1.8 = 7.6

Table 24.—Example: Ranking of mean data

Rank	Laboratory	Mean
1	3	9.4
2	Central	8.8
3	1	8.0
4	2	6.6

and 8.8–1.8 = 7.0), but is not significantly different from the mean of laboratory 1 (8.0–6.6 = 1.4). There is no statistically significant difference between the means of laboratories 1, 3, and the Central Laboratory.

2.4 Significant difference test using t

2.4.1 This test can be applied if it has been decided, before looking at the data, that one mean will be used as the "standard" and the other means will be compared with it (Dunn and Clark, 1974). For example, it is decided, before any samples are mailed to the laboratories, that each contract laboratory's data will be compared to data from a Geological Survey Central Laboratory.

2.4.2 The absolute difference between the central laboratory mean and each of the other means is calculated:

$$\left| \bar{X}_{cl} - \bar{X}_i \right|$$

where

$\bar{X}_{cl}$ = the Central Laboratory mean, and

$\bar{X}_i$ = laboratory means other than the Central Laboratory.

2.4.3 Using the data in table 24, the values are 0.8, 2.2, and 0.6 for the differences between the Central Laboratory mean and the means of laboratory 1, laboratory 2, and laboratory 3, respectively.

2.4.4 Each difference is compared to the significant difference value, calculated as follows:

$$SD = t \sqrt{\frac{WMS}{n_{cl}} + \frac{WMS}{n_i}} \qquad (44)$$

where

SD = the least significant difference,

t = the t statistic, taken from table A11 using the degrees of freedom associated with the "within" mean square,

WMS = the "within" mean square,

n_{cl} = the number of values used in calculating the Central Laboratory mean, and

n = the number of values used in calculating the mean being compared (NOTE 3).

NOTE 3, n_i does not have to equal n_{cl}, although in this example they are equal.

2.4.5 For the example:

$$SD = 2.12 \sqrt{\frac{.95}{5} + \frac{.95}{5}} = 1.31$$

Any mean difference which is larger than 1.31 is significant: The mean reported by laboratory 2 is statistically significantly different from the Central Laboratory mean.

References

Dixon, W. J., and Massey, F. J., 1969, Introduction to statistical analyses (3d ed.): New York, McGraw-Hill, 638 p.

Dunn, O. J., and Clark, V. A., 1974, Applied statistics: analysis of variance and regression: New York, John Wiley, 387 p.

Steiner, E. H., 1975, Planning and analyses of results of collaborate tests, *in* Statistical Manual of the Association of Official Analytical Chemists: Washington, D.C., Association of Official Analytical Chemists, p. 65–88.

Materials Evaluation

In order to have an effective analytical data quality assurance program, it is necessary that materials used in sample collection be of adequate and uniform or known quality. Procedures which can be used in designing a plan to be used in testing materials are described here.

Selection of Sample

1. Application or scope

1.1 This practice describes random sampling from systematically packed material and from bulk packed material. Random sampling techniques must be used to select the sample to be tested.

2. Practice

2.1 Systematically-packed material

2.1.1 Assign a sequence number to each carton, to each tray within a carton and to each row and column within a tray. For example, a sample in the first row and third column of the fifth box in the second carton opened (or received) could be assigned the number 2–5–1–3.

2.1.2 Since most vendors pack a specific material the same way each time it is sent, the numbers can be assigned once and records retained for subsequent shippings. Thus if it is known that there are always five rows and five columns in every box and that there are always six boxes in one carton, the item assigned 2–5–1–3 will always be in the same spot of the second carton opened (or second carton received in shipment).

2.2 Bulk-packed material

2.2.1 Assign each carton a separate number.

2.2.2 Arrange items within a carton in 10 groups (for example, if carton contains 1,000 items, arrange 100 in each group). Assign each item a number or arrange in columns and rows and assign the rows and columns a number.

2.2.3 Since vendors usually pack the same number of items in each carton, the numbers can be assigned once and the records retained for subsequent shippings.

2.3 Random sampling

2.3.1 Use a table of random numbers (available in most statistics books), or a calculator or computer to generate random numbers.

2.3.2 If using a table, arbitrarily put a finger on the table and record subsequent numbers.

2.3.3 Select the items indicated by the table and use for quality assurance testing. Thus, the number 2,513 would designate the 2nd carton, 5th box, 1st row, and 3rd column.

Selected References

Dixon, W. J. and Massey, F. J., Jr., 1969, Introduction to statistical analyses (3d ed.): New York, McGraw-Hill, p. 39–42.

Wiesen, J. M., 1974, Sampling by attributes, *in* Juran, J. M., and others, eds., Quality Control Handbook (3d ed.): New York, McGraw-Hill, p. 24–1—24–44.

Single Sampling With Operating Characteristic Curves

1. Application or scope

1.1 This practice describes the calculations needed to prepare operating characteristic (OC) curves for "single sampling" plans and gives some examples. It can be used in setting up a plan to test the quality of materials.

1.2 Although the number of items which must be tested will usually be greater using a single sampling plan than with other sampling plans (such as double or sequential plans), record keeping will usually be simpler and less time-consuming. Single sampling plans are particularly useful when test analyses are time-consuming and results are desired immediately.

1.3 An OC curve gives the best description of the sampling plan (Miller and Freund, 1977). It will define the risks associated with accepting a "bad" lot or rejecting a "good" lot. Most published sampling plans, such as the Dodge-Romig plans (Dodge and Romig, 1959) and those in Mil-Std-105D (U.S. Department of Defense, 1963) show the applicable OC curve.

2. Practice

2.1 Calculation of OC curve.

2.1.1 An OC curve can be calculated using a hypergeometric distribution. The hypergeometric distribution can be (and, in acceptance sampling, usually is) approximated by the binomial distribution if the sample size n, is small compared to the lot size N, that is $n<\frac{1}{10}N$ (Miller and Freund, 1977).

2.1.2 Calculate the points for the OC curve:

$$A(d;n,p)=\sum_{k=0}^{d}\binom{n}{k}p^k(1-p)^{n-k}$$

$$=\sum_{k=0}^{d}\frac{n!}{k!(n-k)!}p^k(1-p)^{n-k} \qquad (45)$$

where

$A(d; n,p)$ = probability of accepting the lot,
k = number of defectives in the sample,
d = maximum number of defectives in sample,
n = number of items in sample, and
p = proportion of lot which is defective.

2.1.3 The values are tabulated for $n=20$ in Miller and Freund (1977).

2.1.4 Plot the probability of accepting the lot on the vertical axis and the proportion of lot which is defective on the horizontal axis to obtain the OC curve (see figs. 28–31).

2.2 Sampling risks

2.2.1 The risk of rejecting a "good" lot must be decided and the percent of "bad" items which will be allowed in satisfactory lots must be determined. This risk is also called the "producer's risk" and the percent is the "acceptable quality level" (AQL) (NOTE 1).

NOTE 1. In most cases, the AQL to be used initially will have to be set arbitrarily. However, after preliminary data are obtained it may be found that, due to costs involved or other factors, it is necessary to change the AQL.

2.2.2 The risk of accepting a bad lot must be decided and the percent of "bad" items which makes the lot bad must be determined. This risk is also called the "consumer's risk" and the percent is the "lot tolerance percent defective" (LTPD) (NOTE 2).

NOTE 2. The consumer's risk does not give the probability that the consumer will actually receive a product of the specified LTPD. Obviously, if there are zero defects in the lot, there will be no defects.

2.3 Figures 28–31 show examples of OC curves for several sample sizes.

2.3.1 Figure 28 shows OC curves for a sample size of 10 and requires a minimum lot size of 100. If no defective items are allowed in the sample, there is a 10 percent chance of

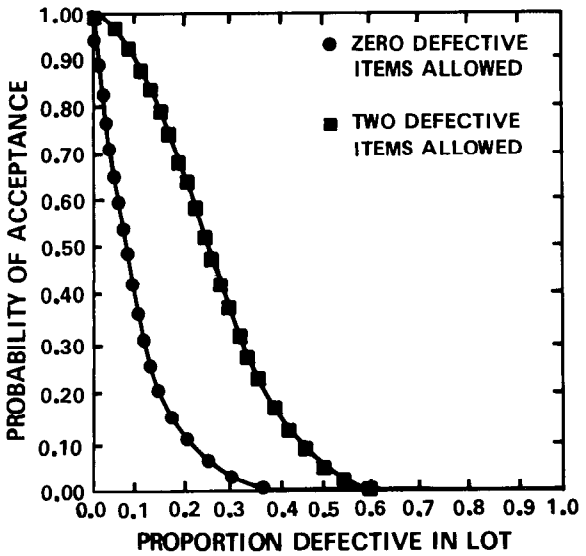

Figure 28.—Operating characteristic curves for sample size of 10.

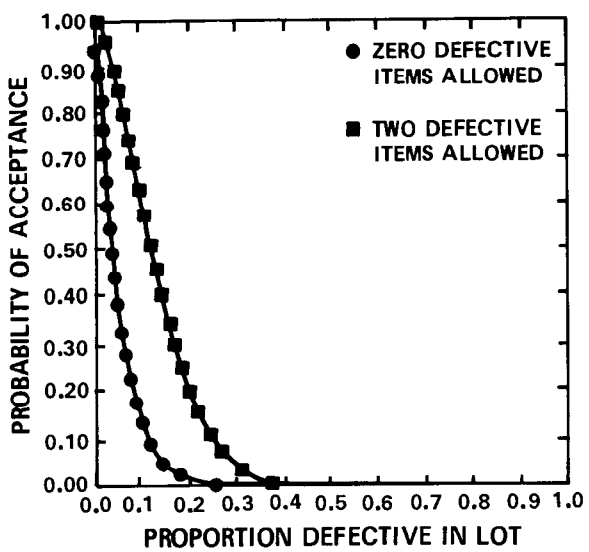

Figure 29.—Operating characteristic curves for sample size of 20.

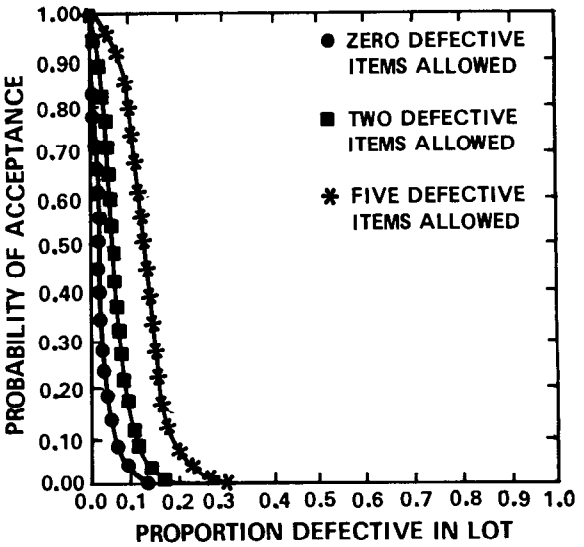

Figure 30.—Operating characteristic curves for sample size of 50.

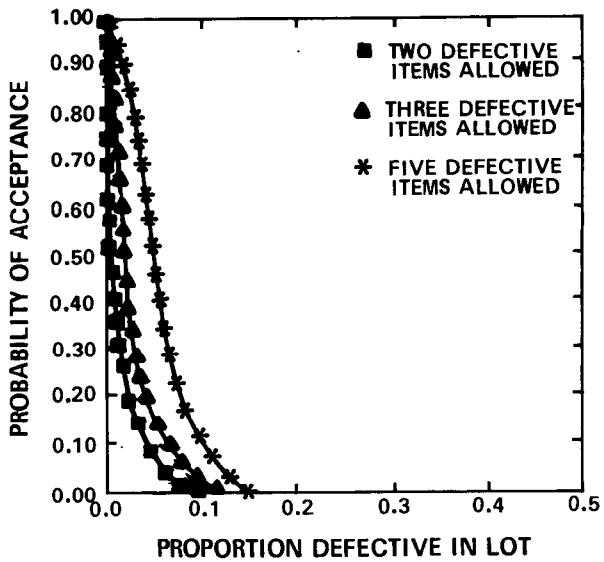

Figure 31.—Operating characteristic curves for sample size of 100.

accepting a lot with 21 percent defective items and a 10 percent chance of rejecting a lot with only 1 percent defective items. If two defective items are allowed in the sample, there is a 10 percent chance of accepting a lot with 45 percent defective items. There is essentially no chance of rejecting a lot with only 1 percent defective items.

2.3.2 By contrast, figure 29 shows OC curves for a sample size of 20 and requires a minimum lot size of 200. If no defective items are allowed in the sample, there is a 10 percent chance of accepting a lot with 11 percent defective items and a 10 percent chance of rejecting a lot with only 1 percent defective items. If two defective items are allowed in the sample, there is a 10 percent chance of accepting a lot with 24 percent defective items. There is a 10 percent chance of rejecting a lot with only 5 percent defective items, but essentially no chance

of rejecting a lot with only 1 percent defective items.

2.3.3 Figure 30 shows OC curves for a sample size of 50 and requires a minimum lot size of 500 and figure 31 shows OC curves for a sample size of 100 and requires a minimum lot size of 1,000. As can be seen by the examples, a change in sample size or a change in the number of defective samples allowed can make a considerable difference in the OC curve and in the risks of accepting a bad lot or rejecting a good lot.

References

Crow, E. L. and others, 1960, Statistics Manual: New York, Dover Publications p. 209–226.

Dixon, W. J., and Massey, F. J. Jr., 1969, Introduction to statistics: New York, McGraw-Hill, p. 410–415.

Dodge, H. F. and Romig, H. G., 1959, Sampling inspection tables, single and double sampling (2d ed.): New York, John Wiley, 224 p.

Enrick, N. L., 1972, Quality control and reliability, (6th ed.): New York, Industrial Press, p. 306.

Miller, Irwin, and Freund, J. F., 1977, Probability and statistics for engineers: Englewood Cliffs, New Jersey, Prentice-Hall, p. 60–63, 436–446, 477–481.

U.S. Department of Defense, 1963, American national standard sampling procedure and tables for inspection by attributes: Mil-Std-105D, 64 p.

Weisen, J. M., 1974, Sampling by attributes, *in* Juran, J. M., and others, eds., Quality control handbook (3rd ed.): New York, McGraw-Hill, p. 24–1—24–44.

Single Sampling Plans, to Obtain Lots of Acceptable Quality

1. Application or scope

1.1 This practice can be used in setting up a specific plan to test the quality of materials. The sampling plan detailed here is a portion of the Military Standard 105D plan. For lot quality which is equal to the acceptable quality level (AQL) specified, the probability of accepting the lot will range from 89 to 99.5 percent (Juran, 1965). This practice is particularly useful when test analyses are time-consuming and results are desired immediately.

1.2 Although the number of items which must be tested will usually be greater using a single sampling plan than with other sampling plans (such as double or sequential plans), record keeping usually will be simpler and less time-consuming.

2. Practice

2.1 Choose the acceptable quality level (AQL) by choosing the maximum percent of "bad" items which will be allowed for satisfactory lots (NOTE 1).

NOTE 1. The AQL choosen may have to be a compromise between what is desirable and what is economically possible to attain. See practice "Single sampling with operating characteristic curves" for more information on the AQL.

2.2 Depending upon the size of the lot, randomly select the number of samples specified in table 25. If sample size specified exceeds lot size, do 100 percent inspection.

2.3 If number of "defective" items found is ≥ value tabulated as an "R" value, reject the

Table 25.—Excerpt from Mil-Std-105D, single sampling plan

		Acceptable quality levels																							
		.10		.15		.25		.40		.65		1.0		1.5		2.5		4.0		6.5		10		15	
Lot size	Sample size	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R
26 to 50	8											↓		0	1			↓		1	2	2	3	3	4
51 to 90	13									↓		0	1	↑		↓		1	2	2	3	3	4	5	6
91 to 150	20									0	1	↑		↓		1	2	2	3	3	4	5	6	7	8
151 to 280	32							0	1	↑		↓		1	2	2	3	3	4	5	6	7	8	10	11
281 to 500	50					0	1	↑		↓		1	2	2	3	3	4	5	6	7	8	10	11	14	15
501 to 1,200	80			0	1	↑		↓		1	2	2	3	3	4	5	6	7	8	10	11	14	15	21	22
1,201 to 3,200	125	0	1	↑		↓		1	2	2	3	3	4	5	6	7	8	10	11	14	15	21	22	↑	
3,201 to 10,000	200	↑		↓		1	2	2	3	3	4	5	6	7	8	10	11	14	15	21	22	↑			
10,001 to 35,000	315	↓		1	2	2	3	3	4	5	6	7	8	10	11	14	15	21	22	↑					
35,001 to 150,000	500	1	2	2	3	3	4	5	6	7	8	10	11	14	15	21	22	↑							
150,001 to 500,000	800	2	3	3	4	5	6	7	8	10	11	14	15	21	22	↑									

↓ = Use sampling plan below arrow. If sample size exceeds lot size, do 100 percent inspection.

↑ = Use sampling plan above arrow.

A = Accept lot if number of defective items ≤ number tabulated.

R = Reject lot if number of defective items ≥ number tabulated.

lot. If number of "defective items found is ≤ value tabulated as an "A" value, accept the lot.

2.4 If 10 lots have been inspected and have not been rejected, refer to Military Standard 105D for procedures to follow to reduce inspection (U.S. Department of Defense, 1963). See also practice "Reducing sample inspection."

References

Juran, J. M. and others, eds.,1965, Quality Control Handbook: New York, McGraw-Hill, p. 24–1—24–44.

Miller, Irwin, and Freund, J. F., 1977, Probability and statistics for engineers: Englewood Cliffs, New Jersey, Prentice-Hall, p. 436–446.

U.S. Department of Defense, 1963, American national standard sampling procedures and tables for inspection by attributes: Mil-Std-105D, 64 p.

Double Sampling Plans, to Obtain Lots of Acceptable Quality

1. Application or scope

1.1 This practice can be used in setting up a specific plan to test the quality of materials. The sampling plan detailed here is a portion of the Military Standrd 105D plan.

1.2 A smaller-sized sample is initially used than would be used in a single sampling plan. If it is possible to accept or reject the lot based on this sample, the overall sample size will be smaller than for single sampling, otherwise a second sample must be selected and the overall sample size will be larger.

2. Practice

2.1 Choose the acceptable quality level (AQL) by choosing the maximum percent of "bad" items which will be allowed for satisfactory lots (NOTE 1).

NOTE 1. The AQL chosen may have to be a compromise between what is desirable and what is economically possible to attain. See practice "Single sampling with operating characteristic curves" for more information on the AQL.

2.2 Depending upon the size of the lot, randomly select the number of samples specified

Table 26.—Excerpt from Mil-Std-105D, double sampling plan

Lot size	Sample set	Sample size	Acceptable quality levels																							
			.10		.15		.25		.40		.65		1.0		1.5		2.5		4.0		6.5		10		15	
			A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R
26 to 50	First	5												↓		.		.		↓		0		0		1	
	Second	5																				1		3		4	
51 to 90	First	8												.		↑		↓		0		0		1		2	
	Second	8														↑				1		3		4		5	
91 to 150	First	13										.		↑		↓		0		0		1		2		3	
	Second	13																1		3		4		5		7	
151 to 280	First	20									.		↑				0			1		2		3		5	
	Second	20												↓			1			4		5		7		9	
281 to 500	First	32								.		↑					0			2		3		5		7	
	Second	32															1			3		4		6		8	
501 to 1,200	First	50				.				↑																	
	Second	50										↓															
1,201 to 3,200	First	80		.																							
	Second	80				↑																					
3,201 to 10,000	First	125						↓																			
	Second	125		↑																							
10,001 to 35,000	First	200																									
	Second	200																									
35,001 to 150,000	First	315																									
	Second	315																									
150,001 to 500,000	First	500																									
	Second	500																									

↓ = Use sampling plan below arrow. If sample size exceeds lot size, do 100 percent inspection.

↑ = Use sampling plan above arrow.

A = Acceptance number.

R = Rejection number.

. = Use corresponding single sampling plan.

in table 26. If sample size specified exceeds lot size, do 100 percent inspection.

2.3 If for the first sample set the numbers of "defective" items found is ≥ value tabulated as an "R" value, reject the lot. If number of "defective" items found is ≤ value tabulated as an "A" value, accept the lot. If the number of "defective" items found is between the "A" and "R" values, select a second set of samples.

2.4 If the number of "defective" items found in first and second set combined is ≥ the value tabulated as an "R" value, reject the lot. If the number is ≤ the value tabulated as an "A" value, accept the lot.

2.5 If 10 lots have been inspected and have not been rejected, refer to Military Standard 105D for procedures to follow to reduce the number of items to be inspected (U.S. Dept. of Defense, 1963). See also practice, "Reducing sample inspection."

References

Juran, J. M. and others, eds., 1965, Quality Control Handbook: New York, McGraw-Hill, p. 24–1—24–44.

Miller, Irwin, and Freund, J. F., 1977, Probability and statistics for engineers: New Jersey, Prentice-Hall, p. 436–446.

U.S. Department of Defense, 1963, American national standard sampling procedures and tables for inspection by attributes: Mil-Std-105D, 64 p.

Sequential Sampling Plans, to Obtain Lots of Acceptable Quality

1. Application or scope

1.1 This practice can be used for testing the quality of materials where it is practical to test one item at a time.

1.2 It may be used to test physical properties of materials prior to accepting their delivery (for example, in testing pesticide bottles which must meet certain size criteria to be used in samplers). Since results from each test must be evaluated before deciding whether to test the next sample, this practice should not be used when time is a critical factor and it is inconvenient or costly to wait for the results from tests of one item at a time.

2. Practice

2.1 Construction of graph

2.1.1 Indicate the number of items tested (n) along the horizontal axis and the number of defective items found (d) along the vertical axis (fig. 32).

2.1.2 Calculate and draw parallel lines, d_1 and d_2, to define areas of acceptance and rejection (Grant and Leavenworth, 1974):

$$d_1 = sn - h_1 \tag{46}$$

$$d_2 = sn + h_2 \tag{47}$$

where

d_1 = lower line, below which is region of acceptance,

d_2 = upper line, above which is region of rejection,

n = number of items tested,

$$h_1 = \frac{\log \frac{1-\alpha}{\beta}}{\log \frac{P_2}{P_1} + \log \frac{1-P_1}{1-P_2}},$$

$$h_2 = \frac{\log \frac{1-\beta}{\alpha}}{\log \frac{P_2}{P_1} + \log \frac{1-P_1}{1-P_2}},$$

$$s = \frac{\log \frac{1-P_1}{1-P_2}}{\log \frac{P_2}{P_1} + \log \frac{1-P_1}{1-P_2}},$$

where

α = probability of rejection of a "good" lot (producer's risk or alpha error),

β = probability of accepting a "bad" lot (consumer's risk or beta error),

P_1 = acceptable quality level (AQL), and

P_2 = lot tolerance percent defective (LTPD)

2.2 Examples of graphs

2.2.1 Figure 33 can be used when willing to take a 2 percent chance of rejecting a lot with 5 percent defective pieces and a 5 percent chance of rejecting a lot with 1 percent defective pieces.

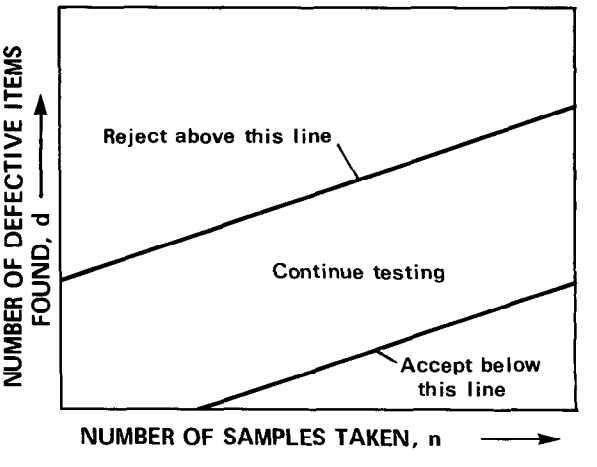

Figure 32.—Sequential sampling.

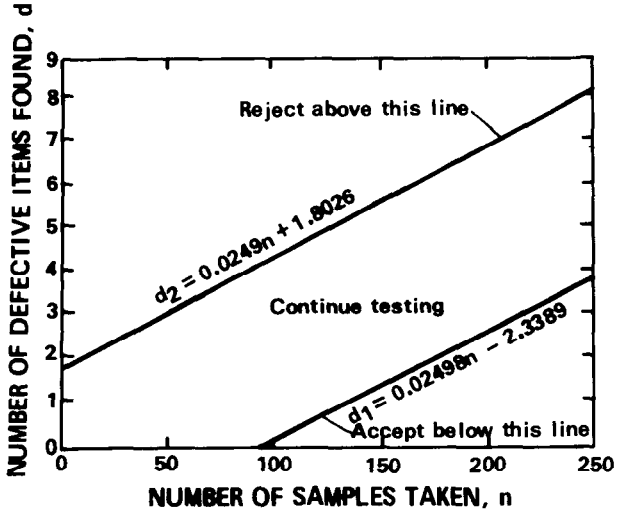

Figure 33.—Sequential sampling: 2-percent chance of accepting a lot with 5-percent defective items, and 5-percent chance of rejecting a lot with 1-percent defective items.

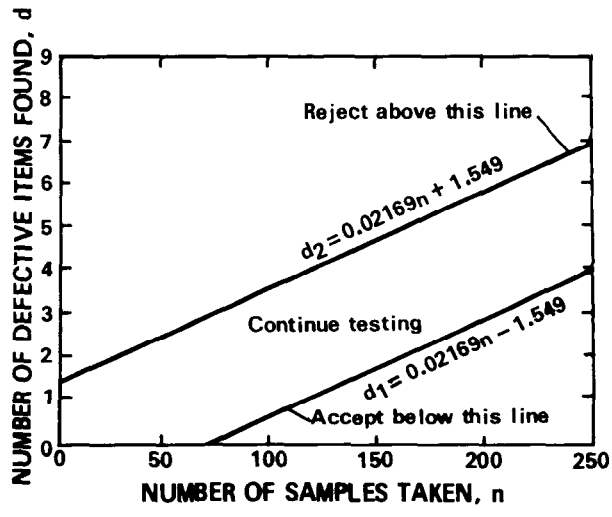

Figure 35.—Sequential sampling: 10-percent chance of accepting a lot with 4-percent defective items, and 10-percent chance of rejecting a lot with 1-percent defective items.

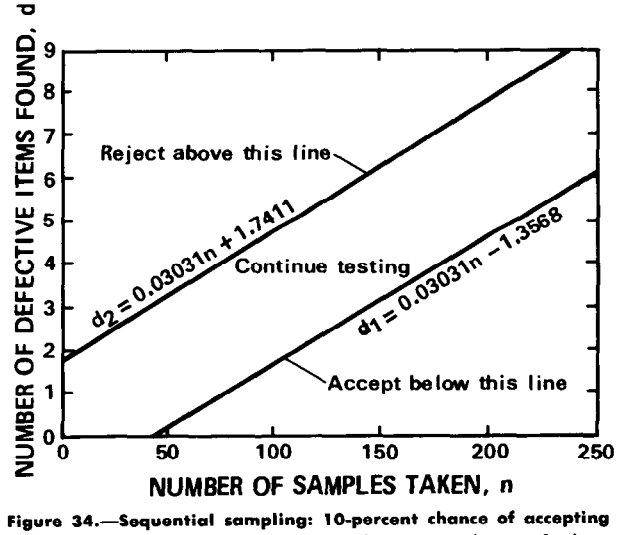

Figure 34.—Sequential sampling: 10-percent chance of accepting a lot with 5-percent defective items, and 5-percent chance of rejecting a lot with 1-percent defective items.

Figure 34 can be used when willing to take a 10 percent chance of accepting a lot with 5 percent defective pieces and a 5 percent chance of rejecting a lot with 1 percent defective pieces. Figure 35 can be used when willing to take a 10 percent chance of accepting a lot with 4 percent defective pieces and a 10 percent chance of rejecting a lot with 1 percent defective.

2.3 Maximum n

2.3.1 It would be possible, particularly if the lot is of "borderline" quality, to continue sequential sampling indefinitely. If an extremely large sample is undesirable, a value for n may be selected at which sampling is to stop.

2.3.2 One value which may be used (Crow and others, 1960) is to calculate and agree to stop sampling at a maximum n such that:

$$n_{max} = \frac{3\left(\log\frac{1-\beta}{\alpha}\right)\left(\frac{1-\alpha}{\beta}\right)}{\left(\log\frac{P_2}{P_1}\right)\left(\log\frac{1-P_1}{1-P_2}\right)} \qquad (48)$$

where

n_{max}=maximum number of samples to be taken, and α, β, P_1 and P_2 are as previously defined (NOTE 1).

NOTE 1. Maximum values would be 517, 241 and 339 for the examples given in figures 33, 34, and 35.

2.3.3 When n_{max} is reached, accept the lot if the distance between n_{max} and the lower line, d_1, is less than the distance between n_{max} and the upper line, d_2. Otherwise, reject the lot (NOTE 2).

NOTE 2. Rarely will it be necessary to test n_{max} number of samples before deciding whether to accept or reject the lot (Crow and others, 1960).

References

Crow, E. L., Davis, F. A., and Maxfield, M. W., 1960, Statistics manual: New York, Dover Publications, p. 209–226.

Dixon, W. J., and Massey, F. J., Jr., 1969, Introduction to statistics: New York, McGraw-Hill, p. 262–375.

Enrick, N. L., 1972, Quality control and reliability (6th ed.): New York, Industrial Press, p. 306

Grant, E. I., and Leavenworth, R. S., 1972, Statistical quality control (4th ed.): New York, McGraw-Hill, p. 456–459.

Miller, Irwin, and Freund, J. F., 1977, Probability and statistics for engineers: New Jersey, Prentice-Hall, p. 436–446.

Reducing Sample Inspection

1. Application or scope

1.1 This practice describes methods which can be used to reduce the size of the sample (and cost) necessary for quality assurance testing when lots are received repeatedly from the same vendor (NOTE 1).

NOTE 1. If vendor cooperation is necessary, it usually will be necessary to specify the type of cooperation needed from the vendor in any contract issued.

2. Practice

2.1 Vendor selection of sample

2.1.1 Require the vendor to select the sample. The size of sample, frequency of sampling, definition of a lot, and so forth, must be agreed upon beforehand (Fitzgibbons, 1974).

2.1.2 Require the vendor to identify the sample as to its lot and give any other pertinent information. Have the sample shipped prior to or along with shipment of the lot.

Table 27.—Excerpt from Mil-Std-105D, maximum number of defective items allowed for reduced inspection

Number of sample units from last ten lots or batches	Acceptable quality level									
	0.25	0.40	0.65	1.0	1.5	2.5	4.0	6.5	10	15
20-29	.	.	.	.	.	.	.	.	0	0
30-49	.	.	.	.	.	.	.	0	0	1
50-79	.	.	.	.	.	.	0	0	2	3
80-129	.	.	.	.	.	0	0	2	4	7
130-199	.	.	.	.	0	0	2	4	7	13
200-319	.	.	.	0	0	2	4	8	14	22
320-499	.	.	0	0	1	4	8	14	24	39
500-799	.	0	0	2	3	7	14	25	40	63
800-1,249	0	0	2	4	7	14	24	42	68	105
1,250-1,999	0	2	4	7	13	24	40	69	110	169
2,000-3,149	2	4	8	14	22	40	68	115	181	
3,150-1,999	4	8	14	24	38	67	111	106		
5,000-7,999	7	14	25	40	63	110	181			
8,000-12,499	14	24	42	68	105	181				
12,500-19,999	24	40	69	110	169					
20,000-31,499	40	68	115	181						
31,500-49,999	67	111	186							
50,000 > Over	110	181	301							

. Denotes that the number of sample units from the last ten lots or batches is not sufficient for reduced inspection for this AQL.

Table 28.—Excerpt from Mil-Std-105D, reduced inspection

		Acceptable quality levels (percent)																			
		.25		.40		.65		1.0		1.5		2.5		4.0		6.5		10		15	
Lot size	Sample size	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R
26 to 90	2										↓	0	1				↓	0	2	1	3
91 to 150	3								↓	0	1	↑			↓	0	2	1	3	1	4
151 to 280	5						↓	0	1	↑			↓	0	2	1	3	1	4	2	5
281 to 500	8				↓	0	1	↑		↓		0	2	1	3	1	4	2	5	3	6
501 to 1,200	13		↓	0	1	↑		↓		0	2	1	3	1	4	2	5	3	6	5	8
1,201 to 3,200	20	0	1	↑		↓		0	2	1	3	1	4	2	5	3	6	5	8	7	10
3,201 to 10,000	32	↑		↓		0	2	1	3	1	4	2	5	3	6	5	8	7	10	10	13
10,001 to 35,000	50	↓		0	2	1	3	1	4	2	5	3	6	5	8	7	10	10	13		↑
35,001 to 150,000	80	0	2	1	3	1	4	2	5	3	6	5	8	7	10	10	13		↑		
150,001 to 500,000	125	1	3	1	4	2	5	3	6	5	8	7	10	10	13		↑				

↓ = Use sampling plan below arrow.

↑ = Use sampling plan above arrow.

A = Accept lot if number of defective items ≤ number tabulated.

R = Reject lot if number of defective items ≥ number tabulated.

2.1.3 Initially, draw a separate independent sample from the lot received. Check the independent sample and the vendor's selected sample.

2.1.4 If results from the independent sample and vendor's sample agree for several shipments, assume that the vendor is selecting a representative sample. Then subsample and test the vendor's sample instead of the lot; occasionally also test the lot to ensure results continue to agree.

2.2 Vendor quality control data

2.2.1 Require the vendor's quality control data to be submitted with each lot.

2.2.2 Initially, select a sample to be tested from each lot and compare with the vendor's data.

2.2.3 If results from the samples tested agree with the vendor's data, assume the vendor's data is adequate. Then rely on the vendor's data for most shipments; occasionally test a lot to verify data integrity.

2.3 Military Standard 105D—reduced sampling

2.3.1 If at least 10 consecutive lots from a vendor have been acceptable and the total number of defective items does not exceed the numbers in table 27, reduced sampling may be used for the Military Standard 105D plan.

2.3.2 Using table 28, select the sample size depending on the size of the lot. Accept the lot if the number of "bad" samples is less than or equal to the value under A. Reject the lot if the number of "bad" samples is equal to or greater than the value under R.

2.3.3 If a lot is rejected, resume normal sampling for Military Standard 105D (See practice "Single sampling plans, to obtain lots of acceptable quality").

References

Fitzgibbons, R. G., 1974, Vendor relations, *in* Juran, J. M., and others, eds., Quality control handbook (30th ed): New York, McGraw-Hill, p. 10–1—10–35.

Juran, J. M., and Gryna, F. M., Jr., 1976, Quality planning and analysis: New York, McGraw-Hill, 684 p.

U.S. Department of Defense, 1963, American national standard sampling procedures and tables for inspection by attributes: Mil-Std-105D, 64 p.

Appendix
Statistical Tables

Table A1.—Critical Values for T[a]

Number of observations, n	2.5 Percent significance level[b]	5 Percent significance level[b]
3	1.155	1.153
4	1.481	1.463
5	1.715	1.672
6	1.887	1.822
7	2.020	1.938
8	2.126	2.032
9	2.215	2.110
10	2.290	2.176
11	2.355	2.234
12	2.412	2.285
13	2.462	2.331
14	2.507	2.371
15	2.549	2.409
16	2.585	2.443
17	2.620	2.475
18	2.651	2.504
19	2.681	2.532
20	2.709	2.557
21	2.733	2.580
22	2.758	2.603
23	2.781	2.624
24	2.802	2.644
25	2.822	2.663
26	2.841	2.681
27	2.859	2.698
28	2.876	2.714
29	2.893	2.730
30	2.908	2.745
31	2.924	2.759
32	2.938	2.773
33	2.952	2.786
34	2.965	2.799
35	2.979	2.811
36	2.991	2.823
37	3.003	2.835
38	3.014	2.846
39	3.025	2.857
40	3.036	2.866
41	3.046	2.877
42	3.057	2.887
43	3.067	2.896
44	3.075	2.905
45	3.085	2.914
46	3.094	2.923
47	3.103	2.931
48	3.111	2.940
49	3.120	2.948
50	3.128	2.956
51	3.136	2.964
52	3.143	2.971
53	3.151	2.978
54	3.158	2.986
55	3.166	2.992
56	3.172	3.000
57	3.180	3.006
58	3.186	3.013
59	3.193	3.019
60	3.199	3.025
61	3.205	3.032
62	3.212	3.037
63	3.218	3.044
64	3.224	3.049
65	3.230	3.055
66	3.235	3.061
67	3.241	3.066
68	3.246	3.071
69	3.252	3.076
70	3.257	3.082
71	3.262	3.087
72	3.267	3.092
73	3.272	3.098
74	3.278	3.102
75	3.282	3.107
76	3.287	3.111
77	3.291	3.117
78	3.297	3.121
79	3.301	3.125
80	3.305	3.130
81	3.309	3.134
82	3.315	3.139
83	3.319	3.143
84	3.323	3.147
85	3.327	3.151
86	3.331	3.155
87	3.335	3.160
88	3.339	3.163
89	3.343	3.167
90	3.347	3.171
91	3.350	3.174
92	3.355	3.179
93	3.358	3.182
94	3.362	3.186
95	3.365	3.189
96	3.369	3.193
97	3.372	3.196
98	3.377	3.201
99	3.380	3.204
100	3.383	3.207
101	3.386	3.210
102	3.390	3.214
103	3.393	3.217
104	3.397	3.220
105	3.400	3.224
106	3.403	3.227
107	3.406	3.230
108	3.409	3.233
109	3.412	3.236
110	3.415	3.239
111	3.418	3.242
112	3.422	3.245
113	3.424	3.248
114	3.427	3.251
115	3.430	3.254
116	3.433	3.257
117	3.435	3.259
118	3.438	3.262
119	3.441	3.265
120	3.444	3.267
121	3.447	3.270
122	3.450	3.274
123	3.452	3.276
124	3.455	3.279
125	3.457	3.281
126	3.460	3.284
127	3.462	3.286
128	3.465	3.289
129	3.467	3.291
130	3.470	3.294
131	3.473	3.296
132	3.475	3.298
133	3.478	3.302
134	3.480	3.304
135	3.482	3.306
136	3.484	3.309
137	3.487	3.311
138	3.489	3.313
139	3.491	3.315
140	3.493	3.318
141	3.497	3.320
142	3.499	3.322
143	3.501	3.324
144	3.503	3.326
145	3.505	3.328
146	3.507	3.331
147	3.509	3.334

[a] Reprinted with permission from the "Annual Book of ASTM Standards, Part 41." Copyright, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103; with data from "Extension of sample sizes and percentage points for tests of outlying observations" by Frank E. Grubbs and Glenn Beck, in "Technometrics," volume 14, number 4, American Statistical Association.

[b] For testing either positive or negative side of the distribution (not both sides).

Table A2.—Criteria for testing outlying value [a]

n	95 percentile	99 percentile
3	.941	.988
4	.765	.889
5	.642	.780
6	.560	.698
7	.507	.637
8	.554	.683
9	.512	.635
10	.477	.597
11	.576	.679
12	.546	.642
13	.521	.615
14	.546	.641
15	.525	.616
16	.507	.595
17	.490	.577
18	.475	.561
19	.462	.547
20	.450	.535
21	.440	.524
22	.430	.514
23	.421	.505
24	.413	.497
25	.406	.489

[a] From "Introduction to Statistical Analysis" by Wilfred J. Dixon and Frank J. Massey, Jr. Copyright (c) 1951, 1957, 1969 by McGraw-Hill, Inc. Used with the permission of McGraw-Hill Book Company.

Table A3.—Significant values for $\sqrt{b}$ [a]

n	1 percent significance level	5 percent significance level
5	1.34	1.05
10	1.31	0.92
15	1.20	0.84
20	1.11	0.79
25	1.06	0.71
30	0.98	0.66
35	0.92	0.62
40	0.87	0.59
50	0.79	0.53
60	0.72	0.49

[a] Reprinted with permission from the "Annual Book of ASTM Standards, Part 41." Copyright, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. As noted in Part 41, values for n of 5 through 20 were obtained by Ferguson.

Table A4.—Significant values for b_2 [a]

n	1 percent significance level	5 percent significance level
5	3.11	2.89
10	4.83	3.85
15	5.08	4.07
20	5.23	4.15
25	5.00	4.00
50	4.88	3.99
75	4.59	3.87
100	4.39	3.77

[a] Reprinted with permission from the "Annual Book of ASTM Standards, Part 41." Copyright, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. As noted in Part 41, values for n of 5 through 25 were obtained by Ferguson.

Table A5.—Approximate 5 percent limits for ranking scores[a] (two-sided test)

Number of labs, n	Number of materials, M[b]												
	3	4	5	6	7	8	9	10	11	12	13	14	15
3		4 12	5 15	7 17	8 20	10 22	12 24	13 27	15 29	17 31	19 33	20 36	22 38
4		4 16	6 19	8 22	10 25	12 28	14 31	16 34	18 37	20 40	22 43	24 46	26 49
5		5 19	7 23	9 27	11 31	13 35	16 38	18 42	21 45	23 49	26 52	28 56	31 59
6	3 18	5 23	7 28	10 32	12 37	15 41	18 45	21 49	23 54	26 58	29 62	32 66	35 70
7	3 21	5 27	8 32	11 37	14 42	17 47	20 52	23 57	26 62	29 67	32 72	36 76	39 81
8	3 24	6 30	9 36	12 42	15 48	18 54	22 59	25 65	29 70	32 76	36 81	39 87	43 92
9	3 27	6 34	9 41	13 47	16 54	20 60	24 66	27 73	31 79	35 85	39 91	43 97	47 103
10	4 29	7 37	10 45	14 52	17 60	21 67	26 73	30 80	34 87	38 94	43 100	47 107	51 114
11	4 32	7 41	11 49	15 57	19 65	23 73	27 81	32 88	36 96	41 103	46 110	51 117	55 125
12	4 35	7 45	11 54	15 63	20 71	24 80	29 88	34 96	39 104	44 112	49 120	54 128	59 136
13	4 38	8 48	12 58	16 68	21 77	26 86	31 95	36 104	42 112	47 121	52 130	58 138	63 147
14	4 41	8 52	12 63	17 73	22 83	27 93	33 102	38 112	44 121	50 130	56 139	61 149	67 158
15	4 44	8 56	13 67	18 78	23 89	29 99	35 109	41 119	47 129	53 139	59 149	65 159	71 169

[a] From W. J. Youden's "Statistical techniques for collaborative tests" in the Statistical Manual of the AOAC," 1975. Copyright 1975 by the Association of Official Analytical Chemists. Reprinted with permission.

[b] Assign ranks 1 to n for each material. Sum the ranks to get the score for each laboratory. The mean score is $M(n + 1)/2$. The entries are lower and upper limits that are included in the approximate 5 percent critical region.

Table A6a.—Five percent values for the distribution of F^{α}

Degrees of freedom (for denominator) \ Degrees of freedom (for numerator)	1	2	3	4	5	6	7	8	9	10	11	12	14	16	20	24	30	40	50	75	100	200	500	∞
1	161	200	216	225	230	234	237	239	241	242	243	244	245	246	248	249	250	251	252	253	253	254	254	254
2	18.51	19.00	19.16	19.25	19.30	19.33	19.36	19.37	19.38	19.39	19.40	19.41	19.42	19.43	19.44	19.45	19.46	19.47	19.47	19.48	19.49	19.49	19.50	19.50
3	10.13	9.55	9.28	9.12	9.01	8.94	8.88	8.84	8.81	8.78	8.76	8.74	8.71	8.69	8.66	8.64	8.62	8.60	8.58	8.57	8.56	8.54	8.54	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.93	5.91	5.87	5.84	5.80	5.77	5.74	5.71	5.70	5.68	5.66	5.65	5.64	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.78	4.74	4.70	4.68	4.64	4.60	4.56	4.53	4.50	4.46	4.44	4.42	4.40	4.38	4.37	4.36
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.03	4.00	3.96	3.92	3.87	3.84	3.81	3.77	3.75	3.72	3.71	3.69	3.68	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.63	3.60	3.57	3.52	3.49	3.44	3.41	3.38	3.34	3.32	3.29	3.28	3.25	3.24	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.34	3.31	3.28	3.23	3.20	3.15	3.12	3.08	3.05	3.03	3.00	2.98	2.96	2.94	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.13	3.10	3.07	3.02	2.98	2.93	2.90	2.86	2.82	2.80	2.77	2.76	2.73	2.72	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.97	2.94	2.91	2.86	2.82	2.77	2.74	2.70	2.67	2.64	2.61	2.59	2.56	2.55	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.86	2.82	2.79	2.74	2.70	2.65	2.61	2.57	2.53	2.50	2.47	2.45	2.42	2.41	2.40
12	4.75	3.88	3.49	3.26	3.11	3.00	2.92	2.85	2.80	2.76	2.72	2.69	2.64	2.60	2.54	2.50	2.46	2.42	2.40	2.36	2.35	2.32	2.31	2.30
13	4.67	3.80	3.41	3.18	3.02	2.92	2.84	2.77	2.72	2.67	2.63	2.60	2.55	2.51	2.46	2.42	2.38	2.34	2.32	2.28	2.26	2.24	2.22	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.77	2.70	2.65	2.60	2.56	2.53	2.48	2.44	2.39	2.35	2.31	2.27	2.24	2.21	2.19	2.16	2.14	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.70	2.64	2.59	2.55	2.51	2.48	2.43	2.39	2.33	2.29	2.25	2.21	2.18	2.15	2.12	2.10	2.08	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.45	2.42	2.37	2.33	2.28	2.24	2.20	2.16	2.13	2.09	2.07	2.04	2.02	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.62	2.55	2.50	2.45	2.41	2.38	2.33	2.29	2.23	2.19	2.15	2.11	2.08	2.04	2.02	1.99	1.97	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.37	2.34	2.29	2.25	2.19	2.15	2.11	2.07	2.04	2.00	1.98	1.95	1.93	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.55	2.48	2.43	2.38	2.34	2.31	2.26	2.21	2.15	2.11	2.07	2.02	2.00	1.96	1.94	1.91	1.90	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.52	2.45	2.40	2.35	2.31	2.28	2.23	2.18	2.12	2.08	2.04	1.99	1.96	1.92	1.90	1.87	1.85	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.28	2.25	2.20	2.15	2.09	2.05	2.00	1.96	1.93	1.89	1.87	1.84	1.82	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.47	2.40	2.35	2.30	2.26	2.23	2.18	2.13	2.07	2.03	1.98	1.93	1.91	1.87	1.84	1.81	1.80	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.45	2.38	2.32	2.28	2.24	2.20	2.14	2.10	2.04	2.00	1.96	1.91	1.88	1.84	1.82	1.79	1.77	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.43	2.36	2.30	2.26	2.22	2.18	2.13	2.09	2.02	1.98	1.94	1.89	1.86	1.82	1.80	1.76	1.74	1.73
25	4.24	3.38	2.99	2.76	2.60	2.49	2.41	2.34	2.28	2.24	2.20	2.16	2.11	2.06	2.00	1.96	1.92	1.87	1.84	1.80	1.77	1.74	1.72	1.71

Degrees of freedom (for denominator)	Degrees of freedom (for numerator)																							
	1	2	3	4	5	6	7	8	9	10	11	12	14	16	20	24	30	40	50	75	100	200	500	∞
26	4.22	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.18	2.15	2.10	2.05	1.99	1.95	1.90	1.85	1.82	1.78	1.76	1.72	1.70	1.69
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.30	2.25	2.20	2.16	2.13	2.08	2.03	1.97	1.93	1.88	1.84	1.80	1.76	1.74	1.71	1.68	1.67
28	4.20	3.34	2.95	2.71	2.56	2.44	2.36	2.29	2.24	2.19	2.15	2.12	2.06	2.02	1.96	1.91	1.87	1.81	1.78	1.75	1.72	1.69	1.67	1.65
29	4.18	3.33	2.93	2.70	2.54	2.43	2.35	2.28	2.22	2.18	2.14	2.10	2.05	2.00	1.94	1.90	1.85	1.80	1.77	1.73	1.71	1.68	1.65	1.64
30	4.17	3.32	2.92	2.69	2.53	2.42	2.34	2.27	2.21	2.16	2.12	2.09	2.04	1.99	1.93	1.89	1.84	1.79	1.76	1.72	1.69	1.66	1.64	1.62
32	4.15	3.30	2.90	2.67	2.51	2.40	2.32	2.25	2.19	2.14	2.10	2.07	2.02	1.97	1.91	1.86	1.82	1.76	1.74	1.69	1.67	1.64	1.61	1.59
34	4.13	3.28	2.88	2.65	2.49	2.38	2.30	2.23	2.17	2.12	2.08	2.05	2.00	1.95	1.89	1.84	1.80	1.74	1.71	1.67	1.64	1.61	1.50	1.57
36	4.11	3.26	2.86	2.63	2.48	2.36	2.28	2.21	2.15	2.10	2.06	2.03	1.98	1.93	1.87	1.82	1.78	1.72	1.69	1.65	1.62	1.59	1.56	1.55
38	4.10	3.25	2.85	2.62	2.46	2.35	2.26	2.19	2.14	2.09	2.05	2.02	1.96	1.92	1.85	1.80	1.76	1.71	1.67	1.63	1.60	1.57	1.54	1.53
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.07	2.04	2.00	1.95	1.90	1.84	1.79	1.74	1.69	1.66	1.61	1.59	1.55	1.53	1.51
42	4.07	3.22	2.83	2.59	2.44	2.32	2.24	2.17	2.11	2.06	2.02	1.99	1.94	1.89	1.82	1.78	1.73	1.68	1.64	1.60	1.57	1.54	1.51	1.49
44	4.06	3.21	2.82	2.58	2.43	2.31	2.23	2.16	2.10	2.05	2.01	1.98	1.92	1.88	1.81	1.76	1.72	1.66	1.63	1.58	1.56	1.52	1.50	1.48
46	5.05	3.20	2.81	2.57	2.42	2.30	2.22	2.14	2.09	2.04	2.00	1.97	1.91	1.87	1.80	1.75	1.71	1.65	1.62	1.57	1.54	1.51	1.48	1.46
48	4.04	3.19	2.80	2.56	2.41	2.30	2.21	2.14	2.08	2.03	1.99	1.96	1.90	1.86	1.79	1.74	1.70	1.64	1.61	1.56	1.53	1.50	1.47	1.45
50	4.03	3.18	2.79	2.56	2.40	2.29	2.20	2.13	2.07	2.02	1.98	1.95	1.90	1.85	1.78	1.74	1.69	1.63	1.60	1.55	1.52	1.48	1.46	1.44
55	4.02	3.17	2.78	2.54	2.38	2.27	2.18	2.11	2.05	2.00	1.97	1.93	1.88	1.83	1.76	1.72	1.67	1.61	1.58	1.52	1.50	1.46	1.43	1.41
60	4.00	3.15	2.76	2.52	2.37	2.25	2.17	2.10	2.04	1.99	1.95	1.92	1.86	1.81	1.75	1.70	1.65	1.59	1.56	1.50	1.48	1.44	1.41	1.39
65	3.99	3.14	2.75	2.51	2.36	2.24	2.15	2.08	2.02	1.98	1.94	1.90	1.85	1.80	1.73	1.68	1.63	1.57	1.54	1.49	1.46	1.42	1.39	1.37
70	3.98	3.13	2.74	2.50	2.35	2.23	2.14	2.07	2.01	1.97	1.93	1.89	1.84	1.79	1.72	1.67	1.62	1.56	1.53	1.47	1.45	1.40	1.37	1.35
80	3.96	3.11	2.72	2.48	2.33	2.21	2.12	2.05	1.99	1.95	1.91	1.88	1.82	1.77	1.70	1.65	1.60	1.54	1.51	1.45	1.42	1.38	1.35	1.32
100	3.94	3.09	2.70	2.46	2.30	2.19	2.10	2.03	1.97	1.92	1.88	1.85	1.79	1.75	1.68	1.63	1.57	1.51	1.48	1.42	1.39	1.34	1.30	1.28
125	3.92	3.07	2.68	2.44	2.29	2.17	2.08	2.01	1.95	1.90	1.86	1.83	1.77	1.72	1.65	1.60	1.55	1.49	1.45	1.39	1.36	1.31	1.27	1.25
150	3.91	3.06	2.67	2.43	2.27	2.16	2.07	2.00	1.94	1.89	1.85	1.82	1.76	1.71	1.64	1.59	1.54	1.47	1.44	1.37	1.34	1.29	1.25	1.22
200	3.89	3.04	2.65	2.41	2.26	2.14	2.05	1.98	1.92	1.87	1.83	1.80	1.74	1.69	1.62	1.57	1.52	1.45	1.42	1.35	1.32	1.26	1.22	1.19
400	3.86	3.02	2.62	2.39	2.23	2.12	2.03	1.96	1.90	1.85	1.81	1.78	1.72	1.67	1.60	1.54	1.49	1.42	1.38	1.32	1.28	1.22	1.16	1.13
1000	3.85	3.00	2.61	2.38	2.22	2.10	2.02	1.95	1.89	1.84	1.80	1.76	1.70	1.65	1.58	1.53	1.47	1.41	1.36	1.30	1.26	1.19	1.13	1.08
∞	3.84	2.99	2.60	2.37	2.21	2.09	2.01	1.94	1.88	1.83	1.79	1.75	1.69	1.64	1.57	1.52	1.46	1.40	1.35	1.28	1.24	1.17	1.11	1.00

[a] Reprinted by permission from "Statistical Methods" by George W. Snedecor and William G. Cochran, 6th edition, (c) 1967 by the Iowa State University Press, Ames, Iowa 50010.

Table A6b.—One percent values for the distribution of F^a

Degrees of freedom (for denominator)	Degrees of freedom (for numerator)																						
	1	2	3	4	5	6	7	8	9	10	11	12	14	16	20	24	30	40	50	75	100	200	500	∞
1	4,052	4,999	5,403	5,625	5,764	5,859	5,928	5,981	6,022	6,056	6,082	6,106	6,142	6,169	6,208	6,234	6,258	6,286	6,302	6,323	6,334	6,352	6,361	6,366
2	98.49	99.00	99.17	99.25	99.30	99.33	99.34	99.36	99.38	99.40	99.41	99.42	99.43	99.44	99.45	99.46	99.47	99.48	99.48	99.49	99.49	99.49	99.50	99.50
3	34.12	30.82	29.46	28.71	28.24	27.91	27.67	27.49	27.34	27.23	27.13	27.05	26.92	26.83	26.69	26.60	26.50	26.41	26.35	26.27	26.23	26.18	26.14	26.12
4	21.20	18.00	16.69	15.98	15.52	15.21	14.98	14.80	14.66	14.54	14.45	14.37	14.24	14.15	14.02	13.93	13.83	13.74	13.69	13.61	13.57	13.52	13.48	13.46
5	16.26	13.27	12.06	11.39	10.97	10.67	10.45	10.27	10.15	10.05	9.96	9.89	9.77	9.68	9.55	9.47	9.38	9.29	9.24	9.17	9.13	9.07	9.04	9.02
6	13.74	10.92	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.79	7.72	7.60	7.52	7.39	7.31	7.23	7.14	7.09	7.02	6.99	6.94	6.90	6.88
7	12.25	9.55	8.45	7.85	7.46	7.19	7.00	6.84	6.71	6.62	6.54	6.47	6.35	6.27	6.15	6.07	5.98	5.90	5.85	5.78	5.75	5.70	5.67	5.65
8	11.26	8.65	7.59	7.01	6.63	6.37	6.19	6.03	5.91	5.82	5.74	5.67	5.56	5.48	5.36	5.28	5.20	5.11	5.06	5.00	4.96	4.91	4.88	4.86
9	10.56	8.02	6.99	6.42	6.06	5.80	5.62	5.47	5.35	5.26	5.18	5.11	5.00	4.92	4.80	4.73	4.64	4.56	4.51	4.45	4.41	4.36	4.33	4.31
10	10.04	7.56	6.55	5.99	5.64	5.39	5.21	5.06	4.95	4.85	4.78	4.71	4.60	4.52	4.41	4.33	4.25	4.17	4.12	4.05	4.01	3.96	3.93	3.91
11	9.65	7.20	6.22	5.67	5.32	5.07	4.88	4.74	4.63	4.54	4.46	4.40	4.29	4.21	4.10	4.02	3.94	3.86	3.80	3.74	3.70	3.66	3.62	3.60
12	9.33	6.93	5.95	5.41	5.06	4.82	4.65	4.50	4.39	4.30	4.22	4.16	4.05	3.98	3.86	3.78	3.70	3.61	3.56	3.49	3.46	3.41	3.38	3.36
13	9.07	6.70	5.74	5.20	4.86	4.62	4.44	4.30	4.19	4.10	4.02	3.96	3.85	3.78	3.67	3.59	3.51	3.42	3.37	3.30	3.27	3.21	3.18	3.16
14	8.86	6.51	5.56	5.03	4.69	4.46	4.28	4.14	4.03	3.94	3.86	3.80	3.70	3.62	3.51	3.43	3.34	3.26	3.21	3.14	3.11	3.06	3.02	3.00
15	8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.73	3.67	3.56	3.48	3.36	3.29	3.20	3.12	3.07	3.00	2.97	2.92	2.89	2.87
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69	3.61	3.55	3.45	3.37	3.25	3.18	3.10	3.01	2.96	2.89	2.86	2.80	2.77	2.75
17	8.40	6.11	5.18	4.67	4.34	4.10	3.93	3.79	3.68	3.59	3.52	3.45	3.35	3.27	3.16	3.08	3.00	2.92	2.86	2.79	2.76	2.70	2.67	2.65
18	8.28	6.01	5.09	4.58	4.25	4.01	3.85	3.71	3.60	3.51	3.44	3.37	3.27	3.19	3.07	3.00	2.91	2.83	2.78	2.71	2.68	2.62	2.59	2.57
19	8.18	5.93	5.01	4.50	4.17	3.94	3.77	3.63	3.52	3.43	3.36	3.30	3.19	3.12	3.00	2.92	2.84	2.76	2.70	2.63	2.60	2.54	2.51	2.49
20	8.10	5.85	4.94	4.43	4.10	3.87	3.71	3.56	3.45	3.37	3.30	3.23	3.13	3.05	2.94	2.86	2.77	2.69	2.63	2.56	2.53	2.47	2.44	2.42
21	8.02	5.78	4.87	4.37	4.04	3.81	3.65	3.51	3.40	3.31	3.24	3.17	3.07	2.99	2.88	2.80	2.72	2.63	2.58	2.51	2.47	2.42	2.38	2.36
22	7.94	5.72	4.82	4.31	3.99	3.76	3.59	3.45	3.35	3.26	3.18	3.12	3.02	2.94	2.83	2.75	2.67	2.58	2.53	2.46	2.42	2.37	2.33	2.31
23	7.88	5.66	4.76	4.26	3.94	3.71	3.54	3.41	3.30	3.21	3.14	3.07	2.97	2.89	2.78	2.70	2.62	2.53	2.48	2.41	2.37	2.32	2.28	2.26
24	7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.25	3.17	3.09	3.03	2.93	2.85	2.74	2.66	2.58	2.49	2.44	2.46	2.33	2.27	2.23	2.21
25	7.77	5.57	4.68	4.18	3.86	3.63	3.46	3.32	3.21	3.13	3.05	2.99	2.89	2.81	2.70	2.62	2.54	2.45	2.40	2.32	2.29	2.23	2.19	2.17

Degrees of freedom (for denominator)	Degrees of freedom (for numerator)																							
	1	2	3	4	5	6	7	8	9	10	11	12	14	16	20	24	30	40	50	75	100	200	500	∞
26	7.72	5.53	4.64	4.14	3.82	3.59	3.42	3.29	3.17	3.09	3.02	2.96	2.86	2.77	2.66	2.58	2.50	2.41	2.36	2.28	2.25	2.19	2.15	2.13
27	7.68	5.49	4.60	4.11	3.79	3.56	3.39	3.26	3.14	3.06	2.98	2.93	2.83	2.74	2.63	2.55	2.47	2.38	2.33	2.25	2.21	2.16	2.12	2.10
28	7.64	5.45	4.57	4.07	3.76	3.53	3.36	3.23	3.11	3.03	2.95	2.90	2.80	2.71	2.60	2.52	2.44	2.35	2.30	2.22	2.18	2.13	2.09	2.06
29	7.60	5.42	4.54	4.04	3.73	3.50	3.33	3.20	3.08	3.00	2.92	2.87	2.77	2.68	2.57	2.49	2.41	2.32	2.27	2.19	2.15	2.10	2.06	2.03
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	3.06	2.98	2.90	2.84	2.74	2.66	2.55	2.47	2.38	2.29	2.24	2.16	2.13	2.07	2.03	2.01
32	7.50	5.34	4.46	3.97	3.66	3.42	3.25	3.12	3.01	2.94	2.86	2.80	2.70	2.62	2.51	2.42	2.34	2.25	2.20	2.12	2.08	2.02	1.98	1.96
34	7.44	5.29	4.42	3.93	3.61	3.38	3.21	3.08	2.97	2.89	2.82	2.76	2.66	2.58	2.47	2.38	2.30	2.21	2.15	2.08	2.04	1.98	1.94	1.91
36	7.39	5.25	4.38	3.89	3.58	3.35	3.18	3.04	2.94	2.86	2.78	2.72	2.62	2.54	2.43	2.35	2.26	2.17	2.12	2.04	2.00	1.94	1.90	1.87
38	7.35	5.21	4.34	3.86	3.54	3.32	3.15	3.02	2.91	2.82	2.75	2.69	2.59	2.51	2.40	2.32	2.22	2.14	2.08	2.00	1.97	1.90	1.86	1.84
40	7.31	5.18	4.31	3.83	3.51	3.29	3.12	2.99	2.88	2.80	2.73	2.66	2.56	2.49	2.37	2.29	2.20	2.11	2.05	1.97	1.94	1.88	1.84	1.81
42	7.27	5.15	4.29	3.80	3.49	3.26	3.10	2.96	2.86	2.77	2.70	2.64	2.54	2.46	2.35	2.26	2.17	2.08	2.02	1.94	1.91	1.85	1.80	1.78
44	7.24	5.12	4.26	3.78	3.46	3.24	3.07	2.94	2.84	2.75	2.68	2.62	2.52	2.44	2.32	2.24	2.15	2.06	2.00	1.92	1.88	1.82	1.78	1.75
46	7.21	5.10	4.24	3.76	3.44	3.22	3.05	2.92	2.82	2.73	2.66	2.60	2.50	2.42	2.30	2.22	2.13	2.04	1.98	1.90	1.86	1.80	1.76	1.72
48	7.19	5.08	4.22	3.74	3.42	3.20	3.04	2.90	2.80	1.71	2.64	2.58	2.48	2.40	2.28	2.20	2.11	2.02	1.96	1.88	1.84	1.78	1.73	1.70
50	7.17	5.06	4.20	3.72	3.41	3.18	3.02	2.88	2.78	2.70	2.62	2.56	2.46	2.39	2.26	2.18	2.10	2.00	1.94	1.86	1.82	1.76	1.71	1.68
55	7.12	5.01	4.16	3.68	3.37	3.15	2.98	2.85	2.75	2.66	2.59	2.53	2.43	2.35	2.23	2.15	2.06	1.96	1.90	1.82	1.78	1.71	1.66	1.64
60	7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63	2.56	2.50	2.40	2.32	2.20	2.12	2.03	1.93	1.87	1.79	1.74	1.68	1.63	1.60
65	7.04	4.95	4.10	3.62	3.31	3.09	2.93	2.79	2.70	2.61	2.54	2.47	2.37	2.30	2.18	2.09	2.00	1.90	1.84	1.76	1.71	1.64	1.60	1.56
70	7.01	4.92	4.08	3.60	3.29	3.07	2.91	2.77	2.67	2.59	2.51	2.45	2.35	2.28	2.15	2.07	1.98	1.88	1.82	1.74	1.69	1.62	1.56	1.53
80	6.96	4.88	4.04	3.56	3.25	3.04	2.87	2.74	2.64	2.55	2.48	2.41	2.32	2.24	2.11	2.03	1.94	1.84	1.78	1.70	1.65	1.57	1.52	1.49
100	6.90	4.82	3.98	3.51	3.20	2.99	2.82	2.69	2.59	2.51	2.43	2.36	2.26	2.19	2.06	1.98	1.89	1.79	1.73	1.64	1.59	1.51	1.46	1.43
125	6.84	4.78	3.94	3.47	3.17	2.95	2.79	2.65	2.56	2.47	2.40	2.33	2.23	2.15	2.03	1.94	1.85	1.75	1.68	1.59	1.54	1.46	1.40	1.37
150	6.81	4.75	3.91	3.44	3.14	2.92	2.76	2.62	2.53	2.44	2.37	2.30	2.20	2.12	2.00	1.91	1.83	1.72	1.66	1.56	1.51	1.43	1.37	1.33
200	6.76	4.71	3.88	3.41	3.11	2.90	2.73	2.60	2.50	2.41	2.34	2.28	2.17	2.09	1.97	1.88	1.79	1.69	1.62	1.53	1.48	1.39	1.33	1.28
400	6.70	4.66	3.83	3.36	3.06	2.85	2.69	2.55	2.46	2.37	2.29	2.23	2.12	2.04	1.92	1.84	1.74	1.64	1.57	1.47	1.42	1.32	1.24	1.19
1000	6.66	4.62	3.80	3.34	3.04	2.82	2.66	2.53	2.43	2.34	2.26	2.20	2.09	2.01	1.89	1.81	1.71	1.61	1.54	1.44	1.38	1.28	1.19	1.11
∞	6.64	4.60	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32	2.24	2.18	2.07	1.99	1.87	1.79	1.69	1.59	1.52	1.41	1.36	1.25	1.15	1.00

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Table A7.—Factor c_2, for use in estimating control chart limits[a]

Number of observations in subgroup n	c_2	Number of observations in subgroup n	c_2
		21	0.9638
2	0.5642	22	0.9655
3	0.7236	23	0.9670
4	0.7979	24	0.9684
5	0.8407	25	0.9696
6	0.8686	30	0.9748
7	0.8882	35	0.9784
8	0.9027	40	0.9811
9	0.9139	45	0.9832
10	0.9227	50	0.9849
11	0.9300	55	0.9863
12	0.9359	60	0.9874
13	0.9410	65	0.9884
14	0.9453	70	0.9892
15	0.9490	75	0.9900
16	0.9523	80	0.9906
17	0.9551	85	0.9912
18	0.9576	90	0.9916
19	0.9599	95	0.9921
20	0.9619	100	0.9925

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Table A8.—Factors d_2 and A_2, for use in estimating control chart limits[a]

Number of observations in subgroup n	d_2	$A_2 = 3/d_2\sqrt{n}$
2	1.128	1.88
3	1.693	1.02
4	2.059	0.73
5	2.326	0.58
6	2.534	0.48
7	2.704	0.42
8	2.847	0.37
9	2.970	0.34
10	3.078	0.31
11	3.173	0.29
12	3.258	0.27
13	3.336	0.25
14	3.407	0.24
15	3.472	0.22
16	3.532	0.21
17	3.588	0.20
18	3.640	0.19
19	3.689	0.19
20	3.735	0.18

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Table A9.—Factors B_3 and B_4, for use in estimating control chart limits[a]

Number of observations in subgroup n	Factors for s chart	
	Lower control limit B_3	Upper control limit B_4
2	0	3.27
3	0	2.57
4	0	2.27
5	0	2.09
6	0.03	1.97
7	0.12	1.88
8	0.19	1.81
9	0.24	1.76
10	0.28	1.72
11	0.32	1.68
12	0.35	1.65
13	0.38	1.62
14	0.41	1.59
15	0.43	1.57
16	0.45	1.55
17	0.47	1.53
18	0.48	1.52
19	0.50	1.50
20	0.51	1.49
21	0.52	1.48
22	0.53	1.47
23	0.54	1.46
24	0.55	1.45
25	0.56	1.44
30	0.60	1.40
35	0.63	1.37
40	0.66	1.34
45	0.68	1.32
50	0.70	1.30
55	0.71	1.29
60	0.72	1.28
65	0.73	1.27
70	0.74	1.26
75	0.75	1.25
80	0.76	1.24
85	0.77	1.23
90	0.77	1.23
95	0.78	1.22
100	0.79	1.21

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Table A10.—Factors D_3 and D_4, for use in estimating control chart limits[a]

Number of observations in subgroup n	Factors for R chart	
	Lower control limit D_3	Upper control limit D_4
2	0	3.27
3	0	2.57
4	0	2.28
5	0	2.11
6	0	2.00
7	0.08	1.92
8	0.14	1.86
9	0.18	1.82
10	0.22	1.78
11	0.26	1.74
12	0.28	1.72
13	0.31	1.69
14	0.33	1.67
15	0.35	1.65
16	0.36	1.64
17	0.38	1.62
18	0.39	1.61
19	0.40	1.60
20	0.41	1.59

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Table A11.—*t*-distribution[a]

Degrees of freedom	Probability of a value which is greater (when testing both positive and negative sides of the distribution)[b]					
	0.500	0.200	0.100	0.050	0.020	0.010
1	1.000	3.078	6.314	12.706	31.821	63.657
2	.816	1.886	2.920	4.303	6.965	9.925
3	.765	1.638	2.353	3.182	4.541	5.841
4	.741	1.533	2.132	2.776	3.747	4.604
5	.727	1.476	2.015	2.571	3.365	4.032
6	.718	1.440	1.943	2.447	3.143	3.707
7	.711	1.415	1.895	2.365	2.998	3.499
8	.706	1.397	1.860	2.306	2.896	3.355
9	.703	1.383	1.833	2.262	2.821	3.250
10	.700	1.372	1.812	2.228	2.764	3.169
11	.697	1.363	1.796	2.201	2.718	3.106
12	.695	1.356	1.782	2.179	2.681	3.055
13	.694	1.350	1.771	2.160	2.650	3.012
14	.692	1.345	1.761	2.145	2.624	2.977
15	.691	1.341	1.753	2.131	2.602	2.947
16	.690	1.337	1.746	2.120	2.583	2.921
17	.689	1.333	1.740	2.110	2.567	2.898
18	.688	1.330	1.734	2.101	2.552	2.878
19	.688	1.328	1.729	2.093	2.539	2.861
20	.687	1.325	1.725	2.086	2.528	2.845
21	.686	1.323	1.721	2.080	2.518	2.831
22	.686	1.321	1.717	2.074	2.508	2.819
23	.685	1.319	1.714	2.069	2.500	2.807
24	.685	1.318	1.711	2.064	2.492	2.797
25	.684	1.316	1.708	2.060	2.485	2.787
26	.684	1.315	1.706	2.056	2.479	2.779
27	.684	1.314	1.703	2.052	2.473	2.771
28	.683	1.313	1.701	2.048	2.467	2.763
29	.683	1.311	1.699	2.045	2.462	2.756
30	.683	1.310	1.697	2.042	2.457	2.750
40	.681	1.303	1.684	2.021	2.423	2.704
60	.679	1.296	1.671	2.000	2.390	2.660
120	.677	1.289	1.658	1.980	2.358	2.617
∞	.674	1.282	1.645	1.960	2.326	2.576

[a] Data are taken from Table III (Distribution of *t*) of Fisher and Yates: "Statistical Tables for Biological, Agricultural and Medical Research," published by Longman Group Ltd. London (1974) 6th edition, (previously published by Oliver & Boyd Ltd. Edinburgh) and by permission of the authors and publishers.

[b] If testing only positive or negative side of distribution (one-tailed test), probability of a greater value is half that tabulated.

Table A12.—Percentiles of the *q* distribution[a]

Degrees of freedom	Test level (percent)	Number of values used to compute each mean											
		2	3	4	5	6	7	9	10	12	16	20	24
1	90	8.93	13.4	16.4	18.5	20.2	21.5	22.6	24.5	25.9	28.1	29.7	31.0
	95	18.0	27.0	32.8	37.1	40.4	43.1	45.4	49.1	52.0	56.3	59.6	62.1
	99	90.0	135	164	186	202	216	227	246	260	282	298	311
2	90	4.13	5.73	6.77	7.54	8.14	8.63	9.05	9.73	10.3	11.1	11.7	12.2
	95	6.09	8.33	9.80	10.9	11.7	12.4	13.0	14.0	14.8	16.0	16.8	17.5
	99	14.0	19.0	22.3	24.7	26.6	28.2	29.5	31.7	33.4	36.0	38.0	39.5
3	90	3.33	4.47	5.20	5.74	6.16	6.51	6.81	7.29	7.67	8.25	8.68	9.03
	95	4.50	5.91	6.83	7.50	8.04	8.48	8.85	9.46	9.95	10.7	11.2	11.7
	99	8.26	10.6	12.2	13.3	14.2	15.0	15.6	16.7	17.5	18.8	20.0	20.5
4	90	3.02	3.98	4.59	5.04	5.39	5.68	5.93	6.33	6.65	7.13	7.50	7.79
	95	3.93	5.04	5.76	6.29	6.71	7.05	7.35	7.83	8.21	8.79	9.23	9.58
	99	6.51	8.12	9.17	9.96	10.6	11.1	11.6	12.3	12.8	13.7	14.4	14.9
6	90	2.75	3.56	4.07	4.44	4.73	4.97	5.17	5.50	5.76	6.16	6.47	6.71
	95	3.46	4.34	4.90	5.31	5.63	5.90	6.12	6.49	6.79	7.24	7.59	7.86
	99	5.24	6.33	7.03	7.56	7.97	8.32	8.61	9.10	9.49	10.1	10.5	10.9
8	90	2.63	3.37	3.83	4.17	4.43	4.65	4.83	5.13	5.36	5.72	6.00	6.21
	95	3.26	4.04	4.53	4.89	5.17	5.40	5.60	5.92	6.18	6.57	6.87	7.11
	99	4.75	5.64	6.20	6.63	6.96	7.24	7.47	7.86	8.18	8.66	9.03	9.32
10	90	2.56	3.27	3.70	4.02	4.26	4.47	4.64	4.91	5.13	5.47	5.73	5.93
	95	3.15	3.88	4.33	4.65	4.91	5.12	5.31	5.60	5.83	6.19	6.47	6.69
	99	4.48	5.27	5.77	6.14	6.43	6.67	6.88	7.21	7.49	7.91	8.23	8.48
12	90	2.52	3.20	3.62	3.92	4.16	4.35	4.51	4.78	4.99	5.31	5.55	5.74
	95	3.08	3.77	4.20	4.51	4.75	4.95	5.12	5.40	5.62	5.95	6.21	6.41
	99	4.32	5.05	5.50	5.84	6.10	6.32	6.51	6.81	7.06	7.44	7.73	7.96
16	90	2.47	3.12	3.52	3.80	4.03	4.21	4.36	4.61	4.81	5.11	5.33	5.52
	95	3.00	3.65	4.05	4.33	4.56	4.74	4.90	5.15	5.35	5.66	5.90	6.08
	99	4.13	4.79	5.19	5.49	5.72	5.92	6.08	6.35	6.56	6.90	7.15	7.36
20	90	2.44	3.08	3.46	3.74	3.95	4.12	4.27	4.51	4.70	4.99	5.21	5.38
	95	2.95	3.58	3.96	4.23	4.45	4.62	4.77	5.01	5.20	5.49	5.71	5.89
	99	4.02	4.64	5.02	5.29	5.51	5.69	5.84	6.09	6.29	6.59	6.82	7.01
24	90	2.42	3.05	3.42	3.69	3.90	4.07	4.21	4.45	4.62	4.91	5.12	5.29
	95	2.92	3.53	3.90	4.17	4.37	4.54	4.68	4.92	5.10	5.38	5.59	5.76
	99	3.96	4.55	4.91	5.17	5.37	5.54	5.69	5.92	6.11	6.39	6.61	6.79
30	90	2.40	3.02	3.39	3.65	3.85	4.02	4.16	4.38	4.56	4.83	5.03	5.20
	95	2.89	3.49	3.85	4.10	4.30	4.46	4.60	4.82	5.00	5.27	5.48	5.64
	99	3.89	4.46	4.80	5.05	5.24	5.40	5.54	5.76	5.93	6.20	6.41	6.57
40	90	2.38	2.99	3.35	3.61	3.80	3.96	4.10	4.32	4.50	4.75	4.95	5.11
	95	2.86	3.44	3.79	4.04	4.23	4.39	4.52	4.74	4.90	5.16	5.36	5.51
	99	3.83	4.37	4.70	4.93	5.11	5.27	5.39	5.60	5.76	6.02	6.21	6.36
60	89	2.36	2.96	3.31	3.56	3.76	3.91	4.04	4.25	4.42	4.68	4.86	5.02
	95	2.83	3.40	3.74	3.98	4.16	4.31	4.44	4.65	4.81	5.06	5.24	5.39
	99	3.76	4.29	4.60	4.82	5.00	5.13	5.25	5.45	5.60	5.84	6.02	6.16
120	90	2.34	2.93	3.28	3.52	3.71	3.86	3.99	4.19	4.35	4.60	4.78	4.92
	95	2.80	3.36	3.69	3.92	4.10	4.24	4.36	4.56	4.71	4.95	5.13	5.27
	99	3.70	4.20	4.50	4.71	4.87	5.01	5.12	5.30	5.44	5.66	5.83	5.96
	90	2.33	2.90	3.24	3.48	3.66	3.81	3.93	4.13	4.29	4.52	4.69	4.83
	95	2.77	3.31	3.63	3.86	4.03	4.17	4.29	4.47	4.62	4.85	5.01	5.14
	99	3.64	4.12	4.40	4.60	4.76	4.88	4.99	5.16	5.29	5.49	5.65	5.77

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