An American National Standard

Standard Guide for
Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[1]

This standard is issued under the fixed designation D 3856; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide provides information on consensus good laboratory practices for laboratories that provide services in the sampling and analysis of water. As consensus standards, these are the minimum criteria that all laboratories should consider in establishing their good laboratory practices.

1.2 This guide is designed to be used by those responsible for the selection, operation, or control of laboratory organizations engaged in sampling and analysis of water.

1.3 This guide presents features of organization, facilities, resources, and operations which affect the usefulness of the data generated.

1.4 This guide presents criteria for selection and control of the features described in 1.3 and also makes recommendations for the correction of unacceptable performance.

1.5 This guide describes methodology and practices intended to be completely consistent with the International Organization for Standardization (ISO) 9000 series of standards and Guide 25 – 1990 (1). [2]

1.6 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

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

2. Referenced Documents

2.1 *ASTM Standards:*
D 1129 Terminology Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[4]
D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]
D 4375 Terminology for Basic Statistics in Committee D-19 on Water[3]
D 4447 Guide for the Disposal of Laboratory Chemicals and Samples[5]
D 4840 Guide for Sampling Chain-of-Custody Procedures[3]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]
D 5172 Guide for Documenting the Standard Operating Procedures Used for Analysis of Water[3]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[4]
E 456 Terminology Relating to Quality and Statistics [6]
E 548 Guide for General Criteria Used for Evaluating Laboratory Competence[6]

3. Terminology

3.1 For definitions of terms used in this guide, refer to Terminologies D 1129, D 4375, and E 456, Guide E 548, and *ASTM MNL 7* (2).

4. Summary of Guide

4.1 This guide describes the criteria, guidelines, and recommendations for physical and human resources and data validation for the operation of a laboratory.

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[1] This guide is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.02 on General Specifications and Technical Resources.
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[2] The boldface numbers in parentheses refer to the list of references at the end of this guide.
[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.02.
[5] *Annual Book of ASTM Standards*, Vol 11.04.
[6] *Annual Book of ASTM Standards*, Vol 14.02.

4.2 Although, philosophically, this guide is intended to apply to all analyses of water, there may be certain test methods to which parts of this guide are not applicable due to the nature of the samples, for example, microbiological analyses.

5. Significance and Use

5.1 Data on the composition and characteristics of water are frequently used to evaluate the health and safety to humans and the environment.

5.2 Moreover, such data are frequently used for process control or to ascertain compliance with regulatory statutes that place limits on acceptable compositions and characteristics of waters.

5.3 Laboratories that conduct water sampling and generate analytical data, and those persons who have the responsibility for selecting a laboratory to perform water quality studies, need to use criteria, guidelines, and recommendations that have been developed by consensus and are well accepted in making this selection.

5.4 Demonstration and documentation by a laboratory that there was judicious selection and control of organization, facilities, resources, and operations will enhance the credibility of the data produced and promote its acceptance.

6. Aspects of Quality Assurance

6.1 *General*—The function of a laboratory is to provide analytical results and related information which are adequate for the intended use. This function is achieved through effective use of a quality assurance program. Every laboratory should develop a written quality assurance program, plan, or manual that demonstrates the effectiveness of its procedures and practices in assuring this quality. In addition to addressing any applicable regulatory requirements, the program should consider the following:

6.2 *Organizational Structure*—A table of the organization should be available which shows the lines of authority, areas of responsibility, and job functions. The laboratory should also provide a description of its capabilities. Laboratory management should demonstrate and foster a positive quality assurance attitude and provide the analytical staff with a written policy to carry out a defined quality assurance program.

6.2.1 *Human Resources*— The key personnel of the organization should be described by means of personal résumés presenting the education and work experience appropriate to the table of organization and the qualifications of the position. For each employee, provision should be made for update of records to reflect additional education, work experience, and continuing training.

6.2.2 *Physical Resources*—The laboratory facilities should provide a working environment that is clean, comfortable, and safe. The instrumentation and equipment must be suitable for the operational needs of the laboratory.

6.3 *Methodology*— Written procedures should be readily available to personnel.

6.3.1 Written sample collection, handling and storage requirements should be followed.

6.3.2 Analytical procedures should be written.

6.3.3 There should be a document control system to track the currency and completeness of procedures.

6.4 *Metrology*—Systems for making measurements should have the following:

6.4.1 Written calibration procedures, including traceability and schedule.

6.4.2 Written preventive maintenance procedures with scheduled intervals.

6.4.3 Records available to document any repair or service of equipment, replacement or change of reagents, or modification of procedures.

6.5 *Data Recording*— The laboratory should keep records of sample source disposition and analyses to provide information on sample collection and preservation, analytical procedures and results, and the persons responsible for the sampling and analysis. All laboratory data sheets should be dated and signed by the analyst and his supervisor or a suitable colleague.

6.6 *Data Validation*— To assess and demonstrate a suitable level of analytical performance, the laboratory should keep records of audit procedures, reference sample programs, and interlaboratory tests. One criterion for measurement of analytical performance should be the precision and bias data contained in the analytical method being used. Where applicable, quality control charts as described in Practice D 4210 should be used.

6.7 *Trouble Shooting*— The organization should provide the authority and the responsibility to a designated person or persons for investigation of out-of-control results and for informing the laboratory management of any problems that occur.

6.7.1 A current log should be kept of analytical deficiencies and the action taken to correct them.

7. Organization

7.1 *General*—The production of reliable data is effected through the effort of everyone involved with the service. It is paramount, therefore, that personnel have a clear understanding of their duties and responsibilities and their relationship to the product produced. Management has the responsibility for defining function and goals as applied to the individual. A formal document describing objectives, staff functions and responsibilities, should be distributed and explained to all staff members.

7.1.1 The personnel in a laboratory will vary with the specific functions that are to be served, but minimal qualifications and duties generally will be as described in 7.2 through 7.3.5.11.

7.2 *Human Resources/Personnel Duties and Responsibilities*:

7.2.1 *The Director*— The director should have a working knowledge of the laboratory and its scope of activities. The director should have earned a baccalaureate degree in science or engineering from an accredited college or university or the equivalent (Note 1) and have at least five years experience in laboratory work.

NOTE 1—The purpose of the "equivalent" requirement is to allow the assignment of persons who have comparable skills obtained through qualified training which did not result in the award of a baccalaureate degree. Interpretation of the term "equivalent" will necessarily require

careful judgment by the user of these guidelines. Certification by professional boards is to be encouraged.

The laboratory director or manager should be a full-time employee that operates the laboratory with at least the responsibilities outlined in 7.2.1.1-7.2.1.6.

7.2.1.1 Establishment of long-term program plans and shorter term work plans and assignments to meet the program objectives.

7.2.1.2 Operation and maintenance of the physical plant (building, equipment, instrumentation, services, etc.).

7.2.1.3 Selection, training, and development of personnel.

7.2.1.4 Overview and approval of methods of sampling and analyses.

7.2.1.5 Development and implementation of a quality assurance (QA) program to monitor and maintain the quality of laboratory performance. In larger laboratories, this function is frequently delegated to an individual or organization separate from the laboratory operation. This includes ensuring staff participation in appropriate interlaboratory quality control activities, intercalibration checks, performance audit programs, etc. Such interlaboratory checks are the most effective measure of comparative performance and should demonstrate the worth of a good quality assurance program to upper management or regulator agencies. A QA program also provides each laboratory staff member with a copy of the quality assurance plan for the laboratory, which documents responsibilities and kind and frequency of quality control checks. The plan should also specify the monitoring and overview responsibilities of management.

7.2.1.6 Establishment of a development and operational performance appraisal system for the staff and an individual career development plan for each staff member. Performance standards should be developed and agreed to jointly by each staff member and their supervisor. The director should be responsible for assuring a periodic review of performance of all staff members by supervisors, for rewarding good quality performance, and for implementing and encouraging on-the-job or off-site training. This joint development of performance standards is key to obtaining an understanding between the worker and the supervisor, as to what is expected for satisfactory performance. It also paves the way for rewarding outstanding performance or identifying unsatisfactory performance. These standards should be used to evaluate performance frequently but informally, and formally on a less frequent (annual or semiannual) basis.

7.2.2 *Senior Staff*— The senior professional staff of the laboratory conduct the difficult and non-routine sampling and analyses, resolve analytical problems, and modify and develop analytical procedures.

7.2.2.1 Senior staff supervise and assist the technical staff in analyses, other laboratory operations and training.

7.2.2.2 Senior staff members should have earned a baccalaureate degree in science or engineering from an accredited college or the equivalent (see Note 1) and have at least two years experience at the bench level in a water laboratory.

7.2.3 *Technical Staff*— The technical staff are personnel who perform routine and specialized sampling and analyses.

7.2.3.1 Where appropriate, technical staff members should have formal training in the sampling and analytical methodology, and quality control, as applied to the specific sample types and concentration levels of analytes which are of interest to the laboratory.

7.2.3.2 Technical staff may be required to satisfactorily complete analytical tests to qualify initially and to periodically requalify throughout their work career. Qualification should be based on the generation of analytical results with precision and bias recovery within limits known to be possible for the particular method and which meet the data user's requirements.

7.2.4 *Laboratory Support Staff*—The support staff are nontechnical workers who perform routine field and laboratory services in support of the professional and technical staff. In the field, they may collect samples, and they may transport, handle and maintain records of collection and storage, including chain of custody. The support staff also maintains sampling and other field equipment.

7.2.4.1 In the laboratory, they wash glassware, operate laboratory reagent water systems, autoclaves, drying ovens, and incubators. The support staff also receives, stores, and ships samples, materials, and laboratory equipment.

7.2.5 *Office Support Staff*—The office staff are nontechnical clerical or secretarial personnel who are trained either on the job or by formal schooling in keyboarding, filing, recordkeeping, communications by telephone or personal visits, payroll, travel, or some combination thereof.

7.2.5.1 The laboratory or office support staff may be an integral part of the laboratory or may be provided as part of the administrative function in a larger organization.

7.3 *Physical Resources and Related Operating Procedures*:

7.3.1 *General*—The laboratory environment can significantly affect the results of water analyses; therefore, the laboratory facility should be carefully designed and periodically inspected and reevaluated. In general, the physical conditions in the laboratory should comply with the applicable U.S. OSHA requirements, or their equivalent, and other safety and legal requirements. For further information see *Laboratory Planning for Chemistry and Chemical Engineering* (**3**).

7.3.2 *Equipment and Supplies*—The specific instrumentation, equipment, materials, and supplies needed for the performance of a standard test method are usually described in the written standard. If the laboratory proposes to perform a new analytical procedure, it must be prepared to acquire the necessary instrumentation, supplies and space, and to conduct an appropriate training period prior to its routine use.

7.3.3 *Laboratory Environment*—The laboratory should be kept as free from environmental contamination as possible in order to protect the samples and instrumentation. Specific procedures should be established for monitoring the quality of the laboratory reagent water per Specification D 1193. By doing so, the laboratory ensures the opportunity to produce quality data. The production of valid data not only depends on the collection of representative samples, but also on maintaining such samples as closely as possible to their original condition through careful handling and storage. If the sample cannot be analyzed at once, it should be preserved and stored

as required for the analytes of interest. Recommended procedures for collecting, transporting and handling water and wastewater samples are described in this guide or in Practices D 3370 and D 3694. Recommended chain of custody procedures are described in Guide D 4840. Whenever sample holding times must be determined, recommended procedures are described in Practice D 4841.

7.3.4 *Ventilation System*—Laboratories should be well ventilated and free of dust, drafts, and extreme temperature changes. Central air conditioning is recommended because: 1) incoming air is filtered, reducing the likelihood of airborne laboratory contamination; 2) uniform temperature is conducive to stable operation of instrumentation and equipment; and 3) low humidity reduces moisture problems with hygroscopic chemicals, samples, and corrosion problems with analytical balances and other instrumentation.

7.3.4.1 In order for the hoods to be effective in removing fumes and aerosols from the laboratory environment, they must be operating at their designed capacity. Proper hood performance cannot be assumed. Hoods should be tested periodically for proper air flow by qualified support staff or a professional maintenance contractor. Hoods should not be located in areas of countervailing drafts, such as between two open doors. Under usual operating conditions, hoods require from 50 to 125 CFM/ft^2 (15 to 38 m^3/min/m^2) of face area. For a more detailed treatment of ventilation consult *Industrial Ventilation—A Manual of Recommended Practice* (**4**).

7.3.5 *Facilities*—Ideally, the areas provided for cleaning of glassware and portable equipment should be separated from the laboratory working area but located close enough for convenience.

7.3.5.1 Laboratories conducting trace organic analyses which use organic solvents in extraction and clean-up procedures must separate these activities from analytical instrumentation rooms to avoid contamination and reduce hazards.

7.3.5.2 Laboratories conducting analyses with a wide range of concentrations must take care to avoid cross contamination among samples in storage or analysis. Relatively clean samples, highly polluted samples and reagents should be stored separately from each other in vented cabinets and hoods to avoid cross-contamination.

7.3.5.3 Calibration standards should be stored separately from all samples.

7.3.5.4 *Laboratory Design*—Limited facilities and restricted work space may affect the quality and validity of results. Visitors and incidental traffic should be discouraged in work areas. Through traffic can be prevented by good laboratory design.

7.3.5.5 Bench tops should be set at heights of 36 to 38 in. (91 to 97 cm) with a depth of 28 to 30 in. (71 to 76 cm). This height is comfortable for work in a standing or sitting position. Desk tops or sit-down benches should be set at 30 to 31 in. (76 to 79 cm) height to accommodate calculations and writing activities. Bench tops should be constructed of stainless steel, epoxy plastic, or another smooth impervious material that is inert, corrosion-resistant, and has minimal seams.

7.3.5.6 Walls should be covered with waterproof paint, enamel, tile, or other surface materials that provide a smooth finish that is easily cleaned or disinfected, or both. Floors should be covered with good quality tiles or other heavy duty material, which can be maintained by wet-mopping or scrubbing machine and application of a skid-proof wax. Bacteriostatic agents contained in some wall or floor finishes increase the effectiveness of disinfection. Floors should never be swept or dry-mopped.

7.3.5.7 High standards of cleanliness should be maintained and monitored for contamination in work areas and the laboratory. If there is any doubt about the effects of the surrounding laboratory facility upon the analytical results, blanks that have been protected against the laboratory environment should be compared periodically against sample blanks that have been exposed to the laboratory environment.

7.3.5.8 A complete set of material safety data sheets (MSDSs), or equivalent safety information for all chemicals used in the laboratory, should be on file in a location accessible to all employees. Samples, reagents, and solvents that may contain harmful or interfering fumes shall be used in a properly operating hood or glove box. Smoking, eating, and drinking should not be allowed in the work area. Soiled hands should be washed before handling analytical materials. Sinks shall not be used for sample or reagent disposal. Laboratories shall dispose of waste in accordance with applicable environmental and safety regulations and standards. Standard operating procedures (SOPs) as described in Guide D 5172 for handling, storage, and disposal of hazardous reagents and samples shall be defined. Additional information is available in Guide D 4447, MSDSs, and Refs (**5-13**), but this information is for reference purposes only and is not intended to be exhaustive or to supersede regulations. Short courses on handling hazardous and toxic chemicals are available from chemical companies and others.

7.3.5.9 *Working Area*—Adequate bench space or working areas should be provided for each analyst. As a general guideline, there should be 150 to 300 ft^2(14 to 28 m^2) per analyst or 12 to 25 linear ft (3.6 to 7.6 m) of bench space per analyst. The space requirement per analyst will vary with the instrumentation or equipment in use, the sample load, and the number of operations that are to be performed by a single analyst. The laboratory may require specialized facilities such as a perchloric acid hood. The lighting level may vary between 50 and 100 fc (535 and 1070 1x), depending upon the closeness of the tasks being performed in the area.

7.3.5.10 *Electric Power Supply*—The reliability of the instruments is affected by the electrical power supply. Some instruments require separate circuits or a regulated power supply for stable operation. The line voltage and stability should be monitored periodically and not assumed as based on records. Surge suppressors should be installed for any sensitive instrumentation or computers. An isolated ground for individual instruments and antistatic pads are helpful in eliminating stray currents.

7.3.5.11 *Safety Considerations*—The laboratory should be supplied with fire extinguishers suitable for Class *A, B,* or *C* fires; spill control materials for acids, bases, and flammables; eye wash and safety shower facilities; and other safety devices that may be consistent with the particular laboratory operation.

The facilities should provide for the safe disposal of reagents and samples with written instructions for the utilization of these procedures by all personnel. Wearing of safety glasses, goggles, or face shields should be required for everyone entering the laboratory. A senior staff member should be assigned the responsibility for monitoring laboratory safety, including periodic inspection of facilities and fire extinguishers. Staff should be trained and have the training documented in the following: handling and disposal of potential chemical or biological hazards, or both; use of appropriate safety and personal protection equipment; and general laboratory safety and hygiene.

8. Methodology

8.1 *General*—The use of written procedures is an essential element in providing useful data. The use of published procedures is usually not sufficient to guarantee reliable and reproducible analytical performance. Each laboratory performing an analysis should reduce the methodology to a SOP that clearly and completely delineates the exact steps followed. The use of SOPs helps ensure uniform performance among different analysts using them.

8.1.1 The quality assurance program should clearly identify the duties of the following: the laboratory staff for routine quality control (QC) checks, the senior staff for continuing review of the quality control activities, and the laboratory director for periodic quality control reviews.

8.2 For ease of cross-referencing methods and ensuring completeness of methods, all SOPs should follow the same format.

8.3 Strict adherence to the method SOP shall be maintained and checked using a system of method performance audits. When deviations are necessary, the SOP should be rewritten to reflect the changes. If time does not permit a rewrite, the necessary deviations from the SOP shall be recorded and approved in writing by supervision before proceeding with the analysis.

8.4 Whenever a deviation from a written SOP is necessary, it should be noted in the final data report along with identification of the person who authorized the change.

8.5 A file of SOPs should be maintained by the laboratory director or manager. Each new SOP or revised SOP should carry its effective date so that recorded data may be related to the appropriate SOP. Outdated SOPs should be kept on file for reference purposes.

9. Metrology

9.1 A set of Class *S* weights or better must be available to make periodic checks on balances. A National Institute of Standards and Technology (NIST) certified thermometer should be used periodically to check temperature measurement devices. A set of color standards may be used to check the wavelength calibration and the stray light characteristics of a spectrophotometer or colorimeter. Systems such as balances and spectrometers can be maintained and certified under an annual service contract.

9.2 The laboratory providing analytical services on the characterization of water may wish to make additional measurements, such as water flow. The calibration of the flow measurement system, used in the field, should be traceable to standard weights and measures.

9.3 All metrology systems should have a record of calibration and maintenance schedules and should note configuration changes that may have occurred in such a system. Records of significant changes in calibration should be noted and reviewed periodically.

10. Data Recording

10.1 Any system is acceptable as long as it meets the requirements outlined in 6.5. A commonly used method of recording laboratory data is a notebook specifically designed for this purpose. The pages of the laboratory notebook are generally lined in a grid pattern with provision for information such as project identification, date, and signatures of the analyst and supervisor. The analyst should record information on the analyte, method of analysis, analytical conditions and results, and remarks. There should be an example of the calculations. Entries shall be in ink with no erasures or whiteout. Revisions should be indicated by a single line through the original entry with the correction alongside or referenced. Changes or corrections shall be dated and initialed.

10.2 When data are generated using an automated or semi-automated instrumentation, it is generally displayed on a strip chart recorder or printed tape. Chart paper should contain the signature of the analyst, the date, the sample identification, and the operational parameters of the instrument. Chart papers and tapes should be retained as a part of the permanent record. Some laboratories prefer to use microfilm for record retention.

10.3 Laboratory sampling, analyses, and data recording are increasingly automated and computerized. Projections into the future indicate an even more rapid transition to computerized operations of almost all sampling and analyses in water chemistry as has begun in clinical chemistry. Universities, colleges, and technical schools now require chemists to take courses in computer logic, programming, and operation so that graduated chemists and technicians are computer literate and able to utilize the advances already available. Instrument responses to samples, quality control checks, and blanks are now directly entered into the computer. Results and limits are calculated, and data acceptability is indicated immediately. Results are reviewed by the analyst on a video screen, and a hard copy is printed out only as desired. Results, evaluations, and summaries are archived off-line. Use of hard disks, floppy disks, and streamer tape back-ups provide the necessary redundancy to avoid loss from system crashes. A wealth of versatile software programs for personal computers permits statistical evaluations, spread sheets, scheduling, complete record-keeping for cost monitoring, supply management, quality control monitoring, report writing, and laboratory management. For further information and recommendations for ensuring data integrity in automated laboratory operations, consult the U.S. EPA *Good Automated Laboratory Practices* (**14**).

10.4 The recording of the data and the analytical results should be in a format that is agreed to by the laboratory and the data user. The laboratory should have a written protocol regarding the number of significant figures, detection limits, reporting convention for nondetection, analytical range, etc.

11. Data Validation

11.1 *General*—The validation of data will require a variety of techniques due to the variety of ways in which data are produced. If the data are collected manually, the validation procedures should take into account the sampling, the sample handling, the calibration and performance of the analytical system, and the calculations. The sampling, the calibration, and the instrument performance should be taken into account if the data are generated by instrumental means.

11.2 *Sampling*—Because the sampling of water (Practices D 3370), whether performed manually or by instrumental means, involves operations upon a heterogeneous mass under uncontrolled conditions, reliable conclusions can seldom be drawn from one or a few samples. The sampling plan must provide an adequate number and volume of samples to permit statistical evaluation of the data produced. Information on the number of samples from which a final result is derived should be available to the data user. The reasons for obtaining the information, the methods of obtaining it, and the desired levels of confidence in the information cannot be addressed within this guide for all situations. For further information, see the U.S. EPA *Handbook for Sampling and Sample Preservation* **(15).**

11.3 *Sample Handling and Identification*—To ensure that proper procedures are observed, to track sample collection, transportation, storage, and analysis, and to protect against loss, misidentification, tampering, or other errors that may be introduced, the sampler is responsible for providing the following information for every sample collected:

11.3.1 Collection date, time, and location;

11.3.2 Weather conditions and other remarks considered appropriate;

11.3.3 Sample identification number and the name of sampler;

11.3.4 The analytes to be tested and the sample preservation techniques utilized, if applicable; and

11.3.5 Appropriate warnings whenever the samples are time, light, or temperature sensitive, coupled with an indication of the allowable holding time. If it is necessary to estimate appropriate holding times, refer to Practice D 4841.

11.4 *Chain of Custody*— The laboratory should record the available history of every sample received, including its collection, preservation, transportation, transfers, analysis, and final disposal. This record will assist the laboratory in the investigation of any problems regarding the sample. If the sample is to meet regulatory or legal requirements, a formal chain of custody is a must. For details regarding chain of custody procedures see Guide D 4840.

11.5 *Analytical Quality Control (AQC)*—Items stated in 11.6 through 11.12 are recommended as the basis for a routine within laboratory analytical quality control program. SOPs for each method should contain the QC specifications appropriate for that method. The QC program described in 11.6 through 11.12 will be superseded by the QC section that will ultimately appear in each ASTM Committee D-19 test method. These QC sections will be prepared in accordance with Practice D 5847. If the method will be used to compare results between different laboratories, see Practice D 2777. For further information, see the U.S. EPA *Handbook for Analytical Quality Control in Water and Wastewater Laboratories* **(16)**.

11.6 *Calibration* — For each analyte, prepare a calibration curve which covers the entire working range of the method. Construct the curve using at least three points, including one near the upper limit of the concentration range and one near the lower limit with a reasonably equitable distribution of the remaining points. The actual minimum number of calibration points depends upon the width of analytical range and the shape of the calibration curve. For example, a broad range or a curve not known to be linear might require calibration at five to seven points. The difference (D) between the value observed for each calibration standard (X_{OBS}) and the value predicted for that standard using the fitted calibration curve (X_{PRED}) can be evaluated as follows:

11.6.1 After 20 to 25 initial values of $D = X_{OBS} - X_{PRED}$ are available, calculate the mean ($\bar{D}$) and standard deviation (S_D) for each concentration.

11.6.2 If a subsequent D value is not within the interval $\bar{D} \pm 3 (S_D)$, the system calibration is out of control and the system shall be recalibrated before continuing routine analyses.

11.6.3 If the calibration curve was fitted by minimizing the sum-of-squares of the absolute deviations of each calibration point from the curve, then the D values should also be in absolute units. However, if *percentage* deviations were minimized, then the D's also should be percentages of the predicted value.

11.6.4 If there is no obvious reason to require recalibration, instead of following steps in accordance with 11.6, an existing calibration curve may be verified at the beginning of the analytical run by measuring two calibration standards, one in the lowest quarter of the total range of the existing calibration curve and one in the highest quarter of the range.

11.6.5 Evaluate the difference $D = X_{OBS} - X_{PRED}$ for each calibration standard using the criteria developed in 11.6 and recalibrate if results are not within the control limits. As in the step described in 11.6, whether the D values are percentages or absolute units depends on how the calibration curve was fitted.

11.6.6 Record the D values for all acceptable calibration analyses and, after 20 to 25 additional results, revise related control limits by recalculating $\bar{D}$ and S_D from the new data.

11.6.7 It is important to preserve the sign of all D values.

11.7 *Method Blank*:

11.7.1 A method blank should be run to identify sources of contamination arising from the reagents or handling procedures used in performing the analysis. Determine reagent water, reagents, and solvent blanks for each set of samples analyzed, when there is a change in the reagent water system, or whenever a new source (newly prepared reagent or solvent) is introduced into the analytical system. Reagents or solvents, or both, should also be checked for purity prior to use.

11.7.2 Carry each method blank through the entire procedure.

11.7.3 Response to a significant method blank depends a great deal on the method, but the associated data shall certainly be evaluated, and every effort should be made to resolve or

minimize system contaminants. For each method, establish a maximum limit for the method blank based on end user's requirements.

11.8 *Field Blank*:

11.8.1 Different types of field blanks may be used during sampling to distinguish among potential sources of contamination that can affect the sampling process. Transport aliquots of analyte-free water or solvent to the field in sealed containers as field blanks for later return to the laboratory with the samples. Designate a specific number of field blanks as trip blanks, which are not opened in the field but are used to detect any contamination arising from handling, transport, or site storage. Designate a specific number of field blanks as equipment blanks, which are passed through the sampling equipment to detect any contamination from the equipment itself or the conditions during sampling.

11.8.2 Analyze appropriate field blanks with each set of samples from a given source. Carry each field blank through the entire procedure.

11.8.3 When interferences occur, it is best to discard the associated analytical results, investigate the cause so such losses may be avoided in the future, and resample. In situations where it is impossible to resample, however, it may be necessary to report the available results along with a note explaining the extent of the interference and its affect upon the data.

11.9 *Precision*—Precision is the closeness of agreement between the results of repeated analysis on the same sample.

11.9.1 *General*—Develop the necessary initial data by randomly selecting routine samples to be analyzed twice in order to provide duplicate analyses. Consider the steps in 11.9.1.1-11.9.8 .

11.9.1.1 Develop these data over a reasonable period of time to reflect day-to-day operations.

11.9.1.2 Choose the samples that are most representative of the interference potential of the sample type. If the laboratory handles multiple sample types with different precision characteristics, it will be necessary to establish and maintain separate background data and evaluation criteria for each sample type.

11.9.1.3 Ultimately, samples representing the entire concentration range should be included within each sample type if necessary.

11.9.2 From each pair of duplicate analytes (X_1 and X_2) calculate their relative range value (R):

$$R = \frac{|X_1 - X_2|}{(X_1 + X_2)/2}$$

where:
$|X_1 - X_2|$ = means the unsigned difference between X_1 and X_2.

11.9.3 After 50 to 100 R values are available for an analyte, order the R values by their related sample concentration estimates, organize the values into concentration ranges that seem to have a similar underlying R value, and calculate the average R value ($\bar{R}$) for each of these concentration ranges. Minimize the number of concentration ranges as much as practical.

11.9.4 Calculate the upper control limit (UCL) for each concentration range as follows:

$$UCL = 3.27 \, (\bar{R})$$

(See Note 2.)

Note 2—This factor may be found in Table 2, p. 83 of Ref. **(2)**.

11.9.5 Review the initial data for R values greater than the UCL value for the appropriate concentration range. If such values are found, they should be discarded and the related UCL value should be recalculated from the remaining R values within that concentration range.

11.9.6 Within each set of 20 or fewer samples to be analyzed together, evaluate system precision by conducting duplicate analyses on one of the samples selected at random. If the relative range value (R) calculated from these duplicates is greater than the appropriate UCL value, system precision is judged to be out-of-control and analyses must stop until the problem has been resolved. Problems with these data may indicate the need for stricter adherence to accepted laboratory practices.

11.9.7 After obtaining 20 to 25 additional acceptable pairs of data within each concentration level for a sample type, periodically update the table of critical relative range values by repeating the step described in 11.9.4 using the new data. Review the criteria being maintained and combine any which are very similar for related concentrations or sample types. If the criteria for adjacent concentration ranges are quite different, further subdivision by concentration may be necessary.

11.9.8 Table A1.1 gives an example of precision estimates from duplicate analyses within specific concentration ranges for three analytes.

11.10 *Bias Check Using Standard Solutions*:

11.10.1 Analyze at least one standard through the complete method for every subset of 20 or fewer routine samples to be analyzed together. This standard of known concentration can be purchased from an external source or prepared in house from materials or solutions of known purity. It should come from a source of material different from that used for the calibration.

11.10.2 To provide a complete record of the calibration and recovery for each analytical run, one of these standard samples should be the last sample analyzed.

11.10.3 Use concentrations that approximate those found in the related routine samples. Calculate percent recovery (P) as follows:

$$P = \frac{100 \, (\text{observed value})}{(\text{true value})}$$

11.10.4 After 20 to 25 standards are analyzed over time, calculate average percent recovery ($\bar{P}$) and standard deviation (S_P) of the resulting P values.

11.10.5 If subsequent standards for percent recovery are not within the interval $\bar{P} \pm 3 \, S_P$, the analytical system should be checked for problems. If problems exist, resolve them before continuing the analyses. Problems with these data often require greater care in sample processing prior to actual measurement.

11.10.6 Runs of seven or more successive points, all either above or below $\bar{P}$, also indicate the system is out-of-control. Use of a Shewhart $\bar{X}$-chart is recommended to facilitate evaluation of percent recovery results. An example of the

calculation of percent recovery and development of a Shewhart $\bar{X}$-chart is given in Table A1.2 and Fig. A1.1.

11.10.7 Record recovery of all acceptable check standards and, after 20 to 25 additional results, revise the related control limits by recalculating P and S_P from the new data. As in 11.9.7, the criteria subdivisions by sample type and concentration range should be periodically reviewed to judge their appropriateness.

11.11 *Bias Check Using Recovery of Spikes*:

11.11.1 Do essentially the same thing for recovery as was done in 11.10, except that a concentrate spike is added to a randomly selected *routine environmental sample* from the current analytical run rather than to *reagent water*. Different types of routine environmental samples may have to be dealt with separately if the samples exhibit different spike recovery characteristics. From this point on, this discussion is in terms of a specific identified sample type. P values for the recovery data are calculated as follows:

$$P = \frac{100 \, [A(V_s + V) - (BV_s)]}{CV}$$

where:
A = measured concentration of the component in the spiked sample,
B = measured background concentration of component in the sample,
C = concentration of component in spiking solution,
V_s = volume of sample before spiking, and
V = volume of spiking solution used.

11.11.2 In spiking samples, make sure that:

11.11.2.1 Sufficient spike is added to at least double the background concentration or to reach a concentration for which the calibration curve has been established. If the background concentration is higher than the midpoint of the standard curve, the background water should be diluted into the lower half of the calibration range and reanalyzed before spiking.

11.11.2.2 The volume of a spike should be kept to a minimum and not exceed 5 % of the sample volume. In organic analyses, the volume of spike should be no greater than 150 mL so that the solubility of the standard in the water will not be affected.

11.11.3 Resulting P values must fall within $\bar{P} \pm 3 \, S_P$ calculated from previous related spike recovery data. If not, the system may be out-of-control, and the cause must be found and corrected before continuing the analyses. Problems with these data often indicate sample matrix interferences. Related spike recovery data are developed from a particular environmental matrix, that is, groundwater, wastewater, etc. These limits may differ from the limits calculated in 11.10.3-11.10.5.

11.11.4 As in 11.10.6, runs of seven or more results on the same side of X indicate the system is out-of-control, and the use of a Shewhart X-chart is recommended to facilitate evaluation of results.

11.11.5 By simply calculating P from P values calculated as specified in either 11.11.1 or 11.10.3, percent recoveries of a spike can be treated as shown in the example given in Table A1.2 and Fig. A1.1.

11.11.6 Periodically review and update the recovery criteria similarly to 11.10.7.

11.12 *Summary of the Analytical Quality Control*—The following recommended analytical quality control program should be the standard practice in any laboratory.

11.12.1 Three or more standards are needed to develop a calibration curve in concentrations covering the working range, as necessary, or measurement of two calibration standards to verify the existing calibration curve.

11.12.2 One method blank per run.

11.12.3 One field blank per set of samples.

11.12.4 One duplicate for precision check (at least one every 20 routine samples).

11.12.5 One standard sample for recovery and calibration check (at least one every 20 routine samples). A standard should be the last sample analyzed in each run.

11.12.6 One spiked sample for recovery check in the presence of a sample matrix (at least one every 20 routine samples).

11.12.7 *Total*—Depending on the end use of the data, seven to ten analytical quality control analyses may be required for runs of up to 20 routine samples; 10 to 13 analytical quality control analyses may be required for runs of 21 to 40 routine samples, etc.

11.12.8 *Minimal Analytical Quality Control*—For very small operations or small sample loads, the described analytical quality control program may not be practical or necessary for all analytes. Whenever analytical quality control must be reduced below the level recommended, the following minimal analytical quality control program should be maintained.

11.12.9 Continue calibration or calibration checks as described in 11.6.

11.12.10 Analyze one field blank per set of samples to check for contamination. If an out-of-control situation is indicated, a method blank should be run to find out whether the contamination problem is in the laboratory or the field.

11.12.11 Analyze one spiked sample at the end of each analytical run to check for recovery or precision problems. If an out-of-control situation is indicated, analyze a standard to find out whether the problem is basic recovery or calibration, or both. Successful recovery of the standard would suggest either a matrix problem or a precision problem. A precision problem would produce random out-of-control indications, probably caused by poor or inconsistent analytical techniques or instrumentation.

11.13 *Performance Review*—Analysts should maintain a permanent record of the quality control checks which are performed. The laboratory supervisor should hold frequent meetings to review the quality control program with analysts to discuss the quality control checks performed and the resolution of any problems which are detected. Deficiencies which are detected should be documented in the record book indicating the analytes involved, the problem, the action taken, and the date of the action.

12. Trouble Shooting

12.1 Extreme, unexpected or questionable results are normally detected and reported by the analyst, or are noted by the supervisor in the daily reviews of results. When a deviation is noted, the train of sampling and analytical methods and quality

control shall be investigated. The documented intralaboratory quality control checks provide the primary means for the investigation.

12.1.1 Review the records of the sample collection. Check the preservation technique used, the chain of custody record, the time in transit, and comments on the conditions of the samples upon arrival at the laboratory, for example, temperature upon arrival, etc.

12.1.2 *Analytical Procedure*—Check calculations for transposition of numbers and mathematical error. Any significant positive blank result indicates field or laboratory contamination of sample, sampling device, sample container, reagents, reagent water, etc. Check monitoring data on reagent water. Check reagents for changes in bottle and lot and expiration dates. Analyze or reanalyze samples to confirm source and resolution of problem. Confirm recoveries with analyses of known reference samples.

12.2 The investigation may indicate good field and laboratory practices were not followed, such as the following:

12.2.1 The field sampling team should keep a bound field logbook for recording field measurements, time, temperature, sampling location, weather conditions, and other pertinent information.

12.2.2 The analyst should keep records on incoming chemicals and reagents, and the preparation of reagents, with estimated shelf lives. Reagent containers should be properly labeled and dated. A mechanism should be established for reorder of chemicals within the estimated shelf lives.

12.2.3 Reagent blanks should be carried through all sampling and analytical procedures. In colorimetry, the reagent blank should be compared with reagent water to detect an unusual reagent blank response.

12.2.4 When the data are obtained through the use of a standard curve, the points on the curve should be treated statistically and a regression line should be developed for the analytical method.

12.2.5 Use of reference materials of known quality from sources such as NIST, or others, should be used to confirm the adequacy of the technique and the analyst.

12.3 Senior analysts must maintain a permanent log of quality control checks performed. The laboratory supervisor shall hold frequent quality assurance review meetings with senior analysts to discuss the quality control checks performed and the resolution of problems detected. Deficiencies and corrective actions must be recorded in a log indicating the analytes involved, the problem, the action taken, and the date of the action. Only when the deficiencies have been discovered, corrected, and confirmed as corrected is the real benefit of a quality assurance plan realized, that is, improved data quality.

13. Keywords

13.1 analytical practices; analytical resources; good laboratory practice; quality assurance; quality control; trouble shooting

ANNEX

(Mandatory Information)

A1. QUALITY CONTROL EXAMPLES

A1.1 Table A1.1 presents the results of carrying out the steps described in 11.9.2 through 11.9.4 for three different analytes to illustrate use of the UCL values. If duplicate chromium results of 31.2 and 33.7 were obtained, the system precision would be checked as follows:

$$R = \frac{|31.2 - 33.7|}{(31.2 + 33.7)/2} = \frac{|-2.5|}{64.9/2} = \frac{2.5}{32.45} = 0.0770 \quad (A1.1)$$

Since the appropriate UCL from Table A1.1 is 0.109 and the current R values are not greater, precision of the analytical system is judged to be within control.

A1.2 The following calculations result from carrying out the step described in 11.11.3 using the data in Table A1.2:

$$\bar{P} = \frac{1}{n}\sum_{i=1}^{n} P_i = \frac{2105.27}{21} = 100.25 \quad (A1.2)$$

$$S_p = \sqrt{\frac{\Sigma(P_i - \bar{P})^2}{n-1}} = \sqrt{\frac{719.839}{20}} = 5.999 \quad (A1.3)$$

$$\bar{P} \pm 3\ S_p = 100.25 \pm 18.00 = 82.25\ to\ 118.25 \quad (A1.4)$$

A1.3 Therefore, as specified in 11.11.3, percent recovery values for total PO_4-P standards roughly within the concentration range from 0.34 to 4.9, that occurred below 82.2 % or above 118 %, would indicate that the accuracy of the analytical system is under control. The related Shewhart $\bar{X}$-Chart is illustrated in Fig. A1.1.

ASTM D 3856 – 95 (Reapproval 2000)

TABLE A1.1 Precision Estimates from Duplicate Analyses Within Specific Concentration Ranges for Three Analytes

Analytes	Concentration Range	No. of Sets of Duplicates	Average Concentration of Data	Average Relative Range (R)	R for Combined Concentration Ranges	Final UCL Results
BOD, 5-Day (mg/L) L	1 to <10	21	5.85	0.1776		
	10 to <25	30	17.6	0.1104	0.1381	0.452
	25 to <50	27	36.1	0.0924		
	50 to <150	29	102.0	0.0638		
	150 to <300	17	197.0	0.0564	0.0652	0.213
	300 to <1,000	12	520.0	0.0232		
	1,000 up	3	3341.0	0.0528		
Chromium (μg/L) L	5 to< 10	32	6.15	0.0612	0.0612	0.200
	10 to <25	15	16.7	0.0340		
	25 to <50	16	36.2	0.0310		
	50 to <150	15	85.1	0.0446	0.0334	0.109
	150 to <500	8	240.0	0.0218		
	500 up	5	3170.0	0.0240		
Copper (μg/L) L	5 to <15	16	11.1	0.1234		
	15 to <25	23	19.1	0.0736	0.0940	0.307
	25 to< 50	21	35.4	0.0338		
	50 to< 100	26	65.9	0.0354		
	100 to< 200	10	134.0	0.0210	0.0313	0.102
	200 up	3	351.0	0.0130		

TABLE A1.2 Analysis [A] of Total Phosphate-Phosphorus Standards, in mg/L Total PO$_4$-P

Point	Known	Obtained	% Recovery = P_i	$(P_i - \bar{P})^2$
1	0.34	0.33	97.06	10.176
2	0.34	0.34	100.00	0.062
3	0.40	0.40	100.00	0.062
4	0.49	0.49	100.00	0.062
5	0.49	0.49	100.00	0.062
6	0.50	0.47	94.00	39.063
7	0.50	0.53	106.00	33.062
8	0.50	0.56	112.00	138.063
9	0.52	0.59	113.46	174.504
10	0.66	0.70	106.06	33.756
11	0.66	0.60	90.91	87.236
12	0.67	0.65	97.01	10.498
13	0.68	0.65	95.59	21.716
14	0.83	0.80	96.39	14.900
15	1.30	1.20	92.31	63.044
16	1.30	1.30	100.00	0.062
17	1.60	1.70	106.25	36.000
18	2.30	2.30	100.00	0.062
19	2.30	2.40	104.35	16.810
20	3.30	3.30	100.00	0.062
21	4.90	4.60	93.88	40.577
		SUMS:	2105.27	719.839

[A] Using a colorimetric method with persulfate digestion.
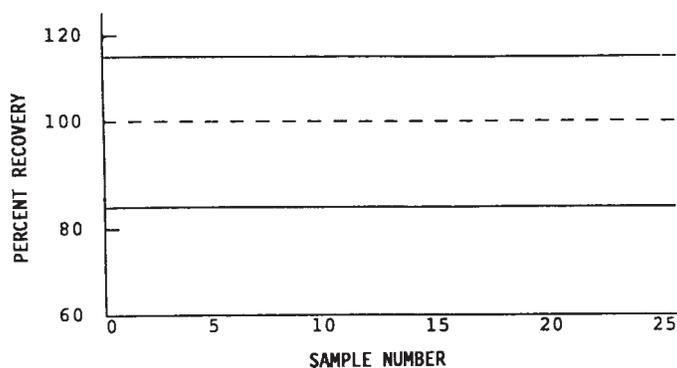
FIG. A1.1 Shewart Control Chart for Percent Recovery Data

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