

Standard Guide for On-Line Monitoring Systems for Water Analysis¹

This standard is issued under the fixed designation D3864; 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 covers the selection, establishment, application, and validation and verification of monitoring systems for determining water characteristics by continual sampling, automatic analysis, and recording or otherwise signaling of output data. The system chosen will depend on the purpose for which it is intended: whether it is for regulatory compliance, process monitoring, or to alert the user of adverse trends. If it is to be used for regulatory compliance, the method published or referenced in the regulations should be used in conjunction with this guide and other ASTM methods.

1.2 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. Specific hazard statements are given in Section 7.

2. Referenced Documents

- 2.1 ASTM Standards:²
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D3370 Practices for Sampling Water from Closed Conduits
- D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)³
- D5540 Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis
- E178 Practice for Dealing With Outlying Observations

2.2 *ASTM Special Technical Publication:* **STP 442 Manual on Water**⁴

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 Calibrations:

3.2.1.1 *laboratory calibration curve for flow-through systems*—calibration curve calculated from withdrawn samples or additional standards that may be spiked or diluted and analyzed using the appropriate laboratory analyzer.

3.2.1.2 *laboratory calibration curve for flow-through systems*—type of sample used to generate a laboratory calibration curve for flow-through systems.

3.2.1.3 *line sample calibration*—coincidental comparison of a line sample and adjustment of a continuous analyzer to the compared laboratory analyzer or a second continuous analyzer.

3.2.1.4 *multiple standard calibration* —where the calibration curve is calculated from a series of calibration standards covering the range of the measurements of the sample being analyzed.

3.2.1.5 *probe calibration*—where the probe is removed from the sample stream and exposed to a calibration solution and the analyzer is adjusted to indicate the appropriate value. Alternately, two probes are exposed to the same solution and the on-line analyzer is adjusted to coincide with the pre-calibrated laboratory instrument.

3.2.1.6 *reference sample calibration* —coincidental comparison of a reference sample and adjustment of a continuous analyzer to the compared laboratory analyzer results.

3.2.2 *cycle time*—the interval between repetitive sample introductions in a monitoring system with discrete sampling.

3.2.3 *drift*—the change in system output, with constant input over a stated time period of unadjusted, continuous operation; usually expressed as percentage of full scale over a 24-h period.

3.2.3.1 *span drift*—drift when the input is at a constant, stated upscale value.

3.2.3.2 zero drift-drift when the input is at zero.

¹ This guide is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved June 1, 2012. Published October 2012. Originally approved in 1979. Last previous edition approved in 2006 as D3864 – 06. DOI: 10.1520/D3864-12.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

 $^{^{3}\,\}text{The}$ last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from ASTM Headquarters. Contact Customer Service, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

3.2.4 *full scale*—the maximum measuring limit of the system for a given range.

3.2.5 *input*—the value of the parameter being measured at the inlet to the analyzer.

3.2.6 *interference*—an undesired output caused by a substance or substances other than the one being measured.

3.2.6.1 *Discussion*—The effect of interfering substance(s) on the measured parameter of interest should be expressed as a percentage change (\pm) in the measured component as the interference varies from 0 to 100 % of the measuring scale. If the interference is nonlinear, an algebraic expression should be developed (or curve plotted) to show the varying effect.

3.2.7 *laboratory analyzer*—a device that measures the chemical composition or a specific physical, chemical, or biological property of a sample.

3.2.8 *limit of detection*—a concentration of twice the criterion of detection when it has been decided that the risk of making a Type II error is equal to a Type I error as described in Practice D4210.

3.2.9 *linearity*—the extent to which an actual analyzer reading agrees with the reading predicted by a straight line drawn between upper and lower calibration points—generally zero and full-scale. (The maximum deviation from linearity is frequently expressed as a percentage of full-scale.)

3.2.10 *monitoring system*—the integrated equipment package comprising sampling system, analyzer, and data output equipment, required to perform water quality analysis automatically.

3.2.10.1 *analyzer*—a device that continually measures the specific physical, chemical, or biological property of a sample.

3.2.10.2 *data acquisition equipment*—analog or digital devices for acquiring, processing, or recording, or a combination thereof, the output signals from the analyzer.

3.2.10.3 *sampling system*—equipment necessary to deliver a continual representative sample to the analyzer.

3.2.11 *output*—a signal, usually electrical, that is related to the parametric measurement and is the intended input to data acquisition equipment.

3.2.12 *range*—the region defined by the minimum and maximum measurable limits.

3.2.13 *repeatability*—a measure of the precision of one analyzer to repeat its results on independent introduction of the same sample at different time intervals.

3.2.14 *reproducibility*—a measure of the precision of different analyzers to repeat results on the same sample.

3.2.15 *response time*—the time interval from a step change in the input or output reading to 90 % of the ultimate reading.

3.2.15.1 *lag time*—the time interval from a step change in input to the first corresponding change in output.

3.2.15.2 *total time*—the time interval from a step change in the input to a constant analyzer signal output.

3.2.16 *sample port*—that point in the sample-conditioning system where samples for laboratory analysis are taken.

3.2.17 *samples*:

3.2.17.1 *line sample*—a process sample withdrawn from the sample port (3.2.16) during a period when the process stream flowing through the continuous analyzer is of uniform quality and the analyzer result displayed is essentially constant. Laboratory tests or results from a second continuous analyzer are obtained from each sample and compared with the continuous analyzer results obtained at the time of sampling.

3.2.17.2 *reference sample*—can be a primary standard or a dilution of a primary standard of known reference value. The reference value must be established through multiple testing using an appropriate ASTM or other standard laboratory test method. Bulk quantities of the reference sample must be stored and handled to avoid contamination or degradation. One or more reference samples encompassing the range of the analyzer may be required.

Note 1—It is essential that the laboratory analyzer be checked carefully before these tests are performed to ensure compliance with the requirements of the standard test procedure. To further ensure proper operation it is recommended that a previously calibrated reference sample or an in-house control standard of known concentration be tested to validate the operations of the laboratory analyzer.

3.2.18 *validations*—a one-time comprehensive examination of analytical results.

3.2.18.1 reference sample validations—a reference sample is analyzed a minimum of seven times by an appropriate continuous analyzer and by an appropriate laboratory analyzer. A comparison is made between the average continuous analyzer results and the average laboratory results using the Student's *t* test at 95 % confidence coefficient, two-tailed test as described in 14.1. Passing the Student's *t* test signifies the continuous analyzer's average analysis of the reference sample is not statistically significantly different from the laboratory analyzer's average analysis of the same reference sample (validation test acceptable). Failing the "*t*" test signifies a statistically significant difference exists (validation test not acceptable).

3.2.18.2 *line sample validations*—a line sample is analyzed coincidentally a minimum of seven times by an appropriate continuous analyzer and an appropriate laboratory analyzer or a second continuous analyzer. A comparison is made on the differences between the coincidental results using the Student's *t* test at 95 % confidence coefficient, two-tailed test, to evaluate whether the average difference is statistically significantly different from zero difference as described in 14.2.

3.2.19 *verification*—a periodic or routine procedure to ensure reliability of analytical results.

3.2.19.1 *line sample verification*—a line sample is analyzed as described in 3.2.18.2, and the results of the difference between the continuous analyzer and the laboratory analyzer or a second continuous analyzer is plotted on a control chart. If the calculated difference between the continuous analyzer and the laboratory analyzer or a second continuous analyzer is within $\pm 3 S_d$, the continuous analyzer is considered verified. If the calculated difference is outside $\pm 3 S_d$ the continuous analyzer is considered out of control (not verified).

3.2.19.2 *reference sample verification*—a reference sample is analyzed as described in 3.2.18.1 and the results of the

differences between the continuous analyzer and the laboratory analyzer are plotted on a control chart. If the calculated difference between the continuous analyzer and the laboratory analyzer is within $\pm 3 S_d$ the continuous analyzer is considered verified.

Discussion— If the calculated difference is outside $\pm 3 S_d$ the continuous analyzer is considered out of control (not verified).

3.3 *Symbols:*— S_d = standard deviation

4. Summary of Guide

4.1 This guide provides a unified approach to the use of on-line monitoring systems for water quality analysis. It presents definitions of terms, safety precautions, system design and installation considerations, calibration techniques, general operating procedures, and comments relating to validation and verification procedures.

5. Significance and Use

5.1 Many of the manual and automated laboratory methods for measurement of physical, chemical, and biological parameters in water and waste water are adaptable to on-line sampling and analysis. The resulting real-time data output can have a variety of uses, including confirming regulatory compliance, controlling process operations, or detecting leaks or spills.

5.2 This guide is intended to be a common reference that can be applied to all water quality monitoring systems. However, calibration, validation, and verification sections may be inappropriate for certain tests since the act of removing a sample from a flowing stream may change the sample.

5.3 Technical details of the specific methodology are contained in the pertinent ASTM standard test methods, which will reference this practice for guidance in selection of systems and their proper implementation.

5.4 This guide complements descriptive information on this subject found in the ASTM Manual on Water.⁴

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. ⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*— Unless otherwise indicated, the reference to water shall be understood to mean reagent water that meets the purity specification of Specification D1193 Type I or Type II water.

7. Hazards

7.1 Each analyzer installation shall be given a thorough safety engineering study. 6

7.2 Electrically, the monitoring system as well as the individual components, shall meet all code requirements for the particular area classification.

7.2.1 All analyzers using 120 V, alternating current, 60 Hz, 3-wire systems shall observe polarity and shall not use mechanical adapters for 2-wire outlets.

7.2.2 Check the neutral side of the power supply at the analyzer to see that it is at ground potential.

7.2.3 Connect the analyzer's ground connection to earth ground and check for proper continuity.

7.2.4 The metallic framework of the analyzer shall be at ground potential.

7.2.5 Consider additional protection in the form of properly sized ground fault interrupters for each individual application.

7.2.6 Analyzers containing electrically heated sections shall have a temperature-limit device.

7.2.7 The analyzer, and any related electrical equipment (the system), shall have a properly sized power cutoff switch and a fuse or breaker on the "hot" side of the line(s) of each device.

7.3 Give full consideration to safe disposal of the analyzer's spent samples and reagents.

7.4 Provide pressure relief valves, if applicable, to protect both the analyzer and monitoring system.

7.5 Take precautions when using cylinders containing gases or liquids under pressure. Helpful guidance may be obtained from Refs (1-2).⁷

7.5.1 Gas cylinders must be handled by trained personnel only.

7.5.2 Fasten gas cylinders to a rigid structure.

7.5.3 Take special safety precautions when using or storing combustible or toxic gases to ensure that the system is safe and free from leaks.

7.6 Gas piping, where possible, shall be metallic, especially inside the analyzer housing.

8. Measurement Objectives

8.1 Carefully define the measurement objective for the monitoring system before selecting components of the system and set specifications realistically, to meet the objective. Terms used as specifications shall be consistent with the terminology in Section 3.

8.2 If the monitoring system is intended primarily to determine compliance with regulatory standards, the accuracy, precision, frequency of sampling, and response time may be dictated by the requirements of the regulations. A high degree of stability and on-line reliability is generally required. The

⁵ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁶ The user, equipment, supplier, and installer should be familiar with requirements of the National Electrical Code, any local applicable electrical code, U.L. Safety Codes, and the Occupational Safety and Health Standards (*Federal Register*, Vol 36, No. 105, Part II, May 29, 1971).

⁷ The boldface numbers in parentheses refer to the list of references at the end of this standard.