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Standard Guide for On-Line Monitoring Systems for Water Analysis[1]

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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D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data (Withdrawn 2002)[3]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3.2.1.1 *laboratory calibration curve for flow-through systems*—calibration curve calculated from withdrawn samples or additional standards that may be spiked or diluted and analyzed using the appropriate laboratory analyzer.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.

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[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] 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 (±) 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.

analyzer response for a specific parameter must be referenced to a recognized or specified laboratory method approved by the regulatory agency.

8.3 Monitoring systems intended to detect leaks and uncontrolled discharges, that is, spills, to protect treatment plants or receiving waters, require short sampling cycles and rapid response. Typically, these will activate alarms to alert operating personnel. They then may cause flow to be diverted from normal channels until the upset has passed or has been corrected. Frequently, the monitoring system is used in some way to locate and identify the source of the spill.

8.4 Systems that monitor the performance of process operations such as waste treatment, may have varying degrees of sophistication and complexity, depending on the specific nature of the application.

8.4.1 Simple, inexpensive, and low-precision analyzers with indicating or recording devices and alarms are acceptable for monitoring trends in operating parameters and for alerting operating personnel to off-standard performance.

8.4.2 Monitoring systems that provide data to be used to manually control process operations or to manually set automatic controllers are generally more complex and frequently require that outputs be transmitted long distances.

8.4.3 Monitoring systems intended to process data for operating guidance or management presentation and to provide varying degrees of automatic process control must be compatible with digital computers or telemetering systems. The reliability and stability of such systems, particularly the data output equipment, shall be high.

9. Sample System Design Considerations

9.1 Carefully examine the measurement objectives of the monitoring system and select a sampling system that matches these requirements.

9.2 Review all sample requirements with the equipment supplier. Be sure to define accurately all conditions of intended operation, the components in the sample and expected variations in the measured parameters.

9.3 Choose materials of construction for the parts that will be in contact with the sample, that do not react with the sample to cause subsequent contamination, corrosion, or other damage to critical parts or sorption of measurable components and maintain sample integrity.

9.4 Select the sampling point(s) so as to provide a representative and measurable sample as close as possible to the sample system and analyzer, and as outlined in Practices D3370.

9.5 Design the sample probe to be consistent with the measurement objective and to require a minimum of maintenance.

9.6 Select the sample transfer system, including pumps and transfer lines, so that the integrity of the sample is maintained from sampling point to analyzer, especially with respect to suspension of solids and biological growth.

9.7 Provide necessary sample conditioning equipment (for example, filters, diluters, homogenizers, stream splitters), that is consistent with the defined measurement objective.

9.8 Provide a connection, when necessary, for introducing standard samples or withdrawing check samples immediately upstream of the analyzer.

9.9 Keep single- or multiple-sample streams that interface a single analyzer flowing all the time. Keep the manifold close to the analyzer to minimize cross-contamination.

9.10 Always keep sample lines as short as possible.

9.11 Provide appropriate protection of sample lines from extremely hot or freezing temperatures.

10. Considerations for Analyzer Selection

10.1 The analyzer selected must meet the measurement objective of the system over the complete range of application.

10.1.1 Precision and accuracy of measurement and response time for the parameter of interest shall coincide with system specifications at all levels of measurement.

10.1.2 Interference shall be insignificant relative to the measured component or shall be controllable. When used for regulatory compliance, known interferences shall not affect the reading more than 5 % from the true value.

10.1.3 If required for compliance, the analyzer shall be capable of validation by calibration with approved and certified standard reference materials using standard ASTM (or equivalent) tests.

10.2 In choosing a specific analyzer for a specific application, on line reliability of the instrument is of prime concern.

10.2.1 Downtime for maintenance because of component failures or other malfunction shall be minimal. Ease, promptness, minimal cost of repair or replacement are essential.

10.2.2 The analyzer shall be stable. Drift and changes in response with changes in conditions such as flow and temperature shall be insignificant or means for compensation shall be provided. Sample flow variations may have a significant effect on measured analyte concentrations. Flow rate control shall be established as specified in Practice D5540. Sample flow rate shall be maintained within limits to maintain the necessary precision of the continuous on line monitor.

10.2.3 The analyzer shall be relatively simple and easy to operate and maintain at a satisfactory level of performance.

11. Data Output Equipment Considerations

11.1 Equipment for the acquisition of output data from the analyzer shall meet the requirements of the measuring objectives for the monitoring system.

11.2 Visual or audible alarms and simple output meters are acceptable and desirable in many applications.

11.3 The analyzer output can be recorded locally at the field location. The digital or analog signal is frequently transmitted to a centralized location, such as a control room, often by a data line shared with other instruments.

11.4 Records or real-time data can be transferred to computers for storage, process control, or report generation.

11.5 Process equipment such as valves and pumps can be actuated by output generated by analyzers in a number of ways:

11.5.1 Recorded and output meters can have set points as integral parts of their design which actuate the equipment directly for either on-off or proportional control.

11.5.2 Controllers can be manually adjusted in response to analyzer signals read from a recorder or from output presented in a data report, typed or displayed on a cathode ray tube.

11.5.3 Direct digital process control is possible in more complicated and sophisticated systems, where real-time analyzer output is integrated with other process data and used to maintain desirable process conditions.

12. Installation of Monitoring System

12.1 Obtain information required for installation and operation of the monitoring system from the supplier.

12.2 Study operational data and design parameters furnished by the supplier before installation.

12.3 Choose materials of construction and components of the monitoring system to withstand the environment in which it is installed.

12.4 Select a location for the analyzer that is as close as possible to the sample intake and which provides adequate protection from extremes of temperature and humidity, where this is essential for proper performance.

12.5 Provide a convenient access to the entire monitoring system.

12.6 Provide proper outlets for the analyzer's exit streams so that no liquid or gas pressure buildup occurs (see 7.4).

12.7 After the installation has been completed, allow the analyzer to stabilize and calibrate before testing performance specifications.

13. Calibration

13.1 Establish a written calibration procedure and frequency consistent with the parameter being measured and the accuracy and reliability demanded by the measurement or control objectives based on the following:

13.1.1 Consult the analyzer supplier to determine the best calibration procedure to use with the specific analyzer in a particular application.

13.1.2 When required for regulatory compliance, use calibration procedures specified by the appropriate agency.

13.1.3 Refer to ASTM standards, where applicable, to determine appropriate calibration standards.

13.1.4 Provide calibration standards at concentrations and compositions as close as possible to those of the sample stream being analyzed.

13.1.5 Before calibration, ensure that the sampling system and output instrumentation are functioning properly and that all preliminary adjustments to the analyzer required by the procedure have been made.

NOTE 2—Flow rate changes may affect continuous on line analyzer measured analyte concentration. If flow rates cannot be maintained constant, the effect of flow rate variation on measured analyte concentration shall be evaluated. Limits for flow rate variation shall be established to maintain the necessary precision of the continuous on line monitor.

13.2 *Reference Sample Calibration :*

13.2.1 With the reference sample flowing uniformly through the analyzer sampling line, allow the continuous analyzer readout to equilibrate.

13.2.2 Record time, sample number, date, and the corresponding continuous analyzer readout, and immediately analyze the reference sample using the appropriate laboratory analysis test method.

13.2.3 Determine the continuous analyzer calibration adjustment required so that results of laboratory analysis and the continuous analyzer readout coincide. Adjust the analyzer controls accordingly.

13.2.4 Repeat this procedure until no further change is needed, consistent with the quality of data required.

13.3 *Line Sample Calibration:*

13.3.1 With the sample flowing through the continuous analyzer sampling line uniformly and the continuous analyzer readout as close as possible to an equilibrium value, connect a second on line analyzer either downstream or on a parallel sample line, or withdraw a sample from the inlet stream as described in Practices D3370.

NOTE 3—The connection should be made in such a way so as not to contaminate the flowing sample.

13.3.2 Record time, date, continuous analyzer results and the second on line analyzer results, or immediately analyze the withdrawn sample using the appropriate laboratory analysis test method.

13.3.3 Determine the continuous analyzer calibration adjustment required so that the results of the on line continuous analyzers agree with the second on line analyzer or the laboratory analysis.

NOTE 4—It is essential that the second on line continuous analyzer be checked carefully before this calibration is performed to ensure compliance with the requirements of the standard test procedure. To further ensure proper operation it is recommended that a reference sample or in-house control standard of known quality be tested to validate the operation of the second on line continuous analyzer.

13.3.4 Adjust the continuous analyzer with the analyzer controls accordingly.

13.4 *Multiple Standard Calibration :*

13.4.1 Prepare a series of calibration standards covering the range of measurements for the sample being analyzed, following instructions in the test method or in the analyzer supplier's instructions.

13.4.2 Check all operating conditions of the system in accordance with the analyzer specifications, and allow sufficient time for instrument equilibrium.

13.4.3 Introduce a calibration standard of a concentration level recommended by the instrument supplier into the analyzer using the recommended instrument operating procedure. Activate the readout equipment.

13.4.4 After sufficient sample has been allowed to flow through the analyzer, adjust the readout to conform to the desired value.

13.4.5 Repeat 13.3.3 for the remaining standards from the calibration series, recording the equilibrium readout value each time.

13.4.6 Plot a calibration curve of standard value versus readout response from the above data.

13.4.7 Discard any standard when any change of composition is detected.

13.5 *Laboratory Calibration Sample for Flow-Through System:*

13.5.1 Withdraw from the spot sampling line or otherwise obtain directly from the sample stream sufficient sample for calibration, representative of one concentration within the range of measurement of the analyzer (see Practices D3370).

13.5.2 Analyze the sample for the parameter of interest using the appropriate laboratory analysis test method.

13.5.3 If necessary, prepare additional standards to cover the range of interest by dilution with reagent water or by "spiking" with known amounts of an appropriate standard.

13.5.4 Serially, introduce the standards into the continuous analyzer, using the recommended instrument operating procedures. Allow the continuous analyzer readout to reach equilibrium, and record the equilibrium readout value each time.

13.5.5 Plot a calibration curve of concentration of parameter being determined versus readout response from the readout data.

13.6 *Probe Calibration:*

13.6.1 Provide special calibration procedure for continuous analyzers for which the instrumental measuring technique utilizes a sensor that is inserted directly into the sample, for example, pH, dissolved oxygen, conductivity.

13.6.2 Prepare two calibration solutions in accordance with the appropriate test method, selecting them to bracket the anticipated value of measurement.

13.6.3 Remove the probe from the sample stream, clean if appropriate and perform any necessary maintenance.

13.6.4 Fill a test container with the first calibration solution. The container shall have the means for monitoring temperature and, where appropriate, provide and maintain an adequate flow of sample past the sensor.

13.6.5 Insert the probe in the container containing the calibration solution and, using the procedure provided by the suppliers, adjust controls so that the analyzer output coincides with the accepted value of the standard. Make necessary adjustments for temperature compensation.

13.6.6 Rinse the probe thoroughly, place it in a second container containing the other calibration solution and readjust the controls, if necessary, so that the output agrees with the value of this guide.

13.6.7 Recheck with both solutions at least once. If either point differs from the true value by a significant amount, as determined by the quality of measurement required, perform necessary maintenance, and recalibrate.

13.6.8 Alternatively, insert a second probe, with independent readout equipment and previously calibrated, into the sample alongside the probe and calibrate in situ, by adjusting its controls until the outputs of the two probes coincide.

13.7 After initial calibration with standard solutions or actual samples, as in 13.2 through 13.5, analyzer calibrations can be rechecked with secondary standards.

13.7.1 An electrical signal may be imposed to produce an analyzer output corresponding to a specific value produced by the parameters being analyzed.

13.7.2 A solution containing material other than the component of interest, but producing the same analyzer output as that component, may be used in place of the standard solution.

13.7.3 An optical filter may be placed in the beam of a photometric analyzer to produce an output equivalent to that produced by the component of interest.

14. Validation Procedures

14.1 *Reference Sample Validation Procedure:*

14.1.1 Obtain the reference sample and determine the reference value in accordance with 3.2.18.2.

14.1.2 Store the reference sample under conditions that will not cause contamination or degradation of the reference sample concentration. Because storage conditions and factors that affect sample stability change with time, confirm the reference value at periodic intervals. The frequency of confirmation can best be determined by the user of the analyzer.

14.1.3 Obtain a minimum of seven coincidental laboratory and continuous analyzer results of the reference sample, by introducing the reference sample into the continuous analyzer or laboratory analyzer and recording the results. Preferably use different qualified operators to make the multiple determinations over a period of time, with routine testing in the interim, until sufficient data have been obtained for analysis.

14.1.4 More than seven test results on the reference sample are often necessary to attain an average value with acceptable confidence limits. This will vary significantly for different laboratory procedures and reference sample concentrations. This applies for both laboratory and continuous analysis.

14.1.5 Tabulate the laboratory and continuous analyzer results and their differences. Check for outliers using the Grubbs test criterion in Annex A1.

14.1.6 Calculate the laboratory analyzer variance from the individual test results, excluding any outliers found in 14.1.5, as follows:

$$S_L^2 = \frac{\left[\sum_{i=1}^{n} X_L^2 - \frac{\left(\sum X_L\right)^2}{n_L}\right]}{\left(n_L - 1\right)} \quad (1)$$

where:

S_L^2 = variance of the laboratory test results,
X_L = individual laboratory analyzer test results on the reference sample,
n_L = number of laboratory analyzer test results, and
$\bar{X}_L$ = $\frac{\sum X_L}{n_L}$ = arithmetic average of the laboratory analyzer test results.

14.1.7 Determine whether the precision of the laboratory test results on the reference sample is statistically significantly different from the historical precision of the laboratory test method. The statistical criterion for this purpose is the F test as follows:

$$F = \frac{S_B^{\,2}}{S_s^{\,2}} \tag{2}$$

where:

$S_B^{\,2}$ = larger variance, either $S_L^{\,2}$ or $S_h^{\,2}$,
$S_s^{\,2}$ = smaller variance, either $S_L^{\,2}$ or $S_h^{\,2}$,
$S_L^{\,2}$ = variance of the laboratory test results on the reference sample as determined in 14.1.6,
v_L = degrees of freedom for laboratory analysis of reference sample ($n_L - 1$),
$S_h^{\,2}$ = historical variance for the laboratory analysis with n_h determinations, and
v_h = degrees of freedom for historical laboratory analyzer tests ($n_L - 1$).

14.1.8 Compare the calculated F value with the critical F value given in Table 1 for the appropriate degrees of freedom in the numerator (v_L or v_h) and appropriate degrees of freedom in the denominator (v_h or v_L).

14.1.8.1 If the calculated F value exceeds the critical F value obtained from Table 1, there is at least a 95 % probability that the reference sample laboratory analyzer data precision is statistically significantly different from the historical precision for that laboratory analyzer. In this event, the reasons for the substandard test precision should be determined, appropriate corrective actions to the procedure or laboratory analyzer, or both, and a minimum of seven new tests on the reference sample repeated in accordance with 14.1.3 through 14.1.8 until acceptable laboratory test precision is obtained.

14.1.9 Calculate the variance of the continuous analyzer excluding outliers rejected in 14.1.5 as follows:

$$S_c^{\,2} = \frac{\left[\sum_{i=1}^{n} X_c^{\,2} - \frac{\left(\sum X_c\right)^2}{n_c}\right]}{(n_c - 1)} \tag{3}$$

or

$$\sum_{i=1}^{n} \left(X_c - \bar{X}_c\right)^2 \frac{}{n_c - 1} \tag{4}$$

where:

X_c = individual continuous analyzer results on the reference sample,
n_c = number of continuous analyzer test results, and
$\bar{X}_c$ = $\frac{\sum X_c}{n_c}$ = arithmetic average of the continuous analyzer test results.

14.1.10 Apply the F test as follows to determine whether the variance of the laboratory analyzer ($S_L^{\,2}$) and the variance of the continuous analyzer ($S_c^{\,2}$) are statistically significantly different:

$$F = \frac{S_B^{\,2}}{S_s^{\,2}} \tag{5}$$

where:

$S_B^{\,2}$ = larger variance, either $S_L^{\,2}$ or $S_c^{\,2}$,
$S_s^{\,2}$ = smaller variance, either $S_L^{\,2}$ or $S_c^{\,2}$,
$S_L^{\,2}$ = variance of the laboratory test results on the reference sample as determined in 14.1.6,
v_L = degrees of freedom for laboratory analysis of reference sample ($n_L - 1$),
$S_c^{\,2}$ = variance of the continuous analyzer test results on the reference sample in 14.1.9, and
v_c = degrees of freedom for the continuous analyzer, ($n_c - 1$).

14.1.11 Compare the calculated F value with the critical F value given in Table 1 for the appropriate degrees of freedom in the numerator (v_L or v_h) and the appropriate degrees of freedom in the denominator (v_h or v_L).

TABLE 1 *F*-Distribution: Degrees of Freedom for Numerator

d/n [A]	1	2	3	4	5	6	7	8	9	10	12	15	20 [B]
1	161	200	216	225	230	234	237	239	241	242	244	246	248
2	18.5	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4
3	10.1	9.55	9.28	9.12	9.01	8.94	8.87	8.85	8.81	8.79	8.74	8.70	8.66
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.81	4.77	4.74	4.68	4.62	4.56
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.61	3.44
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94
10	4.96	4.10	3.70	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.33
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57

[A] Where: n = degrees of freedom in the numerator and d = degrees of freedom in the denominator (for example, if $n = 6$ and $d = 15$ the critical F value is 2.79).
[B] Expanded tables may be found in statistical reference books, see also “Standard Probability and Statistics,” CRC Press, 1991.

14.1.12 If the calculated F value is equal to or less than the critical F value obtained from Table 1, apply the Student's t test to determine if there is a statistically significant difference between the average continuous analyzer results and the average laboratory analyzer result. If the computed F is greater than the critical F value proceed to 14.1.16.

$$t = \frac{\left|\bar{X}_c - \bar{X}_L\right|}{S_p} \tag{6}$$

$$S_p = \sqrt{\frac{(v_L)\,S_L{}^2 + (v_c)\,S_c{}^2}{n_L + n_c - 2} \times \left(\frac{1}{n_L} + \frac{1}{n_c}\right)} \tag{7}$$

where:

S_p = pooled standard deviation for the difference between $\bar{X}_L$ and $\bar{X}_c$,
$\bar{X}_L$ = arithmetic average laboratory analyzer results,
$\bar{X}_c$ = arithmetic average continuous analyzer results,
v_L = degrees of freedom for laboratory analysis $(n_L - 1)$,
v_c = degrees of freedom for the continuous analyzer results $(n_c - 1)$,
$S_L{}^2$ = variance of laboratory analyzer results, and
$S_c{}^2$ = variance of the continuous analyzer results.

14.1.13 Compare the calculated t value from Eq 6 with the critical t value from Table 2 for the $(n_L + n_c - 2)$.

14.1.14 If the calculated t value is equal to or less than the critical t value, the continuous analyzer can be expected to give essentially the same average results as the laboratory analyzer.

14.1.15 If the calculated t value exceeds the critical t value there is at least a 95 % probability that the continuous analyzer and the laboratory analyzer are not giving the same average test results. Continuous analyzer validity is therefore suspect. Further investigation of the continuous analyzer function and operation should be made to correct the probable bias.

14.1.16 Calculate the t value as follows:

$$t = \frac{\left|X_C - X_L\right|}{\sqrt{\frac{S_L{}^2}{n_L} + \frac{S_C{}^2}{n_C}}} \tag{8}$$

TABLE 2 Table of *t* at 5 % Probability Level

Degrees of Freedom $(N - 1)$	t
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228
11	2.201
12	2.179
13	2.160
14	2.145
15	2.131
16	2.120
17	2.110
18	2.101
19	2.093
20	2.086

14.1.16.1 Compute the degrees of freedom for the t test as follows:

$$\text{degrees of freedom} = \frac{\left[\left(\frac{S_L{}^2}{n_L} + \frac{S_C{}^2}{n_C}\right)\right]^2}{\frac{\left(\frac{S_L{}^2}{n_L}\right)^2}{n_L + 1} + \frac{\left(\frac{S_C{}^2}{n_C}\right)^2}{n_C + 1}} - 2 \tag{9}$$

round the computed value to the nearest whole number.

14.1.17 Compare the calculated t value from above with the critical t value from Table 2 for the degrees of freedom computed above.

14.1.18 Refer to 14.1.14 and 14.1.15 for the proper interpretation of the comparison in 14.1.17.

14.1.19 Calculate the t value for the differences as follows:

$$t = \frac{\bar{d}\sqrt{n_d}}{S_d} \tag{10}$$

where:

$\bar{d}$ = average difference,
n_d = number of differences, and
S_d = standard deviation of the differences.

14.1.20 Compare the calculated t value from above with the critical t value from Table 2 for $n_d - 1$ degrees of freedom.

14.1.21 Refer to 14.1.14 and 14.1.15 for the proper interpretation of the comparison in 14.1.20.

14.2 *Line Sample Validation Procedure:*

14.2.1 The line sample method is used primarily for the validation of the continuous analyzer operation where the process stream is in service and available. The line sample method therefore is not applicable for predelivery validation of the continuous analyzer or for calibration before start-up and is not a viable alternative to the reference sample method under these conditions.

14.2.2 For continuous analyzer applications or process stream conditions, or both, that negate the practical use of the reference sample method for predelivery or initial validation, the line sample method is used for the analyzer validation and is applied at appropriate times in the process when the process stream corresponds to low, midscale, and high concentrations within the range of continuous analyzer operation.

14.2.3 Obtain a minimum of seven line samples, preferably during times of stable continuous analyzer results, using different qualified operators, over a period of time, with routine testing in the interim, until sufficient samples have been obtained.

14.2.4 Record the continuous analyzer results at the time each sample is withdrawn.

14.2.5 Determine the laboratory analyzer results using an appropriate ASTM or standard test method.

14.2.6 Tabulate the difference between each continuous analyzer result and its corresponding laboratory analyzer result as follows:

$$d_i = X_c - X_L \tag{11}$$

where:

d_i = individual difference,

X_c = continuous analyzer result, and
X_L = laboratory analyzer result.

14.2.7 Check the set of differences for outliers by the Grubbs test as described in Annex A1.

14.2.8 Compute the average difference and the standard deviation of the individual differences excluding outliers rejected in 14.2.6 as follows:

$$\bar{d} = \frac{\sum d_i}{n_d} \tag{12}$$

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} d_i^2 - \frac{(\sum d_i)^2}{n_d}}{(n_d - 1)}} \tag{13}$$

where:

$\bar{d}$ = average differences,
d_i = individual differences,
n_d = number of differences, and
S_d = standard deviation of the differences.

14.2.9 Apply the *t* test as follows to check for a possible systematic difference (bias) between the continuous analyzer results and the laboratory analyzer results:

$$t = \frac{\bar{d}\sqrt{n_d}}{S_d} \tag{14}$$

14.2.10 Compare the calculated t value to the critical *t* value from Table 2 for $(n_d - 1)$ degrees of freedom.

14.2.11 If the calculated *t* value is equal to or less than the critical *t* value, the continuous analyzer can be expected to give essentially the same average results as the laboratory analyzer.

14.2.12 If the *t* value is greater than the critical *t* value, there is at least a 95 % probability that the continuous analyzer and the laboratory analyzer are not giving the same average results. Therefore, the continuous analyzer validity is suspect. Make further investigations of the continuous analyzer function and operation to resolve the probable bias indicated.

15. Verification Procedures

15.1 *Reference Sample Verification Procedure:*

15.1.1 Tabulate the differences between the continuous analyzer results and the laboratory analyzer results to the reference sample in 14.1 as follows:

$$d_i = X_c - X_L \tag{15}$$

where:

d_i = individual difference,
X_c = continuous analyzer result, and
X_L = laboratory analyzer result.

15.1.2 Apply the Grubbs test for outliers to the tabulated differences in accordance with Annex A1.

15.1.3 Calculate the average difference and the standard deviation of the individual differences excluding outliers rejected in 15.1.2 as follows:

$$\bar{d} = \frac{\sum d_i}{n_d} \tag{16}$$

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} d_i^2 - \frac{(\sum d_i)^2}{n_d}}{(n_d - 1)}} \tag{17}$$

where:

$\bar{d}$ = average of differences,
d_i = individual differences,
n_d = number of differences, and
S_d = standard deviation of the differences.

15.1.4 Apply the Student's *t* test to determine if a statistical significant bias exists between the average difference and zero difference as follows:

$$t = \frac{\bar{d}\sqrt{n_d}}{S_d} \tag{18}$$

15.1.5 Compare the calculated *t* value to the critical *t* value from Table 2 for $(n - 1)$ degrees freedom.

15.1.6 If the calculated *t* value is equal to or less than the critical *t* value, center the control chart around zero difference.

15.1.7 If the calculated *t* value is greater than the critical *t* value, center the control chart around the average difference ($\bar{d}$). Make further investigations of the continuous analyzer function and operation to resolve the probable bias indicated.

15.1.8 Calculate the upper and lower control chart limits as follows:

$$UCL = 0 \text{ or } \bar{d} + 3 \times S_d \tag{19}$$

$$LCL = 0 \text{ or } \bar{d} + 3 \times S_d \tag{20}$$

where:

UCL = upper control limit,
LCL = lower control limit,
0 = center line if pass *t* test,
$\bar{d}$ = center line if fail *t* test, and
$3 \times S_d$ = 99 % confidence interval, where S_d is the standard deviation of the differences.

15.1.9 Periodically, by introducing the reference sample, compare the calculated differences between the continuous analyzer and the coincidental analysis results from the laboratory analyzer. The frequency for the periodic check will depend on the stability of the continuous analyzer. The frequency should be short enough to detect instrument drift or malfunction but long enough so as to not be a nuisance to the operator of the continuous analyzer.

15.1.10 If the calculated difference is within the *UCL* and *LCL*, the continuous analyzer is considered verified.

15.1.11 If the calculated difference is outside the *UCL* or *LCL*, the continuous analyzer is considered out of control. Further investigation of the continuous analyzer function and operation should be made to correct the problem.

15.2 *Line Sample Verification Procedure:*

15.2.1 Calculate the upper and lower control chart limits as follows:

$$UCL = 0 \text{ or } \bar{d} + 3 \times S_d \tag{21}$$

$$LCL = 0 \text{ or } \bar{d} + 3 \times S_d \tag{22}$$

where:

UCL = upper control limit,
LCL = lower control limit,
0 = center line if pass t test,
$\bar{d}$ = center line if fail t test, and
$3 \times S_d$ = 99 % confidence interval, where S_d is the standard deviation of the differences.

15.2.2 Periodically, compare the calculated differences between the continuous analyzer and a coincidental laboratory analysis or a second continuous analyzer. The frequency for the periodic check depends on the stability of the continuous analyzer. The frequency should be short enough to detect instrument drift or malfunction but not long enough to be a nuisance to the operator of the continuous analyzer.

15.2.3 If the calculated difference is within the *UCL* and *LCL*, the continuous analyzer is considered verified.

15.2.4 If the calculated difference is outside the *UCL* or *LCL*, the continuous analyzer is considered out of control. Further investigation of the continuous analyzer function and operation should be made to correct the problem.

16. Calculation

16.1 Each individual monitoring system and ASTM test method chosen determines the calculations necessary to perform on the output signal. Most analyses are recorded as direct readouts based on instrument calibration.

17. Precision

17.1 Preferably, each laboratory standard test method that is applied to on line monitoring shall include its own precision section based on cooperative test program results.

17.2 If it is desirable to validate the monitoring system results relative to the laboratory method, statistical equivalency of the data generated by the two techniques shall be demonstrated by applying the" *t*" test for mean differences of the paired observations at the 95 % ($P \leq 0.05$) confidence level ($t_{0.025}$ – two-tailed). This shows whether any significant difference exists between the mean values of the differences and zero for paired observations having different values. The procedure for this test is given in the annex.

18. Keywords

18.1 automatic analysis; continuous sampling; monitoring systems; on line; validation; verification; water analysis

ANNEX

(Mandatory Information)

A1. REJECTION OF INDIVIDUAL OUTLIERS

A1.1 *Rejection of Individual Outliers*—Absolutely no data should be discarded unless valid statistical criteria show them clearly to be erroneous or aberrant. Control charts and variance analyses may be misleading in some cases. Statistical references provide valid criteria for excluding data from precision evaluations. When the experimenter is aware that a gross deviation from prescribed experimental procedure has occurred, the resultant observation should be discarded. Otherwise the most extreme value among the data at each concentration of material may be tested by calculating its T value.

A1.1.1 If the T value is greater than the critical value recorded in Table A1.1 at the selected significance level (see Practice E178), the outlier may be rejected (the selection of the significance level is left up to the collaborative study chairman). The test criterion for the suspected outlier, x_l or x_n, is as follows:

$$T_n = (x_n - \bar{x})/s_t$$

$$T_n = (\bar{x} - x_l)/s_t$$

where: $\bar{x}$ and s_t are the current estimates of the mean and overall standard deviation for all retained data at the concentration of material associated with x_n (the highest data) and x_l (the lowest data).

A1.1.1.1 Because the direction of the value being tested is not known beforehand and because the experimenter is interested in detecting values that could be either high or low, a two-sided test is being performed (see Grubbs **(3)** for detailed explanation).

A1.1.2 If the suspected outlier fails the test in 10.5.1, recalculate the $\bar{x}$ and s_t from the remaining data at this concentration of material.

A1.1.3 If there is another suspected value among the remaining data for a specific concentration level, a second iteration of 10.5.1 may be justified but is generally not recommended.

A1.1.4 A completed example is shown in X1.3.

TABLE A1.1 Grubbs Distribution

Critical Values for *T* (Two-Sided Test) When Standard Deviation is Calculated from the Same Samples (for Outliers) [A]				
Number of Observations, *n*	10 % Significance Level	5 % Significance Level	2 % Significance Level	1 % Significance Level
3	1.15	1.15	1.15	1.15
4	1.46	1.48	1.49	1.50
5	1.67	1.71	1.75	1.76
6	1.82	1.89	1.94	1.97
7	1.94	2.02	2.10	2.14
8	2.03	2.13	2.22	2.27
9	2.11	2.21	2.32	2.39
10	2.18	2.29	2.41	2.48
11	2.23	2.36	2.48	2.56
12	2.29	2.41	2.55	2.64
13	2.33	2.46	2.61	2.70
14	2.37	2.51	2.66	2.75
15	2.41	2.55	2.70	2.81
16	2.44	2.58	2.75	2.85
17	2.47	2.62	2.78	2.89
18	2.50	2.65	2.82	2.93
19	2.53	2.68	2.85	2.97
20	2.56	2.71	2.88	3.00
21	2.58	2.73	2.91	3.03
22	2.60	2.76	2.94	3.06
23	2.62	2.78	2.96	3.09
24	2.64	2.80	2.99	3.11
25	2.66	2.82	3.01	3.13
30	2.75	2.91	3.10	3.24
35	2.82	2.98	3.18	3.32
40	2.87	3.04	3.24	3.38
45	2.92	3.08	3.29	3.43
50	2.96	3.13	3.34	3.48
60	3.03	3.20	3.41	3.56
70	3.09	3.26	3.47	3.62
80	3.14	3.30	3.52	3.67
90	3.18	3.35	3.56	3.72
100	3.21	3.38	3.60	3.75

[A] Values of *T* for $N \leq 25$ are based on those given in Ref **(3)**. For $n > 25$, the values of *T* are approximated. All values have been adjusted for division by $n - 1$ instead of *n* in calculating *s* . Tabulated values come from Practice E178 and may also be found in Grubbs **(3)**. Levels of significance shown in Practice E178 were doubled, since this is a two-sided test for significance instead of a one-sided test.

APPENDIXES

(Nonmandatory Information)

X1. REFERENCE SAMPLE VALIDATION DETERMINATION

X1.1 The following is a sample calculation for determining the validity of continuous analyzer system results relative to a reference sample analyzed on both a continuous and laboratory analyzer or a second continuous analyzer in accordance with 14.1.

X1.2 Tabulate continuous and laboratory analyzer or a second continuous analyzer results for at least seven matched paired analysis of the reference sample, as in Table X1.1.

X1.3 Check the extreme outliers using the Grubbs rejection criterion in A1.1 for continuous, laboratory, and difference values.

X1.3.1 *Laboratory:*

TABLE X1.1 Reference Sample Tabulated On Line and Laboratory Results

On line Response	Laboratory Response	Difference
26.8	27	–0.2
20	17	3
26	31	–5
25	26	–1
21.3	20	1.3
21	20	1
20.9	18	2.9
20.8	20	0.8
20.5	19	1.5
15	15	0
21.3	19	2.3
$\bar{X} = 21.69$	21.09	0.60
$S = 3.269$	4.826	2.244

$$T_N = \frac{X_{nr} - \bar{X}_r}{S_r} = \frac{31 - 21.09}{4.826} = 2.053$$

$$T_l = \frac{\bar{X}_r - X_{lr}}{S_r} = \frac{21.09 - 15}{4.826} = 1.262$$

$T_{(\alpha/2=0.05,11)} = 2.36$, conclude data are not outliers

where:

X_{nr} = highest laboratory data,
$\bar{X}_r$ = average of the laboratory data,
S_r = standard deviation of the laboratory data, and
X_{lr} = lowest laboratory data.

Continuous:

$$T_N = \frac{X_{nc} - \bar{X}_c}{S_c} = \frac{26.8 - 21.69}{3.269} = 1.563$$

$$T_N = \frac{\bar{X}_c - X_{lc}}{S_c} = \frac{21.69 - 15}{3.269} = 2.046$$

$T_{(\alpha/2=0.05,11)} = 2.36$, conclude data are not outliers

where:

X_{nc} = highest continuous data,
$\bar{X}_c$ = average of the continuous data,
S_c = standard deviation of the continuous data, and
X_{lc} = lowest continuous data.

Difference:

$$T_N = \frac{X_{nd} - \bar{X}_d}{S_d} = \frac{2.9 - 0.60}{2.244} = 1.025$$

$$T_l = \frac{\bar{X}_d - X_{ld}}{S_d} = \frac{0.60 - (-5)}{2.244} = 2.495$$

$T_{(\alpha=0.05,11)} = 2.36$, conclude data are not outliers

where:

X_{nd} = highest difference data,
$\bar{X}_d$ = average of the difference data,
S_d = standard deviation of the difference data, and
X_{ld} = lowest difference data.

Reject this data pair, and recalculate Grubbs values from data shown in Table X1.2.

Laboratory:

$$T_N = \frac{27 - 20.10}{3.725} = 1.852$$

TABLE X1.2 Reference Sample Tabulated On Line and Laboratory Results without Outliers

On line Response	Laboratory Response	Difference
26.8	27	−0.2
20	17	3
25	26	−1
21.3	20	1.3
21	20	1
20.9	18	2.9
20.8	20	0.8
20.5	19	1.5
15	15	0
21.3	19	2.3
$\bar{X}$ = 21.26	20.10	1.160
S = 3.099	3.725	1.327

$$T_l = \frac{20.10 - 15}{3.725} = 1.369$$

$T_{(\alpha/2=0.05,10)} = 2.29$, conclude data are not outliers

Continuous:

$$T_N = \frac{26.8 - 21.26}{3.099} = 1.788$$

$$T_l = \frac{21.26 - 15}{3.099} = 2.020$$

$T_{(\alpha/2=0.05,10)} = 2.29$, conclude data are not outliers

Difference:

$$T_N = \frac{3 - 1.160}{1.327} = 1.386$$

$$T_l = \frac{1.160 - (-1)}{1.327} = 1.628$$

$T_{(\alpha/2=0.05,10)} = 2.29$, conclude data are not outliers

X1.4 Determine whether the precision of the laboratory test results on the reference sample are statistically significantly different from the historical precision of the laboratory of the analysis as follows:

$$F = \frac{S_r^2}{\sigma_r^2}$$

$$F = \frac{(4.826)^2}{(3.575)^2} = 1.822$$

$F_{(\alpha=0.05,9,9)} = 3.18$, conclude variances are not statistically significantly different

where:

S_r^2 = variance of laboratory results from the reference sample validation $(S_r)^2$, and
σ_r^2 = historical variance for this laboratory method, from previous quality control data.

If the *F* test is failed, evaluate, investigate, and eliminate the reason for failure.

X1.5 Determine whether the precision of the laboratory analysis of the reference sample are statistically significantly different from the precision of the continuous analysis as follows:

$$F = \frac{S_L^2}{S_S^2}$$

where:

S_L^2 = larger variance, and
S_S^2 = smaller variance.

$$F = \frac{(3.725)^2}{(3.099)^2} = 1.445$$

$F_{(\alpha=0.05,9,9)} = 3.18$, conclude variances are not statistically significantly different

X1.6 Calculate the Student's *t* test for the averages as follows:

$$t = \frac{\bar{X}_c - \bar{X}_l}{S_p}$$

$$S_p = \sqrt{\frac{v_l\,(S_l^2)+v_c(S_c^2)}{n_l+n_c-2}\times\left(\frac{1}{n_l}+\frac{1}{n_c}\right)}$$

$$v = n_l+n_c-2$$

$$t = \frac{21.26-20.10}{1.532} = 0.757$$

$$S_p = \sqrt{\frac{9\,(3.099)^2+9\,(3.725)^2}{10+10-2}\times\left(\frac{1}{10}+\frac{1}{10}\right)} = 1.532$$

$t_{(\alpha/2=0.05,9)} = 2.262$, conclude no statistically significantly difference. Instrument pairs are not statistically significantly different.

X1.7 Calculate the Student's t test for the difference as follows:

$$t = \frac{\bar{d}\sqrt{n_d}}{S_d} = \frac{1.160\sqrt{10}}{1.327} = 2.762$$

$t_{(\alpha/2=0.05,9)} = 2.262$, conclude there is a statistical significant bias in the difference values. Instrument pair can not be used for validation.

NOTE X1.1—If the Student's t test fails in either X1.6 or X1.7, the instrument pair can not be validated.

X2. LINE SAMPLE VALIDATION DETERMINATION

X2.1 The following is a sample calculation for determining the validity of continuous analyzer system results relative to a laboratory or second continuous analyzer in accordance with 14.2.

X2.2 Tabulate continuous and laboratory analyzer or a second continuous analyzer results for at least seven matched paired analysis of the process stream, as in Table X2.1.

TABLE X2.1 Line Sample Tabulated On Line and Laboratory Results

Continuous Analyzer Response	Second Continuous Analyzer Response	Difference
8.37	8.33	0.04
4.61	4.52	0.09
5.87	6.06	–0.19
5.80	5.81	–0.01
6.86	6.81	0.05
6.03	5.33	0.70
5.45	5.04	0.41
$\bar{X}$ = ...	...	0.155
S = ...	...	0.299

X2.3 Check for extreme outliers using the Grubbs rejection criterion in A1.1 for difference values.
Differences:

$$T_n = \frac{X_{nd}-\bar{X}_d}{S_d} = \frac{0.70-0.155}{0.299} = 1.822$$

$$T_l = \frac{\bar{X}_d - X_{ld}}{S_d} = \frac{0.155-(-0.19)}{0.299} = 1.154$$

$T_{(\alpha=0.05,7)} = 2.02$, conclude data are not outliers

X2.4 Calculate the Student's t test for the difference as follows:

$$t = \frac{\bar{d}\sqrt{n_d}}{S_d} = \frac{0.155\sqrt{7}}{0.299} = 1.372$$

$t_{(\alpha/2=0.05,6)} = 2.447$, conclude no statistical significant difference. Instrument pair can be used for validation.

NOTE X2.1—If the t test fails, the instrument pair cannot be used for validation.

X3. REFERENCE SAMPLE VERIFICATION

X3.1 Develop a control chart centered at zero difference $\pm 3\,S_d$
where: S_d = standard deviation of the differences.

X3.2 Periodically compare, calculate, and plot the difference between the continuous analyzer and the coincidental laboratory analysis or a second continuous analyzer to the reference sample.

X3.3 If the difference value is within $\pm 3\,S_d$, the continuous analyzer is considered verified. If not, the continuous analyzer should be considered out-of-service until the difference is resolved.

X4. LINE SAMPLE VERIFICATION

X4.1 Develop a control chart centered at zero differences $\pm 3\ S_d$ where:

S_d = standard deviation of the differences

X4.2 Periodically compare, calculate, and plot the difference between the continuous analyzer and the coincident laboratory or second continuous to the process stream.

X4.3 If the difference value is within $\pm 3\ S_d$, the continuous analyzer is considered verified. If not, the continuous analyzer should be considered out-of-service until the difference is resolved.

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