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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Practice for Validation of Process Stream Analyzers[1]

This standard is issued under the fixed designation D 3764; 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 practice serves as a guide for the validation of process stream analyzers used in determining the physical or chemical characteristics of petroleum and petrochemical products.

1.2 Procedures for treating data from automatic process stream analyzers are outlined. Definitions, terms, calibration techniques, and applicable statistical tests for validation are described.

1.3 The implementation of this process requires that the analyzer be installed in compliance with the principles set forth in *Part II Process Stream Analyzers* of the "Manual on Installation of Refinery Instruments and Control Systems" APIRP-550 of the American Petroleum Institute and in agreement with the supplier's recommendation. In addition it assumes that the analyzer is designed to monitor the specific quality parameter of interest and at the time of validation the analyzer is operating at the conditions specified by the manufacturer.

1.4 The units of measure used in this practice shall be the same as those applicable to the laboratory test standard used as the reference for analyzer validation.

1.5 *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 1265 Practice for Sampling Liquified Petroleum (LP) Gases—Manual Method[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[3]

F 307 Practice for Sampling Pressurized Gas for Gas Analysis[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

Time Units

3.1.1 *Lag Time, n*—The time interval from a step change in the measured variable at various points in the system to the first corresponding change in the analyzer signal readout.

3.1.1.1 *Discussion*—It is a function of system design (length and diameter of lines, number of fittings, flow restrictions, etc.) and the flow rate of the process or product stream. (See Fig. 1 and Fig. 2.) It consists of the following elements:

3.1.2 *Sample Loop Lag Time, n*—The time required for a step change in process or product stream quality to traverse the distance between the start of the process or product stream sample loop to the inlet of the sample conditioning unit.

3.1.3 *Sample Conditioning Unit Lag Time, n*—The time required for a step change in the process or product stream quality to pass through the sample conditioning unit from the junction with the sample loop to the inlet of the analyzer unit.

3.1.4 *Analyzer Lag Time, n*—A function of the analyzer's operating characteristics.

3.1.4.1 *Discussion*—Where the analyzer is designed to operate at a specific flow rate, the sum of the elements contributing to the analyzer lag time 3.1.4.2 *(1)* and 3.1.4.3 *(1)* will be a constant value. For the analyzer designed for variable flow rates the analyzer lag time and its elements must be determined for each of the flow rates used. These elements are as follows:

3.1.4.2 *(1) Analyzer Dead Time, n*—The time interval between the introduction of a step change in quality at the inlet of the analyzer unit and the initial indication of analyzer response to this change at a specific sample flow rate.

3.1.4.3 *(1) Analyzer Time Constant* (See Fig. 2)—The time interval between the initial response of the analyzer unit and the time required for the analyzer output to reach a value of 63 % of the final output value for a step change in sample quality.

Analyzer Parameters

3.1.5 *Analyzer Output, n*—A signal that is proportional to the quality parameter being measured and suitable for input to readout instrumentation. It can be either a pneumatic, an electrical, or a digital signal.

[1] This practice is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.25 on Validation of Process Analyzers.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 10.05.

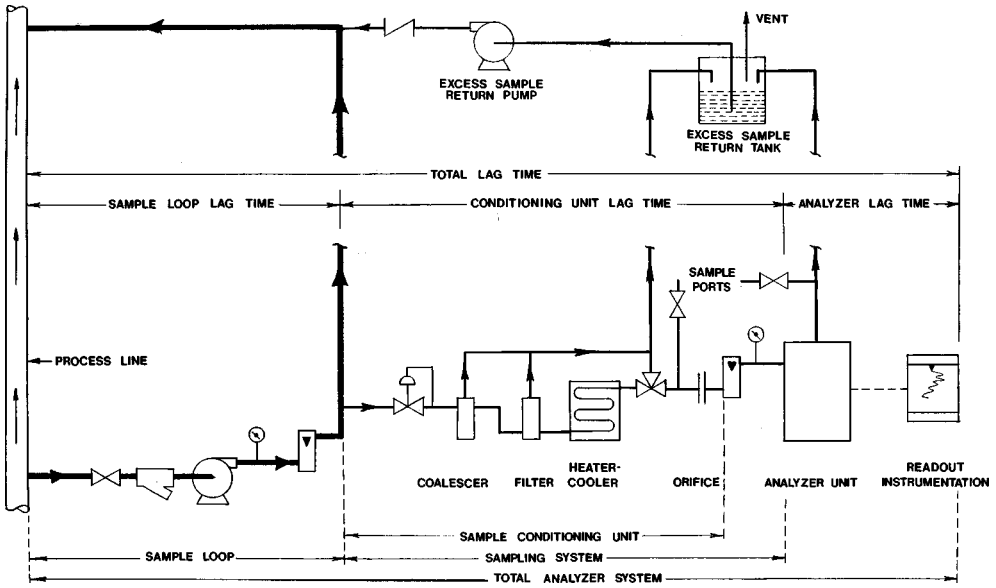


FIG. 1 Total Analyzer System

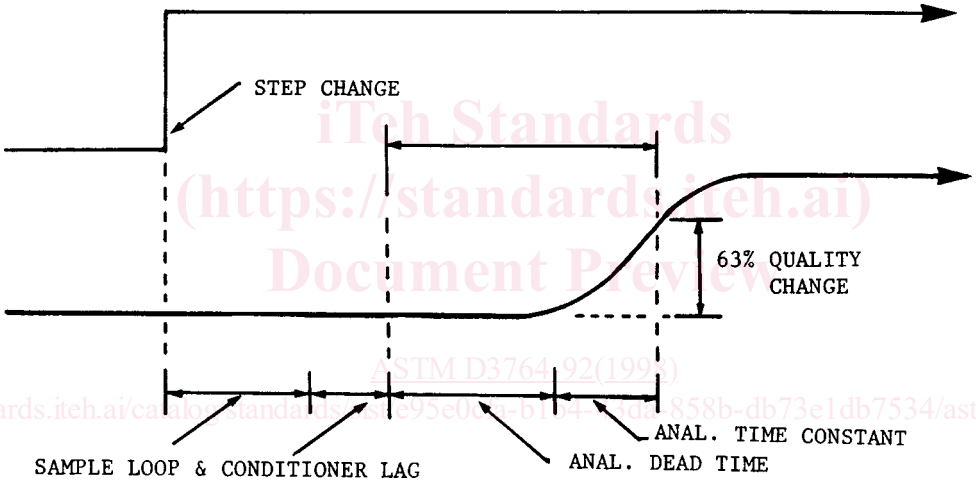


FIG. 2 Analyzer Time Units

3.1.6 *Analyzer Result, n*—The measured quality parameter displayed by the analyzer readout instrumentation in terms of the accepted quality units.

3.1.6.1 *Reference Sample Procedure Result, n*—The average of the intermittent or continuous analyzer readings recorded during a specific time interval after the analyzer is at equilibrium.

3.1.6.2 *Line Sample Procedure Result, n*—The average of the intermittent or continuous analyzer readings recorded during the time interval required to draw one line sample. This time interval starts at one analyzer dead time after sample port valve opening and continues until one analyzer dead time after the required sample has been drawn. The line sample must be drawn only when the entire analyzer system is in operation and when there is no significant change in the measured property. If a quality change occurs during the sample collection time interval as defined above, the sample must be discarded and a new sample collected when the measured property is in equilibrium.

3.1.7 *Sensitivity, n*—The least discernible change in the quality parameter being measured that is not masked by background noise as displayed by the readout instrumentation.

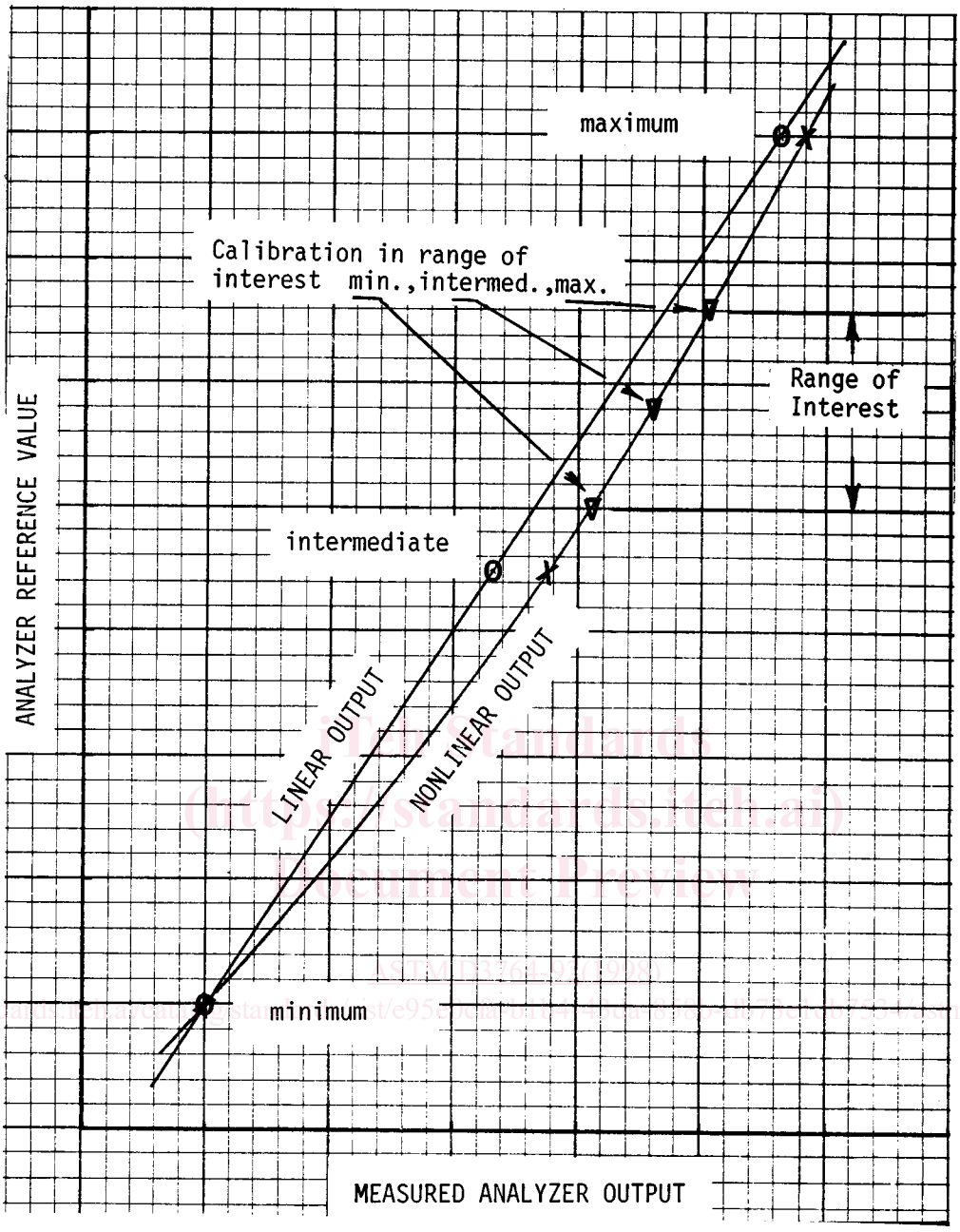
3.1.8 *Linearity, n*—The degree of closeness to which a plot of the analyzer output, over the analyzer operating range approximates a straight line.

3.1.8.1 *Discussion*—It is expressed as the maximum deviation between an average measured output versus a known input and a straight line, where the straight line is drawn through both terminal points of the known input and measured output ranges. Linearity of the analyzer over the quality range of interest must be established and the analyzer output, if nonlinear, adjusted manually or automatically so that the analyzer result displayed is a true indication of the measured quality. See Fig. 3.

Precision Parameters

3.1.9 *Precision, n*—The degree of agreement of reported measurements of the same chemical or physical property of a given material, expressed in terms of dispersion of test results around the arithmetic mean.

3.1.10 *Analyzer Repeatability, n*—The difference between



NOTE 1—The illustration shows two examples of analyzer output; a linear and a nonlinear system when considering the entire potential analyzer range. Even though linearity over the entire range is the ideal condition, a nonlinear system can be used effectively when the approximate process or product quality is known and the operating range of the analyzer can be selected and confined to a small segment of the entire range. By segmentation of the curvilinearity of the input, output relationship can be considered a constant slope and any deviations from linearity thereby will be insignificant. The selection of the range segment, however, will require calibration with one or more reference samples representing the minimum, intermediate and maximum operating range quality to establish the degree of linearity and to institute corrective measures when the deviations from a straight line are excessive.

FIG. 3 Measured Analyzer Output

two successive analyzer results that would be exceeded in the long run in only 1 case in 20 when a single analyzer system is operated on a flowing sample of uniform quality.

3.1.10.1 *Discussion*—The value is related to the repeatability standard deviation as determined from many sets of successive repeat analyzer results from single analyzers.

3.1.11 *Analyzer Reproducibility, n*—The difference between a single result from each of two analyzer systems that would be exceeded in the long run in only 1 case in 20 when the two systems are operated at different sites, by different operators, but on identical samples.

3.1.11.1 *Discussion*—The value is related to the reproducibility standard deviation as determined from testing the same samples on many analyzer systems.

3.1.12 *Historical Standard Deviation, n*—A test method

standard deviation established by averaging the standard deviations of many samples tested by many laboratories.

3.1.13 *Line Sample, n*—A process or product sample withdrawn from the sample port (6.1.3.3) in accordance with Practices D 1265, D 4057, D 4177, and F 307, whichever is applicable during a period when the material flowing through the analyzer is of uniform quality and the analyzer result displayed (3.1.6) is essentially constant.

3.1.13.1 *Discussion*—The laboratory tests are obtained for each sample of this material and compared with the analyzer result obtained (3.1.6) at the time of sampling.

3.1.14 *Reference Sample, n*—A pure compound or a mixture of compounds of known properties that have a reference value for the quality to be measured.

3.1.14.1 *Discussion*—It can also be an isolated batch of process or product with chemical or physical properties approximating the quality level to be monitored by the analyzer. In this event a reference sample value (3.1.15) for the monitored property must be established through multiple testing by an appropriate ASTM or other standard laboratory test method. Bulk quantities of the reference sample must be stored and handled with care to avoid contamination or degradation of the quality of interest. One or more reference samples encompassing the minimum, intermediate, and maximum range of the expected operating range of the analyzer will be required for both the reference sample and line sample procedures.

3.1.15 *Reference Sample Value, n*—The quality value established by appropriate ASTM or other standard laboratory test methods on representative pure compounds, mixtures thereof and process or product samples.

3.1.15.1 *Discussion*—The laboratory apparatus shall be checked carefully before these tests are run to assure compliance with the requirements of the standard test procedure. To further assure proper operation it is recommended that a previously calibrated reference sample or an in-house control standard of known quality be tested to validate the operation of the laboratory equipment.

4. Summary of Practice

4.1 Two procedures have been included; either or both can be applicable in a given situation.

4.1.1 *Reference Sample Procedure* covers the use of a laboratory calibrated reference sample, which is introduced into the analyzer, and the analyzer result compared with the reference value.

4.1.2 *Line Sample Procedure* covers withdrawal of samples from the analyzer system in accordance with Practices D 1265, D 4057, D 4177, and F 307, whichever is appropriate. Analyzer results obtained at the time of sampling are compared with laboratory analyses of the samples using the applicable ASTM or other test method.

5. Significance and Use

5.1 This practice can be used to establish the validity of the results obtained by a process stream analyzer upon commissioning or during routine use, or both.

5.2 This practice provides statistically based methodology to quantify the analyzer system variability and any bias relative to the applicable test method standard.

5.3 This practice addresses analyzer calibration in the range of interest and in accordance with the manufacturer's instructions so that the sensitivity and linearity to process or product quality change are established and adjusted to produce a meaningful analyzer result.

6. System Components

6.1 Fig. 1 illustrates a total analyzer system incorporating a selection and arrangement of components that are typical but not specific for any particular analyzer system. A total analyzer system design must consider the chemical and physical properties of the process or product stream in selecting the components required. These must meet the requirements of the analyzer, and provide a representative sample, without adversely affecting the value of the specific quality parameter of interest (1.3).

6.1.1 *Total Analyzer System* consists of all piping, hardware, and instrumentation required to automatically perform on-stream analysis of a process or product stream including the analyzer unit, readout instrumentation, sampling conditioning devices, sample stream, and sampling port.

6.1.2 *Analyzer Unit* is the instrumental hardware necessary to automatically measure the physical or chemical property of a process or product stream and to provide either an intermittent or a continuous output signal.

6.1.2.1 *Intermittent Analyzer* is an analyzer that tests the sample and produces the prime output signal at discrete time intervals.

6.1.2.2 *Continuous Analyzer* is an analyzer that tests the sample and produces the prime output signal on an instantaneous or continuously updated basis.

6.1.3 *Sampling System* is that assembly of valves, lines, containers, regulator, and gages which constitutes the equipment employed to obtain a proper sample from the sample loop or to introduce a reference sample into the analyzer, or both.

6.1.3.1 *Sample Loop* is that portion of the sampling system which takes the sample from the process or product line to the sample conditioning unit and returns most of the flow back to the line of origin or to waste.

6.1.3.2 *Sample Conditioning Unit* is one or more devices that properly prepare a portion of the sample from the sample loop for testing by the process analyzer consistent with the requirements of the analyzer. This preparation can consist of temperature or pressure adjustment, change of state (liquid, vapor), or removal of contaminates to assure consistent treatment of the sample prior to testing by the analyzer.

6.1.3.3 *Sample Port* is that point on the sampling system, located between the sample conditioning unit and the analyzer or at the outlet of the analyzer from which samples for laboratory analysis are taken. A sample port location at the outlet of the analyzer can be used only if the properties of the sample are unchanged as it passes through the analyzer or if the sample is a slip stream identical to the sample tested. It is important that the sample port is located as close as possible to the inlet or outlet of the analyzer to minimize lag time.

6.1.4 *Readout Instrumentation* is any device used to accept the prime signal from the analyzer to produce and display the quality parameter in acceptable quality units.

7. Procedure for Establishing Reference Sample Value

7.1 A minimum of six laboratory determinations are required on each reference sample, preferably in several laboratories using different operators and test apparatus to minimize laboratory bias.

7.1.1 When it is necessary to run multiple tests in the same laboratory, it is recommended that different operators and apparatus combinations be utilized to the maximum extent possible.

7.1.2 When only one testing unit is available, make the multiple determinations over a period of time, with routine testing in the interim, until sufficient data have been collected for analysis. In these circumstances it is recommended that a number of different qualified operators be used for the individual test determinations to reduce the influence of possible operator bias or procedural errors in the test results.

7.2 More than a minimum of six test results on a 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 properties. This applies to the laboratory determination as well as to the analyzer results.

7.2.1 Controlling factors in the number of tests obtained are: degree of precision desired, testing costs, precision of the laboratory method, and the criticality of analyzer accuracy and precision.

7.2.2 For guidance in determining the number of test results required to establish a desired confidence limit for the reference sample value, refer to Fig. X1.1 and the instructions for use given in X1.2.

7.3 Tabulate the laboratory data obtained on the reference sample and check for extreme values or outliers by an accepted statistically based rejection criterion. As an example, the details for application of Dixon's Rejection Criterion are included in Appendix X1, Typical Statistical Procedures.

7.4 Determine the arithmetic average value ($\bar{X}_r$) and the variance (S_r^2) of the reference sample test data.

7.4.1 Calculate the arithmetic average by the following equation:

$$\bar{X}_r = \frac{\Sigma X_r}{N_r} = \text{arithmetic average test result} \quad (1)$$

where:
X_r = individual test results on the reference sample, and
N_r = number of test results.

7.4.2 Calculate the variance by either of the following equations:

$$S_r^2 = \frac{\left[\Sigma X_r^2 - \frac{(\Sigma X_r)^2}{N_r}\right]}{(N_r - 1)} \quad (2)$$

$$S_r^2 = \frac{\Sigma (X_r - \bar{X}_r)^2}{(N_r - 1)} \quad (3)$$

7.5 Compare the variance of the reference sample data to that used to establish the precision statement of the applicable test method. The statistical criteria for this judgment is the F Test, which is based on the ratio of variances as follows:

$$F = \frac{S_r^2}{\sigma_t^2} \quad (4)$$

where:
S_r^2 = variance of reference sample data, and
σ_t = historical standard deviation of the laboratory test method as utilized to define the reproducibility of the method. When the precision statement is in the form of a reproducibility limit, divide the limit value by 2.772 to obtain the standard deviation.

7.5.1 Determine the limiting F value from the statistical F Distribution (5 % Significance Level) tables for $(N_r - 1)$ degrees of freedom in the numerator and infinite degrees of freedom for the denominator. (See Table X1.2 in Appendix X1 for a condensed portion of the aforementioned F Distribution Table).

7.6 Compare the calculated F value to the limiting F value.

7.6.1 If the calculated F value is equal to or less than the limiting F value, the variance of the reference sample data is as good or better than the test method predicts, the qualification is complete. Proceed to 7.7.

7.6.2 If the calculated F value is larger than the limiting F value, the variance of the reference sample data is not as good as the test method predicts and the difference is statistically significant.

7.6.3 When a significant difference in variance exists, the reasons for the substandard test precision shall be determined, appropriate corrections made to the procedure or apparatus, or both, and the complete reference sample procedure qualification repeated until acceptable laboratory test precision is obtained.

7.7 When a satisfactory reference sample value is achieved, the arithmetic average result shall be the assigned value for the reference sample.

7.8 Reference samples shall be stored under conditions that will not cause changes in the critical characteristics. Because storage conditions and the factors that affect sample stability can change with time, confirm the reference sample value at periodic intervals. The frequency of confirmation can best be determined by the user of the analyzer.

8. Preliminary Analyzer Adjustments

8.1 Check the entire system to assure that the analyzer is installed, operating, and adjusted properly.

8.2 Check linearity 3.1.8 over the quality range of expected operation through the use of one or more qualified reference samples to cover the minimum intermediate and maximum quality ranges.

8.2.1 Plot the analyzer results obtained and draw a line through the points as illustrated in Fig. 3 (see Fig. A1.3).

8.3 Adjust the analyzer to obtain the linearity specified by the manufacturer or to establish linearity over the specific range of interest.

8.4 Adjust the analyzer to obtain the optimum required sensitivity.

9. Reference Sample Procedure

9.1 *Procedure*:

9.1.1 Select the applicable qualified reference sample(s) in

sufficient quantity to permit operation of the analyzer system for a time period adequate to collect the required data for validation.

9.1.2 Provide suitable means for introducing the reference sample into the inlet of the analyzer or, where required, the sample conditioning system. The flow rate, temperature, and pressure used in introducing the reference sample shall be consistent with the analyzer requirements.

9.1.3 Operate the analyzer system on the reference sample and observe the analyzer results. Do not record results until a period of time equivalent to at least one analyzer lag time has elapsed after equilibrium is reached.

9.2 *Data Collection*:

9.2.1 For an intermittent analyzer, record a minimum of seven analyzer results and discard the first as illustrated in Fig. 4.

9.2.2 For a continuous analyzer, obtain a minimum of seven averaged analyzer results allowing at least one analyzer time constant interval for each analyzer result. Discard the data obtained during the first analyzer time constant interval. See Fig. 5.

9.3 *Data Analysis for Analyzer Validation*:

9.3.1 Tabulate the selected analyzer results obtained on the reference sample and check for extreme values or outliers by an accepted statistically based rejection criterion. (See Appendix X1.)

9.3.2 Determine the arithmetic average value (X_a) and the variance (S_a^2) of the accepted analyzer results.

9.3.2.1 Calculate the arithmetic average by the following equation:

$$\bar{X}_a = \text{arithmetic average analyzer result} = \frac{\Sigma X_a}{N_a} \quad (5)$$

where:

X_a = individual analyzer results, and
N_a = number of analyzer results obtained.

9.3.2.2 Calculate the variance by either of the following equations:

$$\text{Analyzer result variance} = S_a^2 \quad (6)$$

$$S_a^2 = \frac{\left[\Sigma X_a^2 - \frac{(\Sigma X_a)^2}{N_a}\right]}{(N_a - 1)}$$

$$S_a^2 = \frac{\Sigma (X_a - \bar{X}_a)^2}{(N_a - 1)} \quad (7)$$

9.3.3 Apply the statistical *F* test to determine whether or not the variance of the analyzer results (S_a^2) and the laboratory reference sample results (S_r^2) are from the same population with the same (but unknown) variance.

9.3.3.1 Establish the calculated *F* ratio by the following equation:

$$F \text{ value} = L/M \quad (8)$$

where:

L = larger variance (S_a^2 or S_r^2), and
M = smaller variance.

9.3.3.2 Determine the limiting *F* value from a 95 % Probability, *F* Distribution Table. (See Table X1.2 in Appendix X1 for a condensed portion of the *F* Table.)

9.3.3.3 Compare the calculated *F* value to the limiting *F* value and follow the instructions given in either 9.3.4 or 9.3.5, whichever applies.

9.3.4 If the calculated *F* value is equal to or less than the limiting *F* value, the variances are essentially the same. Proceed to apply Student's *t* test to determine if there is a statistically significant difference between the average analyzer result and the average laboratory reference sample result.

9.3.4.1 The appropriate equations to establish the calculated *t* for this set of variance conditions are as follows:

$$t \text{ value} = \frac{(\bar{X}_a - \bar{X}_r)}{S_d} \quad (9)$$

$$S_d = \sqrt{\frac{(N_a - 1)S_a^2 + (N_r - 1)S_r^2}{N_a + N_r - 2}\left(\frac{1}{N_a} + \frac{1}{N_r}\right)} \quad (10)$$

where:

S_d = pooled standard deviation of the difference,
$\bar{X}_a$ = arithmetic average analyzer result,
$\bar{X}_r$ = arithmetic average laboratory reference sample result,
N_a = number of analyzer results,
N_r = number of laboratory reference sample results,
S_a^2 = variance of analyzer results (Eq 6 or Eq 7), and
S_r^2 = variance of laboratory reference sample results (Eq 2 or Eq 3).

9.3.4.2 Determine the critical *t* value from a Table of *t* at

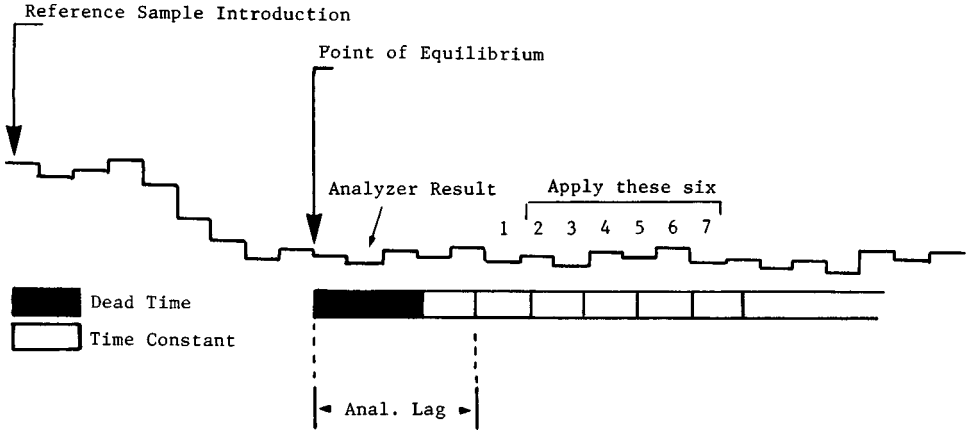


FIG. 4 Intermittent Analyzer Test Run—Reference Sample Procedure