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Standard Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials[1]

This standard is issued under the fixed designation D6621; 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~~ Scope*

1.1 This practice serves as a practical guide for the performance testing of process stream analyzers specifically for measuring chemical or physical characteristics of liquid aromatic hydrocarbon materials for production or certification of these materials. The practice may be applicable to other hydrocarbon stream analyzers as well.

1.2 Only external methods (complete substitution of the process stream with a standard) of control sample introduction are included. Internal methods are beyond the scope of this practice.

1.3 Methods for resetting key operational parameters of analyzers to match predefined limits are provided by vendors and are not included in this practice.

1.4 Analyzer validation procedures are covered in Practices D3764 and D6122, not in this practice.

1.5 Procedures for statistically interpreting data from automatic sampling process stream analyzers are outlined.

1.6 The implementation of this practice requires that the analyzer be installed according to APIRP-550 (**1**),[2] and be in agreement with the analyzer supplier's recommendations. Also, it assumes that the analyzer is designed to monitor the specific material parameter of interest, and that at the time of initial or periodic validation, the analyzer was operating at the conditions specified by the manufacturer and consistently with the primary test method.

1.7 The units of measure used in this practice shall be the same as those applicable to the test primary method used for analyzer validation.

1.8 *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~~ safety, health, and ~~health~~environmental practices, and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

[1] This practice is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.09 on On-Line Analysis.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this practice.

***A Summary of Changes section appears at the end of this standard**

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D3437 Practice for Sampling and Handling Liquid Cyclic Products
D3438 Practice for Sampling and Handling Naphthalene, Maleic Anhydride, and Phthalic Anhydride
D3764 Practice for Validation of the Performance of Process Stream Analyzer Systems
~~D4177~~D3852 Practice for ~~Automatic~~ Sampling ~~of Petroleum and Petroleum Products~~and Handling Phenol, Cresols, and Cresylic Acid
D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems
E456 Terminology Relating to Quality and Statistics
E1655 Practices for Infrared Multivariate Quantitative Analysis

3. Terminology

3.1 *Definitions:*

3.1.1 *accuracy, n*—closeness of agreement between a test result and an accepted reference value.

3.1.2 *analyzer output, n*—signal that is proportional to the quality parameter being measured and suitable for input to readout instrumentation.

3.1.2.1 *Discussion*—
It may be pneumatic, electrical, digital, etc., and expressed as psi, mv, sec., etc.

3.1.3 *analyzer result, n*—numerical estimate of a physical, chemical, or quality parameter produced by applying the calibration model to the analyzer output signal.

3.1.4 *bias, n*—the difference between the expectation of the results and an accepted reference value.

3.1.5 *control sample, n*—material similar to the process stream that is stable over long periods of time so that its parameters may be measured reproducibly in performance tests to characterize analyzer precision and accuracy.

3.1.5.1 *Discussion*—
May be a pure compound, standard mixture, or a sample from the process stream. Its parameters are used to plot statistical process control charts to define analyzer precision in normal operation.

3.1.6 *external performance testing, n*—procedure involving complete substitution of the process/product stream measured by the analyzer with a control sample stream to measure the analyzer's precision and possibly accuracy (if the control sample's true value is known).

3.1.7 *internal performance testing, n*—procedure involving the addition of a known quantity of a standard material homogeneously into the process/product stream measured by the analyzer to measure the analyzer's precision and possibly accuracy (if the sample material's true value is known).

3.1.8 *linearity, n*—parameter ranges where the analyzer's results do and do not approximate a straight line.

3.1.9 *performance testing of an analyzer, n*—mechanical and statistical procedure for routinely checking the accuracy and precision of an analyzer's results against historical accuracy and precision for a control sample.

3.1.10 *precision, n*—closeness of agreement of independent test results of the same chemical or physical property of a given material obtained under stipulated conditions.

3.1.10.1 *Discussion*—
Expressed in terms of dispersion of test results around the arithmetic mean, usually as variance, standard deviation, repeatability or reproducibility, or both.

[3] 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.

3.1.11 *repeatability of an analyzer, n*—difference between two successive analyzer results measured in a short time interval that would be exceeded in the long run in only 1 case in 20 (5 % of the time) when the analyzer is operated on a flowing sample of uniform quality.

3.1.12 *reproducibility of an analyzer, n*—difference between a single result from each of two identical analyzer systems that would be exceeded in the long run in only 1 case in 20 (5 % of the time) when the two systems are operated at different sites by different operators, but on identical samples.

3.1.13 *rule violation, n*—condition when a point value or pattern of points in a statistical process control chart statistically exceeds the defined probability of its occurrence, as defined by the Western Electric rules **(2)** being used.

3.1.14 *spot sample, n*—representative material resembling the stream being monitored, an identical portion of which is analyzed both in a process analyzer and by a laboratory test on a non-scheduled basis for periodic validation testing.

3.1.14.1 *Discussion*—
May be the same material as the control sample.

3.1.15 *validation of an analyzer, n*—process to identify how comparable an analyzer's results are statistically to results from the primary method, or to define how the analyzer's results compare to the primary method's results in precision and accuracy.

3.1.15.1 *Discussion*—
Must be done when the analyzer is first configured or reconfigured (initial validation), and then on a periodic basis (periodic validation), as described in Practice D3764.

3.2 For additional definitions, see Appendix X1.

4. Summary of Practice

4.1 This practice standardizes aromatic hydrocarbon process-analyzer performance testing practices, or processes for maintaining accurate and precise analyzer measurements. It is used with methods for the measurement and certification of aromatic hydrocarbon materials applied to continuous on-line analyzers. These methods are generally under the control of Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals. It is meant as a practical guide for persons setting up and maintaining these analyzers in a process (non-laboratory) environment. They should apply it, with their knowledge of the analyzer's operation and of how the process analyzer results are to be used, to maintain and optimize analyzer operation.

5. Significance and Use

5.1 Performance testing of on-line analyzers is critical to their proper performance within predictable levels of precision and accuracy. This practice can affect production efficiency and certification of aromatic hydrocarbon materials.

6. System Components

6.1 Process analyzers ~~(Fig. 1)~~ for measuring the chemical composition of aromatic hydrocarbons, their purity, or physical properties often replace existing laboratory test methods, using the same or similar chemical measurement techniques. Fig. 1 shows several possible analyzer configurations for on-line process testing of aromatic hydrocarbon materials. Aromatic hydrocarbon stream analyzers are often based on chromatography, but they may also perform physical measurements, wet chemistry, or other methods described in new or existing Committee D16 methods. This practice is intended to be generally applicable to any of them.

7. Performance Guidelines Before Calibration

7.1 At startup, validate any process analyzer against an existing analytical method, typically in this case, one overseen by Committee D16.

7.2 The capability measurement (c_m) for a given analyzer **(3)** shall be less than 0.2, as defined in Eq 1:

$$c_m = \sigma_a^2/\sigma_p^2 < 0.2 \quad (1)$$

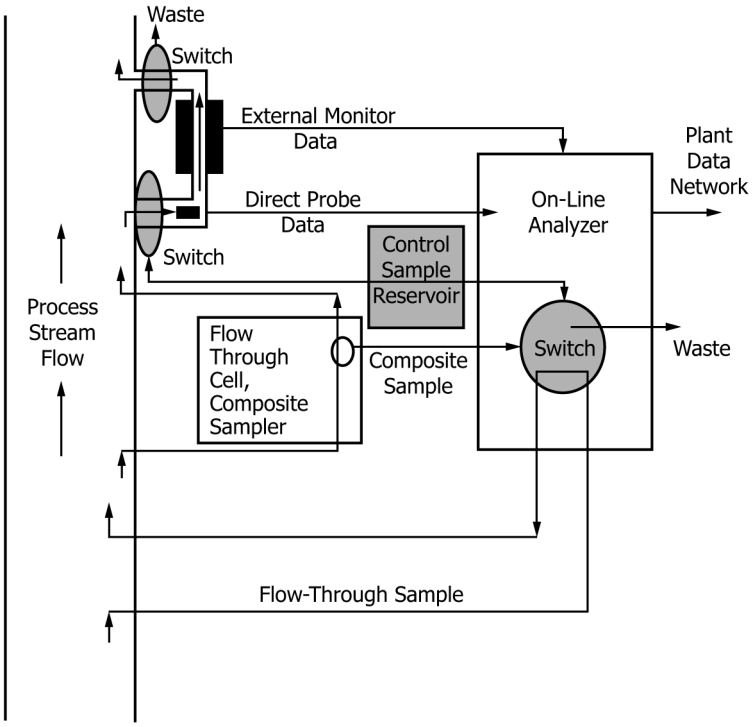

FIG. 1 Possible Process Analyzer Configurations

where:

σ_a = standard deviation of the analyzer measurement, and
σ_p = standard deviation of the process.

The variance (standard deviation squared) of the analyzer should be less than 20 % of the variance of the process, so that the analyzer measurement can be useful for detecting changes in the process. The expected capability for a process analyzer measurement may be available from the vendor for a specific application before installation of the analyzer (advertised analyzer capability). Actual process stream measurement capability should be measured on the process/product stream, usually after initial analyzer validation.

7.3 Automated analyzer sampling practices for aromatic hydrocarbon liquid streams shall follow those referenced in ~~Practice~~ Practices ~~D4177~~D3437, D3438, or D3852.

7.4 Determine the linearity of the process analyzer by using at least three calibration standard materials with known compositions/responses for the components of interest. Each component should be present at a high, low, and medium concentration/amount level with respect to the concentration/amount range expected for the parameter (analyzer operating range). A plot of the component concentration/amount versus analyzer response will determine if the analyzer has a linear response over the concentration range of interest. If analyzer response is nonlinear, additional calibration standards must be analyzed to clearly determine the nonlinear behavior of each analyzer and component, if the analyzer is to be used in the nonlinear range.

7.5 If a process analyzer is to be used only for trend information, the data generated by it is in a form that does not impart compositional information, but relative information only, that is, peak area, peak height, counts, millivolts, etc. Initial validation and frequent performance testing are still required to define precision, as well as to maintain proper analyzer operation.

8. Performance Test Procedure

8.1 Determine analyzer performance using external check samples, which are substituted for the process material stream during performance test runs.

8.2 Process analyzers are routinely performance tested by using control samples. These may be primary or secondary standard materials, or actual portions from the process stream. These portions must be representative of normal process conditions, and be

stored to remain physically and chemically stable over time. The control sample should be repeatedly analyzed by the process analyzer, and then using statistical process control (SPC), to define the actual analyzer result's precision.

8.3 Analyzer performance test frequency can be done at a fixed time interval, based on analyzer reliability and operator experience. Typically, once per shift, day, or week are used, but it may be more or less frequent. Unscheduled control sample analyses may be performed whenever the unit operator feels that something has changed in the process or process analyzer, or at a convenient time.

8.4 The control sample material container shall be located at a point in the process to allow for its simple and regular introduction into the process analyzer's sample introduction system (if appropriate) by the process operator. A sufficient quantity must be available for many repetitive analyses.

8.5 Perform an external analyzer performance test by switching the analyzer sample source from the process stream to the control sample, followed by sampling and analysis of the control sample.

8.6 Monitor the analyzer's output from the control sample until it stabilizes, that is, the difference between successive readings is at or below the repeatability of the ~~analyzer,~~analyzer (which is measured as described in 8.10). If this does not occur, the repeatability of the analyzer has changed and should be remeasured.

8.7 After stabilization of the analyzer, measure at least three successive results on the control sample and average the results. Plot the average of these three results in a SPC chart using any statistically correct method of data handling and control chart construction **(4)**.

8.8 SPC charts of the control sample data shall be used to help decide if the analyzer needs to have its response parameters reset, **(5)** or if it is working within previous statistical levels and should be left alone. SPC results and operator experience should be used to determine subsequent actions, such as determining the cause for any rule violation and correcting it.

8.9 SPC charts of control samples help the operator to differentiate between normal (random) and abnormal (nonrandom) analyzer variation due to changes in analyzer operation.

8.9.1 Charts may be maintained manually or with commercially available SPC software, preferably as part of the analyzer data acquisition and control software.

8.9.2 Control limits should be set at three (3) sigma (standard deviations) from the mean value, warning limits at two (2) sigma, and suitable Western Electric rules **(2)** invoked, consistent with plant/facility statistical policy.

8.9.3 All rule violations shall be investigated and eliminated if possible, with all causes and actions documented with the charts.

8.9.4 If a cause cannot be determined, analyzer operation should continue without any parameter adjustment until the next performance test.

8.9.5 If there are no rule violations, analyzer parameter adjustment is not needed.

8.9.6 If a rule violation's cause is determined and eliminated, and if the operator feels that the analyzer's accuracy has changed as a result, proceed to reset analyzer parameters, as discussed in Section 9. If precision needs to be redefined for the analysis process, follow the procedure listed in 8.10.

8.10 To determine the repeatability of the analyzer, follow the following procedure:

8.10.1 Switch a control sample into the analyzer and wait for stabilization as discussed in 8.6.

8.10.2 Measure at least eleven **(6)** successive analyses on the control sample over at least 1 h or reasonable interval on the same day. The control sample should be switched into and out of the analyzer stream for each determination.

8.10.3 The 95 % repeatability limit of the measurement for the analyzer equals the standard deviation of these 11 successive runs multiplied by 2.8, in accordance with Terminology E456.