



Standard Practice for Performance Testing of Process Analyzers for Aromatic Hydrocarbon Materials¹

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1. 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 D 3764 and D 6122, 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 API RP-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 and health practices, and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

¹ This practice is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons 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.

D 3764 Practice for Validation of Process Stream Analyzers³

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³

D 6122 Practice for Validation of Multivariate Process Infrared Spectrophotometers⁴

E 456 Terminology Relating to Quality and Statistics⁵

E 1655 Practices for Infrared, Multivariate, Quantitative Analysis⁶

3. Terminology

3.1 Definitions:

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

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

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

3.1.5 *control sample*—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*—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*—procedure involving the addition of a known quantity of a standard material

³ *Annual Book of ASTM Standards*, Vol. 5.02.

⁴ *Annual Book of ASTM Standards*, Vol. 5.04.

⁵ *Annual Book of ASTM Standards*, Vol. 14.02.

⁶ *Annual Book of ASTM Standards*, Vol. 3.06.

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

3.1.9 *performance testing of an analyzer*—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*—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.

3.1.11 *repeatability of an analyzer*—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*—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*—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*—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*—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 D 3764.

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 Hydrocarbons 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 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:

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

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 D 4177.

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

ABC Portland Cement Company
Qualitytown, N. J.

Plant Example Cement Type II Date March 9, 1998

Production Period March 2, 1998 - March 8, 1998

STANDARD REQUIREMENTS
ASTM C 150 Tables 1 and 3

CHEMICAL			PHYSICAL		
Item	Spec. Limit	Test Result	Item	Spec. Limit	Test Result
SiO ₂ (%)	20.0 min	21.3	Air content of mortar (volume %)	12 max	8
Al ₂ O ₃ (%)	6.0 max	4.6	Fineness (m ² /kg) (Air permeability)	280 min	377
Fe ₂ O ₃ (%)	6.0 max	3.4		Autoclave expansion (%)	0.80 max
CaO (%)	<i>A</i>	63.2	Compressive strength (MPa) min: 1 Day 3 Days 7 Days 28 Days	<i>A</i>	
MgO (%)	6.0 max	2.2		<i>A</i>	
SO ₃ (%)	3.0 max	2.7		7.0	23.4
Loss on ignition (%)	3.0 max	1.2		12.0	29.8
Na ₂ O (%)	<i>A</i>	0.19	Time of setting (minutes) (Vicat) Initial	Not less than 45 Not more than 375	124
K ₂ O (%)	<i>A</i>	0.50			
Insoluble residue (%)	0.75 max	0.27			
Potential compounds (%)					
C ₃ S	<i>A</i>	52			
C ₂ S	<i>A</i>	22			
C ₃ A	8 max	6			
C ₄ AF	<i>A</i>	10			
C ₄ AF+2(C ₃ A)	<i>A</i>	22			

^ANot applicable.

OPTIONAL REQUIREMENTS
ASTM C 150 Tables 2 and 4

CHEMICAL			PHYSICAL		
Item	Spec. Limit	Test Result	Item	Spec. Limit	Test Result
C ₃ S + C ₃ A (%)	58 max	58	False set (%)	50 min	82
Equivalent alkalies(%)	<i>B</i>	0.52	Heat of hydration (kJ/kg) 7 days	<i>B</i>	300
			Compressive strength (MPa) 28 days	28.0 min	39.7

^BLimit not specified by purchaser. Test result provided for information only.

^CTest result for this production period not yet available.

We certify that the above described cement, at the time of shipment, meets the chemical and physical requirements of the ASTM C 150-97 or (other) _____ specification.

Signature: _____ Title: _____

FIG. 1 Possible Process Analyzer Configurations

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, (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 E 456.

8.10.4 Recalculate the analyzer's control limits based on this new set of data, and reset the SPC chart's parameters. Continue to collect data for subsequent performance tests, and reevaluate the SPC chart control limits after 20 additional points have been collected.

8.10.5 Repeatability should be measured any time the analyzer's precision is suspected to have significantly changed, as indicated by the control sample SPC chart, or if the analyzer's response variation is excessive after an analyzer stream change. An indication of analyzer precision should always be made available to persons receiving data from the analyzer. Any large changes in an analyzer's precision should immediately be brought to the attention of the user of the analyzer's data.

8.11 Perform periodic analyzer validation on a scheduled basis over a longer time (for example, weekly or monthly) than performance testing, or whenever some significant aspect of the analyzer has changed (see Table 1). This activity reestablishes the analyzer's statistical performance with the primary method.

9. Analyzer Parameter Adjustment

9.1 Adjust analyzer response parameters only when the analyzer's control sample SPC chart indicates one or more rule violations, and after investigation, causes have been found and eliminated. Then, if in the opinion of the operator the response accuracy of the analyzer has changed, parameter adjustment may be performed.

9.2 Methods for adjusting analyzer parameters depend on the type of analyzer, and are specifically available from the

TABLE 1 Process Analyzer Changes That Can Trigger Revalidation

Analyzer cell changed or cleaned
Analyzer plumbing reconfigured or cleaned
New electrical component added or existing one replaced
Flow rate through the analyzer significantly changed
Replacement of a key component, like a chromatography column or detector
Movement of the analyzer to a different location in the process
Significant change in the analyzer's operating temperature
Significant changes in the content of the process stream
Analyzer electrical component adjustment
Significant change in the concentration of the analyte or interfering species
New/revised analyzer data collection software
The operator has specific evidence of change in analyzer accuracy

analyzer vendor. For this reason, analyzer parameter adjustment guidelines are beyond the scope of this practice.

9.2.1 It may be necessary to revalidate the analyzer instead of adjusting its parameters, depending on the reasons for analyzer accuracy changes. If the basic setup or operation of the analyzer have changed, it should be revalidated.

9.2.2 A rule violation is NOT an automatic signal for parameter adjustment! Most rule violations will not signal a need for changing the analyzer's parameters. Rather, they are indicators of change that must be investigated and used, with the operator's knowledge of the process and analyzer, to decide further action. Doing nothing, adjusting analyzer parameters, performing analyzer maintenance, or revalidation are options.

9.3 Whenever analyzer parameters are changed, all information relating to it must be recorded in a log book or computer file for the analyzer. Records should include current analyzer settings, changes in analyzer settings, maintenance service performed, any causes of change and repair, or any

other relevant information.

9.4 A spot sample, an identical material analyzed both in the analyzer and in the laboratory by the primary test method, may be analyzed at any time to check analyzer accuracy. However, these results generally should not be used to determine the need for analyzer parameter adjustment. Rather, if the laboratory and analyzer results differ by more than test method reproducibility, a subsequent analyzer performance test should be performed. If that run produces a control chart rule violation, the cause is identified and corrected. If then the operator feels that analyzer accuracy has changed, only then should analyzer parameter changes be considered (see 9.2).

9.5 If a statistical bias between laboratory and process analyzer results has been previously well-characterized during analyzer validation, and it has been monitored continuously by SPC (for example, from an SPC chart of the difference between the laboratory and analyzer on the check sample), a spot sample result may be used to trigger analyzer parameter changes. (**Warning**—the laboratory and process analyzer must be analyzing the same material as the spot sample). *Under these conditions*, if the difference between the spot sample and laboratory results are statistically different (for example, differ by more than test method reproducibility), then the operator may consider changing analyzer parameters appropriately (see 9.2).

10. Keywords

10.1 analyzer; on-line; performance testing; process stream analyzer

APPENDIX

(Nonmandatory Information)

X1. ADDITIONAL TERM DEFINITIONS

X1.1 Definitions:

X1.1.1 *analyzer*—all piping, hardware, computer, software, instrumentation, and calibration models required to automatically perform an analysis of a process or a product stream.

X1.1.1.1 *Discussion*—It may include the sampling system and any other hardware that is an integral part of the analyzer.

X1.1.2 *calibration of an analyzer*—determination of the relationship between the analyzer's output signal and the analyzer's result value.

X1.1.3 *calibration factors*—parameters that directly control the accuracy of analyzer results, for example, chromatographic peak response factors, voltage offsets, etc.

X1.1.4 *calibration standards*—materials similar to the process stream that contain known amounts of the analyte/parameter of interest.

X1.1.4.1 *Discussion*—Multiple concentration calibration standards may be needed to represent the operating range of the analyzer at the low, medium and high ends.

X1.1.5 *capability measurement (c_m)*—ratio of the square of

the standard deviation (variance) of the analyzer's result to the variance of the overall process for the stream being analyzed.

X1.1.6 *certificate of analysis (COA)*—document that demonstrates that a standard material has been analyzed by a specific accepted technique or techniques to contain a specific amount of analyte.

X1.1.7 *normal*—the usual, occurs in everyday practice.

X1.1.8 *normal variation*—differences between identical measurements on identical samples caused by random events in the complete testing process, that is, sampling, instrument changes due to temperature, gas bubbles, etc.

X1.1.9 *primary method*—analytical procedure used to generate the reference values against which the analyzer is both calibrated and validated (called "reference method" in accordance with Practice E 1655).

X1.1.9.1 *Discussion*—For aromatic hydrocarbons, many of these methods are under the jurisdiction of Committee D16.

X1.1.10 *primary standard materials*—materials prepared from first principles, generally obtainable from an external

vendor, and traceable to a national standard reference (for example, NIST).

X1.1.10.1 *Discussion*—Each standard shall be accompanied by a certificate of analysis (COA), indicating results from one or more independent techniques.

X1.1.11 *secondary standard materials*—materials that are similar to the process stream, having a known amount of the parameter of interest from in-house preparation (for example, gravimetrically or volumetrically), not necessarily traceable to a national reference.

X1.1.11.1 *Discussion*—They should be analyzed in a laboratory by the primary method to establish the “true” value for the parameter, must be stable over time, homogeneous, and present in large quantity (usually barrels).

X1.1.12 *standard deviation*—positive square root of the measurement’s variance observed for an analyzer under normal operation, when the analyzer is under statistical control.

X1.1.13 *statistical stability/control*—state of a process in which the variability is attributable to a constant system of chance causes.

X1.1.14 *systematic bias*—difference in average analyzer results for a parameter measured over the long term and the true, assigned, or accepted reference value for the analyte.

X1.1.15 *validation of an analyzer*—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.

X1.1.15.1 *Discussion*—Must be performed when the analyzer is first configured or reconfigured (initial validation), and then on a periodic basis (periodic validation).

X1.1.16 *variance*—measure of the squared dispersion of observed values or measurements, expressed as a function of the sum of squared deviations from the population mean or sample average.

X1.1.16.1 *Discussion*—It should always be accompanied by the degrees of freedom ($n - 1$) on which it is based, where n is the number of measurements.

X1.1.17 *Western Electric rules (2)*—conditions based on statistical probabilities developed at this company, where individual points or patterns of points occur at specified levels of confidence.

X1.1.17.1 *Discussion*—These are used to identify out-of-control conditions on statistical process control charts.

REFERENCES

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