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Standard Practice for
Validation of the Performance of Process Stream Analyzer Systems[1]

INTRODUCTION

Operation of a process stream analyzer system typically involves four sequential activities. *(1)* **Analyzer Calibration**—When an analyzer is initially installed, or after major maintenance has been performed, diagnostic testing is performed to demonstrate that the analyzer meets the manufacturer's specifications and historical performance standards. These diagnostic tests may require that the analyzer be adjusted so as to provide predetermined output levels for certain reference materials. *(2a)* **Correlation for the Same Material**—Once the diagnostic testing is completed, process stream samples are analyzed using the analyzer system. For application where the process analyzer system results are required to agree with results produced from an independent (primary) test method (PTM), a mathematical function is derived that relates the analyzer results to the primary test method results (PTMR). The application of this mathematical function to an analyzer result produces a predicted primary test method result (PPTMR), for the same material. *(2b)* **Correlation for Material including Effect from Additional Treatment to the Material**—The PPTMR in *(2a)* can be used as an input to a mathematical model to predict the effect of an additive and/or a blendstock added to a basestock material as measured by a PTM. *(3)* **Probationary Validation**—After the correlation(s) relationship between the analyzer results and primary test method results has been established, a probationary validation is performed using an independent but limited set of materials that were not part of the correlation activity. This probationary validation is intended to demonstrate that the PPTMRs agree with the PTMRs to within user-specified requirements for the analyzer system application. *(4)* **General and Continual Validation**—After an adequate amount of PPTMRs and PTMRs have been accrued on materials that were not part of the correlation activity, a comprehensive statistical assessment is performed to demonstrate that the PPTMRs agree with the PTMRs to within the tolerances established from the correlation activities. Subsequent to a successful general validation, quality assurance control chart monitoring of the differences between PPTMR and PTMR is conducted during normal operation of the process analyzer system to demonstrate that the agreement between the PPTMRs and PTMRs established in the General Validation is maintained. This practice deals with the third and fourth of these activities.

"Correlation for material including effect from additional treatment to the material" as outlined in this standard is intended primarily to be applied to biofuels where the biofuel material is added at a terminal or other facility and not included in the process stream material sampled by the analyzer at the basestock manufacturing facility. The correlation shall be specific for a constant percentage addition of the biofuels material to the basestock for each model. This practice may not apply for physical properties where the source material for the biofuel material or the denaturant/diluent material used with the biofuel material can significantly affect the finished biofuel's physical property. The user of the standard should investigate the effect of changes to biofuels material blend ratios, biofuels material source material, and blendstock material composition when using this practice. Limits to any of these may need to be applied when the correlation is used.

1. Scope*

1.1 This practice describes procedures and methodologies based on the statistical principles of Practice D6708 to validate whether the degree of agreement between the results produced by a total analyzer system (or its subsystem), versus the results produced by an independent test method that purports to measure the same property, meets user-specified requirements. This is a performance-based validation, to be conducted using a set of materials that are not used a priori in the development of any correlation between the two measurement systems under investigation. A result from the independent test method is herein referred to as a Primary Test Method Result (PTMR).

1.1.1 The degree of agreement described in 1.1 can be either for PPTMRs and PTMRs measured on the same materials, or for PPTMRs measured on basestocks and PTMRs measured on these same basestocks after constant level additivation.

1.1.2 In some cases, a two-step procedure is employed. In the first step, the analyzer and PTM are applied to the measurement of the same blendstock material. If the analyzer employed in Step 1 is a multivariate spectrophotometric analyzer, then Practice D6122 is used to access the agreement between the PPTMRs and the PTMRs for this first step. Otherwise, this practice is used to compare the PPTMRs to the PTMRs measured for this blendstock to determine the degree of agreement. In a second step, the PPTMRs produced in Step 1 are used as inputs to a second model that predicts the results obtained when the PTM is applied to the analysis of the finished blended product. Since this second step does not use analyzer readings, the validation of the second step is done independently. Step 2 is only performed on valid Step 1 results. Note that the second model might accommodate variable levels or multiple material additions to the blendstock.

1.2 This practice assumes any correlation necessary to mitigate systemic biases between the analyzer system and PTM have been applied to the analyzer results. See Guide D7235 for procedures for establishing such correlations.

1.3 This practice assumes any modeling techniques employed have the necessary tuning to mitigate systemic biases between the analyzer PPTMR and PTMR have been applied to the model results. Model form and tuning is not covered by this practice, only the validation of the model output.

1.4 This practice requires that both the primary method against which the analyzer is compared to, and the analyzer system under investigation, are in statistical control. Practices described in Practice D6299 should be used to ensure this condition is met.

1.5 This practice applies if the process stream analyzer system and the primary test method are based on the same measurement principle(s), or, if the process stream analyzer system uses a direct and well-understood measurement principle that is similar to the measurement principle of the primary test method. This practice also applies if the process stream analyzer system uses a different measurement technology from the primary test method, provided that the calibration protocol for the direct output of the analyzer does not require use of the PTMRs (see Case 1 in Note 1).

1.6 This practice does not apply if the process stream analyzer system utilizes an indirect or mathematically modeled measurement principle such as chemometric or multivariate analysis techniques where PTMRs are required for the chemometric or multivariate model development. Users should refer to Practice D6122 for detailed validation procedures for these types of analyzer systems (see Case 2 in Note 1).

NOTE 1—For example, for the measurement of benzene in spark ignition fuels, comparison of a Mid-Infrared process analyzer system based on Test Method D6277 to a Test Method D3606 gas chromatography primary test method would be considered Case 1, and this practice would apply. For each sample, the Mid-Infrared spectrum is converted into a single analyzer result using methodology (Test Method D6277) that is independent of the primary test method (Test Method D3606). However, when the same analyzer uses a multivariate model to correlate the measured Mid-Infrared spectrum to Test Method D3606 reference values using the methodology of Practice E1655, it is considered Case 2 and Practice D6122 applies. In this case 2 example, the direct output of the analyzer is the spectrum, and the conversion of this multivariate output to an analyzer result require use of Practice D6122, hence it is not independent of the primary test method.

1.7 Performance Validation is conducted by calculating the precision and bias of the differences between results from the analyzer system (or subsystem) after the application of any necessary correlation, (such results are herein referred to as Predicted Primary Test Method Results (PPTMRs)), versus the PTMRs for the same sample set. Results used in the calculation are for samples that are not used in the development of the correlation. The calculated precision and bias are statistically compared to user-specified requirements for the analyzer system application.

1.7.1 For analyzers used in product release or product quality certification applications, the precision and bias requirement for the degree of agreement are typically based on the site or published precision of the Primary Test Method.

NOTE 2—In most applications of this type, the PTM is the specification-cited test method.

1.7.2 This practice does not describe procedures for establishing precision and bias requirements for analyzer system applications. Such requirements must be based on the criticality of the results to the intended business application and on contractual and regulatory requirements. The user must establish precision and bias requirements prior to initiating the validation procedures described herein.

1.8 Two procedures for validation are described: the line sample procedure and the validation reference material (VRM) injection procedure.

1.9 Only the analyzer system or subsystem downstream of the VRM injection point or the line sample extraction point is being validated by this practice.

1.10 The line sample procedure is limited to applications where material can be safely withdrawn from the sampling point of the analyzer unit without significantly altering the property of interest.

1.10.1 The line sample procedure is the primary option for when the validation is for (2b) materials including effect from additional treatment to the material.

1.11 Validation information obtained in the application of this practice is applicable only to the type and property range of the materials used to perform the validation.

1.12 Two types of validation are described: General Validation, and Level Specific Validation. These are typically conducted at installation or after major maintenance once the system mechanical fitness-for-use has been established.

1.12.1 General Validation is based on the statistical principles and methodology of Practice D6708. In most cases, General Validation is preferred, but may not always be possible if the variation in validation materials is insufficient. General Validation will validate analyzer operation over a wider operating range than Level Specific Validation.

1.12.2 When the variation in available validation materials is insufficient to satisfy the requirements of Practice D6708, a Level Specific Validation is done to validate analyzer operation over a limited range.

1.12.3 The validation outcome are considered valid only within the range covered by the validation material. Data from several different Validations (general or level-specific) can potentially be combined for use in a General Validation.

1.13 Procedures for the continual validation of system performance are described. These procedures are typically applied at a frequency commensurate with the criticality of the application.

1.14 This practice does not address procedures for diagnosing causes of validation failure.

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

1.16 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D3606 Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography

[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.

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

D6122 Practice for Validation of the Performance of Multivariate Online, At-Line, and Laboratory Infrared Spectrophotometer Based Analyzer Systems

D6277 Test Method for Determination of Benzene in Spark-Ignition Engine Fuels Using Mid Infrared Spectroscopy

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6708 Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material

D7235 Guide for Establishing a Linear Correlation Relationship Between Analyzer and Primary Test Method Results Using Relevant ASTM Standard Practices

D7278 Guide for Prediction of Analyzer Sample System Lag Times

D7453 Practice for Sampling of Petroleum Products for Analysis by Process Stream Analyzers and for Process Stream Analyzer System Validation

D7808 Practice for Determining the Site Precision of a Process Stream Analyzer on Process Stream Material

E456 Terminology Relating to Quality and Statistics

E1655 Practices for Infrared Multivariate Quantitative Analysis

F307 Practice for Sampling Pressurized Gas for Gas Analysis

3. Terminology

3.1 *Definitions:*

3.1.1 *accepted reference value (ARV), n—* a value that serves as an agreed-upon reference for comparison, and which is derived as: *(1)* a theoretical or established value, based on scientific principles, *(2)* an assigned or certified value, based on experimental work of some national or international organization, or *(3)* a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group. **E456**

3.1.2 *between-method reproducibility (R_{XY}), n—*a quantitative expression of the random error associated with the difference between two results obtained by different operators using different apparatus and applying the two methods *X* and *Y*, respectively, each obtaining a single result on an identical test sample, when the methods have been assessed and an appropriate bias-correction has been applied in accordance with this practice; it is defined as the 95 % confidence limit for the difference between two such single and independent results. **D6708**

3.1.2.1 *Discussion—*Within the context of this practice, R_{XY} is interpreted to be the 95 % confidence limit for the prediction deviation between any single Primary Test Method Result (PTMR) and the Predicted Primary Test Method Result (PPTMR) produced by the analyzer system that is deemed

acceptable on the assumption that both the analyzer system and primary test method are in statistical control, and that the correlation relationship applied to the analyzer results to produce the PPTMR is fit-for-purpose.

3.1.3 *precision, n*—the closeness of agreement between independent test results obtained under stipulated conditions. **E456**

3.1.4 *repeatability conditions, n*—conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time. **E456**

3.1.5 *reproducibility conditions, n*—conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment. **E456**

3.1.6 *site precision conditions, n*—conditions under which test results are obtained by one or more operators in a single site location practicing the same test method on a single measurement system using test specimens taken at random from the same sample of material, over an extended period of time spanning at least a 15 day interval. **D6299**

3.1.6.1 *Discussion*—A measurement system may comprise multiple instruments being used for the same test method.

3.1.7 *site precision, n*—2.77 times the standard deviation of results obtained under site precision conditions. **D6299**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Analyzer System Items:*

3.2.1.1 *analyzer output, n*—a signal (pneumatic, electrical, or digital), proportional to the property being measured that is suitable for readout or control instrumentation external to the analyzer system.

3.2.1.2 *analyzer system result, n*—the measured property reading, in the accepted property measurement units, that is displayed by the analyzer unit readout instrumentation or transmitted to end user of the analyzer system.

3.2.1.3 *analyzer unit, n*—the instrumental equipment necessary to automatically measure the physical or chemical property of a process or product stream sample using either an intermittent or a continuous technique.

3.2.1.4 *analyzer unit repeatability, n*—2.77 times the standard deviation of results obtained from repetitive analysis of the same material directly injected into the analyzer unit under repeatability conditions.

3.2.1.5 *continuous analyzer unit, n*—an analyzer that measures the property value of a process or product stream on a continuous basis and dynamically displays the instantaneously updated analyzer output.

3.2.1.6 *intermittent analyzer unit, n*—a cyclic type analyzer that performs a measurement sequence on samples from a process or product stream and displays a new analyzer output at the conclusion of each cycle.

3.2.1.7 *total analyzer system, n*—the complete analyzer system inclusive of the sample loop, sample conditioning unit, analyzer unit, readout instrumentation, and excess sample return system (see Fig. 1).

3.2.2 *Time Unit Items—General Terms:*

3.2.2.1 *analyzer unit cycle time, n*—for intermittent analyzers, the time interval between successive updates of the analyzer output.

3.2.2.2 *analyzer unit dead time, n*—the time interval between the introduction of a step change in property characteristic at the inlet of the analyzer unit and the initial indication of analyzer response to this change.

(1) Discussion—For intermittent analyzers, if the analyzer dead time is less than one analyzer unit cycle time, the analyzer unit dead time cannot be directly measured.
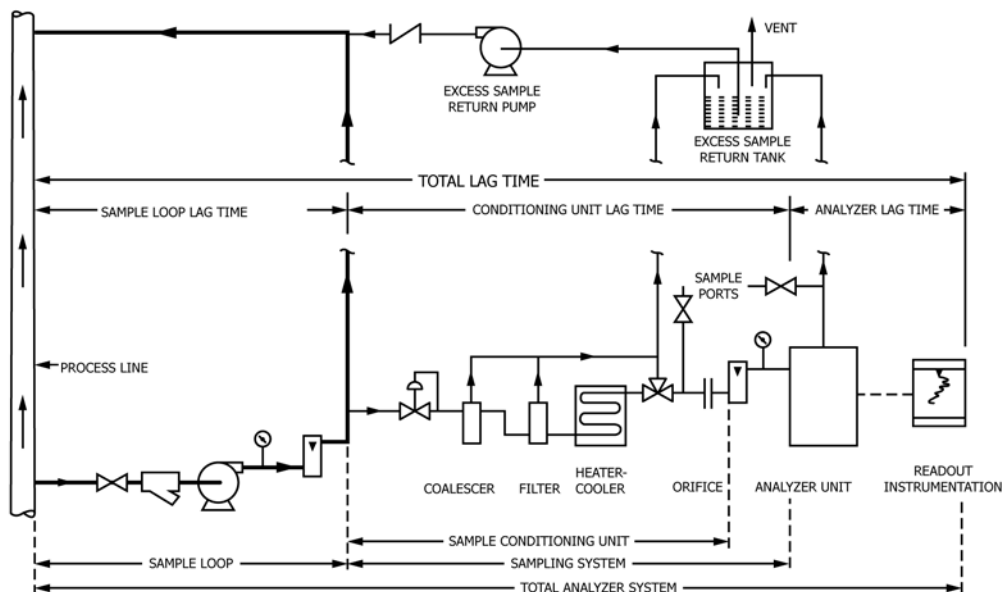

FIG. 1 Total Analyzer System

3.2.2.3 *analyzer unit response time, n*—(see Fig. 2) the time interval between the introduction of a step change in property characteristic at the inlet of the analyzer unit and when the analyzer output indicates a value corresponding to 99.5 % of the subsequent change in analyzer results.

(1) Discussion—For continuous and intermittent analyzers with sufficiently short cycle times, the total analyzer response time is the analyzer dead time plus three times the analyzer unit time constant. For intermittent analyzers with long cycle times, the analyzer unit response time is effectively equal to the analyzer unit cycle time. For intermittent analyzers with intermediate cycle times, the analyzer unit response time should be defined as the multiple of the analyzer unit cycle time needed to exceed 99.5 % response.

3.2.2.4 *analyzer unit time constant, n*—(see Fig. 2) the time interval between the initial response of the analyzer unit to a step change in property characteristic and when the analyzer output indicates a value corresponding to 63 % of the subsequent change in analyzer results.

(1) Discussion—For intermittent analyzers, if the analyzer unit time constant is less than one analyzer unit cycle time, the analyzer time constant cannot be directly measured.

3.2.2.5 *lag time, n*—the time required for material to travel from Point A to Point B in the total analyzer system (Points A and B are user-defined).

(1) Discussion—Lag time is a function of an analyzer system design parameters such as length and diameter of lines, number of fittings, flow restrictions, and the flow rate of the material (process or product stream) through the analyzer system (see Figs. 2 and 1). See Guide D7278 for procedures for predicting analyzer system lag times.

3.2.2.6 *sample conditioning unit lag time, n*— the time required for material to travel from the start of the sample conditioning unit to the analyzer unit inlet.

3.2.2.7 *sample loop lag time, n*—the time required for material to travel from the process takeoff point of the sample loop to start of the sample conditioning unit.

3.2.2.8 *total analyzer system response time, n*—(see Fig. 2) The time interval between when a step change in property characteristic at the sample loop inlet and when the analyzer

output indicates a value c corresponding to the 99.5 % of the subsequent change in analyzer results; the total analyzer system response time is the sum of the sample loop lag time, the same conditioning loop lag time, and the total analyzer response time.

3.2.3 *General Terms:*

3.2.3.1 *composition-specific VRM, n*—a validation reference material consisting of a single, pure compound, or a known, reproducible mixture of compounds for which an accepted reference value or site assigned value can be calculated or measured.

(1) Discussion— A composition-specific VRM may be a commercial standard reference material (SRM) having a certified accepted reference value.

3.2.3.2 *continual validation, n*—the quality assurance process by which the bias and precision performance determined during initial validation are shown to be sustained.

3.2.3.3 *direct measurement, n*—a quantitative measurement result obtained using a principle or principles that express the characteristic property of interest in its defining units.

3.2.3.4 *indirect measurement, n*—a correlated quantitative measurement result obtained using a measurement principle that produces values that do not express the desired characteristic property but which can be modified empirically, using mathematical modeling techniques, to estimate the necessary defining units of the property of interest.

(1) Discussion—Methods that utilize chemometric or multivariate analysis are indirect measurements for generating correlative characteristic property measurement results.

3.2.3.5 *line sample, n*—process material that can be safely withdrawn from a sample port and associated facilities located anywhere in the total analyzer system without significantly altering the property of interest that is intended to be used to perform analyzer system validation as per this practice.

3.2.3.6 *prediction deviations (Δ), n*—calculated differences (including algebraic sign) between predicted primary test method result and primary test result, defined as (PPTMR – PTMR).

(1) Discussion—This is also referred to as prediction residuals in Practice D6708.
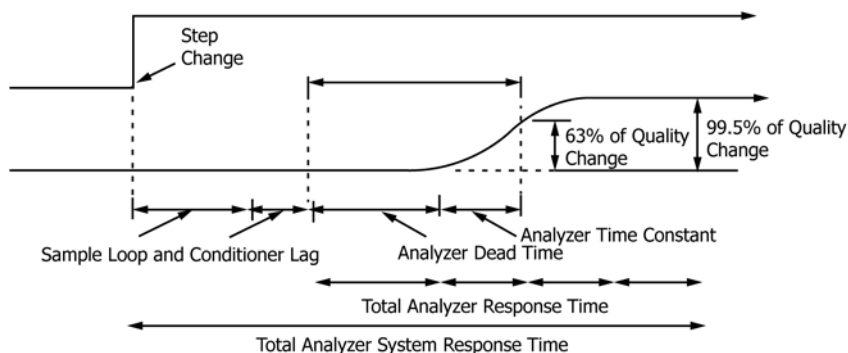

FIG. 2 Analyzer Time Units

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3.2.3.7 *primary test method results (PTMR), n—* test results produced from an ASTM or other established standard test method that are accepted as the reference measure of a property.

3.2.3.8 *predicted Primary Test Method Results (PPTMR), n—*results from the analyzer system, after application of any necessary correlation, that is interpreted as predictions of what the primary test method results would have been, if it was conducted on the same material.

3.2.3.9 *process-derived VRM, n—*a validation reference material derived from an isolated batch of process or product stream material with chemical or physical characteristics, or both, that is suitable for determination of an accepted reference value or site assigned value for the property of interest.

3.2.3.10 *site assigned value (SAV), n—*a property value of a reference material that is based on multiple results from either the analyzer unit or a primary test method, obtained under site precision conditions.

3.2.3.11 *validation, n—*the statistically quantified judgment that the analyzer system or subsystem, in conjunction with any correlation applied, can produce acceptable precision and bias performance on the prediction deviations (Δ) for materials that were not used to develop the correlation.

3.2.3.12 *validation reference material (VRM), n—*for validation and quality assurance testing, a material having an accepted reference value or site assigned value for the property of interest.

4. Summary of Practice

4.1 PPTMRs from the total analyzer system or its subsystem are compared to the corresponding PTMRs on at least 15 materials. PPTMR and PTMR are statistically assessed relative to each other using the methodology of Practice D6708, recognizing that this is only a preliminary Practice D6708 assessment. Precision and bias statistics on the prediction deviations (Δ) are generated and the bias is assessed against pre-specified performance criteria. The system or subsystem performance is considered to be probationary validated for materials and property ranges representative of those used in the validation if the prediction deviations are in statistical control, and bias performance statistic meets pre-specified criterion.

4.2 After probationary validation is achieved, continued statistical quality control chart monitoring and analyses on Δ are carried out with new production samples to ensure on-going prediction performance of the PPTMR meets the levels established from the probationary validation.

4.3 Once the total number of samples with completed datasets (PPTMR , PTMR , Δ) from probationary and continual validation reaches 30, a general validation is conducted using the statistical methodology of Practice D6708. The objective of the general validation is to demonstrate performance with at least 30 samples over a wider operating envelope, or, to confirm outcome from probationary validation with more accrued data.

4.4 If the variation among the 30 samples is inadequate to conduct the Practice D6708 assessment, a level specific vali-

dation may be performed to validate the agreement between PPTMR and PTMR over a narrow operating range. As additional (PPTMR / PTMR / Δ) datasets are collected covering a wider operating range, the general validation may again be attempted.

4.5 After general validation has been achieved, continue to monitor Δ using statistical quality control charts at a frequency commensurate with the criticality of the application.

5. Significance and Use

5.1 This practice can be used to quantify the performance of a process stream analyzer system or its subsystem in terms of precision and bias relative to those of a primary test method for the property of interest.

5.2 This practice provides developers or manufacturers of process stream analyzer systems with useful procedures for evaluating the capability of newly designed systems for industrial applications that require reliable prediction of measurements of a specific property by a primary test method of a flowing component or product.

5.3 This practice provides purchasers of process stream analyzer systems with some reliable options for specifying acceptance test requirements for process stream analyzer systems at the time of commissioning to ensure the system is capable of making the desired property measurement with the appropriate precision or bias specifications, or both.

5.4 PPTMR from Analyzer Systems validated in accordance with this practice can be used to predict, with a specified confidence, what the PTMR would be, to within a specified tolerance, if the actual primary test method was conducted on the materials that are within the validated property range and type.

5.5 This practice provides the user of a process stream analyzer system with useful information from on-going quality control charts to monitor the variation in Δ over time, and trigger update of correlation relationship between the analyzer system and primary test method in a timely manner.

5.6 Validation information obtained in the application of this practice is applicable only to the material type and property range of the materials used to perform the validation. Selection of the property levels and the compositional characteristics of the samples must be suitable for the application of the analyzer system. This practice allows the user to write a comprehensive validation statement for the analyzer system including specific limits for the validated range of application. This practice does not recommend extrapolation of validation results beyond the material type and property range used to obtain these results. In addition, users are cautioned that for measurement systems that show matrix dependencies, bias information determined from pure compounds or simple mixtures of pure compounds may not be representative of that achieved on actual process or product samples.

6. System Components

6.1 Fig. 1 illustrates a total analyzer system incorporating a selection and arrangement of components that are typical but