

THE ENGINEERING EQUIPMENT AND MATERIALS USERS' ASSOCIATION

EEMUA Code of Practice

Calibration and validation of process analysers

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ENGINEERING EQUIPMENT AND MATERIALS USERS' ASSOCIATION

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Contents

Preface	ix
1. Scope: calibration and validation	1
2. Definitions	3
2.1 Equipment	3
2.2 Measurement	3
2.3 Calibration and validation	4
2.4 Statistical terms	5
3. General considerations: calibration and validation.....	9
4. Preconditions for analyser calibration and validation	11
4.1 General.....	11
4.2 Factory Acceptance Testing (FAT)	11
4.3 Site installation	11
4.4 Site Acceptance Testing (SAT)	12
4.5 Site precision	12
4.6 Read-out instrumentation	12
5. Principles of initial calibration, correlation and initial validation.....	13
5.1 Initial calibration and correlation.....	13
5.2 Probationary/initial validation	14
5.3 Analyser result and accepted reference value comparison methods.....	14
6. Principles of routine validation and calibration adjustment	15
6.1 General.....	15
6.2 Analyser result and reference test/primary test method comparison techniques	16
6.2.1 Reference sample method.....	16
6.2.2 Paired sample method	16
6.3 Routine validation (scheduled check of continuing performance).....	17
6.4 Calibration adjustment (adjustment, if required, to re-establish analyser results within performance limits).....	17
6.5 Routine validation and calibration adjustment intervals	18
6.6 Number of result values required for routine validation and calibration adjustment	19
6.7 Routine validation and calibration adjustment of model based/chemometric process analysers.....	20
7. Comparison methods: reference sample method and paired sample method	21
7.1 Comparing analyser and reference method results.....	21
7.2 Routine validation and calibration adjustment using the reference sample method	21
7.2.1 Advantages and limitations	21
7.2.2 Choice of reference samples	22
7.2.3 Testing of reference samples	23
7.3 Routine validation and calibration adjustment using the paired sample method	23
7.3.1 Advantages and limitations	23
7.3.2 Collecting paired sample results.....	25
8. Evaluation of routine validation and calibration adjustment results: use of statistical tools and control charts	27
8.1 General.....	27
8.2 Use of statistical tools	27
8.3 Routine validation and calibration adjustment: use of control charts.....	27
8.3.1 CUSUM approach	29
8.4 Control chart limits	30

8.5 Control chart limits derived from analyser reference sample or paired sample laboratory data.....	31
Appendix 1: Example interpretation of control chart readings	33
Appendix 2: Determination of control chart limits by measuring standard deviations of differences.....	35
References and Bibliography	37

Figures

Figure 1 Example of a control charting diagram.....	28
Figure 2 Examples of analyser results in a CUSUM chart.....	29
Figure 3 Example of accurately distributed control chart reading.....	33
Figure 4 Example of biased control chart reading.....	33
Figure 5 Example of drifting control chart reading.....	33
Figure 6 Example control chart reading; value outside warning limit.....	34
Figure 7 Example determination of control chart limits by measuring standard deviations.....	36

Tables

Table 1 Sample validation uncertainty results.....	19
Table 2 Example of the control chart limits for a distillation analyser.....	35

Preface

This Code of Practice has been prepared by the EEMUA On-Line Analysers Committee. It replaces the First Edition of this Publication, previously named 'Calibration and checking of process analysers', which in turn replaced the following historical IP Codes of Practice relating to analysers: IP 340/92, 341/82, 347/82, 348/82, 349/82 and 353/82.

Other associated EEMUA publications are:

EEMUA 138 - Design and installation of on-line analyser systems.

EEMUA 226 - Design and installation of on-line analyser systems - a guide to technical enquiry and bid evaluation.

EEMUA 187 - Analyser systems - a guide to maintenance management.

The word analyser has been used throughout this Publication to refer to instruments, variously known as on-line analysers, process stream analysers, process analysers, quality analysers, quality measuring instruments and process quality monitors.

1. Scope: calibration and validation

This Publication is a general guide to the principles and methods used for the calibration and validation (verification) of process (on-line) analysers. It covers the principles of initial calibration and correlation, in the factory or on the plant, and initial validation. The detailed guidance is focussed on continued (routine) validation (in-service checking) and calibration adjustment (only if required, based on appropriate validation results) including the use of control charts.

The content and presentation of this Publication recognises that the effort available for routine validation and calibration adjustment is limited. The simplified approaches recommended are therefore intended to require only a reasonable expenditure of effort in order to maintain assurance that the initial calibration and correlation of the analyser to the reference method is still valid.

In some cases the simplified approaches will produce procedures, which although adequate, may be less rigorous than could be evolved on purely technical and theoretical grounds. The approaches should be amended to ensure that they meet the individual business needs of the manufacturing or other process to which they are applied.

It should be noted that this Publication is primarily intended for use by those directly involved with supplying, using and maintaining on-line/process analysers. These individuals are generally not specialists in quality measurement principles and the associated statistical calculations. Therefore, as far as possible, this Publication avoids the explicit use of statistical methods and favours descriptions and explanations of a more practical nature. In order to remain consistent with the theoretical approach these practical approaches are assumed to exhibit random statistical behaviour with a normal/Gaussian distribution.

This Publication is not intended to cover Continuous Emissions Monitoring Systems (CEMS). These systems have calibration, validation, on-going quality assurance (routine validation and calibration adjustment) and the associated statistical tools defined by other standards, e.g. BS EN 14181 - Stationary source emissions: quality assurance of automated measuring systems⁽¹⁾.

This Publication is not intended to cover automatic or semi-automatic instruments used mainly in laboratories to analyse discrete samples. However, the principles and techniques described can also be applied to laboratory instruments.

For consistency with BS EN 60359 - Electrical and electronic measurement equipment expression of performance⁽²⁾, this Publication treats the definitions of validation and verification as equivalent.

2. Definitions

The following glossary aims to add further definition to the terms used in the text in the context of their use when describing activities associated with process analysers.

The definitions are grouped by a usage category (additional external references are shown in brackets). Similar words or phrases are listed with a common description.

2.1. Equipment

Analyser / on-line analyser / process analyser / process stream analyser / quality analysers / Quality Measurement Instruments (QMI). An instrument used to measure continuously and automatically a particular property or chemical composition of a process stream. The input to the instrument is a sample or portion of the process stream, either introduced continuously or at specific points in the analyser operating cycle. The sample is conditioned in a particular way, for example; flow, pressure, temperature or cleanliness. The output is a transmitted result or reading displayed on suitable read out instrumentation such as a control system screen or other operator interface. The analyser is normally located permanently within the process area.

Analyser system / total analyser system (ASTM D3764⁽³⁾). The complete instrumentation system, including sample extraction and return, sample conditioning, analytical measurement, and result display/readout/operator interface. The analyser system typically comprises the sampling system, the analyser, the read-out instrumentation and all associated piping, wiring and data communications and operator displays.

Analyser time constant. For a continuous analyser this is the time interval between the initial response and the time to reach 63 per cent of the final output value with a step change in the measured property. For cyclically sampling analysers the time constant is the analyser cycle time.

Readout instrumentation. The device used to accept the signal transmitted from the analyser and display it for use in process operation or other decision making. Displayed as a measured property or concentration in the accepted units of that property or concentration.

2.2 Measurement

Absolute property. Where the measurement result is independent of the type of equipment and the method used for its measurement. The result from the analyser and the reference/standard test should be identical.

Analyser range / measuring range / range (IEC 60050-311⁽⁴⁾). The smallest and largest values that can be represented as an analyser result. The range is defined by two values of the measurement within which the limits of uncertainty of the measuring instrument are specified.

Analyser result / analyser system result (ASTM D3764) / result / result value. The measured property or concentration reading, in the measurement

units of that property or concentration displayed or recorded by the analyser and transmitted to the read out instrumentation.

Bias (ASTM E456⁽⁵⁾). The difference between the analyser results and the accepted reference value. A consistent offset between the analyser result and the accepted reference value.

Dead band (IEC 60050-311). The finite range of values within which a variation of the input variable does not produce any measurable change in the output variable.

Direct measurement (BS EN 60359). The value of the analyser result is detected directly, without the need for other calculations from a relationship between the measurement and the property being measured.

Drift (BS EN 61207-1⁽⁶⁾, IEC 60050-311). Change in the indication of a measuring instrument, generally slow, continuous, not necessarily in the same direction and not related to a change in the properties or composition of the sample being measured.

Empirical property. Where the measurement is only definable in terms of the reference/standard test. The result from the analyser and the reference/standard test may differ, and the analyser should be calibrated to agree with the reference test result.

Indirect measurement (BS EN 60359). The value of the analyser result is obtained indirectly using a calculation that represents a known mathematical relationship combined with a directly measured/detected property. This can include chemometric models based on a statistical or mathematical analysis of multiple reference samples to develop a calibration model for the analyser based on several measurement parameters, e.g. multiple wavelengths for a spectrometer.

Linearity (IEC 60050-311). The ability of a measuring instrument to provide an indication having a linear relationship with a defined quantity.

Property. The characteristic or compositional parameter that is required to be indicated by the analyser result.

Relative sensitivity (IEC 60050-311). Change in the indication divided by the corresponding change in the value of the property or concentration measured.

Sensitivity. The value of the smallest measurement that can be made and seen on the read out instrumentation.

2.3 Calibration and validation

Accepted reference value (ASTM D3764) / reference / reference test / validation reference value. The numerical value of the particular property reference material against which the analyser result is compared. A value that serves as an agreed reference for comparison, which can be an established theoretical value based on scientific principles, and assigned more certified value based on experimental work of some national or international organisation, or a

consensus value based on collaborative experimental work under the auspices of a scientific or engineering group.

Analyser calibration / calibration (ASTM E456, BS EN 60359). The process, or set of operations that establishes a relationship between an instrument indication and a known standard value under specified conditions.

Calibration adjustment. The process of adjusting the results of an analyser to match the accepted reference value of a reference sample presented to it. This is usually done after the reason for the exceptional difference between the analyser result and the accepted reference value has been investigated and any faults corrected, or based on a set of laboratory cross check sample results.

Certified reference material / reference sample / validation reference material (ASTM D3764). A material having an accepted reference value assigned for the property or composition of interest.

Checking / continual validation (ASTM D3764) / on-going validation / routine validation / verification. The assurance process by which the bias and precision performance determined during initial validation are shown to be maintained. The presentation of a reference sample to an analyser in order to determine the difference between the analyser result and the accepted reference value. A routine procedure to monitor the performance of the analyser over an extended period using control charts. No adjustment to the calibration of the analyser is made unless the control charts indicate a real change has occurred.

Correlation (ASTM D3764). Derivation of the mathematical relationship between the analyser measurement output and the accepted reference values of the reference samples.

Initial calibration. Statistically based calibration to establish the relationship between the analyser results across its entire range using a significant number of reference materials. To accurately establish the relationship between the analyser and the corresponding standard test result or certified reference material.

Initial validation / probationary validation (ASTM D3764). Validation performed using a range of reference materials that were not part of the initial calibration. Not part of the initial calibration to determine normal expected variation (precision), for use in future routine validations.

Primary test method (ASTM D3764) / reference method / standard test. Test results produced from an ASTM or other established standard test method that are accepted as the reference measure of property or composition.

Validation. The presentation of a reference sample to an analyser of a reference sample or by using a laboratory cross check to determine the difference between the analyser result and the accepted reference value. To confirm that initial calibration has not changed and is still valid.

2.4 Statistical terms

Accuracy (ASTM E456). The closeness of agreement between a test result and its accepted reference value.

Analyser calibration uncertainty. The expanded uncertainty or quantification of the cumulative errors within the measurement, calibration, and validation processes, including the uncertainty associated with laboratory results and those of certified standard materials expressed in the measured output units. Also, at a stated confidence level (e.g. 95%, two standard deviations, etc.).

Analyser equipment uncertainty. The uncertainty or quantification of the cumulative errors associated with the analyser result as stated by the equipment supplier/manufacturer. Expressed in the measured output units, and at a stated confidence level (e.g. 95%, two standard deviations, etc.).

Analyser precision / analyser site precision. The closeness of agreement between a sequence of analyser results obtained using the same analyser and same sample within a short interval of time under normal site operating conditions. A quantitative measure of the normal expected variability associated with the same analyser in a given location obtaining successive repeat results on identical reference material. It can be defined as that difference between two such single results that would only be exceeded in the long run in one case in twenty. Equivalent to plus or minus two standard deviations or the measurement uncertainty with a 95% confidence level.

Analyser result standard deviation / analyser standard deviation / sample standard deviation (ASTM E456). Representation of the spread of readings (values/results) over a limited number of observations, and how an individual reading may differ from the average value of a much greater number of observations. Calculated as the square root of the sum of squared differences of a variable from its mean, or accepted reference value, divided by the number of observations minus one.

Analyser uncertainty component. A source of error in a test result to which is attached a particular uncertainty. The uncertainty is expressed as two standard deviations at 95% confidence.

Average / mean (ASTM E456). An average or expected value of a characteristic in an entire population or for all of samples/results. Sum of all of the observed values in the population divided by the number of results in the population.

Certified reference material uncertainty / certified reference method uncertainty / laboratory uncertainty. The overall uncertainty or quantification of the cumulative errors within the laboratory results and those of the certified standard materials used in its calibration. Expressed in the measured output units and at a stated confidence level (e.g. 95%, two standard deviations, etc.).

Confidence interval (BS EN 60359). An interval (confidence interval) expressed as a half width (plus or minus value) with a coverage factor of two times the uncertainty component (two standard deviations). Equivalent to a level of confidence of 95%.

Control chart (ASTM E456) / statistical control chart. A chart on which is plotted a statistical measure of a value versus time of sampling, along with limits based on the statistical distribution of that measure to indicate how much, and the type of variation that is inherent in the measurement process.

Control limits (ASTM E456). A set of boundaries on a control chart that are used as criteria for signalling the need for action or judging whether a set of data does or does not indicate a state of statistical control. If all values are within the control chart control limits this indicates a state of statistical process control. Normally three standard deviations above and below the control chart centre line, equivalent to a level of confidence of 99%. Only 1 result in 100 is expected to exceed the limit.

Deviation (BS EN 60359) / difference. / error. The difference between a single analyser result indication and the laboratory reference test result (or certified reference material value) when sampling an identical test material. Analyser result minus the accepted reference value.

Estimated average / estimated mean. Average or expected value of a characteristic in a limited number of samples/results from within a larger population of all results. Sum of the result values divided by the number of samples/results.

Level of confidence (ASTM E456). A value expressed as a percentage representing the probability associated with a confidence interval. Probability of a measured value being within stated confidence limits.

Lower control limit (ASTM E456). Minimum value boundary of the control chart statistic that indicates statistical control.

Lower warning limit. Minimum value boundary of the control chart statistic that indicates statistical control.

Measurement uncertainty / overall analyser uncertainty. The sum of all of uncertainty components affecting an analyser result. Uncertainty expressed in the units of measurement. The extent of the confidence limits. Confidence limits are generally plus or minus one confidence interval. Generally two standard deviations, equivalent to a level of confidence of 95%. The level of confidence should be recorded along with any quoted uncertainty value.

Normal (Gaussian) distribution (NPL G11). Result values from individual readings, measuring the same property or concentration, are most likely to be near the average value of a significant number of such readings. The highest and lowest values are the least likely to occur.

Performance action limit. Condition derived from the control chart that requires action. A value exceeds the Upper or Lower Control limit or a series of values exhibit a pattern that indicates drift, bias, or a particular recognised analyser fault.

Precision (ASTM E456). The closeness of agreement between independent test results obtained under stipulated conditions. The degree of agreement between measurements of the same property or concentration expressed in terms of the dispersion of test results around their arithmetic mean.

Random error (ASTM E456). A part of the error that in the course of a number of test results remains constant or varies in an unpredictable way.

Repeatability (ASTM E456) / repeatability conditions (ASTM E456). Precision obtained where independent test results are obtained with the same