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Water quality — On-line sensors/analysing equipment for water — Specifications and performance tests

Qualité de l'eau — Matériel d'analyse/capteurs directs pour l'eau — Spécifications et essais de performance

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 15839 was prepared by Technical Committee ISO/TC 147, *Water quality*.

Water quality — On-line sensors/analysing equipment for water — Specifications and performance tests

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

This International Standard describes the performance testing of on-line sensors/analysing equipment for water. The standard is applicable to most sensors/analysing equipment, but it is recognized that, for some sensors/analysing equipment, certain performance tests cannot be carried out. This International Standard

- defines an on-line sensor/analysing equipment for water quality measurements;
- defines terminology describing the performance characteristics of on-line sensors/analysing equipment;
- specifies the test procedures (for laboratory and field) to be used to evaluate the performance characteristics of on-line sensors/analysing equipment.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 6879:1995, *Air quality — Performance characteristics and related concepts for air quality measuring methods*

ISO 8466-1:1990, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO/TR 13530:1997, *Water quality — Guide to analytical quality control for water analysis*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
accepted reference value
value that serves as an agreed reference value for comparison, and which is derived as:

a) an assigned or certified value based on experimental work of some national or international organization;

b) a consensus or certified value based on collaborative experimental work;

c) a theoretical or established value based on scientific principles;

d) when a), b) and c) are not available, the expectation of the (measurable) quantity, i.e. the mean of a number of measurements.

[Adapted from ISO 5725-1:1994]

3.2
accuracy
closeness of agreement between a measured value and the accepted reference value

NOTE The term accuracy, when applied to a set of measured values, involves a combination of random components and a common systematic error or bias component.

[Adapted from ISO 5725-1:1994]

3.3
analytical chain
set of instruments and actions covering all the steps involved in determining a reference value in a field test, including sampling, fractioning, conditioning, storage and transportation of the sample to the laboratory for analysis

3.4
availability
⟨measurement chain⟩ percentage of the full measurement period during which the measurement chain is available for making measurements

NOTE The full measurement period is the period which includes all specified automatic or manual maintenance operations at least once

cf. **up-time** (3.42)

3.5
bias
consistent deviation of the measured value from an accepted reference value

NOTE Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value.

[Adapted from ISO 5725-1:1994]

3.6
blank solution
solution, free of determinand, to which the on-line sensor/analysing equipment is exposed in the same way as calibration or sample solutions

NOTE The value of the measurement is known as the “blank value”.

3.7
calibration solution
solution containing a substance or mixture of substances giving a defined value of the determinand and used for calibration of the on-line sensor/analysing equipment

cf. **reference material** (3.30)

3.8
calibration procedure
set of operations that establishes, under specified conditions, the relationship between the amount or quantity of calibrant and the response indicated by the on-line sensor/analysing equipment

3.9
coefficient of variation
ratio of the standard deviation of the on-line sensor/analysing equipment to the mean of the working range of the equipment

[Adapted from ISO 8466-1:1990]

3.10
day-to-day repeatability
precision under day-to-day repeatability conditions

3.11
day-to-day repeatability conditions
conditions whereby 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 and reagents over several days

3.12
delay time
time interval between the instant when the on-line sensor/analysing equipment is subjected to an abrupt change in determinand value and the instant when the readings pass (and remain beyond) 10 % of the difference between the initial and final value of the abrupt change

NOTE For on-line sensor/analysing equipment with a sample-handling system the delay time frequently depends on the time needed to convey the sample from the sampling point to the analyser inlet.

cf. **response time** (3.33)

3.13
determinand
property/substance that is required to be measured and to be reflected by/present in a calibration solution

3.14
fall time
difference between the response time and the delay time when the abrupt change in determinand value is negative

cf. **delay time** (3.12) and **response time** (3.33)

3.15
interference
undesired output signal caused by a property(ies)/substance(s) other than the one being measured

[ASTM D 3864-96]

3.16
interferent
component of the sample, excluding the determinand, that affects the output signal

3.17
limit of detection
LOD
lowest value, significantly greater than zero, of a determinand that can be detected

3.18
limit of quantification
LOQ
lowest value of a determinand that can be determined with an acceptable level of accuracy and precision

3.19
linearity
condition in which measurements made on calibration solutions having determinand values spanning the stated range of the on-line sensor/analysing equipment have a straight-line relationship with the calibration solution determinand values

3.20
long-term drift
slope of the regression line derived from a series of differences between reference and measurement values obtained during field testing, expressed as a percentage of the working range over a 24 h period

3.21
lowest detectable change
LDC
smallest significantly measurable difference between two measurements

3.22
period between maintenance operations
time between successive maintenance operations on the measurement chain

NOTE The shortest period between maintenance operations will typically be of the order of a few hours (between two automatic rinse operations). The longest period between maintenance operations will typically be of the order of a few months (between services).

3.23
measurement
mean value of at least 10 consecutive readings

cf. **reading** (3.29)

3.24
measurement chain
set of instruments and actions that covers all the steps involved in measuring a determinand, including the on-line sensor/analysing equipment, sampling and pretreatment, transportation and storage of the sample

3.25
memory effect
temporary or permanent dependence of readings on one or several previous values of the determinand

[Adapted from ISO 6879:1995]

3.26
on-line sensor/analysing equipment
automatic measurement device which continuously (or at a given frequency) gives an output signal proportional to the value of one or more determinands in a solution which it measures (see Annex B)

3.27
performance characteristics
set of parameters describing the performance of the on-line sensor/analysing equipment and measurement chain

3.28
precision
the closeness of agreement between independent measured values obtained under stipulated conditions

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results. Less precision is reflected by a larger standard deviation.

[Adapted from ISO 5725-1:1994]

3.29
reading
manual or automatic registration of the on-line sensor/analysing equipment response

NOTE Readings are taken with a frequency which depends on the dynamics of the on-line sensor/analysing equipment (i.e. on the response time — see 3.33 and 5.1.2).

3.30
reference material
substance, or mixture of substances, the composition of which is known within specified limits, and one or more of the properties of which is sufficiently well established, over a stated period of time, to be used for the calibration of an instrument or the assessment of a measurement method

3.31
repeatability
precision under repeatability conditions

[ISO 5725-1:1994]

3.32
repeatability conditions
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 and reagents within short intervals of time (e.g. one day)

[Adapted from ISO 5725-1:1994]

cf. **day-to-day repeatability conditions** (3.11)

3.33
response time
time interval between the instant when the on-line sensor/analysing equipment is subjected to an abrupt change in determinand value and the instant when the readings cross the limits of (and remain inside) a band defined by 90 % and 110 % of the difference between the initial and final value of the abrupt change (see 5.2.1)

NOTE In laboratory testing, the response time of the on-line sensor/analysing equipment is measured. In field testing, it is the whole measurement chain which is tested.

3.34
rise time
difference between the response time and the delay time when the abrupt change in determinand value is positive

cf. **response time** (3.33)

3.35
ruggedness
on-line sensor/analysing equipment stability when the equipment is subjected to different environmental conditions which could possibly affect its performance

NOTE Ruggedness also describes the behaviour of the equipment in the hands of different operators who will inevitably introduce small variations in operations such as calibration and maintenance which may or may not have a significant influence on performance.

3.36
selectivity
extent to which the on-line sensor/analysing equipment can determine a particular determinand in a complex mixture without interference from the other components in the mixture

NOTE On-line sensor/analysing equipment which is perfectly selective for a determinand is said to be specific.

3.37
short-term drift
slope of the regression line derived from a series of measurements carried out on the same calibration solution during laboratory testing, and expressed as a percentage of the measurement range over a 24 h period

3.38
signal
conveyor of information about one or more determinands

NOTE An input signal is a signal applied to the on-line sensor/analysing equipment. An output signal is a signal delivered by the equipment.

3.39
stated range
range covered by the on-line sensor/analysing equipment as stated by the manufacturer/supplier

3.40
test procedure
series of measurements performed to determine the value of a performance characteristic

3.41
test bench
test facilities which are necessary to test on-line sensor/analysing equipment or a complete measurement chain

3.42
up-time
⟨measurement chain⟩ percentage of a full measurement period during which the measurement chain is actually measuring during field testing

cf. **availability** (3.4)

3.43
working range
range between the lowest and highest determinand value for which tests to determine precision and bias have been carried out

4 Determining on-line sensor/analysing equipment performance characteristics — An overview

Determination of the performance characteristics of on-line sensors/analysing equipment has, for practical reasons, to be divided into two parts: a laboratory test under controlled conditions and a field test under real-life conditions. However, the route followed in each of the tests, and the information/materials needed, can be described with the same diagram as shown in Figure 1.

The manufacturer/supplier who provides the on-line sensor/analysing equipment will also provide relevant information concerning operation of the equipment as indicated in Annex A. Based on the equipment properties and the different needs of measurement chains as given in Annex B, the appropriate test bench facilities shall be constructed (recommendations for this are given in Annex C).

After construction of the test bench facilities, a preliminary determination of the sensor/analysing equipment response time shall be carried out, providing information necessary for the timing of measurements. The performance characteristics shall be determined in accordance with the test procedures given in Clauses 5 and 6. The test schedule shall take into account the automatic and/or manual maintenance of the sensor/analysing equipment (see Annex D for an example). Finally, a test report shall be written (see Annex E for examples).

Use of the guidelines outlined in ISO/TR 13530 will ensure that the precision of the results of the laboratory tests is sufficiently high. During testing, use only reagents of recognized analytical grade.

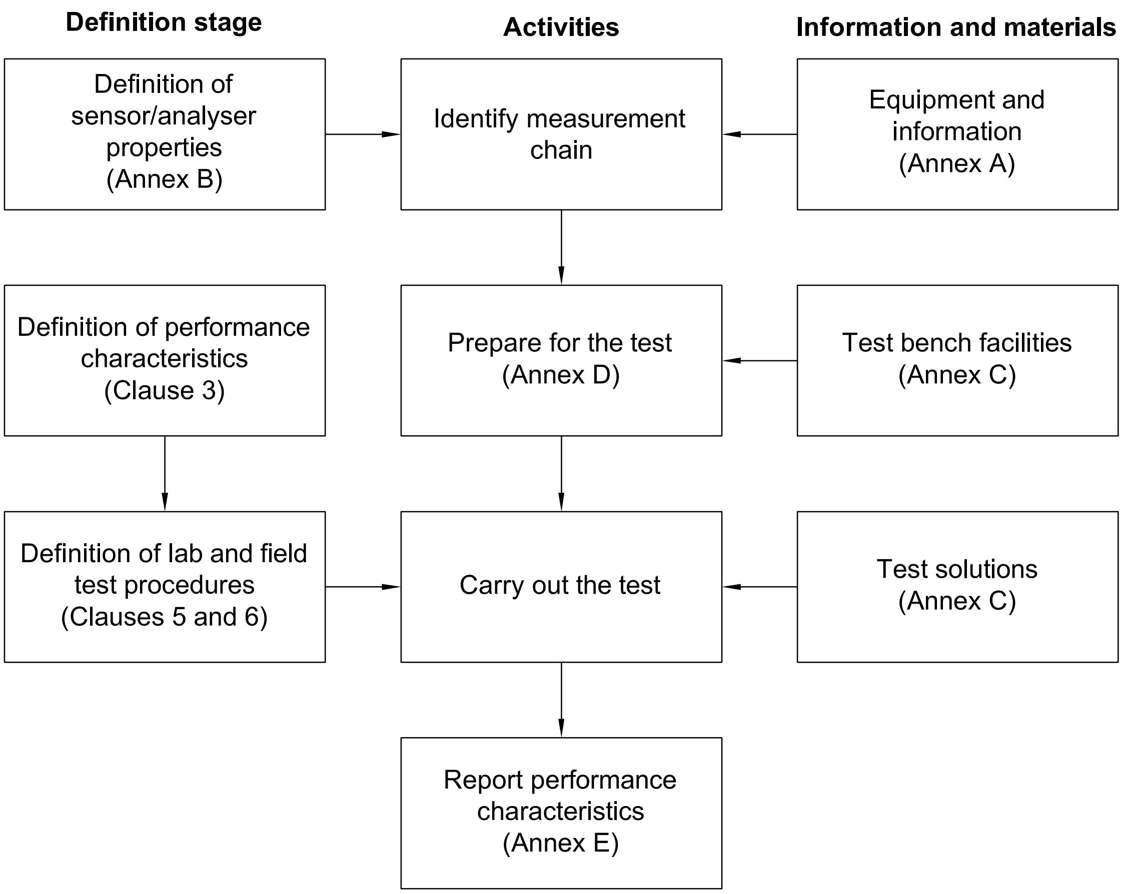


Figure 1 — Overview of test

5 Determination of performance characteristics in the laboratory

5.1 Preparation for the test

5.1.1 Equipment

The test bench facilities (see Annex C) may be different for different on-line sensors/analysing equipment. However, the following conditions shall be fulfilled for all on-line sensors/analysing equipment:

— The test bench facilities shall match the requirements specified for the sensor/analysing equipment by the manufacturer/supplier.

— The facilities shall include the ability to record (manually or automatically) readings of the sensor/analysing equipment in analog or digital form.

— Where appropriate, it shall be possible to change the calibration solution determinand value measured by the sensor/analysing equipment within less than 10 % of the response time declared by the manufacturer/supplier. (Typical examples where this is not appropriate are the determination of turbidity and electrical conductivity.)

— The facilities shall include laboratory instruments for analysis of the required determinand(s). The methods used and their precision shall be reported (see Annex E).

After receipt of the on-line sensor/analysing equipment to be tested, set up the sensor/analysing equipment together with the appropriate test bench facilities. Report the details of the test set-up (see Annex E). Use and maintain the sensor/analysing equipment in accordance with the instructions given by the manufacturer/supplier. Before testing is started, prepare a test schedule taking the measurement and maintenance periods into account (see Annex D).

5.1.2 Determination of details of measurement procedure

The working range used shall be within the declared working range. Carry out a preliminary determination of the sensor/analysing equipment response time by changing from one calibration solution to another, thus inducing an abrupt change. The calibration solutions used for this shall have determinand values of approximately 20 % and 80 %, respectively, of the working range. (A typical example where this is not appropriate is the determination of dissolved oxygen).

Expose the sensor/analysing equipment to the first calibration solution for a period equal to at least five times the response time declared by the manufacturer/supplier before changing to the second calibration solution. After the changeover, expose the sensor/analysing equipment to the second solution for the same length of time. During these two periods and the changeover, record the readings of the sensor/analysing equipment. The frequency at which readings are taken shall be at least 20 readings for each period corresponding to the response time as declared by the manufacturer/supplier.

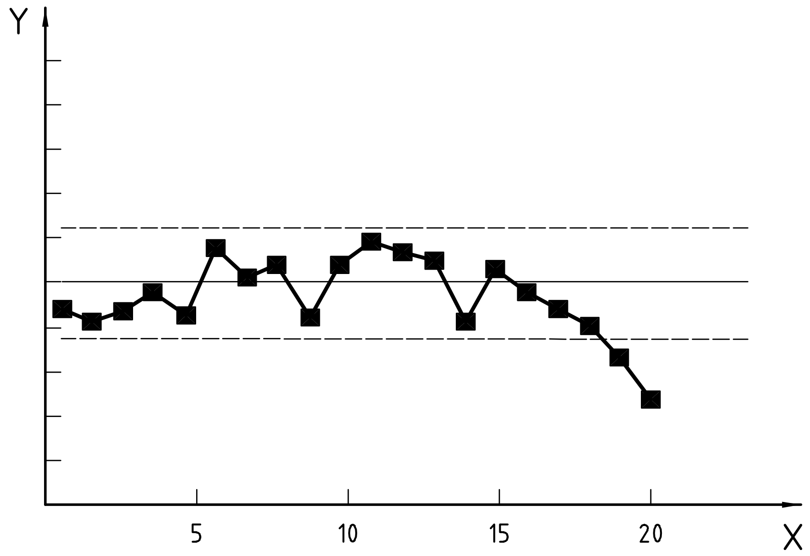
From the record of the readings, determine the preliminary response time as described in 5.2.1. The time interval between readings in the subsequent laboratory test shall be approximately 10 % of the preliminary response time. A measurement shall consist of the mean of ten consecutive readings of the sensor/analysing equipment output signal after the signal has become stable, e.g. after a period equal to three times the preliminary response time.

To be sure that the calibration solutions have remained stable during the test, analyse samples of the calibration solutions before and after each test. No significant difference shall be found.

5.1.3 Monitoring the test

Although sensor/analysing equipment malfunction may be indicated automatically by the equipment's own diagnostic system, monitor the general performance of the sensor/analysing equipment during the test using a response chart (Figure 2). At least once a day during the test, carry out a measurement on one of the calibration solutions (the same strength solution each time).

Plot the measurements on a response chart, along with agreed limits. If the sensor/analysing equipment fails to comply with the limits, contact the manufacturer/supplier. Include the response chart, and details of any corrective action taken, in the test report.



Key

X measurement No.

Y determinand value

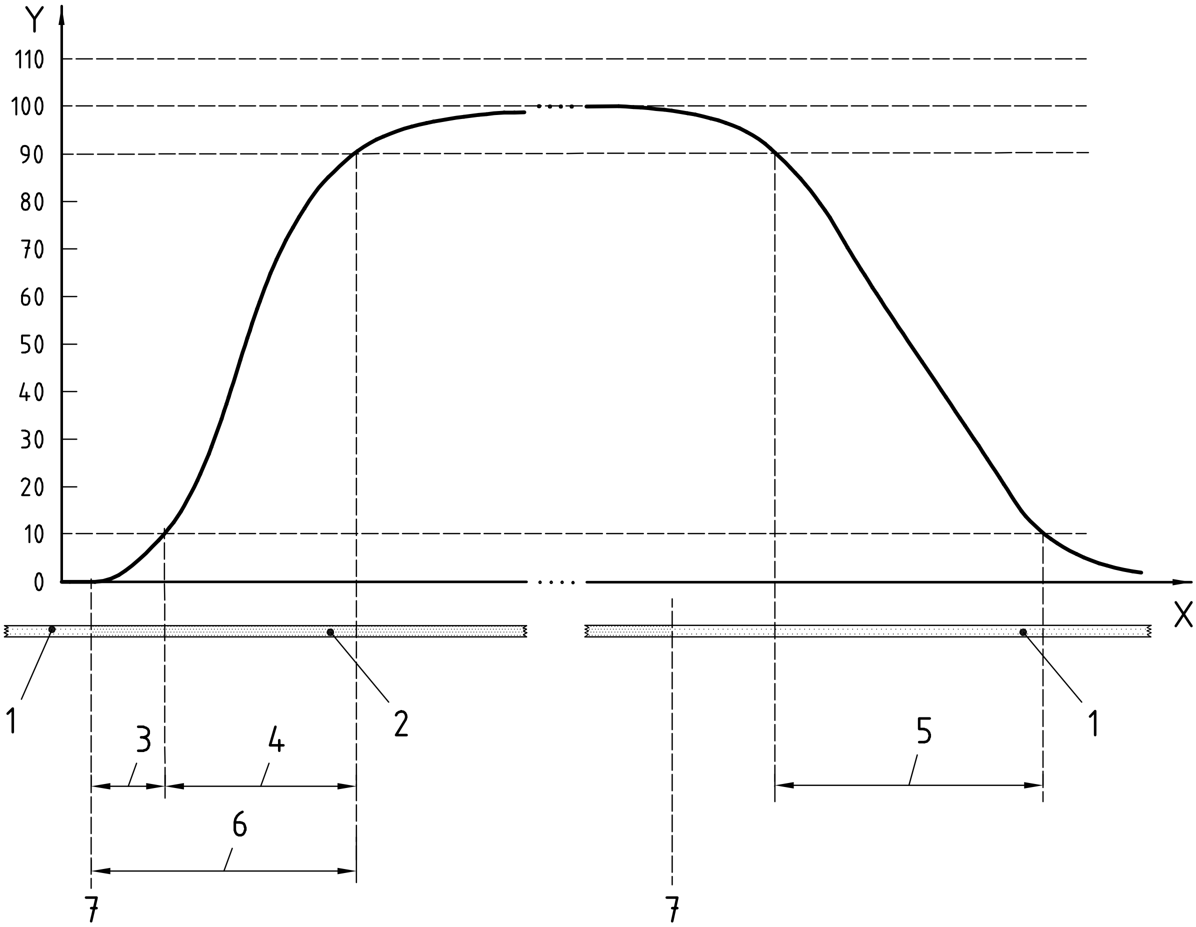
Figure 2 — Response chart

5.2 Test procedure

5.2.1 Response times, delay times and rise and fall times

Response times, delay times and rise and fall times are derived from the record of readings made when the calibration solution to which the sensor/analysing equipment is exposed is changed. In the laboratory, the results apply directly to the sensor/analysing equipment, because no external sampling/sample preparation systems, which might be necessary for field applications, are used.

Figure 3 illustrates the four different periods for an idealized record of readings made with a continuous-reading system. If the response curve is asymmetric, the rise time and fall time may be different, i.e. the sensor/analysing equipment may have different response and delay times for positive and negative changes.



Key

X time

Y response (%age of value of abrupt change)

1 test solution (20 %)

2 test solution (80 %)

3 delay time

4 rise time

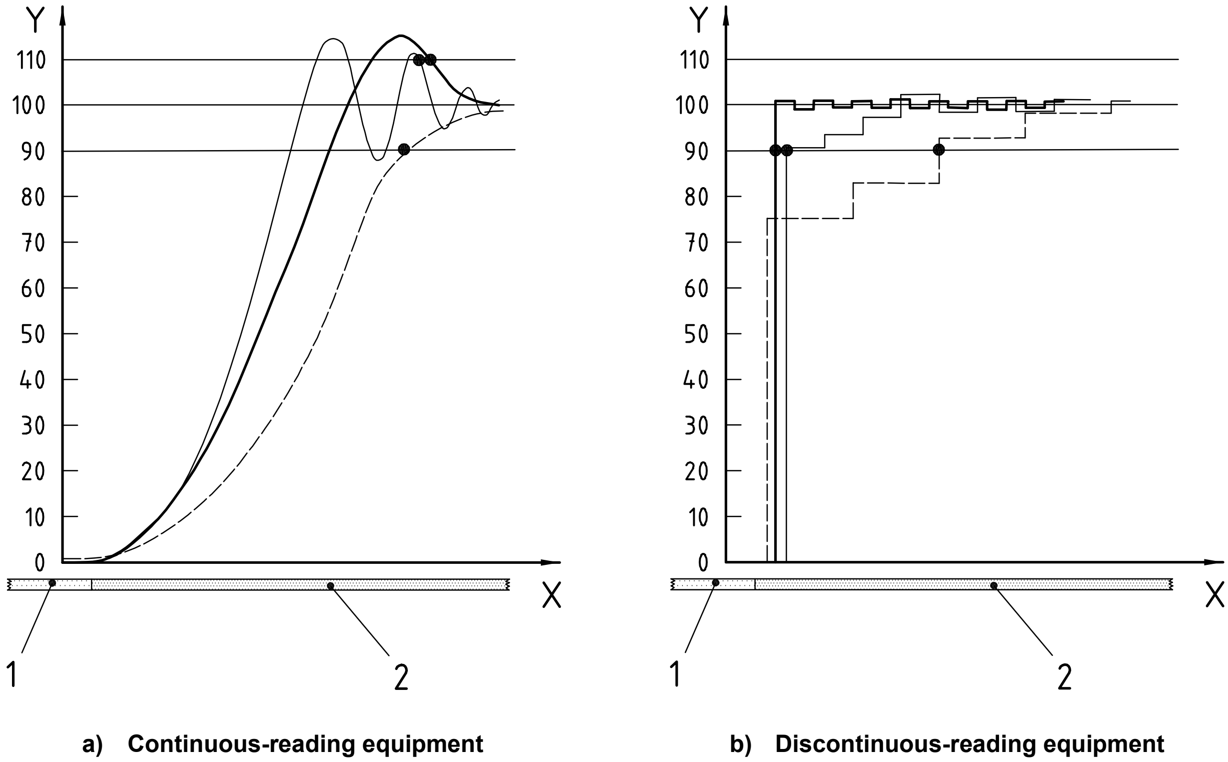
5 fall time

6 response time

7 change

Figure 3 — On-line sensor/analysing equipment response to an abrupt change in determinand value

Figure 4 shows typical responses from real sensors/analysing equipment to a positive change and indicates the correct way of determining the response time. Continuous-reading systems may give curves which differ from the idealized curve in Figure 3, in which case the curve usually takes the form of an oscillating response. Discontinuous-reading systems will always have a response time equal to or longer than the analysis time, longer response times being caused by a carryover effect or by the fact that sampling and the change of calibration solutions are not carried out simultaneously. The shortest response time is therefore obtained by synchronizing the change of calibration solutions with sampling by the sensor/analyser equipment.



Key

X time

Y response (%age of value of abrupt change)

1 test solution (20 %)

2 test solution (80 %)

Figure 4 — Determination of the response time $t_{Response}^{+}$ from recorded readings
(the points on the graphs indicate the response times determined)

Prepare two calibration solutions with determinand values of 20 % and 80 % of the working range. Start the test procedure by exposing the on-line sensor/analysing equipment to the 20 % solution for a period equal to three times the preliminary response time, and then changing to the 80 % solution. Three preliminary response times after the changeover, change back to the 20 % solution. Repeat the procedure six times, recording the readings throughout.

Table 1 — Data sheet for recording response times and delay times

Sequence No.	1	2	3	4	5	6
Response time for positive change, $t_{Response}^{+}$						
Delay time for positive change, t_{Delay}^{+}						
Response time for negative change, $t_{Response}^{-}$						
Delay time for negative change, t_{Delay}^{-}						

From the readings, determine (for i = 1 to 6) the values of $(t_{Response}^{+})_i$, $(t_{Response}^{-})_i$, $(t_{Delay}^{+})_i$ and $(t_{Delay}^{-})_i$, as indicated in Table 1. Calculate each rise time as $(t_{Response}^{+})_i - (t_{Delay}^{+})_i$ and each fall time as $(t_{Response}^{-})_i - (t_{Delay}^{-})_i$. Report the final result for each of the characteristics as the mean value of the determined/calculated values together with the standard deviation.

5.2.2 Linearity, coefficient of variation, limit of detection, limit of quantification, repeatability, lowest detectable change, bias, short-term drift and day-to-day repeatability

The test procedures to be carried out to determine the linearity, coefficient of variation, limit of detection, limit of quantification, repeatability, lowest detectable change, bias, short-term drift and day-to-day repeatability of performance characteristics are summarized in Table 2, which includes all the measurements necessary to calculate these performance characteristics, and in Table 3 which indicates the uses of the measurements and the constraints to be respected when scheduling the test.

Table 2 — Data sheet for linearity, coefficient of variation, limit of detection, limit of quantification, repeatability, lowest detectable change, bias, short-term drift and day-to-day repeatability

i	x_i	$y_{i,1}$	$y_{i,2}$	$y_{i,3}$	$y_{i,4}$	$y_{i,5}$	$y_{i,6}$
1	5						
2	20						
3	35						
4	50						
5	65						
6	80						
7	95						

where

i is the determinand value level;

x_i is the value of the determinand in the ith calibration solution, expressed as a percentage of the working range;

$y_{i,j}$ is the jth measurement of the determinand value x_i, expressed in units of x.

Table 3 — Use of measurements and constraints on scheduling

i	x_i	**Determinand level used for**	**To be measured**
1	5	LOD, LOQ	On the same day separated by blanks
2	20	Repeatability, LDC, bias	On the same day separated by blanks
3	35	Day-to-day repeatability	On different days
4	50	Short-term drift	Equally distributed over shortest period between maintenance operations
5	65	Day-to-day repeatability	On different days
6	80	Repeatability, LDC, bias	On the same day separated by blanks
7	98	Linearity check only	On the same day separated by blanks
$y_{i,1}$	Measurements used for linearity check and determination of coefficient of variation		

Prepare eight calibration solutions covering the working range at determinand values of 0 % (blank), 5 %, 20 %, 35 %, 50 %, 65 %, 80 % and 95 %, using appropriate volumes as required by the on-line sensor/analysing equipment. Ensure adequate mixing. Expose the on-line sensor/analysing equipment to the 5 %, 20 %, 35 %, 50 %, 65 %, 80 % and 95 % solutions, with the blank solution between each and, after the signal has become stable, carry out the measurements in accordance with Tables 2 and 3.

Linearity

Check for linearity in accordance with ISO 8466-1 using the data set $(x_i, y_{i,1})$ where i = 1 to 7.

Coefficient of variation

Calculate the coefficient of variation in accordance with ISO 8466-1 using the data set $(x_i, y_{i,1})$ for i = 1 to 7. Express the result as a percentage. It can be compared to coefficients of variation of other on-line sensor/analysing equipment.

Limit of detection (LOD)

Calculate the limit of detection as three times the standard deviation of the measurements $y_{1,j}$ for j = 1 to 6.

Limit of quantification (LOQ)

Calculate the limit of quantification as ten times the standard deviation of the measurements $y_{1,j}$ for j = 1 to 6.

Repeatability

Determine the repeatability for both high and low determinand values and report as two different results (subscripts 20 and 80, respectively) calculated as the standard deviation of the measurements $y_{2,j}$ for j = 1 to 6 and of the measurements $y_{6,j}$ for j = 1 to 6.

Lowest detectable change (LDC)

Determine the lowest detectable change for both high and low determinand values and report as two different results (subscripts 20 and 80, respectively) calculated as three times the standard deviation of the measurements $y_{2,j}$ for j = 1 to 6 and of the measurements $y_{6,j}$ for j = 1 to 6.

Bias

Determine the bias for both high and low determinand values and report as two different results (subscripts 20 and 80, respectively) calculated as the difference between the mean value of the measurements $y_{2,j}$ for j = 1 to 6 and the value of x_2, and as the difference between the mean value of the measurements $y_{6,j}$ for j = 1 to 6 and the value of x_6.

Short-term drift

Determine the short-term drift in the middle of the working range, calculated as the slope of the regression line for the data set $(t_j, y_{4,j})$ for j = 1 to 6, where t_j corresponds to measurements equally distributed over the shortest time period between any maintenance operations (e.g. rinsing, autocalibration, etc.). Express the result as a percentage of the working range over a 24 h period.

Day-to-day repeatability

Determine the day-to-day repeatability both in the upper half and in the lower half of the working range and report as two different results (subscripts 65 and 35, respectively) calculated as the standard deviation of the measurements $y_{3,j}$ for j = 1 to 6 and of the measurements $y_{5,j}$ for j = 1 to 6.

5.2.3 Memory effect

The memory effect in on-line sensor/analysing equipment is typically observed as a saturation effect caused by the fact that a determinand value is well above the working range of the equipment. Memory effect can either be temporary or permanent, but in both cases the fall time after the equipment has experienced a peak determinand value above its working range will be increased. If the memory effect is a permanent one, it will typically introduce a positive offset in the equipment.

Expose the on-line sensor/analysing equipment to a calibration solution with a determinand value of 200 % of the working range for a period equal to five times the response time, and then change to a 20 % calibration solution. Three response times after the changeover, carry out a measurement. Repeat this procedure six times (see Table 4). Between the peak loads, bring the equipment back to a memory-effect-free state.

Table 4 — Data sheet for memory effect

x	y_1	y_2	y_3	y_4	y_5	y_6
20						

Report the memory effect as the difference between the mean value of the six measurements y_j for j = 1 to 6 and the determinand value of the 20 % calibration solution (i.e. 20). The on-line sensor/analysing equipment is said to have a memory effect if the calculated value is bigger than the lowest detectable change (LDC_{20}).

5.2.4 Interference

Information on interferents affecting the performance of the on-line sensor/analysing equipment shall be obtained from knowledge and experience relevant to the nature of the water and the determinand (i.e. literature, manufacturer/supplier statements, etc.). Possible interferents and the expected interference levels shall be reported. If several interferents are identified, check the interference level of at least two by spiking the 20 % and 80 % calibration solutions with increasing concentrations of the interferent, as follows:

Expose the on-line sensor/analysing equipment to the 20 % calibration solution spiked with interferent at 0 %, 25 %, 50 %, 75 %, 100 %, 125 %, etc., of the expected interference level. Perform a measurement at each spiking level (see Table 5), stopping this stepwise procedure when the difference between the reading at the actual spiking level and the reading without spiking is bigger than the lowest detectable change (LDC_{20}). Report the last spiking level as the interference level for the interferent tested. Repeat the procedure for the 80 % calibration solution using LDC_{80} as the threshold value.

Table 5 — Data sheet for interference

Calibration solution	**Interferent No.**	**Interferent concentration** % of expected interference level							
		0	**25**	**50**	**75**	**100**	**125**	**150**	**etc.**
20 %	1								
80 %	1								
20 %	2								
80 %	2								
20 %	3								
80 %	3								

5.2.5 Environmental and operating conditions

Information on the required environmental and operating conditions, such as the upper and/or lower limits for the ambient temperature, the time between calibrations, the time between cleaning, the stability of the sample supply and the stability of the power supply, can usually be found in manufacturer/supplier literature. All these requirements shall be reported and at least two shall be checked in order to verify the ruggedness of the on-line sensor/analysing equipment with respect to them.

Expose the on-line sensor/analysing equipment to the 50 % calibration solution and carry out a measurement under conditions of “best compliance” with the requirement. Increase/decrease the requirement being checked to its limit and perform a new measurement on the 50 % calibration solution (see Table 6). If the difference between these two measurements is less than the lowest detectable change (mean of LDC_{80} and LDC_{20}), the equipment is said to be compliant with the stated requirement. If the difference is bigger than the lowest detectable change, the equipment is said to be non-compliant with the stated requirement and the difference between the two measurements shall be reported.

Table 6 — Data sheet for environmental and operating conditions

Calibration solution	Requirement No.	Requirement level		
		Neutral	Upper	Lower
50 %	1			
50 %	2			
50 %	3			

6 Determining performance characteristics in the field

6.1 Preparation for field tests

6.1.1 General

Field testing is complementary to laboratory testing and shall include the whole measurement chain consisting of the on-line sensor/analysing equipment and all the necessary sampling, pumping and conditioning devices. The aim of field testing is to determine (in terms of months) the long-term ability of a measurement chain to produce reliable measurements.

Field tests are considered as site-specific in terms of the sample's dynamic range and the nature of the water, and event-dependent with respect to the environmental conditions. Therefore, the operating conditions as stated by the manufacturer/supplier shall be adhered to throughout the test, and the performance characteristics determined shall always be stated in conjunction with details of the test site and the actual operating conditions during the test.

Comparison of different on-line sensors/analysing equipment is only possible at the same time and under the same conditions. Furthermore, the length of the test period shall be based on operational, practical and economic considerations.

6.1.2 Equipment

The test bench facilities (see Annex C) may be different for different measurement chains (see Annex B). However, the following requirements shall be met for all measurement chains.

— The test bench facilities shall match the requirements specified for the measurement chain by the manufacturer/supplier.

— The facilities shall include the ability to record (manually or automatically) readings of the sensor/analysing equipment in analog or digital form.

— The facilities shall include the ability to produce representative samples for laboratory analysis. The sampling procedures used shall be reported.

— Where appropriate, it shall be possible to change the calibration solution determinand value measured by the sensor/analysing equipment within less than 10 % of the response time determined in laboratory testing. (Typical examples where this is not appropriate are the determination of turbidity and electrical conductivity.)

— The facilities shall include laboratory instruments for analysis of the required determinand(s). The methods used and their precision shall be reported (see Annex E).

After receipt of the items included in the measurement chain, the measurement chain shall be set up together with the appropriate test bench facilities and subsequently calibrated and maintained in accordance with the routines recommended by the manufacturers/suppliers. Details of the set-up shall be reported (see Annex E). Before testing is started, a test schedule shall be prepared taking the measurement and maintenance periods into account (see Annex D) and adhered to throughout the test.

6.1.3 Determination of the measurement procedure

As it is the measurement chain — and not only the on-line sensor/analysing equipment — that is under test, determinand reference values shall represent the true values of the determinand just before measurement. Determinand reference values shall be determined at least every second day during the test period.

The timing of measurements made by the measurement chain (10 consecutive readings taken at the same frequency as in laboratory testing) shall be synchronized with the sampling undertaken for the laboratory determination of the reference values (i.e. taking the response time of the measurement chain into account, see 6.2.1).

A preliminary response time shall be determined three times during the first two days of testing, using the procedure described in 6.2.1. This preliminary value shall be used for the timing of the measurements and updated during the test by the results obtained from 6.2.1.

The procedures used to determine the precision of the reference values shall be well documented and meticulously carried out.

6.1.4 Monitoring the test

Malfunctioning of the measurement chain may be indicated by the on-line sensor/analysing equipment's internal diagnostic system, the blockage of sample pretreatment units, the breakdown of pumps, etc. However, in all cases, the malfunction will be demonstrated by significant differences between the measurements and the reference values (see Table 7).

The general performance of the measurement chain shall therefore be monitored. The relative or absolute difference between the measurements and the reference values shall be plotted on a response chart along with agreed limits. The relative difference shall be used if the typical value of the determinand at the test site is larger than 20 % of the working range of the on-line sensor/analysing equipment, otherwise the absolute difference shall be used. Only measurements within the chosen part of the working range shall be used.

If the measurement chain fails to comply with the limits, the manufacturer/supplier shall be contacted. The response chart and the actions taken shall form part of the report, and the cause of non-compliance shall also be recorded (see also 6.2.4).

Table 7 — Data sheet for reference values and measurements

i	Date	Time	x_i	y_i
1				
2				
3				
4				
n				

where

i is the data set No.;

n is the number of data sets (not less than 30);

x_i is the ith reference value of the determinand;

y_i is the ith measurement value of the determinand.

6.2 Procedures for field testing

6.2.1 Response time, delay time, rise time and fall time

The response times, delay times and rise and fall times of the measurement chain shall be derived from readings taken before, during and after an abrupt change in the determinand value of the real sample introduced into the measurement chain (see Annex C).

This change shall be such that it brings the determinand value up to approximately 80 % of the working range and the determinand value shall remain at this level until the readings are stable, whereupon spiking shall be stopped. This procedure shall be repeated six times during the test period (twice just before maintenance operations, twice after maintenance operations and twice in between maintenance operations, Table 8).

Table 8 — Data sheet for response times, delay times, rise time and fall time

Spike No.	1	2	3	4	5	6
Response time for positive change, $t_{Response}^{+}$						
Delay time for positive change, t_{Delay}^{+}						
Response time for negative change, $t_{Response}^{-}$						
Delay time for negative change, t_{Delay}^{-}						

Determine/calculate the different times (a plus sign indicating a positive change and a minus sign indicating a negative change) as described in 5.2.1 and report the final result for each of the characteristics as the mean value of the determined/calculated values together with the standard deviation.

6.2.2 Bias

Determine the bias as the mean of the differences calculated in 6.1.4 (i.e. the mean of the values plotted in the response chart). Continue the test until at least 30 measurements have been obtained within the chosen part of the working range. Report the bias together with the range chosen (i.e. whether relative or absolute differences were used). Measurements below the limit of quantification as determined in laboratory testing shall not be taken into account.

6.2.3 Long-term drift

Determine the long-term drift as the slope of the linear regression performed on the differences calculated in 6.1.4 as a function of time (i.e. the regression line which can be drawn on the response chart). Express the result as a percentage of the working range over a 24 h period.

6.2.4 Availability and up-time

Calculate the equipment availability from the equation:

$$\text{Availability} = 100 \times \left(1 - \frac{\sum t_{\text{Scheduled stop time}}}{t_{\text{Total}}} \right)$$

where

$t_{\text{Scheduled stop time}}$ includes all stops for manual and/or automatic maintenance stated by the manufacturer/supplier as being necessary for reliable operation of the measurement chain (see Annex D);

t_{Total} covers the whole period during which maintenance is necessary.

EXAMPLE 1 A measurement chain requires the following scheduled manual and/or automatic maintenance operations:

M1 automatic rinsing every 6 h, duration 20 min;

M2 automatic calibration every day, duration 40 min;

M3 manual cleaning of filter unit every week, duration 2 h (120 min);

M4 reagent renewal every 4 weeks, duration 60 min.

Based on these figures, the availability is:

$$100 \times \left[1 - \frac{(4 \times 7 \times 4 \times 20) + (4 \times 7 \times 40) + (4 \times 120) + 60}{4 \times 7 \times 24 \times 60} \right] = 90,3\ \%$$

Calculate the up-time as:

$$\text{Up-time} = 100 \times \left(1 - \frac{\sum t_{\text{Measured stop time}}}{t_{\text{Total}}} \right)$$

where $t_{\text{Measured stop time}}$ is a measure of the time used for scheduled and unscheduled automatic or manual maintenance of the measurement chain during the test period. Breakdown of parts of the measurement chain and the time needed to repair these shall not be included in the calculation. However, all such events shall be reported.

EXAMPLE 2 During the operation of a measurement chain, the following measurements were made of the scheduled and unscheduled manual and/or automatic maintenance operations:

M1 automatic rinsing every 6 h, duration 20 min;

M2 automatic calibration every day, duration 45 min;

M3 manual cleaning of filter unit every week, duration 4 h (240 min);

M4 reagent renewal every 4 weeks, duration 60 min.

Based on these figures, the up-time of the measurement chain is:

$$100 \times \left[1 - \frac{(4 \times 7 \times 4 \times 20) + (4 \times 7 \times 45) + (4 \times 240) + 60}{4 \times 7 \times 24 \times 60} \right] = 88{,}8\ \%$$

Compare the up-time and availability. The availability is a preliminary estimate of the up-time at the start of the test. If the up-time is significantly different from the availability, a new maintenance schedule shall be proposed.

Annex A
(informative)

Manufacturer/supplier information

The manufacturer/supplier should be invited to inspect the condition of the sensor/analysing equipment prior to testing to discuss technical details of their equipment. In addition, the manufacturer/supplier should be invited to inspect the installation of their equipment prior to the start of the formal test period. At this time, any modifications to the installation should be discussed.

Prior to the start of the formal laboratory and field test period, the manufacturer/supplier should be allowed to make final adjustments to their instruments. The manufacturer/supplier should not be allowed to visit the test facility during testing without prior agreement.

The manufacturer/supplier should provide, at least, the following information (indicated in Table A.1) required to set up and perform the laboratory and field test of the on-line sensors/analysing equipment and the possible measurement chains they may be a part of. Furthermore, the manufacturer/supplier should provide other information material such as manuals and specification sheets.

Table A.1 — On-line sensor/analysing equipment information

Stated range(s):	Response time:
Signal output(s):	
Known interferences:	
Environmental requirements:	
Maintenance requirements:	
Brief description of sensor/analysing equipment:	
Suggested equipment to be used for sampling/pretreatment of sample (if any):	
Other information:	

Annex B
(informative)

On-line measurement chains

The requirements of an on-line measurement chain can be defined as a combination of the properties of the on-line sensor/analysing equipment. These properties are shown in Table B.1.

Table B.1 — On-line sensor/analysing equipment properties

	Property	Examples
1	Location of sensor	On-line, in-line, off-line, *in situ*, etc.
2	Sampling	External sampling, no external sampling
3	Sample pretreatment	No treatment, filtration, sedimentation, centrifuging, etc.
4	Principle of measurement	Continuous, batch, etc.
5	Measurement method	Photometric, colorimetric, enzymatic, titrimetric, etc.
6	Number of determinands	One, several
7	Need for supplies	Consumables needed, no consumables needed
8	Service intervals	Long intervals, medium intervals, short intervals

The properties of on-line sensor/analysing equipment can be, and often are, used in many different combinations in measurement chains for different applications and determinands. However, most end-users are not concerned with the actual equipment, but are more interested in the measurement and its quality. Users therefore often regard on-line measurement chains as “black boxes”, where the “black box” encapsulates all the other equipment necessary for the measurement.

However, there are three procedures (testing, installation and operation) for which different measurement chains can be defined. These are:

a) No external sampling;

b) External sampling;

c) External sampling and sample pretreatment.

As laboratory tests should be undertaken using known, “clean” test solutions, procedures b) and c) can only be partly tested in the laboratory, and this includes for example response time measurements.

Annex C
(informative)

Recommended test bench facilities

During tests in the laboratory, the on-line sensor/analysing equipment should be exposed to different calibration solutions in different orders, and the response from the equipment should be read and recorded in a way which allows inspection of the resulting readings.

On-line sensor/analysing equipment requiring external sampling often needs to have the calibration solution introduced as a continuous flow, whereas equipment not requiring external sampling can be placed directly in a tank. The size of the tanks containing the calibration solutions can vary from less than a litre to a hundred litres.

The tanks should be protected so that there is no deterioration, such as evaporation or contamination, of the calibration solution, thus ensuring stability during the test. If the tanks are large, it might not be practicable to use de-ionized water as the solvent for the calibration solution. In this case, a “standard solvent” based on tap-water can be used.

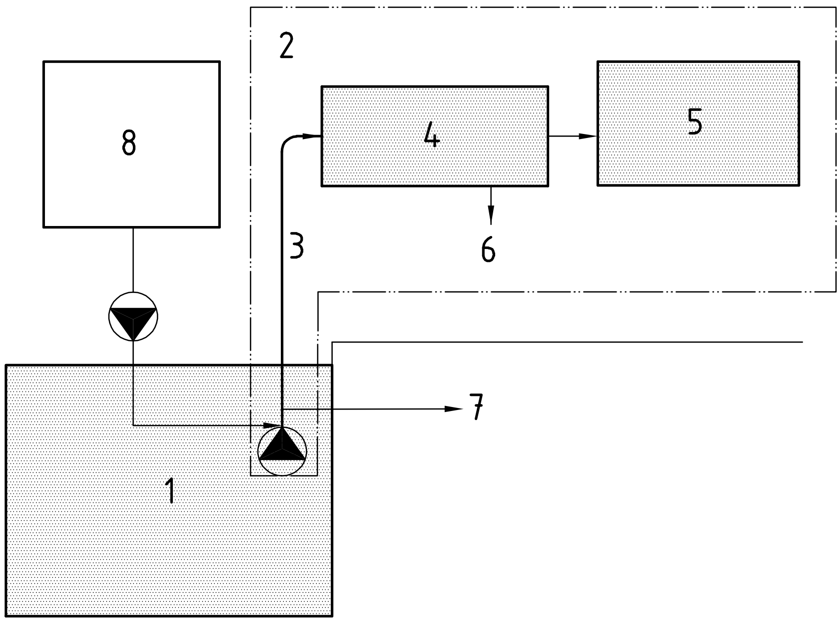
In order to ensure that tap-water is suitable for use, it should be analysed for possible interferents (including the determinand). The values should not exceed the maximum limit for the interferent as stated by the manufacturer. If the limit is exceeded, then de-ionized water should be used to dilute the tap-water until it meets the specification.

It is not possible to use calibration solutions under field test conditions. Therefore, (rapid) sampling and analysis in order to establish reference values and spiking of natural samples should be used.

Figure C.1 shows an example of a test bench for on-line sensor/analysing equipment needing external sampling. It does not take into account the effect of the immersed pump in the measurement chain on the measurements/reference values. However, as the spiking solution is pumped into the main sample stream immediately after the pump, this should not affect the determination of the response time. The on-line sensor/analysing equipment should be installed directly at the site (reservoir, process tank, etc.). The immersed pump should be replaced with a connection to a by-pass if sampling is from a pressurized pipe.

Samples for laboratory analysis (determination of bias and long-term drift) should be taken directly after the immersed pump in the measurement chain. For the determination of response times, no sampling or analysis is required as the sampling line is spiked directly with concentrated solutions of the calibrant (flow of spiking solution very much less than sample supply). For verification purposes, a sample taken from a point after sample pretreatment may be analysed.

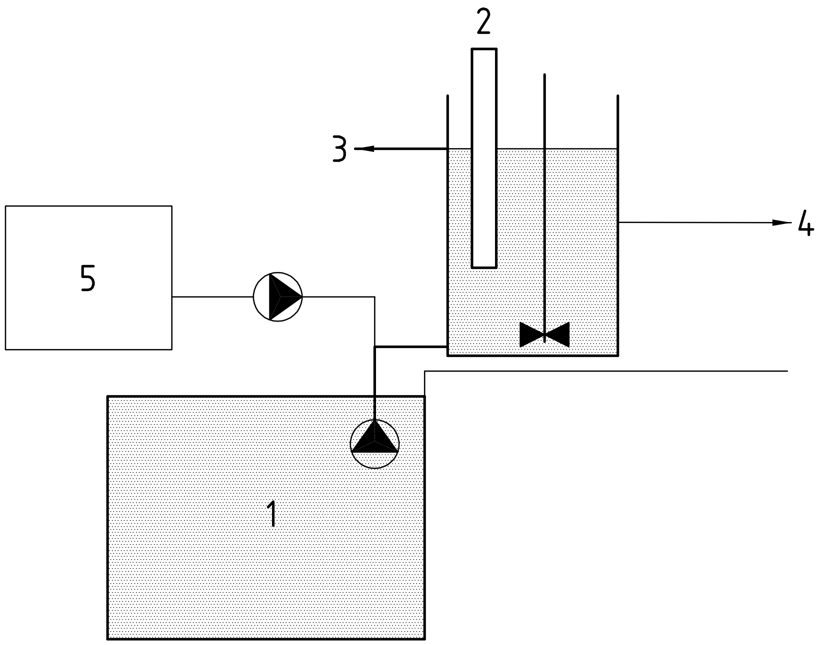
Figure C.2 shows an example of a test bench for on-line sensor/analysing equipment which does not need external sampling. An example of a test bench for a sensor/analyser mounted directly in a pipe is shown in Figure C.3. The method of operation of these test benches is as described above.



Key

1 reservoir, process tank or open channel
2 measurement chain
3 sampling line
4 sample preparation
5 sensor/analysing equipment
6 overflow/waste
7 manual/automatic sampling for measurement of reference values
8 spiking solution for measurement of response times

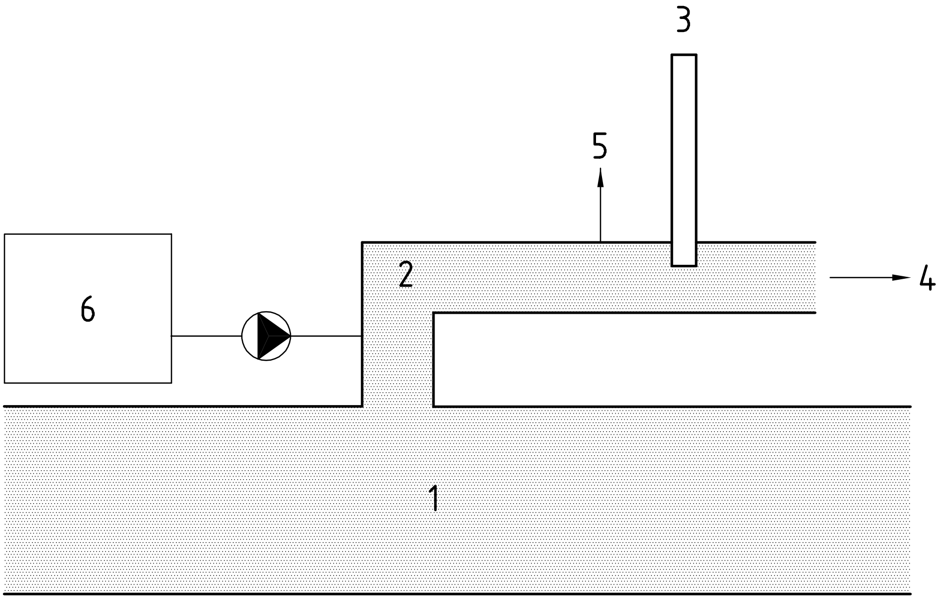
Figure C.1 — Example of field test bench for on-line sensor/analysing equipment requiring external sampling



Key

1 reservoir, process tank or open channel
2 sensor/analysing equipment
3 overflow/waste
4 manual/automatic sampling for measurement of reference values
5 spiking solution for measurement of response times

Figure C.2 — Example of field test bench for on-line sensor/analysing equipment not requiring external sampling



Key

1 main pipe
2 by-pass
3 sensor/analysing equipment
4 overflow/waste
5 manual/automatic sampling for measurement of reference values
6 spiking solution for measurement of response times

Figure C.3 — Example of field test bench for on-line sensor/analysing equipment mounted directly in a pipe

Annex D
(informative)

Scheduling of tests

D.1 Laboratory tests

Table D.1 shows an example of how a complete laboratory test could be scheduled. The shortest period between maintenance operations should exceed the time necessary for a single test, i.e. the on-line sensor/analysing equipment should not be calibrated or an automatic rinse procedure performed during a test.

If an automatic maintenance operation occurs during a repeatability test for instance, the test should be terminated and repeated when the maintenance operation has been completed. However, if an automatic maintenance operation is caused by a change in environmental conditions or is recommended by the manufacturer/supplier, and occurs during testing for these, the test result should be accepted.

Day 1 and day 2: Determination of frequency of reading and of response and delay times.

Day 3 to day 8: Determination of linearity, coefficient of variation, limit of detection, limit of quantification, repeatability, lowest detectable change, bias, short-term drift and day-to-day repeatability as shown in Table D.1.

Table D.1 — Scheduling of laboratory tests

i	x_i	$y_{i,1}$	$y_{i,2}$	$y_{i,3}$	$y_{i,4}$	$y_{i,5}$	$y_{i,6}$
1	5	Day 4	Day 4	Day 4	Day 4	Day 4	Day 4
2	20	Day 6	Day 6	Day 6	Day 6	Day 6	Day 6
3	35	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8
4	50	Day 5	Day ?	Day ?	Day ?	Day ?	Day ?
5	65	Day 4	Day 4	Day 5	Day 6	Day 7	Day 8
6	80	Day 7	Day 7	Day 7	Day 7	Day 7	Day 7
7	95	Day 3	Day 3	Day 3	Day 3	Day 3	Day 3

where

i is the determinand value level;

x_i is the value of the determinand in the ith calibration solution, expressed as a percentage of the working range;

$y_{i,j}$ is the jth measurement of the determinand value x_i;

? indicates a day which is dependent on the length of the period between maintenance operations.

Day 8: Memory effect check.

Day 9 and day 10: Interference checks.

Day 11 and day 12: Checks on environmental and operating conditions.

D.2 Field tests

A schedule for field testing should take into account the maintenance (manual or automatic) required and planned during different periods. The schedule should be used to calculate the availability. As an example, four typical maintenance operations are:

a) M1: automatic rinsing every 6 h;

b) M2: automatic calibration every day;

c) M3: manual filter cleaning every week;

d) M4: reagent renewal every 4 weeks;

resulting in a maintenance schedule as shown in Table D.2.

Table D.2 — Maintenance schedule (example)

	Day number (first week)						
Time	**1**	**2**	**3**	**4**	**5**	**6**	**7**
00:00	M1	M1	M1	M1	M1	M1	M1
02:00	M2	M2	M2	M2	M2	M2	M2
04:00							
06:00	M1	M1	M1	M1	M1	M1	M1
08:00							M3
10:00							
12:00	M1	M1	M1	M1	M1	M1	M1
14:00							
16:00							
18:00	M1	M1	M1	M1	M1	M1	M1
20:00							
22:00							

Day number (fourth week)						
22	**23**	**24**	**25**	**26**	**27**	**28**
M1	M1	M1	M1	M1	M1	M1
M2	M2	M2	M2	M2	M2	M2
M1	M1	M1	M1	M1	M1	M1
						M3
M1	M1	M1	M1	M1	M1	M1
						M4
M1	M1	M1	M1	M1	M1	M1

Annex E
(informative)

Examples of test reports

E.1 Laboratory test

Table E.1 — Example of test report for laboratory test

Performance characteristic	Unit	Results
Response time for positive change, $t_{Response}^{+}$ Response time for negative change, $t_{Response}^{-}$		
Delay time for positive change, t_{Delay}^{+} Delay time for negative change, t_{Delay}^{-}		
Rise time Fall time		
Linearity (including range over which check carried out)		
Coefficient of variation	%	
Limit of detection (LOD)		
Limit of quantification (LOQ)		
Repeatability		
Lowest detectable change (LDC)		
Bias		
Short-term drift	%/day	
Day-to-day repeatability		
Memory effect		If present, give value
Interference caused by interferent 1		
Interference caused by interferent 2		
Environmental and operating conditions: requirement 1 (lower/upper limit) requirement 2 (lower/upper limit)		If non-compliant, give value

Documentation concerning the following items should also be provided:

a) a description of the test bench facilities, including the results of the test carried out to determine the frequency of the readings;

b) the response chart and details of any corrective action taken;

c) the analytical methods used and their precision;

d) graphs of the readings recorded, together with supporting documentation.

E.2 Field test

Table E.2 — Example of test report for field test

Performance characteristic	Unit	Results
Response time for positive change, $t_{Response}^{+}$ Response time for negative change, $t_{Response}^{-}$		
Delay time for positive change, t_{Delay}^{+} Delay time for negative change, t_{Delay}^{-}		
Rise time Fall time		
Bias based on (relative/absolute) differences		
Long-term drift	%/day	
Availability Up-time	% %	

Documentation concerning the following items should also be provided:

a) a description of the test site;

b) a description of any other equipment used in the measurement chain in addition to the sensor/analysing equipment;

c) a description of the test bench facilities, particularly those aspects concerning sampling and the precision of sampling;

d) the response chart and details of any corrective action taken;

e) the methods of laboratory analysis used, including the precision of the methods used to determine the reference values;

f) the maintenance log and the conditions and parameter settings during the whole test period;

g) graphs of the readings recorded, together with supporting documentation.

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