A Common Protocol for Sensor Testing
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Summary

PREPARED, Enabling Change, is an EU-funded Collaborative Project under the Seventh Framework Programme (FP7). The project aims to gather urban utilities in Europe and worldwide to develop an advanced strategy in meeting the upcoming challenges for water supply and sanitation brought by climate change. In Work Area 3 of the project, the project team will contribute to increase the technological capacity and performance of traditional water supply and sanitation systems by better use of sensors and models.

A common protocol was developed for sensor testing under the Task 3.1.3 of the PREPARED project. The common test protocol is used to provide sufficient information to the testing organisation to carry out sensor tests and to make determinations about performance of tested sensors, and can lead to issuance of test reports. The test protocol can also be used as an administrative document that governs all important aspects of the testing and can serve as a test plan template.

The common test protocol was developed for different types of on-line sensors, including optical sensors, electronic noses and biosensors. The test protocol is fully compatible with the EN ISO 15839.

Key words: On-line sensors; Testing; Water and wastewater applications; Common protocol; Technology evaluation
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## Summary

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1 Introduction

1.1 Background
PREPARED, Enabling Change, is a EU-funded Collaborative Project under the Seventh Framework Programme (FP7). The project aims to gather urban utilities in Europe and worldwide to develop an advanced strategy in meeting the upcoming challenges for water supply and sanitation brought by climate change. In Work Area 3 of the project, the project team will contribute to increase the technological capacity and performance of traditional water supply and sanitation systems by better use of sensors and models.

This task is listed as Task 3.1.3 and as Deliverable 3.1.3 under Work Area 3.

This document contains a common protocol to be used for sensor testing or be used as a reference to be adapted in cases it cannot be fully applied.

1.2 Scope of protocol
The objectives of a proposed test shall be specific to the requirements of end users and the desired results of the evaluation. In the PREPARED project, tests will be carried out mainly for new sensors or for existing sensors used for new purposes or with new data processing methods. The sensor tests will include (but not be limited to) evaluation of repeatability, reproducibility, availability of standards, maintenance problems and requirements, uncertainties, and drifts under various conditions, especially those conditions corresponding to demonstration sites in Work Area 1 of the PREPARED project.

This common test protocol is intended to provide sufficient information to the testing organisation to carry out the test and make a determination about the performance of sensors tested at specific sites, and can lead to the issuance of a test report. It is also intended that the test protocol can be used as an administrative document that governs all important aspects of the testing and can serve as a test plan template.

IMPORTANT NOTES
This document is mainly based on the EN ISO standard 15839 (2003), which is fully applicable under laboratory conditions for testing on-line sensors aiming to measure concentrations of various substances in waters (e.g. nitrate, COD, etc.). It should be considered as a reference state-of-the-art approach, but it should also be mentioned that
i) it cannot be fully applied under some field conditions where operating conditions are not under full control or cannot be modified to the extent required by the standard.
ii) it cannot be applied to some sensors which are not measuring concentrations of known substances in water (e.g. turbidimeters, electronic noises, water level meters, flowmeters including e.g. Doppler probes).

For such cases, the approach given in EN ISO standard 15839 shall be adapted to each sensor, keeping in mind that the most important issue is the evaluation of the quality of the measurements delivered by the sensor, especially repeatability, reproducibility, availability of standards, maintenance problems and requirements, uncertainties, and drifts under various conditions.
It shall also be noticed that this common protocol is developed for testing sensors, but not for verifying sensors as in the sense of Environmental Technology Verification (ETV), although actual testing procedures involved can be same. In addition, this common test protocol is developed for calibrated sensors.

1.3 Testing process

The testing process consists of three phases, as shown in Figure 1.

![Flow diagram of a testing process](image)

**Figure 1 Flow diagram of a testing process**

Phase I: Planning – Prior to the test, the test programme must be properly planned. This phase involves a number of activities culminating in the preparation of a site-specific test plan. The main activities include:

- Identification of objectives of the testing
- Identification of testing parties and their responsibilities
- Identification of suitable test sites
- Obtaining and evaluating test site data
- Designing a test programme including evaluation criteria
- Determination of the quality assurance (QA) and quality control (QC) programme
- Determination of how data will be handled and evaluated.

The planning phase is carried out by the technology vendor and the testing organisation. The test facility owner shall be actively involved. The test plan shall be reviewed by an expert group.

Phase II: Testing and data assessment – This phase includes the actual testing activities, using the activities and procedures specified in the planning phase and all data analysis and data evaluation steps. The testing and data assessment is carried out by an independent testing organisation, with logistical and technical support from the technology vendor and the test facility owner. An expert group shall be actively involved in the data assessment.

Phase III: Reporting – This last phase includes test report preparation. An expert group shall be actively involved in the reporting phase.
1.4 Responsible parties and roles

A sensor test will usually involve four parties, each with different responsibilities during the testing. The parties include:

- Vendor of sensors to be tested
- Testing Organisation
- Test facility owner
- Expert Group

A verification test organisation is only required when technology verification is the main objective of the test.

The responsibilities of each party are presented below.

Responsibilities of the Vendor:
- Reviewing and commenting the site-specific test plan
- Provision of logistical and technical support as required
- Assistance to the Testing Organisation in the operation during the testing

Responsibilities of the Testing Organisation:
- Preparation of the site-specific test plan
- Selection of a test site
- Conducting the sensor tests
- Operation and maintenance of the sensor according to the Vendor’s O&M manual(s)
- Scheduling and coordinating all the activities of all testing participants, including establishing a communication network and providing logistical and technical support
- Managing, evaluating, interpreting and reporting on data generated by testing
- Evaluation and reporting on the performance of the tested sensor.

Responsibilities of the Test Facility Owner:
- Provision of logistical and technical support as may be agreed upon by the Testing Organisation, Vendor, and Owner
- Notifying the Testing Organisation of any significant changes in site operation conditions

Responsibilities of the Expert Group:
- Qualification of the test site
- Reviewing and commenting on the site-specific test plan
- Helping on data assessment
- Reviewing and commenting on the testing report.

In an actual test protocol, roles and responsibilities of persons from each party shall be specified. Detail contact information of key personnel shall be included in the protocol.
2 Description of technology and product

2.1 Description of technology

For the purpose of the testing programme, a sensor shall be defined as an automatic measurement device which continuously (or at a given frequency) gives an output signal proportional to the values of one or more determinants in a solution which it measures (EN ISO, 2003).

The sensor technology shall be briefly described here. An example is shown in Example 1.

Example 1. Description of technology

The spectrophotometer probe works according to the principle of UV-VIS spectrophotometry. Substances contained in the medium to be measured reduce the intensity of a light beam going through this medium. The light beam is emitted by a lamp and after contact with the medium its intensity is measured by a detector over a range of wavelengths. Each molecule of a dissolved substance absorbs radiation at certain and known wavelengths. The concentration of substances contained determines the amplitude of the absorption of the sample – the higher the concentration of a certain substance, the more it will reduce the intensity of the light beam.

2.2 Description of product

A detailed description of the sensor product shall be presented here. The description shall cover all main components of the product. A picture or schematic graph shall show how the main components are connected. Detailed description of each main component shall be given. An example is shown in Example 2. Information may be found in both manufacturer fact sheets and general technical literature.

Example 2. Description of product

Every S::CAN Spectrolyser probe consists of three main components: emitter, measuring cell and receiving unit.

The central element of the emitter is a light source – a xenon flash lamp. This is complemented by an optical system to guide the light beam and an electronic control system to operate the lamp.

In the measuring section the light passes through the space between the two measuring windows which is filled with the measuring medium and interacts with it. A second light beam within the probe – called the

1 It may be different for some sensors (flowmeters, odour sensors, turbidimeters, etc.): see important notes on page 5
reference beam – is guided across an internal comparison section with distilled water. Every S::CAN Spectrolyser probe is a dual-beam measuring instrument, allowing for the identification of disturbances in the measuring process (e.g. aging of the flash lamp) which are automatically compensated for.

The receiving unit is located on the side of the spectrometer where the connection cable is attached, and it consists of two major components: the detector and the operating electronics. An optical system focuses the measuring and reference beams on the entrance port of the detector. The light received by the detector is split up into its wavelengths and guided to the 256 fixed photodiodes, making the use of sensitive moving components unnecessary. The operating electronics contained in this part of the probe are responsible for controlling the entire measuring process and all the various processing steps required to edit and check the measuring signal and to calculate fingerprints and parameter values.

2.3 Application and performance parameter definitions

The application and performance parameters are provided by the Vendor’s stated claim of technology capabilities. The performance stated here shall be same as described in the product brochures and/or product manuals.

2.3.1 Application definition

The intended application of the product for testing is defined in terms of matrices, targets, and effects of the product.

The matrices of the application apply to which fields the product is used for and applied specific conditions if there are any.

The targets of the application are generally reported in terms of limit of detection (LoD), limit of quantification (LoQ), precision and uncertainties, trueness, range of application and robustness (see EN ISO 15839 for definition of the above terms). Adaptation may be necessary for some types of sensors.

The effects of the application are all the determinants that the product targets on.

An application definition example is shown in Example 3.

<table>
<thead>
<tr>
<th>Matrices</th>
<th>Effects</th>
<th>Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrolyser is applied for surface water, ground water, drinking water, and wastewater. The matrix tested here is activated sludge tanks in a wastewater treatment plant.</td>
<td>Monitoring of nitrate and COD. Only nitrate was included in the final field tests.</td>
<td>Targets include limit of detection, precision, repeatability, range of application, and robustness of nitrate monitoring.</td>
</tr>
</tbody>
</table>
2.3.2 Performance parameter definitions

It is important for the testing parties to understand differences between an on-line sensor and an on-line measurement chain. An on-line measurement chain can be defined as a combination of the properties of the on-line sensor/analysing equipment. These properties include:

- Location of sensor, e.g. on-line, in-line, in situ, etc.
- Sampling, external sampling or no external sampling
- Sample pre-treatment, e.g. filtration, centrifugation, etc.
- Principle of measurement, e.g. continuous, batch, etc.
- Measurement method, e.g. photometric, colorimetric, enzymatic, etc.
- Number of determinants
- Need for supplies, consumables needed or no consumables needed
- Service intervals, long, medium, or short intervals.

The properties of an on-line sensor can be used in many different combinations in measurement chains for different applications and determinants. However, most end-users are not concerned about the actual equipment, but are most interested in the measurement and its quality. In sensor testing, especially in field testing, performance of an on-line sensor depends not only on the performance of sensor itself but also on the performance of other components in the on-line measurement chain. This is of great importance and, in practice, we recommend that field tests are carried out for the whole measurement chain, i.e. from the transducer in contact with the variable to be measured (i.e. the measurand) to the final output values as recorded in data loggers, SCADA systems, etc.

All important performance parameters required in the EN ISO 15839 are defined in Table 1. They may be adapted to each type of sensor which differs from measurement of dissolved chemical compounds in water.

Table 1 Summary of performance parameters

<table>
<thead>
<tr>
<th>Performance parameters</th>
<th>Definitions (EN ISO 15839: 2003)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time</td>
<td>Time interval between the moment when the on-line sensor/analysing equipment is subjected to an abrupt change in determinant value and the moment 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.</td>
<td>In laboratory testing, the response time is measured. In field testing, it is the whole measurement chain which is tested. Special requirements for certain sensors (e.g. electronic noses) may apply.</td>
</tr>
<tr>
<td>Linearity (range of application)</td>
<td>Condition in which measurements made on calibration solutions (or surrogate tools when standard or certified values are not available) having determinant values spanning the stated range of the on-line sensor have a straight-line relationship with the calibration solution determinant values (or surrogate tools when standard or certified values are not available).</td>
<td></td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>Ratio of the standard deviation of the on-line sensor to the working range of the sensor</td>
<td></td>
</tr>
<tr>
<td>Limit of</td>
<td>Lowest value, significantly greater than zero, of a</td>
<td></td>
</tr>
</tbody>
</table>
detection (LoD) | determinant that can be detected.
---|---
Limit of quantification (LoQ) | Lowest value of determinant that can be determined with an acceptable level of accuracy and precision.
Repeatability (same day) | Precision under repeatability 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 sensor and reagents within short intervals of time (e.g. 24-h).
Day-to-day repeatability | Precision under day-to-day repeatability conditions.
Short time 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.
Long time drift | Slope of the regression line derived from a series of differences between reference and measurements values obtained during field testing, expressed as a percentage of the working range over a 24-h period.
Bias (100%-bias=trueness) | Consistent deviation of the measured value from an accepted reference value. 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.
Availability or up-time | Percentage of the full measurement period during which the measurement chain is available for making measurements. The full measurement period is the period which includes all specified automatic or manual maintenance operations.
Robustness, memory effect | Temporary or permanent dependence of readings on one or several previous values of the determinant
Robustness, interference | Undesired output signal caused by a property(ies)/substance(s) other than the ones being measured. Special requirements for certain sensors (e.g. electronic noses) may apply.

In a test plan, all performance parameters to be verified in the tests shall be quantitative, preferably summarised in a table. For those non-quantitative parameters, such as effects from interference and actions to reduce interference, statement shall be given accordingly. All other clarifications that will help people to understand the performance parameters shall be also stated in the test plan.

Performance of state-of-the-art technologies for the same parameters shall be stated in the test plan and compared to the performance of the sensor to be tested.
Example 4. Description of how to define performance parameters

The ranges of performance parameters to be verified in the test are presented in the table below. The ranges are used for planning the testing only.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit of detection</th>
<th>Range of application</th>
<th>Precision (repeatability)</th>
<th>Precision (reproducibility)</th>
<th>Trueness</th>
<th>Robustness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>0.1 mg NO₃-N/L</td>
<td>LoD-65 mg NO₃-N/L (lab.) LoD-20 mg NO₃-N/L (field)</td>
<td>20% of range: 1 mg NO₃-N/L 80% of range: 5 mg NO₃-N/L</td>
<td>&lt; 10</td>
<td>&lt; 15</td>
<td>100±10</td>
</tr>
<tr>
<td>COD</td>
<td>1 mg COD/L</td>
<td>LoD-1000 mg COD/L</td>
<td>20% of range: 20 mg COD/L 80% of range: 60 mg COD/L</td>
<td>&lt; 25</td>
<td>&lt; 30</td>
<td>100±10</td>
</tr>
</tbody>
</table>

The difference in range of application for laboratory and field test is caused by the background absorbance in wastewater being much higher than in distilled laboratory water. Accordingly, the dynamic range of the instrument is exceeded already from 20 mg NO₃-N/L.

The verified version of the product is designed for controlling a biodenitro wastewater treatment plant. In a biodenitro plant, the concentration of nitrate changes very fast by turning the oxygen on and off, therefore the response time is of importance. A performance parameter for response time is set to < 2 minutes.

Factors such as short term drift, long term drift, availability and up-time will also be evaluated. No relevant range of performance parameters have been set up for these parameters.

According to EN ISO 15839, parameters as limit of quantification (LoQ) and lowest detectable change (LDC) also have to be determined. It has been decided that a relevant range for these performance parameters shall not be set up, since they provide the same basic information as the limit of detection, which has been included in the performance parameters.

EN ISO 15839 requires determination of bias. In this testing, trueness is used instead of bias. Trueness is calculated from bias in percent as 100% minus bias. Reproducibility is tested in the EN ISO 15839 as day-to-day repeatability. For testing of robustness, temperature impact, memory effect and effect from interference on the measurements were tested.

For nitrate, interference is known to occur from nitrite and some substances with strong absorption below 240 nm, such as bromide at sea water concentrations and iodide. In wastewater treatment polyaluminium chloride (PAX) is used. Chloride has similar properties as bromide and iodide. Interference on nitrate measurements will be investigated with:
- Nitrite.
- PAX (PolyAluminum Chloride).

For COD interference is known to occur with substances with strong absorption between 250-350 nm, e.g. ozone. With respect to wastewater, ozone is generally not relevant as interference, as ozone is not added during the relevant part of wastewater treatment. Interference is expected to occur from treatment chemicals such as ferrichloride and PAX. Interference on COD measurements will be investigated with:
- Ferric chloride.
- PAX (PolyAluminum Chloride).

On the market are other similar spectrometer probes. Details on the performance of the two effects with regards to nitrate and COD are compared in the table below.
<table>
<thead>
<tr>
<th>Nitrate</th>
<th>Limit of detection</th>
<th>Repeatability</th>
<th>Trueness</th>
<th>Range of application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>STRP-scan</td>
<td>0.1 mg/L</td>
<td>3% (reproducibility)</td>
<td>± 5% rel. of full scale</td>
<td>0.3-23 mg/L</td>
<td>/5/</td>
</tr>
<tr>
<td>ISIS II</td>
<td>(0.1 mg/L)</td>
<td></td>
<td></td>
<td>0.1-100 mg/L</td>
<td>/6/</td>
</tr>
<tr>
<td>Laboratory (on synthetic samples)</td>
<td></td>
<td>Repeatability 1.2-5.2%</td>
<td></td>
<td></td>
<td>/13/</td>
</tr>
<tr>
<td>Ion-selective electrodes (ISE)</td>
<td></td>
<td>Reproducibility 3.6-15%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>STRP-scan</td>
<td>2 mg/L</td>
<td>3% (reproducibility)</td>
<td>10-2000 mg/L</td>
<td>/5/</td>
</tr>
<tr>
<td>ISIS II</td>
<td>(10 mg/L)</td>
<td></td>
<td>± 5% rel. of full scale</td>
<td>10-100 mg/L</td>
<td>/6/</td>
</tr>
<tr>
<td>Laboratory (on synthetic samples)</td>
<td></td>
<td>Repeatability 2-8%</td>
<td></td>
<td></td>
<td>/13/</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reproducibility 6.5-24%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Note: Detail reference information is not included in this example.)
3 Existing data

3.1 Summary of existing data

If there are any data obtained from previous tests for the same sensors, they shall be presented (or at least referred to) with a quality label in the testing protocol. Data shall be interpreted regarding matrices, effects, and targets. Especially, special testing conditions shall be stated.

3.2 Quality of existing data

The quality of existing data needs to be justified according to how the data were generated in terms of sampling and analytical operation and qualification of the testing laboratories. An ISO standard (ISO 17025:2005), General Requirements for the Competence of Testing and Calibration Laboratories, shall be used for the justification process.

3.3 Acceptance of existing data

Statement for acceptance of existing data shall be stated here.
4 Test site and test facility

4.1 Laboratory tests

The Testing Organisation will select the testing laboratory. Criteria required by the ISO 17025 shall be followed during the laboratory identification process.

Details including name and address shall be described for the selected laboratory. If any other equipment besides the sensor to be tested is going to be used in the test, a detailed description of the equipment shall be given. Comparison of different on-line sensors is only possible at the same time and under the same test conditions.

4.2 Field tests

The criteria for field site selection shall be consistent with the Vendor-specific sensor performance in term of the whole measurement chain, ranges of parameters, sample’s dynamic ranges, natures of the matrix, and other environmental conditions.

Details including name and address shall be described for the selected field site. A detailed description of all necessary sampling, pumping, and conditioning devices shall be given.

An example of test site description is shown in Example 5.

Example 5. Site description and test equipment

The test sites are summarised in the table below.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Address/site</th>
<th>Site details</th>
<th>Test compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laboratory</td>
<td>DHI premises, Aarhus</td>
<td>Activated sludge tank/effluent</td>
<td>Nitrate, DOC</td>
</tr>
<tr>
<td>Field</td>
<td>Aaby Wastewater Treatment Plant, Aarhus</td>
<td>Activated sludge tank</td>
<td>Nitrate</td>
</tr>
</tbody>
</table>

The test equipment includes:

- S::CAN Spectrolyser
- Cooling system: National Lab. ProfiCool

4.3 Test facility preparation

A field test facility may be different for different measurement chains. However, all field test facilities shall meet the following requirements:

- The test facilities shall match the required specification for the measurement chain provided by the Vendor. But special modifications can be done with the test facilities upon agreement between the Vendor and the Test Organisation.
- The facilities shall include the ability to record (manually or preferably automatically) readings of the sensor in analogy or digital forms.
- The facilities shall include the ability to produce representative (in both time and space) samples for laboratory (reference) analysis. The sampling procedures used shall be reported.
After receipt of the items included in the measurement chain, the measurement chain shall be set up together with the appropriate test facilities and subsequently calibrated and maintained according to the routines recommended by the Vendor. Details of the set-up shall be reported. Three recommended test facilities by EN ISO 15839 are described in Example 6.

**Example 6. Three recommended test facilities by EN ISO 15839 for water applications**

![Diagram of field test facility](image)

**Example of field test facility for on-line sensors requiring external sampling**

**Example of field test facility for on-line sensors not requiring external sampling**

**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

**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
Example of a field test bench for on-line sensors mounted directly in a pipe

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
5 Test plan

5.1 Test design

The EN ISO 15839 should be closely followed for determination of the required tests in case it is fully applicable. In other cases, it may be used as a reference document to elaborate a specific test design for types of sensors which cannot be tested adequately with EN ISO 15839. An example of parameters to be tested is shown in Example 7. Detailed design description for certain parameters is summarised in the following sub-sections.

Example 7. Parameters to be tested in laboratory and field sites

<table>
<thead>
<tr>
<th>Test parameters</th>
<th>Laboratory</th>
<th>Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Linearity (range of application)</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Limit of detection (LoD)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Limit of quantification (LoQ)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Repeatability (same day)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Day-to-day repeatability</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lowest detectable change (LDC)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Short time drift</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Long time drift</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias (100%-bias=trueness)</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Availability or up-time</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Robustness, memory effect</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Robustness, interference</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Response time</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

5.2 Determination of performance characteristics in the laboratory

During tests in the laboratory, the on-line sensor should be exposed to different calibration solutions or standards (or surrogate tools when standard or certified values are not available) in different orders, and the response from the equipment should be read and recorded in a way which allows inspection of the resulting readings. However, it shall be noticed that the sensor to be tested in the plan shall be previously fully calibrated and ready for testing. The calibration solutions or standards (or surrogate tools when standard or certified values are not available) used in the test shall have the same characteristics as the solutions used for the sensor calibration. Sensor calibration procedures are addressed in the Task 3.1.5 report of the PREPARED project.

5.2.1 Response times

Response times, including delay times and rise and fall times, are derived from the record of readings made when the testing solution is changed. In the laboratory, the results apply directly to the sensor because no external sampling and sample pre-treatment systems are used.

Test procedure: Prepare two calibration solutions with determinant values of 20% and 80% of the working range. Expose the on-line sensor to the 20% solution for a period equal to three times of the preliminary response time, and then change to the 80% solution. Three
preliminary response times after the changeover, change back to the 20% solution. Repeat the procedure six times, and record the readings in Table 2.

It shall be noted that a special procedure can be used for certain types of sensors (e.g. electronic noses) when standard or certified values are not available. For some sensors (e.g. flowmeters), it may even be extremely difficult (if not impossible) to properly assess their response times as they cannot be exposed to quickly changing conditions as prescribed by EN ISO 15839. In such cases, an adaptation of the test should be defined.

Table 2. Data sheet for recording response times and delay times

<table>
<thead>
<tr>
<th>Sequence No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time for positive change, R+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for positive change, D+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response time for negative change, R-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for negative change, D-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the readings, calculate each rise time as \((R+) - (D+)\) and each fall time as \((R-) - (D-)\). Report the final result for each of the characteristics as the mean value of the calculated values together with the standard deviation.

Figure 2(a) can be referred to as an idealised record of readings obtained in a continuous reading system. If the response curve is asymmetric, the rise time and fall time may be different, i.e. the sensor may have different response and delay times for positive and negative changes. Figures 2(b) and 2(c) show typical responses from real sensors to a positive change and indicate the correct way of determining the response time.
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 for determination of these parameters are summarised in Table 3, which include all the measurements necessary to calculate these performance characteristics, and in Table 4 which indicates the use of the measurements and the constraints to be respected when scheduling the test.

---

Figure 2. Response of on-line sensors to abrupt changes in determinant value
It shall be noted that a special procedure can be used for certain types of sensors (e.g. electronic noses, flowmeters, etc.) when standard or certified values are not available.

Table 3. 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

<table>
<thead>
<tr>
<th>i</th>
<th>( x_i )</th>
<th>( y_{i,1} )</th>
<th>( y_{i,2} )</th>
<th>( y_{i,3} )</th>
<th>( y_{i,4} )</th>
<th>( y_{i,5} )</th>
<th>( y_{i,6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where

- \( i \) is the determinant value level;
- \( x_i \) is the value of the determinant in the \( i \)th calibration solution, expressed as a percentage of the working range;
- \( y_{i,j} \) is the \( j \)th measurement of the determinant value \( x_i \), expressed in units of \( x \).

Table 4. Use of measurements and constraints on scheduling

<table>
<thead>
<tr>
<th>i</th>
<th>( x_i )</th>
<th>Determinant level used for</th>
<th>To be measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>LoD, LoQ</td>
<td>On the same day separated by blanks</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>Repeatability, LDC, bias</td>
<td>On the same day separated by blanks</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>Day-to-day repeatability</td>
<td>On different days</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>Short-term drift</td>
<td>Equally distributed over shortest period between maintenance operations</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>Day-to-day repeatability</td>
<td>On different days</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>Repeatability, LDC, bias</td>
<td>On the same day separated by blanks</td>
</tr>
<tr>
<td>7</td>
<td>95</td>
<td>Linearity check only</td>
<td>On the same day separated by blanks</td>
</tr>
</tbody>
</table>

\( y_{i,j} \): Measurements used for linearity check and determination of coefficient of variation

Prepare eight calibration solutions covering the working range at determinant values of 0% (blank), 5%, 20%, 35%, 50%, 65%, 80%, and 95%, using appropriate volumes as required by the on-line sensor. Ensure adequate mixing. Expose the on-line sensor to the 5%, 20%, 35%, 50%, 65%, 80%, and 95% solutions, with the blank in between each two and, after the signal has become stable, carry out the measurements according to Tables 3 and 4.

The determination methods for other parameters are summarised in Table 5.

Table 5. Summary of determination methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Determination method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearity</td>
<td>Check for linearity according to ISO 8466-1 using the data set ((x_i, y_{i,1})) where ( i = 1 ) to 7.</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>Calculate the coefficient of variation according to ISO 8466-1 using the data set ((x_i, y_{i,1})) where ( i = 1 ) to 7. Express the result as a percentage. It can be compared to coefficients of variation of other on-line sensors.</td>
</tr>
<tr>
<td>Limit of detection (LoD)</td>
<td>Calculate the limit of detection as three times the standard deviation of the measurements ( y_{i,j} ) for ( j = 1 ) to 6.</td>
</tr>
<tr>
<td>Limit of quantification (LoQ)</td>
<td>Calculate the limit of quantification as ten times the standard deviation of the measurements ( y_{i,j} ) for ( j = 1 ) to 6.</td>
</tr>
</tbody>
</table>
Repeatability | Determine the repeatability for both high and low determinant 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 the measurements $y_{6,j}$ for $j=1$ to 6.

Lowest detectable change (LDC) | Determine the lowest detectable change for both high and low determinant 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 the measurements $y_{6,j}$ for $j=1$ to 6.

Bias | Determine the bias for both high and low determinant 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 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 results 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 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 of an on-line sensor is typically observed as a saturation effect caused by the fact that a determinant 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 determinant 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 sensor.

It should be noted that different terms may be used for certain types of sensors. For instance, ultra-high hydrogen sulphide concentrations can cause poisoning effects on metal oxides in the electronic noses.

Expose the on-line sensor to a calibration solution (or surrogate tools when standard or certified values are not available) with a determinant 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 (or surrogate tools when standard or certified values are not available). Three response times after the changeover, carry out a measurement. Repeat this procedure six times (see Table 6). Between the peak loads, bring the equipment back to a memory-effect-free state.

Table 6. Data sheet for memory effect

<table>
<thead>
<tr>
<th>x</th>
<th>y1</th>
<th>y2</th>
<th>y3</th>
<th>y4</th>
<th>y5</th>
<th>y6</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Report the memory effect as the difference between the mean value of the six measurements $y_i$ for $j=1$ to 6 and the determinant value of the 20% calibration solution (i.e. 20). The on-line sensor is indicated to have a memory effect if the calculated value is bigger than the lowest detectable change (LDC$_{20}$).
5.2.4 Interference

Information about interferents affecting the performance of the on-line sensor shall be obtained from knowledge and experience relevant to the nature of the matrix of the concern and the determinant. 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 (or surrogate tools when standard or certified values are not available) with increasing concentrations of the interferent, as the following procedure:

Expose the on-line sensor to the 20% calibration solution (or surrogate tools when standard or certified values are not available) spiked with interferent at 0%, 20%, 50%, 75%, 100%, 125%, etc., of the expected interference level. Perform a measurement at each spiking level (see Table 7), 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 7. Data sheet for interference

<table>
<thead>
<tr>
<th>Calibration solution</th>
<th>Interferent No.</th>
<th>Interferent concentration % of expected interference level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>20%</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>80%</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>80%</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>20%</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>80%</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

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’s literature. However, manufacturer’s information should be considered as indicative only for some specific contexts (e.g. some sensors used in sewers are submitted to very harsh and specific conditions, which may lead to more frequent cleaning, maintenance, calibration and verification).

Expose the on-line sensor equipment to the 50% calibration solution (or surrogate tools when standard or certified values are not available) 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 8). If the difference between these two measurements is less than the lowest detectable change (mean of $LDC_{80}$ and $LDC_{20}$), the sensor is said to be compliant with the stated requirement. If the difference is bigger than the lowest detectable change, the sensor is said to be non-compliant with the stated requirement and the difference between the two measurements shall be reported.

Table 8. Data sheet for environmental and operating conditions
<table>
<thead>
<tr>
<th>Calibration solution</th>
<th>Requirement No.</th>
<th>Requirement level</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>1</td>
<td>Neutral</td>
</tr>
<tr>
<td>50%</td>
<td>2</td>
<td>Upper</td>
</tr>
<tr>
<td>50%</td>
<td>3</td>
<td>Lower</td>
</tr>
</tbody>
</table>

### 5.3 Determination of performance characteristics in the field

#### 5.3.1 General

Field testing is complementary to laboratory testing and shall include the whole measurement chain. The aim of field testing is to determine the long-term ability of a measurement chain to produce reliable measurements. This is why field tests can extend over weeks or months.

The operating conditions as stated by the Vendor 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 actual operating conditions during the test. **Comparison of different on-line sensors is only possible at the same time and under the same conditions.**

As it is the measurement chain (not only the on-line sensor) that is under test, determinant reference value shall represent the true values of the determinant just before the measurement. Determinant reference values shall be determined at least every second day during the test period.

The timing of measurements made by the measurement chains (10 consecutive readings taken at the same frequency as in laboratory testing) shall be synchronised with the sampling undertaken for the laboratory determination of the reference values, i.e. taking the response time of the measurement chain into account. Sampling synchronisation may be a key issue. Due e.g. to pre-rinsing (and also potentially post-rinsing) of sampling tubes and vessels, some auto-samplers require up to 1 minute to collect a sample after the sampling has been ordered. This delay shall be accounted for. Under all circumstances, sampling shall be made in such a way that it maximises the probability that the sample collected has the same properties as the volume of water “explored” by the probe to be tested. This should be explained in the test plan.

A preliminary response time shall be determined three times during the first two days of testing, using the procedure described in Chapter 5.3.3. The preliminary value shall be used for the timing of the measurements and updated during the test by the results obtained from 5.3.3.

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

#### 5.3.2 Monitoring the test

Malfunctioning of the measurement chain may be indicated by the on-line sensor’s internal diagnostic system, the blockage of sample pre-treatment 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 9).
Table 9. Data sheet for reference values and measurements

<table>
<thead>
<tr>
<th>i</th>
<th>Date</th>
<th>Time</th>
<th>( x_i )</th>
<th>( y_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where

- \( i \) is the determinant value level;
- \( n \) is the number of data sets (not less than 30);
- \( x_i \) is the \( i \)th reference value of the determinant;
- \( y_i \) is the \( i \)th measurement value of the determinant.

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 the agreed limits. The relative difference shall be used if the typical value of the determinant at the test site is larger than 20% of the working range of the on-line sensor, otherwise the absolute difference shall be used.

If the measurement fails to comply with the limits, the Vendor 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.

5.3.3 Procedure for field testing

5.3.3.1 Response times

If applicable (see paragraph 5.2.1), the response times, including delay times and rise and fall times, shall be derived from readings taken before, during and after an abrupt change in the determinant value of the real sample introduced into the measurement chain (refer Example 6 for how samples are introduced).

This change shall bring the determinant value up to approximately 80% of the working range, and the determinant value shall remain at this level until the readings are stable, where 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, see Table 10).

It shall be noted that a special procedure can be used for certain types of sensors (e.g. electronic noses) when standard or certified values are not available.

Table 10. Data sheet for recording response times, delay times, rise time and fall time

<table>
<thead>
<tr>
<th>Spike No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time for positive change, ( R^+ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for positive change, ( D^+ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response time for negative change, ( R^- )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for negative change, ( D^- )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Determine the different times as described in Chapter 5.2.1 and report the final result for each of the characteristics as the mean value of the determined values together with the standard deviation.
5.3.3.2 Bias
Determine the bias as the mean of the differences calculated in Chapter 5.3.2 (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 selected part of the working range. Report the bias together with the range selected (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.

5.3.3.3 Long-term drift
Determine the long-term drift as the slope of the linear regression performed on the differences calculated in Chapter 5.3.2 as a function of time (i.e. the regression line drawn on the response chart). Express the result as a percentage of the working range over a 24 h period or any other appropriate time scales.

5.3.3.4 Availability and up-time
Calculate the sensor availability from the following equation:

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

where:
- \(\text{Scheduled stop time}\): Includes all manual and/or automatic maintenance stated by the Vendor as being necessary for reliable operation of the measurement chain (see Chapter 5.5);
- \(\text{Total time}\): Covers the whole period during which maintenance is necessary.

An example for calculation of availability is shown in Example 8.

**Example 8. Calculation of sensor availability (note: this example is NOT for Spectrolyser.)**

A measurement chain requires the following scheduled 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, during 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:

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

where: \(\text{Measured stop time}\) 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.

An example for calculation of up-time is shown in Example 9.

**Example 9. Calculation of up-time (note: this example is NOT for Spectrolyser.)**

A measurement chain requires the following scheduled 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, during 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.

5.4 Reference analysis

Reference analysis is used to check the quality and stability of standard solutions, and the trueness of the tested sensor in the field. Reference analysis shall be done for both the laboratory and the field tests. Equipment used for reference analysis shall be stated in details, including names, models, and key performance parameters.

Proper sampling is critical for ensuring quality of the reference analysis. Necessary preservation of samples shall be taken. Detailed procedures of sampling and preservation shall be reported.

A reference analysis example is shown in Example 10.

**Example 10. Reference analysis for Spectrolyser**

Equipment used for reference tests:

- HP 8453 UV-VIS Spectrophotometer
- Merck Spectroquant NOVA60, using MERCK test kit no. 1.14542.0001 and no. 1.14556.0001 for nitrate
- Ion-Selective Electrode, ISE, nitrate sensor

<table>
<thead>
<tr>
<th>Test kit no.</th>
<th>1.14542.0001</th>
<th>1.14556.0001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring range</td>
<td>0.5-18.0 mg NO₃-N/L</td>
<td>0.1-3.0 mg NO₃-N/L</td>
</tr>
<tr>
<td>Sensitivity: 0.010 A (absorbance)</td>
<td>0.1 mg NO₃-N/L</td>
<td>0.02 mg NO₃-N/L</td>
</tr>
<tr>
<td>Lower limit of detection (LLD)</td>
<td>0.06 mg NO₃-N/L</td>
<td>0.014 mg NO₃-N/L</td>
</tr>
<tr>
<td>Relative standard deviation (RSD)</td>
<td>± 1.5%</td>
<td>± 2.0%</td>
</tr>
<tr>
<td>Trueness</td>
<td>± 0.6 mg NO₃-N/L</td>
<td>± 0.30 mg NO₃-N/L</td>
</tr>
</tbody>
</table>

For measurement of nitrate, it is important to measure concentration right after sampling, due to the biological activity in the activated sludge. Preservation with acid, which is recommended in the standards for measuring nitrate, can dissolve some of the total nitrogen into nitrate and increase the nitrate concentration. It is therefore not possible to preserve the samples and transport them to a reference laboratory for nitrate measurement. Field
measurements were performed instead.

Measurements from an existing nitrate sensor (Ion-Selective Electrode, ISE) at the same location, where the S:-CAN Spectrolyser was located, have also been included in the field test.

5.5 Test and maintenance schedules

Test schedules for laboratory and fields test shall be presented in the test plan.

The rule of thumb for scheduling is that the shortest period between maintenance operations should exceed the time necessary for a single test, i.e. the on-line sensor 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 Vendor, and occurs during testing for these, the test result should be accepted.

An example for the laboratory tests is shown in Example 11.

Example 11. Schedule for laboratory tests

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, day-to-day repeatability as shown in the table below.

<table>
<thead>
<tr>
<th>i</th>
<th>$x_i$</th>
<th>$y_{i,1}$</th>
<th>$y_{i,2}$</th>
<th>$y_{i,3}$</th>
<th>$y_{i,4}$</th>
<th>$y_{i,5}$</th>
<th>$y_{i,6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>Day 4</td>
<td>Day 4</td>
<td>Day 4</td>
<td>Day 4</td>
<td>Day 4</td>
<td>Day 4</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>Day 6</td>
<td>Day 6</td>
<td>Day 6</td>
<td>Day 6</td>
<td>Day 6</td>
<td>Day 6</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>Day 3</td>
<td>Day 4</td>
<td>Day 5</td>
<td>Day 6</td>
<td>Day 7</td>
<td>Day 8</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>Day 4</td>
<td>Day 4</td>
<td>Day 5</td>
<td>Day 6</td>
<td>Day 7</td>
<td>Day 8</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>Day 7</td>
<td>Day 7</td>
<td>Day 7</td>
<td>Day 7</td>
<td>Day 7</td>
<td>Day 7</td>
</tr>
<tr>
<td>7</td>
<td>95</td>
<td>Day 3</td>
<td>Day 3</td>
<td>Day 3</td>
<td>Day 3</td>
<td>Day 3</td>
<td>Day 3</td>
</tr>
</tbody>
</table>

Where
- $i$ is the determinant value level;
- $x_i$ is the value of the determinant in the ith calibration solution, expressed as a percentage of the working range;
- $y_{ij}$ is the jth measurement of the determinant value $x_i$, expressed in units of x.

Day 8: Memory effect check.
Day 9 and day 10: Interference checks.
Day 11 and day 12: Checks on environmental and operating conditions.

A schedule for field testing shall take into account the maintenance (manual or automatic) required and planned during different periods. The schedule should be used to calculate the availability.
5.6 Data management

The test plan shall present the procedures to be followed for data collection, recording, and storage. Data analysis/assessment shall be performed during the course of the tests in order to identify and mitigate problems in time.

Data shall be collected by electronic and/or manual means, whichever the Testing Organisation finds most appropriate for the tests.

- If manual data recording is employed, the Testing Organisation shall record all data by hand in laboratory notebooks. Data logs shall include a description of dates and times, any problems or issues, names of operators, calculations, and other pertinent items.
- Data in electronic format shall be included in commercially available programs for word processing, spreadsheet or database processing or commercial developed especially for data collection and processing on a specific instrument. Backup of the computer database should be performed on a daily basis, if possible.

A database for the test shall be set up in form of the data sheets presented in Chapters 5.2 and 5.3, where EN ISO 15839 is followed. All manually entered data from the laboratory notebooks and data log sheets shall be entered into the designed data sheets on a weekly basis at minimum. All recorded calculations shall also be checked at this time.

5.7 Test report

The results of the entire testing process shall be presented in a Test Report. The report shall include all the test data, problems encountered, and conclusions.

A Test Report template is presented in Appendix 1.
6 Technology evaluation requirements

6.1 Data evaluation

6.1.1 Calculation of performance parameters

All calculations for common parameters are presented in Sections 5.2 and 5.3, based on EN ISO 15839. Any special calculations excluded in EN ISO 15839 shall be described in details. An example for description of special calculations is shown in Example 12.

**Example 12. Description of special calculations**

Special calculations performed for this Spectrolyser test and not included in the EN ISO 15839 are described below:

- **Precision (relative standard deviation):** Calculated as relative standard deviation on repeatability tests performed on 20% and 80% of stated range.
- **Trueness:** Calculated as 100% minus relative bias at 20% and 80% of stated range for laboratory samples.
- **Robustness:** Maximum relative effect from interference, temperature effect and memory effect. Calculated as 100% minus relative bias for 10 samples tested in field.

6.1.2 Performance parameter summary

The results for the performance parameters shall be summarised and presented. Details of important findings in the test shall be discussed.

An example for performance parameter summary is shown in Example 13.

**Example 13. Summary of performance parameter**

The performance parameters found are summarized in the table below. Field testing was in agreement with the EN ISO standard 15839, and due to problems in the field was only performed for nitrate. Therefore field results are only included for robustness of nitrate.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limit of detection mg/L</th>
<th>Range of application mg/L</th>
<th>Precision</th>
<th>Robustness %</th>
<th>Trueness %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>0.19</td>
<td>0.19-62</td>
<td>0.19-0.38</td>
<td>93-111</td>
<td>94-96</td>
</tr>
<tr>
<td>COD</td>
<td>5.7</td>
<td>5.7-950</td>
<td>0.71-1.1</td>
<td>96-104</td>
<td>99-103</td>
</tr>
</tbody>
</table>

The parameter having the highest impact on robustness of nitrate measurements was the temperature and test in field. A decrease in test temperature from 15°C to 5°C gave a robustness of 93%. The bias for the field test of nitrate, was 11% corresponding to a robustness of 111%. For the field tests it shall be noticed that a paired t-test showed no significant difference between the reference method and the S::CAN Spectrolyser, in part due to significant difference between the reference measurements and the S::CAN Spectrolyser values.

The parameter having the highest impact on robustness on COD measurements was 5% PAX interference. The interference caused both low and high measurements. Since it was not possible to perform COD test under field conditions, and knowing that field conditions caused the highest deviation on robustness for nitrate, there is indication of the robustness for COD of 96-104 being too optimistic.

The bias for 80% of concentration range in laboratory test was -5.9%, corresponding to a trueness of 94%. The bias for 20% of concentration range in laboratory test was -1.9%, corresponding to a trueness of 98%.
The bias for COD in the laboratory test was 3.3% and -0.5% respectively for 20% and 80% of concentration range for COD, corresponding to a trueness of 99% and 103%.

The response time is equal to the minimum of period between two measurements offered by the instrument. This results in a response time of 30 seconds in the laboratory and 4 minutes in the field. The difference between laboratory and field response time is due to the need of the hydraulic-pneumatic cleaning between all measurements in the wastewater.

Results for short term drift, long term drift, availability and up-time are presented in the table below.

<table>
<thead>
<tr>
<th>Performance parameter</th>
<th>Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short time drift</td>
<td>Laboratory</td>
<td>-0.10% /day for nitrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0% / day for COD</td>
</tr>
<tr>
<td>Long time drift</td>
<td>Field</td>
<td>0.8% / day</td>
</tr>
<tr>
<td>Availability</td>
<td>Field</td>
<td>100%</td>
</tr>
<tr>
<td>Up-time</td>
<td>Field</td>
<td>100%</td>
</tr>
</tbody>
</table>

6.1.3 Reference control data

Reference data shall be presented here to evaluate performance of the tested sensor. An example is shown in Example 14.

**Example 14. Reference control data for Spectrolyser**

Check for stability of dilutions for laboratory testing was measured as absorbance in the UV areas relevant for nitrate and COD. The trueness and repeatability of the results for standards of 10 ppm NO₃-N and 500 ppm COD are listed in the table below.

<table>
<thead>
<tr>
<th></th>
<th>Repeatability (RSD)</th>
<th>Trueness</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃-N</td>
<td>0.051</td>
<td>100</td>
</tr>
<tr>
<td>COD</td>
<td>1.4</td>
<td>101</td>
</tr>
</tbody>
</table>

6.1.4 Amendments to and deviations from protocol and test plan

Any amendments to and deviation from the Test Plan shall be described here. An example is shown in Example 15.

**Example 15. Amendments to and deviations from protocol and test plan of Spectrolyser**

Suspended solid (SS) had to be excluded from the laboratory testing since it was impossible to produce a stable reference of activated sludge in different concentrations.

In the field it was not possible to retrieve sufficient variation in COD and SS measurements, COD and SS therefore had to be excluded from the field testing.

No verification has therefore been performed for SS, and robustness under field conditions has not been verified for COD.
7 Quality assurance (QA)

The required procedure for QA is described in Figure 1. The QA process and results shall be recorded. An example is shown in Example 16.

<table>
<thead>
<tr>
<th>Name of the Test Organisation</th>
<th>The Expert Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Personnel</td>
<td>Mr. John Smith</td>
</tr>
<tr>
<td></td>
<td>Dr. Alan Brown</td>
</tr>
<tr>
<td>Tasks</td>
<td></td>
</tr>
<tr>
<td>Plan document with application definition and test plan</td>
<td>Reviewed</td>
</tr>
<tr>
<td></td>
<td>Reviewed</td>
</tr>
<tr>
<td>Test report</td>
<td>Reviewed</td>
</tr>
<tr>
<td></td>
<td>Reviewed</td>
</tr>
</tbody>
</table>
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solids</td>
</tr>
<tr>
<td>EN</td>
<td>European Standard</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standardisation Organisation</td>
</tr>
<tr>
<td>ETV</td>
<td>Environmental technology verification</td>
</tr>
<tr>
<td>QA</td>
<td>Quality assurance</td>
</tr>
<tr>
<td>QC</td>
<td>Quality control</td>
</tr>
<tr>
<td>LoD</td>
<td>Limit of detection</td>
</tr>
<tr>
<td>LoQ</td>
<td>Limit of quantification</td>
</tr>
<tr>
<td>LDC</td>
<td>Lowest detectable change</td>
</tr>
<tr>
<td>PAX</td>
<td>Polyaluminum chloride</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>O&amp;M</td>
<td>Operation and maintenance</td>
</tr>
</tbody>
</table>
9 References


10 Appendix I. Template for On-line Sensor Test Report

I. Scope of work

Differing from the test protocol, which serves as a management document covering all the testing phases (planning, testing, and data evaluation), a test report aims to demonstrate key results, findings, and recommendations and present all relevant data generated in the testing.

In this test report template, the main template body summarises all key results, findings, and recommendations from the testing, and appendix contains all relevant data files.

II. Test report template

Front cover

Include name of the report, testing parties, issue data, version

Inside front cover

Include information about authors, project no. Test Organisation contacts, vendor representatives, signatures, key words, documentation classification, etc.

Executive summary

1. Table of contents

2. Introduction

2.1 Test protocol reference

Indicate the responding test protocol used for the testing

2.2 Name and contact of Vendor

2.3 Name and contact of Test Organisation

2.4 Name and contact of Expert Group

3. Test Plan

3.1 Test sites

Include types of test sites (laboratory or field), addresses, and descriptions

3.2 Test design

Include test materials and methods, staffs, schedules, test equipment, type and number of samples, operation conditions, product maintenance, and HSE (health, safety, and environment) details.
4. Reference analysis

Include analytical laboratory, parameters, methods, and performance requirements

5. Data management

Include data storage, transfer and control

6. Quality assurance

Include test plan review, performance control, test system control, data integrity check procedures, and test report review

7. Test results

Include test data summary (both laboratory test and field test), test quality assurance summary, test performance evaluation, and amendments and deviations from test plan

Examples of test results for laboratory and field tests are shown in Tables a1 and a2.

Table a1. Example of test results for laboratory test

<table>
<thead>
<tr>
<th>Performance characteristic</th>
<th>Unit</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time for positive change, / R+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response time for negative change, / R-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for positive change, /D+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for negative change, /D-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rise time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fall time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linearity (including range over which check carried out)</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Limit of detection (LoD)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limit of quantification (LoQ)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Repeatability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lowest detectable change (LDC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short-term drift</td>
<td>%/day</td>
<td></td>
</tr>
<tr>
<td>Day-to-day repeatability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Memory effect</td>
<td>If present, give value</td>
<td></td>
</tr>
<tr>
<td>Inference caused by interferent 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inference caused by interferent 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Environmental and operation conditions:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Requirement 1 (lower/upper limits)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Requirement 2 (lower/upper limits)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table b1. Example of test results for field test

<table>
<thead>
<tr>
<th>Performance characteristic</th>
<th>Unit</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time for positive change, / R+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response time for negative change, / R-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for positive change, /D+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay time for negative change, /D-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rise time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fall time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bias based on (relative/absolute) differences</td>
<td>%/day</td>
<td></td>
</tr>
<tr>
<td>Long-term drift</td>
<td>%/day</td>
<td></td>
</tr>
</tbody>
</table>
8. Conclusions and recommendations

9. References

Appendix 1. Terms, definitions, and abbreviations used in the test report
Appendix 2. Performance parameter definitions and calculations
Appendix 3. Data reporting forms
Appendix 4. Meeting minutes (if applicable)