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Nordic Innovation Centre

NOWATECH

ETV Testnet

DHI

S::CAN Spectrolyser

Verification report

Multiparameter sensor for use in wastewater

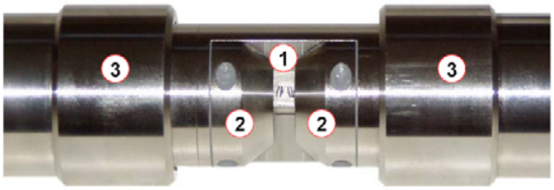
1 Probe's housing (emitter side)
2 Measuring section
3 Probe's housing (detector side)
4 Cable gland
5 Probe cable
6 Connector

Measuring section

1 Optical measuring path

2 cleaning nozzles

3 Fixtures for the measuring path (fixed)



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Version final

S::CAN Spectrolyser

Verification report

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1 TABLE OF CONTENTS

2 INTRODUCTION

Environmental technology verification (ETV) is an independent (third party) assessment of the performance of a technology or a product for a specified application, under defined conditions and quality assurance.

This verification report is a joint effort with the TESTNET project under the 6th Framework Programme for Research of the European Union. The verification has been done and reported under TESTNET, and this report constitutes the transfer of the verification to the Nordic Water Technology Verification Centers (NOWATECH ETV) approach. Accordingly, not all parts of the NOWATECH verification requirements have been fulfilled and an independent NOWATECH verification statement has not been issued.

2.1 Name of product

The product is the S::CAN Spectrolyser probe for water, including wastewater. The S::CAN Spectrolyser for wastewater monitoring is a fairly recently marketed product, and represents the group of multiparameter sensors based on spectral UV-VIS absorbance measurements.

2.2 Name and contact of vendor

S::CAN Messtechnik GmbH, Brigittagasse 22-24, A-1200 Vienna, Austria, phone +43 1 219 73 93 – 0.

Contact: Joep van den Broeke, email: jvandenbroeke@s-can.at

Web site: www.s-can.at

2.3 Name of center/verification responsible

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Verification responsible: Anders Lynggaard-Jensen, email alj@dhigroup.com, phone +45 86 20 51 20.

Test responsible: Ida Rasmussen, e-mail idr@dhigroup.com, phone +45 86 20 51 26.

The verification was done following the suggested ETV verification scheme without a Verification Institute (included in Appendix 6) as suggested by TESTNET. Accordingly, verification and testing have not been separated as prescribed in the NOWATECH approach.

2.4 Verification Test Organization

The verification has been conducted according to the Nordic Water Technology Verification Centers (NOWATECH ETV). Verification was performed by DHI as NOWATECH Water Test Center (DHI WTC) and tests by DHI as TESTNET project partner.

The day-to-day operations of the verification and tests were coordinated and supervised by DHI personnel, with the participation of the vendor, S::CAN. The testing was conducted in the DHI laboratories, Aarhus, Denmark and in the field at a wastewater treatment plant in Aarhus, Denmark. DHI operated the analyzer during the verification. S::CAN provided the analyzer and controller, user manuals and operation instructions. They also participated in development of protocol and plans with DHI.

2.5 Expert group

Within the framework of the ETV Scheme suggested by TESTNET and included in Appendix 6, the Test Laboratory appoints a task group. In this case the task group consisted of the DHI WTC and the Producer, S::CAN. The possibility of including other experts was evaluated. Edu van Naerssen from KIWA in the Netherlands was involved as reviewing expert, but a need for an external expert group besides this was not found, as an internationally accepted ISO (International Standardization Organization) test guideline exists.

2.6 Verification process

The principles of operation with the roles of the verification and test documents and the different sub-bodies responsible are given in Figure 2.1.

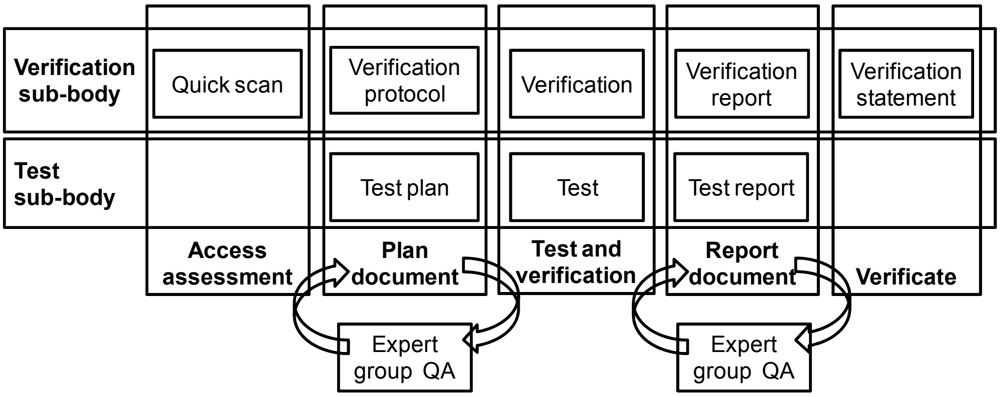

Figure 2.1 Principles of operation of the NOWATECH verification scheme.

The verification and test were performed according to standard in EN ISO 15839 Water quality – On-line sensors/analysing equipment for water – Specifications and performance test. Therefore, the preparation of the test plan was almost covered by the standard.

DHI WTC has performed Quickscan and sent the scan report to the expert at KIWA. KIWA approved the technology as fit for test. DHI WTC formed a task group together with the producer and they made a test protocol fit for use and agreed test plan. DHI WTC performed tests. Verification report was prepared and sent to the expert at KIWA for evaluation.

3 DESCRIPTION OF THE TECHNOLOGY

Spectrometer probes work according to the principle of UV-VIS spectrometry. 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 a certain and known wavelength. The concentration of substances contained determines the size 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.

The absorbance is the logarithm of the ratio of two light intensities: The intensity of light determined after the beam passed through a so-called reference medium (distilled water) and the intensity of light after the beam passed through the medium. There is a linear increase in absorption with higher concentrations.

4 DESCRIPTION OF THE PRODUCT

Every S::CAN Spectrolyser probe consists of three main components: emitter, measuring cell and receiving unit. These can be easily identified from the outside as three different parts of the instrument. The Spectrolyser is shown in Figure 4.1, while the principles are schematically shown in Figure 4.2.

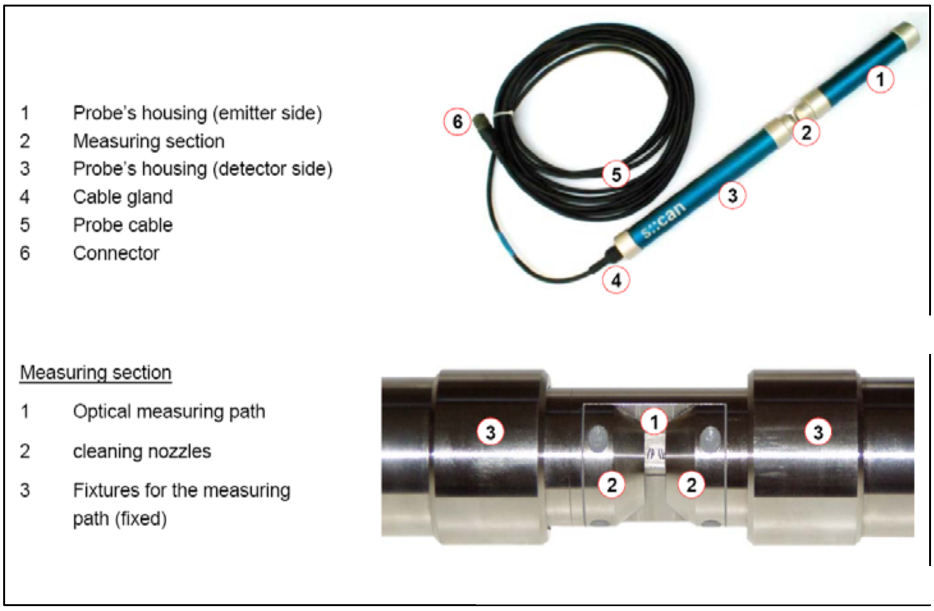

Figure 4.1 Overview of S::CAN Spectrolyser spectrometer probe.

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 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. ageing of the flash lamp) which are automatically compensated for.

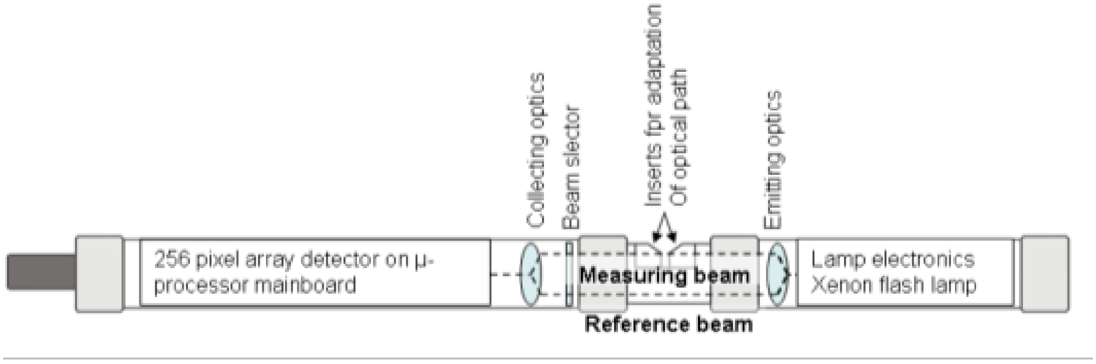

Figure 4.2 Schematic drawing of the main components of the S::CAN Spectrolyser.

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.

5 APPLICATION AND PERFORMANCE PARAMETER DEFINITIONS

The application is defined as detailed in the application definition appendix, Appendix 3, in terms of matrix/matrices for use, targets of monitoring and effects.

5.1 Application definition

An overview of matrix, effect, target and technology for the S::CAN Spectrolyser is given in Table 5.1.

Table 5.1 Description of matrix, effect, targets and technologies for the S::CAN Spectrolyser.

Matrix	**Effect**	**Targets**	**Technology**
Spectrolyser is applied for surface water, ground water, drinking water and wastewater. The matrix verified is activated sludge tanks in a wastewater treatment plant.	Monitoring of nitrate and COD. Only nitrate was included in final field testing	Limit of detection (LoD), precision, repeatability, range of application and robustness of nitrate monitoring	Spectrometer probes according to the principle of UV-Vis spectrometry with a detector covering a range of wavelengths

5.2 Performance parameters for verification

The ranges of performance relevant for the application, as derived in Appendix 3, are presented in Table 5.2. These ranges are used for planning the verification and testing only.

Table 5.2 Relevant ranges of performance parameters in activated sludge tanks.

	Limit of detection	**Range of application**	**Precision (repeatability)**		**Precision (reproducibility)**	**Trueness**	**Robustness**
				%	%	%	%
Nitrate	0.1 mg NO_3-N/L	LoD-65 mg NO_3-N/L(lab.) LoD-20 mg NO_3-N/L (field)	20% of range: 1 mg NO_3-N/L 80% of range: 5 mg NO_3-N/L	< 10	< 15	100±10	100±10
COD	1 mg COD/L	LoD-1000 mg COD/L	20% of range: 20 mg COD/L 80% of range: 80 mg COD/L	< 25	< 30	100±10	100±10

The difference in range of application for laboratory 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 NO_3-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.

According to 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 should not be set up, since they provide the same basic information as the limit of detection, which has been included in the performance parameters.

ISO 15839 requires determination of bias. In NOWATECH verifications trueness is often used instead of bias. Trueness is calculated from bias in percent as 100% minus bias.

Reproducibility is tested in the 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 was 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 was investigated with:

- Ferrichloride.
- PAX (PolyAluminum Chloride).

5.3 Additional parameters

Besides the performance parameters to be obtained by testing, product costs, user manual and occupational health and environment were included for the verification.

6 EXISTING DATA

6.1 Summary of existing data

The performance of the S::CAN Spectrolyser has previously been tested. Several studies have been performed on effluent wastewater and reported e.g. in /9-11/.

Focus has been on the correlation to reference samples and the calibration of the S::CAN Spectrolyser. A graphical result from /11/ is shown in Figure 6.1.

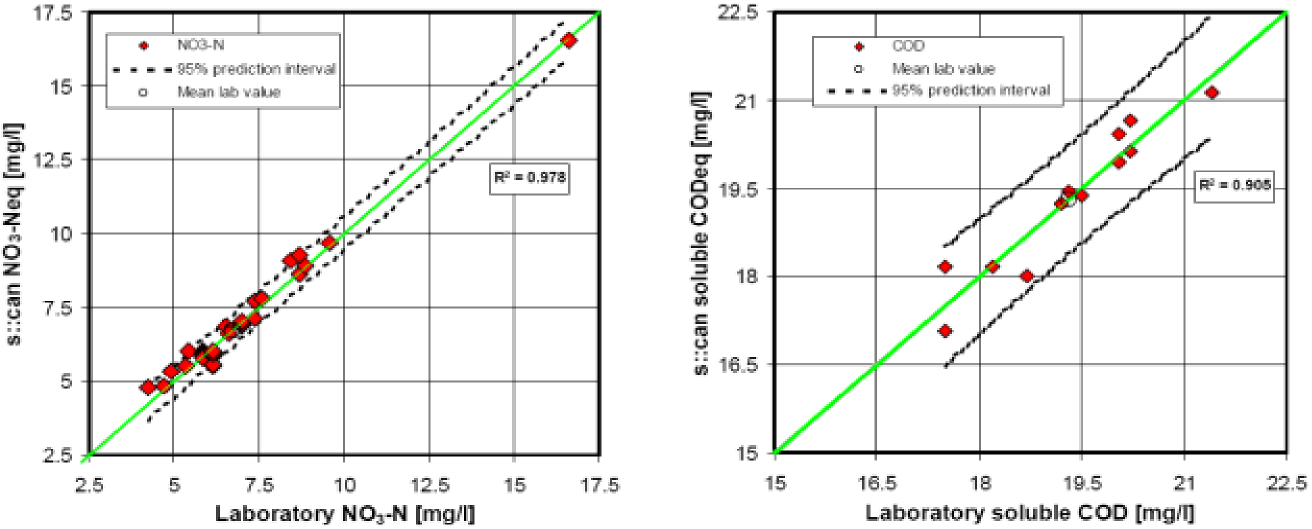

Figure 6.1 Calibration data for nitrate and COD based on Swizz wastewater treatment plant effluent samples /11/.

Table 6.1 Calibration result for nitrate and COD from different references.

Reference	**Range**	**Correlation coefficient**	**95% prediction interval on mean value** %
Nitrate			
/11/	4-17mg NO_3-N/L	0.978	± 8
/10/	0-10 mg NO_3-N/L	0.68	
/9/	1-16 mg NO_3-N/L	0.95	
COD			
/11/	17-22 mg COD/L	0.905	± 5
/10/	0-600 mg COD/L	0.91	
/9/	Not reported	0.77	

It is noticed that the correlation coefficients are generally good and close to 1. The 95% prediction interval on mean value is seen to be good and for both parameters. As seen from Figure 6.1 the measuring range is very limited and these results therefore have to be validated in tests with wider measuring range.

6.2 Quality of existing data

The existing data are limited considering the requirements for verification and have all been produced with focus on equipment calibration.

No raw data are available, so the quality cannot be checked in details.

6.3 Accepted existing data

No existing data are accepted, as part of this verification.

7 TEST PLAN REQUIREMENTS

Based on the application and performance parameter identification, Section 5, the requirements for test design have been set, see below. The detailed test plan is prepared separately based on the specification of test requirements presented below.

7.1 Test design

The outline of the required tests is based on standard EN ISO 15839. An overview of actual tests performed is shown in Table 7.1. The principle behind the design is that two test scales are used: laboratory tests and field tests. Each scale is further described below and provides information on specified performance parameters, with the smallest scale adequate chosen for each parameter in order to maintain simplicity and controlled conditions in the test.

Table 7.1 Parameters to be tested in laboratory and field.

Test parameter	**Laboratory**	**Field**
Response time	X	X
Linearity/Range of application	X	
Coefficient of Variation	X	
Limit of detection (LOD)	X	
Limit of quantification (LOQ)	X	
Repeatability	X	
Lowest detectable change (LDC)	X	
Bias (100% - bias = trueness)	X	X
Short term drift	X	
Long term drift		X
Reproducibility, Day to day repeatability	X	
Availability and up-time		X
Robustness, Memory effect	X	
Robustness, Interference	X	
Robustness, Environmental conditions: Temperature test	X	

7.2 Reference analysis

In the laboratory tests standard solutions were prepared covering the ranges stated by the manufacturer. The solutions contained 0, 5, 20, 35, 50, 65, 80, 95 and 200% of the stated range. Potassium nitrate, KNO_3 was used for the nitrate standard, while potassium hydrogen phthalate, $KHC_8H_4O_4$ was used for the COD standard. No reference analyses of the dilutions were performed. Only the stability of the dilutions was tested, see details in Section 8.3.1.

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.

Reference analyses in the field were made with a spectrofotometric quick test equipment Merck Spectroquant NOVA60, using MERCK test kits for nitrate. The test kits used were no. 1.14542.0001 and no. 1.14556.0001. Data on their performance are listed in Table 7.2.

Table 7.2 Performance parameters for MERCK nitrate test kits /14,15/.

Test kit no.	**1.14542.0001**	**1.14556.0001**
Measuring range	0.5-18.0 mg NO_3-N/L	0.1-3.00 mg NO_3-N/L
Sensitivity: 0.010 A (absorbance)	0.1 mg NO_3-N/L	0.02 mg NO_3-N/L
Lower limit of detection (LLD)	0.06 mg NO_3-N/L	0.014 mg NO_3-N/L
Relative standard deviation (RSD)	± 1.5%	± 2.0%
Trueness	± 0.6 mg NO_3-N/L	± 0.30 mg NO_3-N/L

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 testing.

7.3 Data management

The instrument communicates with a PC via a serial link. The software is delivered by the producer and can be used for manual operation of the instrument, and all readings, measurements and calculations are stored on the PC in the manufacturer's file format. Measurements are transferred from this file to an Excel sheet prepared by the test laboratory.

The Excel sheet is prepared after the guidelines in EN ISO15839. Following this, all calculations etc. as prescribed in EN ISO15839 are added to the Excel sheet and final reports also following the guideline in the standard collect and present the performance characteristics. The filled in sheets are included as appendix in the test report, while the performance characteristics are given in the test report.

7.4 Quality assurance

The quality assurance of the tests has included control of the reference system, control of the test system and control of the data quality and integrity.

The test plan and the test report have been subject to review by the expert at KIWA and the task group as part of the review of this verification report, see Figure 2.1.

7.5 Test report

The test report must follow the principles of the template of the DHI NOWATECH verification center quality manual template /1/ with data and records from the tests presented.

8 EVALUATION

The evaluation includes calculation of the performance parameters, see Section 5.2 for definition, evaluation of the data quality based upon the test quality assurance, and compilation of the additional parameters as specified in Section 5.3.

8.1 Calculation of performance parameters

All calculations are done according to EN ISO15839.

Calculations have been performed in Excel 2007 set-up for the purpose with the equations required.

Special calculations performed for this report 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.

8.2 Performance parameter summary

The performance parameters found are summarized in Table 8.1. Field testing was in agreement with the ISO standard 15839, and was due to problems in the field only performed for nitrate. Therefore field results are only included for robustness of nitrate.

Table 8.1 Actual performance parameters in activated sludge tanks.

Compound	Limit of detection mg/L	Range of application mg/L	Precision		Robustness %	Trueness %
			Repeatability %	Reproducibility %		
Nitrate	0.19	0.19-62	0.19-0.38	0.40-0.91	93-111	94-98
COD	5.7	5.7-950	0.71-1.1	0.94-1.5	96-104	99-103

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 Table 8.2.

Table 8.2 Results for selected parameters from laboratory and field test.

Performance parameter	Test	Result
Short time drift	Laboratory	-0.10% /day for nitrate 0.0% / day for COD
Long time drift	Field	0.6% / day
Availability	Field	100%
Up-time	Field	100%

8.3 Evaluation of test data quality

8.3.1 Reference control data

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 NO_3-N and 500 ppm COD are listed in Table 8.3.

Table 8.3 Repeatability as relative standard deviation (RSD) and trueness.

	Repeatability (RSD) %	**Trueness** %
NO_3-N	0.051	100
COD	1.4	101

8.3.2 Audits

No audit was performed.

8.3.3 Amendments to and deviations from protocol and test plan

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.

8.4 Additional parameter summary

8.4.1 User manual

The verification criterion for the user manual is that it describes the use of the measurement device adequately and understandably for the typical analyst. This criterion was evaluated through evaluation of a number of specific points of importance, see Table 8.4.

A description is complete, if all essential steps are described, if they are illustrated with a figure or a photo, where relevant, and if the descriptions are understandable without reference to other guidance.

Table 8.4 Criteria for user manual evaluation.

Parameter	**Complete description**	**Summary description**	**No description**	**Not relevant**
Product				
Principle of operation	√			
Intended use	√			
Performance expected	√			
Limitations				
Preparations				
Unpacking	√			
Transport	√			
Assembly	√			
Installation	√			
Function test			√	
Operation				
Steps of operation	√			
Points of caution	√			
Accessories	√			
Maintenance	√			
Trouble shooting	√			
Safety				
Chemicals				√
Power	√			

8.4.2 Product costs

The capital investment costs and the operation and maintenance costs were itemized based on a determined design basis /12/, see Table 8.5. Note that the actual cost for each cost item is not compiled and reported.

The scenario is based on one year’s operation of one S::CAN Spectrolyser for online measurements and 2 software packages, to be able to see results on a site and a remote computer.

Table 8.5 List of capital cost items and operation and maintenance cost items per product unit (sample).

Item type	Item	Number	None
Capital			
Site preparation			√
Buildings and land			√
Equipment	Spectrolyser Flow cell Controller Software packages	1 1 1 2	
Utility connections	Compressed air Power	1 1	
Installation	Rod for installation on site	1	
Start up/training	Training (1 day for 2 men)	2 days	
Permits			√
Operation and maintenance			
Materials, including chemicals			√
Utilities, including water and energy	Electricity	4 MWh	
Labour	Labour	3 days	
Waste management			√
Permit compliance			√

8.4.3 Occupational health and environment

No impact on occupational health and environment is identified by using the verified S::CAN Spectrolyser. No chemicals are used during the measurements and the operation of the equipment involves no heavy lifting or other actions requiring special safety precautions.

The risk with regard to occupational health and environment is therefore only seen as normal for operations performed on wastewater treatment plants.

8.5 Recommendations for verification statement

It is recommended to include the performance parameters' summary as listed in Table 8.1.

9 VERIFICATION SCHEDULE

According to the test plans, the tests should be carried out during a period of 6 days for each of the tested variables – in total 12 working days. However, this schedule turned out to be too tight. A total of 14 days were used – mostly due to problems during the interference test using ferrichloride.

10 QUALITY ASSURANCE

The quality assurance of the verification is described in Table 10.1 and Figure 2.1, and the quality assurance of the tests is described in the test plan.

Table 10.1 QA plan for the verification.

	DHI	**Expert Group**
Initials	Anders Lynggaard-Jensen Christian Grøn	Edu van Naerssen
Tasks		
Plan document with application definition, verification protocol and test plan	Review	Review
Report document with test report and verification report	Review	Review

APPENDIX 1

Terms and definitions used in the verification report

The abbreviations and definitions used in the verification protocol and the test plan are summarized below.

Word	**NOWATECH**	**Comments**
Application	The use of a product specified with respect to matrix, target, effect, clarified by statement of any limitations	The application must be defined with a precision that allows the user of a product verification to judge whether his needs are comparable to the verification conditions
Absorbance	The intensity of light at a specified wavelength	
COD	Chemical Oxygen Demand	
DHI WTC	(ETV) Water Test Center at DHI	
Effect	The way the target is affected	The effect could be concentration reduction, decrease in treatment period, pH increase, measurement of a component, etc.
EN	European standard	
Environmental technology	The practical application of knowledge in the environmental area in a technology, the use of which is less environmentally harmful than relevant alternatives	The term technology covers a variety of products, processes, systems and services
ETV	Environmental technology verification (ETV) is an independent (third party) assessment of the performance of a technology or a product for a specified application, under defined conditions and adequate quality assurance	
EU	European Union	
Evaluation	Evaluation of test data for a technology product for performance and data quality	
Experts	Independent persons qualified on a technology in verification or on verification	These experts may be technical experts, QA experts, e.g. for other ETV systems, or regulatory experts
ISO	International Standardization Organization	

Word	**NOWATECH**	**Comments**
Limit of detection LoD	Calculated from the standard deviation of replicate measurements at less than 5 times the detection limit evaluated. Corresponding to less than 5% risk of false blanks	
Limit of quantification LoQ	Calculated from the detection limit, typically 3 times the LoD, the concentration, where the blank variation impacts the precision 20%	
Matrix	The type of material that the product is intended for	Matrices could be soil, drinking water, ground water, etc.
Method	Generic document that provides rules, guidelines or characteristics for tests or analysis	An in-house method may be used in the absence of a standard, if prepared in compliance with the format and contents required for standards
NOWATECH	Nordic Water Technology Verification Centers	
(NOWATECH) test center	Preliminary name for the verification bodies in NOWATECH with a verification and a test sub-body	Name will be changed, when the final nomenclature in the EU ETV has been set
Performance parameters	Parameters that can be documented quantitatively in tests and that provide the relevant information on the performance of an environmental technology product	The performance parameters must be established considering the application(s) of the product, the requirements of society (regulations), customers (needs) and vendor claims
Precision	The standard deviation obtained from replicate measurements, here measured under repeatability or reproducibility conditions	
Procedure	Detailed description of the use of a standard or a method within one body	The procedure specifies implementing a standard or a method in terms of e.g.: equipment used
Producer	The party producing the product	
(Environmental) product	Ready to market or prototype stage product, process, system or service based upon an environmental technology	The product is the item produced and sold and thus the item that a vendor submits for verification
QA	Quality assurance	

Word	NOWATECH	Comments
Range of application	The range from the LoD to the highest concentration with linear response	
Repeatability	The precision obtained under repeatability conditions, that is with the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time	
Robustness	% variation in measurements resulting from defined changes in matrix properties	
RSD	Relative standard deviation in %	
Standard	Generic document established by consensus and approved by a recognized standardization body that provides rules, guidelines or characteristics for tests or analysis	
Target	The property that is affected by the product	The target could be mg N/L of treated wastewater or detection limit for a measurement
Test center, test sub-body	Sub-body of the test center that plans and performs test	May by within same organization as the verification sub-body, or may not
Test center, verification sub-body	Sub-body of the test center that plans and performs the verification	May by within same organization as the test sub-body, or may not
Test/testing	Determination of the performance of a product for parameters defined for the application	
Vendor	The party delivering the product to the customer	Can be the producer
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance	

APPENDIX 2

References

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APPENDIX 3

Application and performance parameter definitions

This appendix defines the application and the relevant performance parameters as input for verification and test of an environmental technology following the NOWATECH ETV method.

1 Applications

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

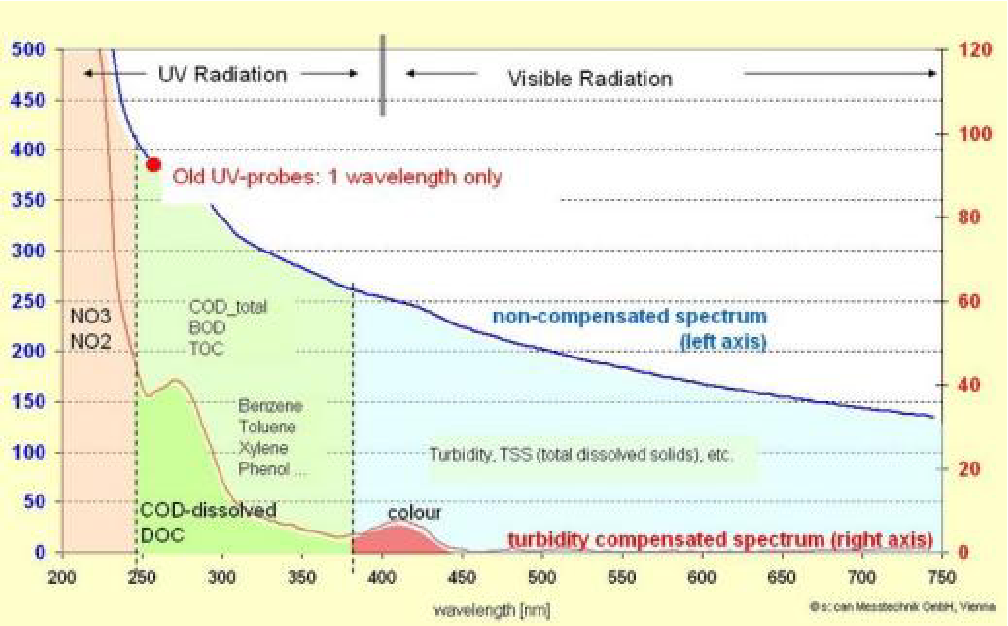
The S::CAN Spectrolyser is an online analyzer which measures directly in the wastewater, in essence combining “sampling” and measurement, and the verification shall accordingly see these two investigation steps as one.

1.1 Matrix/matrices

The S::CAN Spectrolyser can be applied for surface water, ground water, drinking water and wastewater. The matrix of the application verified is activated sludge in a wastewater treatment plant.

1.2 Effect

The S::CAN Spectrolyser can monitor among others nitrate, COD (Chemical Oxygen Demand), DOC (Dissolved Organic Carbon), nitrite, BTX (benzene, toluene and xylene), hydrogen sulphide, SS (suspended solid), ozone, turbidity and colour. Examples hereof are shown in Appendix Fig 1. Further it can also scan for specific fingerprints or be used for giving alarm in case of contaminant or hydrocarbon occurrence.



Appendix Fig 1 Examples of parameters found in the UV-Vis spectrum between 200 and 750 nm.

The effects of the product of this verification are nitrate and COD (Chemical Oxygen Demand). Only nitrate was included in the final field testing.

1.3 Targets

The targets for the application are generally reported in terms of limit of detection (LoD), precision (repeatability), trueness, range of application and robustness. The targets claimed by the vendor are given in Appendix Table 1 for the two target compounds.

The robustness is the change in trueness within the range of application for defined variations in e.g. contaminant concentration.

Appendix Table 1 Vendor claim of performance /4/,/7/.

	Limit of detection mg/L	**Repeatability** mg/L	**Trueness** mg/L	**Range of application** mg/L	**Robustness** %
Laboratory (effluent)					
Nitrate	0.1	± 0.1	Better than ± 0.3	0-65	Not claimed
COD	1	± 5	± 10	0-1000	Not claimed
Field (activated sludge tank)					
Nitrate	0.1	± 0.1	Better than ± 0.3	0-20	Not claimed

1.4 Exclusions

The verification was performed in wastewater, so other media as surface water, groundwater and drinking water are excluded.

Among the list of possible parameters nitrate, COD (Chemical Oxygen Demand) and SS (suspended solid) were chosen as targets for this verification. Suspended solid had later 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 testing it was also planned to include nitrate, COD and SS. However, it was not possible to retrieve sufficient variation in COD and SS measurements, there was only a barely measurable variation in the COD concentration in the active sludge tank. Values could be obtained either with the activated sludge tanks being fully mixed or with the sludge settled at the tank bottom (no COD/SS). It was impossible to take corresponding reference samples during the settling. The results were therefore only no COD/SS and a concentration with tank fully mixed, without any concentrations in between. This is not sufficient for calibration of the S::CAN Spectrolyser, COD and SS therefore had to be excluded from the field testing.

2 General performance requirements

No formal performance requirements for the application have been identified in the European Union.

The conventional performance parameters of analytical and monitoring methods and equipment are limit of detection (LoD), precision (repeatability and reproducibility), trueness, specificity, linearity and matrix sensitivity. The uncertainty of measurements may be used to summarize the performance. Parameters may be added to characterize e.g. online or on-site monitoring instruments.

2.1 Regulatory requirements

Within the field of online measurements of nitrate and COD in activated sludge tanks, no regulatory requirements for monitoring performance exist. Measurements of treated wastewater is regulated by the Danish executive order 1353 from 2006 regarding quality requirements for environmental measurements performed by accredited laboratories, certified personnel, etc. This executive order is based on 3 EU directives: 91/271 21/05-1991, 98/83 03/11-1998 and 76/160 08/12-1975.

The executive order states the maximum total standard deviation ($S_{T\ Max}$) for COD and nitrogen measurements in treated wastewater as follows:

- Nitrogen: $S_{T\ Max} = 0.03$ mg N/L
- COD: $S_{T\ Max} = 10$ mg O_2/L

S_T is defined as:
$S_T = s_w + s_b$

where s_w is the variation within series and s_b is the variation between series.

The detection limit, DL, is defined as:
$DL = s_w * 3$

s_w can maximum be equal to S_T. This therefore results in maximum detection limits for COD and nitrogen:

- Nitrogen: $DL_{Max} = 0.09$ mg N/L
- COD: $DL_{Max} = 30$ mg O_2/L

The regulatory concentration limits in wastewater effluent differ for each country and for each type of recipient. For COD the limit is further transport based, as a rule of thumb a concentration of 75 mg COD/L can be seen as requirement for effluent. There is no specific requirement for nitrate in Denmark, here nitrate is covered in the limit to total nitrogen of 8 mg N/L.

2.2 Application based requirements

For measurements in an activated sludge tank the response time is important whereas the exact concentration levels are secondary. Here the purpose of the measurements is to see changes in concentrations with high resolution.

For effluent wastewater the requirements are opposite. Here the purpose of the measurements is to see absolute concentrations, but not necessarily with high resolution.

The requirement for the analyser is that the precision has to be sufficiently good near the discharge criteria.

3 State-of-the-art performance

On the market are other similar spectrometer probes. Details on the performance of two with regards to nitrate and COD are compared in Appendix Table 2.

Appendix Table 2 Performance parameters for 3 spectrometer probes.

	Limit of detection	Repeatability	Trueness	Range of application	Reference
Nitrate					
STRP-scan	0.1 mg/L	3% (reproducibility)		0.3-23 mg/L	/5/
ISIS II	(0.1 mg/L)		± 5% rel. of full scale	0.1-100 mg/L	/6/
Laboratory (on synthetic samples)		Repeatability 1.2-5.2% Reproducibility 3.6-15%			/13/
Ion-selective electrodes (ISE)				0.4-62,000 mg/L	/8/
COD					
STRP-scan	2 mg/L	3% (reproducibility)		10-2000 mg/L	/5/
ISIS II	(10 mg/L)		± 5% rel. of full scale	10-100 mg/L	/6/
Laboratory (on synthetic samples)		Repeatability 2-8% Reproducibility 6.5-24%			/13/

The ion-selective electrodes (ISE) are used for the reference measurements for the nitrate field test.

4 Performance parameter definitions

Based on the above mentioned performance requirements, a set of relevant ranges of performance parameters for activated sludge tanks (and treated wastewater) have been sat up and are listed in Appendix Table 3.

Appendix Table 3 Relevant ranges of performance parameters in activated sludge tanks.

	Limit of detection	**Range of application**	**Precision (repeatability)**		**Precision (reproducibility)**	**Trueness**	**Robustness**
	mg/L			%	%	%	%
Nitrate	0.1 mg NO_3-N/L(	LoD-65 mg NO_3-N/L (lab.) LoD-20 mg NO_3-N/L (field)	20% of range: 1 mg NO_3-N/L 80% of range: 5 mg NO_3-N/L	< 10	< 15	100±10	100±10
COD	1 mg COD/L	LoD-1000 mg COD/L	20% of range: 20 mg COD/L 80% of range: 80 mg COD/L	< 25	< 30	100±10	100±10

APPENDIX 4

Test report

NOWATECH

S::CAN Spectrolyser

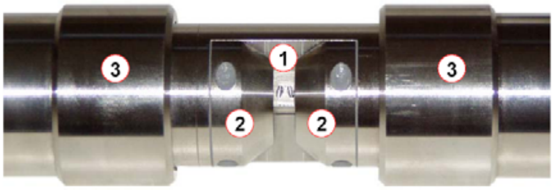
Test report

Multiparameter sensor for use in wastewater

1	Probe's housing (emitter side)
2	Measuring section
3	Probe's housing (detector side)
4	Cable gland
5	Probe cable
6	Connector

Measuring section

1	Optical measuring path
2	cleaning nozzles
3	Fixtures for the measuring path (fixed)



January 2010 **Version final**

S::CAN Spectrolyser

Test report

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Project Nordic Water Technology Verification Centers		Project No 80144/11710744				
Authors Ida Rasmussen, Mette Tjener Andersson, Anders Lynggaard Jensen		Date January 2010				
		Approved by Steen Lindberg				
	Final report	IDR/MTA	CHG	SL	10-01-19	
Revision	Description	By	Checked	Approved	Date	
Key words Environmental technology verification; Online optical analyzer; S::CAN spectrolyser; Wastewater		Classification ☒ Open ☐ Internal ☐ Proprietary				

Distribution		No of copies
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1 TABLE OF CONTENTS

2 INTRODUCTION

This test plan is the implementation of a test design developed for verification of the performance of an environmental technology following the NOWATECH ETV method.

2.1 Verification protocol reference

This test report is prepared in response to the test design established in the S::CAN Spectrolyser, verification report.

2.2 Name and contact of vendor

S::CAN Messtechnik GmbH, Brigittagasse 22-24, A-1200 Wien/Vienna, Austria, phone +43 1 219 73 93 – 0.

Web site: http://www.s:can.at/

Contact: Joep van den Broeke, e-mail jvandenbroeke@s-can.at

2.3 Name of center/test responsible

NOWATECH Water Test Center, DHI, Agern Allé 5, DK-2970 Hørsholm, Denmark.

Test responsible: Ida Rasmussen, e-mail idr@dhigroup.com, phone +45 86 20 51 26.

2.4 Expert group

The expert group assigned to this test and responsible for review of test plan and test report includes:

- Task group consisting of the DHI WTC and the Producer, S::CAN.
- Edu van Naerssen from KIWA, the Netherlands.

3 TEST DESIGN

The test design intended to supply the performance parameters defined in the Verification protocol Section 5.2, and is carried out according to the EN ISO 15839 standard /3/.

The laboratory test has been performed at the DHI WTC using an instrument delivered by the manufacturer incl. a manual sampling device, which can be mounted on the instrument in order to encapsulate the “measuring gap” of the instrument (Figure 3.1 – left). The “measuring gap” of the instrument was selected to be 2 mm in order to cover the ranges of the parameters (nitrate, COD and suspended solids) to be tested in the application: activated sludge tanks on wastewater treatment plants.

However, the instrument was not tested with suspended solids in the laboratory test, as it was deemed impossible to produce a stable reference of activated sludge in different concentrations.

For all tests except for the temperature robustness test, the manual sample device was used. When changing sample, the manual sample device was flushed three times with the new sample, to make sure that the sample was completely changed. This could be carried out within the 30 seconds between measurements. In order to keep the sample and the instrument at the same temperature, the sample was stored in the laboratory next to the probe. During the temperature test, the instrument was submerged (Figure 3.1 – right) – the water being the sample and passing through a cooling system.

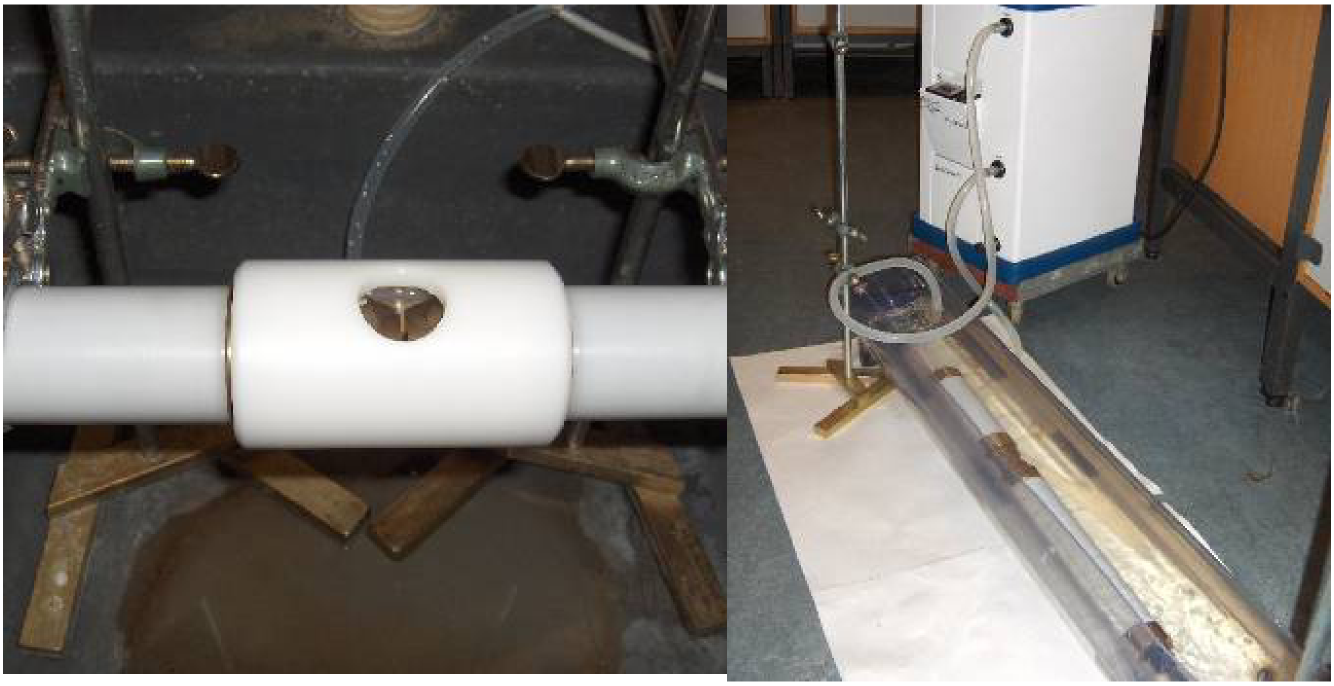


Figure 3.1 Set-up of instrument with manual sample device (left) and set-up for temperature test (right).

3.1 Test sites

The laboratory tests were conducted in the DHI laboratory buildings, Aarhus, Denmark.

The field tests were carried out at Aaby Wastewater Treatment Plant in Aarhus, Denmark.

3.1.1 Types

The test sites are summarized in Table 3.1.

Table 3.1 Summary of test sites.

Scale	Address/site	Site details	Test compounds
Laboratory	DHI premises, Aarhus	Activated sludge tank/ effluent	Nitrate, DOC
Field	Aaby Wastewater Treatment Plant, Aarhus	Activated sludge tank	Nitrate

3.1.2 Addresses

See Table 3.1.

3.1.3 Descriptions

See Table 3.1.

3.2 Tests

3.2.1 Test methods

The S::CAN Spectrolyser multiparameter sensor has been tested according to the EN ISO 15839 standard used for an application on wastewater treatment plants (NOx, and COD in activated sludge) /3/.

3.2.2 Test staff

The test responsible was Ida Rasmussen (IDR) while Niels Eisum (NHE) has participated in the testing.

3.2.3 Test schedule

The test schedule is given in Table 3.2.

Table 3.2 Actual test schedule

Test	Testing period
Nitrate tests in lab	8-16 March 2007, 26 April 2007
COD tests in lab	19-26 April 2007
Nitrate field test	14 September-25 October 2007

3.2.4 Test equipment

The test equipment includes (working procedures):

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

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.

3.2.5 *Type and number of samples*

The types and number of samples are included in Table 3.3.

Table 3.3 Number of samples analysed in laboratory and field tests.

Test parameter	**Laboratory Nitrate**	**Laboratory COD**	**Field Nitrate**
Response time	General evaluation	General evaluation	General evaluation
Linearity	7	7	-
Coefficient of Variation	7	7	-
Limit of detection (LOD)	6	6	-
Limit of quantification (LOQ)	6	6	-
Repeatability	6	6	-
Lowest detectable change (LDC)	6	6	-
Bias (for lab 20%/80%)	6/6	6/6	10
Short term drift	6	6	-
Long term drift	-	-	18
Day to day repeatability (35%/65%)	6/6	6/6	-
Availability and up-time	-	-	General evaluation
Memory effect	6	6	-
Interference (20%/80%) nitrite	4/3	-	-
Interference (20%/80%) $FeCl_3$	-	6/6	-
Interference (20%/80%) PAX	3/3	3/3	-
Environmental conditions: Temperature test	3	3	-

For the field test 22 reference measurements were produced, of which one was higher than the chosen range and three were lower than the detection limit, leaving only 18 reference measurements to be included in the verification.

According to EN ISO15839, the bias shall be calculated as the mean of the differences calculated to produce the response chart, but it also says that: “Measurements below the limit of quantification (LoQ) as determined in laboratory testing shall not be taken into account.” The LoQ in the laboratory test was reported to be 0.63 mg NO_3-N/L, which in fact means that only the 10 out of 18 reference values are acceptable for use.

3.2.6 *Operation conditions*

The operation conditions applied during the verification of the product are:

- Sampling temperature: 5-30°C.
- Sampling media: activated sludge and wastewater effluent.

3.2.7 *Operation measurements*

No additional measurements were performed.

3.2.8 *Product maintenance*

The laboratory tests were done with pure water and over very short time, therefore no maintenance was required.

The S::CAN Spectrolyser uses an automatic cleaning device with cleaning by compressed air, see Figure 3.2, this device was required between all measurements in the field, due to the tests being performed in wastewater.

For the field test, running over several months, the checking of the instruments as required by the vendor was performed /4/. This includes:

- Checking actual status/functionality of the probe.
- Checking the plausibility of readings.
- Checking automatic probe cleaning.
- Checking historical status or system stability.
- Checking unintentional modifications of measuring settings caused by unauthorized access or remote control.
- Checking the probe's mounting.
- Functional check of probe (system check).

Figure 3.2 Effectiveness of hydraulic-pneumatic cleaning of measuring windows.

3.2.9 *Health, safety and wastes*

The use of the product does not imply special health, safety or waste issues.

Laboratory work during testing will be done according to the DHI Safety Rules.

Operation of the equipment gains no waste. Sample solutions containing potassium nitrate, potassium hydrogen phthalate, nitrite, PAX and iron chloride were all disposed of through the laboratory sink.

4 REFERENCE ANALYSIS

In the laboratory, reference analyses were limited to stability check of dilutions.

In the field, reference analyses were performed with test kit on site. Further measurement from the existing nitrate sensor at the wastewater treatment plant was included in the evaluations, although only as graphical evaluation of the S::CAN Spectrolyser data and not included in the calculation of performance parameters.

4.1 Analytical laboratory

No external laboratory analyses were used. The samples used in the laboratory tests were checked at the DHI laboratory in Aarhus using the method described in Section 4.3. Samples from the field were reference tested on-site.

4.2 Analytical parameters

Reference analysis was performed for the two parameters tested: nitrate and COD.

4.3 Analytical methods

Both nitrate and the COD sample follow Beer's law without adding any chemicals, which means that in non-interfering solutions, the concentration can be determined by measuring the absorbance at a specific wavelength and from a calibration curve calculating the concentration. The reference check for stability of dilutions prepared for laboratory test was a measurement of the absorbance in the UV areas relevant for nitrate and COD, 215 and 254 nm respectively. The reference stability test was carried out using a 20 mm cuvette and measured on a HP 8453 UV-VIS spectrophotometer.

Reference analyses in the field were made with a quick test equipment MERCK NOVA60. The MECK nitrate test kits used were no. 1.14542.0001 and no. 1.14556.0001. The reference analyses were performed on filtered samples. The samples were filtered maximum 30 seconds after sampling, and were analysed maximum 1-2 minutes after filtration.

Measurements from the 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 testing.

4.4 Analytical performance requirements

The analytical performance of the reference analysis shall be at the least as good as the relevant ranges for the performance parameters to be verified, see Table 6.1.

Table 4.1 Relevant ranges of performance parameters in activated sludge tanks.

	Limit of detection	**Range of application**	**Precision (repeatability)**		**Trueness**
	mg/L	mg/L	mg/L	%	%
Nitrate	0.1	LoD-65	1-5	< 10	100±10
COD	1	LoD-1000	20-80	< 25	100±10

No preservation and storage can be used as both samples from laboratory test and samples from field test shall be measured at once.

5 DATA MANAGEMENT

In general, the data filing and archiving procedures of the DHI Quality Management System were followed.

5.1 Data storage, transfer and control

The instrument communicates with a PC via a serial link. Measurements and calculations are stored on the PC in the manufacturer's file format. Measurements are transferred from this file to an Excel sheet prepared by the test laboratory.

Following this, all calculations as prescribed in EN ISO15839 are added to the Excel sheet and final reports, also following the guideline in the standard, to collect and present the performance characteristics.

6 QUALITY ASSURANCE

The tests were performed under the quality management system of DHI which is ISO 9001 compliant /1/, but not certified. The DHI laboratories have ISO 17025 accreditations /2/ for sampling of drinking water.

The laboratory test and field tests are not covered by the ISO 17025 accreditation.

6.1 Test plan review

The test plan was subject to internal review by the verification responsible from DHI WTC, Senior Chemist Anders Lynggaard-Jensen, and the rest of the task group.

External review of the test plan was done by the expert at Kiwa in the Netherlands.

6.2 Performance control – reference analysis

The HP 8453 UV-VIS spectrometer was checked by measuring on a 10 mg NO3-N solution at wavelength 215 and 230 nm. The relative standard deviation (RSD) was determined to 0.045% and 0.37% respectively over a test period of 8 days, including 6 measurements. This was adequate for the requirements stated.

The MECK nitrate test kits used were no. 1.14542.0001 and no. 1.14556.0001. Data on their performance are listed in Table 6.1.

Table 6.1 Performance parameters for MERCK nitrate test kits /5,6/.

Test kit no.	**1.14542.0001**	**1.14556.0001**
Measuring range	0.5-18.0 mg NO_3-N/L	0.1-3.00 mg NO_3-N/L
Sensitivity: 0,010 A (absorbance)	0.1 mg NO_3-N/L	0.02 mg NO_3-N/L
Lower limit of detection (LLD)	0.06 mg NO_3-N/L	0.014 mg NO_3-N/L
Relative standard deviation (RSD)	± 1.5 %	± 2.0 %
Trueness	± 0.6 mg NO_3-N/L	± 0.30 mg NO_3-N/L

The upper measuring range reported for nitrate was lower than required and dilution of samples have been required. Limit of detection and precision is adequate as reported, whereas the trueness would be adequate down to 3 mg NO_3-N/L.

No further control of the performance of reference analysis was done.

6.3 Test system control

The laboratory test system is simple, and only analysis of solutions used was done in order to demonstrate stability.

The HP 8453 UV-Vis was checked by measuring on a 10 mg NO_3-N/L solution at wavelength 215 nm and a 500 mg COD/L solution at wavelength 254 nm.

6.4 Data integrity check procedures

All data have been transferred from a data file created by the data logger to an Excel spreadsheet, and all calculations have been performed in the spreadsheet.

The spreadsheet calculations have been checked by the verification responsible: Anders Lynggaard-Jensen from DHI.

6.5 Test system audits

No audit was performed.

6.6 Test report review

The test report was subject to internal review by the verification responsible from DHI WTC: Senior Chemist Christian Grøn.

7 TEST RESULTS

7.1 Test data summary

Below the laboratory and field test results are summarised according to requirements in EN ISO 15839. The complete data set is available in Appendix 5.

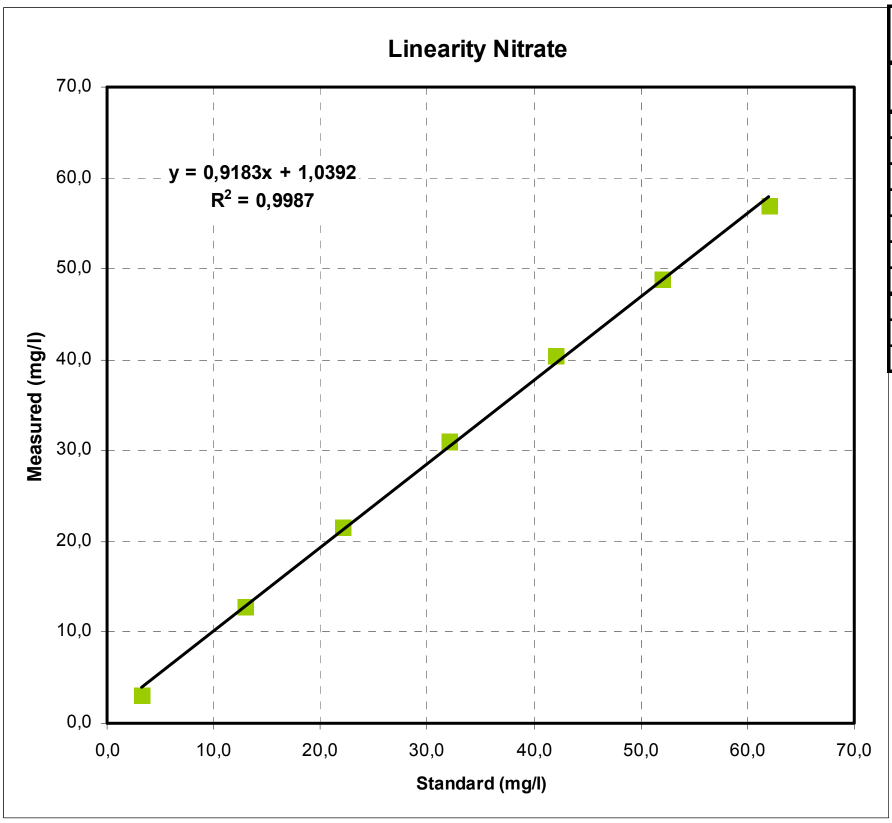
7.1.1 Laboratory test

Response time

The minimum period between two measurements offered by the instrument is 30 seconds, and as the instrument is an in-situ instrument with the light path exposed directly in the sample, measuring absorbance instantly, the response times becomes 30 seconds.

Linearity and coefficient of variation

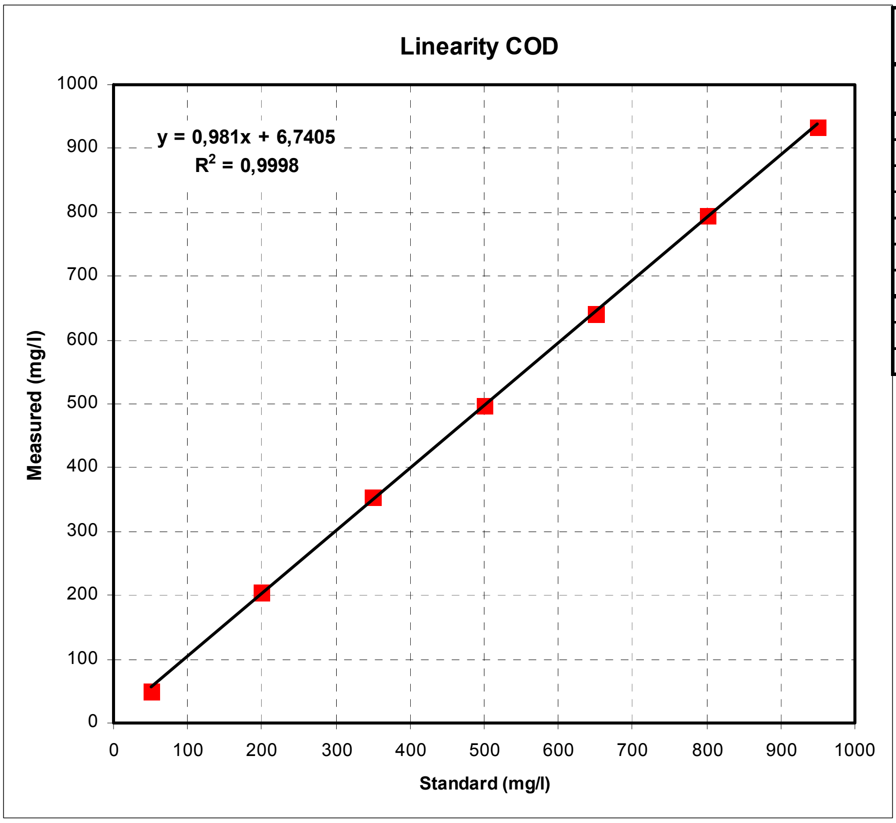
In Figure 7.1 and Figure 7.2 the linearity plot for the two tested parameters nitrate and COD is shown.



Nitrate: Linearity and Coeff. of Var.

Standard mg/l	Measured mg/l
3,2	3,2
13,0	12,8
22,0	21,7
32,0	31,1
42,0	40,4
52,0	48,8
62,0	57,0
Average	30,7
Stddev.	19,5
Result	63,3

Figure 7.1 Linearity for nitrate.



COD: Linearity and Coeff. of Var.	
Standard mg/l	Measured mg/l
50	50
200	206
350	355
500	499
650	642
800	795
950	934
Average	497,2
Stddev.	317,9
Result	63,9

Figure 7.2 Linearity for COD.

Limit of detection (LoD), limit of quantification (LoQ), repeatability, lowest detectable change (LdC) and bias

The determination of limit of detection (LoD), limit of quantification (LoQ), repeatability, lowest detectable change (LdC) and bias for both nitrate and COD are shown in Table 7.1.

Table 7.1 *Determination of limit of detection (LOD), limit of quantification (LOQ), repeatability, lowest detectable change (LDC) and bias for nitrate and COD.*

Nitrate			**Avg.**	**Stddev.**	**Bias**	**LOD**	**LOQ**	**LDC**	**Rep.**
Conc. % of full range	**Conc. mg/l**	**Date 2007**	Nitrate mg/l	Nitrate mg/l	Nitrate mg/l	Nitrate mg/l	Nitrate mg/l	Nitrate mg/l	Nitrate mg/l
5%	3,2	12/3	3,10	0,06		0,19	0,63		
20%	13,0		12,75	0,05	-0,25			0,16	0,05
80%	52,0		48,93	0,10	-3,07			0,31	0,10

COD			**Avg.**	**Stddev.**	**Bias**	**LOD**	**LOQ**	**LDC**	**Rep.**
Conc. % of full range	**Conc. mg/l**	**Date 2007**	COD mg/l	COD mg/l	COD mg/l	COD mg/l	COD mg/l	COD mg/l	COD mg/l
5%	50	20/4	49,1	1,9		5,7	19,0		
20%	200		206,6	0,7	6,5			2,2	0,7
80%	800		795,9	1,9	-4,1			5,7	1,9

Bias can, based on nitrate concentrations, be calculated to respectively -1.9% and -5.9% for 20% and 80% of concentration range and for COD to respectively 3.3% and -0.5% for 20% and 80% of concentration range.

Short term drift and day-to-day repeatability

The short term drift and the day-to-day repeatability have been determined and are shown in Table 7.2.

Table 7.2 Determination of short term drift and day-to-day repeatability for nitrate and COD.

Nitrate: Day-to-day Repeatbility		
Day no.	Conc. 35%	Conc. 65%
1	21,4	39,9
4	21,7	40,4
5	21,4	40,1
6	21,6	40,2
7	21,2	40,0
8	21,2	40,1
Stddev.	0,20	0,17
Result	0,20	0,17

Nitrate: Short term drift	
Day no.	Conc. 50%
1	31,3
4	31,1
5	30,9
6	31,1
7	30,9
8	30,8
Slope	-0,07
Result	-0,10

COD: Day-to-day Repeatbility		
Day no.	Conc. 35%	Conc. 65%
1	359	635
2	355	642
5	349	643
6	359	651
7	349	643
8	359	651
Stddev.	5,1	6,1
Result	5,1	6,1

COD: Short term drift	
Day no.	Conc. 50%
1	503
2	499
5	497
6	506
7	497
8	506
Slope	0,3
Result	0,0

Memory effect

In Table 7.3 the effect on the memory, when the sensor has been subjected to a calibrant solution of 200% of the working range, is given.

Table 7.3 Determination of memory effect for nitrate and COD.

Conc. % of full range	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l	Nitrate mg/l	Nitrate mg/l
200%	130,0	16/3	105,9	102,7	102,8	102,4	102,4	102,8	Avg.	Diff.
20%	13,0		13,0	12,8	12,8	12,8	12,8	12,7	12,82	-0,18

Conc. % of full range	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l	COD mg/l	COD mg/l
200%	2000	26/4	1340,0	1371,0	1410,0	1327,0	1355,0	1342,0	Avg.	Diff.
20%	200		202,1	202,4	201,7	200,5	201,9	202,3	201,8	1,8

Interference

The effect from interference on nitrate and COD measurement are given in Table 7.4 and Table 7.5.

Table 7.4 Determination of effect of interference on nitrate measurement with nitrite and PAX.

Interferent 1: Nitrite	**Concentration in mg/l**			0	0,1	0,2	0,4			Interference
Nitrate	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l	level mg/l
Use diff. conc. of interferent until change ~ LDC (if any)	20%	13,0	14/3	12,9	13,0	13,2	13,4			0,2
	80%	52,0		48,6		48,8	49,2			0,4

Interferent 2: PAX	**% of commercial product concentration**			0	1	5				Interference
Nitrate	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l	level (%)
Use diff. conc. of interferent until change ~ LDC (if any)	20%	13,0	26/4	14,0	14,0	14,0				>5
	80%	52,0		52,5	52,5	52,4				>5

Table 7.5 Determination of effect of interference on COD measurement with $FeCl_3$ and PAX.

Interferent 1: $FeCl_3$*	**% of commercial product concentration**			0	1	0,5	0,25	0,125	0,05	Interference
COD	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l	level (%)
Use diff. conc. of interferent until change ~ LDC (if any)	20%	200	24/4	214,8	223,5	214,9	227,3	267,8	285,7	N/A
	80%	800		800,5	816,9	806,0	816,9	845,7	885,4	N/A

*) Try to clean with 0,2 N HCl between measurements due to deposits of iron on the instrument's optics, but not possible to get consister

Interferent 2: PAX	**% of commercial product concentration**			0	1	5				Interference
COD	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l	level (%)
Use diff. conc. of interferent until change ~ LDC (if any)	20%	200	26/4	207,1	204,6	192,2				5
	80%	800		797,2	797,4	783,5				5

Environmental conditions

Results from testing under different environmental conditions, here different temperatures, are shown in Table 7.6.

Table 7.6 Determination of effect of change in temperature conditions on nitrate and COD measurement.

Nitrate: Environmental conditions	**Temp. deg.C**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Diff. mg/l
Measure at each temperature until measurent is stable using the 50% conc.	5	32,0	08/3	31,0	-2,2
	15	32,0		33,2	-
	30	32,0		35,5	2,3

COD: Environmental conditions	**Temp. deg.C**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Diff. mg/l
Measure at each temperature until measurent is stable using the 50% conc.	5	500	18/4	562,5	3,5
	15	500		559,0	-
	30	500		555,0	-4,0

Performance in laboratory test

The final results of the laboratory tests according to EN ISO 15839 are summarised in Table 7.7 and Table 7.8.

Table 7.7 Overview of performance in laboratory test for nitrate.

Performance Characteristics Nitrate Laboratory Test	Unit	Result	Effect
Response time for positive change, t_{Response}^{+}	Sec.	30	
Response time for negative change, t_{Response}^{-}	Sec.	30	
Linearity: Range	mg/l	3,2 – 62	
Linearity: R^2	-	0,9987	
Coefficient of variation	%	63,3	
Limit of detection (LOD)	mg/l	0,19	
Limit of quantification (LOQ)	mg/l	0,63	
Repeatability 20%	mg/l	0,05	
Repeatability 80%	mg/l	0,10	
Lowest detectable change (LDC) 20%	mg/l	0,16	
Lowest detectable change (LDC) 80%	mg/l	0,31	
Bias at 20%	mg/l	-0,25	
Bias at 80%	mg/l	-3,07	
Short term drift at 50% (% of working range/day)	%/day	-0,10	
Day-to-day repeatability at 35%	mg/l	0,20	
Day-to-day repeatability at 65%	mg/l	0,17	
Memory effect (if > LDC at 20%)	mg/l	-0,18	Yes
Interference level at 20% for Nitrite (level as mg/l Nitrite)	mg/l	0,20	Yes
Interference level at 80% for Nitrite (level as mg/l Nitrite)	mg/l	0,40	Yes
Interference level at 20% for PAX (level as % of commercial solution)	%	>5	No
Interference level at 80% for PAX (level as % of commercial solution)	%	>5	No
Temperature effect at 50% (15^{o}C - 5 ^{o}C) (if > Mean of LDC values)	mg/l	-2,2	Yes
Temperature effect at 50% (15^{o}C - 30 ^{o}C) (if > Mean of LDC values)	mg/l	2,3	Yes

PAX: 1.78 g Al_2O_3 and 2.6 g Cl^- pr. liter

Table 7.8 Overview of performance in laboratory test for COD.

Performance characteristics COD Laboratory Test	Unit	Result	Effect
Response time for positive change, $t_{Response}^{+}$	Sec.	30	
Response time for negative change, $t_{Response}^{-}$	Sec.	30	
Linearity: Range	mg/l	50 - 950	
Linearity: R^2		0,9998	
Coefficient of variation	%	63,9	
Limit of detection (LOD)	mg/l	5,7	
Limit of quantification (LOQ)	mg/l	19,0	
Repeatability 20%	mg/l	0,7	
Repeatability 80%	mg/l	1,9	
Lowest detectable change (LDC) 20%	mg/l	2,2	
Lowest detectable change (LDC) 80%	mg/l	5,7	
Bias at 20%	mg/l	6,5	
Bias at 80%	mg/l	-4,1	
Short term drift at 50% (% of working range/day)	%/day	0,0	
Day-to-day repeatability at 35%	mg/l	5,1	
Day-to-day repeatability at 65%	mg/l	6,1	
Memory effect (if > LDC at 20%)	mg/l	1,8	No
Interference level at 20% for PAX (level as % of commercial solution)	%	5	Yes
Interference level at 80% for PAX (level as % of commercial solution)	%	5	Yes
Temperature effect at 50% (15^{o}C - 5 ^{o}C) (if > Mean of LDC values)	mg/l	3,5	No
Temperature effect at 50% (15^{o}C - 30 ^{o}C) (if > Mean of LDC values)	mg/l	-4,0	Yes

PAX: 1.78 g Al_2O_3 and 2.6 g Cl^- pr. liter

7.1.2 Field test

All recorded results from the 6 weeks' field test period are shown in Appendix 5. Graphs are drawn for each week. They show calibrated S::CAN Spectrolyser measurement logged every 2 minutes as a dark blue line. A yellow curve is representing measurements done with an ISE electrode from WTW which was logging every minute. The WTW is used normally at the treatment plant. The staff at the treatment plant is most interested in the lower values. Calibration of the WTW electrode is always carried out at low values, knowing that this will produce too high measured values for higher real values. A general agreement between the WTW electrode and the S::CAN Spectrolyser (both following the alternating process) is seen at low values (< 2 mg/L). At higher values the difference increases with the concentrations, reflecting an erroneous calibration of the WTW equipment rather than a discrepancy between the two instruments.

In the graphs all reference measurements are also shown. Of the reference measurements for the calibration period, 6 are used for calibration, see Appendix 5.

From the graphs in Appendix 5 it can be seen that the lower values are in fact the typical values in the activated sludge plant, but with increases in some periods.

Finally, the plot from week no. 3 shows that there are no values from the instrument from Friday afternoon until Monday morning. The missing data was caused by a malfunction in the mounted PC – not the instrument - and should therefore not affect the up time.

Response time

In the field the monitor is set to use a sequence of single pulses which are averaged to compensate for fluctuations in the medium. This takes around 70 seconds. Further time is also included for a cleaning with a burst of compressed air, this takes 30-40 seconds. The instrument uses an average of the last 2 measurements, which potentially gives a response time of 4 minutes.

Bias

The calibration and reference measurements and the corresponding S::CAN Spectrolyser values are shown in Figure 7.4. The graph shows the correlation between the reference measurements and the corresponding S::CAN Spectrolyser values.

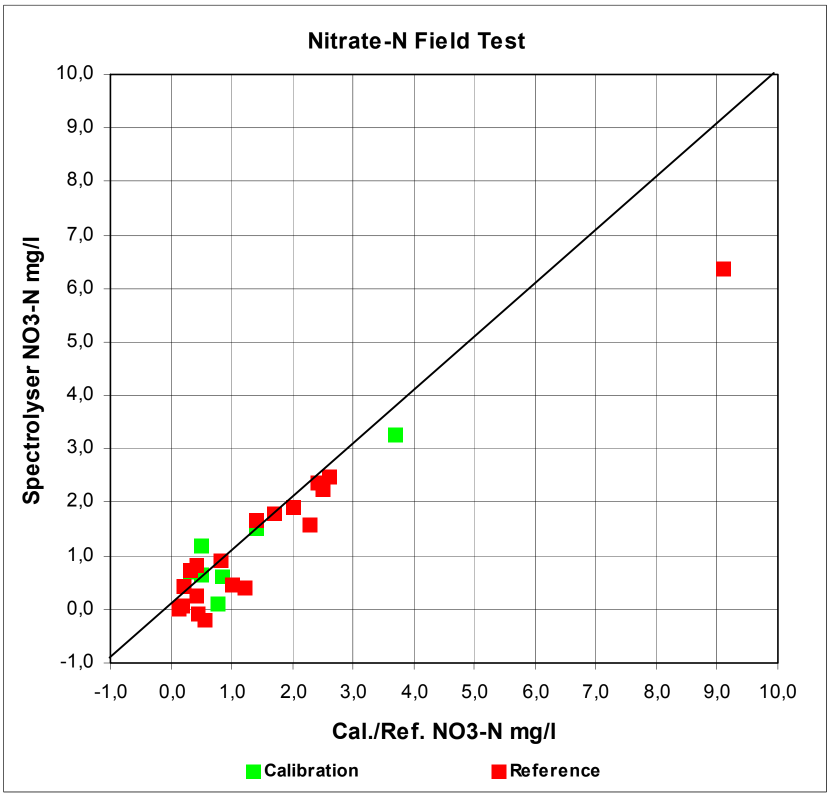


Figure 7.3 Calibration/Reference measurement and the corresponding Spectrolyser values.

According to EN ISO15839, the bias shall be calculated as the mean of the differences calculated to produce the response chart, as in Figure 7.4, but it also says that: "Measurements below the limit of quantification (LoQ) as determined in laboratory testing shall not be taken into account." The LoQ was in the laboratory test reported to be 0.63 mg

NO_3-N/l, which in fact means that only 10 reference values shown in Table 7.9 and Figure 7.4 are acceptable for use. The bias is calculated as 0.2 mg NO_3-N/l. A paired t-test shows that there is no significant difference between the reference method and the S::CAN Spectrolyser.

Table 7.9 Accepted reference and S::CAN Spectrolyser values and calculation of the bias.

Field Test	NO3-N mg/l		
Date andTime	Reference	Spectrolyser	Abs.Diff.
03-10-2007 11:04	1,00	0,48	0,52
05-10-2007 14:08	1,40	1,67	-0,27
05-10-2007 14:18	1,70	1,81	-0,11
05-10-2007 14:35	2,00	1,91	0,09
05-10-2007 14:52	2,50	2,24	0,26
05-10-2007 15:01	2,40	2,37	0,03
05-10-2007 15:10	2,60	2,50	0,10
10-10-2007 10:19	2,28	1,60	0,68
22-10-2007 14:11	1,20	0,41	0,79
24-10-2007 14:48	0,80	0,93	-0,13
Bias = Average of Abs. differences > LOQ			0,20

The average concentration in the reference samples is 1.79 mg NO_3-N/L. The bias of 0.20 mg/L corresponds to 11%.

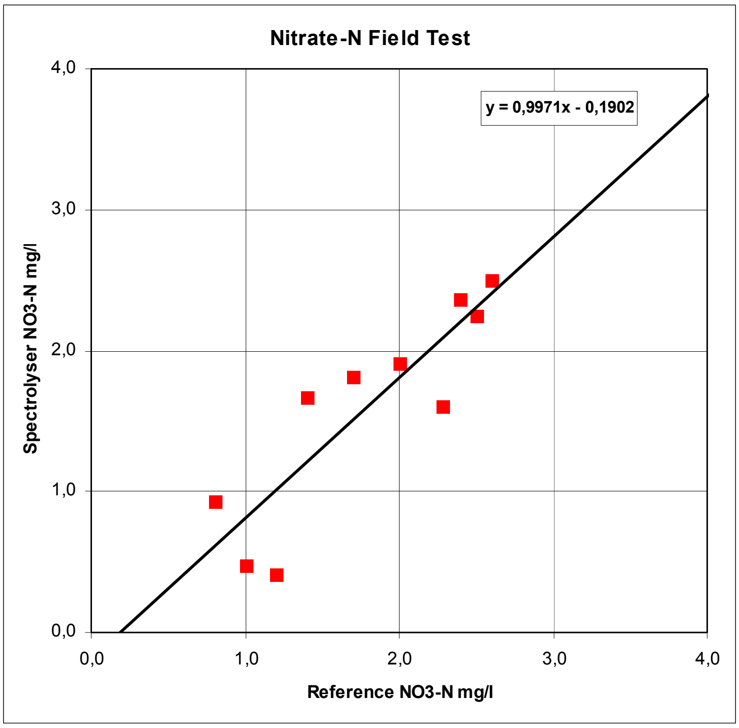


Figure 7.4 Response chart. Accepted reference S::CAN Spectrolyser values and the regression line.

Long term drift

The long-term drift is defined as the slope of the regression line which can be drawn on the response chart, and expressed as a percentage of the working range over a 24 h period, see Figure 7.5. As the slope is 0.0229 mg NO_3-N/L/day and the working range 0-4 mg NO_3-N/L/day the long term drift can be calculated to 0.6%/day.

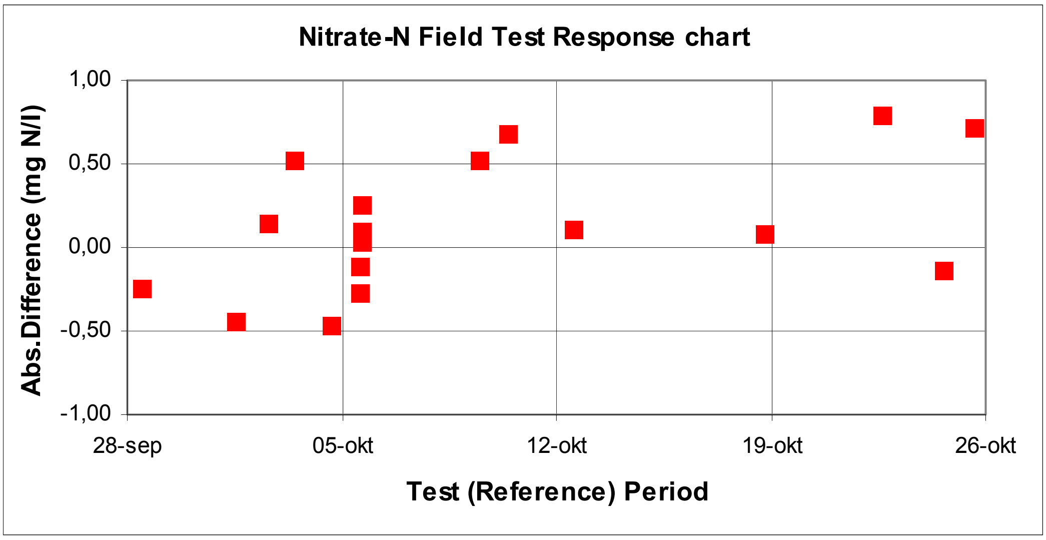


Figure 7.5 Response chart for monitoring of the test.

Availability and up-time

As no maintenance/calibration during the test period is planned and as the automatic rinsing between each measurement does not really give "no-availability", the availability becomes 100% (the recording of the extra calibration value and the following recalibration did not make the instrument un-available at any time). As the instrument did not have any malfunction during the test and the availability is 100%, the up-time also becomes 100%.

Performance in field test

The final results of the field tests according to EN ISO 15839 are summarised in Table 7.10.

Table 7.10 Overview of performance in laboratory test for COD.

Performance Characteristics Nitrate Field Test	**Unit**	**Result**	**Effect**
Response time for positive change, $t_{Response}^{+}$	Min.	4	
Response time for negative change, $t_{Response}^{-}$	Min.	4	
Bias based on absolute differences	mg/l	0,20	
Long term drift (% of working range/day)	%/day	0,6	
Availability	%	100	
Up-Time	%	100	

7.2 Test quality assurance summary

The reference check of stability of dilutions for laboratory test was a measurement of the absorbance in the UV area (215 nm for nitrate and 254 for COD). The results for standards of 10 ppm NO_3-N and 500 ppm COD are listed in Table 7.11.

Table 7.11 Reference check of standards.

Date	**215 nm**	**Concentration NO_3-N** ppm	**Date**	**254 nm**	**Concentration COD** ppm
22 February	0.84165	10.05	18 April	0.75936	506.2
23 February	0.84072	10.04	19 April	0.74274	495.1
26 February	0.84132	10.05	20 April	0.75783	505.1
27 February	0.84097	10.04	23 April	0.73883	492.5
28 February	0.84166	10.05	24 April	0.76025	506.7
01 March	0.84145	10.05	26 April	0.76404	509.3
Average		10.05			502.5
RSD		0.051			1.4

7.3 Test performance observation

7.3.1 Laboratory test

According to the test plans, the tests should be carried out during a period of 6 days for each of the tested variables – in total 12 working days. However, this schedule turned out to be too tight. A total of 14 days were used – mostly due to problems during the interference test using ferrichloride.

Generally speaking, the laboratory test was successful, and no major problems were encountered except for problems with the interference test using ferrichloride, where the iron made deposits on the optical windows – despite the effort to clean the windows between each measurement (incl. blanks) in 0.2N HCl, it was not possible to get consistent results.

The protocol as described in EN ISO15839 was strictly followed, and the operation of the instrument did not require any changes in this except for a minor change during the test of response times.

With regard to response time, the EN ISO15839 states that a measurement consists of the average of 10 readings. However, the instrument offers a measurement value consisting of the average of maximum of 6 readings. A reading is obtained every time the flash lamp is activated, and it is possible to use a series of 6 consecutive activations of the lamp as one measurement.

7.3.2 Field test

In EN ISO 15839 it is stated that: “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 determinant 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."

As the typical value for nitrate is below the 20% value of the working range (= 4 mg/L), the response chart shall be produced using absolute differences (Figure 7.3 and Appendix 5), and the agreed limits are +/- 1 mg NO_3-N/L. Furthermore, the site specific calibration during the first 2 weeks has been has been done at the typical values – although the increase in nitrate values during 19 September has been forced by leaving the aerators on for a much longer period than usual in order to give a larger span for the calibration.

It is stated in EN ISO 15839 that: "Continue the test until at least 30 measurements have been obtained within the chosen part of the working range". Within the test period of 4 weeks (week 3-6) 23 reference values were produced – hereof 1 higher than the chosen range, 3 lower than the detection limit and 1 used for calibration, which leaves only 18 acceptable values for the response chart, which clearly does not fulfil the requirements of the standard.

It was discussed to launch another campaign – during a period with "forced variation" of the nitrate concentration in order to reach a higher number of reference values, but this cannot be generally recommended as reference values should be evenly distributed over the test period. Furthermore, repeating the test for another 4 weeks was not possible due to time constraints in the project. Therefore it was decided to conclude the test with the 18 acceptable reference values and support these results with the plot of all values for the 6 weeks of operation where the general performance of the instrument can be followed.

7.4 Amendments to and deviations from test plan

Suspended solid 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.

APPENDIX 1

Terms and definitions used in the test plan

The abbreviations and definitions used in the test plan are summarized below.

Word	NOWATECH	Comment on NOWATECH approach
Analytical laboratory	Independent analytical laboratory used to analyse test samples	The test center may use an analytical laboratory as subcontractor
Application	The use of a product specified with respect to matrix, target, effect, clarified by statement of any limitations	The application must be defined with a precision that allows the user of a product verification to judge whether his needs are comparable to the verification conditions
CEN	European Committee for Standardization	
COD	Chemical Oxygen Demand	
DHI WTC	(ETV) Water Test Center at DHI	
Effect	The way the target is affected	The effect could be concentration reduction, decrease in treatment period, pH increase, measurement of a component, etc.
EN	European standard	
Environmental technology	The practical application of knowledge in the environmental area in a technology the use of which is less environmentally harmful than relevant alternatives	The term technology covers a variety of products, processes, systems and services
ETV	Environmental technology verification (ETV) is an independent (third party) assessment of the performance of a technology or a product for a specified application, under defined conditions and adequate quality assurance	
EU	European Union	
Evaluation	Evaluation of test data for a technology product for performance and data quality	None
Experts	Independent persons qualified on a technology in verification or on verification	These experts may be technical experts, QA experts, e.g. for other ETV systems, or regulatory experts
ISO	International Standardization Organization	

Word	NOWATECH	Comment on NOWATECH approach
Limit of detection LoD	Calculated from the standard deviation of replicate measurements at less than 5 times the detection limit evaluated. Corresponding to less than 5% risk of false blanks	
Limit of quantification LoQ	Calculated from the detection limit, typically 3 times the LoD, the concentration, where the blank variation impacts the precision 20%	
Matrix	The type of material that the product is intended for	Matrices could be soil, drinking water, ground water, etc.
Method	Generic document that provides rules, guidelines or characteristics for tests or analysis	An in-house method may be used in the absence of a standard, if prepared in compliance with the format and contents required for standards.
NOWATECH	Nordic Water Technology Verification Centers	
(NOWATECH) test center	Preliminary name for the verification bodies in NOWATECH with a verification and a test sub-body	Name will be changed, when the final nomenclature in the EU ETV has been set
Performance parameters	Parameters that can be documented quantitatively in tests and that provide the relevant information on the performance of an environmental technology product	The performance parameters must be established considering the application(s) of the product, the requirements of society (regulations), customers (needs) and vendor claims
Precision	The standard deviation obtained from replicate measurements, here measured under repeatability or reproducibility conditions	
Procedure	Detailed description of the use of a standard or a method within one body	The procedure specifies implementing a standard or a method in terms of e.g.: equipment used
Producer	The party producing the product	None
Performance parameters	Parameters that can be documented quantitatively in tests and that provide the relevant information on the performance of	

Word	NOWATECH	Comment on NOWATECH approach
	an environmental technology product	
(Environmental) product	Ready to market or prototype stage product, process, system or service based upon an environmental technology	The product is the item produced and sold and thus the item that a vendor submits for verification
QA	Quality assurance	
Range of application	The range from the LoD to the highest concentration with linear response	
Repeatability	The precision obtained under repeatability conditions, that is with the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time	
Robustness	% variation in measurements resulting from defined changes in matrix properties	
RSD	Relative standard deviation in %	
Standard	Generic document established by consensus and approved by a recognized standardization body that provides rules, guidelines or characteristics for tests or analysis	
Target	The property that is affected by the product	The target could be mg N/L of treated wastewater or detection limit for a measurement
Test center, test sub-body	Sub-body of the test center that plans and performs test	May by within same organization as the verification sub-body, or may not
Test center, verification sub-body	Sub-body of the test center that plans and performs the verification	May by within same organization as the test sub-body, or may not
Test/testing	Determination of the performance of a product for parameters defined for the application	

Word	NOWATECH	Comment on NOWATECH approach
Vendor	The party delivering the product to the customer	Can be the producer
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance	

APPENDIX 2

References

1. International Standardization Organisation, EN ISO 9001. Quality management systems - Requirements. 15-11-2008.

2. ISO. General requirements for the competence of testing and calibration laboratories. ISO 17025. 2005.

3. EN ISO 15839:2003 "Water Quality – on-line sensors/analysing equipment for water - specifications and performance tests".

4. TESTNET. D3.1b Evaluation Report Test case 1b: Spectrolyser multiparameter sensor for wastewater. DHI. 02-04-2008.

5. MERCK. Certificate of quality. Sectroquant® Nitrate Cell Test, Cat. No. 1.14542. Dated 27.09.2007

6. MERCK. Certificate of quality. Sectroquant® Nitrate Cell Test, Cat. No. 1.14556. Dated 05.06.2009

APPENDIX 3

In-house test methods

Appendix 3.1

Preparation of solutions for reference analysis.

Standard solution NOx: KNO_3 (7,23 g KNO_3 = 1000 mg/L NO_3-N
Standard solution COD: KH_8H_4O ~ 500 mg COD/L

The solid KNO_3 and KH_8H_4O were dried in drying cupboard for one hour. Solutions of one litre of each dilution were prepared.

The COD standard was made according to Danish Standard (DS 217), where a 2,082 mmol/L (0,4251g/L) solution of Potassium Hydrogen Phtalate has a theoretical COD concentration equal to 500 mg/L.

Appendix Table 1.1 Prepared sample solutions.

Percentage of stated range	Nitrate-N (KNO_3)	COD ($KHC_8H_4O_4$)
%	mg/L	mg/L
0	0	0
5	3.2	50
20	13	200
35	22	350
50	32	500
65	42	650
80	52	800
95	62	950
200	130	2000

APPENDIX 4

In-house analytical methods

None

APPENDIX 5

Data reporting forms

Results Lab. Test Spectrolyser	Nitrate								
Tasks	Conc. % of full range	Conc. mg/l	Date 2007	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Response and delay time*, Day to day repeatability, Short term drift	35%	22,0	09/3	21,4					
	50%	32,0		31,3					
	65%	42,0		39,9					
Coefficient of Variation, Linearity, LOD, LOQ, LDC, Linearity, Bias, Repeatability, Day to day repeatability, Short term drift	5%	3,2	12/3	3,2	3,1	3,1	3,1	3,1	3,0
	20%	13,0		12,8	12,8	12,7	12,7	12,8	12,7
	35%	22,0		21,7					
	50%	32,0		31,1					
	65%	42,0		40,4					
	80%	52,0		48,8	48,9	49,0	48,9	49,1	48,9
	95%	62,0		57,0					
Day to day repeatability, Short term drift, Environmental Conditions*	35%	22,0	13/3	21,4					
	50%	32,0		30,9					
	65%	42,0		40,1					
Day to day repeatability, Short term drift, Interferent 1*	35%	22,0	14/3	21,6					
	50%	32,0		31,1					
	65%	42,0		40,2					
Day to day repeatability, Short term drift, Interferent 2*	35%	22,0	15/3	21,2					
	50%	32,0		30,9					
	65%	42,0		40,0					
Day to day repeatability, Short term drift, Memory effect	35%	22,0	16/3	21,2					
	50%	32,0		30,8					
	65%	42,0		40,1					
	200%	130,0		105,9	102,7	102,8	102,4	102,4	102,8
	20%	13,0		13,0	12,8	12,8	12,8	12,8	12,7

*) Special Table for Results

Nitrate: Environmental conditions	Temp. deg.C	Conc. mg/l	Date 2007	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Measure at each temperature until measurent is stable using the 50% conc.	5	32,0	08/3	31,0					
	15	32,0		33,2					
	30	32,0		35,5					

Interferent 1: Nitrite	Concentration in mg/l			0	0,1	0,2	0,4		
Nitrate	Conc. % of full range	Conc. mg/l	Date 2007	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Use diff. conc. of interferent until change ~ LDC (if any)	20%	13,0	14/3	12,9	13,0	13,2	13,4		
	80%	52,0		48,6		48,8	49,2		

Interferent 2: PAX	% of commercial product concentration			0	1	5			
Nitrate	Conc. % of full range	Conc. mg/l	Date 2007	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Use diff. conc. of interferent until change ~ LDC (if any)	20%	13,0	26/4	14,0	14,0	14,0			
	80%	52,0		52,5	52,5	52,4			

Results Lab. Test Spectrolyser	**COD**								
Tasks	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Response and delay time*, Day to day repeatability, Short term drift	35%	350	19/4	359,2					
	50%	500		503,0					
	65%	650		635,2					
Coefficient of Variation, Linearity, LOD, LOQ, LDC, Linearity, Bias, Repeatability, Day to day repeatability, Short term drift	5%	50	20/4	49,6	48,4	52,6	47,9	49,1	47,2
	20%	200		205,8	206,3	207,6	207,3	206,0	206,3
	35%	350		354,9					
	50%	500		498,5					
	65%	650		642,3					
	80%	800		795,4	795,2	794,7	793,7	798,0	798,5
	95%	950		934,1					
Day to day repeatability, Short term drift, Environmental Conditions*	35%	350	23/4	349,0					
	50%	500		496,5					
	65%	650		643,4					
Day to day repeatability, Short term drift, Interferent 1*	35%	350	24/4	359,4					
	50%	500		506,2					
	65%	650		651,3					
Day to day repeatability, Short term drift, Interferent 2*	35%	350	25/4	349,0					
	50%	500		496,5					
	65%	650		643,4					
Day to day repeatability, Short term drift, Memory effect	35%	350	26/4	359,4					
	50%	500		506,2					
	65%	650		651,3					
	200%	2000		1340,0	1371,0	1410,0	1327,0	1355,0	1342,0
	20%	200		202,1	202,4	201,7	200,5	201,9	202,3

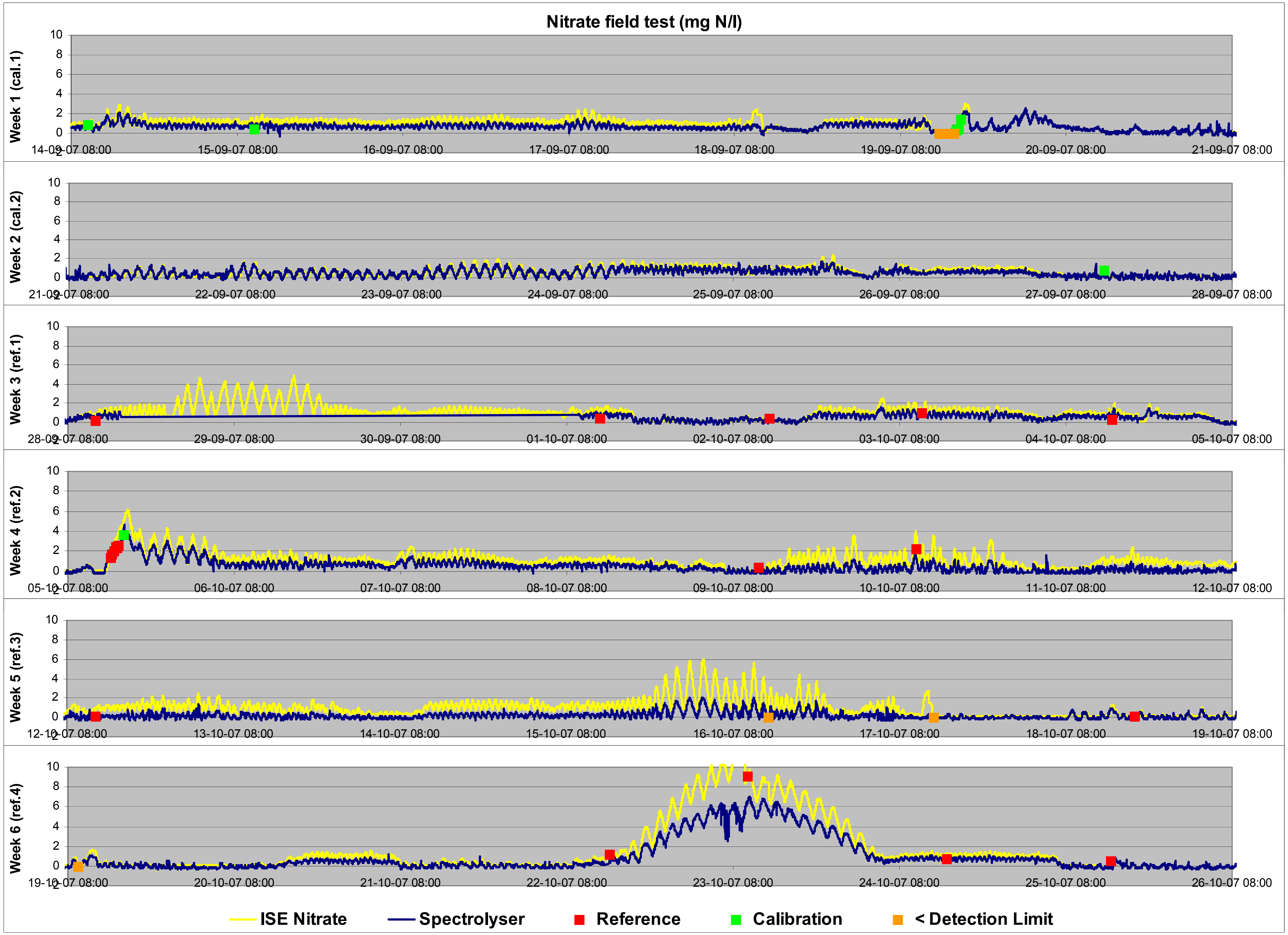
*) Special Table for Results

COD: Environmental conditions	**Temp. deg.C**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Measure at each temperature until measurent is stable using the 50% conc.	5	500	18/4	562,5					
	15	500		559,0					
	30	500		555,0					

Interferent 1: FeCl$_3$*	**% of commercial product concentration**			0	1	0,5	0,25	0,125	0,05
COD	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Use diff. conc. of interferent until change ~ LDC (if any)	20%	200	24/4	214,8	223,5	214,9	227,3	267,8	285,7
	80%	800		800,5	816,9	806,0	816,9	845,7	885,4

*) Try to clean with 0,2 N HCl between measurements due to deposits of iron on the instrument's optics, but not possible to

Interferent 2: PAX	**% of commercial product concentration**			0	1	5			
COD	**Conc. % of full range**	**Conc. mg/l**	**Date 2007**	Meas.1 mg/l	Meas.2 mg/l	Meas.3 mg/l	Meas.4 mg/l	Meas.5 mg/l	Meas.6 mg/l
Use diff. conc. of interferent until change ~ LDC (if any)	20%	200	26/4	207,1	204,6	192,2			
	80%	800		797,2	797,4	783,5			


Nitrate field test (mg N/l)

Spectrolyser Field Test			NO3-N mg/l			Comment
Period	Test week	Date andTime	Cal./Ref.	Spectrolyser	Abs.Diff	
Calibration period	1	14-09-2007 10:26	0,85	0,63		Cal.
		15-09-2007 10:25	0,50	0,66		Cal.
		19-09-2007 13:33	< 0.1	0,13		< Det.limit
		19-09-2007 13:46	< 0.1	0,06		< Det.limit
		19-09-2007 14:38	< 0.1	0,11		< Det.limit
		19-09-2007 14:52	< 0.1	0,12		< Det.limit
		19-09-2007 14:59	< 0.1	0,14		< Det.limit
		19-09-2007 15:25	< 0.1	0,22		< Det.limit
		19-09-2007 15:41	< 0.1	0,55		< Det.limit
		19-09-2007 16:07	0,30	0,72		Cal.
		19-09-2007 16:25	0,50	1,19		Cal.
		19-09-2007 16:39	1,40	1,53		Cal.
	2	27-09-2007 13:28	0,75	0,11		Cal.
Reference period	3	28-09-2007 11:53	0,20	0,45	-0,25	< Lab.LOQ
		01-10-2007 12:47	0,40	0,84	-0,44	< Lab.LOQ
		02-10-2007 13:07	0,40	0,26	0,14	< Lab.LOQ
		03-10-2007 11:04	1,00	0,48	0,53	
		04-10-2007 14:32	0,30	0,76	-0,46	< Lab.LOQ
	4	05-10-2007 14:08	1,40	1,67	-0,27	
		05-10-2007 14:18	1,70	1,81	-0,11	
		05-10-2007 14:35	2,00	1,91	0,09	
		05-10-2007 14:52	2,50	2,24	0,26	
		05-10-2007 15:01	2,40	2,37	0,03	
		05-10-2007 15:10	2,60	2,50	0,10	
		05-10-2007 15:57	3,70	3,27		Cal.
		09-10-2007 11:41	0,45	-0,07	0,52	< Lab.LOQ
		10-10-2007 10:19	2,28	1,60	0,68	
	5	12-10-2007 12:08	0,18	0,07	0,11	< Lab.LOQ
		16-10-2007 13:01	< 0.1	0,02		< Det.limit
		17-10-2007 12:54	< 0.1	-0,06		< Det.limit
		18-10-2007 17:57	0,12	0,03	0,09	< Lab.LOQ
	6	19-10-2007 09:25	< 0.1	0,11		< Det.limit
		22-10-2007 14:11	1,20	0,41	0,79	
		23-10-2007 10:05	9,10	6,39		> Range
		24-10-2007 14:48	0,80	0,93	-0,13	
		25-10-2007 14:23	0,55	-0,17	0,72	< Lab.LOQ

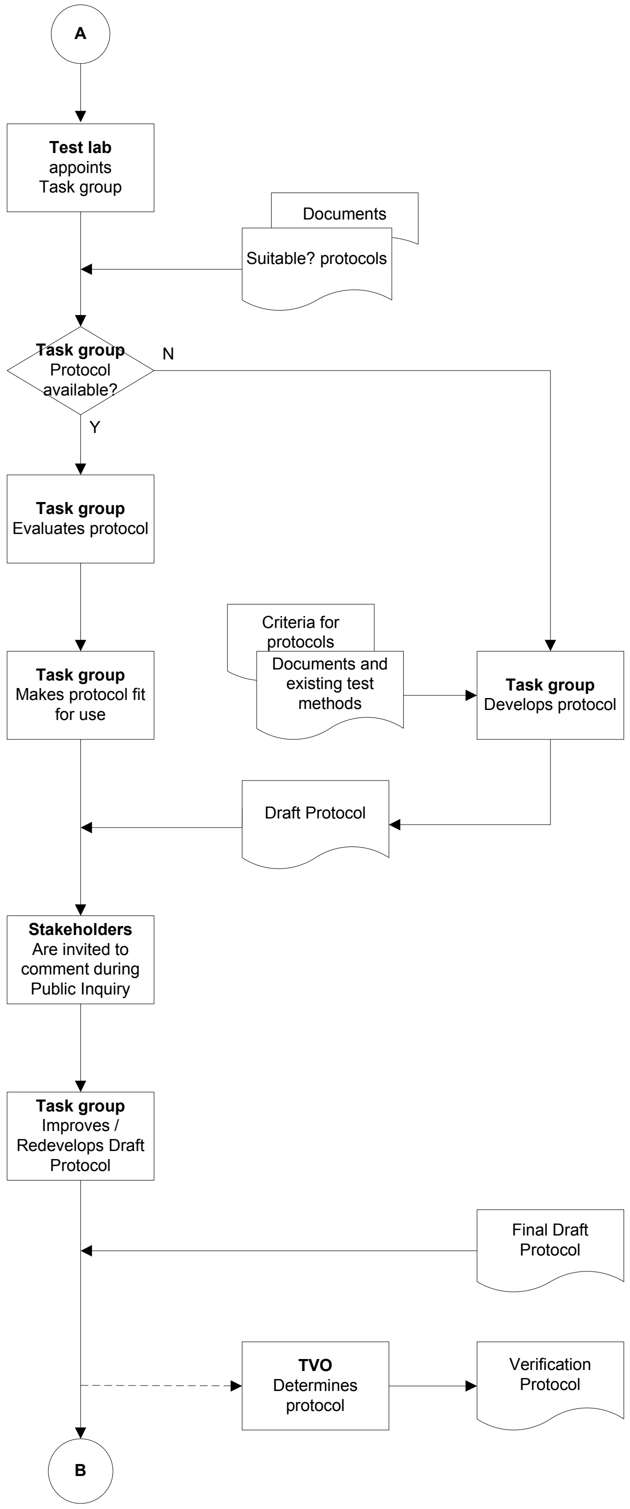
APPENDIX 5

Verification Scheme

European ETV Scheme - Without VI

(flowchart) page 2 (23-08-2006)

PROTOCOL procedure



The Test lab invites members for a (temporary) Task group. The Test lab chairs the group, the producer and eventually other laboratories who are expected to be charged with the testing are q.q. member. But also other experts can be invited.

The Task group first of all checks if the protocols available are suitable. When there is no protocol for this type of technology the Task group has to develop one.

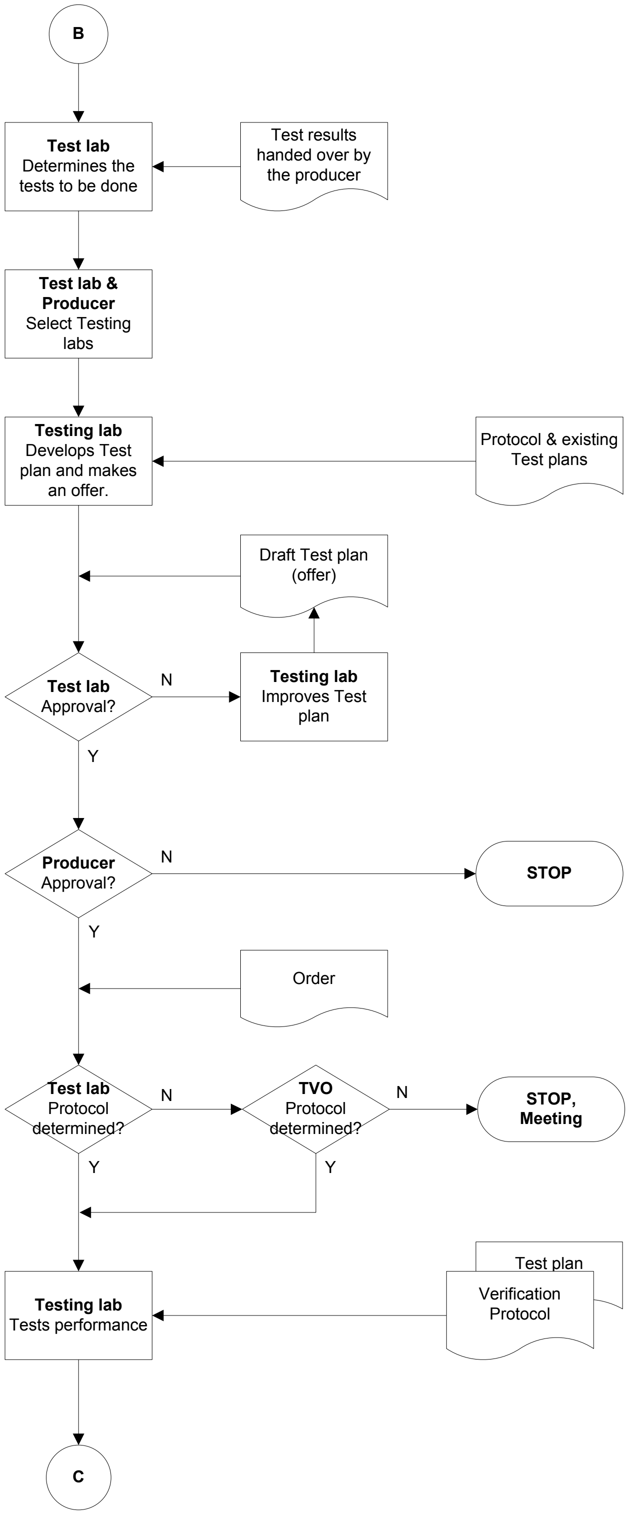
Even when a suitable protocol is available, almost always adjustments have to be made to make it fit for the type of technology/apparatus involved.

Usually the Test lab in charge makes the drafts, to be discussed and approved in the Task group. The protocol has to be as complete and detailed as possible, also with respect to the tests to be performed.

Every stakeholder is asked to comment the draft protocol (during e.g. 1 month) through intermediation of their branch organisations and by publishing in the communication channels of the specific field of technology.
2/3 Weeks after the end of the period of Public Inquiry the Task group has a meeting.

The Task group works the comments into the final draft in a transparent way.
In the end the protocol has to be determined formally by the TVO. Only exceptionally the TVO will send the protocol back to the Test lab for improvement.
To prevent delay meanwhile the testing procedure is started up.

European ETV Scheme - Without VI
(flowchart) page 3 (23-08-2006)
TESTING procedure



The first step for the Test lab is to verify if his judgment about the test results (and the test plan they are based on) handed over by the producer has to be adjusted.
The Test lab determines if and if so which tests have to be repeated/done.

When not all tests can be performed by the Test lab it advises the producer in selecting laboratories. The laboratories who might perform the tests are called Testing labs from now on.
Tendering: in this case more laboratories are invited to make an offer.

The Test plan focuses on quality assurance. Concerning the tests it gives in detail extensions and other deviations of the protocol.

The Test plan forms the main part of the offer; it is the basis for judging the quality and the costs.

The Test lab criticises the Test plan together with the producer.
The Task group appointed by the Test lab stays stand-by to advice during the tendering and the testing procedure in case of problems.

The producer gives an order to the Testing lab based on an agreement about the costs. It is possible that more than one Testing lab gets orders for different tests or even for the same tests.

The Test lab sends a copy of the order to the TVO.
When the protocol has not yet been determined by the TVO, the Test lab urges the TVO to make a decision.
In the (exceptional) case the TVO rejects the protocol commissioning is suspended.
In this case a meeting will be arranged to examine what the consequences are:
Start all over again, redevelop the protocol or go on.

The Testing lab performs the necessary tests, writes the Test report and submits it to the Test lab.
The Test lab may be present during the tests performed by other testing labs.