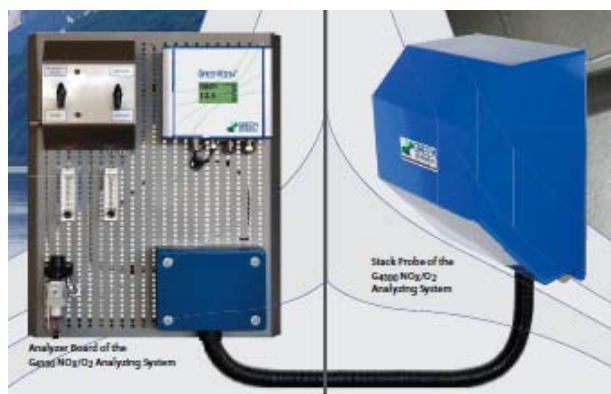




# G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System

Emission Control



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**Verification Protocol**

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Marianne Kyed Ørbæk



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## **Appendices**

- 1 Terms and definitions used in the verification protocol
- 2 References
- 3 Application and performance parameter definitions



## 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.

### 2.1 Name of product

The product is the G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System.

### 2.2 Name and contact of vendor

Green Instruments A/S  
 Erhvervsparken 29  
 9700 Brønderslev  
 Denmark  
 Phone +45 96 45 45 00  
 Contact Poul Kodal Sørensen  
 E-mail pks@greeninstruments.com

### 2.3 Name of centre/verification responsible

The Danish Center for Verification of Climate and Environmental Technologies (DANETV), FORCE Technology DANETV, Air and Energy Center

<b>Verification Test Centre (DANETV)</b>	<b>Verification responsible</b>
FORCE Technology	Marianne Kyed Ørbæk
Park Allé 345	E-mail <a href="mailto:mko@force.dk">mko@force.dk</a>
DK - 2605 Brøndby	Phone +45 4326 7062
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### 2.4 Verification and test organization

The verification will be conducted by the Danish Centre for Verification of Climate and Environmental Technologies, DANETV, which performs independent tests of technologies and products for the reduction of climate changes and pollution.

The verification is planned and conducted to satisfy the requirements of the ETV scheme currently being established by the European Union (EU ETV).

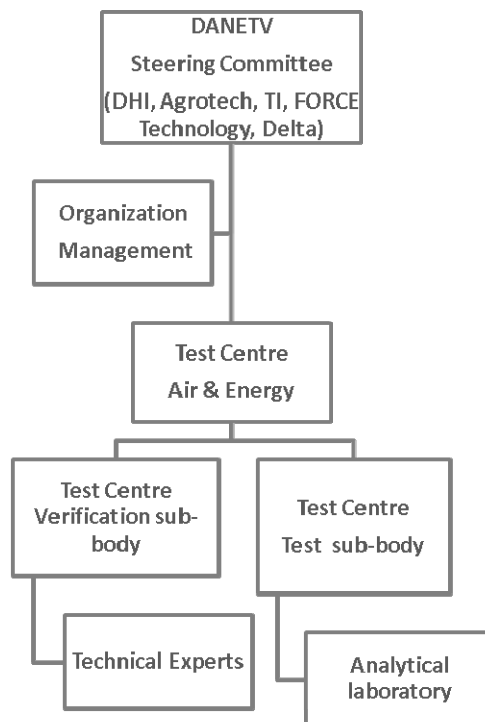
The day to day operations of the verification and tests will be coordinated and supervised by FORCE Technology personnel, with participation of the vendor, Green Instruments. The test will be conducted at MAN Diesel & Turbo A/S, Filial of MAN Diesel & Turbo SE, Germany, R&D Engineering DK Frederikshavn, Denmark. Green Instruments will operate the G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System during the verification. Green Instruments will provide the G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System, user manuals and operation instructions. In addition Green Instruments also participates in the development of the protocol and plans with FORCE Technology.



A technical expert group is established to support FORCE Technology in planning, conducting and reporting the verification and tests, and to review plans and reports.

The organization chart in Figure 1 identifies the relationships of the organization associated with this verification and tests.

**Figure 1 Organization of the verification and tests**



## 2.5 Technical expert

The technical expert assigned to this verification and responsible for review of the test plan and test report documents includes:

Karsten Fuglsang  
 FORCE Technology  
 Park Allé 345  
 DK - 2605 Brøndby  
 Phone: +45 4326 7148  
 E-mail: kfu@force.dk

## 2.6 Verification process



Verification and tests will be conducted in two separate steps, as required by the EU ETV. The steps in the verification are shown in Figure 2.

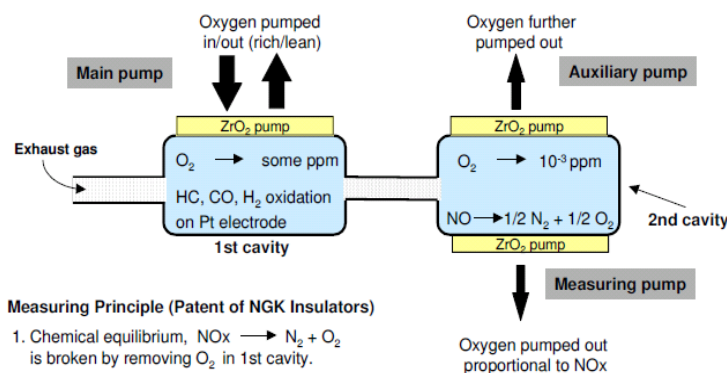
Figure 2 Verification steps

References for the verification process are the Quality Manual for DANETV (Appendix 2 ref.1).

A verification statement will be issued after completion of the verification.

### 3 DESCRIPTION OF THE TECHNOLOGY

The principle of the technology is shown in below figure and further described in the text below the figure.



#### Measuring Principle (Patent of NGK Insulators)

1. Chemical equilibrium,  $\text{NOx} \rightarrow \text{N}_2 + \text{O}_2$  is broken by removing  $\text{O}_2$  in 1st cavity.
2.  $\text{NOx}$  is reduced by catalyst and  $\text{O}_2$  is generated in the 2nd cavity.
3. Measure the generated oxygen, which represents the  $\text{NOx}$  concentration.



Exhaust gas enters a first part of the analysis system. Oxygen ( $O_2$ ) diffuses over a barrier to a ceramic sensor with zirconium electrolyte and is measured. The diffusion reduces the  $O_2$  content to a few ppm before the gas enters the second part of the system. In the first part all oxidizable components are oxidized at a platinum electrode and are thus removed, before the gas enters the second part.

In the second part of the system the equilibrium between NO and  $O_2$  is shifted towards  $O_2$  by removing  $O_2$  by the measuring electrode (also a ceramic sensor with zirconium electrolyte). The reduction of NO is thus forced to completion and the generated  $O_2$  represents the NO concentration of the exhaust gas.

Strictly speaking the equilibrium is between  $NO_x$  and  $O_2$ . Equilibrium between  $NO_2$  and  $O_2$  exists as well. The sensitivity against  $NO_2$  is informed to be 80% (Appendix 2, ref. 6) If the  $NO_x$  concentration in an exhaust gas is rich in  $NO_2$ , the  $NO_x$  concentration will consequently be significantly underestimated. The underestimation is app. 2% for an exhaust gas with 10%  $NO_2$ .

There is no sensitivity against  $N_2O$ , but  $N_2O$  is normally neither regarded as a  $NO_x$  component, nor present in significant concentrations.  $N_2O$  is neither measured by the reference method (ChemiLuminescence Detector (CLD)).

Furthermore there is a minor cross sensitivity (less than 0.5%) to  $O_2$ , CO,  $SO_2$ ,  $CO_2$  and temperature for normal diesel exhaust gas exposure. No water quenching or skewing has been noted. The  $ZrO_2$  sensor is protected from  $PM_{10}$  by mechanical filter. The filter is periodical back-flushed in order to secure correct sample flow.

## 4 DESCRIPTION OF THE PRODUCT

The  $G_{4100}$   $NO_x/O_2$  Analyzing System was newly developed based on experience working with zirconia oxygen ( $ZrO_2$ ) sensors and  $NO_x$  monitoring solutions for the marine industry. Marine instruments have to be very robust and simple in order to be operated by a crew that is met by many and diverse challenges each day.

The sensor is small and robust and can be installed directly in the exhaust duct without special protection. The technology allows real-time measurement of  $NO_x/O_2$  on wet basis at high temperatures. It avoids sampling lines and sampling systems and conversion. The simple plug'n'play design makes it easy and cost-effective to install, operate, and maintain the analyzing system. A complete system includes an automatic back-flushing ejector probe connected to an analyzing board with analyzer and air supply and calibration gas reduction station.



Figure 3 Analyzer board of the G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System

## 5 APPLICATION AND PERFORMANCE PARAMETER DEFINITIONS

The intended application of the G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System is defined as detailed in Appendix 3 in terms of the matrix, the target and the effect of the sensor.

### 5.1 Matrix

The matrix of the application is flue gas from a heavy-duty constant speed engine for ship propulsion.

### 5.2 Target

The target is NO<sub>x</sub> concentration in the flue gas.

### 5.3 Effects

In the case of the G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing System the effect is equivalence with CLD measurements.

### 5.4 Performance parameters for verification

The performance parameter for the verification is the NO<sub>x</sub> emission concentration in terms of g NO<sub>x</sub>/kWh (section 7.1). This value is calculated from the NO<sub>x</sub>-concentration and basically the flue gas flow. The flue gas flow might be calculated from other emission parameters and the fuel consumption.

### 5.5 Additional parameters

Several parameters will be measured or values achieved at the "plant", to convert the parameter into standard and reference conditions as appropriate, and to verify and document the operating conditions during the verification:





- flue gas temperature
- fuel consumption
- oxygen concentration
- power

## 6 EXISTING DATA

On January 15<sup>th</sup> 2009, Green Instruments made a performance test of the instrument with the purpose to make a Type Approval of the NO<sub>x</sub> /O<sub>2</sub> Analyzer type G4100 in accordance with the specifications listed in Resolution MEPC.177(58) – Adopted on 10 October 2008 – Amendment to the Technical Code of Emission of Nitrogen Oxides from Marine Diesel Engines laid down in section 1.6 to 1.10 of appendix 3 of the code.

The test was made by Green Instruments under supervision of Lloyds Register EMEA, Strandvejen 104 A, DK-2900 Hellerup. The results are summarized in below table.

Parameter	Comment	Satisfying
Accuracy	The deviation over the whole range is less than +/- 2% for both the NO <sub>x</sub> and O <sub>2</sub> analyzer	Yes
Precision and repeatability	The precision and repeatability for the NO <sub>x</sub> analyzer is $2.5 * 0.57 = 1.425$ ppm or < 0.1 % of eF.S.	Yes
Precision and repeatability	The precision and repeatability for the O <sub>2</sub> analyzer is $0 * 2.5 = 0\%$ or 0% of F.S.	Yes
Noise	The analyzer peak to peak response for the NO <sub>x</sub> signal is 1 ppm and for the O <sub>2</sub> signal is 0.0 %, which are better than 2% of F.S.	Yes
Zero drift NO <sub>x</sub>	The zero NO <sub>x</sub> drift (difference start–stop) is 1.66 ppm resulting in a zero drift of 0.11%	Yes
Span drift O <sub>2</sub>	The span O <sub>2</sub> drift (difference start–stop) is 0.0 % resulting in a span drift of 0.0%	Yes
Span drift NO <sub>x</sub>	The NO <sub>x</sub> span drift was recorded as 10.33 ppm resulting in a span drift of 0.69%	Yes
Zero drift O <sub>2</sub>	The O <sub>2</sub> zero O <sub>2</sub> drift (difference start–stop) is 0.0% resulting in a zero drift of 0.0%	Yes
Analyzer response time (additional test)	The responses of the analyzer for both NO <sub>x</sub> and O <sub>2</sub> value are all higher than 90% of the measurement range in 30 seconds.	-

It is known (Appendix, ref. 7) that the sensitivity of NO<sub>2</sub> is only 80%, which means that measurements of NO<sub>2</sub>-containing exhaust gasses do not give the correct NO<sub>x</sub>-value. If e.g. the exhaust gas contains 10% NO<sub>2</sub> the NO<sub>x</sub>-value is underestimated by 2%.

## 7 TEST PLAN REQUIREMENTS

### 7.1 Test design



The G<sub>4100</sub> NO<sub>x</sub>/O<sub>2</sub> Analyzing system (the candidate method) will be tested for its ability to yield measurement results equivalent to the results of the reference method (CLD) during stable operation of a reciprocating internal combustion engine.

The test will be performed with reference to ISO 8178-1 and 8178-4 (Appendix 2, ref. 3,4). The test will be based on a seven pair sample of measurement results from measurement on an E2 test cycle (Appendix 2, ref.3,4).

An E2 test cycle consists of four modes (four different engine loads). A mode is defined by a torque and a speed. According to ISO 8178-4 "each test shall be performed in the given sequence of the test modes for a particular test cycle" (Appendix 2, ref.4). It means that the measurement runs through the four modes successively.

Each load is maintained for a stable period long enough to split the measurement period in seven representative intervals (minimum 3 minutes each).

Practically the test is run as one cycle with at least 30 minutes on each mode in the sequence for the chosen test cycle. For each mode the measurement period is split in seven with 3 minutes intervals. The last 60 seconds of each interval is numbered 1 combined to form one pair with four modes (one cycle). All intervals numbered "2" are combined in the same way to form another pair and so on. Using only one cycle with splitting of each mode instead of using 7 cycles is inspired by Germanischer Lloyds (Appendix 2, ref. 7). To our best knowledge this one cycle method conflicts with the intentions and statistical principles in ISO 8178-1 and 8178-4 (Appendix 2, ref. 3, 4). However from a practical and economical perspective the method is accepted, but it is not possible to predict the statistical consequences for the results.

The measurement will be performed simultaneously with both the candidate and reference method.

For each pair the cycle emission in g NO<sub>x</sub>/kWh is calculated by means of a formula using weighting factors for each mode. The cycle emission is calculated for the results from both measurement methods. For each measurement method 28 results yields seven values for the cycle emission (seven pairs).

The seven pairs are statistically compared by means of an s-test (the accuracy) and an F-test (the repeatability) as described in ISO 8178-1, annex D.

## **7.2 Reference analysis**

The test measurement is performed according to FORCE Technology's DANAK accreditation no. 51 according to ISO 17125 (approved by Danish Standards).

## **7.3 Data management**

Data storage, transfer and control must be done in accordance with the requirements described in the DANETV centre quality manual, FORCE Technology (Appendix 2, ref. 1).



## 7.4 Quality assurance

The quality assurance of the tests must include 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 will be subject to review by the technical expert as part of the review of this verification protocol and the verification report, see Figure 2.

## 7.5 Test report

The test report must follow the template of DANETV centre quality manual , FORCE Technology (Appendix 2, ref. 1).

# 8 EVALUATION

The evaluation includes calculation of the performance parameters, see Section 5.4 for definition, evaluation of the data quality based upon the test quality assurance, see Section 7.4 for requirements, and compilation of the additional parameters as specified in Section 5.5.

## 8.1 Calculation of performance parameters

Calculations are done according to generally accepted mathematical and statistical principles such as those described in the standards behind the FORCE Technology's DANAK accreditation number 51 (Appendix 2, ref. 2) and as described in section 7.3 and in NOx Technical Code /6/.

## 8.2 Evaluation of test data quality

The information of the test plan and the test system together with data quality and integrity control will be evaluated against the requirements set in this protocol and the objectives set in the test plan.

## 8.3 User manual

Table 1 User Manual

Parameter	Complete description	Incomplete description	No description	Not relevant
<b>Product</b>				
Principle of operation		X		
Intended use		X		
Performance expected			X	
Limitations		X		
<b>Preparations</b>				
Unpacking				X



Transport				X
Assembly	X			
Installation	X			
Function test			X	
<b>Operation</b>				
Steps of operation	X			
Points of caution			X	
Maintenance	X			
Trouble shooting	X			
<b>Safety</b>				
General instructions	X			
Power and high voltage	X			

#### 8.4 Occupational health and environment

The use of the product does not imply special health, safety and waste issues different from the operation of other analyzers.

## 9 VERIFICATION SCHEDULE

The verification is planned for April 2012. The overall schedule is given in Table 2.

Table 2 Verification schedule (2011 & 2012)

Task	Timing [week]	QA	Expert
Application definition document	40		
Verification protocol	48		
Test plan	17	41	15
Test	20		
Test reporting	24	23	23
Verification report	26		
Verification statement	28		

## 11 QUALITY ASSURANCE

The quality assurance of the verification is described in Table 3 QA plan for the verification and Figure 2 Verification steps, and the quality assurance of the tests in the test plan.

Table 3 QA plan for the verification

	Internal audit	Technical Expert
Task	Initials	
Verification Protocol & Test Plan	OSC	KFU
Test report & Verification Report	OSC	KFU

## Appendix 1



### Terms and definitions

CLD	ChemiLuminescence Detector
Effect	The way the target is affected
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.
Evaluation	Evaluation of test data for a technology product for performance and data quality
Matrix	The type of material that the product is intended for
Method	Generic document that provides rules, guidelines or characteristics for tests or analysis
Performance claim	The effects foreseen by the vendor on the target(s) in the matrix of intended use
Performance parameters	Parameters that can be documented quantitatively in tests and that provide the relevant information on the performance
QA	Quality assurance
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
Test/testing	Determination of the performance of a product for parameters defined for the application
Verification	Evaluation of product performance parameters for a specified application under defined conditions and adequate quality assurance

## Appendix 2

### References



/1/	DANETV Centre Quality Manual, FORCE Technology, February 2009.
/2/	DANAK accreditation no. 51.
/3/	International Standard ISO 8178-1. Reciprocating internal combustion engines / Exhaust emission measurement. Part 1: Test-bed measurement of gaseous and particulate exhaust emissions
/4/	International Standard ISO 8178-4. Reciprocating internal combustion engines / Exhaust emission measurement. Part 4: Steady state test cycles for different engine applications.
/5/	Marpol Annex VI and NOx Technical Code 73/78. Regulations for the prevention of air pollution from ships.
/6/	General Presentation basics "Smart NOx sensor", Continental AG, 15-04-2008
/7/	e-mail correspondence with Fabian Koch, Germanischer Lloyds, July 1 <sup>st</sup> . 2011: Auswertung für Gleichwertigkeitsnachweis

## Appendix 3

### Application and performance parameter definition



This appendix defines the application and the relevant performance parameters application as input for verification and test of the  $G_{4100}$   $\text{NO}_x/\text{O}_2$  Analyzing System following the DANETV method.

#### 1. **Application**

The intended application of the  $G_{4100}$   $\text{NO}_x/\text{O}_2$  Analyzing System is defined in terms of the matrix, the target and the effect of the Analyzer.

##### 1.1. **Matrix**

The matrix is the type of material that the product is intended for.

In the case of the  $G_{4100}$   $\text{NO}_x/\text{O}_2$  Analyzing System the matrix of the system is flue gas.

The analyzing system to be verified is suitable for other types of flue gas.

In this verification the flue gas is produced from a heavy-duty constant speed engines for ship propulsion.

##### 1.2. **Target**

Targets are the properties that are measurable with the product for verification.

In the case of the  $G_{4100}$   $\text{NO}_x/\text{O}_2$  Analyzing System the target is  $\text{NO}_x$  concentration in the flue gas.

##### 1.3. **Effects**

The effects describe how the targets are affected by the product.

In the case of the  $G_{4100}$   $\text{NO}_x/\text{O}_2$  Analyzing System the effect is equivalence with CLD measurements.