NO_X Analyzer for Ships MEXA-820NOx

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NO_X exhaust regulation has been step-by-step applied to maritime engines by IMO (The International Maritime Organization) with MARPOL (The International Convention for the Prevention of Pollution from Ships), and the SCR (Selective Catalytic Reduction) system is implemented to meet the tier 3 regulation from 2016. This report introduces HORIBA's solution: NO_X analyzer for ships MEXA-820NOx which is developed for SCR feedback control and on-board NO_X reduction efficiency monitoring with its principle, configuration, specification and evaluation results.

Introduction

In marine shipping industry, NO_X emission regulations by the International Maritime Organization (IMO) MARPOL 73/78 protocol had been gradually strengthened, and IMO NOx Tier III Regulations have been applied from 2016. Marine engine manufactures had been working on reducing NO_X with advanced combustion improvement of the engines until Tier II Regulations, but it is said that conformity to Tier III Regulations is insufficient by engine technology alone and it is necessary to introduce the after treatment technology, the application of Selective Catalytic Reduction (SCR), which is one of the popular techniques mainly for heavy-duty vehicles. Therefore, we have been promoting the research and development of NO_X analyzer which is capable of on-board measurement for the feedback control of marine SCR and the confirmation of NO_X reduction efficiency. In this report, we introduce the measurement principle, configuration, main specifications, and evaluation results of HORIBA MEXA-820NOx marine NO_X analyzer.

IMO NO_X regulation for marine diesel engine

Figure 1 shows the IMO NO_X emission regulatory value that is specified for rated engine revolution.
The first regulation was enforced in 2005, the second regulation was enforced in 2011 with 20% NO_X reduction against the first regulation, and the third regulation was enforced in 2016 with 80% NO_X reduction against the first regulation.

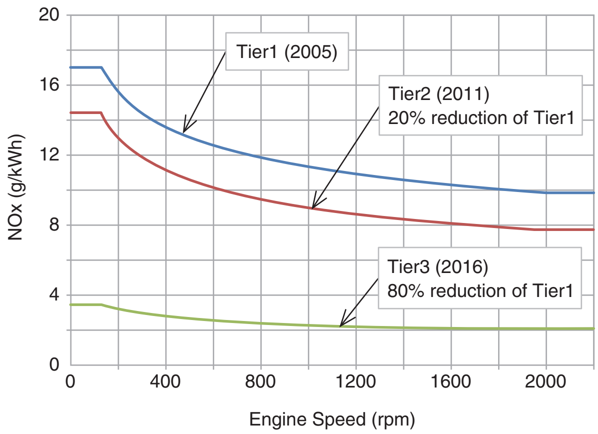

Figure 1 IMO regulation of NO_X in vessels exhaust
(Refer to International Maritime Organization (IMO) Home Page:
http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Nitrogen-oxides-(NOx)-%E2%80%93-Regulation-13.aspx)

Feedback control of SCR by real time NO_X measurement

Figure 2 shows the structure of SCR.
The catalyst unit and urea water injection nozzle are arranged in exhaust duct, and urea water as reducing agent is injected and sprayed to the upstream side of the catalyst unit. Injected urea water is thermally decomposed to ammonia by the heat of the exhaust gas. Thereafter, inflow NO_X exhaust and ammonia react on catalyst and are decomposed into harmless nitrogen and water. When the urea water injection is insufficient against the NO_X concentration of inflow exhaust, sufficient reaction cannot be carried out. On the other hand, when excessive urea water is injected, unreacted excess ammonia will be emitted in the outflow exhaust gas. The optimization of urea

injection quantity is indispensable for the confirmation of NO_X removal efficiency. In this case, by introducing a NO_X sensor at the front stage of the SCR, inflow NO_X concentration can be measured in real time and fed back to the control of SCR to optimize the urea water injection quantity, and to realize highly efficient NO_X removal.

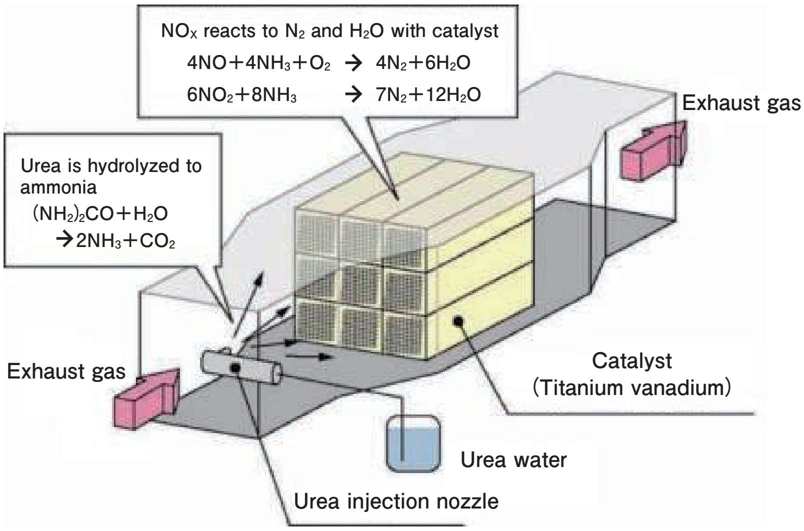

Figure 2 Structure and principle of SCR (Reprinted from National Maritime Institute (NMRI) Home Page: https://www.nmri.go.jp/oldpages/institutes/environment_power_system/power_system_rd/nox.html)

SCR certificate test

There are two methods for SCR certificate test according to Scheme A and Scheme B.

In Scheme A, NO_X emission is measured by combining the engine and SCR on land. EIAPP Certificate (Engine International Air Pollution Prevention Certificate) will be issued if the criterion of regulation is satisfied. IAPP Certificate (International Air Pollution Prevention Certificate) is issued to the ship owner without on board NO_X measurement but with parameter check.

In Scheme B, NO_X emission is confirmed by the engine alone, and the performance of NO_X removal is confirmed on SCR alone with simulated gas or exhaust gas. Assuming that the engine and SCR are combined, if it can be confirmed that NO_X emission is less than the criterion of the regulation, the EIAPP Certificate is issued to the ship manufacturer. If on board NO_X measurement is required, IAPP Certificate will be issued if the NO_X removal efficiency is within 5% compared to the result of EIAPP. Therefore, by arranging NO_X sensors before and after SCR, it is possible to monitor NO_X concentration and to confirm NO_X removal efficiency.

Marine NO_X analyzer "MEXA-820NOx"

Figure 3 shows the equipment configuration of MEXA-820NOx developed for SCR feedback control and confirmation of NO_X removal efficiency.

The sensor is inserted into the guide probe and the guide probe is inserted directly into the exhaust pipe or duct. Since the exhaust gas flowing in the exhaust pipe reaches the sensor by diffusion through the sintered filter at the tip of the guide probe, where additional sampling parts are not necessary. The receiver gets the signal from the sensor and converts it to NO_X concentration in real time. The system has a host interface communication function of RS-485 protocol as external input / output, and it is possible to transmit NO_X concentration to such as upper host PC for SCR control. Also, in the case of a ship equipped with several power generators such as auxiliary machinery, NO_X data of each engine exhaust is available at the same time by arranging NO_X sensors in each exhaust pipe, and by connecting receivers to each sensor with daisy chain function.

Figure 4 shows a picture of the Marine NO_X analyzer

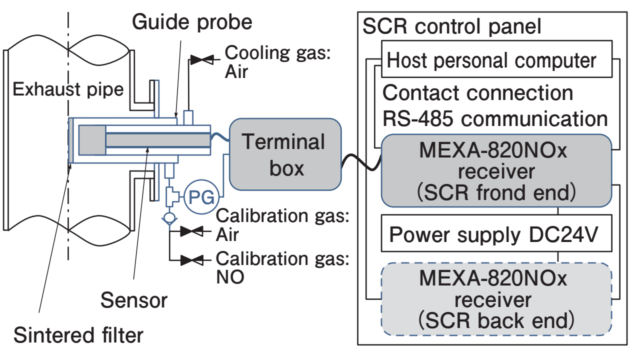

Figure 3 System configuration diagram of MEXA-820NO_X

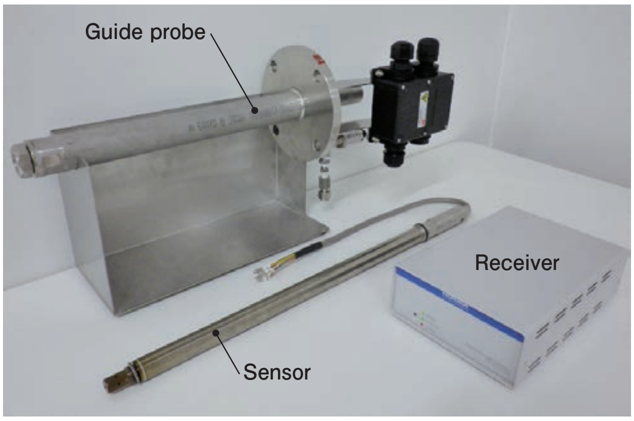

Figure 4 System appearance of MEXA-820NO_X

"MEXA-820NOx".
The sensor, guide probe, and receiver are all compact. The guide probe serves as not only the jig for attaching the sensor to the exhaust pipe, but also piping for supplying the calibration gas to the sensor. In addition, a pressure sensor is provided in order to correct the converted NO_X gas concentration value with measured pressure.
Table 1 shows the main specifications of MEXA-820NOx.

Table 1 System specification of MEXA-820NO_X

Items	Specifications
Measurement items	NO_X, O_2
Measuring range	NO_X: 0-2000 ppm, O_2: 0-25% vol.
Measurement principle	Limiting current type zirconia sensor
Power supply	24 V DC (22 V to 28 V, however the fluctuation should be ±0.2 V or less), 50 VA
Power consumption	20 W approximately
Analog output	Output either NO_X or O_2
	Output current: 4-20 mA (load resistance should be not more than 600Ω)
Contact output	3 points (Sensor maintenance, Upper/lower warning thresholds or Analyzer fault (Pressure sensor abnormality included))
	Dry, 30 V DC, 1 A, isolated
Communication function	RS-485 4-wire type
Measurement accuracy	NO_X: ±40 ppm, O_2: ±0.4%vol
Response time (T_{90})	Within 10 seconds (90% response when switch the gas zero gas [Air] and standard gas [NO 1000 ppm/N2]. The gas put in from Calibration gas inlet at 2 L/min.)
Start-up time	About 3 minutes after power-up
Sensor warranty	Not less than 4000 hours uptime

Measurement Principles

Ion pumping phenomenon and limiting current type oxygen sensor

Figure 5 shows the measurement principle of limiting current type oxygen sensor. Electrodes are formed on the upper and lower surfaces of the plate-shaped zirconia solid electrolyte, then electromotive force (: voltage) arises between these electrodes when the oxygen concentration is different between the upper and lower sides of the zirconia plate. Conversely, when external voltage is applied between these electrodes, oxygen ions can be transported through the zirconia plate by electrochemical reaction, and oxygen concentration become different between the upper and lower sides of the zirconia plate. This phenomenon is called "ion pumping". When oxygen flow onto the zirconia plate is restricted by diffusion control holes such as small holes, the current becomes constant and saturates even if higher voltage is applied between these electrodes.

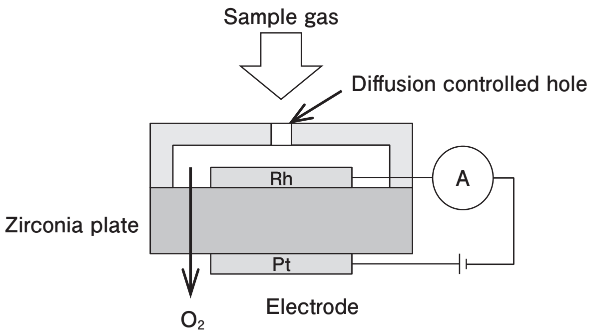

Figure 5 Measurement principle of limiting current type oxygen sensor

This current is called "limiting current" and is proportional to the oxygen concentration contained in the gas. By measuring this current, the oxygen concentration of the sample gas can be detected. This is the principle of limiting current type oxygen sensor that is also applied to the exhaust gas NO_X sensor.

Decomposition of NO and measurement of oxygen concentration

The equilibrium reaction of NO decomposition and re-synthesis is expressed by the following Equation 1.

$$NO \rightleftarrows 1/2N_2 + 1/2O_2 \quad \cdots\cdots (1)$$

Here, by removing oxygen, the reaction proceeds toward decomposition of NO as shown in the following equation.

$$NO \rightarrow 1/2N_2 + 1/2O_2 \quad \cdots\cdots (2)$$

From Equation 2, since the amount of output oxygen is proportional to the amount of decomposed NO, the initial NO concentration can be measured by measuring output oxygen which is removed from the system.

Measurement principle of zirconia NO_X sensor

Measurement principle of the zirconia NO_X sensor is shown in Figure 6.
In order to measure the amount of oxygen generated by decomposition of NO, it is necessary to eliminate foreign oxygen in sample exhaust gas before NO_X measurement. Therefore, the NO_X sensor has two, first and second internal cavities, and each of the internal cavities is equipped with ion pump of different performance. To be more specific, oxygen is pumped out by the ion pump in the first internal cavity to control the oxygen concentration to an extremely low concentration. Thereafter, the sample gas diffuses into the second internal cavity, and the oxygen concentration is reduced to nearly zero level with another ion pump, where the ion pump with rhodium (Rh) electrode which is referred to as "NO detection electrode". Rh is a good catalyst for NO decomposition under almost

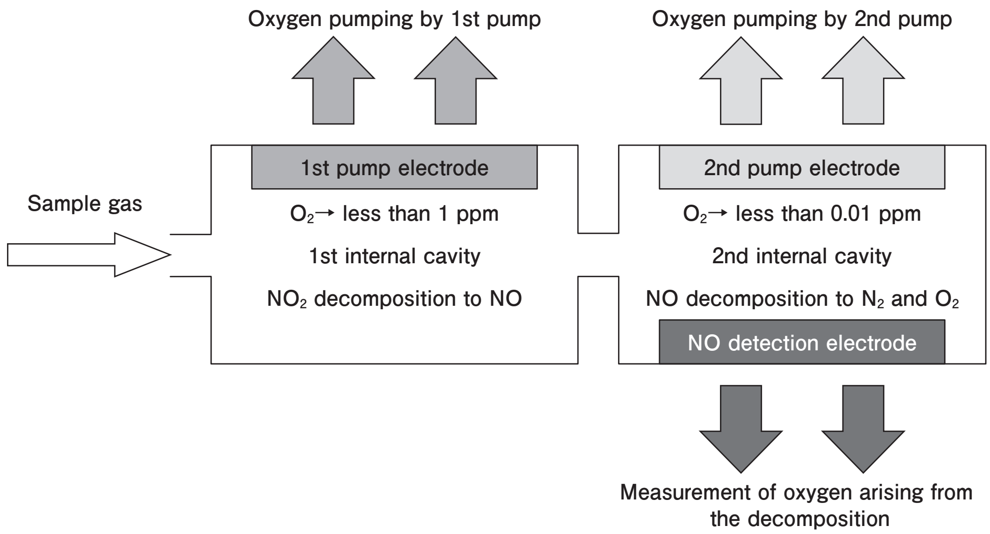

Figure 6 Measurement principle of zirconia NO_X sensor

oxygen-free conditions, and does not decompose NO to N_2 or O_2 on the Rh electrode surface. By pumping oxygen generated from this NO decomposition with ion pump and measuring the Rh electrode current, NO concentration can be provided. Note that NO_2 is reduced to NO in the first internal cavity and then the same decomposition is carried out. Therefore, by measuring the oxygen ion current in the second internal cavity, it is possible to measure the concentration of NO_X (: NO + NO_2) in the sample exhaust gas. Here, assuming that the sensitivity of the sensor to NO is 1, the sensitivity to NO_2 is about 0.8. The cause of this difference is considered to both the NO_2 decomposition into NO in the first internal cavity and the difference of diffusion coefficient between NO and NO_2.

Structure and detection principle of zirconia NO_X sensor

Figure 7 shows the sensor structure of MEXA-820NOx. The sensor of MEXA-820NOx is fabricated by the thick film lamination of zirconia solid electrolyte. In addition, the sensor is equipped with internal heater and is heated to about 700 to 800°C in order to increase the efficiency of ion transfer in the electrolyte. The sensor has air duct other than the first and second internal cavities, and atmospheric reference electrode for measuring the oxygen concentration in the first and second internal cavities is equipped. The oxygen concentration in the first internal cavity is detected by voltage V_0, and the oxygen concentration in the first internal cavity is kept constant (about 1 ppm) by controlling the pump drive current Ip_0, Similarly, the oxygen concentration in the second cavity is detected by voltage V_1, and the oxygen concentration is kept constant (about 0.01 ppm) by controlling the pump drive current Ip_1. A constant voltage is applied between the NO detection electrode and the atmospheric reference electrode. The amount of ion current Ip_2 generated by NO decomposition is measured and converted into NO concentration.

Focusing on the first internal cavity, it has the same structure and function as the limiting current type oxygen sensor, and so it is also possible to measure oxygen concentration.

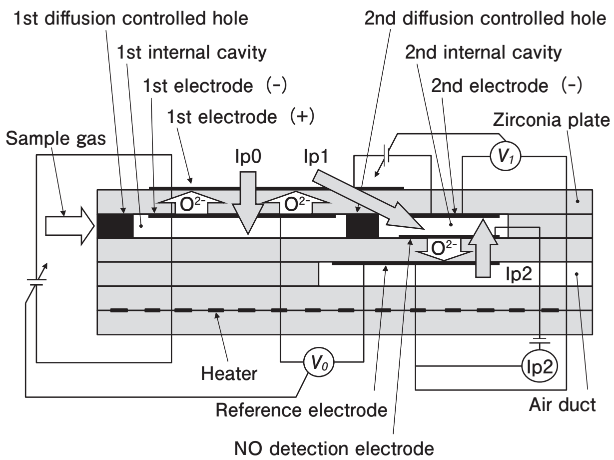

Figure 7 Sensor configuration of MEXA-820NOx

Summary

Test items

Evaluation test items necessary for approval of the classification society of marine electrical equipment are described in publication E10 (Test specification for Type Approval) of Unified Requirements (UR) established by International Association of Classification Societies (IACS). Our evaluation tests were carried out in accordance with E10 (Test specification for Type Approval) aiming to acquire type certification of electrical equipment. The main test items are shown in Table 2.

Table 2 Major test items

Test items	Points	Requirement for type approval
Linearity test	Included in performance test	Required
Damp heat test	Necessary to withstand 55°C and 95%RH	Required
Vibration test	±4.0 G acceleration load on sensor and guide probe	Required
Correlation test	Reference is CLD method, which is the standard NOx measurement method defined in IMO NOx technical code	N/A

Linearity test

Figure 8 shows the results of linearity test for MEXA-820NOx. The gas of known NO concentration (1999 ppm NO in N_2 dilution was divided into 10 with N_2 using a gas divider) was flowed from the calibration gas inlet of the guide probe and NO concentration was measured. It is found that MEXA-820NOx has good linearity and R^2 in a wide concentration range from 0 to 1999 ppm of NO concentration.

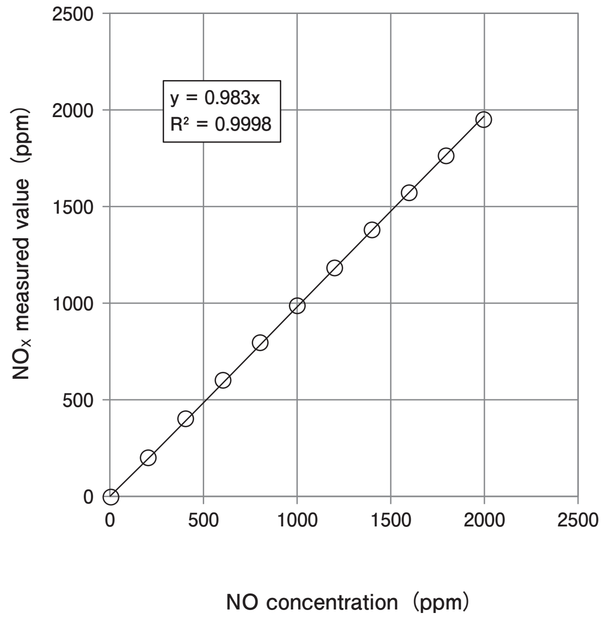

Figure 8 Data linearity of MEXA-820NOx

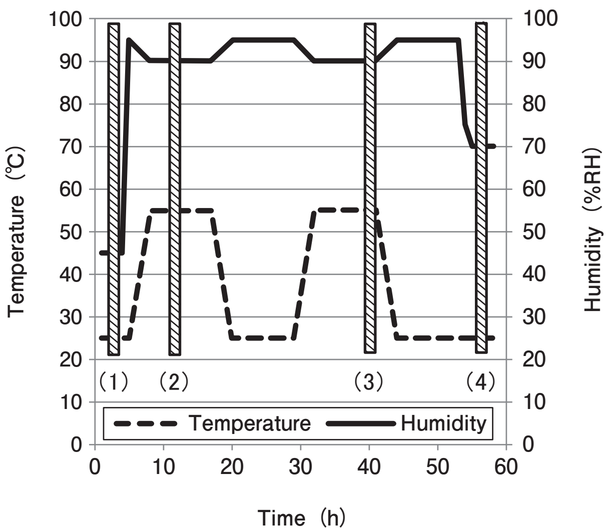

Figure 9 Atmosphere and measurement timing of temperature and humidity test

Temperature and Humidity Test

Figure 9 shows the environmental condition of temperature and humidity test and the timing of measurement. Environment test is total 48 hours long and consist of twice 24 hour cycle where it is 55°C / 90% RH in the first 12 hours, and is 25°C / 95% RH in the second 12 hours. At the timing (1) to (4) shown in Figure 9, NO concentration was measured by flowing 950 ppm NO as the span gas and air as the zero gas alternately from the calibration gas inlet of the guide probe for 10 minutes three times, and measurement reproducibility was confirmed.

Table 3 shows the results of the temperature and humidity test. Reproducibility show sufficiently satisfying ± 10 ppm of the equipment standard at the measurement points of (1) to (4).

Table 3 Result of MEXA-820NOx temperature and humidity test

(Unit: ppm)

	1st	2nd	3rd	Ave.	Dev.	Spec.	Result
(1)	951.5	953.2	954.1	952.9	+1.1/–1.4	±10	Good
(2)	950.1	950.1	950.1	950.1	±0.0	±10	Good
(3)	948.9	948.9	947.1	948.3	+0.6/–1.2	±10	Good
(4)	949.3	949.4	949.2	949.3	+0.1/–0.1	±10	Good

Vibration test

Since the sensor and the guide probe are installed in the exhaust pipe of high power ship engine, particularly high vibration resistance is required. At first, the sweep test was carried out at oscillation frequency of 2 to 100 Hz and 0.5 oct / min while measuring air as the zero gas and confirmed whether a resonance point was exist or not. Figure 10 shows the results of MEXA-820NOx sweep test. No resonance is observed in the entire oscillation frequency range and zero value is also stable.

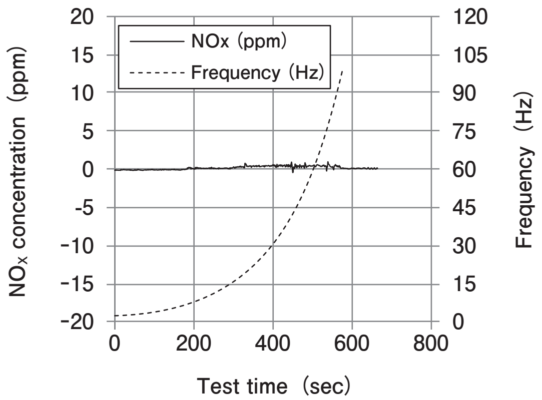

Figure 10 Frequency scanning vibration test of MEXA-820NOx

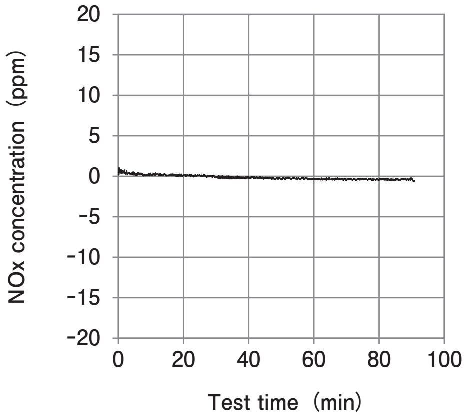

Figure 11 Vibration endurance test of MEXA-820NOx

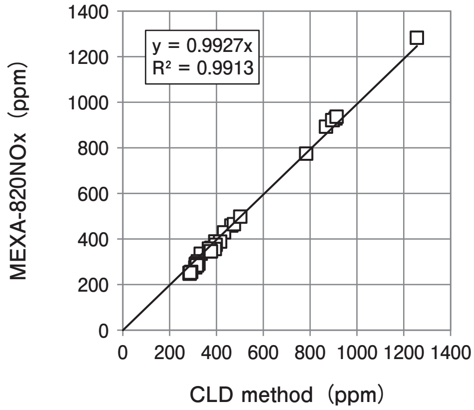

Figure 12 Correlation test with CLD method

Front side

Rear side

Figure 13 MEXA-820NOx arranged in the front and the rear of SCR

Next, while measuring air as the zero gas, vibration durability tests were carried out at vibration frequency of 30 Hz, acceleration of ± 4.0 G of three axes of vibration directions X, Y, Z, and for 90 minutes in each direction. Figure 11 shows the result of vibration durability test of MEXA-820NOx for the vibration direction perpendicular to sensor axis as the representative. It can be seen that the measurement value of zero gas is also stable over the entire measurement time.

Correlation with Chemiluminescence method (CLD)

In IMO NO_X Technical Code (NTC), CLD method is defined as a standard for NO_X measurement. Figure 12 shows the example of correlation test result of zirconia NO_X sensor and the CLD method. As a test engine, a two-stroke marine diesel engine was used. Figure 12 shows that the zirconia NO_X sensor has a good correlation with the CLD method.

Durability of sensors

Figure 13 shows the sensor installation at exhaust pipe during on-board exhaust gas durability test.

Figure 14 shows the continuous evaluation result of sensitivity transition of zirconia NO_X sensor installed before and after the on board SCR where High Sulfa C heavy oil fuel was used. Sensitivity decrease was within 20% through continuous measurement for about 7000 hours, and so continuous monitoring measurement is considered to be possible with proper periodic calibration.

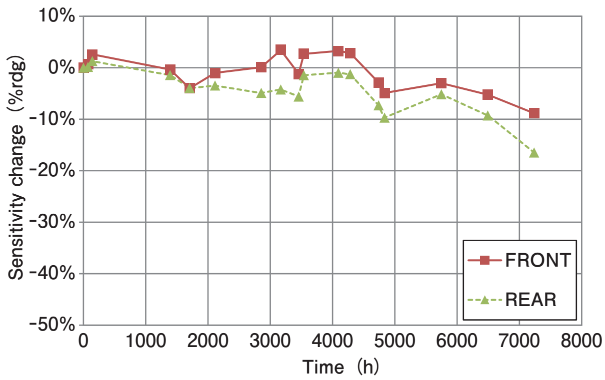

Figure 14 Durability evaluation on actual vessel

Figure 15　Vessel classification certificates by each classification society

Classification certification

Currently we have received certifications of marine electrical equipment from 4 classification society including American Bureau of Shipping (ABS), Nippon Kaiji Kyokai (NK), DET NORSKE VERITAS (DNV) and China Classification Society (CCS). Furthermore, we are operating for EU marine equipment directive (MED) certification of on-board NO_X monitoring system and NO_X reduction efficiency confirmation with our SCR system. Figure 15 shows classification certificates from each classification society.

Conclusion

In this report, we introduced the marine NO_X analyzer “MEXA-820NOx” using zirconia NO_X sensor. We developed compact system with the sensor of sufficient durability against exhaust gas from ships. This system can be applied as not only SCR controller, but also continuous on-board NO_X monitor, and confirmation method of NO_X reduction efficiency.

* This content is based on our investigation at this publish unless otherwise stated.

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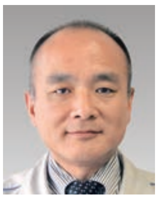

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