NO\textsubscript{X} Analyzer for Ships MEXA-820NOx

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NO\textsubscript{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\textsubscript{X} analyzer for ships MEXA-820NOx which is developed for SCR feedback control and on-board NO\textsubscript{X} reduction efficiency monitoring with its principle, configuration, specification and evaluation results.

Introduction

In marine shipping industry, NO\textsubscript{X} emission regulations by the International Maritime Organization (IMO) MARPOL 73/78 protocol had been gradually strengthened, and IMO NO\textsubscript{X} Tier III Regulations have been applied from 2016. Marine engine manufactures had been working on reducing NO\textsubscript{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\textsubscript{X} analyzer which is capable of on-board measurement for the feedback control of marine SCR and the confirmation of NO\textsubscript{X} reduction efficiency. In this report, we introduce the measurement principle, configuration, main specifications, and evaluation results of HORIBA MEXA-820NOx marine NO\textsubscript{X} analyzer.

IMO NO\textsubscript{X} regulation for marine diesel engine

Figure 1 shows the IMO NO\textsubscript{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\textsubscript{X} reduction against the first regulation, and the third regulation was enforced in 2016 with 80% NO\textsubscript{X} reduction against the first regulation.

Feedback control of SCR by real time NO\textsubscript{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\textsubscript{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\textsubscript{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 NOX removal efficiency. In this case, by introducing a NOX sensor at the front stage of the SCR, inflow NOX 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 NOX removal.

**SCR certificate test**

There are two methods for SCR certificate test according to Scheme A and Scheme B. In Scheme A, NOX 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 NOX measurement but with parameter check.

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

**Marine NOX analyzer “MEXA-820NOx”**

Figure 3 shows the equipment configuration of MEXA-820NOx developed for SCR feedback control and confirmation of NOX 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 NOX 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 NOX 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, NOX data of each engine exhaust is available at the same time by arranging NOX sensors in each exhaust pipe, and by connecting receivers to each sensor with daisy chain function. Figure 4 shows a picture of the Marine NOX analyzer.
“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\textsubscript{x} gas concentration value with measured pressure. Table 1 shows the main specifications of MEXA-820NOx.

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

### 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.

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\textsubscript{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.

\[
\text{NO} \leftrightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2
\]

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

\[
\text{NO} \rightarrow \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2
\]

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\textsubscript{x} sensor**

Measurement principle of the zirconia NO\textsubscript{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\textsubscript{x} measurement. Therefore, the NO\textsubscript{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...
oxygen-free conditions, and does not decompose NO to N₂ or O₂ 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 NO₂ 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 NOₓ (NO + NO₂) in the sample exhaust gas. Here, assuming that the sensitivity of the sensor to NO is 1, the sensitivity to NO₂ is about 0.8. The cause of this difference is considered to both the NO₂ decomposition into NO in the first internal cavity and the difference of diffusion coefficient between NO and NO₂.

Structure and detection principle of zirconia NOₓ 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 V₀, and the oxygen concentration in the first internal cavity is kept constant (about 1 ppm) by controlling the pump drive current Iₚ₀. Similarly, the oxygen concentration in the second cavity is detected by voltage V₁, and the oxygen concentration is kept constant (about 0.01 ppm) by controlling the pump drive current Iₚ₁. A constant voltage is applied between the NO detection electrode and the atmospheric reference electrode. The amount of ion current Iₚ₂ generated by NO decomposition is measured and converted into NO concentration.

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.
Linearity test

Figure 8 shows the results of linearity test for MEXA-820NOx. The gas of known NO concentration (1999 ppm NO in N\textsubscript{2} dilution was divided into 10 with N\textsubscript{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\textsuperscript{2} in a wide concentration range from 0 to 1999 ppm of NO concentration.

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).

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.
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 NOx Technical Code (NTC), CLD method is defined as a standard for NOx measurement. Figure 12 shows the example of correlation test result of zirconia NOx sensor and the CLD method. As a test engine, a two-stroke marine diesel engine was used. Figure 12 shows that the zirconia NOx 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 NOx 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 11 Vibration endurance test of MEXA-820NOx](image)

![Figure 12 Correlation test with CLD method](image)

![Figure 13 MEXA-820NOx arranged in the front and the rear of SCR](image)

![Figure 14 Durability evaluation on actual vessel](image)
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 NOX monitoring system and NOX reduction efficiency confirmation with our SCR system. Figure 15 shows classification certificates from each classification society.

Conclusion

In this report, we introduced the marine NOX analyzer “MEXA-820NOx” using zirconia NOX 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 NOX monitor, and confirmation method of NOX reduction efficiency.

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

References


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