

Product Introduction

Laser Spectroscopic Motor Exhaust Analyzer QL-N2O

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Nitrous Oxide (N₂O) emission reduction has gained large prominence recently due to its contribution to the climate change as a greenhouse gas. The United States Environment Protection Agency together with the United States Department of Transport has already regulated the N₂O emissions from Light-Duty Vehicles and Heavy-Duty Engines. N₂O measurement should be done from sample storage bags. Performance requirement of the analyzer is to be able to measure N₂O gas concentration of sub-ppb order. N₂O gas analyzer, QL-N2O has been developed as one analyzer for integrated to MEXA-ONE. QL-N2O is utilizing Quantum Cascade Laser and this analyzer can measure N₂O concentration of ten ppb order.

Introduction^[1]

Recently, Nitrogen Oxides (NO_x) that results from automobile exhaust emissions have become subject to regulations. With the rise of global environmental consciousness, regulations on automobile exhaust emissions have become more stringent, demanding a further decrease in NO_x emissions. In response, several different NO_x after treatment systems are under research and development. To evaluate the performance of these after-treatment devices, analysis of NO_x compounds should not only include NO and NO₂, but also N₂O and NH₃. For example, NH₃ measurement are integral for the optimization of urea injection rate in heavy-duty diesel vehicles using Selective Catalyst Reduction (SCR) with urea injection systems. In Europe, regulations have already been implemented for NH₃ in the exhaust of SCR equipped vehicles. These regulations are scheduled to be further strengthened in the next term's Euro VI emission standards. On the other hand, new regulations and the requirements for annual emission reports in the United States have resulted in an increased need for N₂O measurement, due to its Greenhouse Gas (GHG) properties.

N₂O is a trace gas that exists naturally in the atmosphere with a level of about 300 ppb. It is the most common tropospheric nitrogen species aside from molecular nitrogen. Because it is a stable molecule, it has a very long

life time, which has been recorded as ranging from 130 to 170 years.^[2] In addition, since N₂O has an even greater propensity for absorbing infrared radiation than CO₂, there is a possibility that N₂O may contribute significantly to global warming.^[3] The EPA/NHTSA has finalized GHGs emissions standards that will cap tailpipe N₂O emissions for Light Duty Vehicles (LDV) at 0.010 g/mile,^[4] and LDVs will be obligated to install sample storage bags for N₂O measurements. For Heavy Duty Engines (HDE), the EPA has established N₂O emission regulations of 0.10 g/bhp-hr.^[5] The newest N₂O regulations for diesel engines will be implemented in 2017. Normally, emissions from HDEs can be measured directly from the exhaust or even after dilution, without the sample storage bags. Hence, in order to comply with exhaust emission regulations of both LDVs and HDEs, there is now a need for analyzer systems that are compatible with diluted exhaust gas bags and continuous measurement. To accurately calculate the values requested in these regulations, concentration readings must have a margin of error less than 50 ppb.

For N₂O measurement, the most commonly used methods are Non-Dispersive Infrared detection (NDIR), Fourier Transform Infrared detection (FTIR), and Gas Chromatography (GC). Although these are all accurate analysis methods, their measuring sensitivity and susceptibility to interference are not necessarily the most optimum to meet the measurement demands for current regulations.

Therefore in 2011, infrared spectroscopy method by using laser was defined as a viable measurement principle in the EPA regulations due to the potential of its laser which is able to improve sensitivity and reduce interference.

In 2012, the MEXA-1100QL-N2O system based on the Mid-Infrared Quantum Cascade Laser Spectroscopy (QCL-IR) was developed for measuring ultra-low concentrations of N₂O in automobile exhaust gas sampled in a sample storage bag.^[6] This system can be utilized either independently, or integrated into the automobile exhaust analysis system MEXA-7000. The system conforms to the 40 CFR Part 1065/1066 GHG standards set by the U.S. EPA. This paper presents the Mid-Infrared Quantum Cascade Laser (QCL-Mid IR) Spectroscopic Motor Exhaust Gas analyzer unit, called MEXA-1100QL-N2O analyzer, which is a part of the integrated MEXA-ONE Motor Exhaust Gas Analysis System, developed to provide one minute measurements corresponding to the current regulatory requirements.

Measurement Principle

Quantum Cascade Laser (QCL) is being recently applied to a new method for laser detection, as an alternative to traditional diode lasers which could not emit light in the mid-infrared range. Due to the mid-infrared laser's inherent properties, QCL-IR is able to scan in the micro-wavelength region

Figure 1a shows the schematic of the measurement principle using QCL-IR. The QCL source irradiates a laser into a gas analysis cell where sample gas is being fed, and the intensity of the laser after traveling through

the cell is monitored. Laser pulses are emitted when current is supplied for fixed intervals into the QCL source. The monitored output waveform for a single pulse is represented in Figure 1b, 1c, where the axes represent time vs. intensity of transmitted light. When a pulse voltage is applied to the QCL source, its temperature begins to rise, resulting in a change on the oscillating wavelength of the laser within the micro-region. As this process is repeated in each pulse, a defined range of oscillation wavelengths can be scanned in one pulse. Hence, each detected waveform of the pulses represented in Figure 1b, 1c can be transformed to wavelength vs. intensity of transmitted light. To quantify the gas component concentration in the QCL-IR, the light source's center wavelength is adjusted so that the absorption peaks of the target components fall within the scan's range. It is also desirable that the absorption peak of the selected target components does not overlap with the absorption peaks of other interference components.

Using a light source with these wavelength ranges, the logarithmic intensity ratios of the detected waveforms from sample gases fed into the cell (Figure 1c) are compared to a previously detected reference waveform of zero gas (Figure 1b) to obtain the absorbance spectrum contained in the scanned range. According to the Beer-Lambert law, light absorbance by a gas is proportional to its concentration. Thus the concentration of target components can be calculated from the detected light spectrum. Moreover, since the actual spectral intensity is affected by the temperature and pressure, compensation of these effects must also be performed. QCL-IR can be applied to a number of components that have absorption in the mid-infrared region. In addition, since a very high definition spectrum can be obtained by depressurization of the cell, the interference between components is expected to decrease as well.

Configuration of the Analyzer

The block diagram of the QL-N2O analyzer unit is presented in Figure 2. The laser beam is split and directed into the cell through a short (0.8 m) and long (30 m) optical paths. For the same sample gas present in the cell, stronger absorption can be observed at the long optical path from which low concentrations can be detected. On the other hand, the short path prevents saturation of light concentration when measuring high concentrations. The long and short optical paths allow for detection ranges of 0.5~5 ppm and 20~200 ppm, respectively. Thus, by gathering spectra from two optical path lengths, a wide range of low to high concentrations can be measured. The detector used in this system is an MCT

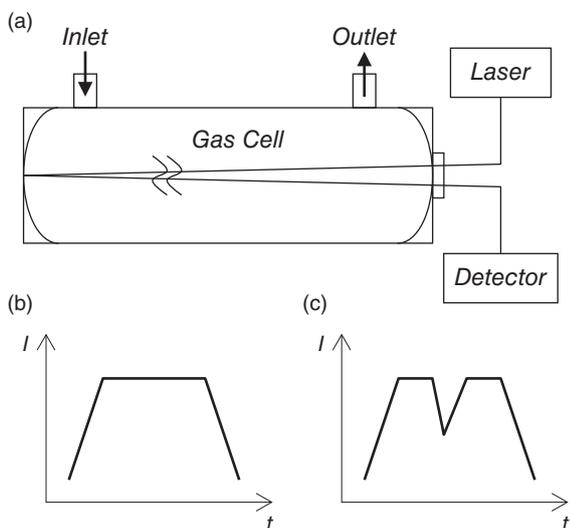


Figure 1 Principle of QCL-IR

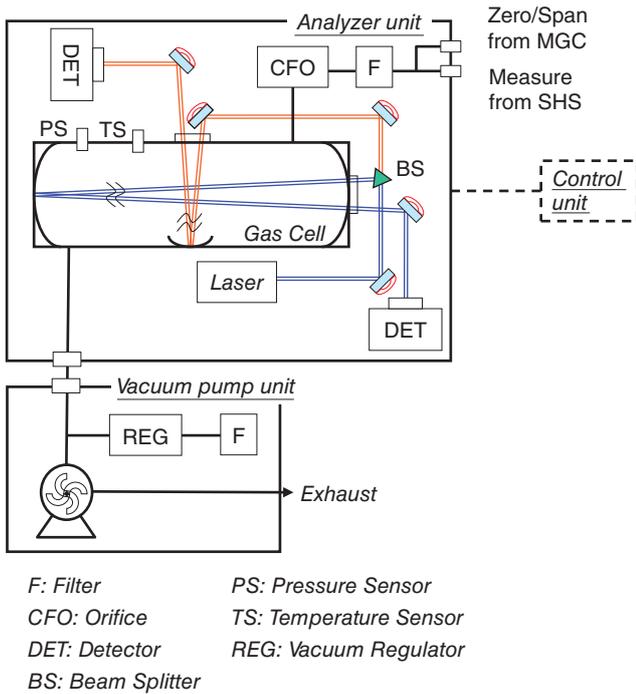


Figure 2 Block diagram of QL-N2O

semiconductor infrared detector, which operates at room temperature.

Sample gas is supplied to the gas cell after passing through a preprocessing filter and a critical flow orifice (CFO). The CFO has the function to maintain a constant flow rate, and combined with the downstream vacuum pump, the cell is maintained at a constant absolute pressure of about 25 kPa. Generally, a sharper absorption peak can be obtained by preserving the optical path in a vacuum state, thus facilitating the separation of spectra from other coexisting gas components, minimizing their interference.

System Configuration

In the MEXA-ONE system, the number of analyzer units

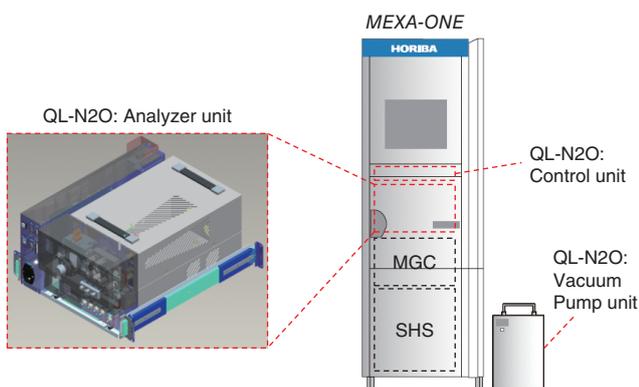


Figure 3 MEXA-ONE with QL-N2O

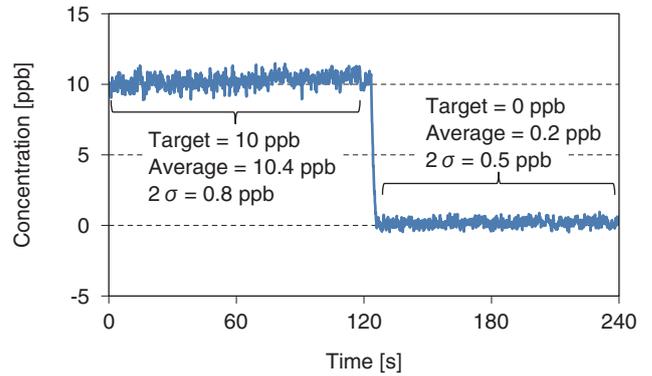


Figure 4 Noise and detection limit

is minimized to achieve one minute measurements. The units are mounted on a 19 inch rack, along with a Multi-Gas Controller (MGC) and a Sample Handling System (SHS), supplied by a calibration and sample gas lines. (Figure 3)

Equipment Performance

Noise and detection sensitivity

The noise of the QL-N2O is defined at double standard deviations (2σ), with a reference zero point below 10 ppb. Figure 4 shows the results when switching N_2O 10 ppb to zero gas (N_2). The 2σ calculated from the data when supplying Zero gas is 0.5 ppb. At a 10 ppb concentration, the 2σ results in 0.8 ppb. The 10 ppb concentration difference here can be clearly seen.

Accuracy and linearity

Measured concentration is corrected by 21 cut points of 5 ppm and 200 ppm ranges, and accuracy is warranted at same 21 cut points. Linearity is evaluated by intercept, slope, and coefficient of determination (R^2) as shown in Figure 5.

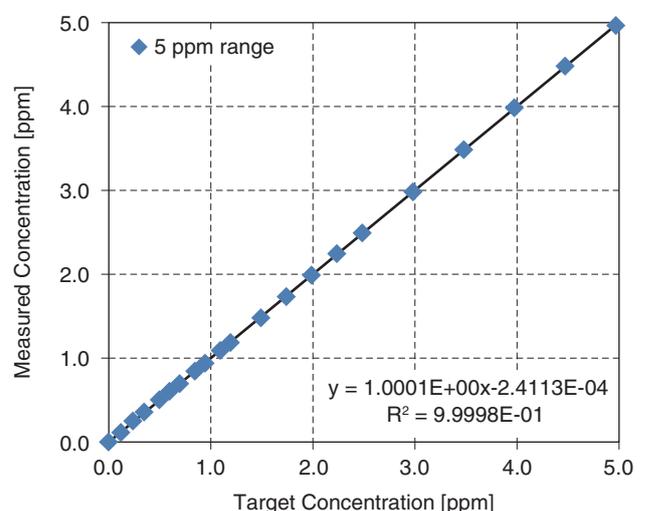


Figure 5 Corrected linearization curve at 5 ppm range

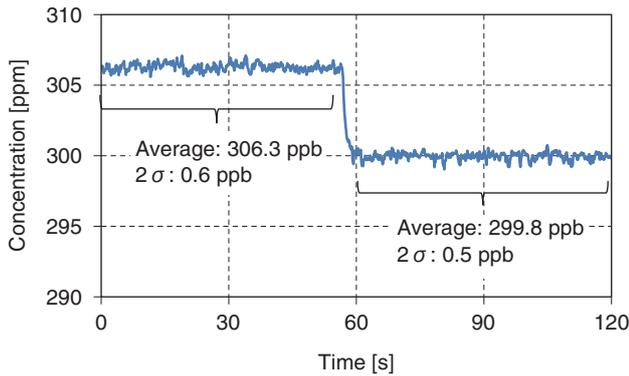


Figure 6 Measurement resolutions at atmospheric N₂O concentration

Figure 6 shows measurement results for atmospheric concentration levels of N₂O. Gases of 300 ppb and 306 ppb were measured, generated from a 600 ppb gas cylinder using a gas divider. The measured average concentrations were 299.8 ppb and 306.3 ppb, with a 2σ value of 0.5 ppb and 0.6 ppb, respectively. From these results it can be seen that N₂O atmospheric concentration levels can be measured with high accuracy.

Effects of interference

Concentration calculation was performed from an absorption peak near 4.7 μm obtained by the QL-N2O. Since CO₂ and H₂O have absorption peaks near the 4.7 μm wavelength, interference from these gases was expected. However, the effects of interference from CO₂ and H₂O absorption peaks have been minimized in this spectrometer, to the specified values of ±10 ppb. The effects of interference from CO₂ and H₂O can be seen in Figure 7. The effects of interference were determined by the difference of the concentration averages when feeding interference component gases (CO₂ and H₂O) and Zero gas. Interference by CO₂ was +3.3 ppb and interference by H₂O was -0.6 ppb.

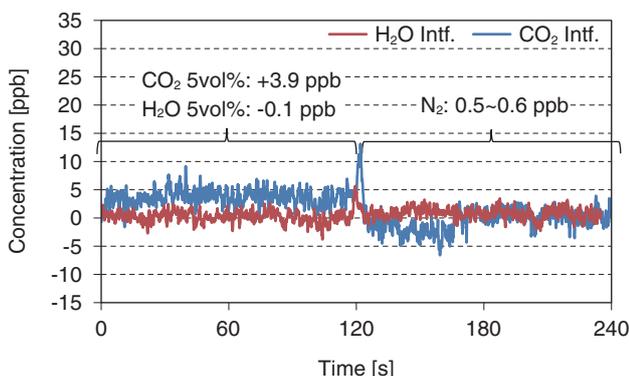


Figure 7 Interference test of CO₂ and H₂O

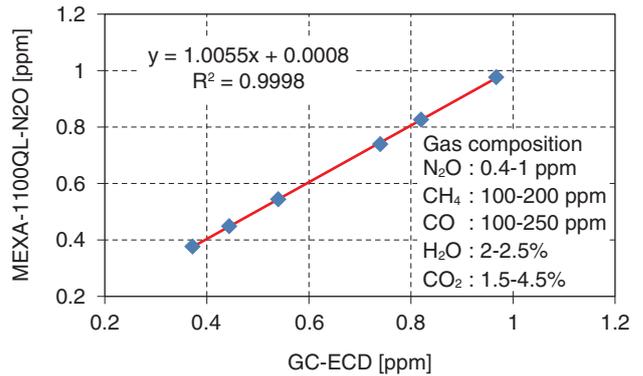


Figure 8 Correlation with GC-ECD in JARI (Standard gases)

Experimental results of interference effects using a similar analyzer to the MEXA-1100QL-N2O are presented in Figure 8. These results were provided by the Japan Automobile Research Institute. In this experiment, five gases (N₂O, CH₄; 100~200 ppm, CO; 100~250 ppm, H₂O; 2.0~2.5%, CO₂; 1.5~4.5%) were sampled in bags, from which six sampling bags were generated by mixing with a 0.4~1 ppm concentration of N₂O. Concentration results from these six sampling bags obtained using GC-ECD and MEXA-1100QL-N2O were compared, giving a 1.0055 slope and 0.0008 intercept, showing excellent correlation between both tests.

Conclusions

This paper presents an outline of the Mid-Infrared Laser Absorption Spectroscopy for Automobile Exhaust Emissions Analysis. The performance of the QL-N2O used in the MEXA-1100QL-N2O proved satisfactory for integration into the one minute measurement MEXA-ONE system. Its features are outlined as follows:

- (1) Highly sensitive measurements
 - Capable of concentration measurements at the 10 ppb level
 - Measuring resolution for atmospheric concentration levels below 6 ppb
- (2) Wide measurement range
 - 10 ppb (lower detection level) ~ 200 ppm (highest measurement range)
- (3) Low interference
 - Interference of CO₂ and H₂O within ±10 ppb

Notes

Through this device, the applications of the MEXA-ONE systems were able to expand. This device is used to meet the GHG regulations according to the U.S. EPA, and will hopefully contribute to the solution of global environmental problems.

References

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