Measurement of Automobile Exhaust N_2O by Mid-IR Laser Spectroscopy

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Nitrous Oxide (N_2O) 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 (EPA) together with the United States Department of Transport (DOT) has already regulated the N_2O emissions from Light-Duty Vehicles (LDV). For LDV, N_2O measurement should be done from sample storage bags over the light-duty FTP drive cycles. N_2O emission standard of 0.10 g/bhp-hr for Heavy-Duty Engines (HDE) is also finalized. The final N_2O standard becomes effective in 2017 model year for diesel engines. Usually raw or diluted exhaust is measured for HDE emission testing. Therefore, an analyzer capable of measuring N_2O from bag and from diluted sample continuously is required to support both LDV and HDE regulations. In this study, comparative measurement of automobile exhaust N_2O in continuous dilute and in sample storage bag has been attempted. A modern vehicle meeting 2008 Japanese emission standards has been evaluated. In this letter, it is found that the laser based exhaust gas analyzer has sufficient detection capability for bag measurement and fast response for continuous dilute measurement.

INTRODUCTION

Nitrous oxide (N_2O) 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 very long life time which has been recorded as being from 130 to 170 years.[1] Since N_2O has an even greater propensity for absorbing infrared radiation than CO_2, there is concern that N_2O contributes significantly to global warming.[2]

The US-EPA together with the DOT has already regulated the N_2O emissions from Light-Duty Vehicles (LDV) under a harmonized and consistent National Program. Under the national program, automobile manufacturers will be able to build a single light-duty national fleet that satisfies all requirements while ensuring that consumers still have a full range of vehicle choices. N_2O emission from light duty LDV has been limited to 0.010 g/mile.[3] For LDV, N_2O measurement should be done from sample storage bags. Similar to the CO_2 standard approach, the N_2O emission level of a vehicle would be a composite of the light-duty FTP cycles. The US-EPA is also finalizing a N_2O emission standard of 0.10 g/bhp-hr for heavy-duty engines (HDE).[4] The final N_2O standard becomes effective in 2017 model year for diesel engines. Usually raw or diluted exhaust is measured for HDE emission testing. An analyzer capable of measuring N_2O from bag and from diluted sample continuously is required for supporting both the LDV and HDE regulations.

An instrument based on mid-infrared quantum cascade laser spectroscopy had been developed for measuring ultra-low level N_2O in automobile exhaust gas sampled in a sample storage bag.[5] This instrument is a pulsed-mode high-resolution narrow band mid-infrared analyzer. It was reported that it has very low detection limit (<5 ppb), excellent linearity, and the response time (t_{10}-t_{90}) is shorter than 4 second (sample flow rate of 4 L/min). Negligible amount of interference from co-existing gases was also confirmed by using real engine exhaust.[5] In this study, the instrument is applied for measuring N_2O emission from a modern gasoline vehicle that meets 2008 Japanese

emission standards. Correlation between N_2O measurement from sample storage bag hereafter called as "bag measurement" and continuous N_2O measurement from CVS hereafter called as "continuous dilute measurement" has been attempted.

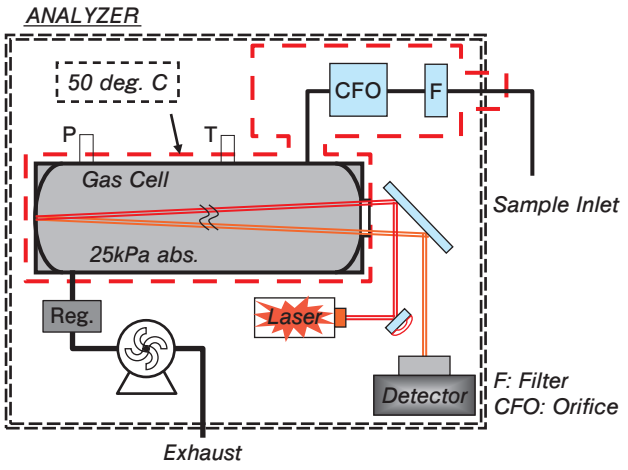

Figure 1 Block diagram of the N_2O measurement system

SYSTEM CONFIGURATION

Figure 1 shows th e block diagram of the analyzer. It mainly consists of a gas cell, a laser unit, a detector, and a vacuum pump. The gas cell is maintained at 50 °C and under high vacuum. The cell volume is about 500 ml where a total optical path length of about 30 m was achieved by multiple reflections between two mirrors in order to achieve low detection limit. The sample gas flow rate is maintained at about 4 L/min at room temperature for bag measurement in this letter.

VEHICLE TEST PROCEDURE

The test vehicle is equipped with a 1.5 L port injection gasoline engine and with dual-TWC after treatment system. The tests were performed on a chassis-dynamometer under FTP test cycles under cold start and hot start condition. In the cold start test, the vehicle was preconditioned and soaked in similar way every time before the test according to the EPA recommended procedure.[6] The hot start test is the test started immediately after completion of a cold start test without any preconditioning and soak. The schematic of the test system is shown in Figure 2. The sample storage bag was purged with nitrogen gas well in advance. In addition, sampling-to-measurement time was also kept constant in all test conditions in order to minimize the variation in bag environment under which transformation of NOx components in the sample storage bag occurs.

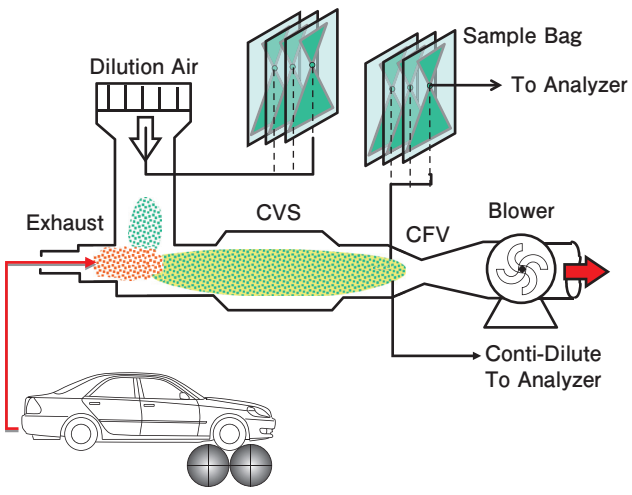

Figure 2 System schematic for vehicle test on chassis dynamometer with CVS

Measurement of N_2O was attempted both from CVS for continuous dilute measurement and from sample storage bag. The dilution air was supplied from ambient through a charcoal plus HEPA filter unit. Diluted sample and dilution air was sampled in two separate bags for background correction. The full FTP driving cycle is separated into 3 phases; phase-1: Cold Transient, phase-2: Stabilized, and phase-3: Hot Transient. In between phase-2 and phase-3 there is a predetermined soak period. Therefore a total of six bags were sampled, 2 bags for each phase in the full driving cycle. Calculation of N_2O

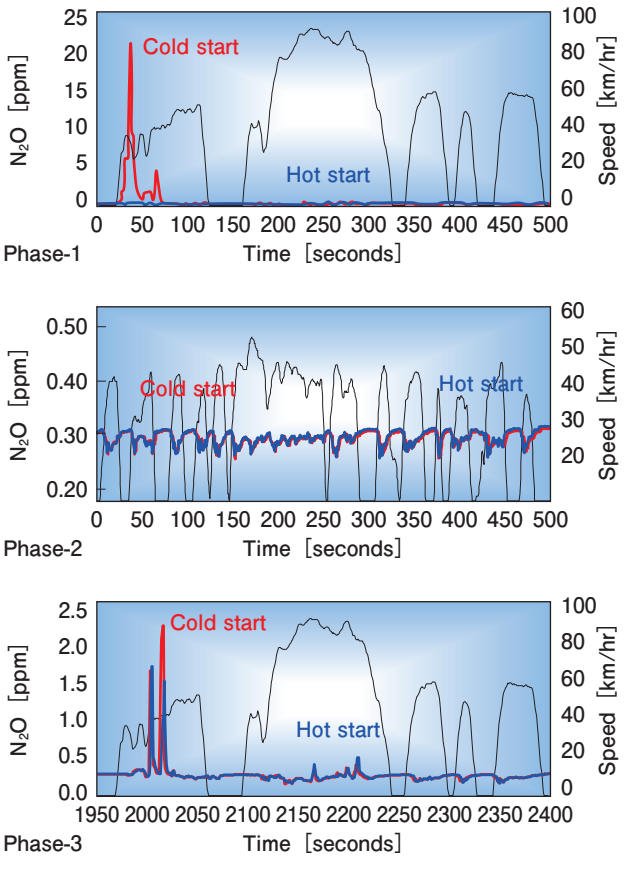

Figure 3 Real-time N_2O emission of the FTP driving cycle

mass emission of was done according to EPA procedure.[7] Only continuous dilution measurement was performed without any bag sampling in this case.

RESULTS AND DISCUSSIONS

Figure 3 shows the real-time N_2O emission in different phases of the FTP driving cycle under cold and hot start condition. The upper side graph shows the real-time N_2O emission in the cold transient phase (Phase-1) while the bottom side graph shows the real-time N_2O emission in the hot transient phase (Phase-3). The graph in the middle shows the real-time N_2O emission in the stabilized phase (Phase-2). There is a predetermined soak period between the stabilize phase and the hot transient phase.

Figure 4 shows the total and individual phase based mass emission of N_2O calculated from the bag measurement data. Calculation of mass emission was done according to the "40CFR Part 86 Subpart B.[6] It shows that during cold start condition most of the N_2O is emitted in cold transient phase of FTP driving cycle. Concentration of N_2O in diluted samples stored in Bag-1 during this phase is about 600 ppb which gives mass emission of about 4.50 mg/mile. However when the test is done under hot started condition, concentration of N_2O in diluted samples stored in Bag-1 during this phase is about 330 ppb which gives a mass emission of about 0.17 mg/mile.

Phase-2 (stabilized phase) shows no N_2O emission at all even if the vehicle is started at either cold or hot condition. Concentration of N_2O in diluted samples stored in Bag-2 during this phase is within 290 to 300 ppb while the ambient background is about 320 ppb. Therefore it gives almost zero mass emission according to the calculation procedure proposed in the "40CFR Part 86 Subpart B.[6] Concentration of N_2O in the Bag-2 may become significantly lower than dilution air background depending on the engine type and driving pattern. Phase-3 shows some positive N_2O mass emissions and hot start condition has almost the same N_2O mass emissions as that of cold start condition. It shows that the total mass emission of N_2O from this test vehicle is about 0.95 mg/mile under cold start condition while it is about 0.14 mg/mile under hot start condition. The cold start emission from this test vehicle is one tenth of the EPA regulatory value.

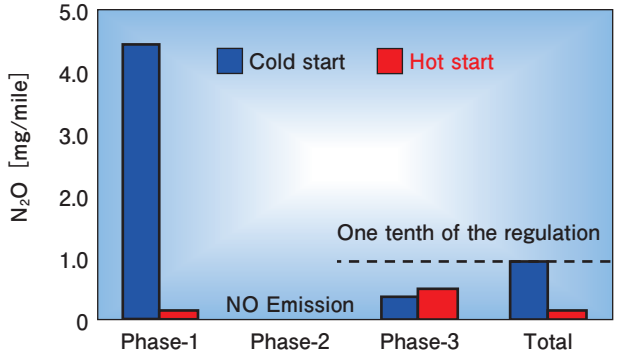

Figure 4 Total and Modal Mass Emission of N_2O

CONCLUSION

A modern clean vehicle has been tested under FTP test cycles. A quantum cascade mid-infrared laser spectroscopic motor exhaust gas analyzer is used to measure the N_2O emission. The analyzer showed promising potential for ultra-low concentration N_2O measurement from bag as well as faster response for continuous dilute measurement. Results revealed the following:

1. Vehicle equipped with conventional port injection gasoline engine and TWC emits very low level of N_2O and concentration of N_2O in diluted samples stored in bag sometimes goes below ambient level. N_2O emission level of the test vehicle is one tenth of the regulatory value. Therefore, compliance test of such low emission vehicle requires very sensitive analyzer with low detection limit.
2. For vehicle equipped with conventional port injection gasoline engine and TWC, most of the N_2O is emitted during first 100 to 200 seconds of any driving cycle if started from cold condition. There is almost no N_2O emission when the vehicle is warmed up.
3. The mid-infrared quantum cascade laser spectroscopic analyzer used in this study has sufficient detection capability for measurement of very low concentration of N_2O from bag. The analyzer has fast response for continuous dilute measurement from CVS. There is excellent consistency between bag measurement and continuous dilution measurement by the analyzer used in this study.

References

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[3] Environmental Protection Agency, "Electronic Code of Federal Regulation, Title 40, Parts 85, 86, 600, 1033, 1036, 1037, 1039, 1065, 1066, and 1068.

[4] Environmental Protection Agency, "Electronic Code of Federal Regulation, Title 49, CFR Parts 523, 534, and 535.

[5] Montajir, R., "Development of an Ultra-Low Concentration N_2O Analyzer Using Quantum Cascade Laser (QCL)," *SAE Technical Paper* **2010-01-1291**, 2010, doi: 10. 4271/2010-01-1291.

[6] "Electronic Code of Federal Regulation, Title 40: Protection of Environment, Part 86: Control of Emission from New and In-Use Highway Vehicles and Engines, Subpart B, Section 86-132-00.

[7] "Electronic Code of Federal Regulation, Title 40: Protection of Environment, Part 86: Control of Emission from New and In-Use Highway Vehicles and Engines, Subpart B, Section 86. 144-94.

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