Feature Article

Sulfur Compounds Analyzer MEXA-1170SX

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The MEXA-1170SX is a continuous gas analyzer for sulfur compounds existing in engine emissions. It can measure SO_2 concentration and the amount of total reduced sulfur compounds (TRS), such as H_2S, separately. It can also measure the total sulfur compounds (TS) that contains both gaseous compounds and liquid compounds in PM, such as SO_3. By utilizing ultra-violet fluorescence (UVF) method and various original analysis techniques such as ozone injection, the MEXA-1170SX achieves reliable measurements with low interference from other co-existing compounds.

Introduction

Sulfur compounds in exhaust gases can be absorbed on particulate matter (PM) and then enter the respiratory system, causing concern as to the effect on human's health. Measurement of sulfur components in vehicle emissions is important in evaluating de-sulfating systems for NOx after-treatment systems, such as a lean NOx trap catalyst, where sulfur poisoning on the surface would cause a serious decay of catalyst activity.

Additionally, in recent years, oil consumption of vehicles has attracted much attention since it is closely related to fuel consumption. For oil consumption measurement, the oil weighing process has been generally used. This method can directly measure the mass of consumed oil, however, it is hard to obtain real-time information about oil consumption. The sulfur tracing method, in which oil consumption is calculated from the sulfur compounds exhausted from an engine, has also been investigated as an alternative method.

The HORIBA MEXA-1170SX is a high-sensitivity and quick response analyzer, which can be used for evaluating sulfur compounds behavior in after-treatment systems and for measuring oil consumption by the sulfur tracing method [1][2]. This article describes the system configuration using ultraviolet fluorescence (UVF) method as measurement principle and examples of engine emission evaluation.

Outline of the System

Specifications

Figure 1 and Table 1 show the overview of the MEXA-1170SX. It can measure SO_2 concentration and the amount of total reduced sulfur compounds (TRS) as "SO_2/TRS measurement mode". It can also measure the total sulfur compounds (TS) that contains both gaseous compounds and liquid compounds in PM as "TS measurement mode". TRS means the sulfur compounds with higher reducibility than SO_2, such as hydrogen sulfide (H_2S),
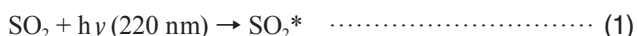

Figure 1　MEXA-1170SX

Table 1   Specification of MEXA-1170SX

Model	MEXA-1170SX
Application	Exhaust gases from engines

Target components	Either of the following modes can be selected (switchable):
	-SO_2, SUM, TRS measurement mode:
	  SO_2: SO_2
	  SUM: SO_2, and total reduced sulfur compounds
	  TRS: Total reduced sulfur compounds
	    (by subtracting "SO_2" from "SUM")
	-TS measurement mode:
	  TS: Total sulfur compounds, in gas phase and liquid phase (such as SO_3)

Principle	Ultra-violet fluorescence (UVF) method
Measuring range	

SO_2/TRS mode	(Standard)
	  SO_2: 0-20 to 2000 ppm
	  SUM: 0-20 to 2000 ppm
	  TRS: 0-20 to 2000 ppm
	    (Ranges for SO_2, SUM and TRS are changed synchronously)
	(Optional)
	  SO_2: 0-20 to 2000 ppm

TS mode	(Standard)
	  TS: 0-10 to 2000 ppm
	(Optional)
	  TS: 0-5 to 100ppm

Principle of Detecting Sulfur Dioxide

Ultraviolet Fluorescent Detector

The UVF method is an analytical technique utilizing fluorescence in the ultraviolet region. Figure 2 shows the principle of the UVF detector. Sample gas introduced into the cell is irradiated by ultraviolet rays from a light source, so that a portion of SO_2 in the gas becomes excited (SO_2*), by absorbing the ultraviolet light of approx. 220 nm (Equation 1). This excited SO_2* then decays back to its original state, by producing fluorescent radiation with a wavelength of approx. 330 nm (Equation 2).

$$SO_2 + h\nu \,(220\ nm) \rightarrow SO_2^* \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$
$$SO_2^* \rightarrow SO_2 + h\nu \,(330\ nm) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

This fluorescent radiation can be detected by a photo-multiplier tube (PMT) perpendicular to the radiating light. This prevents scattered light from the light source from entering into the PMT, therefore only the ultraviolet fluorescence is detected. The detected intensity of fluorescence has a relationship with the concentration of SO_2 in the cell. As a result, the SO_2 concentration can be calculated from the PMT output.
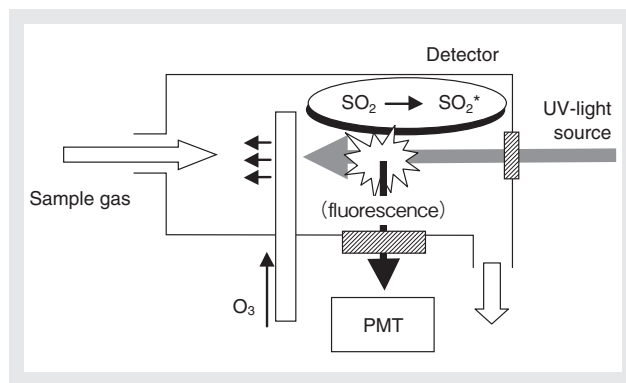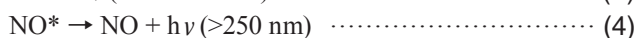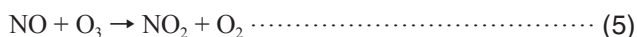

Figure 2   Principle and Configuration of UVF Detector

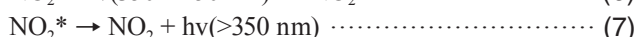## Countermeasure against Interference from NO

The UVF method sometimes receives interference from radiations of other components which show fluorescence near 330 nm. Among the major components in engine exhaust gas, NO should be considered as the most possible interfering component. NO in sample gas absorbs 150 to 250 nm radiations and reaches to an exited state (NO* in Equation 3), and then radiates fluorescence in the relaxation process (Equation 4).

$$NO + h\nu \,(150\sim250\ nm) \rightarrow NO * \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$
$$NO^* \rightarrow NO + h\nu \,(>250\ nm) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$

The wavelength of fluorescent radiation in this process is expected to be close to 330 nm, therefore some of the fluorescent radiation from NO* can be detected by the same PMT. This is the reason why the UVF detector has not been considered to be suitable for measuring sulfur components in vehicle emissions. To prevent such interference from NO, an ozone injection technique has been adopted in the UVF method sulfur analyzer. NO is easily oxidized into NO_2 by O_3 (Equation 5).

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

Although NO_2 also absorbs ultraviolet and emits fluorescent radiation, the radiation wavelength is longer than that from SO_2* (Equation 6, 7). So interference by NO_2 fluorescence can be avoided by placing an optical filter that selectively permeates light from 250-340 nm in front of the PMT.

$$NO_2 + h\nu(350\sim450\ nm) \rightarrow NO_2^* \quad \cdots\cdots\cdots\cdots\cdots\cdots (6)$$
$$NO_2^* \rightarrow NO_2 + h\nu(>350\ nm) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$$

Countermeasure against Interference from HC

Unsaturated hydrocarbons such as the aromatic series are known to emit ultraviolet fluorescence. So hydrocarbons

can be interfering components for SO_2 detection by the UVF method. Interference from such components is prevented by an optical filter installed in front of the PMT. Also, during TS measurements, the sample gas passes through the furnace before entering the detector. So hydrocarbon in the sample is expected to burn off in the furnace, therefore the interference to SO_2 indication can be ignored.

Sampling Configuration for TRS and TS Measurement Modes

TRS/SO_2 Measurement Mode

Figure 3 shows the flow schematic for measuring total reduced sulfur (TRS) and SO_2 simultaneously. In this configuration, sample gas is introduced into the analyzer and split into 2 sample lines, i.e. a line to measure SO_2 only and another line to measure total amount of SO_2 and TRS (SUM line). Then, the sample gas of the SUM line is flowed into a furnace with O_3 to convert the TRS into SO_2. The temperature of the furnace has been set to 600 °C Finally in SUM line, the UVF detector measures the SO_2 concentration that is related to the total amount of SO_2 and TRS originally contained. TRS concentration can be calculated by subtracting the SO_2 concentration from the SUM concentration.
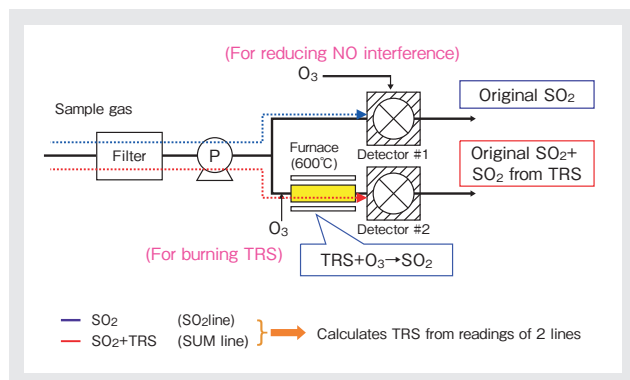

Figure 3   Flow Schematic of TRS Measurement Mode

To limit NO interference, the device injects ozone to the SO_2 line that will not pass through the furnace. Injecting ozone is efficient in reducing NO interference but may oxidize a part of the TRS into SO_2. To prevent this, at the SO_2 line, ozone is injected to the sample gas at the closest possible point to the detector. TRS oxidation speed by the ozone is slower than the NO oxidation speed, so the conversion of TRS into SO_2 within the detector can effectively be ignored.

TS Measurement Mode

Figure 4 shows the flow schematic for measuring the total sulfur (TS). The sampling probe is heated up to temperature of 350 °C to vaporize any sulfuric acid (boiling point 330 °C) in the engine emission. The sample gas passes through two heated furnaces in this analyzer. The primary furnace is heated to 1100 °C. This burns the carbons in PM and HC, and further deoxidizes sulfate in PM into SO_2 by addition of oxygen. A secondary furnace is heated to 600 °C for oxidizing any TRS that remains in the downstream of the primary furnace by addition of ozone. So TRS and sulfate, in addition to the sulfur trioxide (SO_3), is converted into SO_2 by the two furnaces. The sample gas ultimately flows into the SO_2 detector and SO_2, TRS and sulfate in the PM are all detected as TS.
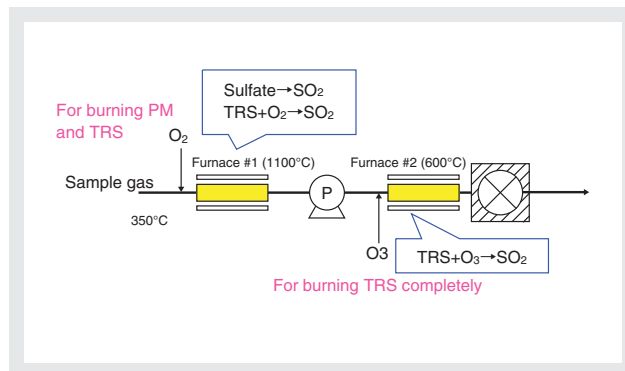

Figure 4   Flow Schematic of TS Measurement Mode

Basic Performance

Response Speed

Figure 5 shows the speed of response during SO_2/TRS, (SO_2/SUM) and TS measurement. SO_2 gas was used for the confirmation tests, and zero / span gases were switched in the device. The response speeds are practically identical for all detectors, approximately 4 seconds to 90% response rate (T_{90}).
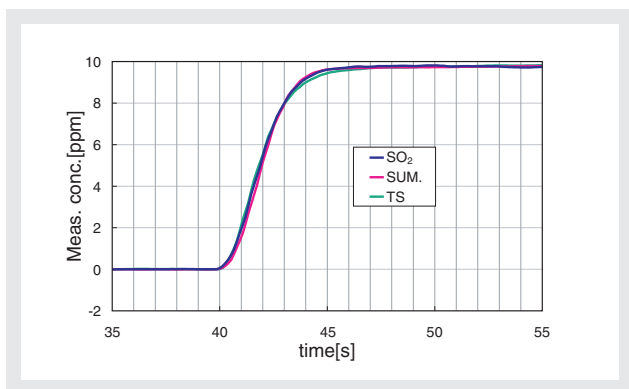
Figure 5   Response Time for SO$_2$ from Calibration Line

With a 10-meter sample line attached to the analyzer when the gas was switched at the sample line entrance, the delay time up to the start of response (T_d) was approximately 3 seconds and T_{90} was approximately 4 seconds.

Oxidation Efficiency for TRS

Table 2 shows the TRS oxidation efficiency in a 600 °C furnace. The "With O$_2$ injection" column shows the efficiency when O$_2$ is injected before the sample gas is introduced into the furnace, and "With O$_3$ injection" shows the efficiency when ozone is injected. Oxidation efficiency is higher when ozone is injected for all components, with generally 90% oxidation. It shows that TRS is oxidized efficiently by injecting ozone before passing the sample gas through the furnace.

Table 2   Example of Oxidation Efficiencies for TRS

Components and concentration		oxidation efficiency in a furnace of 600°C	
		With O$_2$ injection	With O$_3$ injection
H$_2$S	45.9ppm	58.8%	91.3%
CS$_2$	26.5ppm	8.1%	89.9%
COS	50.1ppm	1.7%	92.3%
(CH$_3$)SH	49.3ppm	55.1%	90.7%
(CH$_3$)$_2$S	53.2ppm	11.8%	89.1%
(C$_2$H$_5$)SH	10.4ppm	76.9%	100.0%
(C$_2$H$_5$)$_2$S	52.3ppm	32.7%	90.2%

Temperature Dependency of SO$_3$ De-oxidation

Figure 6 shows the effect of furnace temperature on the de-oxidation efficiency for TS mode. The ◆ symbols in the figure indicate the efficiency when the furnace temperature was changed from 300 °C to 1150 °C. The line shows the theoretical efficiency that is calculated from the equilibrium constant of SO$_3$ and SO$_2$. The reaction formula is expressed in Equation 8.

$$SO_2 + \frac{1}{2}O_2 \longleftrightarrow SO_3 + 23.1\ kcal \quad \cdots\cdots\cdots\cdots\cdots (8)$$

Measured efficiency is lower than calculated efficiency till the furnace temperature rises to 1100 °C. However, the general tendency shows relatively good agreement each other.
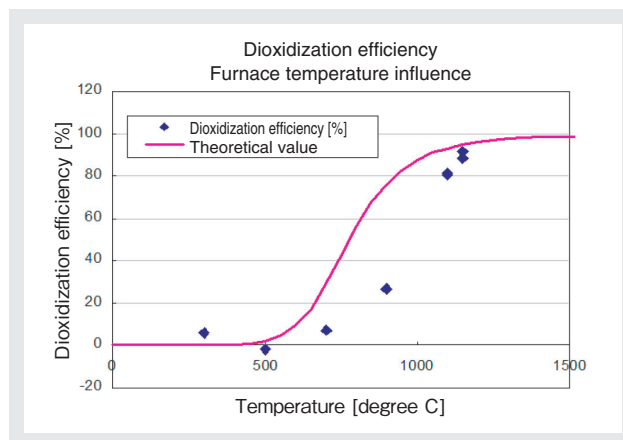

Figure 6   Temperature Dependency of SO$_3$ De-oxidation

Engine Emission Measurement

TRS Measurement

Figure 7 shows an example of SO$_2$/TRS measurement in exhaust gas from a 2.5-liter diesel engine. The sampling point was after the catalyst, and in this case, the sulfur component desorbing from the catalyst by the fuel injection is likely being measured. In the figure, it is apparent that SO$_2$ and TRS show different behaviors in response to the fuel injection.
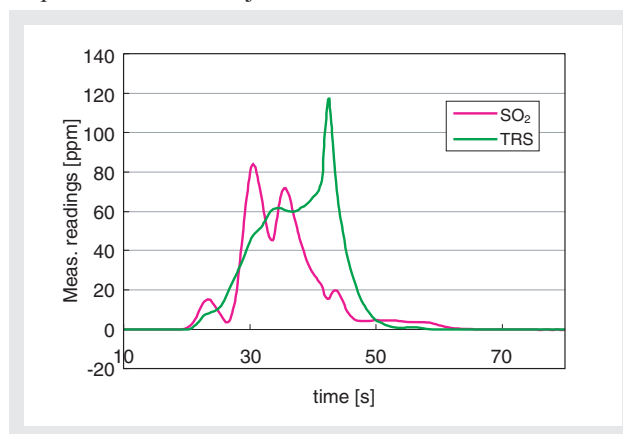

Figure 7   Example of SO$_2$/TRS Measurement in Diesel Exhaust Gas

TS Measurement

Dependency on engine speed

Figure 8 shows a real-time chart for TS measurement. The specimen engine was 2.4 L, 4-cylinder gasoline engine. Mass concentration of sulfur in the fuel was roughly 5 ppm and that in the oil was 0.23%. The engine

speed was varied from 1000 rpm to 5000 rpm. The TS concentration is not so stable; however, it obviously increases when the engine speed increases. The concentration level is around 1 or 2 ppm, and likely includes sulfur from the fuel as well as from the oil. However, assuming the engine exhaust gas flow is proportional to fuel consumption, the TS concentrations derived from fuel are fixed during the each stage. Therefore the rise and fall of TS concentration in Figure 8 is considered to respond to oil consumption. So it can be seen that oil consumption increases with the increase in engine revolutions.
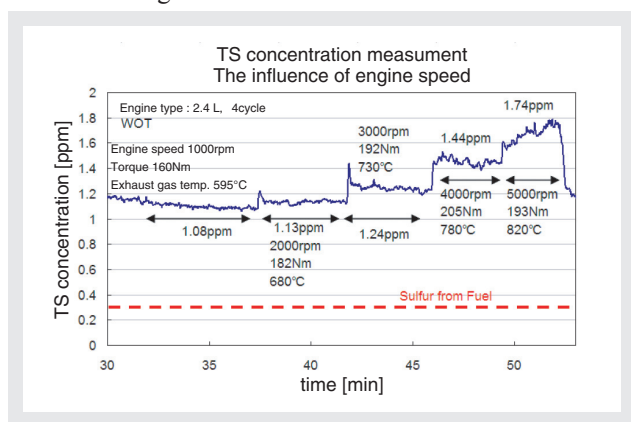

Figure 8   TS Concentration under Various Engine Speed

Dependency on Engine Torque

For measuring oil consumption rate by the sulfur tracing method, special oil containing high sulfur and low-sulfur fuel have to be utilized. The oil consumption rate is calculated from the mass flow rate of fuel and air, and total sulfur concentration in oil, fuel, air and exhaust gas. In general, the oil consumption is calculated as shown in Equation 9.

$$m_{oil} = \frac{m_{fuel}\left([S]_{exh}-[S]_{fuel}\right)+m_{air}\left([S]_{exh}-[S]_{air}\right)}{[S]_{oil}-[S]_{exh}} \cdots\cdots (9)$$

Where,
m_{oil} : mass flow rate of oil (oil consumption rate) [kg/h]
m_{fuel} : mass flow rate of fuel [kg/h]
m_{air} : mass flow rate of intake air [kg/h]
$[S]_{oil}$: sulfur mass concentration in oil [%]
$[S]_{fuel}$: sulfur mass concentration in fuel [%]
$[S]_{air}$: sulfur mass concentration in intake air [%]
$[S]_{exh}$: sulfur mass concentration in engine exhaust [%]

Figure 9 shows an example real-time chart for engine torque and TS concentration (as SO_2), where engine speed was under a fixed condition 1500 rpm. The oil consumption

rate that was calculated from TS concentration is also shown. The specimen engine was 2.2 L, 4-cylinder diesel engine. Mass concentration of sulfur in the fuel was 8 ppm and that in the oil was 1%. It can be seen that TS concentration varied in the order of 0.5 to 2 ppm when engine torque was changed from about 50 N m to 300 N m. This change, in oil consumption rate, is around 5 to 35 g/h. Additionally, as the torque increases, TS concentration and oil consumption ratio increases.
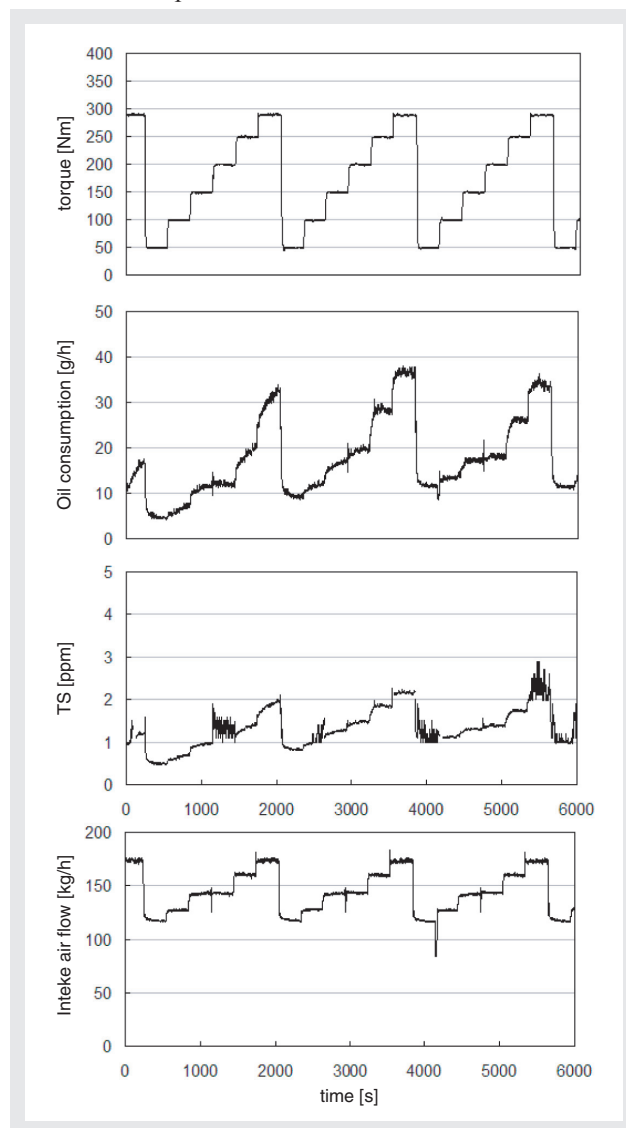

Figure 9   Measurement of Oil Consumption Rate

Conclusion

In this article, system configuration, performance and emission test results of MEXA-1170SX have been shown. The MEXA-1170SX utilizes a UVF detector which has high-sensitivity and quick-response. Generally, an UVF

detector is not suitable to measure sulfur components in vehicle emission due to a significant interference from NO. For the MEXA-1170SX, an O_3 injection technique has been adopted to eliminate NO interference. Since the MEXA-1170SX can be applied for measurement of both TRS and TS, the system is expected to be a beneficial tool for evaluating sulfur compounds behavior in after-treatment systems and for measuring oil consumption by the sulfur tracing method.

References

[1] H.Nakamura, et.al., Development of a new UVF Analyzer with O_3 injection for Measurement of SO_x and TRS in Vehicle Emission, SAE paper 2004-01-1959.

[2] S.Murakami, et.al., Application of Real-time Total Sulfur Analysis with UVF Method to Oil Consumption Measurement, SAE paper 2007-01-2062.

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