

Feature Article

Low-mass PM analyzer MEXA-1370PM

— Improvement of the Performance for PM Composition Analysis —

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Particulate matter (PM) emitted from engines is currently measured by the filter weight method. The filter weight method passes diluted emission gases through a filter collecting the PM, and post test weighs the mass of the collected PM on a precision balance. However, this method is time consuming, and with decreasing PM emission volumes, improvements in accuracy were needed. So the MEXA-1370PM was developed, to measure soluble organic fraction (SOF), soot, sulfate and total PM by vaporizing, thermally decomposing and gasifying (through redox reaction) the PM collected on a filter. The MEXA-1370PM allows easy measurement of collected PM mass, and shows good correlation with the PM weighing results of the precision balance. On the other hand, regarding the separation performance of SOF and soot, dispersion of the detection ratio increased for PM volume of 0.5 mg and under. To prevent the main cause, the mixing of O₂ during SOF measurement, the device composition and criteria were improved; SOF and soot were accurately separated up to 0.2 mg.

Introduction

Recently, after-treatment techniques for diesel engine emission reduction have made remarkable progress. Owing to new techniques such as the diesel particulate filter (DPF), the total amount of particulate matter (PM) collected on filter is rapidly reducing. Conventionally, PM amounts from engine exhaust gas were measured by the weighing method using precision balances⁽¹⁾. However, measurement of low PM samples was difficult, troublesome and time consuming. In addition, the component separation measurement of SOF and soot that requires Soxhlet extraction, making the process even more cumbersome. As an alternative, in 2001, HORIBA released the MEXA-1370PM analyzer, which utilized the vaporization/ thermal decomposition/ oxidation-reduction method (hereinafter, "vaporization method")⁽¹⁾⁻⁽³⁾. The MEXA-1370PM can quickly and easily measure separated components of PM.

The composition and the measurement conditions of the MEXA-1370PM were improved to increase the component separation accuracy even further, for use with low-concentration PM measurements. This report describes the factors considered for improvement as well as the separation accuracy after improvement and the results of

the correlation test with the conventional method.

Outline of MEXA-1370PM

Dimensions and Specifications

Figure 1 and Table 1 show the overview of the MEXA-1370PM.

Table 1 Specification of MEXA-1370PM

Model	MEXA-1370PM
Application	Particulate matter (PM) from engine exhaust gas (collected on a filter)
Principle	Vaporization, oxidation and de-oxidation using NDIR
Component	SOF: Soluble Organic Fraction Soot Sulfate Total PM: SOF+ soot+ sulfate
Analysis time	240 s (per sample)
PM collecting filter	Dedicated quartz filter
Display	CRT displays analysis result in graphic
Output	Files stored in hardware, detector output as analog voltage (0-1V), printer output (analysis result, setting value)

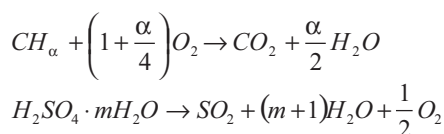


Figure 1 MEXA-1370PM

Measurement Principle

Figure 2 shows a diagram of the flow paths for the MEXA-1370PM. To collect particulate samples for this instrument, sample gas from a dilution tunnel is drawn through a quartz filter, the characteristics of which remain unchanged under high temperature¹⁾.

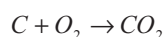
For measurement, the particulate sample collected on the quartz filter is placed into a furnace heated to 980 °C. Volatile organic fraction (VOF) and sulfate in the particles are vaporized in a N₂ atmosphere. The VOF is oxidized into CO₂ by oxygen mixed at the downstream, and the sulfate is de-oxidized and transformed into SO₂ under the high temperature conditions. Concentrations of the generated CO₂ and SO₂ are analyzed by detectors based on the non-dispersive infrared (NDIR) method. The chemical reactions that occur in this process are expressed as follows:



where

- α is the hydrogen to carbon molar ratio
- m is the H₂O to H₂SO₄ molar ratio

After the vaporization of VOF and sulfate, O₂ is introduced into the furnace. The soot remaining on the filter is then oxidized and is measured as CO₂ by the NDIR analyzer. The chemical reaction of this stage is as follows:



The output of the CO₂ analyzer is integrated while

introducing N₂ gas to determine the mass of soluble organic fraction (SOF), and is also integrated while introducing O₂ gas to determine the mass of soot. The SO₂ analyzer output is also integrated to determine the mass of the sulfate.

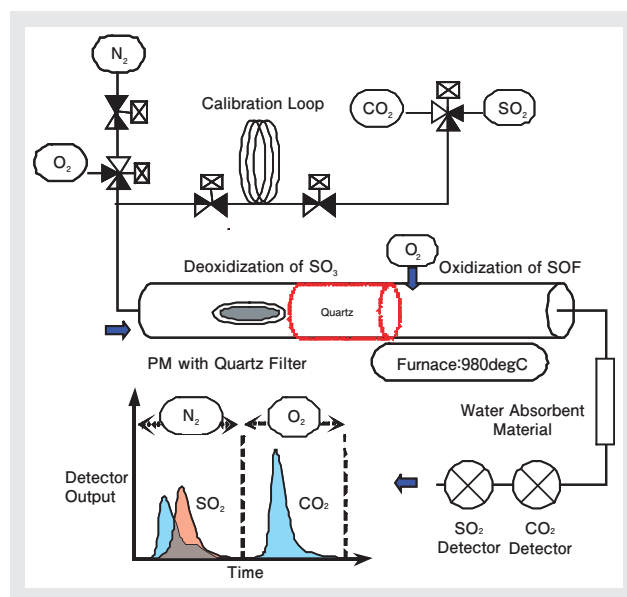


Figure 2 Measurement Principle of MEXA-1370PM

Improvement of the Instrument PM Composition Analysis

Figure 3 shows a typical signal of PM measurement obtained by the previous version of MEXA-1370PM, prior to improvement. The figure shows the CO₂ signal output data only. The first peak around 90 seconds is generated from SOF, and second peak around 350 seconds is generated from soot. To secure the separation accuracy of SOF and soot, it is desirable to separate the two peaks completely. However, as shown in the scale-up plot of Figure 3, the CO₂ analyzer trace exhibits a tail from the

SOF peak that extends beyond the 200 seconds. This device assumes the tail to be SOF, but considering the chemical properties of SOF, such long tailing is improbable, and there is the possibility that portions of the soot remaining on the filter is transformed into CO_2 . For example, the tailing signal area from 200 seconds and 300 seconds corresponds to 0.012 mg SOF approximately. This will significantly bias a soot measurement that simply looks at the area under the curve beyond 120 seconds. In fact, such phenomenon was one reason the lower limit of the separation performance of the MEXA-1370PM before improvements was about 0.5 mg.

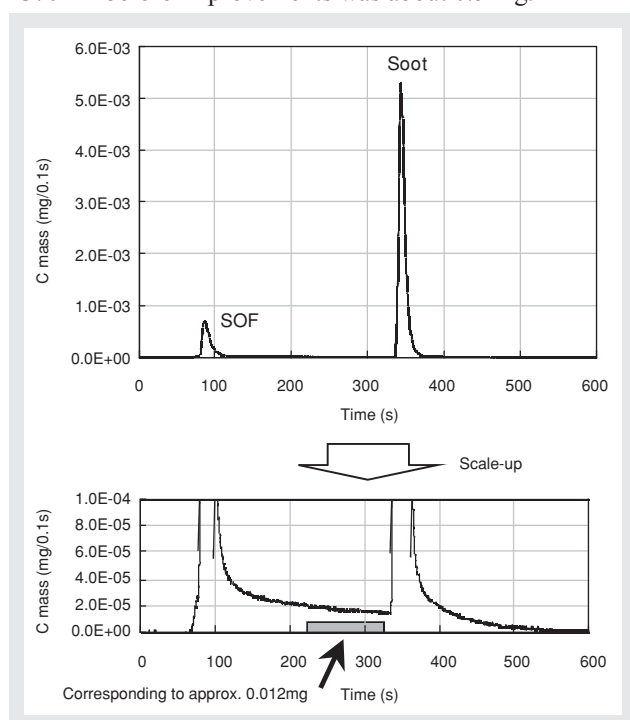


Figure 3 Typical CO_2 Signal of Previous MEXA-1370PM

Improvements

One of the causes of this SOF tail is residual oxygen mixed into the nitrogen carrier gas from several sources. Namely, there is high probability that "soot pre-reaction" occurred, where soot on the filter burned during SOF measurement due to the O_2 mixing into the carrier N_2 . So improvements were made to the following three factors related to O_2 mixing.

- Oxygen diffusion
- Ambient oxygen
- Remaining oxygen in the line

Oxygen Diffusion

In the measurement sequence, nitrogen carrier gas does not flow for the first 60 seconds in order to allow oxygen filling downstream of the furnace. The function of this oxygen is to oxidize the vaporized SOF completely. If this time period is too long, oxygen may diffuse and reach the sample. As described below, this issue has been improved by optimizing the oxygen diffusion time.

A carbon graphite sample was used to determine the appropriate time. The result is shown in Figure 4. In theory, SOF should not be detected from carbon graphite. However, following oxygen diffusion for 60 seconds about 60 μg of SOF is measured. By decreasing the oxygen diffusion time, the detected soot in SOF measuring sequence was reduced until finally no SOF peak was detected below 20 seconds. This suggests that the SOF amount in the figure is originally from soot pre-reaction. From this result, the diffusion time was reduced from 60 seconds to 20 seconds.

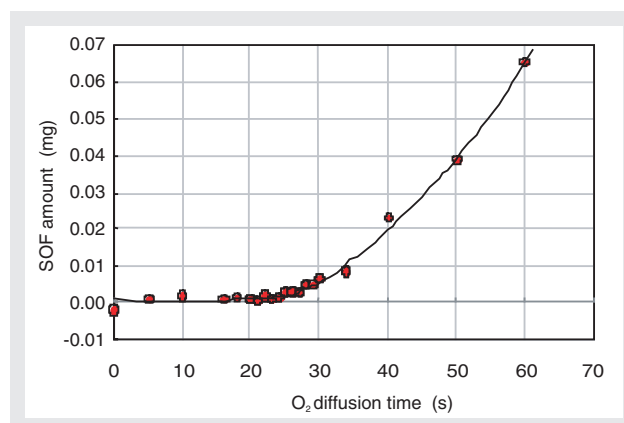


Figure 4 Effect of the Oxygen Diffusion Time

Ambient Oxygen

The cross section of the sample inlet passage is shown in Figure 5. The right side of the figure indicates the front of the equipment, and left side of this figure indicates the furnace. Figure 5 (a) is the shutter open condition and Figure 5 (b) is the closed condition. The shutter moves vertically for opening and closing. The black part in the figure is a cover for the furnace which is moved horizontally by compressed air in order to seal the furnace. There is a narrow space at the left side of the cover block which is not sealed well. Ambient air flows into this space, and when the shutter closes the cover pushes the ambient air into the furnace allowing the oxygen in this ambient air to react with SOF or soot.

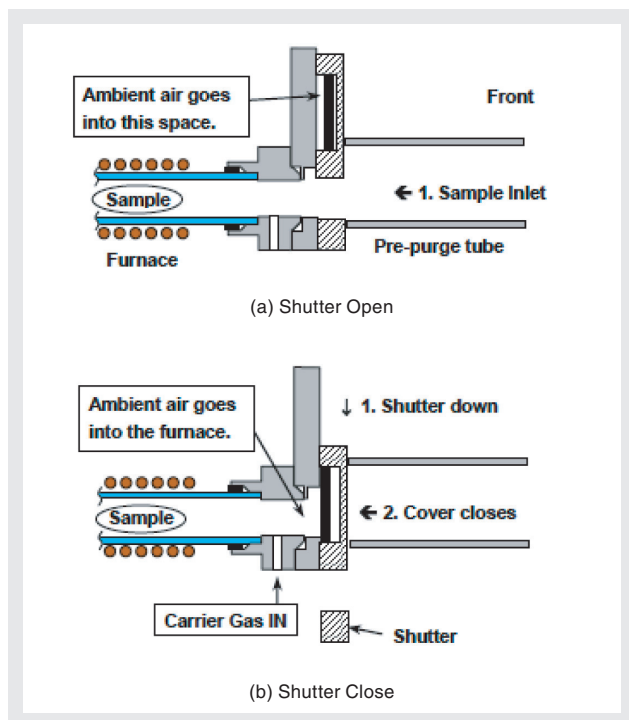


Figure 5 Structure of the Shutter (Cross Section)

Additional nitrogen purge (2 L/min) at the shutter is used to prevent ambient air entering the furnace. Using carbon graphite as a measurement sample, the result of this improvement is shown in Figure 6. Pre-reaction carbon graphite was increased as the shutter opening time increased in the case of no additional nitrogen purge. For example, the amount of pre-reaction carbon graphite is about 10.9 μg when the shutter opens for 5 minutes. However, in the case of additional nitrogen purge, the CO_2 signal remained at zero level and no carbon graphite was detected even when the shutter was opened for 5 minutes. In the actual measurement procedure, the shutter opening time is normally less than 1 minute, therefore the performance of this additional purge should be sufficient.

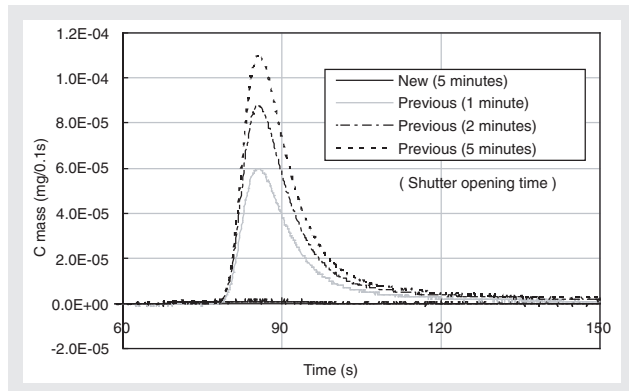


Figure 6 Improvement of Pre-reaction for Soot by Additional Shutter Purge (SOF Peak for Carbon Graphite Measurement)

Remaining Oxygen in the Line

The next improvement focused on the remaining oxygen in the carrier gas lines. The original flow schematic used a common line for both nitrogen and oxygen gases. For all measurements, nitrogen flows at the beginning, followed by oxygen flows for a few minutes through the same gas line, as shown in figure 2. Some oxygen may remain in the line and therefore be included in the nitrogen successive cycle. A small amount of soot will then oxidize with nitrogen flowing causing SOF tailing. To overcome this issue, independent lines have been adopted. Figure 7 shows two signals for a similar amount of standard PM (SRM1650) measurement with both the previous flow schematic and current flow schematic. It shows that the SOF tailing has significantly been improved.

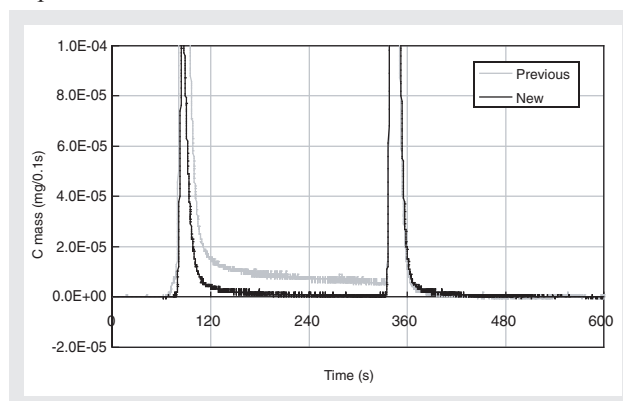


Figure 7 Reduction of SOF Tailing Level by Improvement of the Carrier Gas Line Conditions

Evaluation of the Improvement

PM Composition Analysis

Figure 8 shows the result of composition analysis with standard PM (SRM1650). Figure 8 (b) shows that with updated system. Figure 8 (a) shows the result with the device composition before improvements; large dispersion can be seen overall, and especially at or under 0.5 mg, the composition ratio of SOF and soot greatly veers towards SOF. This shows that if the sample quantity is small, the effects of soot pre-reaction become greater. On the other hand, the results of the updated system Figure 8 (b) shows that stable composition ratio is obtained up to 0.2 mg, signifying the improved SOF/soot separation performance.

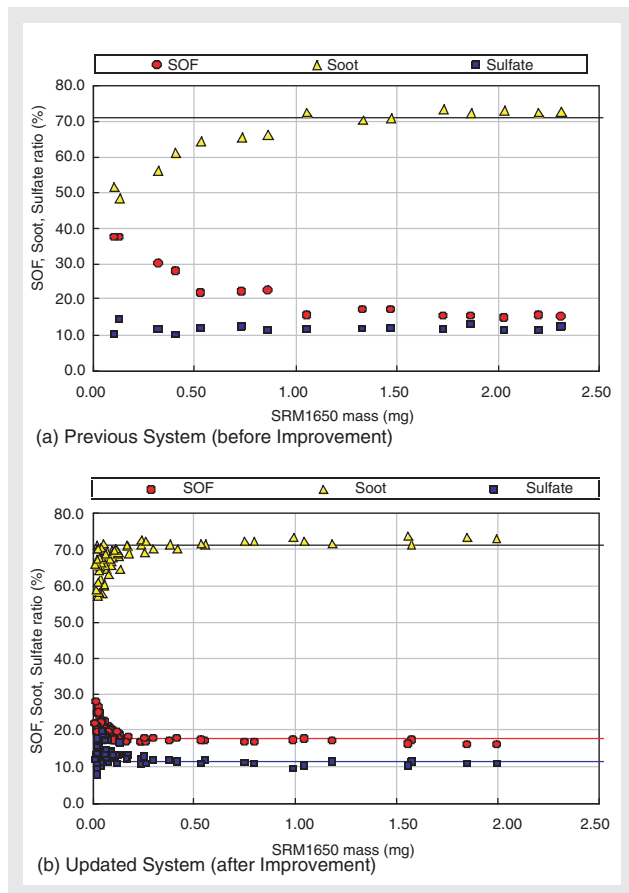


Figure 8 The Result of Standard PM (SPRM1650) Measurement

Correlation with Gravimetric Method

Figure 9 shows the correlation between gravimetric results and updated system results for all components. All horizontal axes are total mass of standard PM sample (SRM2975) weighed by a microbalance while the vertical axes represent the instrument result. Figure 9 (a) shows the correlation for total PM mass. There is good agreement between these two methods. For SOF soot and sulfate the agreements are also good as presented in Figure 9 (b), (c) and (d). The coefficients of determination (R^2) for these components are greater than 0.99.

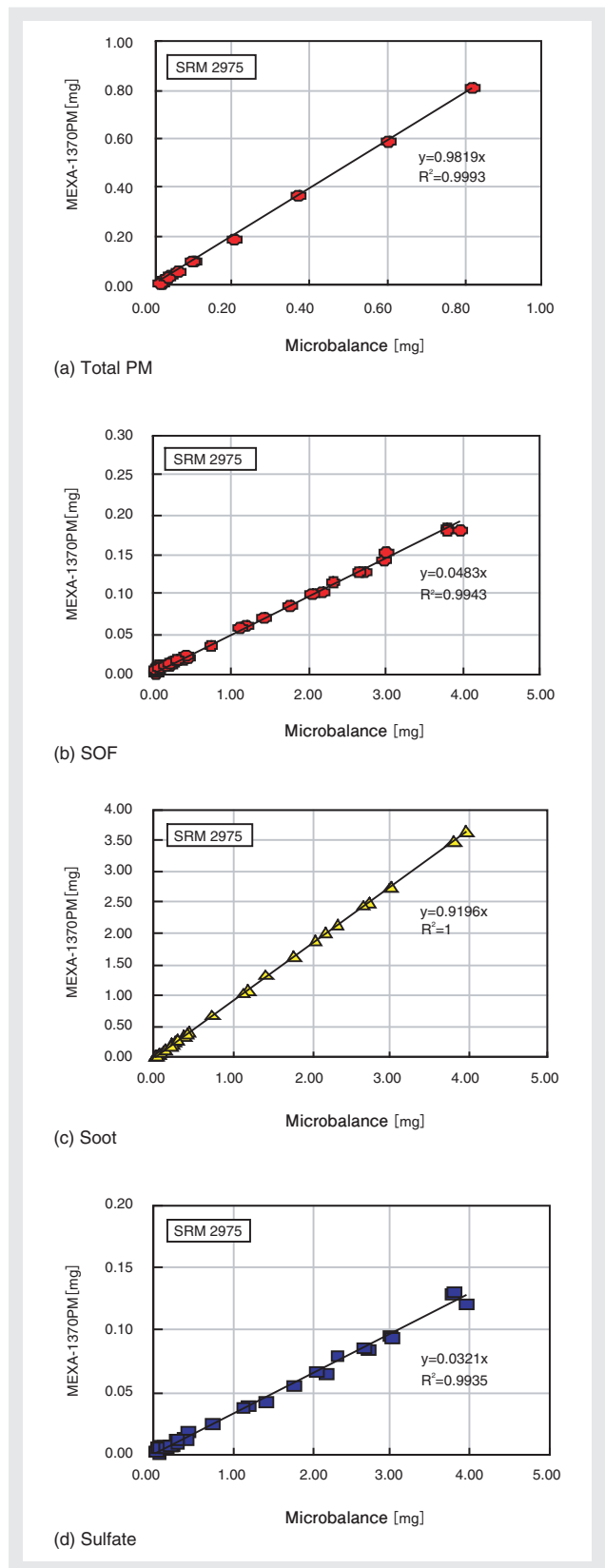


Figure 9 Microbalance and Combustion Method Comparison

Conclusion

This report introduced improvements made to prevent “soot pre-reaction,” the partial transformation of soot into CO₂ during SOF measurements, in order to increase the composition separation accuracy of the MEXA-1370PM. The improvements made were the following:

- Optimization of SOF diffusion time (shortened from 60 seconds to 20 seconds)
- Additional shutter purge function to avoid leakage of ambient air into the furnace
- Independent carrier gas lines for nitrogen and oxygen as a countermeasure for remaining oxygen in the line

By combination of the above countermeasures, the composition separation accuracy of PM was improved significantly up to 0.2 mg. With the recent improvements in both engines and after-treatment systems, the concentration of emitted PM decreases even further, by enabling low-concentration PM analysis, the MEXA-1370PM is expected to contribute to various efforts geared towards PM emission reduction.

References

- [1] S. H. Cadle, et.al., Automated carbon analyzer for particulate samples., Anal. Chem. 1980, 52 (13), 2001-2206.
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