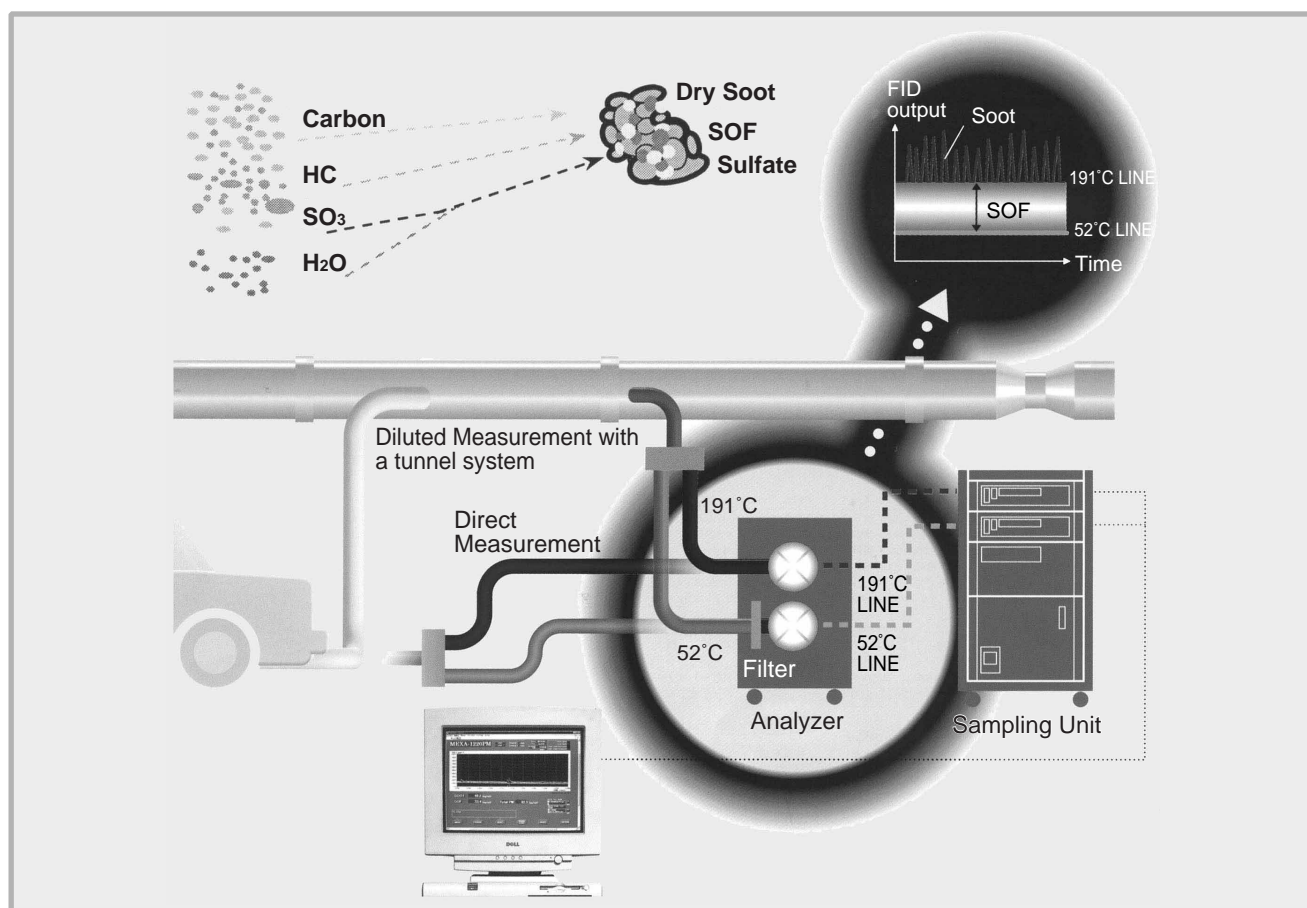


Advanced Function Analyzers: Real-time Measurement of Particulate Matter Using Flame Ionization Detectors

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Abstract

Particulate matter emitted from vehicles is regarded as one of the major problems affecting the environment and human health. The first step toward reducing particulate matter emissions is to determine which vehicle operating conditions cause the formation of particulate matter in exhaust gas. To achieve this, Horiba has developed an instrument that can perform continuous measurement of particulate matter. The instrument uses the flame ionization detection to continuously measure soot concentration. The soluble organic fraction can also be continuously measured by splitting a sample gas line into a low-temperature line and high-temperature line and then determining the difference in total hydrocarbon concentrations between the two lines.

This report discusses the measurement principle and the configuration of this instrument. Based on a large amount of data collected in engine tests, we have established that there is a good correlation between data produced by this method and data produced by conventional methods, and that continuous measurement is indeed possible.

1 Introduction

Demands for reducing the particulate matter (PM) emitted from diesel engines grow stronger and stricter with each passing year. As a result, methods to measure and characterize the instantaneous behavior of the PM emissions have become indispensable to diesel engine developers.

The standard PM measurement method is based on the requirements of current laws and regulations. The method calls for introducing the exhaust gas into a dilution tunnel, collecting the PM on a filter at a temperature of 52°C or less, and weighing the collected PM on a microbalance. Because this is a batch measurement method, it is very difficult to apply this method to the differential analysis of engine conditions related to the production of PM constituents, i.e. soot, the soluble organic fraction (SOF), and total PM (soot plus SOF).

Therefore, in order to continuously monitor the behavior of PM emissions, Horiba has developed the MEXA-1220PM real-time PM analyzer, which uses a flame ionization detector (FID) to perform separate measurements of soot and SOF, as well as total PM. In this report, we discuss the measurement principle of this instrument and the results of measurements made from engines.

2 Measurement Principle

2.1 The Flame Ionization Detector

The FID is commonly used as a high-sensitivity hydrocarbon detector. This detector uses the following measurement principle: a sample gas is discharged from a nozzle and introduced into the flame formed by mixed gas of hydrogen and air. The nozzle is given a fixed high-voltage electrical charge. In the high-temperature environment of the hydrogen flame (1500°K or higher), a portion of the hydrocarbon molecules in the sample gas are ionized and an ion current flows between the nozzle and collector¹⁾²⁾. By detecting and amplifying this ion current, it is possible to measure the concentration of the total hydrocarbons.

2.2 The Measurement of Soot in PM

Generally, when applying the FID to engine exhaust gas measurement, the sample gas flows through a filter, so only the gaseous components reach the FID. On the other hand, when diesel engine exhaust gas that contains PM is sent directly to the FID, without passing through a filter, we see that spike signals occur³⁾. We conducted the following test to verify that these spike signals are the result of carbon particles contained in the PM.

An overview of the experiment layout is shown in Fig.1 We purified powdery carbon (carbon black) in a vacuum at 700°C for 24 hours to obtain pure carbon particles that contained no hydrocarbons. The carbon black was then placed in a container, and the container was vibrated while feeding air into it to make the carbon black to flow directly to the FID. To observe high-speed FID response, the FID output was connected directly to an oscilloscope.

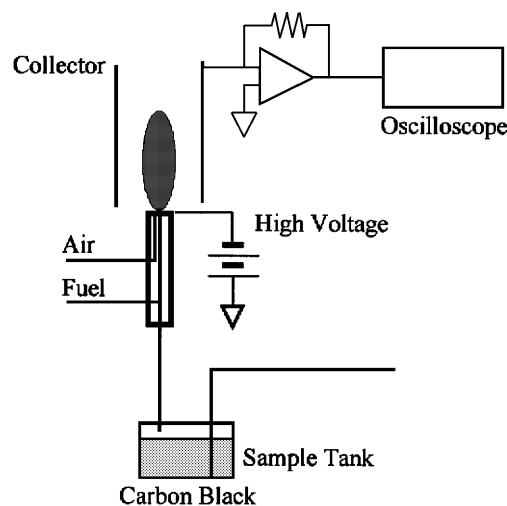


Fig.1 Schematic Diagram of Carbon Sample Introduction into an FID

Fig.2 shows an example of the FID output obtained from the test. In this example, four pulse signals can be observed. The first three pulse signals have the same half-value width, and this value is determined by the time constant of the FID. Because the half-value width is the same, we believe that these pulse signals all occurred when one carbon particle passed through the FID. The differences in the peak heights of the pulse signals are thought to be due to differences in carbon particle size. The fourth pulse signal, between the 6 millisecond and 8 millisecond marks, includes two or more peaks, which is thought to be due to overlapping signals from multiple particles.

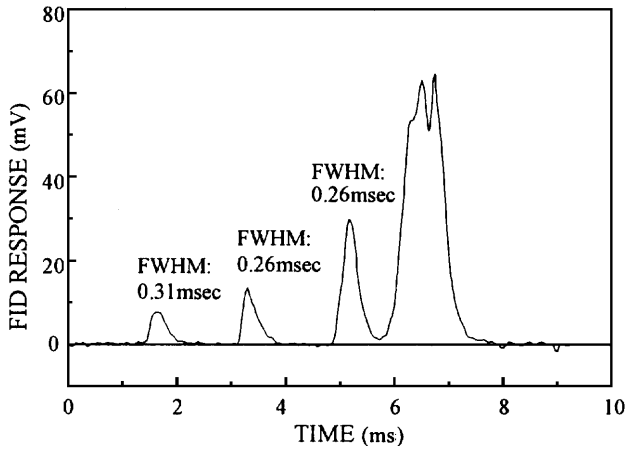


Fig.2 FID Response to Carbon Black

These results prove that the FID produces a pulse signal response to pure carbon particle. Accordingly, by directly feeding the PM emitted by a diesel engine into an FID and detecting only the generated pulse signal, it should be possible to continuously measure just the soot constituent of the PM.

2.3 Measurement of SOF in PM

Fig.3 shows the flow of the process used to obtain a signal from the SOF constituent of PM. Exhaust gas containing PM is split into two flow lines. The “direct” line is heated to 191°C and carries exhaust gas containing PM directly into the FID⁴. The “filtered” line is heated to 52°C and, by removing other PM constituents using a filter, carries only the gaseous components of the exhaust into the FID³.

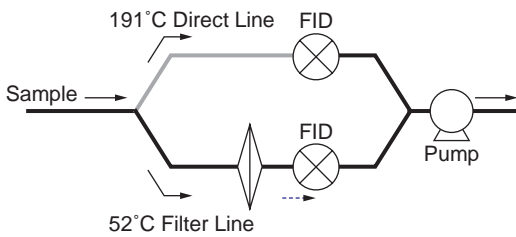


Fig.3 Gas Flow Used in SOF Measurement

Fig.4 shows the signal obtained from two FIDs when exhaust gas from a diesel engine is measured using the flow shown in Fig.3. For the direct line, the FID output caused by the hydrocarbons that have vaporized at 191°C is taken as the base, and then the pulse signal from the soot is added to this base signal. The FID output for the filtered line shows the gaseous hydrocarbons that vaporized at 52°C. Accordingly, the difference between the base signal of the direct (191°C) line and the signal of the filtered (52°C) line indicates the concentration of the

hydrocarbons that were converted from liquids to gases at a temperature range between 52°C and 191°C.

In other words, by calculating the difference in base signals output from the FIDs for the direct line and filtered line, it should be possible to continuously measure only the SOF constituent of the PM.

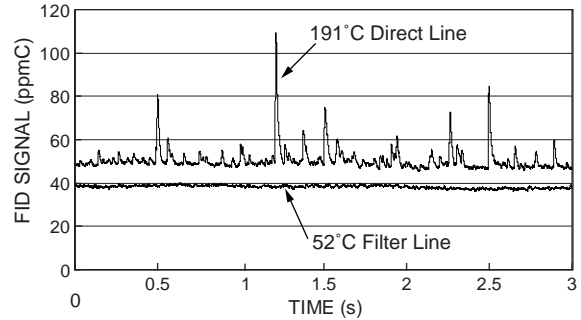


Fig.4 FID Signals From the 191°C Direct Line and the 52°C Filtered Line

3 Real-time PM Analyzer System

3.1 System Configuration

Fig.5 shows a configuration diagram of a real-time PM measurement system that includes a dilution tunnel. The PM analyzer consists of heated sampling tubes, an analyzer unit with two FIDs, a sampling unit, and a personal computer as a control/operation unit.

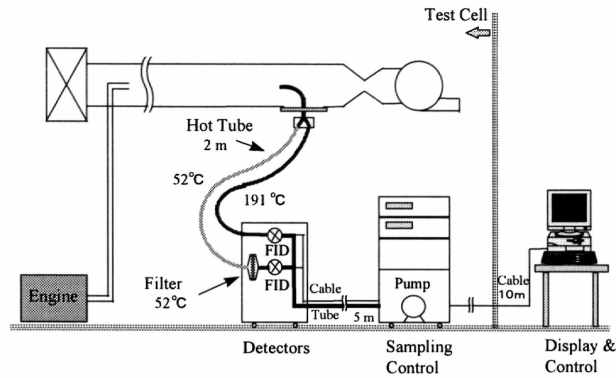


Fig.5 System Block Diagram for PM Measurement

The exhaust gas containing PM, collected by the sampling probe, is split into two flows and fed to two heated tubes, one heated to 191°C and one to 52°C. The 191°C line feeds the exhaust gas directly to the FID. At the 52°C line, the exhaust gas containing PM is passed through a filter heated to 52°C. The PM is filtered out of the flow and only the gaseous components are fed to the FID. In order to prevent the PM from being trapped in the sampling line, the pipings from the sampling point to the FID has been designed to be completely smooth with no level variations, and the pump is installed at the downstream of the FID. Analog outputs from two FIDs are fed to a computer, and the soot, SOF, and total PM are calculated and output every 0.5 seconds. Table 1 shows the outline of the specifications for the MEXA-1220PM real-time PM analyzer.

Model	MEXA-1220PM
Components	Soot, SOF and total PM (soot +SOF)
Principle	Flame ionization detection (FID)
Sample flow rate	7 L/min
Range of FID	0-100/200/500/1000 ppmC as THC output
Response of FID	Less than 1.0 s for C3H8 standard gas
Power supply	100 V AC, 50/60Hz as standard
Dimensions	Analyzer unit : 400(W)×593(D) ×800(H) mm Sampling unit : 570(W)×710(D)×1000(H) mm Control unit : 410(W)×450(D)×520(H) mm

Table 1 Specifications for the MEXA-1220PM

3.2 Mathematical Processing

Analog signals from the two FIDs are fed to the computer at a sampling frequency of 5 kHz, and the following mathematical processing is performed every 0.5 seconds.

The signal from the 191°C line contains pulse signals with information about soot concentration, so it is necessary to extract just that signal. However, a small pulse signal may be buried in noise, making it undetectable. To avoid this problem, the computer performs filter processing. The filtered signal is split into two – the pulse section that contains information about the soot concentration, and the base section that indicates the concentration of the gaseous hydrocarbons. Next, the difference in the 191°C line base signal and the 52°C base signal is calculated, yielding SOF concentration information.

Here, both soot concentration calculated from pulse signal and SOF concentration calculated from difference between the two FIDs base signals are expressed in units of parts per million carbon (ppmC). To convert these values into mass concentration units, the control/operation unit has conversion coefficients for soot and SOF so the final data can be expressed in units of mass concentration (mg/m³) and output. The measured concentrations of the soot, SOF, and total PM can also be saved as digital data.

4 Engine Measurement Results

4.1 Correlation with the Filter Weighing Method

The following test was conducted to verify that there is a sufficient correlation between the soot and SOF values measured with this instrument and the results of measurements made based on current regulations using a dilution tunnel and the filter weighing method.

A diesel engine was connected to a dynamometer and operated under a constant load and at a constant revolution. The exhaust gas, generated during steady-state operation, is fed into the tunnel and the PM in the gas is collected on a filter at a temperature of 52°C or lower. At the same time, samples are fed to the MEXA-1220PM from almost the same sampling point and measurements are carried out.

Fig.6 shows the correlation of these two methods for soot and SOF. The plotted points in the figure indicate the following correlations under the steady-state operation of representative stages in the Japanese diesel 13-stage test cycle:

- Correlation between soot mass concentration (mg/m³) obtained by the filter weighing method and the soot concentration (ppmC) calculated from pulse signal by the MEXA-1220PM
- Correlation between SOF mass concentration (mg/m³) obtained by the filter weighing method and the SOF concentration (ppmC) calculated from base signal differential of the two FIDs used in the MEXA-1220PM

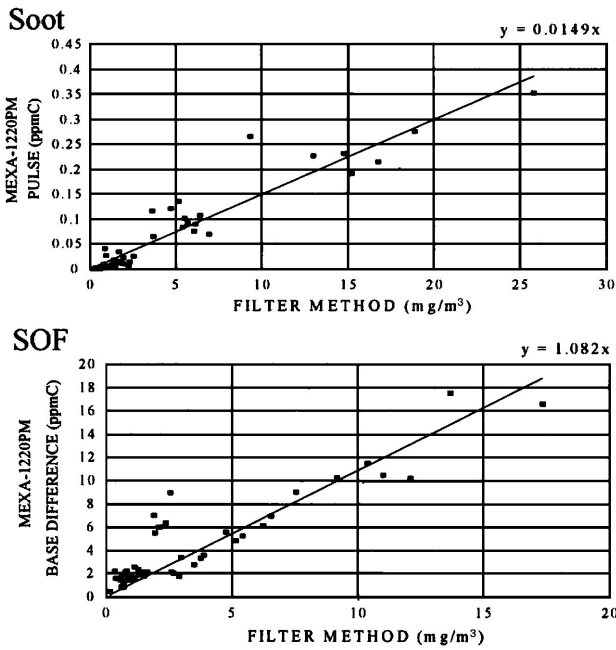


Fig.6 Correlation of the Filter Method and the FID Method

These test results indicate a comparatively strong correlation for both soot and SOF. This verifies that soot mass concentration can be obtained by detecting the pulse signal of the 191°C line FID, and that SOF mass concentration can be obtained by calculating the difference between the base signals of the two FIDs.

At present, there are no standard samples for measuring soot and SOF, so a large amount of data was collected for the filter weighing method and from this instrument, using diesel engines. From this data we were able to determine the conversion coefficient for converting from ppmC to mg/m³, making it possible to calculate the mass concentrations of soot and SOF.

Fig.7 shows a comparison of the total PM mass concentration (mg/m³) obtained from the filter weighing method with representative stages of the Japan diesel 13-stage test cycle, and total PM mass concentration (mg/m³) measured with this instrument.

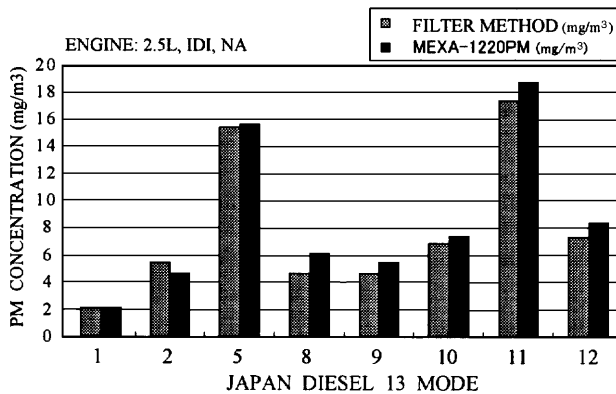


Fig.7 Total PM Concentration Using the Japan 13-stage Test Cycle

The soot and SOF mass concentrations needed to calculate the total PM mass concentration are determined using the conversion coefficients obtained by applying the least squares method to the points plotted in Fig.6. With this method, it is possible for this instrument to achieve mass concentration results that are close to the results of the filter weighing method, even for total PM concentration.

4.2 Continuous Measurements

In order to verify that this instrument can measure fluctuations in PM emissions behavior that occur with fluctuations in engine conditions, a diesel vehicle was operated on a chassis dynamometer and the exhaust gas sampled from the tailpipe. Fig.8 shows the measurement results. In this figure, we can see how soot and SOF behaviors fluctuate with the operating conditions of the vehicle. The results of this test verify that, with this type of instrument, it is possible to analyze the fluctuations in soot and SOF behavior that accompany fluctuations in engine conditions, and that such instruments are effective tools for application to engine developments aimed at reducing PM.

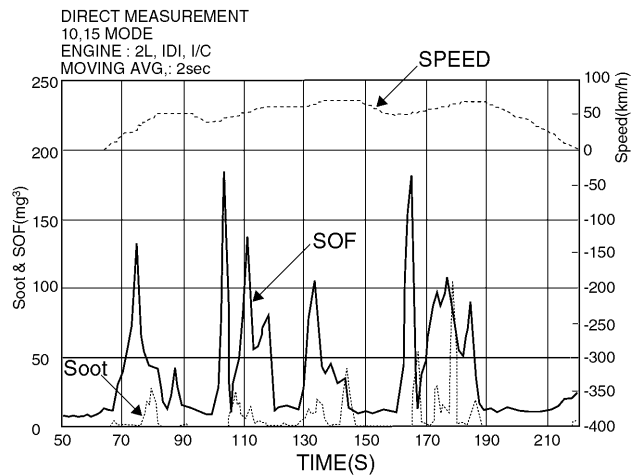


Fig.8 Example of Continuous Measurement Results (Soot & SOF)

5 Conclusion

This report has provided an introduction to the MEXA-1220PM real-time PM analyzer, which uses FIDs. The primary advantage offered by this instrument is that it makes it possible to continuously measure soot, SOF and total PM during fluctuations in engine operating conditions, measurements that were heretofore impossible to obtain. Another way to put this would be to say that, by performing continuous measurements with this instrument, it is possible to easily obtain data needed to reduce PM emissions.

Horiba anticipates that the MEXA-1220PM will serve as an effective tool in efforts to resolve some of the serious environmental problems that confront society, and that it will contribute to the reduction of PM.

Furthermore, although conventional PM measurement methods have focused only on the measurement of mass, much research is now being done on the relationship of PM particle size to harmful effects on the human body. As a manufacturer of analytical and measurement systems, HORIBA shall continue to work to help resolve the world's environmental problems.

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