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Feature Article

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Development of Analyzers for Hazardous Air Pollution Components in Vehicle Emission Gases

Yutaka Yamagishi

Abstract

Acetaldehyde, benzene, benzo(a)pyrene, formaldehyde, 1,3-butadiene and other hazardous air pollution (HAP) components in exhaust gases from vehicles have lately attracted considerable attention. To date, batch measurement using gas chromatography, mass spectrometry, or other methods have generally been used for analysis of these substances. However, real-time analysis of such components is now much in demand for engine-system development, a task for which general-purpose analytical instruments are not well suited. Horiba has overcome many of the drawbacks of these instruments for use in continuous measurement, and has succeeded in developing the MEXA-4000FT FTIR motor exhaust analyzer, and the MEXA-4000MS soft-ionization motor exhaust mass spectrometer. These two products offer improved design and a wide range of enhancements to the sampling system and analyzer, as well as better data processing in the control system, thus enabling the measurement of rapid changes of gas concentrations in samples.

1. Introduction

Regulated exhaust components in vehicle emissions include carbon monoxide (CO), nitrogen oxides (NOx), total hydrocarbons (THC), and other substances. In addition to these, the Environment Agency in Japan has also cited other substances as HAP components, including acetaldehyde, benzene, benzo(a)pyrene, formaldehyde, and 1,3-butadiene. In the United States, the Clean Air Act lists not only these substances, but a total of 189.

Horiba was the first to provide analyzers to measure CO, nitrogen dioxide (CO_2), NOx, and THC in exhaust gases from vehicles, using non-dispersive infrared analysis (NDIR), chemiluminescence detection (CLD), and flame ionization detection (FID). These products were developed as part of Horiba's efforts to contribute to the public interest. These gas analyzers all offer rapid response, and are especially suitable for real-time exhaust emission measurement. However, where the concentrations of HAP components in vehicle emissions are very low, the sensitivities of conventional analyzers are insufficient for precise measurements. The HAP components present in trace quantities have conventionally been measured by general-purpose analytical methods, such as Fourier transform infrared spectrometry (FTIR), mass spectrometry (MS), and gas chromatography. The effort to reduce these components in emissions requires accurate measurement of which HAPs are generated under a variety of conditions. Analyzers for engine emissions must be able to respond to the rapid changes in concentrations during engine test modes, in catalytic temperature when the engine starts up, and other conditions. Because general-purpose analytical instruments are designed to be used offline at a laboratory after samples have been collected using a separate device, they are not suitable for following and measuring rapid changes in exhaust gas concentrations. Horiba has developed the MEXA-4000FT FTIR motor exhaust analyzer and the MEXA-4000MS soft-ionization motor exhaust analyzer to make possible the measurement of these changes in exhaust gas concentrations. In the development of these products, HORIBA adapted the general-purpose analytical instrument for vehicle emission analysis by improving the response speed, adding a wide range of new enhancements and designs to the sampling system, and improving data processing in the control system.

2. FTIR Motor Exhaust Analyzer

The Horiba MEXA-4000FT FTIR motor exhaust analyzer is capable of simultaneous and continuous measurement of various components in engine exhaust gas, including formaldehyde, acetaldehyde, 1,3-butadiene and other HAP components, as well as low boiling point hydrocarbons, sulfur dioxide (SO_2) and ammonia (NH_3). The measurement components, minimum detection limits, and measurement ranges are listed in **Table 1**. In addition, the MEXA-4000FT is capable of assessing catalytic performance by measuring nitrogen compounds such as nitrogen oxide (NO),nitrogen (N_2O), nitrogen dioxide (NO_2) and NH_3.

2.1 Principles of the FTIR Motor Exhaust Analyzer

FTIR is an infrared absorption analysis technique for measuring the gas components of a sample. This technique is based on the fact that each gas molecule absorbs an intrinsic infrared wavelength according to its molecular structure. Inorganic gases such as CO, CO_2 and NH_3, and organic gases such as many types of hydrocarbons and oxygenated hydrocarbons each absorb different wavelength regions because of their different molecule structures.

Since FTIR allows the entire infrared wavelength region to be measured simultaneously, the measured infrared spectrum of the sample gas can be immediately processed by a

Table 1 Measurement Components, MDLs, and theMeasurement Ranges

Component	MDL	Ranges
CO	2ppm	0-200, 1000, 5000ppm, 2, 10%
CO_2	100ppm	0-1, 5, 20%
NO	4ppm	0-200, 1000, 5000ppm
NO_2	2ppm	0-200ppm
N_2O	1ppm	0-200ppm
H_2O	0.12%	0-24%
NH_3	2.5ppm	0-500ppm
SO_2	3ppm	0-200ppm
HCHO	2.5ppm	0-500ppm
CH_3CHO	6ppm	0-200ppm
CH_3OH	2.5ppm	0-500, 2000ppm
CH_3COCH_3	2.5ppm	0-100ppm
$(CH_3)_3COCH_3$	1ppm	0-200ppm
HCOOH	0.5ppm	0-100ppm
CH_4	5ppm	0-500ppm
C_2H_4	2.5ppm	0-500ppm
C_2H_6	4ppm	0-200ppm
C_3H_6	3ppm	0-200ppm
1,3-C_4H_6	2ppm	0-200ppm
iso-C_4H_8	2ppm	0-200ppm
C_6H_6	10ppm	0-500ppm
C_7H_8	10ppm	0-500ppm

computer to yield the speciation of the components and concentrations of the sample gas. The optics used in the MEXA-4000FT are shown in **Figure 1**. The infrared light is emitted from the light source and collimated by the parabolic mirror; it then enters into the interferometer via the aperture. The interferometer scans the mirror every second to generate the interfered light and introduces it to the multi-path reflection gas cell. The gas molecules in the cell then absorb the intrinsic wavelength region of interfered light corresponding to the concentration of gases. This interfered light is then collimated again and enters into the detector. The analog signal of the detector is converted to a digital signal and passed through the fast Fourier transform (FFT) process to obtain the infrared absorption spectrum. A multivariate analysis method is applied to determine the concentrations of the components. The processing procedure is repeated by the computer at one second intervals for continuous measurement.

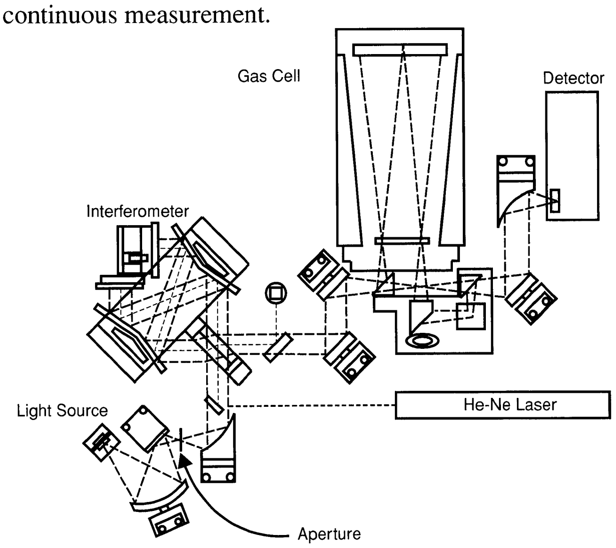

Figure 1 The Optics used in the MEXA-4000FT

2.2Measurement Test of Gasoline Vehicle Emissions

Figure 2 shows the results of a measurement test using the FTIR motor exhaust analyzer, specifically the emission pattern for N_2O and NH_3 in gasoline vehicle exhaust gas, and the velocity pattern showing the running state of the vehicle. This figure shows that N_2O emissions are present from about 50 seconds to 200 seconds after the engine is started, and NH_3 emissions start from about 200 seconds. On the other hand, since no NH_3 is present in the exhaust gas before it passes through the catalyst, NH_3 is likely generated through the catalytic reaction. These results demonstrate how FTIR can be used to analyze the behavior of the catalyst by real-time measurement of the gas components, something that previous analysis techniques

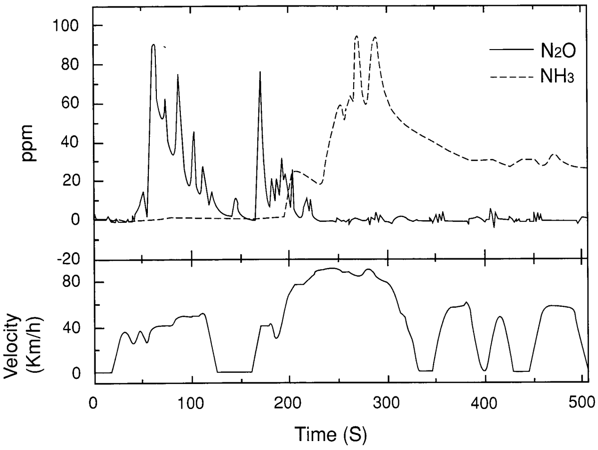

Figure 2 The Emission Pattern for N_2O and NH_3 in Gasolin Vehicle Exhaust Gas

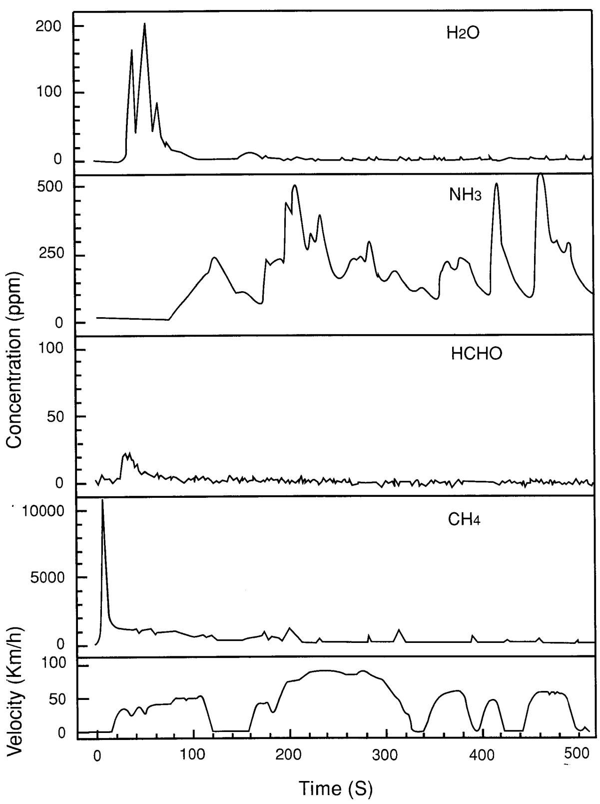

Figure 3 The Emission Pattern for N_2O,NH_3,HCHO, and CH_4 From CNG Vehicle

have been unable to do. This allows the transitions of oxidation and deoxidation reactions in the catalytic heating process to be observed.Tests were also conducted using exhaust gas from a compressed natural gas (CNG).
Figure 3 gives the measurement results for N_2O, NH_3, formaldehyde (HCHO), and methane (CH_4). Except for CH_4, real-time measurement of these components is difficult to perform using conventional analysis techniques. The FTIR motor exhaust analyzer, on the other hand, uses a single gas cell and is able to continuously measure HAP components at the same response time as CO, CO_2, and other such components, as described above.

3. Soft-Ionization Vehicle Emission Mass Spectrometer

While the FTIR motor exhaust analyzer is capable of continuous measurement of moderate amounts of such components as benzene, toluene, and 1,3-butadiene, problems of sensitivity and cross sensitivity when measuring ultra-low-concentration heavy hydrocarbons, such as HAP components, demand a device with ultra high sensitivity and faster response. To meet these requirements, Horiba has taken the mass spectrometry method and developed the MEXA-4000MS soft ionization vehicle emission mass spectrometer.

3.1 Principles of the Mass Spectrometer

Mass spectrometry is a technique for analyzing gas components of a target mass through ionization of gas molecules in a vacuum, and selecting ions based on the mass to electric charge ratio (specific charge: m/q).

The MEXA-4000MS **(Figure 4)** uses soft ionization for ionizing the gas molecules, and a quadrupole for ion selection. Molecules in the sample gas are introduced to the analyzer by the sampling unit and ionized, then pass through the quadrupole to which an electric current is applied. Through the use of radio frequency (RF) and by sweeping the applied voltage in the quadrupole, the passing ions can be selected at high speed. The MEXA-4000MS incorporates

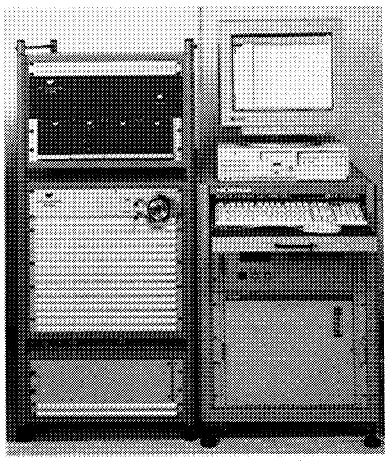

Figure 4 The Exhaust Gas Analyzer Using Mass Spectrometer MEXA-4000FT

a high sensitivity detector and can scan at high speed mass numbers of the gas molecule ions in 0.1 of a second, thereby allowing continuous measurement even of ultra low concentration components on a scale of parts-per-billion (ppb).
In the "soft" ionization method used in the MEXA-4000MS, a thermoelectron discharged from a filament collides with either xenon (Xe), krypton (Kr), or mercury (HG) gas molecule to generate a primary ion. This primary ion then reacts with the sample gas and transfers its charge to the sample gas molecule. In contrast to electron impact (EI) ionization where the sample gas directly reacts with electrons, in soft ionization, the ionization energy of the sample molecule is small due to the reaction with the primary ion, and is limited by the species of the primary ions. As a result, the species of fragment ions generated when the bonds of the gas molecules are broken can be limited by the species of primary gas ions used. It is this characteristic of the soft-ionization method that reduces the influence of cross sensitivity in the MEXA-4000MS. **Figure 5** shows the schematic setup of the instrument.

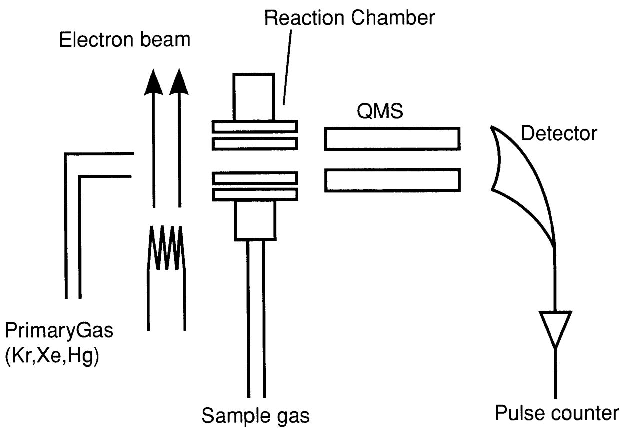

Figure 5 The Principle of the Soft-ionization Mass Spectrometer

3. 2 Features of Exhaust Gas Measurements Using a Mass Spectrometer

Mass spectrometry is an analytical technique with which all gas molecules, both organic or inorganic, led to the analyzer can be detected. Moreover, unlike other analytical methods, mass spectrometry is not affected by the chemical properties of the gases to be measured. For example, the NDIR and FTIR methods, both of which use infrared analysis techniques, do not have sensitivity to hydrogen (H_2), oxygen (O_2), or their diatomic gases and monatomic noble gases. Also, FID has sensitivity to hydrocarbons, while CLD has sensitivity to nitric oxide.

Although mass spectrometry can analyze all components, molecular ions and atoms having the same mass number cannot be discriminated and measured. For example, nitrogen (N_2) and CO both have a mass number of 28, and CO_2 and N_2O share a mass number of 44. These molecules cannot be distinguished one from the other. However, in some cases, even when the molecule ions have the same mass number, the molecules themselves can be distinguished because the mass numbers and quantity of the fragment ions generated are different. For example, n-butane and iso-butane are isomers both having the same molecular formula, C_4H_{10}, and mass number, 58. But among the four species of fragment ions produced by n-butane, $C_3H_7^+$ (mass number 43) is the most common, while $C_4H_9^+$ (mass number 57) is the most common of the three species of fragment ions produced by iso-butane. Horiba's MEXA-4000MS also includes a special mass soft-ionization spectrum library so that the user of the MEXA-4000MS can perform the measurements under the most suitable conditions, including the mass numbers to be used according to the objectives of the analysis.

3. 3 Measurement of HAP Components Using the MEXA- 4000MS

Figure 6 shows measurements for the standard-concentration gases of benzene, toluene, xylene, and 1,3-butadien on a scale of parts-per-billion, while measurements from actual emissions from a vehicle are given in **Figure 7**. In this latter test, the exhaust gas from a gasoline vehicle in LA-4 cold transient test mode was sampled from the end of the tail pipe using a dry sampling unit. Since both the engine and the catalyst were cold when the engine was started, for roughly 200 seconds until the catalyst warmed up, BTX and 1,3-butadiene were emitted in large amounts. This demonstrates how the MEXA-4000MS can be used for the analysis of ultra low concentration HAP components for which continuous measurements were previously very difficult. In addition, this instrument is expected to be applied soon to many other HAP components contained in vehicle emission gas, such as SO_2.

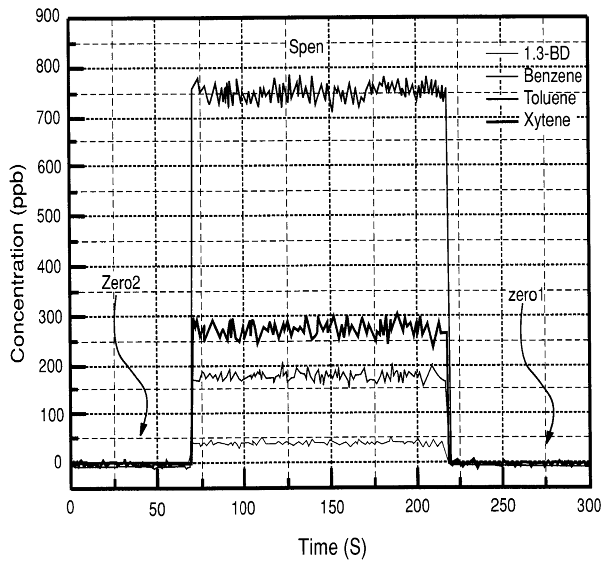

Figure 6 The Measurements Result for the Standard-Concentration Gases of Benzene, Toluene, Xylene, and 1,3-butadien Using the MEXA-4000MS

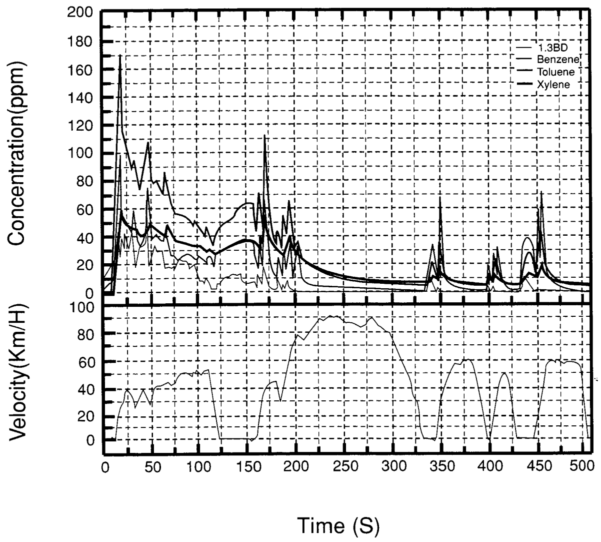

Figure 7 The Measurements Result for BTX and 1,3-buten from a Vehicles

Conclusion

Besides the FTIR and mass spectrometry real-time vehicle emission analyzer introduced in this paper, Horiba has also developed the MEXA-3000GC high-speed GC exhaust gas analyzer, capable of producing a chromatogram in 10 minutes. By combining these methods, the measurement of many HAP components, to date difficult to perform, may soon be realized. However, vehicle emission gas analysis is not simply the measurement of HAP components. Data analysis, engine research, fuel analysis, catalyst performance assessment, and the providing of other information required by the analyzer are also an essential part. In the years to come, Horiba hopes to contribute to the preservation of the global environment through the development of easy-to-use vehicle emission analyzers with the superior performance to meet these requirements.

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