Measurement of Vehicle Emissions with Fourier Transform Infrared (FTIR) Method

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ABSTRACT

A new concept for measuring automotive emissions using FTIR is discussed. This technique is especially notified for the measurements on alternative fuel vehicle. Principle of the technique, measuring conditions, some technical challenges, and results from a methanol engine are presented in this paper.

Correlations between some existing methods show good results and future potential for this technique.

1. INTRODUCTION

Development of alternative fueled vehicle is needed to be accomplished urgently because of the needs for protecting the earth's environment. Especially, methanol fueled vehicle has been investigated from many aspects. [1] The methanol fueled vehicle is reported to have (1) low emission rate of gaseous pollutants such as CO, CO_2, and NOx compared to gasoline fueled vehicle, and (2) extremely low formation rate of particulates compared to Diesel engine vehicle. However, it is also reported that the methanol fueled vehicle has unregulated pollutants such as formaldehyde (HCHO) and unburned methanol (CH3OH). Needless to say, those pollutants are harmful in the atmosphere.

Those new pollutants have been mostly measured with gas chromatography, and the method lacks a capability of time series measurement. Recently much attention have been focused on the measurement with Fourier transform infrared spectroscopy (FTIR) because of the method's capability of continuous data acquisition and multi-component gas analysis. [2]-[8] Formaldehyde, unburned methanol, and existing regulated pollutants can be measured continuously and simultaneously with the FTIR utilizing those capability.

An automotive emission analyzing system using FTIR is consist of emission gas sampling system, FTIR spectrophotometer, and data processing system. Since the system is based on new concept, those components still have many problems that have to be solved soon. Basic parameters that affect the measurement and have to be optimized are (1) optical path length of gas cell, (2) sampling flow rate, (3) temperature of the gas, and (4) pressure of the gas. Furthermore, it is important to look at data correlation with existing conventional method. If good correlations are obtained, the system is considered as an advanced way of measuring emission pollutants.

Discussion of the basic measurement conditions and some correlations with the conventional method are shown in this study.

2. SYSTEM

2.1 Principle

FTIR first acquires an interferogram using the Michelson interferometer as shown in Fig.1. Then the interferogram is converted to infrared absorption spectrum (Fig.2.) by means of Fast Fourier Transform (FFT) and a few other simple calculations.

Multicomponent quantitative measurement can be done because the technique is based on dispersive idea, in other words, entire mid-IR absorption spectrum can be obtained and also each individual absorption shape of the gas of interest can be seen. Lambert-Beer's law will then be applied to this individual shape and gas concentration can be calculated. Even if those gas absorption spectra are overlapped each other, such as HCHO and other hydrocarbons or NO and water, deconvolution of those shapes can be done through mathematical operations based on linear algebra. The higher the resolution, the easier the deconvolution. The reason is that, in high resolution absorption spectrum, one can very easily find differences between the shapes and linear independency in the calculation will be increased. At least 0.25cm-1 or higher resolution seems to be needed for the system.

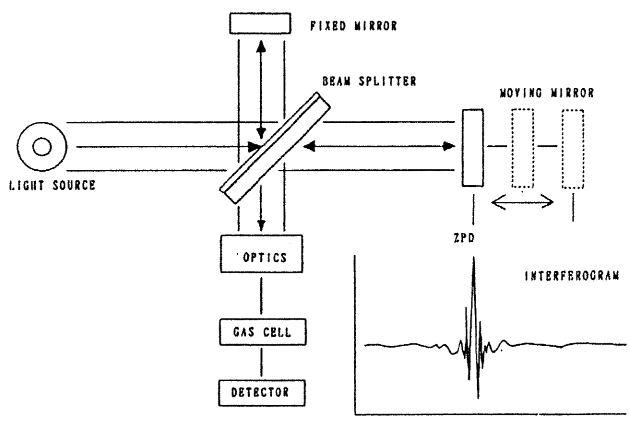

Fig.1 Interferometer and interfergram.

However, some of the gas species such as CO, or in the case of very bad spectrum resolution, Lambert-Beer's law can not totally describe the light absorption. Special mathematical treatments have to be applied for those non-linear cases.

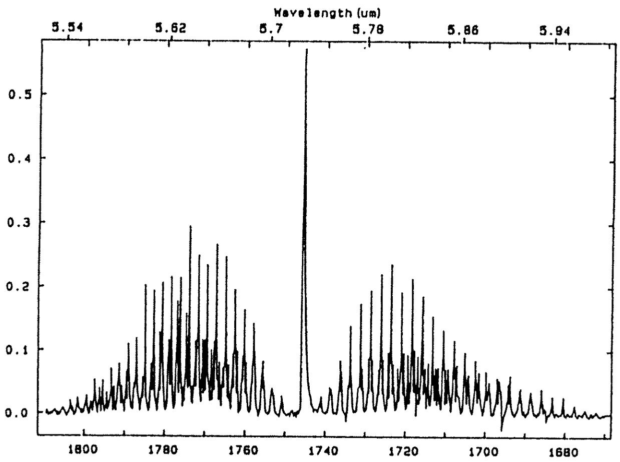

Fig.2 An example of absorption spectrum. (HCHO 0.25cm-1 resolution)

2.2 System Components

Important items in the system are as follows.

(1) How many gas species can be measured simultaneously
(2) Concentration range of each gas
(3) Minimum detectable limit of each gas
(4) Interference
(5) Reproducibility
(6) Drift
(7) Response time
(8) Reliability
(9) Minimum sampling rate

These items are depend on the system's components such as
(1) sampling system,
(2) interferometer and it's controlling electronics,
(3) gas cell,
(4) optics including light source and detector, and
(5) data processing computer system.

Simple explanations of these components and requirements are listed below.

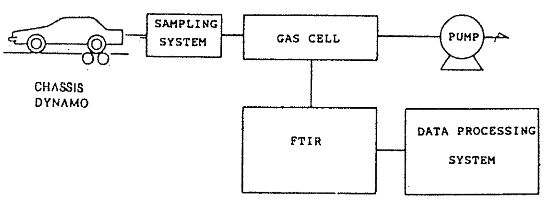

Fig.3 Schematic of the system.

Emission Sampling System

Automotive emission must be introduced into the gas cell without any stoichiometric change such as degeneration and absorption. Since the emission from the methanol fueled vehicle has much more water vapor than gasoline fueled vehicle, it is required to protect the emission from those changes.

Especially, since formaldehyde and methanol have high solubility to water, much more care have to be made in the sampling system. Air dilution in order to avoid vapor saturation and heating samping lines are examples of the sample protection.

FTIR Interferometer

Performance of the interferometer is the most important item in the system. High resolution is needed for the later calculation of multi-component analysis and for the accuracy.

In order to get stable and high resolution spectra, action of the moving mirror has to be very precisely controlled.

Gas Cell

Light absorption due to the emission gas occurrs in the gas cell.

Temperature of gas cell should be maintained at least over room temerature to avoid the condensation of water vapor. Optical path length is also a critical parameter for the cell, and very long path (over 20meter) is needed for the measurement of low concentration gas. Volume of the cell should be as small as possible in order to make response time shorter.

Optics

High energy wide band light source is needed for the system because the gas cell always has a very low through put due to it's multi refrection configuration.

High S/N and fast response is required for the detector. Using Mercury Cadmium Tellride detector at liquid nitrogen temperature is very popular way for this purpose.

Data Processing

FTIR method require a computer system to process the Fast Fourier Transform (FFT), and to calculate gas concentrations with the qualitative analysis algorithm. Performance of array-processor has been improved by recent digital signal processing technique. But load of the cpu is still large and high speed data processing is required to achieve real time emission gas analysis.

Several multi-component qualitative analysis algorithm have been presented elsewhere. PLS (Partial Least Square) method [9], spectral mask method [3], least squares method including P-matrix or K-Matrix method are the well known techniques. Less than 1 second computing time is required for practical system. Although in general, these methods need matrix calculations, and require long computing time.

3. RESULTS

In order to evaluate the potential of this method, linearity, influence of gas cell pressure, the correlation with the existing method and time response have been investigated using Mattson Instruments Co. FTIR emission analyzer and methanol fueled vehicle (passenger car, M85).

3.1 Linearity

Linearity of formaldehyde concentration is shown in Fig.4. Formaldehyde from a standard gas generator using trioxane, was diluted with air to provide appropriate concentrations. This gas was introduced into the gas cell of FTIR, and was measured its concentration.

Result of this test shows that the linearity of formaldehyde analysis is good. The fluctuation of data is about 6ppm at 0-125ppm range.

3.2 Influence of Cell Pressure

Figure 5. shows a influence of the pressure in the gas cell using CO2 gas at room temperature. Indicated values show that the influence of gas pressure is also linear from 100mbar to 1000mbar range. But, this result means that the pressure of gas cell must be controlled to maintain a constant pressure to avoid the fluctuation of output.

Large flow rate is required to get fast response and presice pressure control is required to get high reliability.

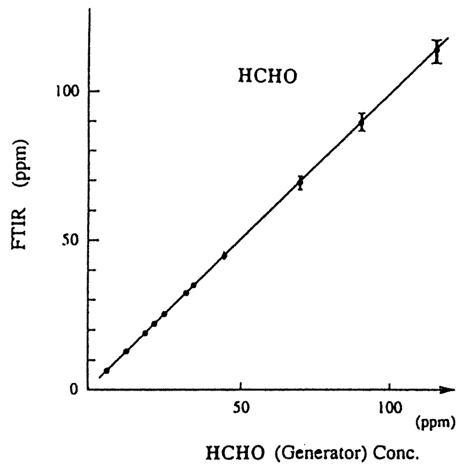

Fig.4 Linearity of absorption. (HCHO)

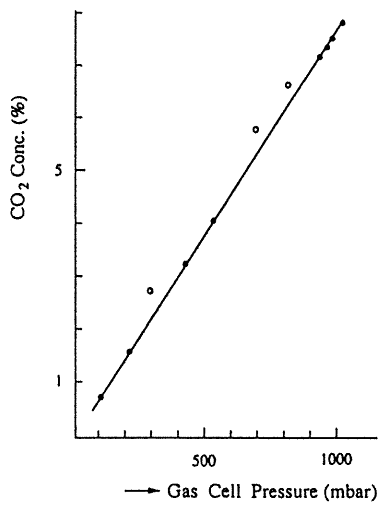

Fig.5 Linearity of cell pressure.

3.3 Correlation Results

Schematic of the correlation test is shown in Fig.6. Formaldehyde (HCHO), unburned methanol (CH3OH), CO, CO_2, NOx, and T.HC were used to evaluate the correlation. Both FTIR method and DNPH method were employed to measure HCHO as shown in Fig.7. Both FTIR and GC were to measure CH_3OH as shown in Fig.8. Comparison of CO and CO2, NOx, and THC data were made with NDIR, CLA, and FIA respectively as shown in Fig.9 through Fig.12.

Time averaged results indicate good correlations for all gas species. Especially, HCHO and CH3OH running mode data have best correlation among all of these tests.

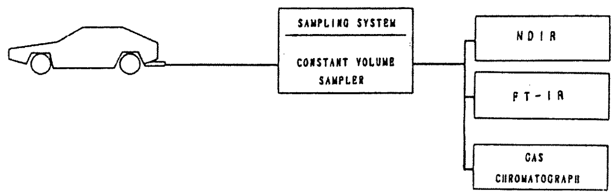

Fig.6 Schematic of correlation test.

Symbols represent following conditions in figures 7 through 12.

○ : Time averaged value of M85 emission 40km/hr constant

△ : Time averaged value of M85 emission LA-4 mode

□ : Time averaged value of gasoline engine emission LA-4 mode

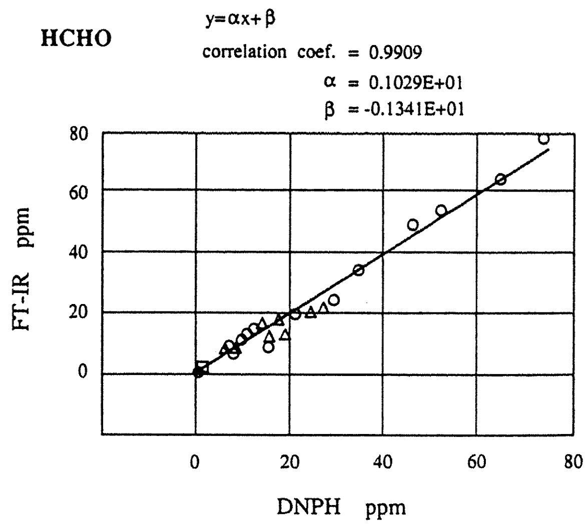

Fig.7 Correlation result, DNPH

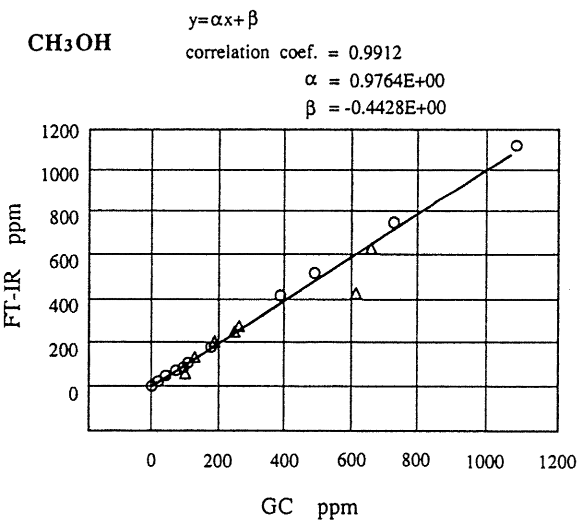

Fig.8 Correlation result, GC

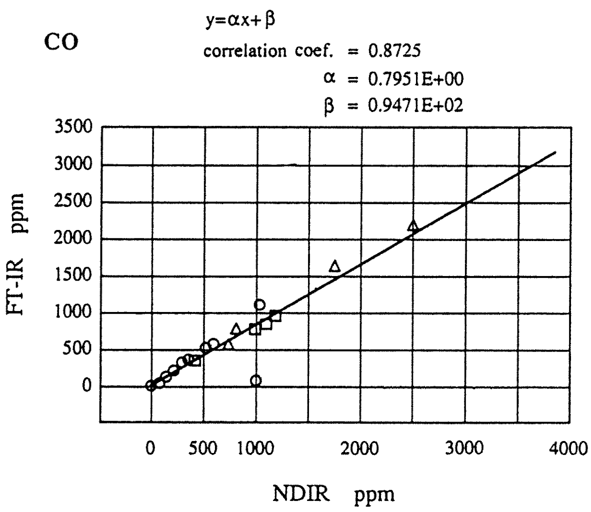

Fig.9 Correlation result, NDIR

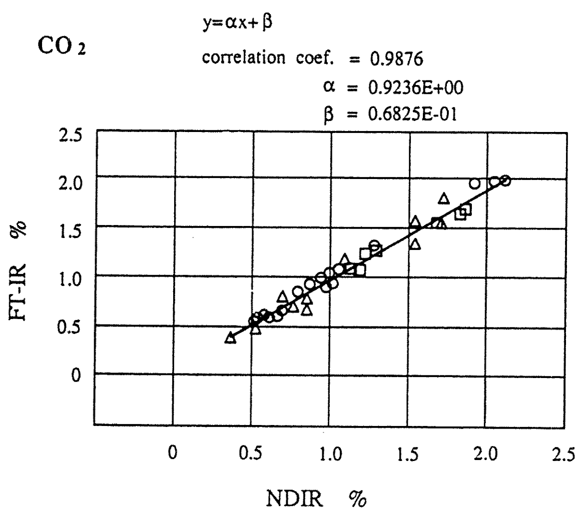

Fig.10 Correlation result, NDIR

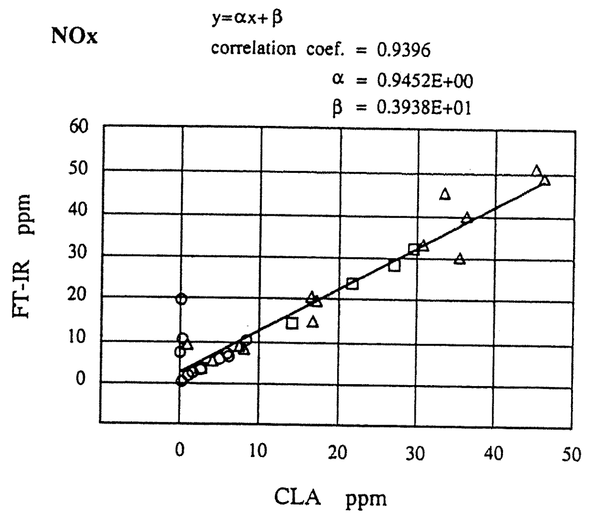

Fig.11 Correlation result, CLA

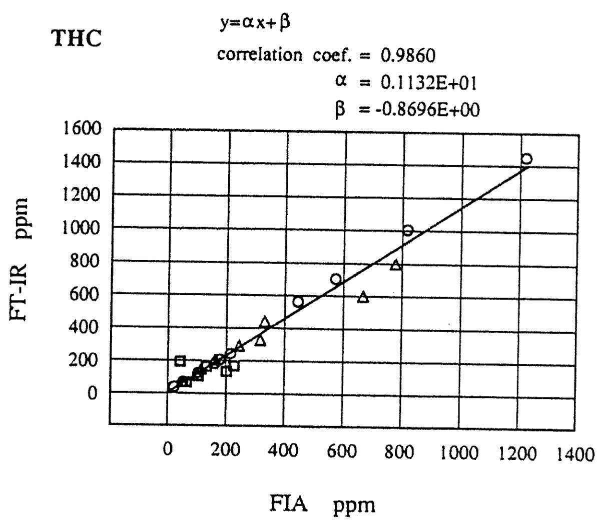

Fig.12 Correlation result, FIA

3.4 Response Time

Fast response is required for practical emission analysis. Most of continuous gas analyzers have T_{90} (response time required for 90% of final value) of within 1 second. Volume of the system's gas cell is 5.4 litter and T_{90} is about 40sec at a flow rate of 20 litter/minute. Figure.13 shows the comparison between this technique and the conventional technique using Federal Test Procedure at sampling flow rate of 13 litter/minute. One can decrease the response time with increasing the flow rate. T_{90} of 3 seconds can be realized by increasing the flow rate up to 100 litter/min. At this much flow rate, not only system becomes more challenging, but many other problems such as noise, interferences, accuracy, etc. will arise It is required to realize the system with fast response at minimum flow rate. Designing the sampling system with fast response is very important.

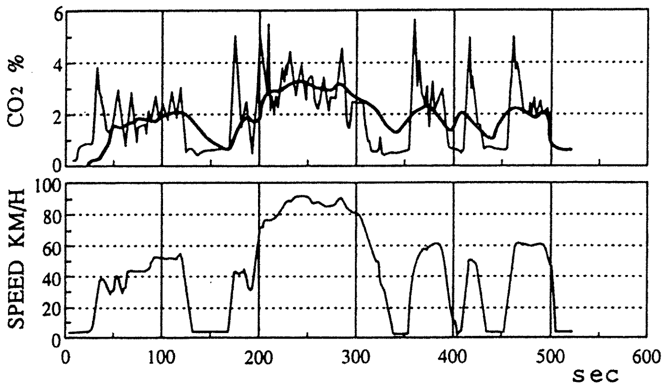

Fig.13 Federal Test Procedure data.

4.SUMMARY

Concept and basic requirements for an automotive emission analyzing system using FTIR have been investigated. And actual data have been collected and analyzed for methanol fueled vehicle (M85) with this system.

Correlations with existing conventional technique show good results for HCHO, CH3OH, CO, CO2, NOx, and THC. The results mean that the system has a high future potential for measuring automotive emissions continuously and simultaneously. However, response time is very slow compared to the existing technique because of the volume of the gas cell. Development of small volume and long path gas cell is needed to be done soon.

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