

Laser Spectroscopic Multi-component Hydrocarbon Analyzer

Yasuhiko Mitsumoto *¹ Masaya Ooyama *¹
Chikara Yatabe *² Nobuhiko Kanbara *²

Yokogawa has developed a prototype of a laser spectroscopic multi-component hydrocarbon analyzer, which can measure the components simultaneously, precisely and rapidly. This analyzer uses a semiconductor laser with a widely tunable wavelength range called micro electro mechanical systems-vertical cavity surface emitting laser (MEMS-VCSEL), and a newly developed spectrum analysis algorithm. This can be applied to the real-time process control. Yokogawa has conducted a field test for measuring the calorific value of the process gas in a calorific adjustment process of town gas as one of its applications. This report outlines this analyzer and introduces the results of the field test.

INTRODUCTION

In recent years, shale gas extraction technology has made rapid progress, inducing a shale gas revolution mainly in the USA. Thus, the need for analysis of hydrocarbon gases, including natural gas, is expected to grow rapidly.

Traditionally gas chromatography has been used for the analysis of hydrocarbon gases; it can accurately measure the concentration of each hydrocarbon component in a sample of natural gas. However, it has disadvantages in that measurement is intermittent, requiring several minutes for each measurement, and that it needs a carrier gas such as helium which, may be exhausted.

Recently, gas analyzers for industrial processes applying spectroscopic analysis technology using semiconductor lasers are becoming popular. They have the advantage that they can measure the concentration of a target component quickly, stably, and with high selectivity, simply by irradiating a laser beam onto a sample gas using a highly reliable semiconductor laser. Yokogawa is manufacturing and selling TDLS series laser gas analyzers, and they are being used for process gas analysis in various industries such as oil refining, chemical and steel industries⁽¹⁾. However the current laser gas analyzers can only measure one or two components simultaneously, as the tunable wavelength range of their lasers is limited to within a few nm.

We have developed a laser spectrometer which can measure absorption spectra of multi-component gases in a period of a few seconds by using the micro electro mechanical systems-vertical cavity surface emitting laser (MEMS-VCSEL) with a wavelength tuning range of approximately 50 nm⁽²⁾ developed by Yokogawa. Furthermore, applying

a method using multivariate analysis, which can calculate concentrations of each component from a measured absorption spectrum in which absorption spectra of various components are overlapping, we have developed a prototype of a laser spectroscopic multi-component hydrocarbon analyzer shown in Figure 1 which can simultaneously measure concentrations of seven saturated hydrocarbon components with a carbon number of from one to five.



Figure 1 External view of the prototype analyzer

This paper first describes the principle and structure of the analyzer and MEMS-VCSEL, the absorption spectra of hydrocarbons, and the calculation algorithm. Then, it introduces the measurement results of the components in gases used in the actual town gas production process and the results of a field test using the analyzer in a calorific value adjustment process of town gases as an example of a process application.

MEASUREMENT PRINCIPLE

Lambert-Beer Law

The measurement principle of the analyzer is based on the Lambert-Beer law expressed in the following equations,

$$A = -\log_{10}(I_1/I_0) \quad (1)$$

$$A = \varepsilon C L \quad (2)$$

where A is the absorbance, I_0 , I_1 are the intensity of light before entering and after passing through the gas medium respectively, ε is the absorption coefficient, C is the concentration of the gas component, and L is the optical path

*1 Core Technology Development Dept.,
Foundation Technology Development Center,
IA Platform Business Headquarters

*2 Research & Development Division, Innovation Headquarters

length. Equation (1) is the definition of the absorbance and is the logarithm of the ratio of light intensities before and after entering the gas medium. The absorbance is proportional to the component concentration and the optical path length as seen in equation (2). When a sample is a mixture of multiple components, equation (2) can be rewritten as follows assuming that the optical path length is constant.

$$A = \left(\sum_{i=1}^n \varepsilon_i \times C_i \right) \times L \quad (3)$$

The wavelength dependences of ε_i for each component are different from each other. Thus, if the calibration curves indicating the relation between absorbance and concentration in a wide wavelength range are created, the concentrations of each component of unknown multi-component samples can be measured.

Absorption Spectra of Hydrocarbons

This analyzer measures the concentration from the absorption spectra of laser light after travelling through hydrocarbon gases. As examples of hydrocarbon spectra, Figure 2 shows absorption spectra of methane, ethane, and n-butane at the 1.7 μm band. This band is the harmonic of the 3.4 μm band in which a fundamental vibration due to coupling of carbon and hydrogen atoms is found. An absorption at the 1.7 μm band is less than that at the 3.4 μm band. However, for the 1.7 μm band, InP-based laser diodes which are proven for optical communications usage can be used, and an optical system can be configured using low-cost and highly reliable optical components and high-performance photo detectors. Thus, the 1.7 μm band was chosen for this analyzer

The shape of a spectrum of a hydrocarbon depends largely on the carbon number. The spectrum of methane with a carbon number of one shows steep and high peaks, and the absorbance between these peaks is nearly zero. On the ethane with a carbon number of two or n-butane with carbon numbers of four, the absorbance does not drop to zero and the spectra are overlapping within the 1.7 μm band. In particular, the spectrum of n-butane shows no steep peaks and is a very smooth curve.

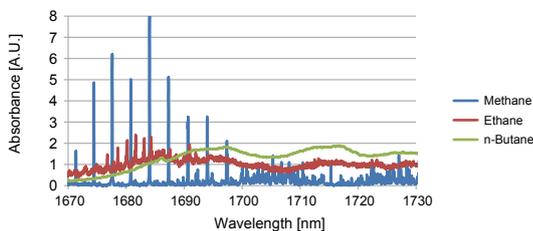


Figure 2 Absorption spectra of hydrocarbons at the 1.7 μm band

CONFIGURATION OF THE LASER SPECTROSCOPIC MULTI-COMPONENT HYDROCARBON ANALYZER

Optical System

Figure 3 illustrates the optical system of this analyzer. The light beam emitted from the MEMS-VCSEL, with a

widely tunable wavelength range, is split into three beams by the beam splitter, and then reaches the photodetectors. The first beam passes through the gas cell containing the sample gas before reaching photodetector 1. The second beam traverses the gas cell for wavelength calibration, in which methane gas is sealed, and irradiates photodetector 2. The wavelength swept by the laser is automatically calibrated by the positions of the steep absorption peaks peculiar to methane. The third beam goes directly into photodetector 3 and is used as the reference for the laser light intensity.

The laser light intensities are converted into electronic signals by the photodetector, and then the absorption spectrum is created by computer, and finally the concentrations are calculated by using the multivariate analysis technique.

Because the shape and magnitude of an absorption spectrum are affected by gas temperature and pressure, the analyzer controls them to make them constant.

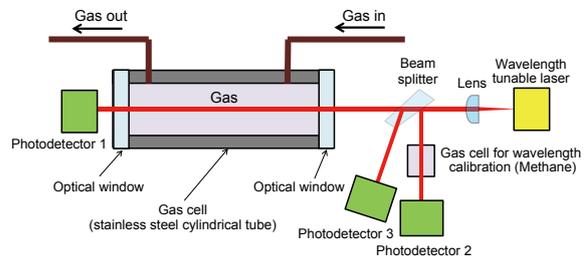


Figure 3 Optical system of the laser spectroscopic analyzer

MEMS-VCSEL with a Widely Tunable Wavelength Range

Figure 4 shows the conceptual diagram of a MEMS-VCSEL with a widely tunable wavelength range developed by Yokogawa, which is used for the light source of this analyzer. This semiconductor laser has a variable resonator structure with a MEMS movable mirror chip bonded to a half-VCSEL chip, the total dimension being approximately 3 mm \times 3 mm \times 1 mm. The movable mirror has a concave shaped dielectric multi-layered thin membrane structure to reduce the diffraction losses. When voltage is applied between the membrane and the lower part of the silicon on insulator (SOI) substrate, the membrane is drawn towards the substrate by the induced electrostatic force. As a result, the optical cavity length, formed by the multi-layered mirror in the VCSEL chip and the dielectric multi-layered mirror on the membrane, becomes longer and thus the lasing wavelength shifts to the longer wavelength side.

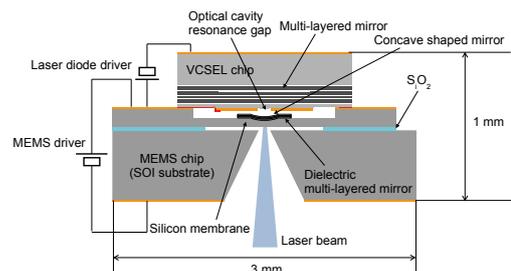


Figure 4 Conceptual diagram of MEMS-VCSEL

This optical cavity length is designed so short as to be about 10 times the laser wavelength. This makes the frequency spacing between longitudinal modes wide enough to allow a single-mode oscillation.

Figure 5 shows an absorption spectrum of methane obtained by using the MEMS-VCSEL as a laser source. Conventional laser gas analyzers can observe only one absorption peak because of the limitation of a wavelength tunable range of a few nanometers. However, the MEMS-VCSEL can measure multiple absorption peaks of methane by sweeping a wide wavelength range. This also enables observation of the spectral characteristics of not only methane but also various hydrocarbons shown in Figure 2.

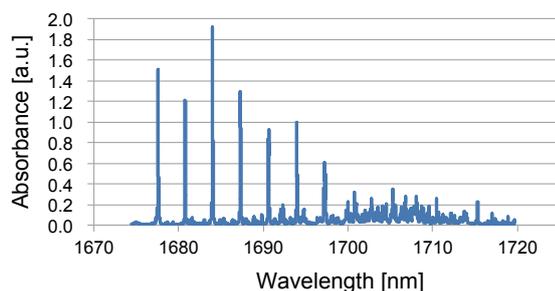


Figure 5 A spectrum of methane obtained by using MEMS-VCSEL

Spectrum Analysis and the Algorithm for Measuring Concentrations of Components

The multivariate analysis technique is used for the spectrum analysis. First, spectra of samples of known concentrations are collected, and then calibration curves for determining concentrations are derived from those known concentrations and measured spectra, by using statistical techniques. For this analysis, a partial least squares (PLS) regression method is used. Unknown concentrations of gases are determined by applying these calibration curves to their spectra.

Conventional laser analyzers generally use the height of the peak or the area near them of absorption for measurement. However, when measuring multiple hydrocarbons simultaneously, because their spectra overlap each other, it is difficult to measure their concentrations solely by the peaks in their spectra.

When using a multivariate analysis, not only the absorption peaks but also the whole spectral information within the range swept by a laser can be used for the concentration analysis. This enables determination of the concentration of gases such as n-butane with little distinct spectral peculiarity.

PRELIMINARY TEST RESULTS

To evaluate the developed prototype laser spectroscopic analyzer, gas samples of a mixture of seven kinds of gases: methane, ethane, propane, i-butane, n-butane, i-pentane and n-pentane, were measured and its results were compared with measurements by a high-precision gas chromatograph used as

a standard. As a result, it was confirmed that its measurement deviation from the measured value by the gas chromatograph is less than 0.1%, that is 2σ , which is the accuracy required for the calorific value adjustment process.

Figure 6 compares the measurement results obtained by the prototype and by a gas chromatograph when concentrations of gas samples are changed. The horizontal axis is the clock time and the vertical axis is the concentration indicating the values measured by the prototype and by the gas chromatograph. It is seen that the prototype can similarly follow slight changes in concentrations of about 0.2% as does the gas chromatograph, and it was proven that it can catch small amounts of changes in concentrations. The interval of the prototype achieved is three seconds, one two-hundredth of that of the gas chromatograph with that of 10 minutes. This shows that the prototype analyzer can perform real-time measurement much more rapidly than a gas chromatograph.

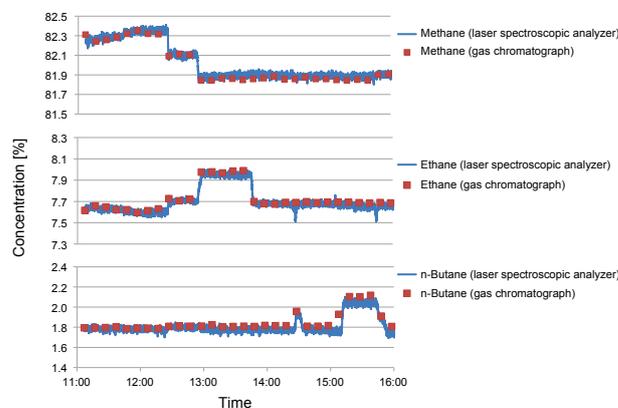


Figure 6 Concentration measurement comparison between that of the prototype laser spectroscopic analyzer and that of a gas chromatograph

APPLICATION TO REAL-TIME MEASUREMENT OF GAS CALORIFIC VALUES

For town gas production, liquid natural gas (LNG) and liquid petroleum gas (LPG) are evaporated, mixed together at the proper ratio to adjust the calorific value, and then delivered to consumers' homes. Traditionally, gas chromatography has been used to measure accurate concentrations of each component included in a gas, and the calorific value of the gas has been calculated from those concentrations and their calorific values per unit. However, this measurement takes about 10 minutes and is not suitable for town gas calorific control. Sometimes other devices with a shorter measurement time such as a gas densimeter are used for calorific value measurement, but this method cannot avoid errors due to inclusion of nitrogen, whose calorific value is zero. Therefore, a high-precision and high-speed calorific value measurement for process gases is expected. A field test for measuring calorific values in real-time has been conducted using the prototype laser spectroscopic analyzer in an actual town gas production process.

Figure 7 shows a conceptual diagram of a town gas production process. LNG is supplied from various countries

or regions as a raw material, and stored in tanks. In the plant where this test was conducted, the LNG from multiple tanks is evaporated, mixed with LPG and finally adjusted so that the calorific value of the mixed gas become 45 MJ/m³N, odorant is added to the mixed gas, and the final gas mixture is delivered to consumers as town gas. In this field test, the calorific value of the mixed gas just after the final calorific value adjustment by mixing LNG and LPG was measured.

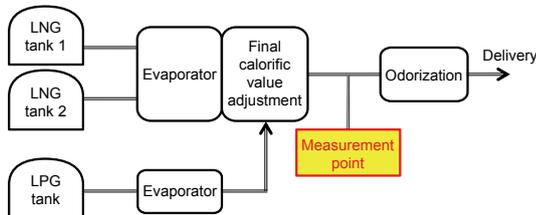


Figure 7 Conceptual diagram of a town gas production process and the calorific value measurement point

Figure 8 shows the one-day long measurement results of the calorific value of the process gas after the adjustment, i.e. at the measurement point shown in Figure 7. The blue line shows the measurements by the prototype laser spectroscopic analyzer and the red squares show those by the gas chromatograph. The prototype measures concentrations of all seven hydrocarbon components: methane, ethane, propane, i-butane, n-butane, i-pentane and n-pentane included in the process gas at three second intervals, and the calorific values are synchronously calculated from those concentrations and their calorific values per unit. It is seen that the measurements by the laser spectroscopic analyzer indicate similar values to those obtained by using the gas chromatograph. It is also seen that the laser spectroscopic analyzer is capable of remarkably quick response to the process fluctuations compared with the gas chromatograph, owing to its short measurement interval.

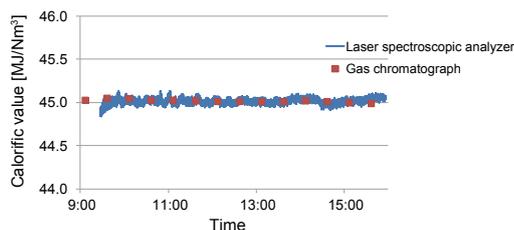


Figure 8 Calorific value measurement results after the adjustment process

In this way, high-speed and high-precision measurement of calorific values using a laser spectroscopic multi-component hydrocarbon analyzer has been achieved. This enables fast control of a calorific value adjustment process and can help enhance the efficiency in town gas production. Of course, this can interlock the calorific value to exceed the control limit.

FUTURE DEVELOPMENT

Although the analyzer is still in the prototype stage, Yokogawa will enhance its usefulness for practical

application and improve it to meet the market demand for commercialization. The following three items are planned for future development:

1) Reducing the delay time caused by sampling

Currently the measurement time is determined by the time required for sampling because the measurement is performed after sampling the process gas. Improvement to enable the analyzer to be directly attached to the piping is planned, to reduce the sampling time

2) Applications to other areas

Hydrocarbon analyzers can be applied to various areas other than the calorific value measurement of town gas. Specifically, measurements in processes in an ethylene plant, natural gas refining processes and processes or pipelines for LNG production, and use for combustion control of gas turbines in thermal electric power plants can be considered to be possible applications. Yokogawa will pursue the effectiveness of this analyzer for these applications.

3) Expanding applications to other gases

Many gases not limited to hydrocarbons absorb infrared light, and so Yokogawa is planning to investigate the feasibility and effectiveness of applications of spectroscopic analysis to other gases, by making use of the accumulated technologies through prototype development.

CONCLUSION

We have developed a prototype of a laser spectroscopic multi-component hydrocarbon analyzer using a MEMS-VCSEL with a widely tunable wavelength range, and succeeded in simultaneously measuring seven hydrocarbons by using the spectral analysis based on multivariate analysis. A field test in a town gas production process has proved that the new analyzer has a high potential for measuring hydrocarbons.

The need for hydrocarbon gas measurement is expected to grow in the future due to the shale gas revolution. We hope that hydrocarbon gas measurement using the new technology described in this paper will contribute to improving the efficiency of process control and reducing running costs for hydrocarbon gas measurement.

Finally, we express our sincere gratitude to persons concerned in Osaka Gas Co., Ltd. for their provision of valuable information to us and for their considerable cooperation with us in measuring process gases at their actual production facilities.

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