# High Sensitive Gas Concentration Measurement using the Infrared Absorption Spectroscopy

赤外吸収分光技術を用いた高感度ガス濃度計測

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The amplitude-to-time conversion (ATT) technique is proposed as a detection method which can achieve a wide dynamic range and a high signal-to-noise ratio. Laser absorption measurement is known for its high sensitivity for a gas concentration. To enhance the sensitivity for detection, it is required that the minute attenuation in a direct signal is amplified. In order to verify the principle and evaluate the performance, a gas concentration measurement system was developed with the quantum cascade laser and the ATT circuit. As a result of the test, the detection limit of NO<sub>2</sub> has been improved by about fifty times in comparison with measurement of amplitude.

## 1. Introduction

Nitrogen oxides  $(NO_x)$  and sulfur oxides  $(SO_x)$  are contained in diesel exhaust gas of ships and vehicles. They are known to cause acid rain and air pollution. Although a catalyst system is often used to reduce these substances, there is a problem in terms of energy efficiency. Therefore, the catalyst-free system with the plasma is expected to solve this problem[1]. In order to realize an efficient exhaust gas treatment, it is important to measure a gas concentration in the field of plasma reaction.

The most commonly used optical method for trace-gas sensing is tunable diode laser absorption spectroscopy (TDLAS)[2]. This is a highly sensitive method to detect specific molecules using a laser with high wavelength accuracy. Recently, quantum cascade lasers (QCLs)[3,4] had been developed. This laser can be directly emitting a light in the infrared band (3-10µm). In order to further increase the sensitivity of such measurements, multiple reflection optics is used typically. In this case, it is possible to measure only an average gas concentration in the optical cell. It is necessary to improve the sensitivity by another method, when a plasma reactor is miniaturized or the measuring area is localized. amplitude-to-time (ATT) The conversion technique is proposed as a detection method which can achieve a wide dynamic range and a high signal- to-noise ratio (SNR).

## 2. Principle of amplitude-to-time conversion

In this technique, the information on amplitude is

converted to delay time. The purpose of the conversion is to improve the SNR by accumulating and averaging on a time axis. Conceptual diagram of ATT was shown in Fig. 1. The waveform was shown in Fig. 2. Since the pulsed light emission is repeated, the delay time  $\Delta t$  is amplified. Random noise in the signal is reduced according to  $1/\sqrt{N}$ , when *N* is repeat number.



Fig.1. Conceptual diagram of amplitude-to-time conversion circuit



Fig.2. Waveform in the conceptual diagram



Fig.3. Block diagram of a gas concentration measurement system with the ATT circuit



Fig.4. NO<sub>2</sub> Spectra at different gas concentration

#### **3. Experimental System**

Block diagram of the experimental system was shown in Fig. 3. The mid-infrared light source was provided by a thermoelectrically cooled distributed feedback QCL. The center wavelength of the laser is  $6.1\mu$ m (for NO<sub>2</sub>). The laser beam was focused on an InSb photoconductive detector with a preamplifier. In order to achieve the ATT conversion, high-speed devices were required. Therefore, emitter-coupled logic (ECL) devices such as high-speed comparators and ripple counters had been implemented.

### 4. Results

The absorption spectra were shown in Fig. 4. When the concentration of  $NO_2$  was decreased, the spectral variation has been reduced. However,

change of the characteristic shape of a spectrum was not observed at this time. There is a possibility of evaluating the specified gas concentration quantitatively through analysis of the spectral shape changes.

#### 5. Conclusions

Amplitude-to-time conversion technique was proposed for highly sensitive measurement with an infrared absorption spectroscopy. This system is suitable for local and in-situ measurement. Furthermore this technique can be applied to another measurements such as microwave or magnetism.

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