HYDROGEN GAS CONCENTRATION MEASUREMENT IN SMALL AREA USING RAMAN LIDAR MEASUREMENT TECHNNOLOGY

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ABSTRACT

When change of hydrogen(H_2) gas concentration in a certain point is measured, non-contact measurement technology with high temporal and spatial resolution is necessary. In this study, H_2 concentration in the small area of <1cm^2 under the gas flow was measured by using a Raman lidar. Raman scattering light at the measurement point of 750mm ahead was detected by the Raman lidar. As a result, it was proved that the H_2 concentration of more than 100ppm could be successfully measured.

1 INTRODUCTION

Hydrogen is expected to become a clean energy in next-generation. Various proof examinations are carried out to create the hydrogen society. From such a background, the demand for hydrogen gas measurement is drastically increasing.

When change of hydrogen gas concentration in a certain point is measured, a gas sensor is fixed at the measurement point, or a syringe is utilized to sample the gas, and it is analyzed by a gas chromatography. However, the gas sensor and the syringe have influence on gas flow and its measurement values. Non-contact measurement technology with high temporal resolution and high spatial resolution is necessary to measure at such a small area.

It is effective to use a Raman lidar, as a non-contact measurement technique of hydrogen gas concentration distribution[1][2]. Hydrogen gas measurement by the Raman lidar doesn't have to install a sensor and a syringe into the gas flow, concentration distribution of hydrogen gas can be measured without interference to the gas flow at a measurement point. When the measurement area is very small of <1cm^2, however, the spatial resolution of the measurement delimits its accuracy. This is because the spatial resolution depends on the pulse width of the laser, and the hydrogen gas concentration measured within the pulse width is the mean value distributed over the range.

Therefore, in this study, for the purpose of non-contact measurement of the hydrogen gas concentration in the small area under the gas flow, a specialized Raman lidar was developed. A laser beam (wavelength 349nm, pulse energy 120μJ, PRF 1kHz) with the beam diameter of 1mmϕ at the measurement spot was irradiated to the hydrogen gas. Raman scattering light at the measurement point of 750mm ahead was focused by a Fresnel lens, which is arranged at the orthogonal direction again the transmitting laser beam. As a result, it was proved that Raman signal intensity showed good linear correlation with hydrogen density of more than 100ppm. The gas concentration in a small area could be quantitatively estimated without interference of the gas flow.

2 METHODOLOGY

2.1 Principle

The remarkable absorption wavelength of hydrogen molecules is less than 110nm[3] and does not have clear absorption lines from ultraviolet to the infrared wavelength. Therefore, although absorption spectroscopy is general technique for gas measurement, it is difficult to adapt it for hydrogen gas measurement. On the other hand, the hydrogen molecule shows strong Raman effect[4]. The Raman scattering is the inelastic scattering, which is caused by the interaction between the incident photon and target gas molecules. The Raman scattering shifts the scattering wavelength to the longer wavelength (Stokes light). When ω_P is an angular frequency of the irradiation light, and ω_S is an angular frequency of the Stokes light, and $\Delta\omega$ is the Raman shift of measurement gas molecules, from the law of the conservation of energy,

$$\omega_s = \omega_p - \Delta\omega \tag{1}$$

is established. The energy difference of the photon is equal with internal energy level differences of molecules of $\Delta\omega$, and it is peculiarity for molecular species[5]. The Raman scattering light intensity is proportional to molecular concentration. Therefore, molecular species are clarified by Raman scattering wavelength, and gas concentration is measured quantitatively by Raman scattering intensity. Raman shift of hydrogen, nitrogen and oxygen, and Raman scattering wavelengths when laser light of 349nm is irradiated towards those gases are shown in table 1.

Table 1 Raman shifts and Raman scattering wavelength when using a laser wavelength 349nm

Molecule species	H_2	N_2	O_2
Raman shift [cm^{-1}]	4160	2331	1556
Raman scattering wavelength [nm]	408.3	377.9	369.0

The Raman scattering light intensity observed from the vertical direction against the laser optical axis is expressed by eq.(2)[6].

$$P_R = \frac{\lambda}{\lambda_R} P_L \chi \rho \sigma_R L N \eta_D \qquad (2)$$

P_R : Intensity of Raman scattering
λ : Wavelength of laser irradiation
λ_R : Wavelength of Raman scattering
P_L : Output power of laser
χ : Molar function
ρ : Number density of molecules
σ_R : Raman scattering cross section
L : Pass length
N : Effective number of passes of the laser beam in field of view
η_D : Efficiency of the collecting and detecting optical system

From eq.(2), the Raman scattering light intensity is proportional to a molar function, namely the gas concentration of target gas. When concentration of hydrogen gas is measured, Raman scattering light intensity of the atmospheric nitrogen gas is also measured as reference. The Raman scattering light intensities of hydrogen gas (subscript H) and the nitrogen gas (subscript N) are expressed like eq.(3), eq.(4) using eq.(2) [1][2][7].

$$P_{RH} = \frac{\lambda}{\lambda_{RH}} P_L \chi_H \rho \sigma_{RH} L N \eta_{DH} \qquad (3)$$

$$P_{RN} = \frac{\lambda}{\lambda_{RN}} P_L \chi_N \rho \sigma_{RN} L N \eta_{DN} \qquad (4)$$

When the ratio of both Raman scattering lights is taken and the equation is expressed the molar function of the hydrogen gas, eq.(5) is provided.

$$\chi_H = \frac{P_{RH}}{P_{RN}} \frac{\lambda_{RH}}{\lambda_{RN}} \frac{\sigma_{RN}}{\sigma_{RH}} \frac{\eta_{DN}}{\eta_{DH}} \chi_N \qquad (5)$$

Nitrogen gas concentration in the atmosphere is 78%, λ_H and λ_N are Raman scattering wavelength shown in Table 1, σ_H and σ_N are known[5], and η_H and η_N are values by the optical efficiency of the collecting and detecting system. Therefore, concentration conversion constant C is decided, and eq.(6) is provided.

$$\chi_H = C \frac{P_{RH}}{P_{RN}} \qquad (6)$$

Therefore, the molar function that represents the concentration of hydrogen gas is calculated.

2.2 Experimental configuration

The experimental configuration in this study is shown in Figure 1.

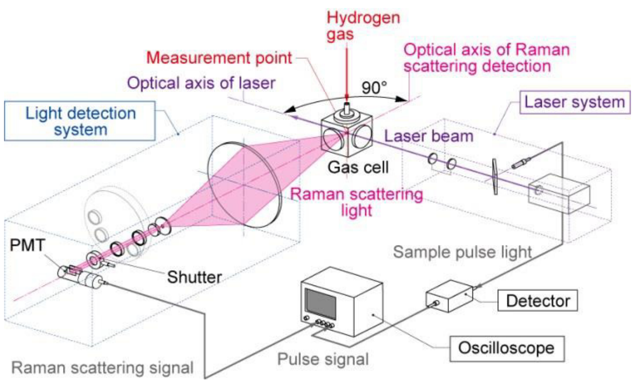

Figure 1 Experimental configuration of hydrogen gas measurement.

Nd:YLF laser (Explorer349 made in Spectra-physics, Wavelength 349nm, Pulse energy 120μJ, Pulse width 5ns, Repetition rate 1kHz) was used as a light source. The beam diameter is 1mmϕ at the measurement spot. Raman scattering light was focused by a Fresnel lens, which is arranged at the orthogonal direction again the transmitting laser beam, and the scattering intensity was measured by a photomultiplier tube (R12829 made in Hamamatsu Photonics). The aperture diameter and the focal distance of the Fresnel lens are 170mm and 230mm, respectively.

The light receiving optical system is shown in Figure 2.

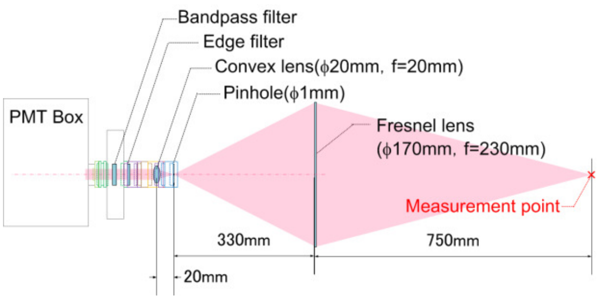

Figure 2 Optical components arrangement of light detection unit.

The light receiving optical system was Kepler type telescope using two convex lenses. The distance between the Fresnel lens and the pinhole was calculated by focus distance of the Fresnel lens of f_1=230mm and the distance to the measurement spot L_1=750mm. The pinhole of aperture diameter 1mmϕ was arranged at 330mm from the Fresnel lens.

The Raman scattering light was delivered to be parallel by a convex lens which was located behind a pinhole, and it was introduced into a photomultiplier tube through an edge filter (Transmissivity <10^{-6} at 349nm, and 95% at 360nm or more) and a band pass filter (Center wavelength 410nm, FWHM 10nm).

The diameter of the receiver's field of view at the measurement spot was calculated as A_M=2.3mm when the pinhole aperture diameter A_P was 1mm, the distance to the measurement spot of L_1=750mm, the distance between Fresnel lens and the pinhole of L_2=330mm and their relationship with the image magnification shown in eq.(7).

$$\frac{A_P}{A_M} = \frac{L_2}{L_1} \tag{7}$$

The gas concentration measurement area of this experimental configuration which was observed from the Fresnel lens side was within the width of 2.3mm, height of 1mm, and depth of 1mm, because the beam diameter of the laser at the measurement spot is 1mmϕ and A_M=2.3mm.

3 RESULTS

In experimental configuration shown in Figure 2, low concentration hydrogen mixed gas (nitrogen gas balance) of known concentration were filled into a gas cell, and its Raman scattering light intensity was measured. Hydrogen gas of the concentration of 1,000ppm was used as standard, and the gas density in the cell was adjusted by changing the filling pressure into the gas cell. Measurement results are shown in Figure 3 and Figure 4.

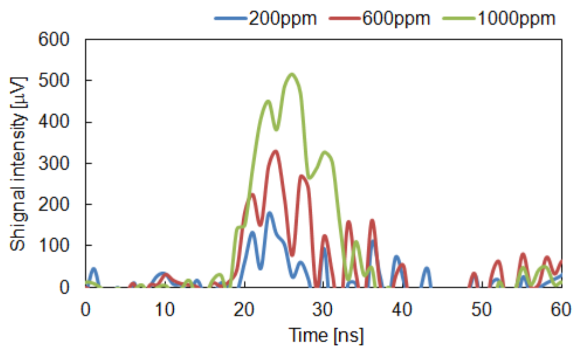

Figure 3 Time responses of Raman scattering intensity.

Figure 3 shows time responses of–Raman scattering signals from hydrogen gas which are measured by the photomultiplier tube. Pulse width of the light source was 5ns. FWHMs (Full Width Half Maximum) of Raman scattering signals were 10ns, it agreed with the time response of the pulsed light to pass through the measurement point.

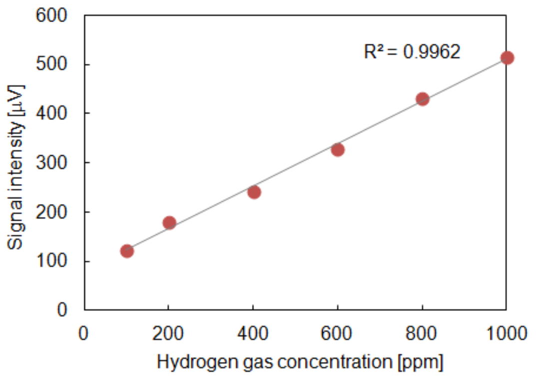

Figure 4 Dependence of Raman scattering intensity on the hydrogen concentration in the gas cell.

Figure 4 shows the peak value of the Raman scattering signal when the hydrogen gas concentration in the gas cell was changed. The Raman scattering signal intensity showed good linear correlation with hydrogen gas concentration of 100ppm or more. It was confirmed that the hydrogen gas concentration measurement in the certain small point was possible with the developed Raman lidar.

4 CONCLUSIONS

Remote measurement technique of gas concentration in the certain small point under its flow was considered, and the experimental system was developed. It was shown that low-concentrated hydrogen gas at the distance of 750mm was measured successfully with the liner correlation up to 100ppm.

From these results, it was shown that the gas concentration remote measurement ~~in~~ at the certain small leak point was possible without interfering the gas flow.

This result can be applied to monitoring of gas diffusion under a case that a gas tank was damaged and gas was leaked. In addition, other gases including oxygen and nitrogen etc. can be also measured by adjusting the observation Raman wavelength.

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