# OBSERVATION OF THE HYDROGEN DISPERSION BY USING RAMAN SCATTERING MESURMENT AND INCREASE OF MEASURABLE DISTANCE

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## ABSTRACT

Preparing for the arrival of the hydrogen society, it is necessary to develop suitable sensors to use hydrogen safely. There are many methods to know the hydrogen concentration by using conventional sensors, but it is difficult to know the behavior of hydrogen gas from long distance. This study measured hydrogen dispersion by using Raman scattering light. Generally, some delays occur when using conventional sensors, but there are almost no delays by using the new Raman sensor. In the experiments, 6mm & 1mm diameter holes are used as a spout nozzle to change initial velocities. To ensure the result, a special sheets are used which turns transparent when it detected hydrogen, and visualized the hydrogen behaviour. As a result, the behaviour of the hydrogen gas in the small container was observed. In addition, measurable distance is increased by the improvement of the device.

## 1 INTRODUCTION

Hydrogen has been expected for long years as one of the next generation energy carriers. In Japan, there are plans to develop infrastructure to promote the use of hydrogen energy at the Tokyo Olympic Games in 2020 and to promote fuel cells dramatically. To promote using hydrogen, we have to pay attention to the risk of explosion. In order to use hydrogen safely, it is necessary to detect hydrogen leak using a sensor, but existing contact type sensor cannot detect hydrogen unless it is installed at exact position where leakage is expected. Therefore, the behaviour of hydrogen was confirmed by measuring the hydrogen concentration changes using a non-contact type Raman sensor, and the possibility of using a new sensor in various places was considered. This sensor has good responsiveness and can measure hydrogen concentration change with sensitivity of about 0.1 second. In this research, since the conventional Raman type sensor had a measurement limit of about 3 m, we improved the equipment to detect from more long distance.

## 2 METHOD FOR MEASUREMENT

### 2.1 Measurement Principle

The gases produce Raman scattering when irradiating a laser. A wavelength of Raman scattering of a gas is specific to the gas because the scattering depends on the internal energy of molecules of the gas and the laser. Therefore the wavelength of Raman scattering differs by gas type [table.1], then the target gas scattering is separated by using an optical filter. The strength of light is known to be proportional to concentration. Therefore, it is possible to distinguish a gas type and possible to calculate gas concentration. 1) A pulsed laser of 355 nm is used as a measuring device. In addition, the signal strength of the Raman scattering is proportional to the amount of gas molecules, then gas concentration is calculated from signal strength. 2)

$$S(L)=\gamma PkG(A/L^2)N\sigma\Delta L\exp\{-(\alpha L+\alpha R)L\} \qquad (1)$$

S: received signal strength, γ: receiving optical efficiency, P: laser strength, k: optical efficiency of the light receiving system (permeability and reflectivity), G: efficiency of the collector optics, A: receiving optical area, L: distance, N: molecular density, σ: Raman scattering sectional area, ΔL: distance resolution, αL & αR: dispersal coefficient in laser wavelength and Raman scattering wavelength.

Table 1. Raman scattering wavelength and relative strength against nitrogen (355nm laser) [3)]

| Gas | Raman scattering strength(nm) | Relative strength against nitrogen(σ/σN2) |
|---|---|---|
| $CO_2$ | 373.1 | 1.5 |
| $O_2$ | 375.4 | 1.6 |
| CO | 383.9 | 1.3 |
| $N_2$ | 386.7 | 1.0 |
| $H_2S$ | 390.9 | 6.8 |
| $H_2$ | 416.1 | 3.1 |

The target gas concentration is calculated based on nitrogen gas. The formula is shown below. [4)]

$$C=\frac{RS(gas)-RS(gas=0)}{RS(N_2=std)-RS(N_2=0)}\times\frac{0.78}{\sigma gas/\sigma N_2}\times 100 \qquad (2)$$

C: Concentration of target gas, RS(gas): Raman scattering strength of target gas, RS(gas=0): Raman scattering strength without target gas, RS(N2=std): Raman scattering strength at standard air condition, RS(N2=0): Raman scattering strength without nitrogen, σgas/σN2: relative strength of target gas against nitrogen.

In the calculation, N2 concentration is assumed 78% in the air, and to measure RS(N2=0) is difficult, however it can be assumed almost same as RS(gas=0).

## 2.2 Measurement Equipment

The laser beam is reflected by two mirrors and irradiated to the target gas. Raman scattering which generated from the gas is focused by Fresnel lens, and it is sent to optical receiver. This light is made parallel by a biconvex lens. The parallel light passes edge filter and interference filter, which remove the light of unnecessary wavelength. The light that passed each filter is converted into an electrical signal by Photo Multiplier Tube (PMT). The electrical signal is sent to AD converter, then the signal strength is displayed on a PC.

The optical receiver is set on a movable rail to easily adjust measurement distance. For example, in the case of doing the long distance measurement, it is necessary to move the optical receiver close to the Fresnel lens.

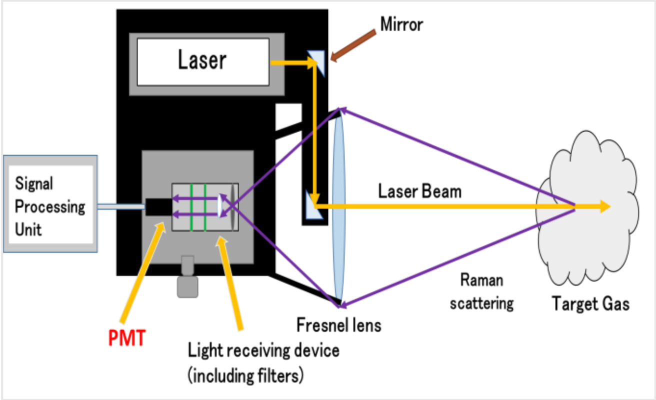


Figure 1. Overall view of the device

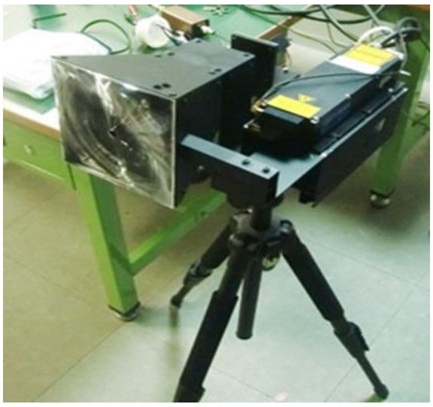


Figure 2. Raman Sensor

## 3 OBSERVATION OF HYDROGEN BEHAVIOR IN SMALL CONTAINER BY MEASURING RAMAN SCATTERED LIGHT

### 3.1 Experimental Description

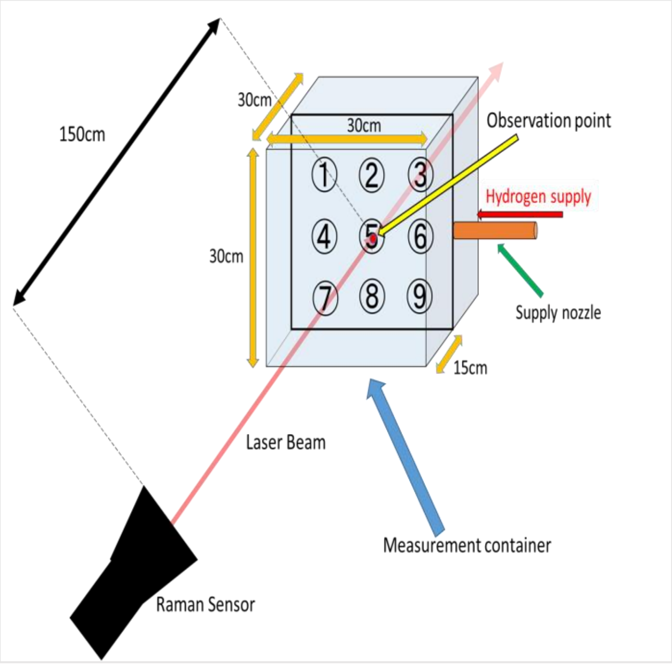
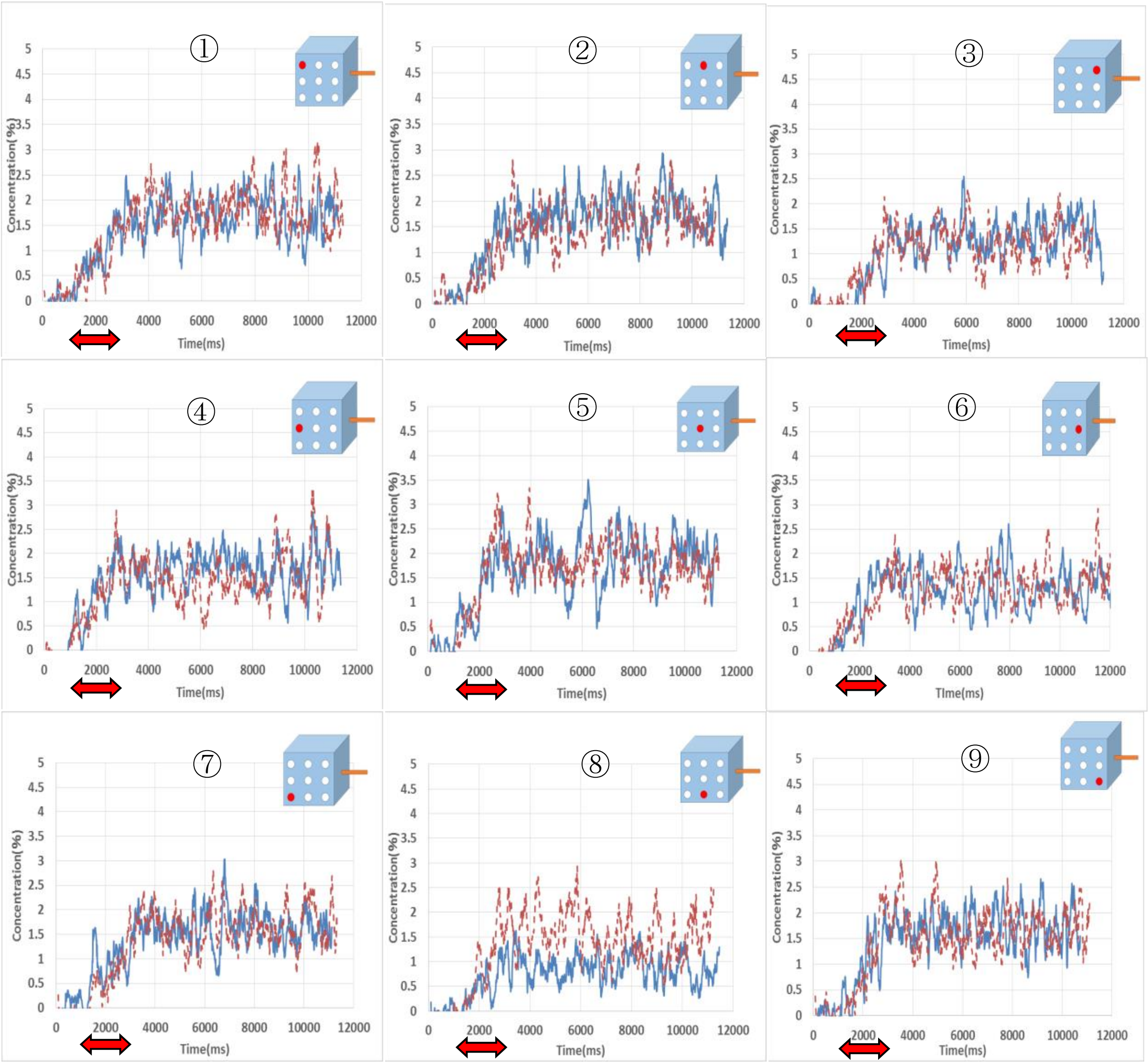


Figure 3. Environment of Experiment

The test container's inner size is 30 cm × 30 cm × 30 cm (27 L), we conducted measuring the hydrogen concentration by the time at 9 points in the container. In front of the container, special acrylic was used because Raman scattered light from the target gas has to transmit. A special quartz glass (d=30mm) was used for the front part irradiated with the laser to decrease the fluorescence. The Raman sensor can focus on one point on the optical axis of the laser, and possible to measure the concentration. As shown in Figure. 3, the measurement position was set to ① to ⑨ as seen from the front. Since the measurement cannot be performed at the same time, we conducted experiments at all 9 points. The back of the container on the optical axis of the laser has holes to avoid the influence of fluorescence. The nozzle was set on the right side, and those with diameters of 1 mm or 6 mm were prepared as hydrogen supply nozzles to investigate the difference depending on the flow rate. Measurements were taken from 150 cm away from the observation location. Hydrogen was supplied for 1,000 to 3,000ms from the start of measurement, namely, for 2 seconds at 40 L / min. The same experiment was carried out twice to confirm reproducibility, and they were displayed on the same graph.

## 3.2 Results and Discussion

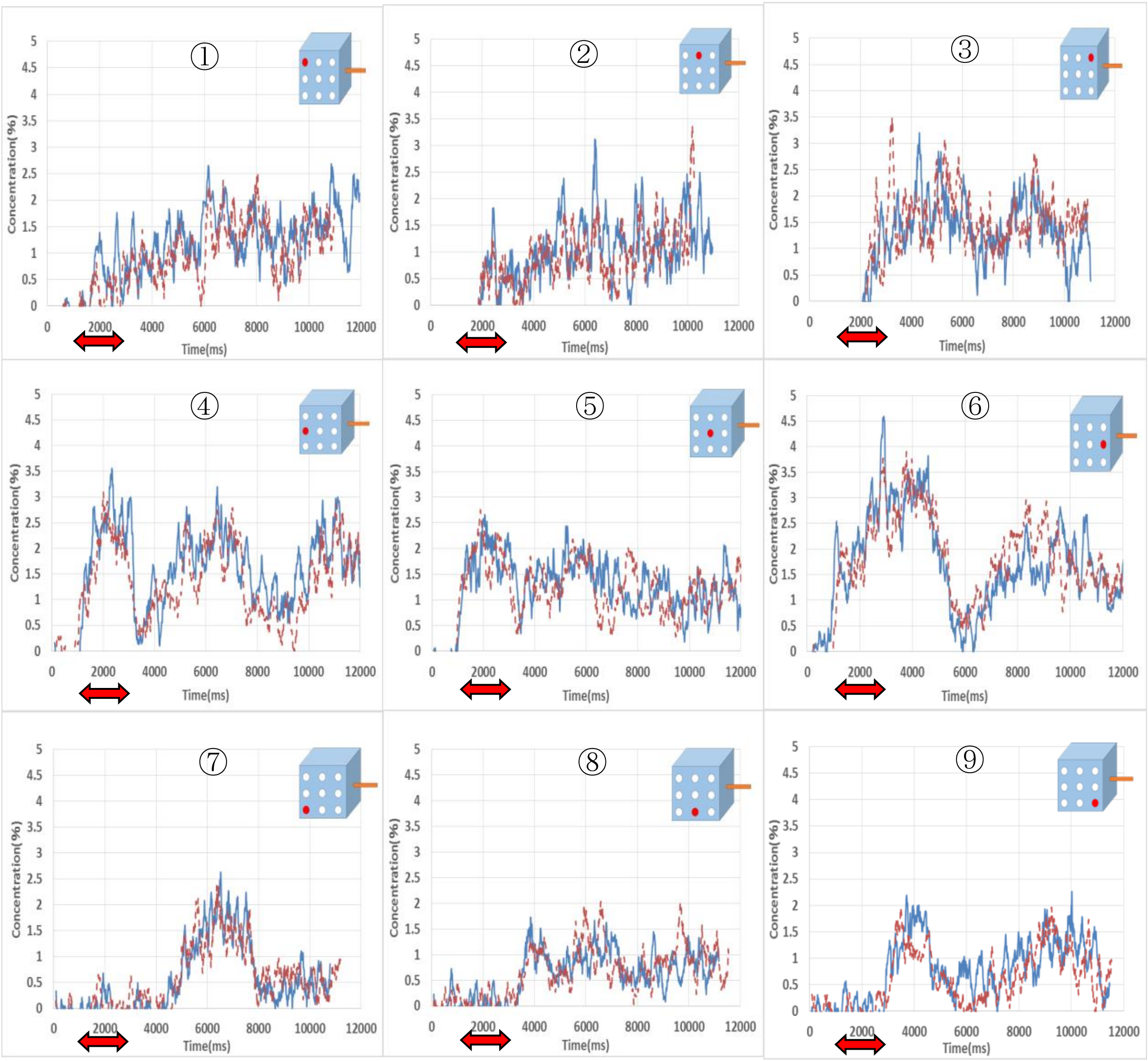
The measurement results of the temporal change in hydrogen concentration using the nozzles 1 mm & 6mm are shown below.



⟺: Hydrogen feeding time

Figure 4. Concentration change with 1mm nozzle
H2:40L/min 2sec supply (1st experiment: red line, 2nd experiment: blue line)

This result shows that hydrogen injected at high speed immediately diffused into the container with air entrained in it. Except for ⑧, reproducibility is guaranteed because of the results of the two experiments are fairly consistent.



↔: Hydrogen feeding time

Figure 5. Concentration change with 6mm nozzle,
H2:40L/min 2sec supply(1st experiment: red line,
2nd experiment: blue line)

From these results, when using a 6 mm diameter nozzle, the hydrogen concentrations are repeated up and down as compared with the case of using the 1 mm nozzle. It is inferred that the hydrogen gas is not immediately diffused into the entire container because the flow rate from the hydrogen nozzle is slower than 1mm nozzle. The highest concentration was observed at ⑥, because it is closest to the supply nozzle, and after the concentration of about 3 to 4% was measured, the concentration decreased as hydrogen supply stopped. Also, paying attention to the time of hydrogen concentration rise, the hydrogen concentration rise seen at ③ starts from 2,000ms, which is about 1,000ms later seen at ⑥ close to the supply nozzle. Concentration rise observed at ③ is different time from ④, ⑤, ⑥, so it seems that hydrogen flew to the wall near ④, and convection was detected. At the position of ⑥, the concentration reaches the peak at 4000ms, whereas in the ⑦ the peak reaches around 6000 to 7000ms. Then, it is found that even in the narrow space, the time to reach maximum concentration varies by 2 to 3 seconds. In the case of ④, ⑥, ⑨, after the hydrogen concentration rises, once it decreases to around 0%, then it is found that the concentration is rising again. This indicates that hydrogen gas has passed these places and then returned again by convection. When comparing the upper part ① ~ ③,a high concentration is observed in ③. It is presumed that a part of supplied hydrogen rises and accumulates, and it hits against the wall, then it gathers at the location of ③ after convection. The hydrogen behaviour assumed from the above results is shown in Figures 6 & 7. In addition, since the transition of the concentration was almost similar in the same experiment conducted several times, the reproducibility of these experiments are high.

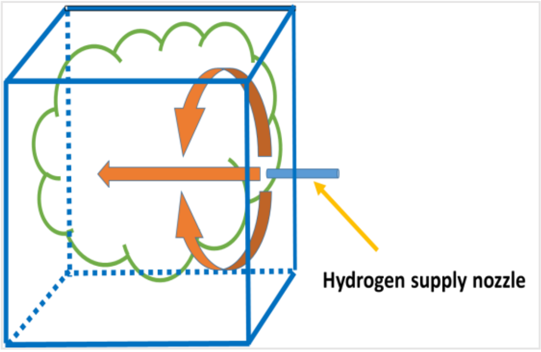


Figure 6. Diagram showing hydrogen behaviour with 1mm nozzle

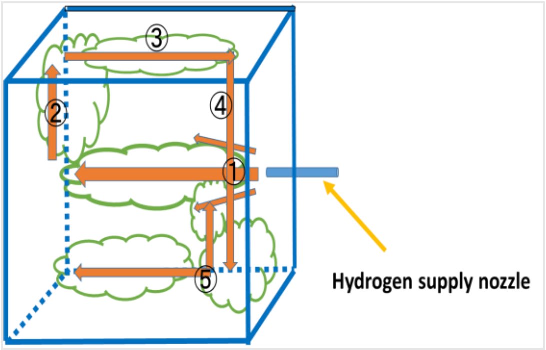


Figure 7. Diagram showing hydrogen behaviour with 6mm nozzle

### 3.3 Verification of Initial Hydrogen Diffusion by Hydrogen Visualization Sheet

Experiment were conducted to visually observe the condition of hydrogen diffusion near the nozzle by using a hydrogen visualization sheets which manufactured by Atsumitec Corporation. Those turn transparent by reacting with hydrogen. The diffusion angle did not change according to the hydrogen supply time, but it changed by the diameter of the nozzle. The state of transparency was clearly confirmed for longer supply time.

For the experiment, the container shown in Figure. 3 was used. The experiment's environment is shown in Figure. 8. Hydrogen was supplied at 40 L / min for 4 seconds. Experimental results using 1 mm & 6 mm nozzles are shown in Figures 9 & 10.

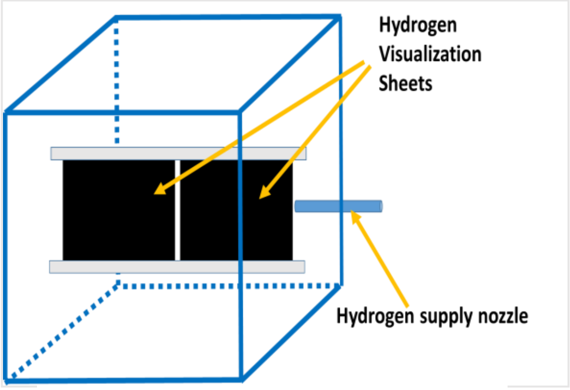


Figure 8. Placement of hydrogen visualization sheets

Figure 9. Hydrogen behaviour near the 1mm nozzle with red line

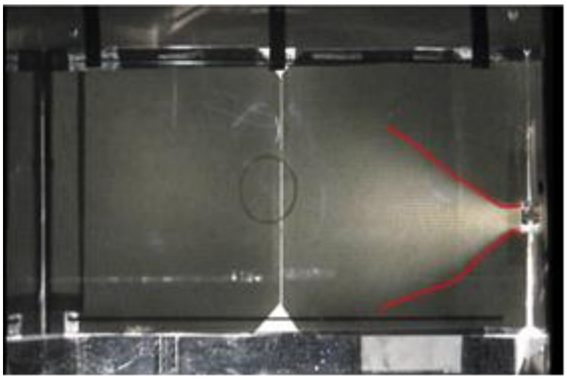


Figure 10. Hydrogen behaviour near the 6mm nozzle with red line

As a result, the experiment using the nozzle with the diameter of 1 mm diffuses larger angle than 6 mm. That is, when 1mm nozzle was used, hydrogen diffused in a wide range inside the vessel, and this result correspond with the result of Raman scattering light measurement which is a stable transition at nine positions.

## 4.0 IMPROVEMENT POSSIBILITY OF RAMAN SENSOR

### 4.1 Measurable Distance

Raman scattering lights are very weak intensity. Therefore, it is necessary to collect by the Fresnel lens, and amplify the light by the PMT in order to fulfil the function of the sensor. If leakage of hydrogen is assumed and a conventional detector is not installed, from the viewpoint of safety, leakage should be detected as far as possible by man. In the sensor of Figure 2, the measurement from 3 to 4 m was the limit. Then, new sensor was developed by improving a Fresnel lens size 15cm to 30 cm diameter that can detect hydrogen from a long distance. A new sensor is shown in Figure 11.

Figure 11. New Raman sensor to measure hydrogen from a distance away

### 4.2 Experimental

It is necessary to be able to detect Raman scattered light of Nitrogen, in order to obtain the concentration of hydrogen. To confirm the performance of the new sensor, the signal intensity of Nitrogen Raman scattered light was compared with the previous one. By changing the focus of this sensor, it is possible to obtain a signal on the laser optical axis. The result of distance measurement of the nitrogen Raman signal is compared with the previous sensor and shown in Figure 12.

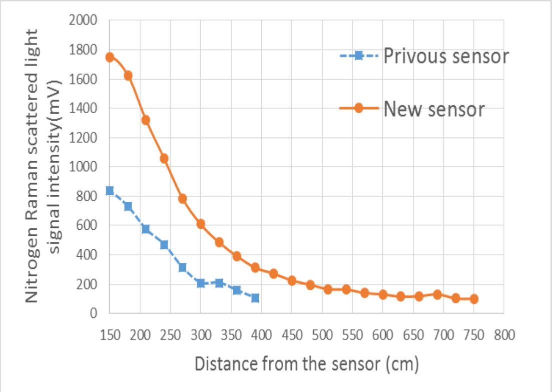


Figure 12. Performance comparison of sensors by strength of Nitrogen Raman signal

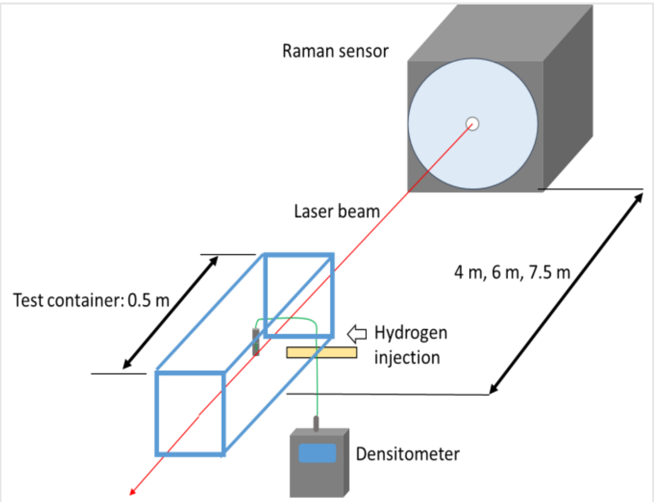


Figure 13. Experimental environment of new sensor

Experiment was conducted using by a new test vessel (50 cm (W) x 20 cm (H) x 20 cm (D)). The state of the experiment is shown in Figure 13. The hydrogen Raman signal intensity on the optical axis was measured after supplying hydrogen at 2 L / min, and 4 L / min for 40 seconds. This measurement was carried out by moving the measurement container position 4 m, 6 m, and 7.5 m. At the same time, the hydrogen concentration is measured by a thermal conduction type sensor. The measurement results are shown in Figure. 14, 15, and 16. For comparison, measurement was carried out when hydrogen was not supplied.

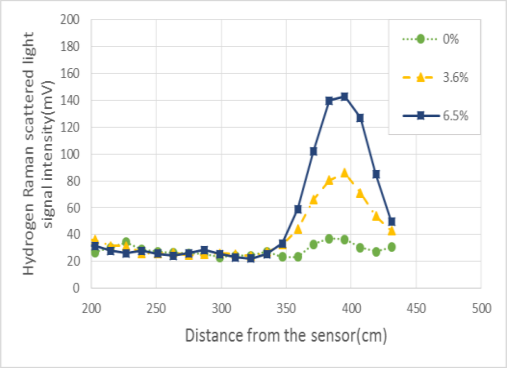


Figure 14. Hydrogen Raman signal intensity on laser optical axis when measuring container is installed at 4 m point

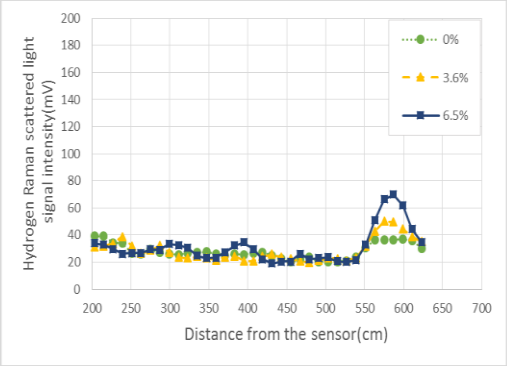


Figure 15. Hydrogen Raman signal intensity on laser optical axis when measuring container is installed at 6 m point

The hydrogen Raman signal becomes smaller as it goes away from the sensor, and the signal becomes larger as the concentration of hydrogen by the thermal conduction sensor becomes larger. The reason why the signal increases also in the case of 0% is that the laser light hits the container, and it is presumed that the fluorescence is also detected.

From the result in Figure. 16, hydrogen Raman signal is found from 7.5 m away. These result show detecting hydrogen from 7.5m away is available.

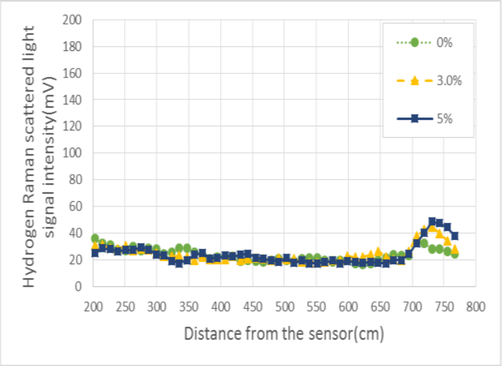


Figure 16. Hydrogen Raman signal intensity on laser optical axis when measuring container is installed at 7.5 m point

## 5 CONCLUSIONS

Simulation is effective way for predicting hydrogen behaviour, but it is also important to conduct real measurement. In conventional sensors, hydrogen behaviour in space could not be measured without contact. There is an infrared sensor as one of gas sensors, but hydrogen is not suitable because it has a low infrared absorption rate, also it cannot measure distances to gas and concentration change. 5) From these experimental results, observation of hydrogen behaviour by Raman scattering light measurement and its development possibility were confirmed. Unlike the infrared sensor, Raman scattering light sensor can get the data not only the gas concentration but also the gas distribution and time. Since hydrogen is the lightest and risky gas, conventional gas safety measures facilities may be inadequate. It is necessary to choose the most appropriate method of hydrogen detection according to the time and location. In the case of the Raman sensor, hydrogen can be detected from a safe location where sensors are not installed, so it is considered to be useful. Moreover, by using a method other than CFD, it is possible to estimate hydrogen behaviour by actual measurement utilizing the rapid response speed. In addition, this sensor can be used not only for hydrogen but also for another type of gas measurement such as methane. In the future, development of practical Raman sensors will be promoted by improving the measurement distance and removing fluorescence noise.

## 5 REFFRENCES

1. Asahi, I., Sugimoto, S., Yejima, S., Y. Ninomiya, H, 2009, “Remote measurement of hydrogen concentration distribution,” Shikoku Research Institute INC, HESS, Proceedings of the 30th Hydrogen Energy Association, pp. 89-92.

2. Ishikawa, H., and Fukui, K., 1999, “Hydrogen Gas Sensors,” Hydrogen energy system, Vol. 24, No. 2.

3. Raymond M. Measures; Laser Remote Sensing: Fundamentals and Applications, Krieger Publishing Company (1992)

4. Tamnaka, T., Inoue, M., Matuo, D., Kudou, K., Nakamoto, A., Ninomiya, H., 2015, “Development of Remote Measuring Equipment for Concentration and Location of Various Gases by LASER,” Japan Society for safety Engineering Vol.54 No.6 pp. 506-511.

5. Kikugawa, T., Kimura, K., Suzuki, T., Mori, H., and Samejima, T., 2006, “Laser-Based Remote Gas Detector,” Anritsu Technical, No. 82, pp. 66-71.