

# APPLICATION OF LASER INDUCED FLUORESCENCE TECHNIQUE FOR ENVIRONMENTAL DETECTION IN COAL FIRED POWER PLANT

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*Abstract: The novel sensing technique using laser induced fluorescence (LIF) for environmental detection to measure carbon monoxide and alkali vapor in the exhaust gas from the coal fired thermal power plant has been developed. High accuracy and short measurement time indicate a possibility of in-situ environmental detection in the real thermal power plant.*

*Keywords: LIF, Carbon Monoxide, Alkali*

## 1 INTRODUCTION

In coal fired power plants, environmental detection has become increasingly important to improve plant efficiency and monitor the life of the plant components. Authors have developed novel sensing technique using laser induced fluorescence (LIF) through Japanese national research project sponsored by MITI. In this paper, the laboratory experimental results to detect carbon monoxide and alkali vapor are presented. The effect of operating parameters such as temperature, pressure and gas contents on LIF signal was studied. And accuracy, measurable lower limit and measurement time were evaluated quantitatively in the simulated gas condition of the real plant.

## 2 NECESSITY OF ENVIRONMENTAL DETECTION IN POWER PLANT

Carbon monoxide is an important index to assess the combustion state in the conventional thermal power plant. Two-dimensional distribution of CO concentration across the boiler economizer outlet section is strongly dependent upon the combustion state of geometrically corresponding burner. Combustion tuning is generally carried out by adjusting each burner with CO distribution measured by traverse gas sampling which takes much time. To measure it rapidly and save time for combustion tuning, real time monitoring of CO distribution is needed.

Alkali vapor concentration is an important index to assess the life of the gas turbine blade from the viewpoint of high temperature corrosion in the advanced coal fired combined cycle plant such as PFBC (pressurized fluidized-bed combustion) unit. Type II hot corrosion in PFBC gas turbine blade could be caused by deposition and condensation of alkali vapor entrained in flue gas.<sup>[1],[2],[3],[4]</sup> Even a small amount of alkali vapor would give significant influence on corrosion of the gas turbine. It was reported that the alkali vapor concentration should be suppressed to less than 24 ppbwt (Na+K) for the conventional oil fired gas turbine to prevent hot corrosion caused by alkali sulphate attack.<sup>[2],[5]</sup> To ensure the life assessment of PFBC gas turbine, various alkali vapor measuring techniques that can detect such a low concentration have been developed.<sup>[6],[7],[8],[9],[10],[11]</sup>

## 3 LABORATORY EXPERIMENTS

### 3.1 Experimental apparatus

Prior to the laboratory experiments, the pilot test furnace was fabricated which could simulate combustion gas environments in actual coal fired power plants completely. Figure 1 illustrates the flow diagram of the test furnace which could be operated with the condition of max. 1.4 MPa X max. 1000. Nitrogen, oxygen, carbon dioxide, carbon monoxide and sulphur dioxide were supplied from gas cylinders through mass flow controllers. Alkali vapor was generated by heating the graphite felt with an electric heater, in which the alkali solution was soaked. Generated alkali vapor was supplied by nitrogen as a carrier gas. Sulphur trioxide was generated by converting

sulphur dioxide through the catalyst. Various gases were collected to the electric furnace, in which the pressure, temperature and gas contents were controlled to simulate the actual boiler environment.

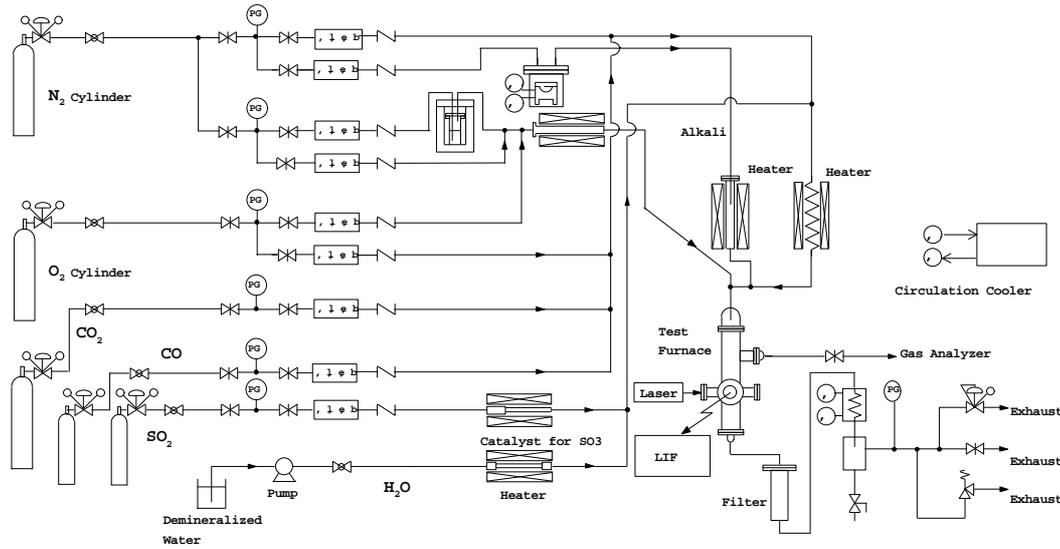


Figure 1. Flow diagram of the Test Furnace

Figure 2 shows the arrangement of LIF system. Nd:YAG/Dye Laser was used as the light source and the fluorescence was detected by the photo-multi tube with gate function. Laser wavelength and optical filter in front of the detector were changed for each gas species. Laser equipment and the detector were synchronized by the pulse generator. Detected signal was integrated with the analog boxcar type integrator and monitored by the oscilloscope.

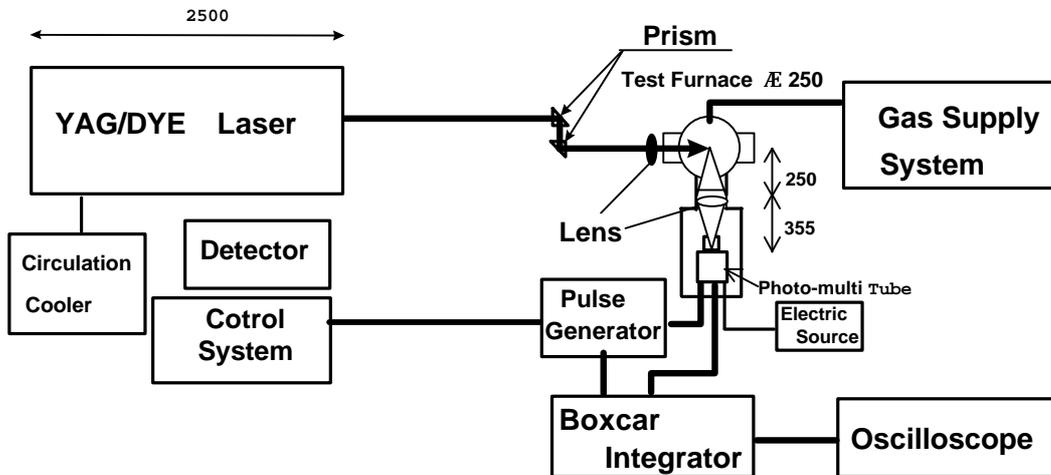


Figure 2. Arrangement of LIF system

### 3.2 Experimental procedures and test conditions

Laser light was inserted and focused towards the measuring point inside the test furnace through the optical window equipped on the test furnace in which the actual boiler exhaust gas was simulated. The fluorescence generated from the target gas was focused towards the detector through the another optical window. Fluorescence detection technique using two-photon absorption was applied to monitor carbon monoxide. Alkali vapor was measured by detecting fluorescence signal through the photo-multi tube by induced photo-fragmentation technique. The test conditions used in the laboratory experiments are shown in Table 1. The concentration of carbon monoxide and alkali vapor were measured by the authorized infrared absorption analyzer and the flame atomic emission spectroscopy method, respectively, together with the laser measurements for the purpose of calibration. This alkali vapor analysis had been developed and verified by authors through the measurement in the real PFBC plant.<sup>[8],[9]</sup>

**Table 1.** Test conditions for the laboratory experiments

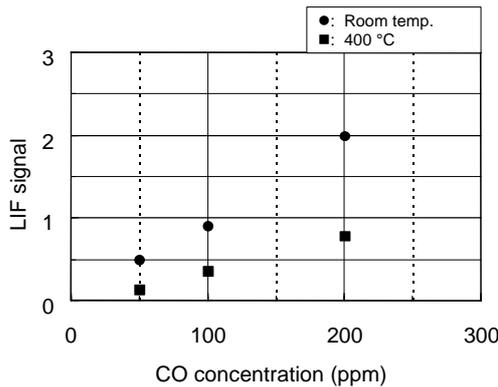
Gas Species		CO	Alkali (Na)
Concentration		10~200ppm	500~500 ppb
Pressure (MPa gauge)		0	0~1.4
Temperature (°C)		200~500	700~1000
Gas Composition	O <sub>2</sub> (%)	0~3.2	
	CO <sub>2</sub> (%)	0~14	
	H <sub>2</sub> O (%)	0~10	
	N <sub>2</sub> (%)	Balance	

## 4 EXPERIMENTAL RESULTS

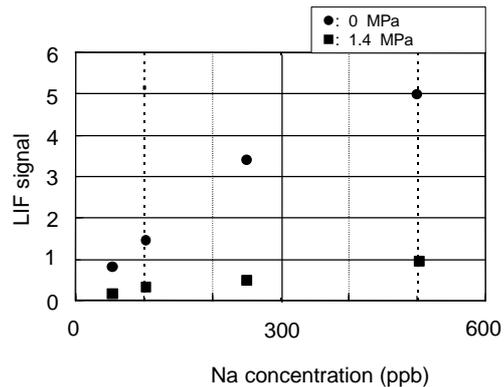
### 4.1 Fundamental test of LIF wavelength

Although there are a lot of reports of measuring nitrogen monoxide for combustion monitoring by LIF, there are a few of reports to detect carbon monoxide by LIF. [12], [13], [14] In this test, we tried to find out the induction wavelength of carbon monoxide in the atmospheric pressure and high temperature condition. Figure 3 shows the relation between LIF signal versus CO concentration after 300 times of integration which was obtained by the laser wavelength of 230.1 nm with CO - N<sub>2</sub> balance gas condition. It is observed from the figure that the relation is a linear one and suggests LIF signal of CO could be obtained properly.

It has been reported by some researchers [10], [11] that induced photo-fragmentation (LIPF) is the most effective measurement technique to detect vapor-state alkali species, which was also used in our experiments. LIPF technique could fragment Na Cl and induce Na simultaneously by the laser energy. In this test, we tried to find out the induction wavelength of vapor-state alkali in high pressure and temperature condition.(1.4 MPa X 850) The relation between LIF signal versus Na Cl concentration after 300 times of integration is shown in Figure 4 which was obtained by the laser wavelength of 210 nm with Na Cl - N<sub>2</sub> balance gas condition. It is observed from the figure that the relation is linear both for atmospheric and high pressure condition, and suggests LIF signal of NaCl could be obtained properly, even though LIF signal would decrease by quenching effect in the high pressure condition.



**Figure 3.** Relation between LIF signal versus CO concentration

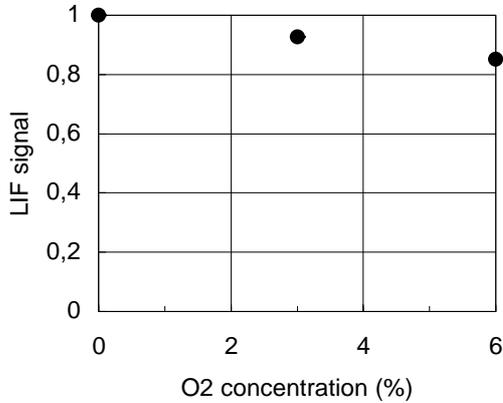


**Figure 4.** Relation between LIF signal versus Na concentration

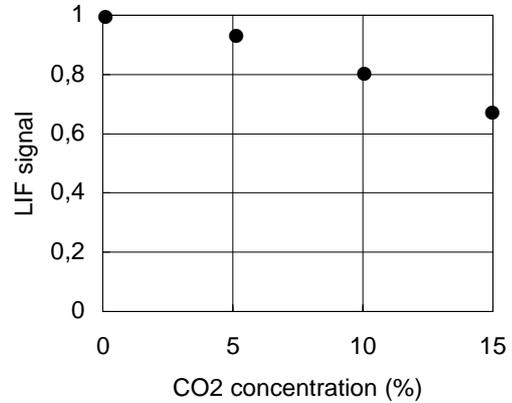
### 4.2 Characteristic test for various operation parameters

Characteristic test using the test furnace was conducted by varying the operation parameters such as gas content, temperature and pressure. Figure 5 – 8 show experimental results for CO. Figure 5 is a relation between LIF signal of CO versus O<sub>2</sub> concentration by changing oxygen content for the base condition. (Base condition: 0MPa, 400, CO 100ppm - O<sub>2</sub> 3.2% - CO<sub>2</sub> 14% - H<sub>2</sub>O 10% - N<sub>2</sub> balance) Plotted data is the average value for three times of measurements and error-bar shows the normalized deviation. The relation between LIF signal of CO

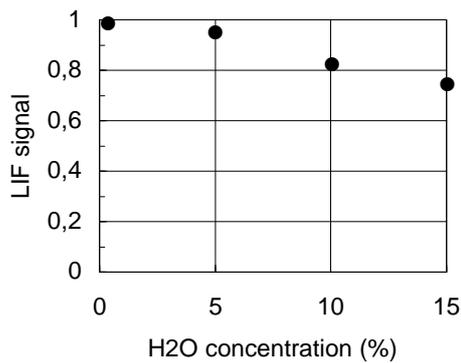
versus CO<sub>2</sub> concentration and H<sub>2</sub>O concentration are shown in Figure 6 and Figure 7, respectively. These results suggest that LIF signal of CO could be slightly affected by other gas concentrations by their quenching effects. Figure 8 shows a relation between LIF signal of CO versus temperature. It is observed that the effect by temperature on LIF signal of CO would be small. Based on the parameter experiments of CO, it is suggested that the allowance caused by variation of operating parameters must be considered for the measurement data by LIF although the operating parameters would be comparatively stable in the actual boiler.



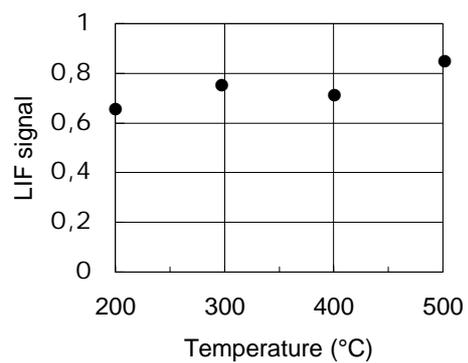
**Figure 5.** Relation between LIF signal of CO versus O<sub>2</sub> concentration



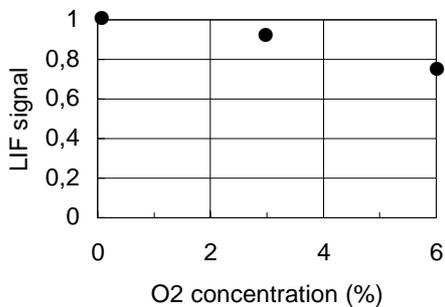
**Figure 6.** Relation between LIF signal of CO versus CO<sub>2</sub> concentration



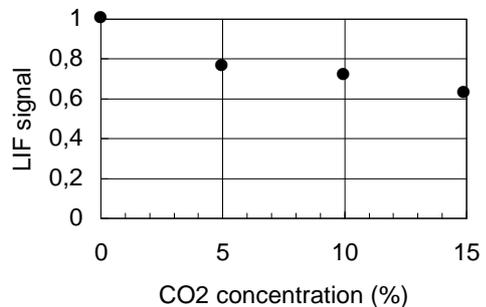
**Figure 7.** Relation between LIF signal of CO versus H<sub>2</sub>O concentration



**Figure 8.** Relation between LIF signal of CO versus temperature



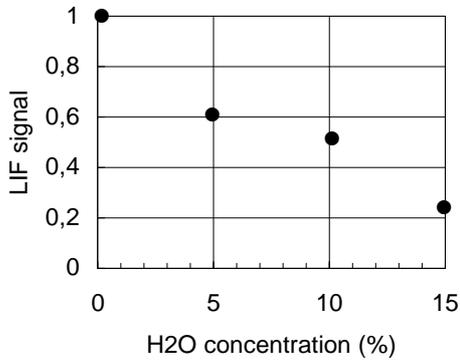
**Figure 9.** Relation between LIF signal of Na versus O<sub>2</sub> concentration



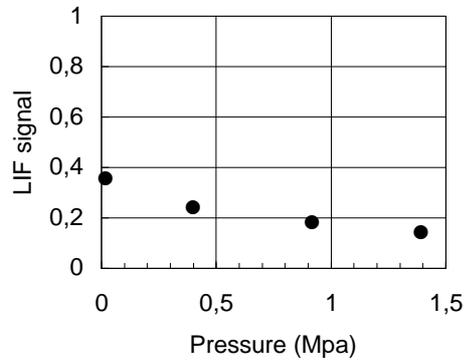
**Figure 10.** Relation between LIF signal of Na versus CO<sub>2</sub> concentration

Experimental results which indicate the effect of operating parameters on alkali (NaCl) vapor measurement are

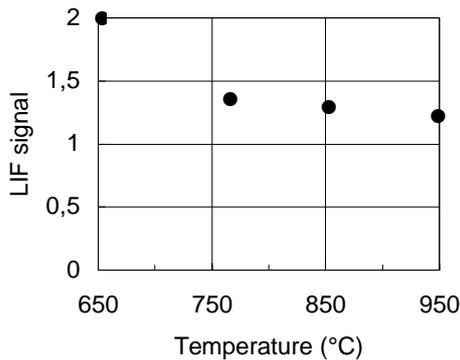
shown in Figure 9-13. Figure 9 is a relation between LIF signal of Na versus O<sub>2</sub> concentration for the base condition. (Base condition : 1.4MPa, 850, NaCl 250ppb - O<sub>2</sub> 3.2% - CO<sub>2</sub> 14% - H<sub>2</sub>O 10% - N<sub>2</sub> balance) Figure 10 and Figure 11 show the relation between LIF signal of Na versus CO<sub>2</sub> concentration and H<sub>2</sub>O concentration, respectively. The relation between LIF signal of Na versus operating pressure and temperature are shown in Figure 12 and 13, respectively. These results reveal that the effect of the variation of operating parameters on LIF signal of Na should be much bigger compared to that for CO and the proper calibration procedure is necessary for the alkali measurement.



**Figure 11.** Relation between LIF signal of Na versus H<sub>2</sub>O concentration



**Figure 12.** Relation between LIF signal of Na versus pressure



**Figure 13.** Relation between LIF signal of Na versus temperature

#### 4.3 Verification test in the simulated environments

Accuracy, measurable lower limit, response time and measuring stability were investigated in the simulated environmental condition using the test furnace. Figure 14 shows the relation between LIF signal and CO concentration in the simulated gas condition. (OMP<sub>a</sub>, 400, CO 10-200ppm - O<sub>2</sub> 3.2% - CO<sub>2</sub> 14% - H<sub>2</sub>O 10% - N<sub>2</sub> balance) It is observed that the relation indicates almost linear even in the real gas composition and the deviation from the linear line was less than 4.8%. And measurable lower limit which could be defined as S/N = 1 was 1.4ppm for 300 times of integration and was 0.7ppm for 1000 times of integration, respectively. Response time defined as required time from the beginning of measurement until LIF signal would become stable, was approx. 50 sec for 300 times of integration and was approx. 130 sec for 1000 times of integration, respectively. Measuring stability defined as variation of LIF signal during one hour of continuous measurement was 3.7%. These specifications required for practical measurement in real plants show satisfactory results.

Figure 15 shows the relation between LIF signal and Na concentration in the simulated gas condition. (1.4MPa, 850, NaCl 50-500ppb - O<sub>2</sub> 3.2% - CO<sub>2</sub> 14% - H<sub>2</sub>O 10% - N<sub>2</sub> balance) It is observed that the relation indicates almost linear even in the real gas composition and the deviation from the linear line was less than 3.3%. And measurable lower limit was 3.1ppb for 300 times of integration and was 1.5ppb for 1000 times of integration, respectively. Response time for alkali measurement was approx. 50 sec for 300 times of integration and was approx. 130 sec for 1000 times of integration, respectively. To obtain the lower limit of 1ppb, total integration of 2240

times, which corresponds to the response time of 300 sec, is necessary. And measurement stability for alkali measurement was 4.6%. Satisfactory results were verified for alkali measurement by LIPF.

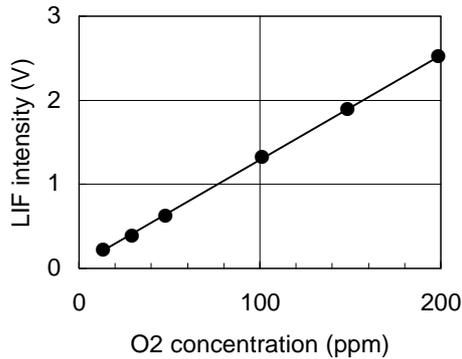


Figure 14. Relation between LIF signal versus CO concentration

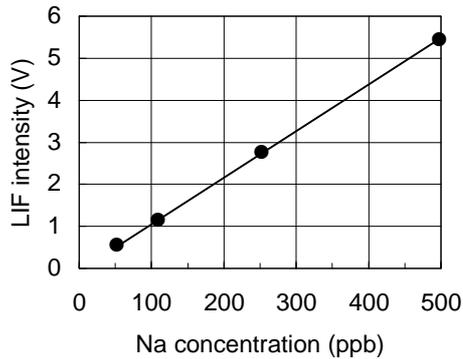


Figure 15. Relation between LIF signal versus Na concentration

## 5 CONCLUSION

The following important results obtained through the laboratory experiments suggests a possibility that the novel sensing technique using laser could be applied to in-situ environmental detection in the thermal power plant.

- 1) Carbon monoxide could be detected by two-photon LIF technique stably in the simulated environment of coal fired boiler combustion gas. (400, 0 MPa, O<sub>2</sub> 3.2% - CO<sub>2</sub> 15% - H<sub>2</sub>O 10% - N<sub>2</sub> balance) with the induction wavelength of 230.1 nm.
- 2) Alkali vapor could be detected by induced photo-fragmentation technique stably in the simulated environment of pressurized fluidized bed combustion gas. (850, 1.4 MPa, O<sub>2</sub> 3.2% - CO<sub>2</sub> 15% - H<sub>2</sub>O 10% - N<sub>2</sub> balance) with the induction wavelength of 210 nm.
- 3) Variation of operation parameters such as gas composition, pressure and temperature could affect LIF signal because of their quenching effects. The degree of the effect is small for CO detection since operation parameters in real plants are stable. However, for alkali vapor detection, the effect by pressure is big and needs proper calibration procedure.
- 4) For CO detection, measurable lower limit was 1.4 ppm for 300 times of integration, which corresponds to the response time of approx. 50 sec. The accuracy and the measuring stability was 4.8% and 3.7%, respectively, and show satisfactory results for practical measurement.
- 5) For alkali detection, measurable lower limit was 1.5 ppb for 1000 times of integration, which corresponds to the response time of approx. 130 sec. The accuracy and the measuring stability was 3.3% and 4.6%, respectively, and show also satisfactory results for practical measurement.

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