

LIBS APPLICATION FOR THERMAL PLANTS MONITORING

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Abstract: A LIBS technique has been applied to detect alkali metals under high pressure and high temperature conditions, and an automated LIBS unit has been developed and applied in a month-long monitoring experiment. The results were compared to those obtained using the conventional sampling method, showing good agreement. LIBS can detect Na and K at ppb levels, even under the high pressure conditions appearing in PFBC and IGCC thermal power plants. LIBS is capable of 1 minute detection time, as compared to the 20 hour sampling time required by the conventional method, and offers various merits as a tool for actual plant monitoring.

Keywords: LIBS, Alkali Metals, Corrosion, Real Time Monitoring

1 INTRODUCTION

It has become increasingly important to monitor plant condition factors in order to improve the operation of industrial plants, and improved on-line monitoring techniques for plant controlling factors are necessary to enhance the controllability of overall plant operations. Alkali metals such as Na and K cause corrosion and deposition in power generation turbines, and ppb level detection is required by safety regulations.

Laser techniques make it possible to monitor these parameters because of their high sensitivity. Because of its strong signal intensity and the simplicity of its apparatus, laser induced breakdown spectroscopy (LIBS) is suitable for composition measurement in gas, liquid, and solid materials [1] [2] [3]. This study demonstrates ppb level detection of Na and K under high temperature and high pressure conditions appearing in PFBC and IGCC plants. Long term monitoring is also demonstrated under actual gas combustion conditions in order to confirm practical plant applicability.

2 LIBS

The LIBS process is shown in Figure 1. A laser beam is focused onto a small area, producing hot plasma. The temperature of the plasma can reach 10,000 K to 20,000 K and the material inside the measurement area is quickly atomized. The atomized material produces an emission dependent upon the material content. The resulting signal is a function of material components, and concentration can be detected by means of analysis. In this study Na and K in a gas phase were detected in the ppb range of detection sensitivity.

The LIBS signal is also a function of the plasma temperature and plasma area produced in the LIBS process. In this study N emission was monitored simultaneously with the Na and K LIBS signal to calibrate these effects.

3 EXPERIMENTAL APPARATUS

An automated LIBS analyzer was developed for actual plant monitoring applications. This unit can be used even in field applications. Alkali metal detection was tested under high temperature and high pressure conditions, and the unit was also applied in a corrosion test combustor for a long term monitoring experiment.

3.1 High Temperature and High Pressure Furnace

Figure 2 (a) illustrates the high temperature and high pressure furnace that was used. This furnace can produce an alkali-added gas in the 300K -1000K and 0.1MPa-3MPa temperature and pressure ranges. Figure 2 (b) shows the optical setup of the automated LIBS unit. Na and K LIBS signals are detected using an ICCD camera. These signals are calibrated by the N LIBS signal which is detected by a gated photomultiplier for correction of the plasma temperature and plasma area.

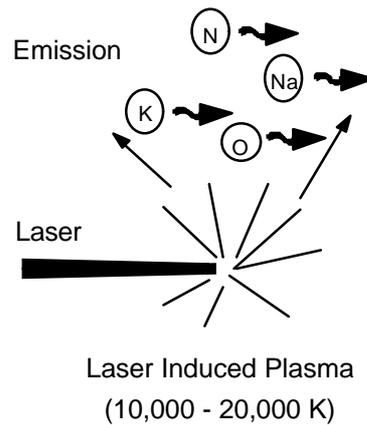
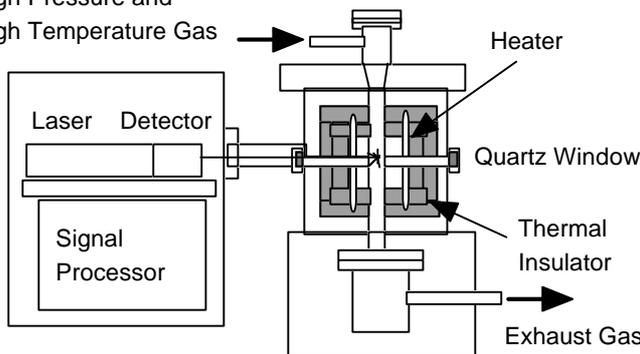


Figure 1. LIBS Plasma Process.

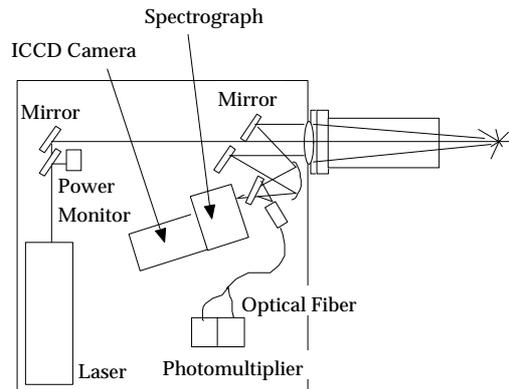
3.2 Corrosion Test Combustor

Figure 3 shows the corrosion test combustor, which was used for the long term monitoring test. This combustor was an oil burner to produce 400-1300K gas conditions at a 280m³N/h flow rate. The alkali components are added within the combustion area to produce a constant alkali concentration. A sampling unit (JIS-K8808,JIS-K0095) was also included to confirm the real alkali concentration in the measurement area.

High Pressure and High Temperature Gas

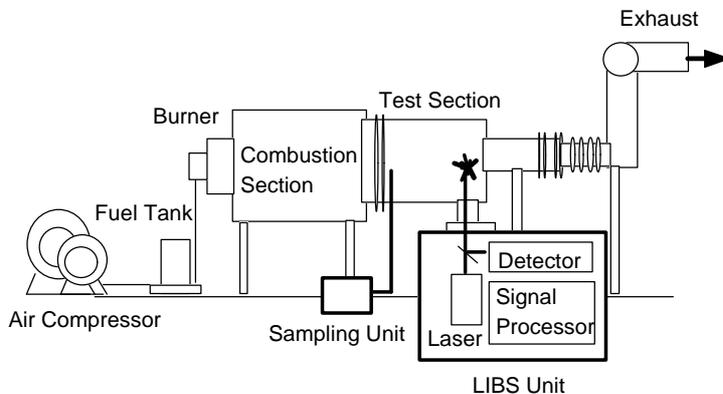


(a) High Temperature and High Pressure Furnace



(b) Optical Setup in LIBS Unit

Figure 2. High Temperature and High Pressure Test Apparatus



(a) Corrosion Test Combustor



(b) Photo of LIBS Unit

Figure 3. Long Term Na Monitoring Test Apparatus.

4 RESULTS AND DISCUSSION

In LIBS plasma process, the atom emission signals appear after a time delay following laser emission. Detection parameters, such as delay time and gate width, were changed according to the measurement field temperature and pressure conditions. Figure 4 shows the Na, K, and N LIBS spectra. N signals were used for the calibration of the Na and K concentration measurements.

4.1 High Pressure and High Temperature Application

Under high temperature and high pressure conditions, LIBS signal characteristics change due to the collisional plasma quenching. Figure 5 shows the Na S/N ratio according to the delay time. As pressure increases plasma quenching because of the high collisional rate, shorter delay times must be chosen to obtain reasonable LIBS signals. Even under high pressure conditions, the S/N ratio is almost the same as that at low pressure. High density results in both high signal and high noise. Plasma quenching also causes the LIBS intensity to decrease. The detection limit is about the same up to 3 MPa, and reaches the ppb level for both Na and K.

Figure 6 shows the LIBS signal intensity at different Na and K input concentrations. These results show the good linear relation between the input Na and K concentration and their LIBS signal intensities.

Table 1 shows the Na, K, and N signal detection conditions. Na and K have almost the same delay time parameter, because the both atoms have almost the same upper states energy. On the other hand, N has a shorter delay time condition. The excited N atom that cause the N LIBS emission at 746.8nm is quenched much faster than those of Na and K because of the sharp temperature decrease in the plasma quenching process.

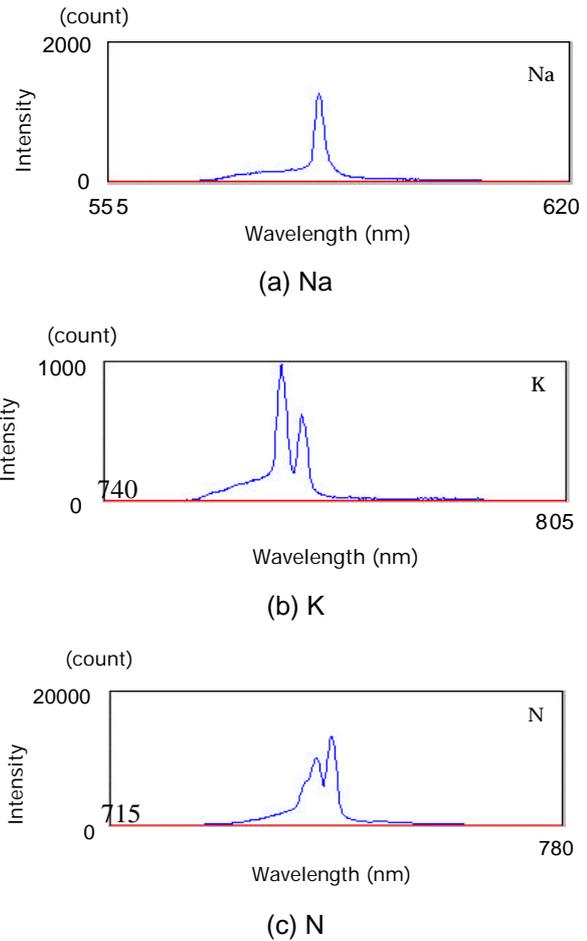


Figure 4. LIBS Spectra

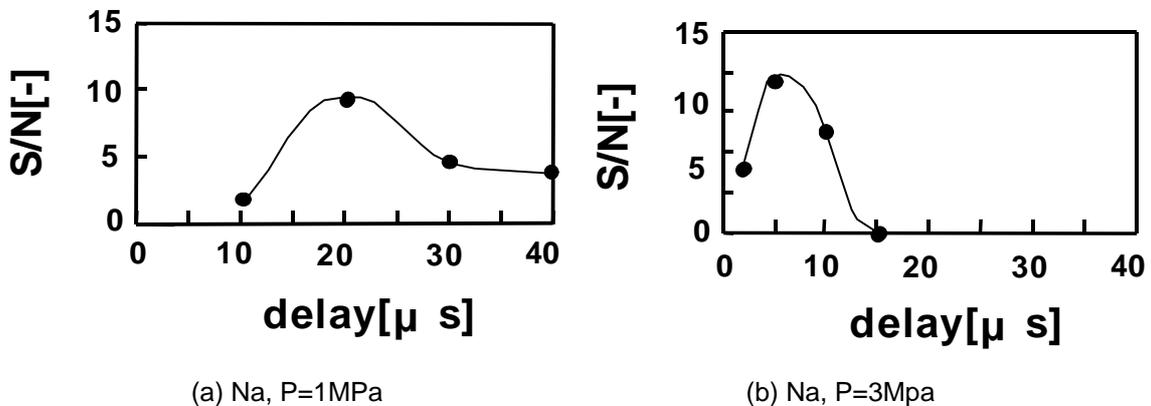
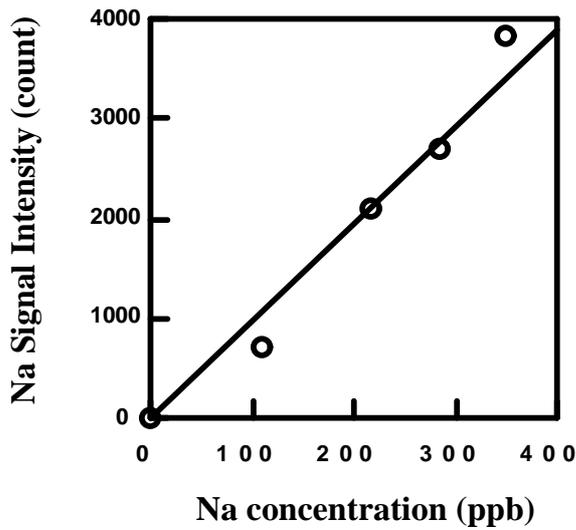
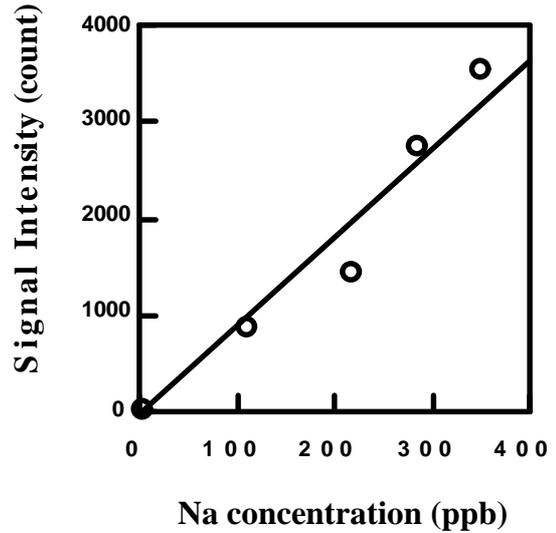


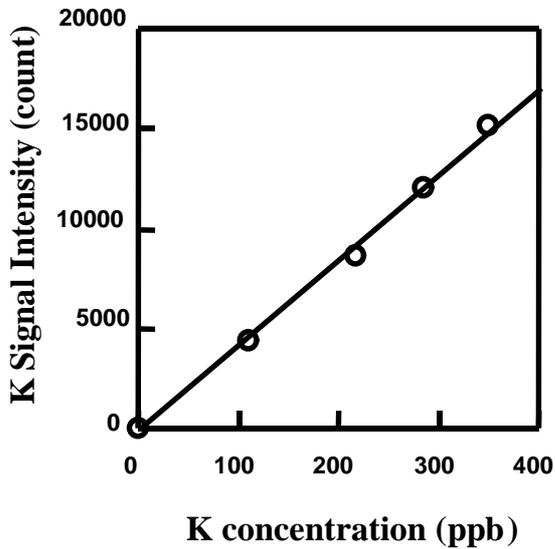
Figure 5. Relationship Between Delay Time and S/N Ratio



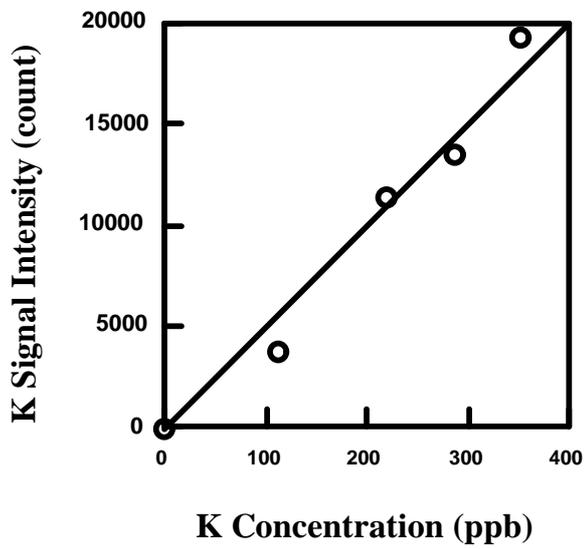
(a) Na, P=1MPa, T=870K



(b) Na, P=3MPa, T=870K



(c) K, P=1MPa, T=870K



(d) K, P=3MPa, T=870K

Figure 6. Relationship between LIBS Signal and Alkali Metal Concentration

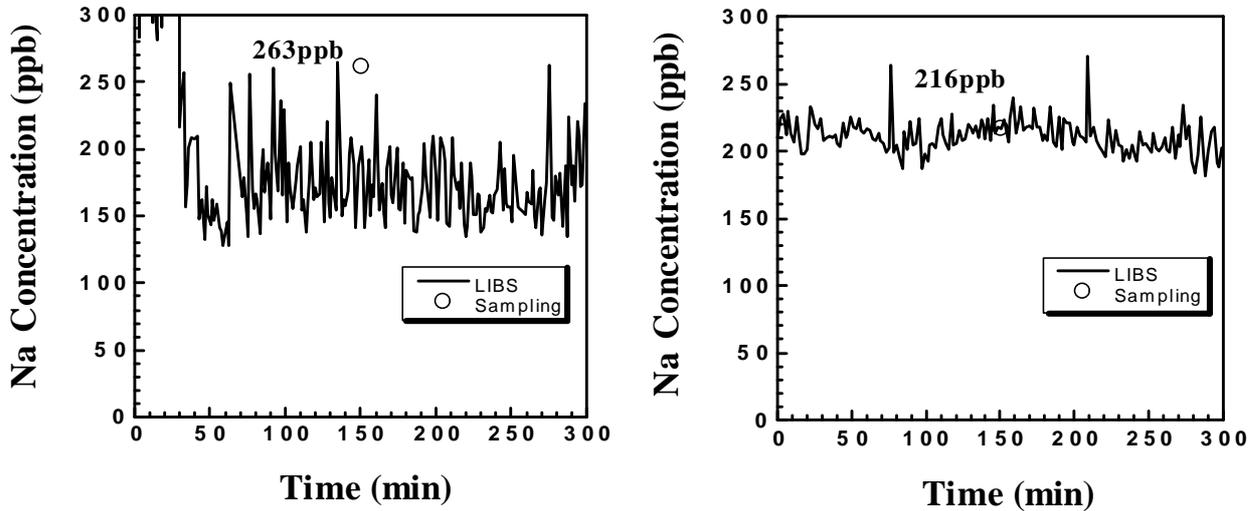
Table 1. Na, K, and N Signal Detection Conditions

Atom	Emission Wavelength (nm)	Upper state Energy (cm ⁻¹)	Delay Time 0.1 MPa (μs)	Delay Time 1Mpa (μs)	Delay Time 3MPa (μs)
Na	589.0	16973	100	20	5
K	766.5	13043	120	30	7
N	746.8	96751	4	0.7	0.3

4.2 Long Term Monitoring

The corrosion test combustor was used for a long term Na monitoring experiment. Background Na concentration was a few ppb and 10, 50, 100, 500 ppb Na input was added to the combustion gas to change the experimental conditions. The burner was operated continuously for about one month, and the LIBS unit was operated automatically using a computer for the same period of time. About a half of the input Na reached the measurement area.

Figure 7 shows the Na detection trend with and without N signal calibration under the same Na input conditions. Comparing the two results, N signal calibration reduces data fluctuation caused by the plasma condition change.



(a) Without N Signal Calibration

(b) With N Signal Calibration

Figure 7. Na Concentration Measurement Stability

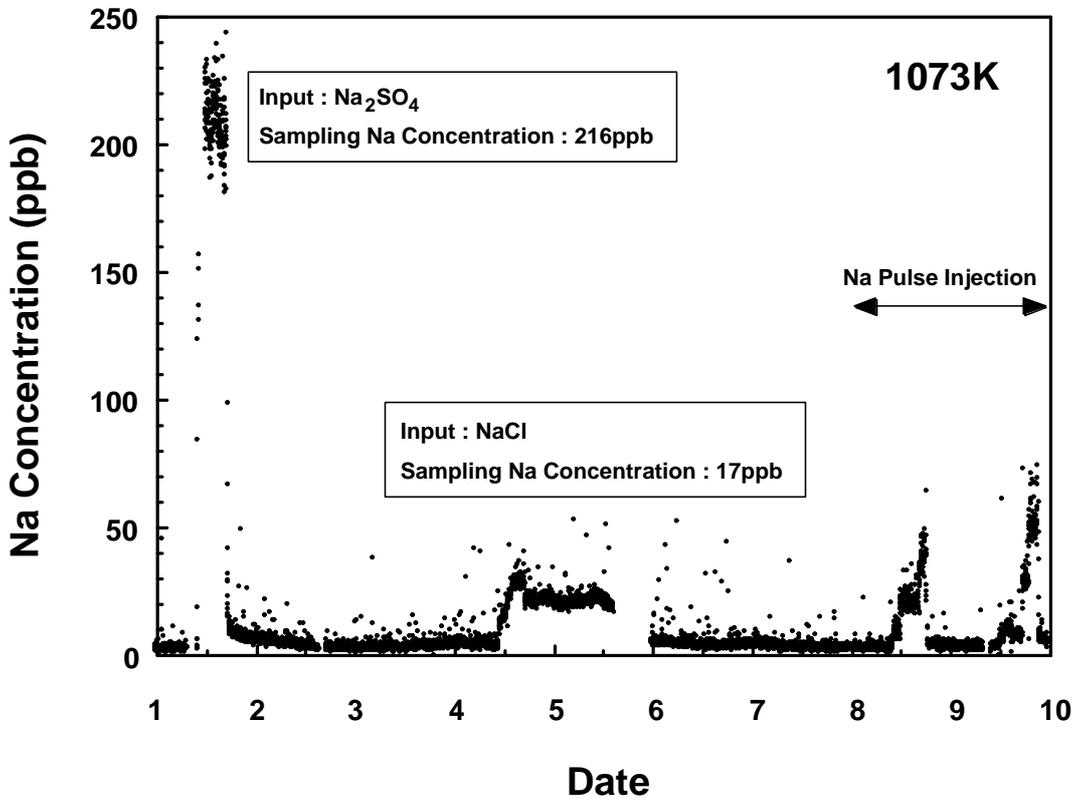


Figure 8. Long Term Monitoring Results.

Figure 8 shows the long term Na monitoring results. LIBS is capable of detecting the sharp rise just after the Na input because of the 1 minute detection time. The comparison between the LIBS and the sampling results is shown in Figure 9, and the LIBS-measured Na concentration agrees well with the results obtained by conventional sampling. Although the conventional sampling method requires 20 hours to monitor a few ppb of Na, LIBS can detect the same concentration within one-minute measurement time and exhibits an excellent monitoring capability.

5 CONCLUSION

LIBS was applied to several materials and its applicability was confirmed in a long-term test under actual gas combustion conditions. It shows better characteristics in terms of on-line capability and sensitivity compared to the conventional sampling method. Combined with solid state laser technology, LIBS appears likely to surpass the conventional method in various fields for improved control of plant performance.

ACKNOWLEDGEMENTS

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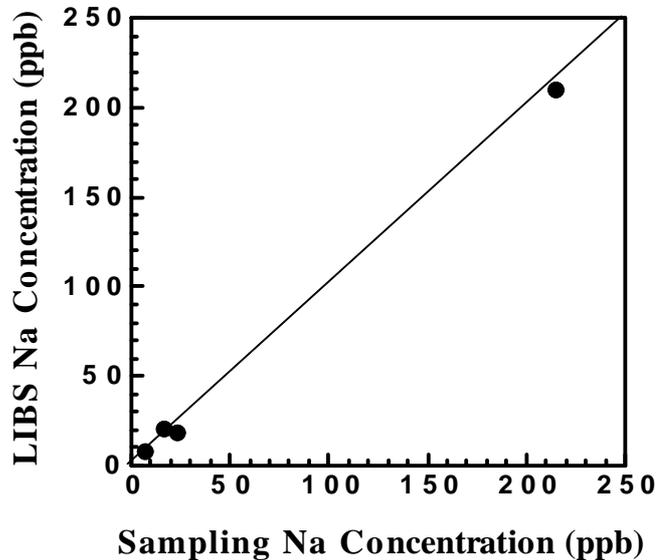


Figure 9. Comparison Between LIBS and Sampling Results.

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