Applications of Laser-Induced Breakdown Spectroscopy and Laser Breakdown Time-of-Flight Mass Spectrometry to Thermal Power Plants

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With the increasingly stringent energy and environmental requirements, it is necessary to improve the efficiency of coal combustion and to reduce the pollution emissions. The pollutants of trace heavy metals in exhaust result in the serious influence on environment and human. First step of the pollution control is the fast and precise measurement of pollutants. Laser-induced breakdown spectroscopy (LIBS) has a great potential application of on-line measurement in thermal power plant. The direct measurement of particles using LIBS was studied. The LIBS method was also improved to measure the gas phase trace species, as well as the combined method of LIBS and time-of-flight mass spectrometry (TOFMS). These results will be useful for the applications of LIBS and TOFMS.

Key Words: Laser-induced breakdown spectroscopy, Laser breakdown, Time-of-flight mass spectrometry, Thermal power plant, Applications

1. Introduction

With the increasingly stringent energy and environmental requirements, it is necessary to improve the efficiency of coal combustion and to reduce the pollution emissions.1,2 Fig. 1 shows the system of a coal-fired power plant and the necessary monitoring items. The coal and fly ash contents, especially unburned carbon in fly ash, are the important factors of efficient combustion. 2D temperature and concentration distributions in the boiler also play an important role. Fly ash produced during coal combustion is one of the sources of fine particles related to PM2.5. It is urgent to evaluate the heavy metal emission in exhausts.

The integrated coal gasification fuel cell combined cycle(IGFC) is a proven means in the next generation thermal power plant with the development of the combined power generation technologies.3 However, fuel impurities in these practical fuels could cause degradation of cell performance and affect system durability.4 The heavy metal contents in the fuel cell are important monitoring factors.

The traditional methods of coal analysis are off-line analyses consisting of sampling, sample preparation and measurement with time consumption. Several on-line analytical systems based on the absorption/scattering or stimulated emission methods haven’t been widely applied in the thermal power plants because of high cost, radiation, accuracy, etc. The unburned carbon in fly ash is measured according to the weight difference after combustion to determine the unburned carbon content, which lags a few hours. The trace heavy metals are the harmful materials in the thermal power plant, especially the Hg emission. Hg can be detected using laboratory and on-line analyses which feature time consumption and specific requirements for applications.

It is necessary to develop the on-line methods with high sensitivity, fast response and multi-elemental detection of coal, fly ash and trace species. Laser diagnostics has attracted a great attention in industries as the qualitative and quantitative detection techniques.5 Laser-induced breakdown spectroscopy(LIBS) is an analytical technique based on atomic emission spectroscopy to measure elemental composition. Time-of-flight mass spectrometry(ToFMS) is another appealing technique for the analysis of atomic and molecular ion signals with the increased sensitivity and rapid analysis features. LIBS and laser breakdown time-of-flight mass spectrometry(LB-TOFMS) were employed in the applications of thermal power plants.

Fig. 1 System of coal-fired power plant.
2. Theory

2.1 Laser-induced breakdown spectroscopy (LIBS)

In LIBS process, a laser beam is focused into a small area, producing hot plasma. The light corresponding to a unique wavelength of each element is emitted from excited atoms in the plasma. A calibration of the LIBS signal is necessary for quantitative analysis. Despite the fact that the LIBS processes involved are complex, the emission intensity from the atomized species can be described by the following equation with the assumption of uniform plasma temperature:

\[ I_i = n_i K_{ij} g_i \exp \left( \frac{-E_{ij}}{kT} \right) \]

In Eq. (1), \( I_i \) is the emission intensity of species \( i \), \( n_i \) is the concentration of species \( i \), \( K_{ij} \) is a variable that includes the Einstein A coefficient from the upper energy level \( j \), \( g_i \) is the statistical weight of species \( i \) at the upper energy level \( j \), \( E_{ij} \) is the upper level energy of species \( i \), \( k \) is the Boltzmann constant and \( T \) is the plasma temperature. There are several factors that affect \( I_i \), including plasma temperature, plasma non-uniformity, and matrix effects, etc. The appropriate correction factors must be contained in \( K_{ij} \) for quantitative results.

There are several plasma temperature correction methods such as the Boltzmann plot method using many emission lines to increase correction precision. Considering the system simplicity and real-time measurement capability, the temperature correction method employing emission pair from the same atom is preferable. It has been demonstrated the method is workable and satisfactory for practical applications.

2.2 Time-of-flight mass spectrometry (TOFMS)

In TOFMS system, a measured sample is introduced into a vacuum chamber. It is atomized and ionized by laser irradiation. The electric field potential is applied for acceleration of ions after ion generation. The accelerated ions enter the drift region with no potential difference and undergo uniform motion. Due to the law of energy conservation, the ions’ electric field potential is equivalent to their kinetic energy. The following formula is established by the energy conservation law:

\[ z e V = \frac{m (L/t)^2}{2} \]

In Eq. (2), \( z \) is the ionic valence, \( e \) is the elementary charge, \( V \) is the acceleration electric field potential, \( m \) is the ion mass, \( L \) is the ion distance of flight, \( t \) is the time of flight.

TOFMS is employed with several ionization processes, such as electrospray ionization (ESI), resonance enhanced multi-photon ionization (REMPI), laser breakdown, etc. Laser breakdown is combined with TOFMS to measure the trace element. The laser breakdown process consists of laser dissociation, multi-photon ionization, electron impact ionization, etc. At low pressure, i.e., less than 1 Pa, laser dissociation and multi-photon ionization processes become useful for the atomic detection.

3. Research of coal and fly ash measurements

The versatile and multi-elemental capability of LIBS have been demonstrated by the analyses of coal and mineral ores. The detectable elements include key inorganic components of coal, such as Fe, Ti, Al, Ca, Na, Cu, Zr, Nd, Yb, Ce, Sm, Dy and Gd, in addition to C and H. The detection limits depend on the particular element. Table 1 shows the detectable elements and the corresponding wavelengths in coal and fly ash.

Fig. 2 illustrates the schematic diagram of LIBS system in coal and fly ash measurements. The experimental setup was composed of laser, beam focusing system, measured sample, detection system and auxiliary devices. There are two types of measured samples including pellet and particle flow.

The sample pellets as the common specimen were prepared for LIBS measurement due to the higher homogeneity of solid sample than that of powdered counterparts. The binders were employed to bind the anthracite powder together to improve the repeatability. Results showed that the optimized binder of \( \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} \) with Si from the binder as the internal calibration element, can yield the overall best measurement precision and accuracy. In order to enhance the repeatability and precision of the fly ash elemental composition, specimens of various forms and different binders were employed for LIBS measurement. The fly ash and bottom ash employing collinear double pulse approach were also analyzed to address the influence of matrix effect on the calibration curves. LIBS has a great potential of on-line application. However, there are several problems to implement this purpose. The samples usually should be prepared as the solid specimens before measurement using LIBS, which cannot be applied for the online measurement.

LIBS has been applied for carbon content detection in fly ash, char and pulverized coal under high-pressure and high-temperature conditions without any sample preparation, which featured a detection time of less than 1 minute. The calibration difficulty of aerosol sample was surpassed by the temperature correction factors. This automated LIBS apparatus was

\[ \text{Table 1 Detection elements in coal and fly ash.} \]

| Atom  | Wavelength (nm) | Atom  | Wavelength (nm) |
|-------|-----------------|-------|-----------------|
| Ca    | 315.9, 393.9, 397.0, 422.7 | Na    | 589.0 |
| Mg    | 280.0, 285.0, 372.3-376.0 | Cu    | 766.5 |
| Fe    | 248.3, 260.9 | Zr    | 337.7 |
| Si    | 252.4, 288.4-9, 372.3-376.0 | Yb    | 279.6 |
| C     | 247.9 | Dy    | 386.9 |
| Al    | 309.6-9 | Gd    | 422.6 |
| Ti    | 453.5 | Sm    | 321.7 |

Fig. 2 Schematic diagram of LIBS system.
also in infancy and should be learned in detail, such as the CO
determination of global anthropogenic Hg emission. Hg behavior in coal-
Coal combustion in power plant constitutes the large share
effect on unburned carbon.

**Table 2 Standard deviation of LIBS measurement.**

| Concentration ratio | Signal stability (corrected %) | Signal stability (no correction %) |
|---------------------|-------------------------------|-----------------------------------|
| Fe$_2$O$_3$/SiO$_2$  | 5.7                           | 12.7                              |
| Al$_2$O$_3$/SiO$_2$  | 12.4                          | 14.6                              |
| CaO/SiO$_2$         | 17.1                          | 32.6                              |
| C/SiO$_2$           | 14                            | 28.1                              |

The fly ash and coal samples were measured to set up the
temperature correction factors under different experimental
conditions, such as delay time. The emission pair of $I_{Mg1}$ and
$I_{Mg2}$ was defined as the temperature indicator. The fluctuation of the concentration ratios of C/SiO$_2$, Al$_2$O$_3$/SiO$_2$, Fe$_2$O$_3$/SiO$_2$ and CaO/SiO$_2$ greatly reduced using the experimentally determined correction factors, as shown in Table 2. 

The quantitative measurement can be improved by choosing the appropriate plasma temperature range, i.e. $I_{Mg1}/I_{Mg2}$. The results at low plasma temperature showed better local thermodynamics equilibrium (LTE) condition with the accurate correction. Size-segregated coal and fly ash were detected employing the temperature correction method. 

A fully software-controlled LIBS system including LIBS apparatus and sampling equipment has been designed for on-line analysis of pulverized coal within 3 minutes. The coal particles in the form of descending flow were directly analyzed with the improved analysis approach. An automated prototype LIBS apparatus has also been developed for on-line analysis of unburned carbon in fly ash without the influence of the type of coal. The measurement accuracy for unburned carbon analysis is estimated to be 0.26%. These studies are still in infancy and should be learned in detail, such as the CO$_2$ effect on unburned carbon.

4. Research of trace species measurement

Coal combustion in power plant constitutes the large share of global anthropogenic Hg emission. Hg behavior in coal-
fired power plants has been studied extensively. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) have been applied to detect trace species with high sensitivity. However there is time consumption for the sample preparation. The trace species has been widely measured using LIBS and TOFMS. Fig. 4 shows the schematic diagram of trace species measurement including detection systems of LIBS and LB-TOFMS.

With the development of lasers and detection systems, LIBS has been applied in various fields including combustion, metallurgy, environment, etc. Environment field is one of the earliest and deepest applications of the monitoring of soil, air, and water.

LIBS was applied to detect the toxic metals of Be, Cd, Cr, Hg, and Pb in exhaust as a continuous emission monitor. The sampling method and data process have been improved to enhance the detection ability. The pressure and buffer gas effects have been also analyzed. The signal to noise ratio and resolution can be improved when decreasing the pressure. Due to the quenching of Hg emission at 253.7 nm in O$_2$, the effect of oxygen on Hg detection using LIBS was discussed in different plasma delay time, which is useful to understand the interactions between plasma and metal species for advancement of real-time monitors.

Short pulse width lasers, such as picosecond and femtosecond lasers, have been employed in LIBS technique. The ablation mechanisms of nanosecond, picosecond and femtosecond pulses are different. Short pulse width lasers allowed for a specificity of excitation that could yield LIBS signals more tightly correlated to particular species and showed significantly lower background emission than that of nanosecond laser.

The trace species were detected at low pressure using nanosecond and picosecond lasers under various conditions. Fig. 5 shows the typical LIBS spectra of Hg in air at low pressure using picosecond laser. These findings suggest the low pressure and short pulse LIBS performs the remarkable detect-
applied to measure the hydrocarbons and nanoparticle constit-
species using TOFMS is often ppb or less. TOFMS has been
ic and molecular ion signals. The detection limit of measured
surement characteristics and great progress for trace s pecies mea-
surement of trace species.
In order to measure the trace elements, the laser breakdown
process combined with TOFMS has been employed in the de-
tection of trace species. Fragmentation of partial break-
down is the major interference to target atomic ion signals.
Measurements employing breakdown induced by 532 nm and
1064 nm lasers display the results without interference of
fragmentations compared to that using 266 nm in the mass re-
gion of 30-300 m/z due to the higher photon energy, which in-
duces the photolysis occurring at lower laser power and partial
fragmentation. 532 nm breakdown ion signals increased com-
parison to 266 nm breakdown ion signals increased com-
pared to 1064 nm breakdown. The mass spectra of Hg$^+$ using
nano-second breakdown at 1064 nm is shown in Fig. 6. The
signal intensity of Hg$^+$ can be enhanced employing short
pulse width laser. Table 3 shows the Hg detection limits of
600 shots (1 min) using low pressure LIBS$^-$ and LB-TOFMS,
which can be enhanced using short pulse width laser.

5. Conclusion
LIBS and LB-TOFMS have been applied to measure the
contents of coal and fly ash, as well as the trace species. In
order to develop the on-line detection system, the direct mea-
surement methods of particles have also been discussed. The
trace species of gas phase were measured using low pressure
and short pulse LIBS and LB-TOFMS with the features of en-
hanced detection limit, which can improve the application and
detection ability in thermal power plants.

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