New Approach to Quantitative Analysis by Laser-induced Breakdown Spectroscopy

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been studied as the technique of choice in some particular situations like screening, in situ measurement, process monitoring, hostile environments, etc. Especially, LIBS can fulfill the qualitative and quantitative analysis for radioactive high level waste (HLW) glass in restricted experimental conditions [1]. Several ways have been suggested to get quantitative information from LIBS. The one approach is to use the absolute intensities of each element. The other approach is to use the elemental emission intensities relative to the intensity of the internal standard element whose concentration is known already in the specimen. But these methods are not applicable to unknown samples. In the present work, we introduce new approach to LIBS quantitative analysis by using H_α (656.28 nm) emission line as external standard.

2. Experimental

A plasma was generated by focusing a Nd:YAG laser (wavelength, 355 nm; pulse width, 6 ns; repetition rate, 20 Hz) onto Standard Reference Materials (SRMs) which contain trace elements in a glass matrix. The laser beam was focused using a 80 mm focal length plano-convex lens and 10 mJ laser pulse less than the threshold energy of air breakdown (14 mJ) was used to create plasma. The plasma emission was collected into the entrance slit of a Czerny-Turner spectrometer (focal length: 303 mm, 1200-line/mm grating, aperture: f/4) and emission spectra was recorded by intensified charge coupled device (ICCD) camera.

3. Result and Discussion

3.1 Optimal laser energy

The plasma initiated by focusing laser pulse onto the surface of glasses generates H_α emission whose source is ambient air. The laser energy was chosen lower than the threshold energy of 14 mJ for air breakdown.

The LIBS intensity of hydrogen line (H_α) at different laser energies is shown in Fig. 1. The emission intensity was increased as the laser energy was raised. The uncertainty of relative emission intensity was obtained by 5 replicate measurements.

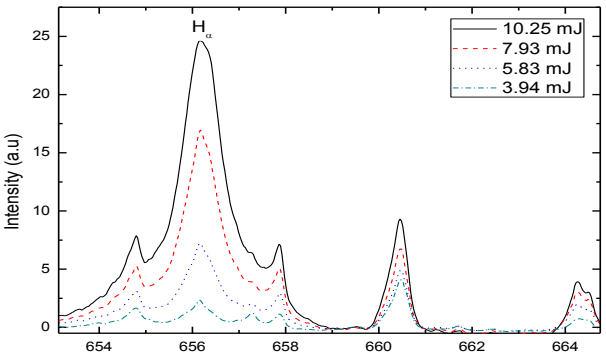

Fig. 1. LIBS spectra for hydrogen emission which was initiated by plasma of sample (SRM611)

When the incident laser energy was 10 mJ, the uncertainty was the lowest. Therefore this pulse energy was selected as optimal laser energy for further LIBS measurements.

3.2 Calibration curve

The spectral emission intensity is determined not only by the elemental concentration of the sample, but also by the properties of the plasma itself, which in turn depend on factors such as the characteristics of the excitation source (energy, power density, wavelength), the sample matrix and the surrounding gas. Furthermore, the laser ablation process (a term includes the processes of evaporation, ejection of atoms, ions, molecular species and fragments, plasma initiation and expansion, etc) influences the amount and composition of the ablated mass and must be understood and controlled in order to achieve accurate and sensitive quantitative analysis [2].

Table I: Nominal concentration of Sr in SRMs from NIST

SRMs	610	612	614	616
Concentration (ppm)	515	78.4	45.8	41.72

Figure 2 shows the strontium and hydrogen signals for different SRMs. Ideally, the hydrogen signals must remain constant due to the same composition of the support matrix of SRMs but there is a strong variation in the hydrogen signal. This variation could be caused by the experimental uncertainties such as surface state of each samples and by changing samples for the next measurement. Even though the experimental conditions were kept constant for all measurements and the variation was attributed to differences in ablation and plasma excitation occurring during experiments [3].

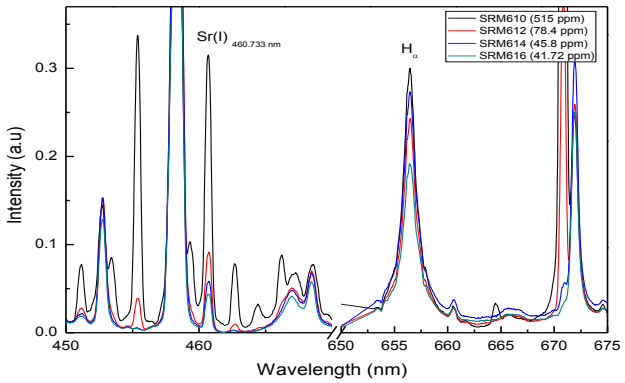

Fig. 2. LIBS Spectra of $Sr(I)_{460.733\ nm}$ from SRMs and $H(I)_{656.28\ nm}$ from ambient air

Figure 3 shows that the calibration curve using the absolute intensity of strontium is not linear, whereas the calibration curve using hydrogen as an external standard is linear. The result indicates that the intensity ratio of strontium to hydrogen strongly suppresses the experimental uncertainty.

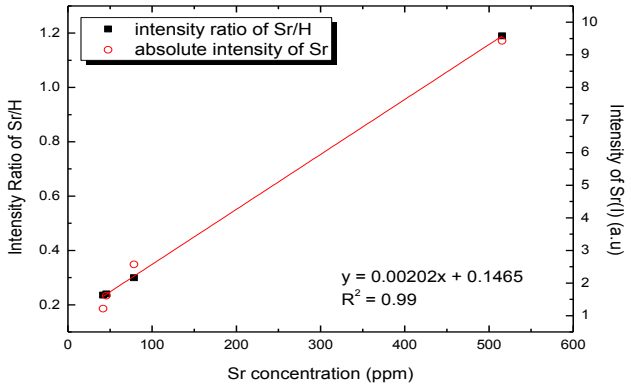

Fig. 3. Calibration curve either with the $H(I)_{656.28\ nm}$ emission line as external standard or with the absolute intensity of $Sr(I)_{460.733\ nm}$

3. Conclusions

The present paper demonstrates that the hydrogen emission line of ambient air generated by plasma of sample has been successfully used as external standard for quantitative analysis of LIBS. The measurement uncertainties could be noticeably reduced by this method.

REFERENCES

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