Semi-quantitative analysis of a Samarium alloys sample using a Laser induced breakdown spectroscopy

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a laser-based sensitive optical technique used to detect certain atomic and molecular species by monitoring the emission signals from a LIP (Laser-induced plasma). The LIBS technique has been applied for a direct qualitative and quantitative determination of the composition of a wide range of different matrices such as solids, liquids, and gaseous samples [1]. In view of an IAEA Safeguards implementation for nuclear materials, the LIBS method has an advantage of a timely analysis of multi elements in a sample taken from a nuclear fuel cycle process when compared to a time consuming chemical analysis method. Also the LIBS technique adopting fiber optics could be a promising method for measuring sensitive nuclear material (such as Uranium, Plutonium and Curium) in a high radiation environment such as a hot-cell. A quantitative analysis of materials has two important issues. First, the measurement conditions for a high fluctuation of a laser induced plasma (LIP) need to be optimized during an actual experiment. It is necessary because of the environmental gas condition, the sample preparation process, and the vibration around the equipment. Second, the positioning of the measurement location in a whole plasma sphere is very important. The plasma sphere is enlarged by the rarefied air, and it is discriminated by the inner sphere and the outer sphere. The inner sphere is brighter than the outer sphere, and it has been shown that the ion particles are superior in number to the neutral atoms. On the contrary, the neutral atoms are superior to the ions in the outer sphere. It is thus proper that the measurement is executed relatively stably in the outer sphere [2-4].

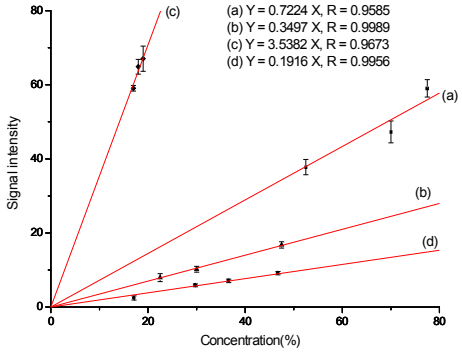

Fig. 1 Calibration curve for (a)Cu, (b)Ni, (C)Cr, (d)Nd

This study is focused on stabilizing a plasma sphere in order to enhance the accuracy of the LIBS and the positioning of a measurement in a whole plasma sphere for the semi-quantitative analysis of a Samarium alloy. Fig.1 shows acquired calibration curve at the former research.

2. Experimental and Results

This study was to derive an optimized measurement condition with a high reproducibility and to grow a plasma sphere to 20 mm high under a 484±3 mtorr vacuum states. The signal intensity measurement was at a 6.0 mm distance in the direction of a plasma sphere from a sample. This point belongs to the outer sphere region in a plasma.

2.1 Instrumentation of Experiment

Fig.2 shows the LIBS system that was used for the experiment in the Lab. The wavelength of the laser was 1064 nm with a Q-switched Nd:YAG laser, having an output full power of 50.0 mJ, 6 ~ 8 ns of a pulse duration, 2% of an energy stability and 2.8 mm of a beam diameter. Spectrometer used a CCD type detector with 14,336 pixels with a 0.1 nm (FWHM) resolution and a 2.1 ms integration time. The gas chamber was manufactured with SUS material having 3 build-in directional quartz windows, and the light emitted from the plasma was collected at a 90° angle by an optical fiber terminated by a lens. The opposite side of the laser input window was located by a sample supporter. A substance motor was installed to minimize a sample surface damage by a high powered laser beam.

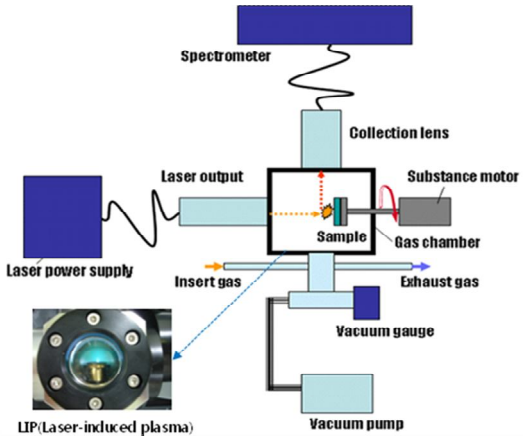

Fig. 2 The composition of actuality LIBS

2.2 Sample Preparation

A preliminary measurement was carried out on the samarium prior to a measurement of the Actinium samples. Five ingot samples which had mutually different components were prepared in a Arc Melting Furnace at 3000℃ starting with a homogeneously mixed powder form of Sm and Cu. Here, Cu is the reference element for each mixed-sample. All of the samples prepared have a thickness of 3.65 ± 0.03 mm for the same measurement condition.

Table.1 The description of mixed-samples

Mixed-Sample	Mixture Ratio (g) Cu : Sm	Atomic Percent (%)		Sample Thickness
		Cu	Sm	
Sm-01	3.2 : 0.4	94.98	5.02	3.65 mm
Sm-02	2.0 : 0.8	85.54	14.46	3.68 mm
Sm-03	2.0 : 1.0	82.56	17.44	3.65 mm
Sm-04	2.0 : 1.4	77.17	22.83	3.64 mm
Sm-05	2.0 : 1.6	74.73	25.27	3.64 mm

2.3 Derivation of optimized measurement condition

To obtain a signal with a high reproducibility a substance motor was introduced to make a sample revalue for less damage to a sample surface by a high procured laser beam. The optimized measurement condition was found to be at an output power of 18.75 mJ with a gradual increase of the laser power at which the reproducibility was the highest [5]. The plasma sphere size was sustained at 484±3 mtorr of a vacuum condition for a plasma sphere stabilization.

2.4 Determination of Standard Signals

The measurement was made in the range of 400 ~ 600 nm signals for the Sm and Cu mixed-sample. The signals were taken selectively based on a non-overlapping and the highest reproducibility. The measurements of the standard signals were determined as 488.3 nm for Sm and 510.6 nm for Cu respectively.

2.5 Measurement & Analysis

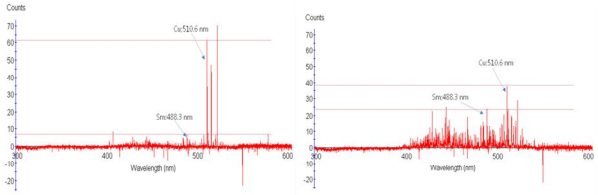

Fig.3 The raw data of LIBS spectrum
; Sm-01(left), Sm-04(light)

Each measurement was performed after 50 laser ablations under the same conditions, and repeated 10 times. An analysis of the measurement was undertaken by an acquisition of the calibration curve that was calculated by the concentration in the sample and the signal intensity for the 'Sm', and the results are shown in Fig.4. The linear regression of this result was R^2=0.9535 and the slope error was 4.78%. At this time, the linear regression of 'Cu' was R^2=0.9523.

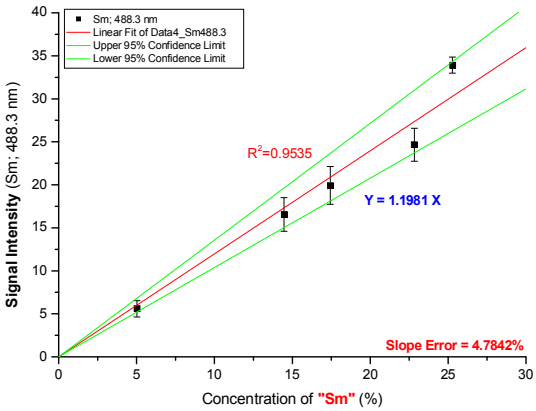

Fig.4 The calibration curve for 'Sm'

3. Conclusions

A real time semi-quantitative analysis of a sample can be possible with LIBS. In a quantitative analysis by the LIBS, an essential point is a location adjustment for the derived plasma. The plasma was distinguished for the inner sphere and the outer sphere, and it was clearly distinguishable at a pressure of 600 mtorr. It is thus proper that the measurement is executed relatively stably in the outer sphere. The calibration curve of 'Sm' was acquired. The linear regression of this result was R^2=0.9535 and the slope error was 4.78%.

Further effort is needed for an enhancement of the measurement reproducibility by means of a quantitative analysis of a varied concentration of the uranium samples.

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