Determination of uranium concentration in an ore sample using laser-induced breakdown spectroscopy

Y.-S. Kim, B.-Y. Han *, H.S. Shin, H.D. Kim, E.C. Jung, J.H. Jung, S.H. Na

Korea Atomic Energy Research Institute, P.O. Box 255, Yuseong, Daejeon 305-353, Republic of Korea

ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has been recognized as a promising technique for analyzing sensitive nuclear materials such as uranium, plutonium, and curium in a high-radiation environment, especially since the implementation of IAEA (International Atomic Energy Agency) safeguards. The uranium spectra of ore samples were quantitatively analyzed prior to analyzing sensitive materials in the nuclear industry. The purpose of this experiment is to extract quantitative information about the uranium in a uranium ore using a standard addition approach. The uranium ore samples containing different concentrations of U were prepared by mixing raw ore powder with natural uranium oxide powders. Calibration sets of 0.2, 0.4, 0.6, 0.8 and 1.0 wt.% uranium concentrations within the uranium ore sample were achieved. A pulsed and Q-switched Nd:YAG laser at a wavelength of 532 nm was used as a light source. An echelle spectrometer that covers a 190–420 nm wavelength range is used to generate a calibration curve and determine the detection limit of uranium in the ore matrix. The neutral atomic-emission peak at a wavelength of 356.659 nm indicated a detection limit of ~158 ppm for uranium, and the uranium concentration was determined in a raw ore sample that has an unknown quantity of uranium.

1. Introduction

Regarding the implementation of safeguards for nuclear materials in electrochemical-processing facilities that handle and dispose of spent nuclear fuels, there has been a request to develop measurement techniques that are applicable in critical environments, such as high-radiation and high-temperature environments. LIBS is applicable in-situ to identify and quantitatively analyze the sensitive nuclear elements such as uranium and plutonium in spent fuel because, unlike other spectroscopy methods, it does not require a preparation of the sample, it can conduct distant measurements, and it uses a semi-nondestructive method of analyzing the sample by focusing a low-energy laser pulse (a few mJ) onto the sample [1–5]. A limited number of studies have been reported that have attempted to use LIBS to detect sensitive nuclear materials [6–13]. A preliminary study was performed that investigated the use of LIBS to monitor the concentrations of U, Pu, Am, and Np being released from a waste processing facility [9]. The isotope ratio determination of uranium by LIBS was reported with the help of high resolution spectrometry by Pietsch [11]. For a quantitative analysis of uranium, Cremers et al. reported that the detection limits obtained using uranium deposited on Al metal, painted metal, plastic, and ceramic tile lie in the range of 13 to 150 μg/cm^2 [12]. Jung et al. reported that LOD for uranium in

a glass matrix was ~150 ppm, and the wavelength-dependent ablation effect resulted in stronger emission intensities for the UV than for the visible radiation [13].

The Korea Atomic Energy Research Institute (KAERI) is currently developing a LIBS technology to monitor and prevent the diversion of nuclear materials in an effort to strengthen the safeguards in electrochemical-processing facilities, which require high-radiation shielding. The main purpose of the application of LIBS to the safeguards is to identify sensitive nuclear elements and to gain quantitative information on them. Thus, preliminary experiments on the materials to be handled in the electrochemical-processing facilities should be performed in a laboratory environment to carry out the feasibility of LIBS application.

For this research, uranium was selected as a target element since it is the most common element in spent nuclear fuel. A uranium ore sample was used to obtain the characteristic information through uranium spectral detection and to perform qualitative and quantitative analyses. Natural uranium ore was mined in Kumsan County in South Korea and contains a small quantity of uranium. Various samples containing different concentrations of uranium were made for the quantitative analysis. LIBS technology was used to determine the limit of detection (LOD) according to the normalized signals for each concentration in the ore samples. The uranium concentration in the raw ore sample was also determined from the calibration curve. The precision of the signal-to-noise (S/N) ratio and non-homogeneous effects of the measurement samples were considered to reduce the measurement uncertainty.

* Corresponding author. Tel.: +82 42 868 8470; fax: +82 42 862 7313.
E-mail address: byhan@kaeri.re.kr (B.-Y. Han).

Table 1
Compositions of uranium ores (wt.%, *ppm).

Si	O	C	Al	Fe	Ca	S	Mg	V	Ni	U*
24.3	38.73	13.8	5.78	2.66	3.52	3.1	2.51	0.18	0.03	288.7

2. Experimental

The standard addition method was used to develop a calibration curve. The samples were prepared by adding a known concentration of uranium into a raw ore containing a small amount of uranium. The nominal composition of the support matrix in the raw uranium ore is listed in Table 1. The raw ore was evenly pulverized into powder and mixed for 30 min with a three-dimensional shaker mixer (Turbula) after adding five uranium concentrations, 0.2, 0.4, 0.6, 0.8, and 1 wt.%, to the raw ore sample. The mixed powder samples were formed into a green pellet type with a pressure of 300 MPa. The compacted green pellets (10 mm in diameter, 10 mm in length, and approximately 4 grams in weight) were sintered in a solid state for 2 h at 1200 °C by raising the temperature by 4 °C per minute in an Ar atmosphere.

In this experiment, a 532 nm Nd:YAG laser (Big Sky Laser Inc., USA) was operated at a pulse width of 6–8 ns and at a pulse repetition rate of 20 Hz. The fluctuation of the laser energy was within 2.5% using a pulse-to-pulse method. The experiment was performed under atmospheric pressure. The laser beam was focused onto the sample ore in a closed chamber to prevent the uranium powders from scattering and contaminating the air. The sample was rotated to produce plasma from a laser ablation on a wider surface area. This can reduce the measurement errors occurring by the non-homogeneity of the sample [14]. The laser beam was focused using a convex lens with a focal length of 100 mm. The focal point was set approximately 2 mm below the surface of the sample to minimize a breakdown above the surface [15]. The emission from the plasma was collected by a lens assembly containing a collimator and convex lens. It was positioned on an XYZ translation stage with manual controls, at a distance of about 75 mm (focal length) from the plasma. The collected light was transferred onto a fiber optic cable (a core diameter of 600 μm), and an emission spectrum was obtained with the elements displayed within the spectral detection region at wavelengths of 190–420 nm using an echelle spectrometer (LLA Instruments GmbH, ESA 4000) which has a combination of an echelle grating and a prism to generate a two dimensional spectral image. The image was detected using an intensified charge-coupled device (ICCD) camera with a 40,000 resolving power ($\lambda/\Delta\lambda$).

It is also well known that an increase in the accumulated number of pulses reduces the relative standard deviation (RSD) [16,17]. A lower RSD value indicates a higher repeatability of the experiment
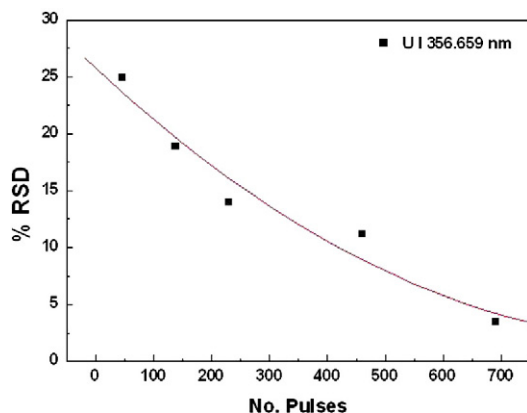

Fig. 1. Measurement precision (%RSD) vs. number of pulses. These data show a significant gain in precision (4%) for the signal ratio using 690 laser pulses.
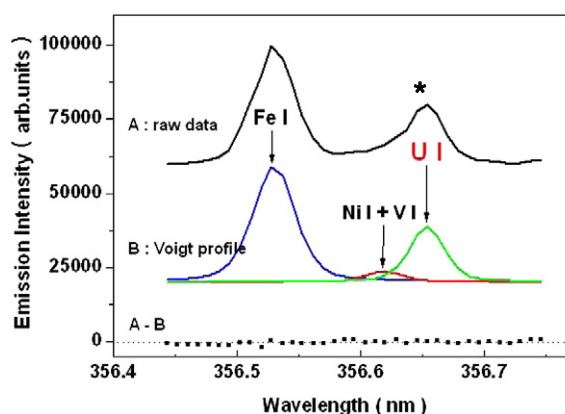

Fig. 2. Uranium and background (Fe, V and Ni) intensities estimated from the Voigt fitting function. The top trace A is the raw spectrum, the middle trace B is the spectrum by fitting method using Voigt function. The bottom trace is the difference between A and B.

and can increase the precision of the experiment. The spectral signals were compared as a function of the numbers of pulses to improve the measurement precision and the accuracy of the determination. Fig. 1 shows a result illustrating the %RSD of the normalized U I emission line at a wavelength of 356.659 nm relative to the accumulated number of pulses, and the signal was determined by the peak height of the emission spectra. The results in Fig. 1 show that the %RSD tends to decline as the number of pulses increases and the experimental repeatability is the highest with approximately 4% RSD when 690 pulses are accumulated. However, the emission intensity showed the maximum value at approximately 500 accumulations of the incident laser pulse at an energy of 10 mJ. When the number of pulses exceeded this value, a smaller emission intensity was detected because the laser ablation decreases owing to the increase of the crater's depth. Thus, the laser pulse of 460 was optimized to determine the LOD in this work.

3. Results and discussion

Uranium has a complicated emission spectrum consisting of a very high density of spectral lines. Based on the results of Refs. [12,13], which reported the LIBS experiments for U, the neutral atomic line at 358.488 nm and the ion line at 409.013 nm were investigated to identify the uranium. However, in the ore sample, the uranium lines at 358.488 nm and 409.013 nm are strongly interfered by the Fe and V elements in the ore matrix. Instead, in this work, the neutral atomic line at 356.659 nm was used for a quantitative analysis of the uranium in the ore sample. Although interference with the Ni and V elements was also found in the neutral uranium atomic line, better spectral separation was achieved owing to the relatively higher intensity of uranium line than both Ni and V elements.

A calibration curve was obtained from the LIBS signal (U I /Ca I) as a function of uranium concentration for quantitative analysis regarding the unknown concentrations in a matrix. For this purpose, the interference from other components should be taken into account. A curve fitting method was applied for the observed spectra to extract pure uranium signals, and the pure signal intensities were obtained by removing the background, which interfered with the uranium

Table 2
Line wavelengths, energy levels for the transitions, and observed relative intensities of the lines present in the observed emission spectrum.

Element (concentration)	Wavelength (nm)	Lower level (cm^{-1})	Upper level (cm^{-1})	Relative intensity
Ca I	299.731	15,210.063	48,563.522	8
Fe I	355.852	7985.785	36,079.372	400