Quantitative Analysis of Uranium concentration in LiCl-KCl salt of Electrorefining Process using LIBS

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) has been developed for the effective and efficient safeguards of pyroprocessing at Korea Atomic Energy Research Institue (KAERI) [1]. LIBS is based on the optical analysis of the plasma generated by concentrating a strong laser beam on the surface of the sample. LIBS has characteristic such as real-time analysis, no sample preparation before the analysis, and possibility of situ implementation.[2-5] In this study, U and lanthanide element in LiCl - KCl salt are measured as electrorefining process material of pyroprocessing via LIBS. In this study, LiCl - KCl based salts $LaCl_3$, $CeCl_3$, $BaCl_2$, $PrCl_3$, $NdCl_3$, YCl_3 , $SmCl_3$ and UCl_3 were added and melted and then sampled the salt in the solid state was measured in order to reduce the measurement error. The purpose of the present study is to explore the applicability of LIBS to quantitatively measure the uranium in the eletrorefining salt.

2. Methods and Results

At first, five LiCl-KCl samples containing UCl_3 were fabricated to obtain the preliminary calibration curve. Sample contained from 1.5wt% to 6.8wt% UCl_3. Composition materials of the samples were placed in the glassy carbon crucible, and they were heated up to 650℃ to melt. The molten salt samples were slowly cooled to solid form in the furnace.
Experiments were conducted in a glove box with an atmosphere of Ar gas with moisture and oxygen content of 100 ppm or less for samples with high deliquescence. The LIBS measurement setup is shown in Figure 1. A laser beam was injected through the port of the glove box and the optical fiber cable was inserted I received it. The sample surface was somewhat irregular and the distance between the sample and the focusing lens was corrected each time the sample surface was changed by interlocking the XYZ moving sample table with a high precision distance meter to match the same focal length. A beam of Q-switched Nd: YAG pulse laser (Brilliant B, Quantel) with a wavelength of 532 nm is focused on the sample surface to generate plasma and Echelle spectroscopy with 20,000($\lambda/\Delta\lambda$) resolution to detect plasma emission line and ICCD camera was used. The emission lines of U and other emission line were selected in the wavelength region of 200 to 400 nm where spectroscopy is permitted. The number of laser pulses in the measurement was 100. After collecting of LIBS spectrum at a position, the sample was moved horizontally to obtain the scan data of the sample surface. The measured U spectrum in the wavelength 357.005nm, 294.189nm, 297.101nm, 304.403nm and 385.952nm were analyzed. The U peak intensity is normalized with peak intensity of the K 399.180 nm line. Figure 2 is the LIBS spectrum of 356.5 nm to 357.5 nm range, clearly shows the 356.654 nm peak and 357.005 nm peak are from U. Figure 2 shows a spectrum of the Comparison of U with varying concentration sample and the sample without U.

Fig. 1. LIBS system used in the present work

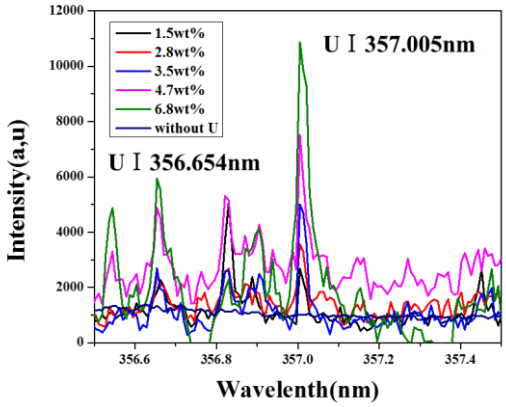

Fig. 2. U spectrum in a sample containing from 1.5 wt% to 6.8 wt% UCl_3 in LiCl-KCl.

The U 385.952 nm line had the smallest Limits of detection (LOD,) 0.0576wt%, and the 304.413nm line had the highest LOD, 0.1820wt%. For better analysis of

the performances, Partial least-squares (PLS) regression modeling was also conducted to obtain a multivariate calibration curve. The root mean squares error of calibration (RMSEC) for the U model as a function of the latent variables used are shown in Figure 3a. In this case seven latent variables were used to best capture the behavior of the spectral data. The PLS calibration curve for U is shown in Figure 3b. The RMSEC is 0.4152wt%, which is smaller than the univariate case.

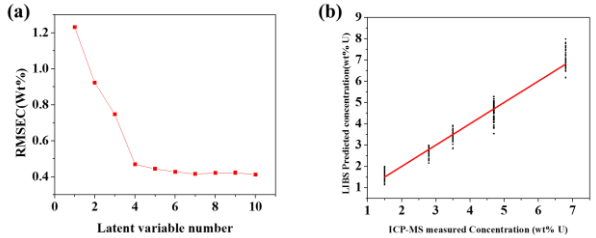

Fig. 3. (a) The RMSEC as a function of the number of latent variables used in the U PLS model, (b) The PLS calibration curve for U.

3. Summary

LIBS is a promising technology as the process monitoring technology applicable to the pyroprocessing safeguards. The uranium concentration in LiCl-KCl salt were measured using LIBS system, and the quantitative analysis performance of LIBS. U concentrations in the samples ranged from 1.5 wt% to 6.8 wt%, and the achieved values of accuracy and LOD are 2 ~ 8 % and 0.0576wt% respectively. Our result is promising for application of the LIBS to the safeguards. Between the univariate and the PLS analysis, the univariate approach showed better results. The benefit of the PLS grows as the spectrum get complex, and PLS analysis will play important role in the salt analysis of the spent fuel processed salt.

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