Measurement of Uranium in LiCl-KCl Salt Using LIBS

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1. Introduction

The Korea Atomic Energy Research Institue (KAERI) has explored Laser Induced Breakdown Spectroscopy (LIBS) as a promising technique for pyroprocessing safeguards measures because a remote, in-situ analysis of a material is possible.[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, multi elements analysis and no sample preparation before the analysis.[2-5] In this study, U and lanthanide element in LiCl - KCl salt are measured as electrorefining process material of pyroprocessing via LIBS.

2. Methods and Results

In this experiment, simulated electro-refining salt samples were made by adding $LaCl_3$, $CeCl_3$, $BaCl_2$, $PrCl_3$, $NdCl_3$, YCl_3 , $SmCl_3$ and UCl_3 to LiCl-KCl salt. Five LiCl-KCl samples containing UCl_3 were fabricated. The concentration of U in the samples were from 1.5wt% to 6.8wt%. Composition materials of the samples were placed in the glassy carbon crucible, and they were heated up to 650℃ to melt. This temperature was maintained for two hours, after which the samples were slowly cooled to a solid form in a 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. 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 410 nm where spectroscopy is permitted. The number of laser pulses in the measurement was 100 shot. 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 357.005 nm, 294.189 nm, 297.101 nm, 304.403 nm and 385.952 nm were analyzed. The U peak intensity is normalized with peak intensity of the K 399.180 nm line.

The U 385.952 nm line had the smallest LOD, 0.0576wt%, and the 304.413 nm 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.

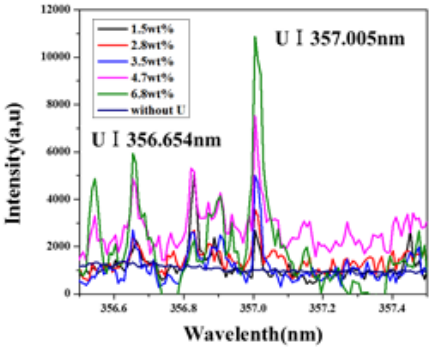

Fig. 1. U spectrum in a sample containing from 1.5 wt% to 6.8 wt% UCl_3 in LiCl-KCl.

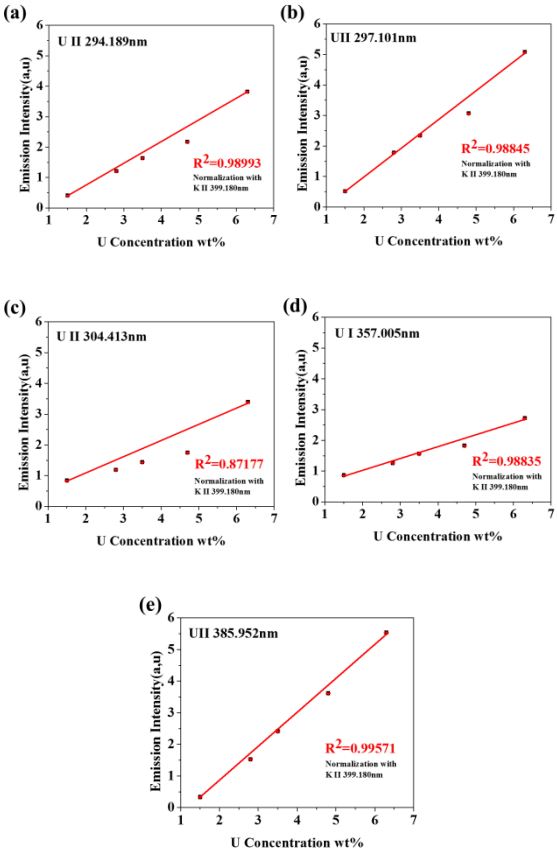

Fig. 2. Univariate calibration curves for U: (a) 294.189 nm line, (b) 297.101 nm line, (c) 304.413 nm line, (d) 357.005 nm line, and (e) 385.952 nm line.

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 1.5wt% to 6.8wt%, the limits of detection (LOD) was 0.0576wt% and R^2 was 0.99 at the 385.952 nm. Our result is promising for application of the LIBS to the safeguards.

ACKNOWLEDGEMENT

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