ANALYSIS OF URANIUM-BEARING MATERIALS BY LASER-INDUCED BREAKDOWN SPECTROSCOPY

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1. INTRODUCTION

In recent years, laser-induced breakdown spectroscopy (LIBS) finds more and more applications in the nuclear field. Among the samples for the analysis of which LIBS was successfully tested are reactor structural materials, nuclear fuel, contraband radioactive materials, forensic samples, etc. [Li 2016, Maurya 2020] Although quantitative isotope analysis is not the strong suit of LIBS due to the small isotopic effect of atomic emission spectral lines and their pressure broadening, but with some limitations it is also within reach recently via laser ablation molecular isotope analysis (LAMIS). Similarly to other fields, LIBS was found particularly useful for the qualitative discrimination of sample types, elemental distribution studies and trace analysis [Galbács 2015].

In the present project, commissioned by the International Atomic Energy Agency (IAEA), we investigated the capability of LIBS for the in-field analysis of uranium-bearing materials, more specifically whether or not it can provide quantitative trace analytical results for contaminants in compliance with the ASTM C753-04 standard. Our presentation gives a brief overview of the project's results.

2. EXPERIMENTAL

In order to maintain portability and in-field applicability of the instrumentation, we used a portable LIBS system (LIBScan 25+, Applied Photonics, UK) for spectral data collection and compact (mostly self-developed) devices for sample preparation or ablation control. In accordance with this effort we developed a laser ablation chamber and an electronic chamber ambient gas pressure control unit adapted to the LIBS setup and for the

purposes of the project. Spectral coverage was from the UV to NIR range (240 to 940 nm, with a small gap around 460-470 nm), with a spectral resolution of <0.1 nm. The samples involved in the experiments included the NBL CRM 124 set of reference materials (U_3O_8 matrix); IAEA 874501, IAEA 8747-01 and IAEA 9064-07-01 standards uranium ore concentrates; several uranium-bearing inter-laboratory samples as well as pure, common metals (as targets used in optimization experiments). The powdered samples were pressed into pellets before LIBS analysis. All gases used as ablation ambient gases were of 99.995% grade purity (Messer Hungarogáz, Hungary). All LIBS experiments on uranium-bearing materials were performed in the laboratory of the Nuclear Security Department, Atomic Energy Research Institute (NSD-AERS), whereas experimental planning, optimization experiments and data evaluation was performed at the University of Szeged. Reference compositional measurements on inter-laboratory samples were done also at the (NSD-AERS), using a Thermo Element 2 sector field ICP-MS instrument.

3. RESULTS AND DISCUSSION

Prior to all further works, a selection of prominent spectral lines for the elements included in ASTM C753 was performed, based on theoretical considerations (with priorities on selectivity and sensitivity). We found that analytically the 460 to 800 nm range is the most promising and that most elements in the standard have potentially suitable lines for the analysis in this matrix. We also studied the potential of diminishing spectral interferences from the uranium matrix by using sample dilution [Chinni 2009]. It was found that it is highly adviseable to dilute the samples 100-fold using e.g. spectrographic carbon or other suitable binder/diluent powder.

We carried out experimental testing of several LIBS signal enhancement methodologies that can potentially be applied in the field (e.g. argon gas purge and pressure control, spatial and magnetic plasma confinement, timing optimization, etc.). It was found that gas control is the most reliable and practical enhancement methodology. By using argon gas purging and lower than normal pressure (ca. 100 mbar), a three-fold signal enhancement was achieved. It was also established, that a light collection setup different from the built-in one in the portable LIBS instrument used is needed to fully exploit the signal enhancement methodologies [Palásti 2017].

Several signal calibration and normalization approaches were also theoretically evaluated. It was established that the use of uranium as an internal standard and matrix-matched external calibration are the most practical. Extensive attempts were also made to prepare homogeneous pelletized external samples by mixing metal salts and pure UO_2 powder in order to make calibration standards, but it was not deemed to be reliable.

The analytical performance of the LIBS measurement setup, under optimized conditions was assessed. Calibration plots were constructed for 64 spectral lines of 17 elements, common in both the standard samples and ASTM C753. It was found that most of the spectral lines suffer from interferences from elements outside the focus of the

project, therefore only Fe, Zn, K, Mg, Ca, Mn could be properly calibrated (depending on the sample matrix). Limits of quantitations (LOQs) of 50-100 ppm were achieved, which level is more than adequate for the quantitative analysis of the elements according to ASTM C753, which dictate 200 ppm limits of quantitation or less. The dynamic range of the method was found to be 2-3 orders of magnitude. The signal scatter, which is influenced by many parameters (including laser pulse energy jitter, sample microhomogeneity, matrix composition, etc.), is significant, ca. 10-20 RSD%, with signal normalization, but this is reasonable for portable instrumentation and for compliancy testing [Palásti 2019].

The matrix effect was studied for at least three uranium-bearing matrices (e.g. UO_2, U_3O_8, ammonium-diuranate) and it was found to be significant, as expected. This is primarily caused by the different light absorption of the chemical compounds making up ca. 99% of the samples at the wavelength of the laser, as well as – to a less extent - the density and porosity of the samples. Since plasma characteristics are determined by the matrix (and the gas environment), therefore the influence of the matrix is far from neglectable in the analysis of the trace components. The matrix effect manifested itself in the calibration plots as either different signals for the same analyte concentration (when the plot was linear) and different curvature of the plots (for the same spectral line, in all cases) was found. This finding stresses the importance of matrix-matched calibration.

Quantitative accuracy was tested by analyzing inter-laboratory uranium-bearing samples, using solution-based ICP-MS measurements as reference (after the acid-digestion of the samples). A 20-25% relative inaccuracy was found, which is a fair value considering the factors involved [Galbács 2019].

4. CONCLUSIONS

The LIBS method was generally found to be quite suitable for the quantitative trace analysis of uranium-bearing materials, at the level of detection capabilities and accuracy dictated by ASTM C753-04. The analytical task is fully feasible by portable instrumentation, although some sample preparation (powder dilution) may be needed, but this can potentially also be performed on site.

5. ACKNOWLEDGEMENTS

6. REFERENCES

[Li 2016]   C. Li, C. L. Feng, H. Y. Oderji, G. N. Luo, H. B. Ding,
Front. Phys., 11 (2016) 114214.

[Maurya 2020]   G. S. Maurya, A. Marín-Roldán, P. Veis, A. K. Pathak, P. Sen,
J. Nucl. Mat., 541 (2020) 152417.

[Galbács 2015] G. Galbács, *Anal. Bioanal. Chem.*, 407 (2015) 7537.

[Chinni 2009]   R. C. Chinni, D. A. Cremers, L. J. Radziemski, M. Bostian,
C. Navarro-Northrup, *Appl. Spectrosc.*, 63 (2009) 1238.

[Palásti 2017]   D. J. Palásti, É. Kovács-Széles, A. Berlizov, G. Galbács,
poster presentation P95, *International Symposium on Analytical and Environmental Problems*, Szeged, Hungary, 2017.

[Palásti 2019]   D. J. Palásti, Á. Bélteki, É. Kovács-Széles, A. Berlizov, G. Galbács,
poster presentation WP-43, *European Winter Conference on Plasma Spectrochemistry*, Pau, France, 2019.

[Galbács 2019] G. Galbács, D. J. Palásti, A. Metzinger, É.-Kovács Széles, A. Berlizov,
oral presentation FT-1, *10th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy*, Brno, Czech Republic, 2019.