



# Multivariate approach to the chemical mapping of uranium in sandstone-hosted uranium ores analyzed using double pulse Laser-Induced Breakdown Spectroscopy

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## ABSTRACT

The goal of this work is to provide high resolution mapping of uranium in sandstone-hosted uranium ores using Laser-Induced Breakdown Spectroscopy (LIBS) technique. In order to obtain chemical image with highest possible spatial resolution, LIBS system in orthogonal double pulse (DP LIBS) arrangement was employed. Owing to this experimental arrangement the spot size of 50  $\mu\text{m}$  in diameter resulting in lateral resolution of 100  $\mu\text{m}$  was reached. Despite the increase in signal intensity in DP LIBS modification, the detection of uranium is challenging. The main cause is the high density of uranium spectral lines, which together with broadening of LIBS spectral lines overreaches the resolution of commonly used spectrometers. It results in increased overall background radiation with only few distinguishable uranium lines. Three different approaches in the LIBS data treatment for the uranium detection were utilized: i) spectral line intensity, ii) region of apparent background and iii) multivariate data analysis. By utilizing multivariate statistical methods, a specific specimen features (in our case uranium content) were revealed by processing complete spectral information obtained from broadband echelle spectrograph. Our results are in a good agreement with conventional approaches such as line fitting and show new possibilities of processing spectral data in mapping. As a reference technique to LIBS was employed X-ray Fluorescence (XRF). The XRF chemical images used in this paper have lower resolution (approximately 1–2 mm per image point), nevertheless the elemental distribution is apparent and corresponds to presented LIBS experiments.

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## 1. Introduction

The global demand for energy is rising and the future generation will need a range of options if greenhouse gas emissions are to be reduced [1]. One of the basic source of energy comes from nuclear processes, especially uranium fission. Sufficiency of uranium reserves found on the Earth can contribute to energy sustainability.

Uranium accumulations are formed in various ways, the most important include magmatic, hydrothermal and sedimentary processes, which create a wide range of deposit types and formations. The widespread hydrothermal types are sandstone-hosted uranium deposits constituting approximately 18% of the world's known reserves. It is distributed in more than six hundred deposits [2,3] and contributes to

more than half of a current uranium production. Orebodies of this type are commonly low to medium grade (0.05–0.35% U) and the number of operating deposits (50) considerably exceeds other deposit types. Rather than conventional methods (underground and opencast mining), the chemical extraction (*in-situ* leaching) is chiefly used for economic valuation [4].

Czech Republic does not belong any more to the world's most valuable uranium provinces, but especially in European and regional scale it has considerable ore reserves. These are represented by penconcordant sandstone-hosted uranium deposits in the North Bohemian Cretaceous Basin. These deposits are defined as U-Zr-P-Ti type and represent a remarkable elemental as well as mineral associations, that makes this area worldwide unique.

The study of ore mineralization is difficult for the size of mineral phases (in  $\mu\text{m}$ ), gel nature of components *etc.* and hence application of traditional geological instruments such as optical microscopy, electron microprobe, scanning electron microscopy or x-ray diffraction is often

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**Table 1**  
Some analytical methods utilized for uranium detection.

Method	Stand-off detection	Chemical mapping	Reference
ICP-MS	No	No	[6]
ICP-AES	No	No	[6]
XRF	No	Yes	[7]
Raman spectroscopy	Yes	Yes	[8]
LIF	Yes	Yes	[9,10]
Gamma ray spectroscopy	Yes	No	[11]
LIBS	Yes	Yes	[12–16]

ICP-MS – Inductively Coupled Plasma Mass Spectrometry; ICP-AES – Inductively Coupled Plasma Atomic Emission Spectrometry; XRF – X-ray Fluorescence; LIF – Laser-Induced Fluorescence, LIBS – Laser-Induced Breakdown Spectroscopy.

limited due to the low-grade ore, particle size or colloidal nature of uranium and uranium-bearing phases [5]. These methods need extensive sample preparation prior the analysis. Some analytical methods typically used for uranium detection and their capabilities are listed in Table 1. However, for direct *in-situ* and/or *stand-off* detection, the aforementioned methods are inconvenient. Analytical method with great potential to satisfy above discussed demands is Laser-Induced Breakdown Spectroscopy (LIBS). Thus this paper aims to study the possibilities of LIBS concerning the detection of uranium precipitated in sandstones, and consequently selects and also suggests new approaches enabling fast and accurate chemical mapping of elements of interest.

The scope of advantages of LIBS in comparison to other methods routinely used for ore mineralization studies comprises mainly the relatively simple and robust equipment, possibility to detect broad spectrum of elements, no necessity of sample preparation, relatively high sensitivity and possibility of spatially resolved measurements [17–19]. Moreover LIBS is capable of *in-situ* and *stand-off* measurements [13,20]. Despite unquestionable advantages of LIBS, the detection of some elements is challenging due to various reasons. One of these difficult-to-detect elements is uranium. The main challenge in uranium detection is its complex emission spectrum with very high density of spectral lines. As it is stated in ref. [12] the number of uranium lines measured using a hollow cathode discharge lamp exceeds 5000 in the range 384.8 to 908.4 nm. Considering the spectral line broadening such line density may cause interference of spectral lines. In this paper it is suggested to use this feature of uranium emission spectrum to determine the relative content of uranium in the studied specimen.

This approach enables obtaining and isolating optimal areas of the sample with ore-bearing material. Moreover, elemental mapping brings additional information as it gives us a basic idea about the distribution of ore-phases and their possible associations (based on the correlation of elements). Furthermore, it is an interesting mean of monitoring of the ore-forming solutions fluxes, which create metallic accumulation within the sandstones. This study is focused on multiple ways of data processing concerning monitoring of spatial distribution of uranium only.

## 2. Experimental

### 2.1. Samples and sample preparation

Břevniště deposit is one of the uranium deposits of sandstone type situated within geological structure called the Stráž block (in the area of northern part of the Bohemian Cretaceous Basin). Unique association of elements U-Zr-P-Ti characterizes the ore field and forms mostly fine-grained mineralization bonded to the Cenomanian sediments (especially sandstones and siltstones) [21]. These host rocks are composed mainly from quartz, clay matrix and accessory minerals (such as oxides, sulfides or carbonates). Mineralization formed in these rocks is a result of infiltration of ore-forming solutions into the open or clay matrix filled pores between quartz grains. Specific nature of this deposit consist in the occurrence of uraniferous hydrozircon and leucogenes *s. l.*

(alteration products and mixtures of Fe-Ti oxides) and partial colloidal to meta-colloidal nature of ore minerals [22].

Preparation of samples included several specific steps, which are necessary for application of different methods. Ten samples collected at the site were cut, dried, and cemented with Araldite epoxy. For XRF elemental mapping it was required to create a flat surface and circumference of the sample. This was achieved by grinding an excess of epoxy from the rock surface and cropping edges.

The final step comprised of the selection of most interesting sample and its region respectively for the consecutive LIBS analysis, based on the uranium content.

### 2.2. X-ray Fluorescence (XRF) analysis

Results described in this article were obtained with the XRF system designed and operated at the Czech Technical University in Prague. XRF system consists of an exchangeable X-ray source, a spectrometric X-ray detector (Si-PIN), and a positioning stage for sample investigation. The Si-PIN detector (Amptek Inc.) provided X-ray spectrometry in the energy range approximately from 2 keV up to 30 keV. System utilizes a beryllium window 25.4  $\mu\text{m}$  in thickness and with a sensitive volume of 6 mm<sup>2</sup>  $\times$  0.5 mm. Window distance from the measured sample was less than 1 cm. Sample stage is movable in both horizontal directions with a step down to 10  $\mu\text{m}$  and the maximum range of operation is approximately 50 cm.

This XRF analyzer was equipped with Au anode Mini-X X-ray tube that was operated at the voltage of 35 kV and the current of 0.1 mA. The X-ray beam was collimated with a narrow collimator and filtered with 1 mm of pure aluminum. The aperture diameter of the shipped collimator is 2 mm and the lateral resolution in scanning mode is 3 mm (FWHM determined with knife-edge scan). Resulting lateral resolution was achieved by adding copper collimators.

This technique was used for mapping of the largest possible surface of ore samples to determine the most abundant spheres of occurrence the elements of interest. At a lateral resolution 1–2 mm per image point and dwell time from 8 to 20 s, it has been, in a relatively short time, possible to examine the sample surfaces of roughly 2500–4000 mm<sup>2</sup>.

### 2.3. Laser-Induced Breakdown Spectroscopy (LIBS)

The experimental double-pulse (DP) LIBS setup was utilized in order to reach high sensitivity, maintaining low crater diameter, subsequently enabling high spatial resolution chemical mapping. High energy Nd:YAG laser LQ 529A (Solar LS, Belarus), operating on its second harmonic (532 nm, 12 ns pulse duration), was introduced into the LIBS interaction chamber (AtomTrace, CZ) by a series of mirrors and then focused by a 20 mm focal length glass triplet (Sill Optics, Germany) collinearly with the sample surface normal. Secondary laser, Brilliant b (Quantel, FR) operated at the fundamental wavelength (1064 nm, 8 ns pulse duration), was introduced into the chamber perpendicularly with respect to the first laser pulse axis using mirrors and then focused into the emerging plasma with 40 mm focal length lens. Such arrangement resulted in the orthogonal DP LIBS, where the first laser pulse

**Table 2**  
Experimental parameters of DP LIBS measurements.

Parameter	Value
Ablation laser energy (mJ)	30
Secondary laser energy (mJ)	80
Spot size ( $\mu\text{m}$ )	50
Interpulse delay ( $\mu\text{s}$ )	0.5
Gate delay ( $\mu\text{s}$ )	1.5
Gate width ( $\mu\text{s}$ )	20
Spatial resolution ( $\mu\text{m}$ )	100

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