Analysis of geological materials containing uranium using laser-induced breakdown spectroscopy

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) is a rapid atomic emission spectroscopy technique that can be configured for a variety of applications including space, forensics, and industry. LIBS can also be configured for stand-off distances or in-situ, under vacuum, high pressure, atmospheric or different gas environments, and with different resolving-power spectrometers. The detection of uranium in a complex geological matrix under different measurement schemes is explored in this paper. Although many investigations have been completed in an attempt to detect and quantify uranium in different matrices at in-situ and standoff distances, this work detects and quantifies uranium in a complex matrix under Martian and ambient air conditions. Investigation of uranium detection using a low resolving-power LIBS system at stand-off distances (1.6 m) is also reported. The results are compared to an in-situ LIBS system with medium resolving power and under ambient air conditions. Uranium has many thousands of emission lines in the 200–800 nm spectral region. In the presence of other matrix elements and at lower concentrations, the limit of detection of uranium is significantly reduced. The two measurement methods (low and high resolving-power spectrometers) are compared for limit of detection (LOD). Of the twenty-one potential diagnostic uranium emission lines, seven (409, 424, 434, 435, 436, 591, and 682 nm) have been used to determine the LOD for pitchblende in a dunite matrix using the ChemCam test bed LIBS system. The LOD values determined for uranium transitions in air are 409.013 nm (24,700 ppm), 424.167 nm (23,780 ppm), 434.169 nm (24,390 ppm), 435.574 nm (35,880 ppm), 436.205 nm (19,340 ppm), 591.539 nm (47,310 ppm), and 682.692 nm (18,580 ppm). The corresponding LOD values determined for uranium transitions in 7 Torr CO_2 are 424.167 nm (25,760 ppm), 434.169 nm (40,800 ppm), 436.205 nm (32,050 ppm), 591.539 nm (15,340 ppm), and 682.692 nm (29,080 ppm). The LOD values determine for uranium emission lines using the medium resolving power (10,000 $\lambda/\Delta\lambda$) LIBS system for the dunite matrix in air are 409.013 nm (6120 ppm), 424.167 nm (5356 ppm), 434.169 nm (5693 ppm), 435.574 nm (6329 ppm), 436.205 nm (2142 ppm), and 682.692 nm (10,741 ppm). The corresponding LOD values determined for uranium transitions in a SiO_2 matrix are 409.013 nm (272 ppm), 424.167 nm (268 ppm), 434.169 nm (402 ppm), 435.574 nm (1067 ppm), 436.205 nm (482 ppm), and 682.692 nm (720 ppm). The impact of spectral resolution, atmospheric conditions, matrix elements, and measurement distances on LOD is discussed. The measurements will assist one in selecting the proper system components based upon the application and the required analytical performance.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been used to analyze the elemental composition and concentration of many complex environmental samples. Elements from hydrogen to the heavy elements including actinides (uranium, plutonium, americium, neptunium, and thorium) have been investigated [1–19]. LIBS is a highly configurable technique based on the needs of the application. In-situ measurements can be readily replaced with stand-off measurements for hard to reach samples due to rough terrain or a hazardous area by changing laser beam launching and emission light collection optics. LIBS measurements under different atmospheric conditions such as under vacuum, gas pressure, or even other planetary atmospheres have also been achieved for applications on Mars or to reduce atmospheric interferences [19]. An important experimental parameter for performing a LIBS measurement is the resolving power of the spectrometer. This aspect of the system tends to be a balance between size restrictions and

spectral assignment and sensitivity requirements. Low resolving power spectrometers typically have a 200–1000 nm spectral range and tend to be much smaller in size. However, sensitivity and/or accuracy in emission line assignment due to several emission lines being convoluted in a single spectral feature are the major downfall. High resolving power spectrometers tend to be much larger and have more narrow spectral regions but are capable of baseline separation of elemental isotopes [21]. Other novel techniques for the detection and analysis of uranium have been reported by Ko and Jovanovic [30]. In summary, the application, the chemical environment of the sample (matrix), and the quantitative or qualitative needs dictate the system requirements.

The focus of this work is to detect and quantify uranium and determine limit of detection (LOD) under different measurement schemes. The measurements will assist one in selecting the proper system components based upon the application and the required analytical performance. The detection and analysis of uranium in complex matrices have been the subject of many investigations since the work of Wachter and Cremers in 1987 [7]. In that investigation, LIBS was used to determine a LOD of 100 ppm for uranium in a nitric acid solution. A review of the result from previous investigations to quantify uranium in a variety of matrices is shown in Table 1. In summary, LIBS has been used to identify and provide semi-quantitative determinations of uranium in many different matrices at in situ and standoff distances. Most of the experimental results reported so far have been conducted under ambient air conditions. The primary challenge in using LIBS to accurately identify and assign atomic emission spectral signatures for uranium is to exploit the complex interplay between experimental parameters (delay time, gate width, laser power, atmospheric compositions including ambient air, Ar, He, and CO_2) and concentration to determine the lowest LOD for uranium in a matrix. For example, isolating an atomic emission line from neighboring transitions that have different concentration dependencies on integrated intensity is of high importance. Therefore, resolving power of dispersion devices (spectrometers) and signal to noise (background) ratios are extremely important instrument and experimental parameters.

Another important factor is the data analysis method used to determine LOD. Kim et al. found that normalization to Ca I or Fe I using the same 356.659 nm U I line resulted in LODs of 158 or 186 ppm respectively [12]. Others use mathematical techniques such as multi-component curve fitting and partial least squares to de-convolute the partially resolved peaks in the spectrum [13]. This technique results in reported LOD of 17–51 ppm for U II 409 and 3–12 ppm for U I 682 with a NIST 1872 SRM, where the resolving power of the spectrometer was reported as 34,000 [13]. In this work, the LOD is defined as 3.3 σ/m where σ is the standard deviation of the y-intercept of the calibration curve based on the regression analysis and m is the linear slope of the calibration curve [22]. This approach is a better indicator of the LOD at

low concentrations rather than averages derived at higher concentrations from the residual standard deviations. Other methods to calculate LOD are described by Lasue et al. [23].

Although many investigations have been completed in an attempt to detect and quantify uranium in different matrices at in situ and standoff distances, this is the first report of detecting and quantifying uranium in a complex matrix under Martian conditions. The ChemCam test bed LIBS system is used as the low resolving-power standoff LIBS system to identify and assign uranium atomic emission lines [20]. Several uranium atomic emission lines are measured and discussed to quantify uranium at a standoff distance of 1.6 m. These results are compared to medium resolving power LIBS in-situ measurements under ambient air conditions. The roles that spectral resolution, environmental conditions (7 Torr CO_2 versus air), and matrix elements play on LOD are also reported.

2. Experimental Set-up

2.1. Instrumentation

2.1.1. Standoff LIBS system

A detailed description of the ChemCam test bed LIBS system used in this investigation has been previously described by Maurice et al. [24] and Wiens et al. [25], therefore only a brief description will be provided in this paper. The excitation source was a diode pumped Nd:KGW laser (designed and built by CNES and Thales Optronics, France) operating at 1067 nm producing pulses of 5 ns width at a repetition rate of 3 Hz. The maximum output energy was 13 ± 1 mJ per pulse. The output excitation energy from this laser was focused to a spot size of 300 μm on target using a beam expander at a standoff distance of 1.6 m. A Schmidt Cassegrain telescope was used to collect the emission from the plasma and transfer it to three spectrometers via a de-multiplexer. The spectrometers cover three spectral regions: 240.8–340.8 nm, 382.1–469.1 nm, and 473.1–905.6 nm with resolving powers of 1930, 2125, and 1150 respectively [20,24]. Compared to traditional time-gated LIBS systems, this system is operated in a non-gated mode with an integration time of approximately 3 ms. Each time the laser is fired, the shutter on the spectrometers opens for 3 ms and spectral data is collected. A total of 50 laser shots are acquired and the average spectrum is reported. The samples used in this investigation were analyzed in a vacuum chamber containing 7 Torr CO_2 gas to simulate the atmospheric conditions on Mars and in air under standard atmospheric conditions.

2.1.2. In-situ LIBS system

A medium resolving power echelle spectrometer from LLA Instruments (ESA 4000) was also used to collect LIBS spectral data between 220 and 780 nm. The resolving power of the spectrometer system is

Table 1
A list of detection and analysis results of uranium in different matrices from previous work.

Author	Transition (nm)[1]	Matrix	Resolving power	LOD (ppm)
Wachter/Cremers [7]	409 II	Nitric acid	4000	100
Chinni/Cremers [9]	409 II	Silica	6000	2600 (in situ)/5000 (@30 m)[2]
Sarkar [10]	263 II	Thoria	2000	37,000
	367 II	Thoria	2000	38,000
	447 I	Thoria	2000	NR[3]
	454 II	Thoria	2000	34,000
Jung [11]	358 I	Silica	40,000	150
Kim [12]	356 I	Silica	40,000	158
Choi [13]	409 II	Pb-germanate glass	34,000	17–51
	682 I	Pb-germanate glass	34,000	3–12

[1] I and II refer to the neutral and 1st ionization state of the uranium atom.
[2] 30 m is 30 meter standoff measurement distance.
[3] NR is defined as not reported.

Table 2
Comparison of LIBS systems used in this study.

Specifications	ChemCam test bed LIBS system	In-situ LIBS system
Laser power	13 ± 1 mJ	10 mJ
Repetition rate	3 Hz	10 Hz
Wavelength (nm)	1067	1064
Pulse width	5 ns	8 ns
Configuration	Standoff, 1.6 m	in-situ
No. laser shots per spectrum	50	200
Spectrometer	Czerny–Turner	Echelle
Spectral resolving power	1150–2125 [1]	10,000
Spectral region	240.8–340.8 nm, 382.1–469.1 nm, 473.1–905.6 nm	200–780 nm
Gate delay	–	100 ns
Gate width	3 ms	1 μs
Atmosphere	7 Torr CO_2, Standard atmospheric conditions	Standard atmospheric conditions

[1] The resolving powers for the three spectral regions are 1930, 2125, and 1150 respectively.