

QUANTITATIVE ROCK ANALYSIS BY LASER-INDUCED BREAKDOWN SPECTROSCOPY AT THE SURFACE OF MARS.

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Overview: Remote Laser-Induced Breakdown Spectroscopy (LIBS) has been selected as part of the ChemCam instrument package for the Mars Science Laboratory (MSL) rover, scheduled to be launched in 2009. LIBS has been under development for planetary science applications because based on laser ablation, it can remove dust layers remotely or perform depth profile through weathering coatings at stand off distances [1,2] and thus provide analyses on the pristine rock samples. The LIBS technique allows both qualitative and quantitative elemental analysis of a wide range of materials. However, as for any method of solid samples analysis, the accuracy of quantitative results is often compromised by the so called matrix effects, in which the analytical response is influenced by the physical properties of the sample and by its overall chemical composition. In a laboratory, matrix effects can be partially overcome by applying one calibration curve for each element contained in any substrate of interest. This approach requires an *a priori* knowledge of the matrix composition and several corresponding reference samples. Consequently, it is not compatible with field analyses of complex and unknown samples, as for the case of soils and sediments on Mars surface. Hence, it is of prime importance for the ChemCam project to develop a methodology for correcting the matrix effects in order to perform quantitative analysis of inhomogeneous and unknown samples representative of Martian rocks. The aim of the present work was to identify the matrix effects occurring in LIBS analyses of several types of natural rocks under the simulated Mars atmosphere (9 mbar CO₂) and to develop an analytical procedure enabling correction of these matrix effects for quantitative stand-off analysis (3 meters). For this purpose, we tested different methods: the realisation of multi-matrix calibration curves, the external normalization with correction for the 100% total concentrations, the internal normalization by a major element and the application of the Calibration Free (CF) LIBS approach [3].

Experiment: The studies were performed on a series of natural rock samples: basalt (ES9206), limestone (RJ3), gabbro (OT9101), trachy-andesite (ES9106), trachyte (ES9101) and obsidian (LMG Little Mountain Glass). Their "reference" elemental compositions, determined by the ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and ICP-MS (ICP-Mass Spectrometry) techniques, are given with uncertainties in Refs. [4-6]. These samples were analyzed in Martian conditions using the setup presented in Fig. 1. The Q-switched Nd:YAG laser operating at 1064 nm and 10 Hz was expanded by a 3x telescope and focused with a 3000 mm focal length lens onto the sample surface through the quartz window of a vacuum chamber. This cell was filled with a flowing stream of CO₂ gas and the pressure was adjusted to 9 mbar with a pumping device to simulate the Martian atmosphere. The laser energy on the sample was 25 mJ, value considered to

be achievable by a compact laser likely to be used in spatial missions. The plasma light was collected along the same path as the laser beam and then focused with a lens of 100 mm focal length onto an optical fiber (200 μm core diameter, 500 mm length). The end of this fiber was directly connected to the entrance slit of an Echelle spectrometer equipped with an ICCD (Intensified Charge-Coupled Device) camera detector system and sensitive in the 280-1000 nm spectral range. The plasma light was recorded with a time delay of 200 ns, a gate width of 500 ns and the maximum gain of the intensifier. To minimize the heterogeneity problem of natural rock samples, each LIBS spectrum was produced by integrating spectra from 400 plasmas on the same spot (integration of depth heterogeneity) and the acquisition was replicated 50 times at different places on the surface.

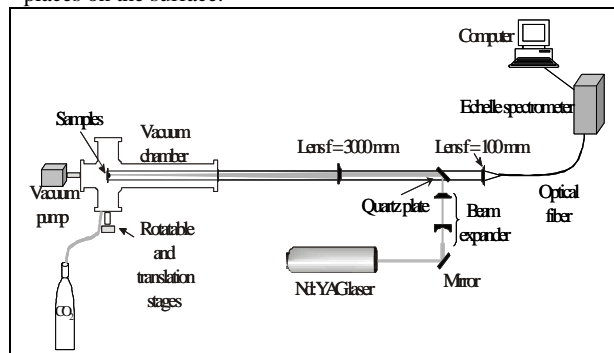


Fig. 1: LIBS experimental setup for geological samples analysis at a distance of 3 meters.

Results: To evaluate the LIBS response as a function of concentrations, we performed multi-matrix calibration curves for the elements Si, O, Ca, Fe, Mg, Al, Na, K, Ti, Ba and Sr (Fig. 2).

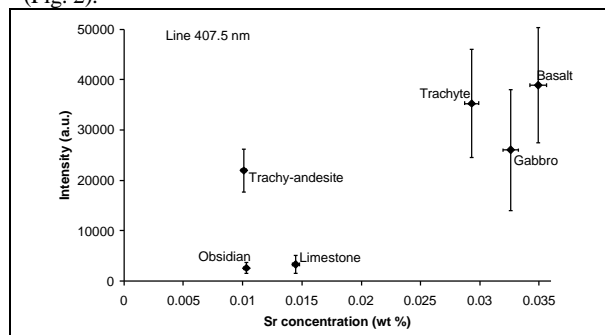


Fig. 2: Multi-matrix calibration curve prepared for Sr. The points representative of basalt, gabbro, trachy-andesite and trachyte are placed on a same calibration curve indicating that no matrix effects are observable between these different rocks. On the contrary, the lines intensity of plasma created on obsidian

ian and limestone samples is lower than that obtained from other rock samples. This is characteristic of matrix effects which imply the need for developing a methodology allowing to compensate these effects.

The first method considered to correct for matrix biases within the determination of rocks elemental concentrations consists to use one reference sample with known composition (trachyte in our work) and to apply normalization to 100% of the sum of all elemental concentrations. Fig. 3 shows the good agreement between the calculated concentrations and the certified values, except for limestone (apart for its major components O and Ca).

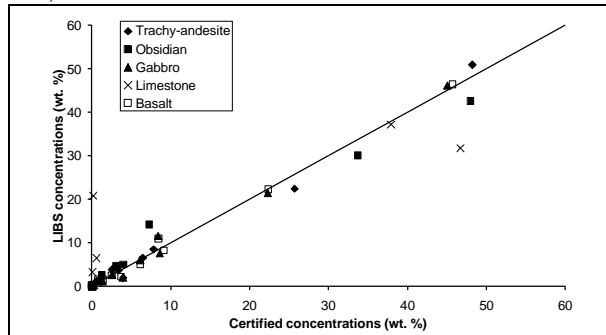


Fig. 3: First method: Concentrations calculated from a reference sample and normalization to 100% of the sum of all elemental concentrations.

The second approach, widely used in spectrochemistry to correct from matrix effects, is based on internal standardization with a major component of the matrix. We chose the oxygen (at 777.2 nm) as normalization element because it was the major element common to all studied rocks. Fig. 4 presents the correlation between the Sr intensity normalized to the O signal and the Sr elemental concentration divided by the O concentration.

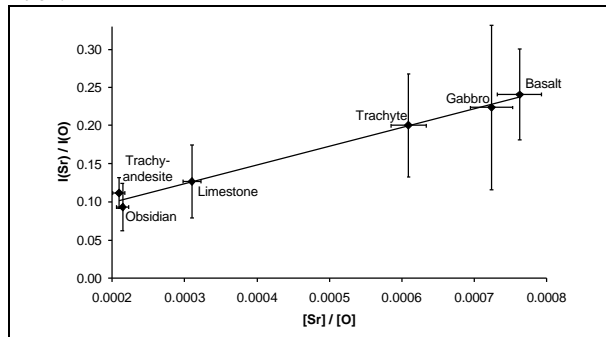


Fig. 4: Correlation between the intensity normalized to the O signal and the concentration ratio for Sr.

By comparison with Fig. 2, it can immediately be seen that the intensity ratios measured on obsidian and limestone are in good agreement with the results obtained on other matrices. That is a good indication of a proper correction of matrix effects. Equation of each calibration curve was then used to calculate the relative concentrations (Fig. 5). Despite the good agreement between the calculated concentrations and the certified values, the results are generally less accurate than those obtained with the previous method, except for limestone where Ca, Na and Sr are determined very accurately.

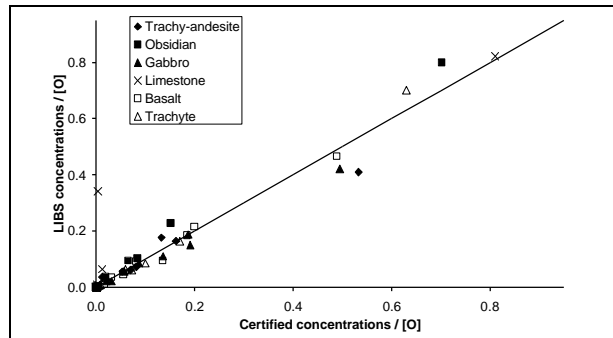


Fig. 5: Second method: Concentrations relative to O concentration.

The third method which allows to establish a measurement protocol not affected by the matrix effects is based on the basic physics of the laser-induced plasma. This CF LIBS approach [3] was proposed for quantitative elemental analysis of materials without use of calibration curves or need of reference samples and was applied to our rock samples (Fig. 6).

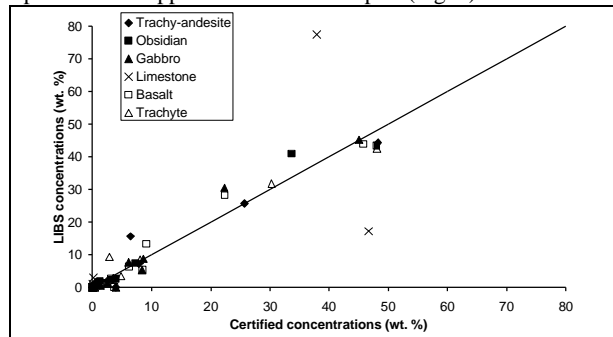


Fig. 6: Third method: Concentrations calculated with the CF LIBS method.

For the siliceous rocks, an overall agreement is achieved between the results of the CF method and the certified values. On the contrary, for the limestone sample the discrepancy is very large. Whatever the studied material, there is a huge deviation between the calculated concentrations and the standard ones for the Mg, Sr and Ba elements. The results obtained with this method are generally less accurate than those obtained with the two previous ones (maybe due to the uncertainties on the knowledge of spectroscopic parameters used in the CF method).

Conclusion: Finally the methodologies evaluated in this work allow to determine concentrations with accuracy compatible with the ChemCam requirements (10% for major elements). The three methods appear complementary and all present an interest for ChemCam. Each one has to be used in scenario to be defined in future work.

References: [1] Cremers D.A. (1987) *Appl. Spectrosc.* 41, 572-578. [2] Palanco S. et al. (2002) *Spectrochim. Acta Part B* 57, 591-599. [3] Palleschi V. et al. (1999) *Patent n°WO99/49301*. [4] Poitrasson F. et al. (1998) *Bull Volcanol* 60, 213-223. [5] Poitrasson F. et al. (1995) *J. Petrology* 36, 1251-1274. [6] Cantagrel F. et al. (1994) *Geostand. Newslett.* 18, 123-138.