LASER-INDUCED BREAKDOWN SPECTROSCOPY: A NEW METHOD FOR STAND-OFF QUANTITATIVE ANALYSIS OF SAMPLES ON MARS. B. Sallé[1], P. Mauchien[2], J.-L. Lacour[2], S. Maurice[3], R. C. Wiens[4]. [1]CESR, Université Paul Sabatier (Toulouse, France, salle@carnac.cea.fr), [2]CEA Saclay, DEN/DPC/SCP/LRSI (91191 Gif sur Yvette Cedex, France, mauchien@carnac.cea.fr), [3]CESR, Observatoire Midi-Pyrénées (9 avenue du Colonel Roche, 31400 Toulouse, France; sylvestre.maurice@cesr.fr), [4]Space and Atmospheric Sciences Group (MS D466, Los Alamos, NM 87545; rwiens@lanl.gov)

Introduction: ChemCam, Laser Induced Remote Sensing for Chemistry and Micro-Imaging, has been selected by NASA for the mobile Mars Science Laboratory (MSL) rover, scheduled for launch in 2009 [1,2]. ChemCam's Laser-Induced Breakdown Spectroscopy (LIBS) instrument will ablate surface coatings from materials at stand-off distances of up to 10 meters and measure elemental composition of underlying rocks and soils. The LIBS technique uses high powered laser pulses focused on the target at stand-off to obtain a plasma which emits light. Collection of the plasma light, followed by spectral dispersion and detection, permits identification of the elements present in the sample via their characteristic spectral lines. Advantages of the method compared to conventional elemental analysis methods, in the context of Mars exploration, include: - stand-off analysis capability [3], - no sample preparation, - rapid analysis (few minutes), - simultaneous multi-element detection of major, minor and trace elements, - ability to clean thin layer of dust and measure composition through depth profiling. Quantitative elemental analysis of materials is possible by comparing the LIBS signal obtained for a given element to a suitable calibration curve. However, the LIBS signal emitted by the same element depends on the matrix in which it is embedded [4-9]. This matrix effect leads to the necessity of many calibration curves, in principle, one for any substrate composition. This quantitative method can not be applied in the case of unknown samples that will be encountered on Mars. Recently, a new quantitative method has been developed to determine, without calibration curves, the concentration of atomic components in solid, liquid and gaseous samples [10]. This calibration free LIBS approach was tested in Ref. [11] on several samples of terrestrial origin, mostly volcanic rocks, which could be analogue to expected Martian samples. Results for main constituents were found in agreement with an EDX analysis. They demonstrate that the calibration free LIBS method can be of very great help for any first search in a mineralogical analysis. The aim of this work was first to evaluate the capabilities of the calibration free LIBS method in air at atmospheric pressure and close distance. The application of this method to LIBS experiments at stand-off distances in environmental Martian conditions on geological samples is in progress.

Brief description of the method: To use the calibration free LIBS method, some assumptions should be made concerning the theoretical representation of the plasma conditions. We suppose that the plasma composition is representative of the material composition prior to the ablation (as-

sumption well realized in the range of laser irradiances used in LIBS experiments). In the temporal and spatial observation window, the plasma is supposed to be in Local Thermal Equilibrium (LTE) and optically thin. In an LTE approximation, population of the excited atomic levels follows a Boltzmann distribution. This study will consider only the spectral lines that are not self-absorbed. In typical LIBS experimental conditions, only lines generated by neutral species and single ionized species can be detected. Given these conditions, the method comprises: (a) obtaining the plasma temperature from at least one species of the emitted radiation by the Boltzmann plot (for that species, we need to know the LIBS intensity of different lines, the corresponding degeneracy levels and the transition probabilities); (b) calculating the partition function of each species at the plasma temperature; (c) determining the concentration value of each species times an experimental factor by using several spectral lines at different energies; (d) calculating the concentration of the species that have not been detected by using the Saha equation; (e) calculating the concentration of atomic components by eliminating the experimental factor through normalization to units of the sum of all species' concentration; (f) determining the elemental composition by adding the values corresponding to the neutral and single ionized species of the same element.

Results: Fig. 1 shows the Boltzmann plots obtained from the different species observed in the plasma. The slope of the Boltzmann plot obtained for Fe(I) yields a plasma temperature of 11070 K. The results presented here were obtained in air at atmospheric pressure and close distance (25 cm) for a Fe/Ni alloy whose composition in % is given in Table 1.

	Standard (%)	CF-LIBS (%)	Accuracy (%)
Fe	44.64	46.399	4
Ni	32.30	37.56	16
Cu	0.29	0.369	27
Cr	20.65	13.392	35
Co	0.13	0.105	19
Mo	0.26	0.252	3
Ti	0.30	0.316	5
Mn	0.85	1.017	20
Si	0.30	0.277	8
Al	0.28	0.312	11

Table 1: Concentrations of standard Fe/Ni alloy compared with the values obtained by the calibration free LIBS method (CF-LIBS).

According to the calibration free method proposed by Palleschi et al., we impose this same temperature for all the species to deduce the elemental composition of the sample. Results presented in Table 1 are in good agreement with the known concentrations although relative accuracy strongly depends on the element: it varies between 4 and 35%. We are now evaluating this calibration free method for geological samples ablated at stand-off distances in simulated Martian environment. The experimental set-up used for this application is described below.

Typical laboratory set-up: To evaluate performance of LIBS for Mars soil and rock analyses, special care is taken to reproduce the configuration expected at Mars, especially for the laser in terms of wavelength, repetition rate and energy. Thus, our experimental set-up (Fig. 2) is composed of a Q-switched Nd:YAG laser at 1064 nm with a repetition rate of 10 Hz. The laser beam is transported to the sample by one reflective mirror and a quartz plate at 45°, which allows collection of plasma emission light along the same optical axis as the laser beam and reduction of the laser energy to a value of approximately 40 mJ, the same energy as proposed for the ChemCam laser. Between the reflective mirror and the quartz plate, we use a 3x laser beam expander composed of two lenses of -100 and 300 mm focal length. The laser pulses are focused at normal incidence on the sample surface through a lens of focal length fixed at 5 meters. The sample is placed in a chamber filled with a flowing stream of mixture of CO_2 (95.3%), N_2 (2.7%) and Ar (1.6%) and the pressure is adjusted to 7 Torr to simulate the Martian atmosphere. The plasma emission light is focused by a 10-cm focal length lens into a 1-m-long fiber optic. This optical fiber is directly connected to the entrance slit of an echelle spectrometer (LLA ESA 3000, Gmbh, Germany) equipped with an Intensified CCD camera (KAF 1000, Kodak) detector system. The advantage of this spectrograph is its ability to simultaneously collect the entire 200-780 nm spectral range with a resolving power $\lambda/\Delta\lambda\sim 10,000$. The use of this kind of spectrometer is strongly preferred for the calibration free procedure which requires all the atomic components of a sample to be detected by measuring at least one of their characteristic spectral lines. Spectra are recorded with time resolution, controlled by a programmable pulse delay generator (DG 535, Stanford Research Systems) to eliminate the continuum emitted at the beginning of the plasma emission. As the response curve of the detection system is a characteristic of the experimental apparatus, it needs to be determined in order to normalize the spectral intensities in the whole spectral range considered. It has been done by using a continuous standard lamp (S-638, Optronic Laboratories) with a known spectral intensity profile ($\mu W/cm^2$ nm) to the place of the sample. Once the spectra have been acquired for the samples being analyzed and the peaks assigned to the corresponding species, the intensity values are normalized by taking into account the efficiency of the experimental apparatus at the considered wavelength.

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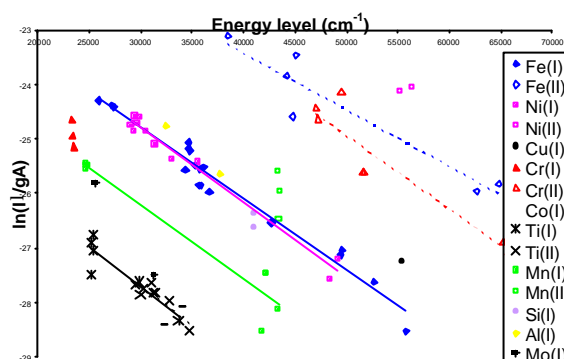

Fig. 1: Boltzmann plots to determine the plasma temperature from the slope of the curves.
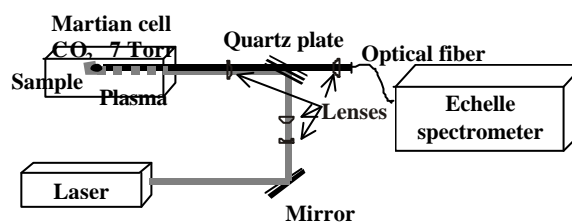

Fig. 2: Experimental set-up used for LIBS experiments at stand-off distances in Martian conditions.