

**EVALUATION OF THE ELEMENTAL AND MOLECULAR HOMOGENEITY OF THE SUPERCAM CALIBRATION TARGETS.** L. Gómez-Nubla<sup>1</sup>, J. Aramendia<sup>1</sup>, G. Arana<sup>1\*</sup>, F. Rull<sup>2</sup>, A. Cousin<sup>3</sup>, S. Fdez-Ortiz de Vallejuelo<sup>1</sup>, K. Castro<sup>1</sup>, M. Maguregui<sup>1</sup>, J.A. Manrique<sup>2</sup>, G. Lopez-Reyes<sup>2</sup>, J.M. Madariaga<sup>1</sup>, J. Medina<sup>2</sup>, V. Garcia-Baonza<sup>4</sup>, J. Laserna<sup>5</sup>, S. Maurice<sup>3</sup> and R. Wiens<sup>6</sup>. <sup>1</sup>Department of Analytical Chemistry, University of Basque Country (UPV/EHU), Bilbao, Spain ([gorka.arana@ehu.eus](mailto:gorka.arana@ehu.eus)), <sup>2</sup>University of Valladolid, Spain, <sup>3</sup>IRAP, Toulouse, France, <sup>4</sup>Complutense University, Madrid, Spain, <sup>5</sup> Malaga University, Spain, <sup>6</sup>LANL, Los Alamos, USA.

**Introduction:** Mars 2020 is the new mission of NASA to Mars whose main objective is the detection of life evidences by means of the analysis of superficial and in depth samples belonging to the Planet. For this purpose, SuperCam will be used as one of the instruments selected. This instrument is designed to perform remote analysis on the Mars surface employing several spectroscopic techniques such as Laser Induced Breakdown Spectroscopy (LIBS), Raman, Time-Resolved Fluorescence (TRF) and Visible and InfraRed (VISIR) reflectance. In addition, SuperCam also acquires high-resolution images using a color remote micro-imager (RMI). This system replaces and improves the ChemCam, its precursor, only focused on LIBS analysis [1].

In order to analyse the samples collected from Mars, it is essential to perform previous in-situ calibration using targets with known elemental and molecular composition. Thus, it will be possible to assess the presence or absence of certain elements or compounds in Mars, and their concentrations as well.

A set of 25 calibrations targets will be loaded in the SuperCam instrument. A set of six replicates for each sample will be prepared [2]. A correct interpretation of the data obtained from the diverse spectroscopic techniques requires that calibration targets must be sufficiently homogeneous with respect to their elemental and molecular composition.

**Instruments:** In this work, a new methodology was developed to verify the physico-chemical homogeneity of the selected calibration targets. It is based on micro energy dispersive X-Ray Fluorescence ( $\mu$ -ED-XRF) and Raman spectroscopy analysis, so both elemental and molecular composition of the samples can be analyzed. A M4 TORNADO  $\mu$ -ED-XRF spectrometer (Bruker Nano GmbH, Berlin, Germany) was used, which implements an energy-dispersive SDD detector with 30 mm<sup>2</sup> sensitive area and resolution of 142 eV for Mn K $\alpha$  line, and two air-cooled Rh tubes powered by a low power high voltage (HV) generator. One of the tubes is capable to operate at voltages in the range of 10-50 kV and 100-600  $\mu$ A, which is mounted on a polycapilar lens that provides lateral resolution of 25 microns for the Mo K $\alpha$  line, and was employed to verify the elemental homogeneity. Besides. A MV 10 N VARIO-B diaphragm pump was used to improve the detection of light elements. The pressure inside the

chamber of the instrument was 20 mbar. A Zr disc was used to calibrate the equipment daily. Moreover, XRF data were acquired using a measuring time of 20-50 ms, 2 cycles and a distance of 20 $\mu$ m between points of measurement. The treatment of data was carried out by M4 TORNADO software.

The Raman spectrometer used was a fully automated Renishaw InVia system. The 532 nm excitation diode laser was selected for the experiments, and the spectra were collected in a thermally-cooled high sensibility and ultra low noise CCD detector. The nominal power of the laser can be modulated (from 0.0001 % to 100 % of its maximum power) to prevent the thermodecomposition of the samples. The spectrometer is coupled to a microscope and different objectives of 5x, 20x and 50x were used. This microscope mounts an optical camera for an improved focusing of the laser spot on the sample. Besides, the device is equipped with a class 1 enclosure to minimize spurious or sun light effects. In addition, the instrument is mounted on an vibration-isolated table. The mean spectral resolution is around 1 cm<sup>-1</sup>. The calibration of the equipment was performed daily by measuring the 520.5 cm<sup>-1</sup> band of a silicon. The laser beam was centered also once per day to ensure a proper analysis. The software used for data collection was the Wire 4.2 (Renishaw, UK). After several analysis, the optimized acquisition parameters were 5 seconds and 1 accumulation using the 1800 l/mm grating (60-1800 cm<sup>-1</sup> spectral range) at 10% of the maximum power laser and using 10x objective. These integration parameters were optimized considering the signal-to-noise ratio and minimizing the exposure times required for the analysis.

**Methodology:** The methodology followed with the two techniques slightly differed depending on the specifications of the two instruments. However, with the aim of being comparable the sampling for the determination of the homogeneity were exactly the same for both. First of all, Raman and XRF images of the whole targets were measured following a point-by-point methodology. The images were extremely useful to detect hotspots at first glance (Figure 1). Once these images were obtained, areas of 100 x 100  $\mu$ m were limited to determine whether the calibration targets were homogeneous or not within the established tolerances. These dimensions were selected by taking into

account the working-spot of the SuperCam spectroscopic techniques. For instance, the LIBS's spot is around 300 microns, so if the calibration targets were homogeneous for 100 microns, they would be also homogeneous for 300 microns. Besides, in order to ensure the statistical significance of the results, 10 areas were randomly selected in each calibration target (it means that the same procedure was repeated ten times). In this way, several quantitative data were acquired and statistical treatment was able to be applied.

The final quantification data were subsequently obtained in both techniques with different acquisition parameters depending on the instrument and software.

In the case of Raman spectroscopy, the Wire 4.2 software includes a chemometric algorithm based on Direct Classical Least Squares (DCLS). This algorithm approximates the experimental spectrum of each pixel in the map by combining different scaled copies of reference spectra of all the compounds detected in the target. The scaling factor is automatically selected to fit as best as possible the spectra of the Raman map. To perform the best fit, the reference spectrum of each compound on the pellet (target) was recorded at the exactly same experimental and instrumental conditions. After that step, a quantification of the different compounds present in the pellet was carried out following a Fraction Estimation procedure. Thus, a percentage of each phase present in the sample was obtained, from the fit performed by DCLS. It is crucial to perform an automatic pre-treatment to all the spectra (baseline correction and cosmic ray removal) following the same criteria in order to obtain a repetitive method.

In the case of XRF, the semi-quantitative data were obtained from the spectral results using a Fundamental Parameters based-method included in the M4 TORNADO software. The numerical values are given according to the signal of the elements, and the statistical treatment is carried out then.

The obtained data were statistically weighted equally for both techniques. In this way, a decision making tool was developed based on the Relative Standard Deviation (RSD) obtained with the different replicas. With the value for each element/compound for all the areas in the same target, the average and standard deviation were calculated. Finally, the RSD for each element/compound in each target was calculated to decide whether a given target can be considered homogeneous or not for that element/compound with respect to a threshold value.

Apart from the homogeneity validation of the targets, Raman spectroscopy was also used to assess possible thermal-induced changes in the original composition either by the sinterization (process employed for the manufacture of the pellets) or by the LIBS pulses.

This fact is crucial to verify whether the target's performance will be preserved after the LIBS analysis once in the Martian surface.

Most of the samples studied showed a good homogeneity for many of the elements according to the XRF results obtained. Samples were later analyzed by microprobe to obtain the concentration of the elements [3].

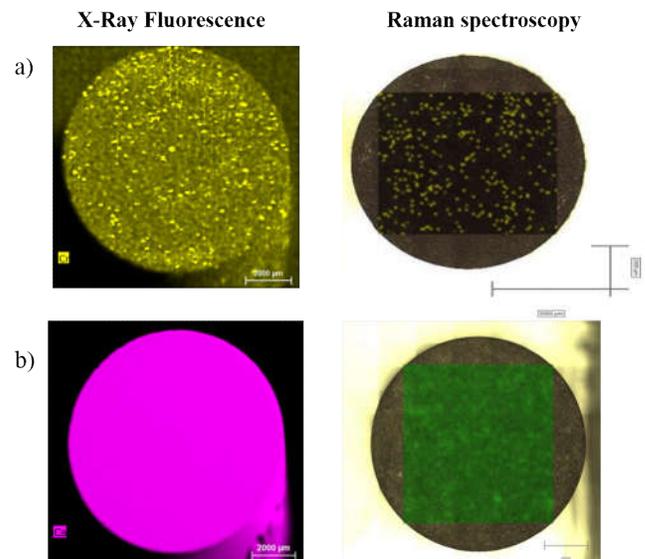


Figure 1. Heterogeneous (a) and homogeneous (b) calibration targets from X-Ray Fluorescence and Raman spectroscopy analyses.

**Conclusions:** The methodology developed here is an essential previous step for an adequate collection of data of the spectroscopic techniques loaded into the SuperCam instrument. This protocol allows us to verify the homogeneity of the targets (pellets) used to calibrate the equipments, so the result will not be affected by the location of the target where the analysis will be performed.

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#### References:

- [1] <https://mars.nasa.gov/mars2020/mission/instruments/supercam/for-scientists/> [2] Cousin A. et al. (2017) Lunar and Planetary Science XLVIII. [3] Cousin A. et al. (2018) Lunar and Planetary Science XLIX.