IN-SITU RAMAN-LIBS COMBINED SPECTROSCOPY FOR SURFACE MINERAL ANALYSIS AT STAND-OFF DISTANCES. F. Rull[1], A. Vegas[2] , F. Barreiro[2] . [1] Centro de Astrobiologia, Unidad Asociada UVa-CSIC. Ed.INDITI P.203 Parque Tecnologico de Boecillo, E47151 Boecillo (VA) (Spain) [2] TCP Sistemas e Ingenieria, C/ Fernández Caro, 7 E28027 Madrid (Spain)

Introduction: Mineral phase identification, molecular detection combined with chemical composition at stand-off distances constitute a very important field of application of the spectroscopic techniques. Remote Raman detection has proved to be feasible up to 200 meters distance [1-3] and combination of Raman with other complementary techniques as LIBS or fluorescence show an enormous potential for planetary surface analysis as well as for other Earth applications as drugs and explosive detection and work in harsh and remote environments [4,5].

In the case of the future sample return missions precise remote analysis of surface targets will be an extreme valuable tool for selecting the appropriate samples, simplifying the operation strategy and allowing a faster screening of the surroundings of a rover or lander in particular approaching outcrops.

A particular aspect in which remote Raman spectroscopy (RRS) could be applied with great advantage extending its potential to Astrobiological applications is in the study of water and ice at the field and in particular in the case of glaciers, icebergs and other natural ice formations. The possibility to analyze ice at distances ranging from several meters to 100-200 meters could allow obtaining in-situ structural information of ice formation and transformations in big icewalls which are in general quite difficult for robotic close analysis and sampling. This potential has been explored in several expeditions at the Arctic (Svalbard Islands, Norway) in the context of AMASE activities (Arctic Mars Analog Svalbard Expedition) during 2007-2008 and 2009 analyzing ice in-situ with a field prototype in the range 20-150 meters and obtaining very good results.

A natural extension of Raman capabilities is the combination with LIBS (Laser Induced Breakdown Spectroscopy). This combination allow the identification of molecules and mineral phases with elemental analysis at the same spot. Nevertheless LIBS need to induce a plasma on the sample surface which is not easy a longer distances limiting the use with portable systems at the reasonable range of several meters.

In this work remote Raman-LIBS results obtained with a new version of the remote Raman prototype used in AMASE expeditions in the Arctic are presented and discussed. Particular attention is devoted to the capability to obtain spectra in daylight conditions without the use of gated i-CCD's at the nanosecond scale which represent also a limiting factor in planetary exploration.

Experimental: The remote Raman-LIBS instrument consists on a pulsed laser used for excitation, a Raman spectrometer and the appropriate optics to focus the illuminated target on the spectrometer entrance. The laser is an Nd-YAG pulsed laser emitting at 532nm and a maximum rate of 20Hz with 32 mJ energy and 4ns width pulses. In the only remote Raman configuration the laser beam is coaxially aligned with the telescope or telephoto optical path (Figure 1). In the combined Raman-LIBS mode the laser pulse is focused on the sample for plasma excitation in LIBS and defocused for Raman in order to avoid thermal damage. The collection optics is focused on the laser spot in both cases and the incoming light projected to the fiber optic entrance which is coupled with the spectrometer (Figure 2). The spectrometer used is a transmission spectrograph built in our laboratory following the same design parameters than those envisaged for the Raman spectrometer selected for the Exomars mission. Two configurations has been tested for comparison purposes. In one case using a double holographic transmission grating (Kaiser Optical) and in another case using a single transmission grating from Wasatch Photonic. The detection has been also tested in two modes. A gated CCD Andor iStar camera able to gate up to 2ns and a non gated CCD Newton DU940N-BV also from Andor able to acquire single spectra in the order of 10 micro seconds. The distances used for test range between 5 to 30 meters for the remote only system and 4 to 15 meters for the combined Raman-LIBS system. In the field operation mode the whole system is mounted in a pan and tilt computer controlled device and a panoramic camera control the target selection.

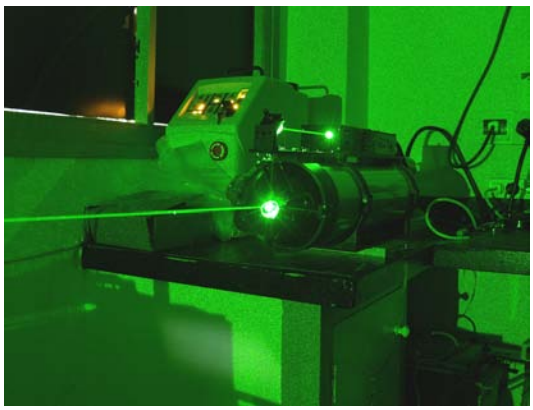

Figure 1. Coaxial alignment of the excitation and collection paths in Remote Raman Spectroscopy

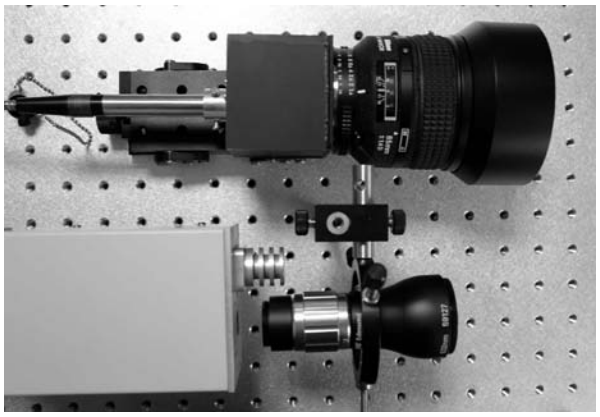

Figure 2. Excitation and collection paths for the combined remote Raman-LIBS spectroscopy.

Results and discussion: One of the main aims of the present work is to assess the performance of the systems tested on comparing the gated detection in the nanosecond scale with the detection with non gated detection which show more intense response and some advantages for planetary exploration use. Nevertheless non gated mode show important limitations when the spectra are taken under daylight conditions. In figure 3 some spectra obtained with the telescope and the iCCD detector at distances of 30 meters under sunny conditions are presented. Typical gate width used is 20ns and 100 spectral accumulations. In Figure 4 spectra of calcite and Ba(ClO4)2_3H2O at 4.5 meters distance obtained with the non gated CCD are presented. Calcite spectrum was obtained under partially clouded daylight conditions with 200 microseconds integration time and 200 spectral accumulations. Ba(ClO4)2_3H2O spectrum was obtained under incandescent lamp (60W/m2) illumination with 10 microseconds integration time and 200 accumulations. In Figure 5 LIBS spectra of calcite and basalt form Calatrava Volcanic Field (Spain) obtained at 15 meters are presented. In these cases conditions are similar to those used for calcite Raman experiment: partially clouded daylight conditions. The integration time was 10 microseconds and 100 spectral accumulations. These results show the real possibility to obtain combined Raman-LIBS spectra at the field under some daylight conditions with non gated detectors and in the microsecond range. This methodology simplify the technical limitations imposed by detection in the nanosecond scale. Nevertheless our results also show that while for LIBS a wide range of integration time can be used it is not the case for Raman. Integration time in the order of milliseconds preclude in general obtain spectra with acceptable signal top noise ratio under daylight conditions even in cloudy days.

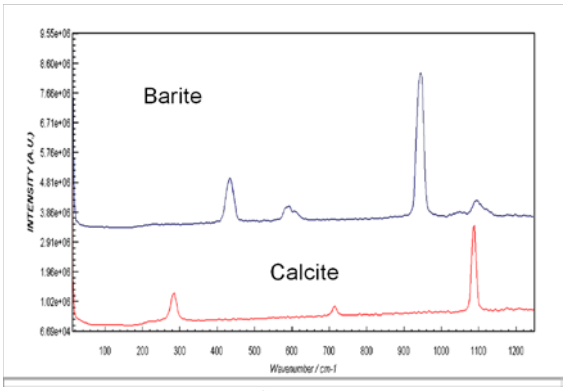

Figure 3. Raman spectra of calcite and barite obtained in daylight conditions (intense sunny light) in gated mode.

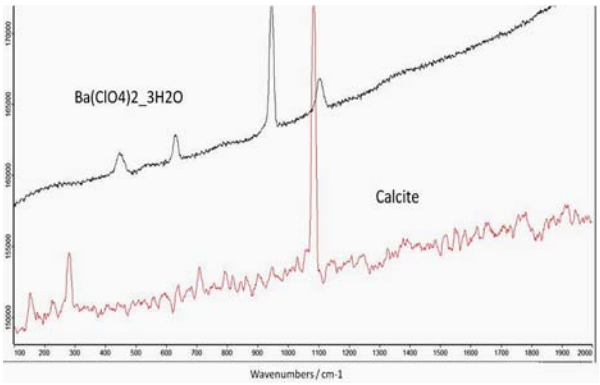

Figure 4. Raman spectra of calcite and Ba(ClO4)2_3H2O at 4.5 meters distance obtained with the non gated CCD. Partially cloudy conditions.

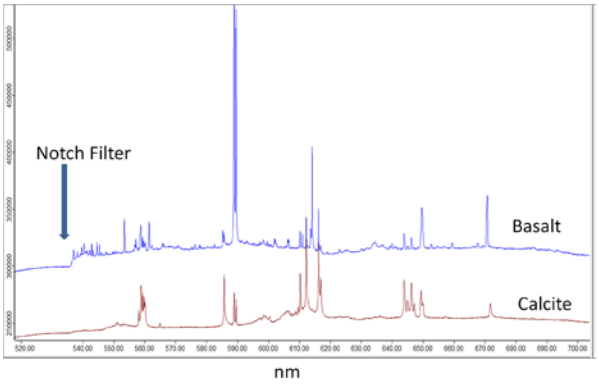

Figure 5. LIBS spectra of calcite and Ba(ClO4)2_3H2O at 4.5 meters distance obtained with the non gated CCD. Partially cloudy conditions.

References:

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