Validating the performance of a Raman laser spectrometer (RLS) instrument under Martian conditions

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Obtaining a better understanding of Mars' geologic history and the search for evidence of past or present life on Mars are the principal objectives of ESA's first mission of the Aurora programme, ExoMars. Water plays an essential role in supporting all types of terrestrial life forms; consequently a major scientific focus of most Martian missions is to search for evidence of water. In addition, in the context of postulated future manned missions to the planet, an "on-site" source of H_2O would be crucial. Quantifying the amount of water on the planet's surface, its spatial distribution and its occurrence, either as liquid or ice or bound in hydrated silicate or sulphate minerals such as clay and sulphates is therefore a key requirement of instrumentation on current and future Mars missions.

A combined Raman-laser induced breakdown spectroscopy (LIBS) (RLS) instrument was initially chosen as one of the instruments of the Pasteur analytical package of the ExoMars rover. As such it was proposed to be one of the most important analytical tools on the mission being a first contact instrument. Raman spectrometry would be used to characterise mineralogy and organic compounds and simultaneously, the LIBS would determine multi-elemental compositions of minerals. The combination of mineralogy and compositional data had the capability to both constrain the location of water and understand petrogenetic processes that form rocks and minerals. Due to scaling back of the ExoMars mission, the RLS has been replaced by a Raman only instrument. However, the potential powerful analytical capability of a combined RLS system is widely recognised and development of a RLS continues in the context of potential future missions to both Mars and Moon.

This PhD project is designed to determine the optimum analytical strategy for the Raman and Laser Induced Breakdown Spectroscopy (LIBS) (RLS) instrument on Mars. Therefore, the first objective of this PhD research was to design, manufacture and test a Mars Atmosphere Simulation Chamber (MASC) large enough for instrument testing and capable of reproducing the atmospheric conditions of Mars. The MASC is a temperature and atmosphere controlled chamber (200 l). In order to reproduce Mars' atmosphere and temperature inside the MASC, an innovative heating-cooling system was coupled to a vacuum and gas control system. The MASC chamber can simulate planetary atmospheres and by doing so we are able to perform *in situ* sample analysis and test the performance of space instruments.

The second objective of this PhD research was to validate the performance of the RLS instrument within the MASC under Martian conditions. Therefore, the RLS instrument was installed inside the MASC and the performance of the RLS instrument was evaluated and tested. The performance of the spectrometer was initially assessed based on the calibrations of the spectrometer at different temperatures. For the calibration, visible light (~400-800 nm) was directed at the RLS instrument to localise the position of the visible spectrum on the charge coupled device (CCD) and the visible spectrum from 660 to 800 nm was used for Raman analyses for this research. The calibration established that the position of the spectrum on the CCD was influenced by the temperature of the spectrometer. We conclude that the prism of the RLS instrument was significantly affected by thermal changes. In other word, the most probable causes of the change in the position of the orders on the CCD are (the unwanted) movement of the prism or (unwanted) change(s) in the properties of the prism due to thermal expansion. A key observation is that the spectrum did not shift horizontally on the

CCD so that wavelength calibrations were not affected. From these observations we conclude that the grating was not affected by temperature. Consequently, we can summarise that the RLS instrument can be operated under Martian atmospheric conditions provided that temperature variations only vary in the range +10 to -20 °C.

The final objective of this PhD research was to assess the effectiveness of the RLS instrument in obtaining Raman spectra from different group of minerals under Martian conditions. The results of the experiments show that the influences of temperature and pressure on mineral Raman spectra were not detected at Martian conditions. In fact, the different structures of minerals result in distinct Raman spectra. Importantly it has been shown that it is possible to use detect changes in Raman spectra using the RLS instrument to determine compositional variations of specific mineral groups, e.g. Mg-Fe substitution in olivine. However, the poor identification of a group of minerals by the RLS instrument confirm that, the RLS instrument is far less effective at producing and detecting Raman signals than commercially available instruments; e.g., Renishaw InVia Raman microscope.

We recommend extensive further testing of the RLS instrument and the newly designed Raman-only instrument for ExoMars on samples that will be more typical of Mars's surfaces. The work carried out to date, although under Martian conditions, was essentially under laboratory conditions. More rigorous assessments of the effects of variable grain size and surface morphology are needed. This is because the intensity of the Raman peak is determined not only by instrument optics, but also by the sample properties. The influence of the crystals properties (such as grain size, surface relief, colour and absorption coefficient) on the peaks intensity needs to be studied.

We evaluated key aspects of performance of the RLS instrument that were sub-optimal and made a series of suggestions for improvement of RLS instrument's performance for future planetary missions.

Recommendation	**Goal**
- Select a suitable stable Raman laser source	- Accurate and reproducible Raman spectra
- Increase the laser power	- Improving the detection limits of minerals
- Decrease the RLS instrument spot size	- Ability to identify minerals of small grain size
Improving the RLS optical design - Re-design spectrometer - Shorter optical fibres - Use less connectors	- To increase SNR and optical transmission

- Improve the CCD cooling system	- Increasing SNR (decrease thermal noise)
- Change the angle of the grating or apply a shorter wavelength laser source	- To expand the Raman spectral range to above 3000 cm^{-1} to include water

Coupled with the proposed improvements above we are confident that the use of a combined Raman-LIB spectrometer will be a valuable addition to the contact instrument package of future planetary missions.