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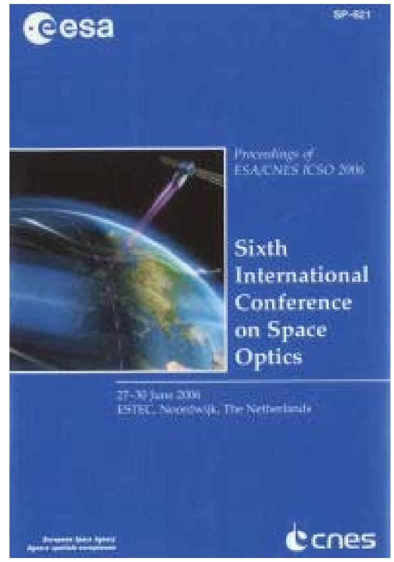

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COMBINED RAMAN SPECTROMETER/ LASER-INDUCED BREAKDOWN SPECTROMETER DESIGN CONCEPT

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ABSTRACT

Amongst the different instruments that have been pre-selected to be on-board the Pasteur payload on ExoMars is the Raman/ *Laser Induced Breakdown Spectroscopy* (LIBS) instrument. Raman spectroscopy and LIBS will be integrated into a single instrument sharing many hardware commonalities.
An international team under the lead of TNO has been gathered to produce a design concept for a combined Raman Spectrometer/ LIBS *Elegant Bread-Board* (EBB). The instrument is based on a specifically designed extremely compact spectrometer with high resolution over a large wavelength range, suitable for both Raman spectroscopy and LIBS measurements. Low mass, size and resources are the main drivers of the instrument's design concept. The proposed design concept, realization and testing programme for the combined Raman/ LIBS EBB is presented as well as background information on Raman and LIBS.

1 GENERAL SPECIFICATIONS

ExoMars (planned launch 2011) is the first flagship mission of the Aurora programme of the *European Space Agency* (ESA).
Its aim is to further characterise the biological environment on Mars by deploying a mobile exobiology instrumentation package (Pasteur payload) inside a rover on the Martian surface performing in-situ soil sample analysis. The main scientific objective of the Pasteur payload is the search for signs of past and/or present life on Mars.

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Fig. 1. Pasteur Payload artist impression [1].

Amongst the different instruments that have been pre-selected to be on-board the Pasteur payload is the Raman/ LIBS instrument, which is regarded as a fundamental, next-generation instrument for organic, mineralogical and elemental (atomic) characterization of Martian soil and rock samples. The Raman spectrometer is dedicated to molecular analysis of organics and minerals and will participate in the geological and mineralogical context analysis. The LIBS provides information on the sample's elemental composition. The capability of simultaneous multi-element detection, rapid analysis, high sensitivity, and spatial resolution are among the advantages of these active techniques over other passive systems.

Raman spectroscopy and LIBS will be integrated into a single instrument. They share many hardware commonalities, e.g. pointing capability, light collection, spectral analysis. For science objectives, the synergy is evident: the capability to analyse the local structure of a substance, with its chemical composition, is essential in the mission. Measurements will be made in two different contexts: outside the rover laboratory (using the rover's robotic arm) and inside the rover laboratory (samples provided by a drill system). Fig. 2 shows the functional block diagram for the EBB.

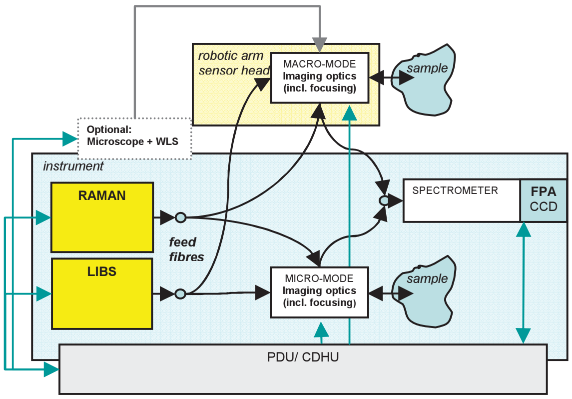

Fig. 2. Functional block diagram.

2 SCIENCE OBJECTIVE

In recent years, our knowledge of Mars has enormously progressed, at kilometre-scales from orbital distances, as well as centimetre-scale from rovers. However, vast areas of investigations are still at their commencement, at the cross-cut major themes of climate, geology, and life.

2.1 Geology & mineralogy

The current knowledge of Mars geology and mineralogy comes from two main sources, the SNC meteorites, the different remote sensing and rover-surface missions. Mars Global Surveyor, Mars Odyssey and Mars Express together with Viking, Pathfinder and Mars Exploitation Rovers Spirit and Opportunity paved the way with data from which the knowledge on mineralogy, chemical elemental composition and geological processes has been developed.

Evidence of volcanic, hydrothermal, fluvial and glacial related geological processes have been reported. The existence of water has also been proved and the scientific community is waiting for more precise details from the MARSIS-radar on-board the Mars Express orbiter.

The most important argument supporting the water activity on Mars surface comes from the Mars Exploration Rover Opportunity's Moessbauer spectrometer. It showed the presence of an iron-bearing mineral called Jarosite in the set of rocks dubbed "El Capitan" in Mars' Meridiani Planum. "El Capitan" is located within the rock outcrop that lines the inner edge of the small crater where Opportunity landed. The occurrence of this mineral has been interpreted as:

- Environmental conditions including episodic inundation by shallow surface water, evaporation, and desiccation, suggesting that conditions were suitable for biological activity for a period of time in Martian history;
- Mineralogical evidence for aqueous processes on Mars, probably under acid-sulphates conditions;
- Possible existence of a volcanism-related mineralising hydrothermal system, and
- Indicative of a wet, oxidizing and acidic environment, but followed by arid conditions.

The Mini-*Thermal Emission Spectrometer* (TES) instruments on Spirit and Opportunity have studied the mineralogy and thermo-physical properties at Gusev Crater and the Meridiani Plains. At Gusev undisturbed soil spectra showed features interpreted to be due to minor carbonates and bound water. At Meridiani, the Mini-TES has confirmed the presence of coarse crystalline hematite and olivine basalt sands predicted from orbital TES spectroscopy.

In general rocks are olivine-rich basalts with varying degrees of dust and other coatings. Pyroxene, plagioclase and oxides (mainly hematite) are also present (in agreement with the data from SNC meteorites). And some sulphates (Ca, Mg, and Fe) and carbonates have been also identified.

Nevertheless, the total amount of mineral phases identified (about a dozen) compared with the phases identified on Earth, stresses the needs of developing new rovers with more instrumental capacity and new types of instruments with more sensitivity and analytical capacities.

2.2 Organics & search for life

Viking started the search for organics on Mars. Results were puzzling due to three aspects. First, was the total absence of organics as measured by the *Gas Chromatography/ Mass Spectrometry* (GCMS) [1 and 2]. The second unexpected result was the rapid release of O_2 when soil samples were exposed to water vapour in the *Gas Exchange Experiment* (Gex) [3]. The third unexpected result was that organic material in the *Labelled Release Experiment* was consumed as would have been expected if life was present [4] in apparent contradiction with the results from the GCMS. Currently, the most widely held explanation for the reactivity of the Martian soil is the presence of one or more inorganic oxidants [5, 6, 7]. The question of the search for organics on Mars is still open, with all its implications for astrobiology.

3 RAMAN AND LIBS ON MARS

Characterisation of the elemental chemical composition and structure of the minerals forming the rocks and soils at the surface and subsurface of Mars is essential to identify the genesis and the geological processes related with the evolution of the “red planet”. Moreover, characterisation of possible organic compounds as well as secondary weathering mineral processes, in particular those related with possible biogenic activity are also essential in the assessment of traces of present or past life on Mars.

The combination of Raman and LIBS constitutes a powerful tool for the analysis of minerals and biomarkers in the exploration of Mars. Raman is sensitive to the phase (composition and structure) while LIBS is sensitive to the elemental chemical composition of any mineral or organic compound. In Raman spectroscopy, the vibrational transitions undergone by the chemical bonds of a compound are analysed after excitation by a monochromatic light source, normally a continuous or pulsed laser. In LIBS the emitted electronic transitions of atoms ablated by small laser-pulse induced plasma on the sample are analysed.

Raman is a completely non-destructive technique and LIBS only induces small perturbations on the samples at microscopic level. Nevertheless, these perturbations (ablation craters) can also be used to study coated minerals (as it is the case of many rocks on Mars) by performing in-deep analysis. The pulsed laser used with LIBS does ablation and so permits to get a profile along the optical axis of the system. Therefore, adsorbed particles and minerals resulting from alteration can be distinguished from the unaltered and uncoated initial rock.

Finally, samples in the solid, liquid or gas state can be analysed with both methods.

3.1 Raman

Raman spectroscopy is well recognised as a powerful tool for the chemical and structural identification of materials in the solid, liquid or gas state. Its analytical capability, both macro- and micro- without the need to perturb a sample, have made this technique unique for many applications where the materials are scarce or very valuable and rare. In Fig. 3, the Raman Spectrum of Ferricopiapite from Rio Tinto is shown. Fig. 4 presents the Raman spectrum of Jarosite from the world-type locality Barranco del Jaroso. These figures are illustrating the vibrational features at low, medium and high wavenumber spectral ranges [9].

Raman spectroscopy suffers from some limitations, which are mainly those derived from the fluorescence emission induced in the samples by the laser excitation.

The choice of the Raman excitation wavelength is a very important issue to consider. Excitations with wavelength over 700 nm have in general a very limited detection capability for ν(CH) and ν(OH) bands, which in their turn are essential to characterise hydrated phases and biomarkers. This fact is illustrated in Fig. 3. Raman spectroscopy can easily distinguish between OH from hydroxyl groups and OH from hydration water [Fig. 3].

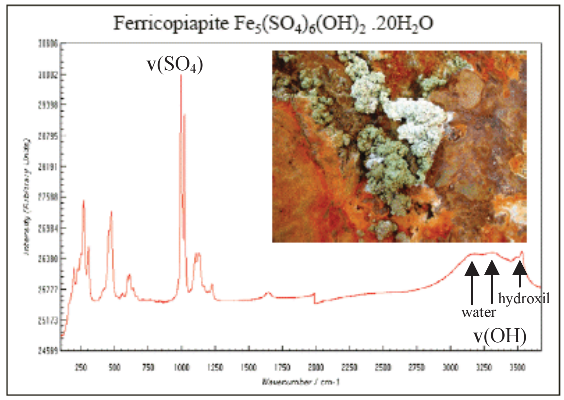

Fig. 3. Raman spectrum in macro-mode of ferricopiapite mineral from Rio Tinto [9].

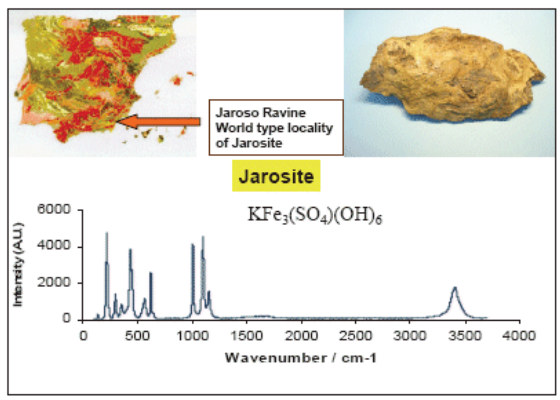

Fig. 4. Raman spectrum in macro-mode of Jarosite from the Jaroso Ravine [9].

On the other hand, excitation at short wavelengths in some cases induces several fluorescence processes on the samples. The large experience on Raman spectroscopy of minerals, polymers and biomarkers of the scientific team involved in this project proves that most of the fluorescence effects are present in the laser excitation range from 532 to 785 nm.
Fluorescence is mostly avoided using *Fourier Transform* (FT)-Raman spectrometry with *infrared* (IR) (typically 1064 nm) excitation. Nevertheless, FT-

Raman suffers from the above-mentioned limitations in identifying OH vibrations and it has important technical difficulties if combined with LIBS. Another possibility is to use gated mode with acquisition times of the order of few nanoseconds when excited with lower wavelengths, in particular with 532 nm pulsed laser.
Previous experimental research performed in the frame of the *Mars Surveyer Rover* (MSR) payload by Alian Wang [10] showed that the dark and red compounds emit a quite weak Raman scattering when illuminated with red to IR excitations as compared with green excitation (in fact this is a classical absorption effect). On the opposite, the light compounds emit in general more fluorescence. For these reasons, laser excitation that avoids absorption limitations as the 532 nm and avoids fluorescence as the gated mode is considered as the ideal.

This approach has however not be considered for the Mars mission, as it presents high technical risks particularly related to the lack of maturity of intensified detection systems for space applications.

Consequently for Mars application the choice of the Raman excitation wavelength should be a compromise between the minimum detection capabilities necessary to analyse important vibrations as the ν(CH) for organics and the negative possible fluorescence effects.

3.2 LIBS

LIBS is based on the focusing of a high-power pulsed laser beam (>1 GW/cm^2) onto a sample surface leading to the creation of a plasma composed of excited species which emit light.

Collection of the plasma light, followed by spectral dispersion and detection, permits identification of the elements present in the sample using their characteristic spectral lines and allows quantitative analysis. For space exploration, this method possesses several advantages including stand-off analysis capability, no sample preparation required, rapid analysis (few minutes), simultaneous multi-elemental detection (major, minor and trace elements), and the ability to measure the composition of weathered layers and the underlying bulk rock composition through depth profiling (repeated ablation).

Fig. 5 [11] presents the LIBS spectrum of a Basalt standard. It is worth noticing that the density of lines is higher at low wavelengths than at high wavelengths. To achieve such a spectrum typical resolution needs to be smaller than 0.1 nm in the *ultra-violet* (UV) and could be between 0.1 nm and 0.2 nm in the near IR.

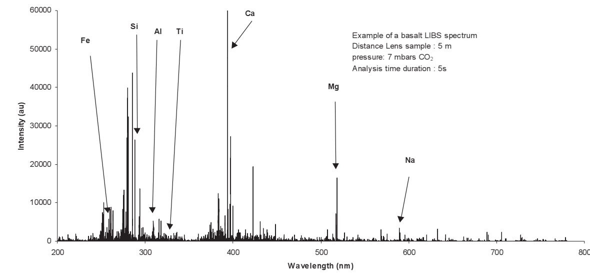

Fig. 5. Echelle spectrum of a basalt standard in LIBS at a distance of 3 m. Note that trace elements, such as Li, Ba, and Sr, are visible.

4 INSTRUMENT CONCEPT

Fig. 6 gives an overview of the design concept for a combined Raman Spectrometer/ LIBS *Elegant Bread-Board* (EBB).

The instrument is based on a specifically designed extremely compact spectrometer with high resolution over a large wavelength range, suitable for both Raman and LIBS measurements. Other subsystems are imaging optics (for micro- and macro-mode application), lasers and fibre optics for light transfer. Optionally a microscope/ close-up imager can be integrated in the current design concept.
An overview of Spectrometer and the imaging optics design concepts is given in the following.

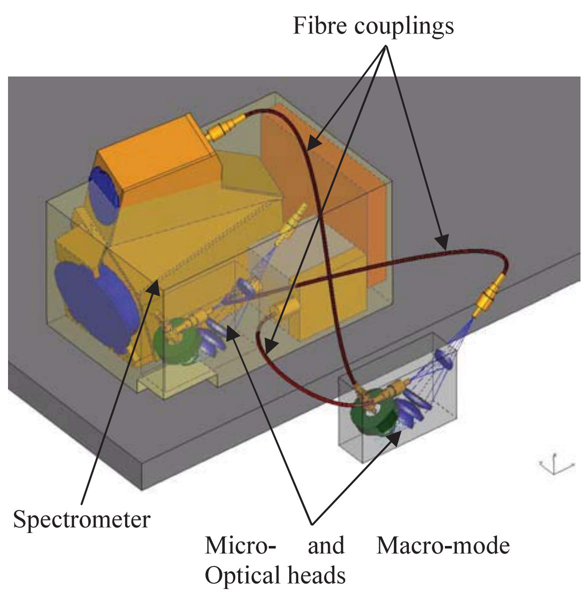

Fig. 6. EBB mechanical layout [8].

4.1 Spectrometer

The design is based on a concept of a cross dispersion spectrometer. As a result of the cross dispersion there are six spectra (see Fig. 7), separated in cross dispersion direction, imaged on a 2D detector array. The spectrometer covers continuously a range varying from the UV to the NIR. Its spectral resolution is varying from less than 0.1 nm in the UV to 0.2 nm in the NIR.

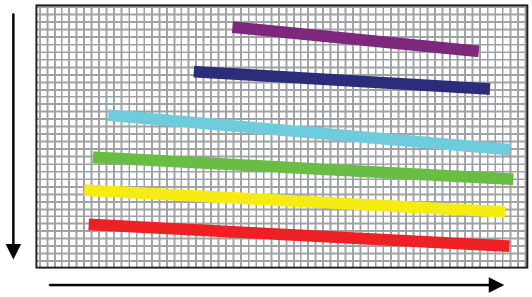

Fig. 7. Dispersed lines on detector.

4.2 Optical head

The optical head consists of two optical systems: a condenser part for sample illumination and an imaging system (relay imager optics). The light path goes from two fibres (one for Raman and one for LIBS) through the condenser lens to the sample and from the sample through the relay imager to another fibre, which feeds the spectrometer.

The spot diameters for the Raman and the LIBS experiments have to be independently optimised, since the spatial resolution requirements of the two experiments differ:

- For Raman, depending on the operation mode (micro or macro-mode) of the instrument, the spot diameter requirement may vary. For micro-mode application (inside the rover laboratory) a small spot diameter is appropriate for individual mineral phase identification in most cases where the grain size ranges between 20 and 100 µm. For macro-mode application (outside the rover in the robotic arm), larger scale Raman experiment can be performed on element mixtures for fast, qualitative analysis. Then a larger spot diameter (e.g. a few hundreds of micrometers) is required.

- For the LIBS the size of the optical source is defined by the plasma size which is not identical to the laser spot size such as in Raman or in fluorescence techniques. The plasma size which depends on experimental parameters such as spot size, irradiance environmental conditions can expend up to millimetres dimensions in Martian atmospheric pressure where the plasma expands a lot [12]. This geometrical aspect is of great importance to determine the photon collection efficiency. To achieve this source characterisation, a LIBS experimental set-up, present in the CEA laboratory, will be adapted to be representative of the Martian conditions and also of the currently selected LIBS laser irradiance. The geometry of the plasma, dimensions and spatial distribution of the luminosity will be measured.

5 CONCLUSION AND OUTLOOK

This paper gives an overview of a project currently implemented at TNO (NL) to design, manufacture and test a combined Raman Spectrometer/ LIBS EBB for the ESA's ExoMars mission (launch 2011).

The Raman LIBS instrument is regarded as a fundamental, fundamental, next-generation instrument for organic, mineralogical and elemental characterisation of Martian soil and rock samples.

The current activity performed at TNO aims to ensure the timely definition of the Raman/LIBS system for a 2011 launch. The objective of the current activity is to develop and construct an advanced laboratory breadboard /engineering model, able to verify the instrument's end-to-end functional performance -with natural samples- under mission-representative conditions. This prototype is intended to become the basis for realizing the instrument's flight model.

The instrument is based on a specifically designed extremely compact spectrometer with high resolution over a large wavelength range, suitable for both Raman spectroscopy and LIBS measurements. Low mass, size and resources are the main drivers of the instrument's design concept.

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