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Combined Raman/LIBS spectrometer elegant breadboard: built and tested - and flight model spectrometer unit

B. Ahlers

I. Hutchinson

R. Ingley



COMBINED RAMAN/ LIBS SPECTROMETER ELEGANT BREADBOARD – BUILT AND TESTED - AND FLIGHT MODEL SPECTROMETER UNIT

B. Ahlers⁽¹⁾, I. Hutchinson⁽²⁾, R. Ingle⁽²⁾ and Raman LIBS EBB Team.

⁽¹⁾TNO Science and Industry, Space and Science, Stieltjesweg 1, 2600 AD Delft, The Netherlands, berit.ahlers@tno.nl.

⁽²⁾Brunel University, Imaging for Space and Terrestrial Applications Group, United Kingdom, Uxbridge, Middlesex UB8 3PH.

ABSTRACT

A spectrometer for combined Raman and *Laser Induced Breakdown Spectroscopy* (LIBS) is amongst the different instruments that have been pre-selected for the Pasteur payload of the ExoMars rover. It is regarded as a fundamental, next-generation instrument for organic, mineralogical and elemental characterisation of Martian soil, rock samples and organic molecules. Raman spectroscopy and LIBS will be integrated into a single instrument sharing many hardware commonalities [1]. The combined Raman / LIBS instrument has been recommended as the highest priority mineralogy instrument to be included in the rover's analytical laboratory for the following tasks: Analyse surface and sub-surface soil and rocks on Mars, identify organics in the search for life and determine soil origin & toxicity. The synergy of the system is evident: the Raman spectrometer is dedicated to molecular analysis of organics and minerals; the LIBS provides information on the sample's elemental composition. An international team, under ESA contract and with the leadership of TNO Science and Industry, has built and tested an *Elegant Bread Board* (EBB) of the combined Raman / LIBS instrument. The EBB comprises a specifically designed, extremely compact, spectrometer with high resolution over a large wavelength range, suitable for both Raman spectroscopy and LIBS measurements. The EBB also includes lasers, illumination and imaging optics as well as fibre optics for light transfer. A summary of the functional and environmental requirements together with a description of the optical design and its expected performance are described in [2]. The EBB was developed and constructed to verify the instruments' end-to-end functional performance with natural samples. The combined Raman / LIBS EBB realisation and test results of natural samples will be presented.

For the *Flight Model* (FM) instrument, currently in the design phase, the Netherlands will be responsible for the design, development and verification of the spectrometer unit, while the UK provides the detector. The differences between the EBB and the FM will be demonstrated.

1 INTRODUCTION

The design concept for a combined Raman / LIBS instrument has been presented at the last *International Conference on Space Optics* (ICSO) in 2006 [3]. Since then, the instrument has been built and tested. The planned launch for ExoMars has been shifted to 2013, as the first flagship mission of the Aurora programme of the *European Space Agency* (ESA). The rover design as depicted in Fig. 1 has slightly changed and full scale bread board tests of the vented airbag have been performed [4]. The rover comprises the *Analytical Laboratory Drawer* (ALD) in which the Raman LIBS spectrometer is going to be located.

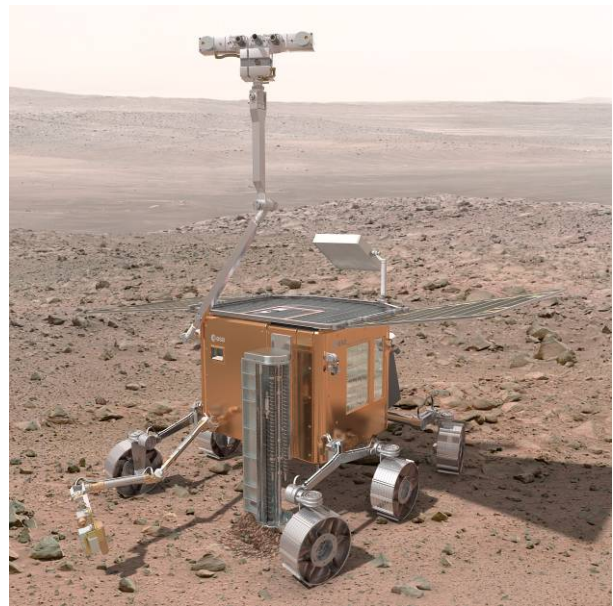


Fig. 1. ExoMars rover (courtesy of ESA).

The main science objectives as gathered in [3] geology, mineralogy, organics and search for life, as well as the principles and goals for Raman spectroscopy and LIBS on Mars are described.

The challenge was to combine these two techniques in a single instrument with stringent mass, volume and power requirements for a suitable space application.

The *Flight Model* (FM) will use Raman and possibly LIBS outside the rover on the robotic arm, and Raman spectroscopy will be used for first identification inside the rover in the ALD.

2 COMBINED RAMAN / LIBS SPECTROMETER EBB INSTRUMENT

The functions of the instrument are to illuminate a sample with laser light that generates physical phenomena (Raman shift and a luminous plasma plume/ablation for LIBS) with light emission, to collect and relay the emitted light to a spectrometer, and to record a spectrum that provides the means for sample identification. The two experiments, Raman spectroscopy and LIBS, are performed at the same location (spot) on the sample.

The solution realised consists of a spectrometer located inside the *Analytical Laboratory Drawer* (ALD) with an optical fibre link to an optical head and another link to an optical head located at the end of the robotic arm.

The modular approach as shown in Fig. 2 allows a consistent thermal design of the EBB by splitting the assembly that is source of thermal disturbance (electronic assembly) from the optical assembly, which needs to stay a-thermal as much as possible. More flexibility for implementation on the rover and an easier approach for planetary protection are additional factors.

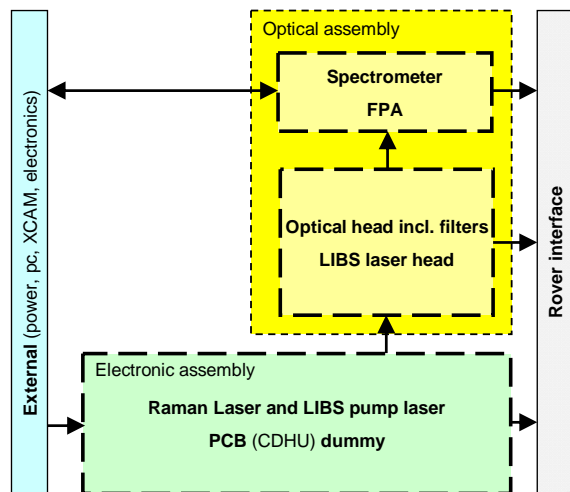


Fig. 2. Assembly layout of the Raman/ LIBS EBB.

Low mass, size and resource usage were the main drivers of the EBB design. The volume and mass values are given in Table 1. The subsystems are described in detail in [2].

Table 1. Low mass, size and resource usage were the main drivers of the instrument design with a total mass of smaller than 2 kg.

Sub-systems	Volume [mm ³]	Mass [g]
Spectrometer incl. CCD	185 x 144 x 187	840
Optical head	83 x 70 x 95	240
Electronics	78 x 103 x 40	505

The optical assemblies as depicted in Fig. 2 are described in the following.

2.1 EBB Spectrometer unit

The spectrometer unit incorporates a *Focal Plane Assembly* (FPA) that contains a *Charged Coupled Device* (CCD), a preamplifier and a cold finger. A cold strap and a Peltier cooler are also used to enable measurements to be made with a cooled detector under terrestrial laboratory conditions. The CCD is a back-illuminated, e2v technologies device with 2048 x 2048, 13.5 μm pixels and a UV coating which optimises its sensitivity within the 240 to 840 nm wavelength range. The device is operated in pseudo frame transfer mode (with half the area of the device optically shielded) in order to avoid image smear during readout.

Different stages, i.e. opto-mechanical design [Fig. 3], the optical design with its components prepared for integration [Fig. 4] and the spectrometer during assembly [Fig. 5] are realised before testing started in 2007/2008.

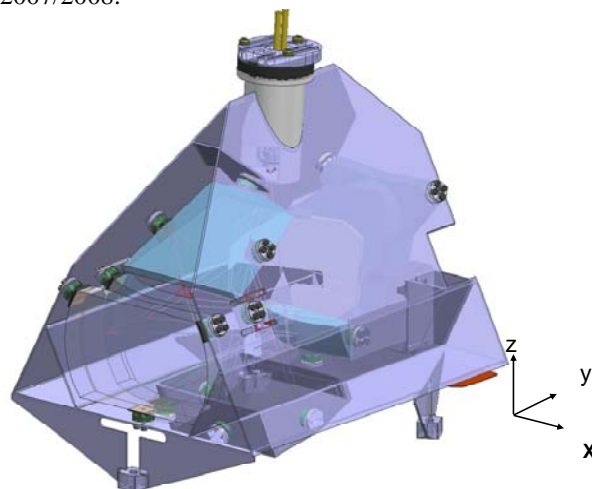


Fig. 3. Combined Raman LIBS EBB spectrometer design incl. housing.

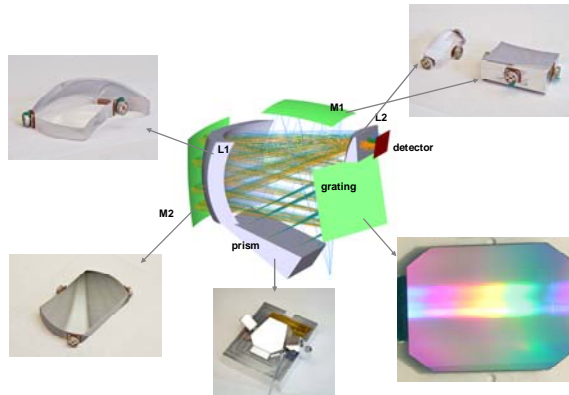


Fig. 4. 3D-view of the EBB spectrometer optical design (M – Mirror; L – Lens) with components as prepared for integration.

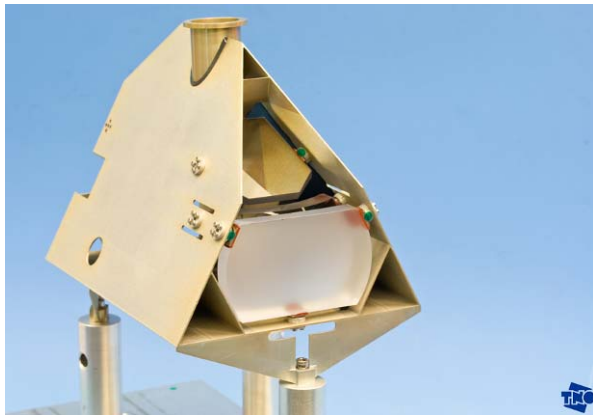


Fig. 5. EBB spectrometer during assembly and integration.

LIBS driven design parameters include almost continuous coverage from 240 to 840 nm with a spectral resolution of 0.1 nm in the ultra-violet to 0.2 nm in the near-infrared. The Raman shift signal is detected in diffraction order 3 (650 to 840 nm) only. For LIBS diffraction orders 3 to 9 are used. The different wavelength ranges per diffraction order are listed in Table 2. While the orders 1, 10 and 11 are not visible on the detector due to sensitivity and optical throughput in the ultra-violet, the silicium based CCD is sensitive to about 1100 nm, thus diffraction order 2 is partly visible in the detector image.

Table 2. Wavelength range of different diffraction orders imaged on the detector.

Diffraction order	Wavelength range on detector [nm]
1	1950 to 2520 (CCD not sensitive)
2	975 to 1260 (CCD sensitive to 1100, visibility of LIBS laser)
3	650 to 840 (Raman shift detection)
4	504 to 630
5	406 to 504
6	345 to 406
7	300 to 345
8	265 to 300
9	240 to 265
10	195 to 252
11	177 to 229

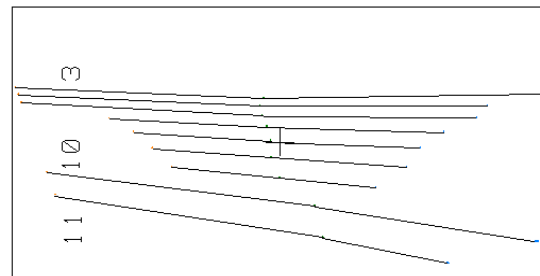


Fig. 6. Diffraction orders imaged on detector.

To retrieve the desired *Signal-to-Noise Ratio* (SNR), the CCD can be actively cooled to -10°C , i.e. baseline temperature with acceptable dark current contribution. The CCD is thermally isolated from the spectrometer structure. The FPA cooling system is designed to cool the CCD to the baseline temperature and down to -40°C , i.e. the minimum operational temperature.

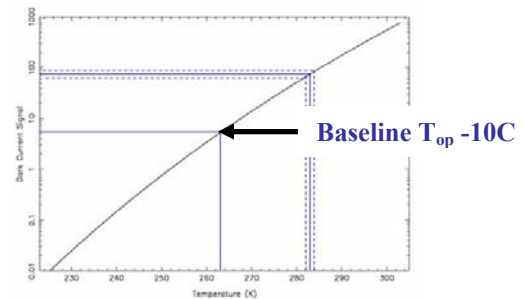


Fig. 7. Dark current signal as a function of temperature for CCD42-40.

2.2

EBB optical head breadboard

The concept of the optical head is depicted via a block diagram in Fig. 8. The LIBS illumination optics are totally independent of the optics for the other paths. The LIBS illumination [left in Fig. 8] is the only channel that looks orthogonally to the sample's surface. The other paths share commonalities. The Raman laser light transferred by an optical fibre is filtered by a dedicated band-pass to reduce the scattering effects in the optical fibre, the so-called "Raman filter". The Raman illumination and viewing are separated by a beam-splitter, which is used as a notch filter to isolate the excitation wavelength with a far stronger intensity, from the weak Raman shift signals that need to be detected. The Raman channels and the LIBS viewing optics look at the sample at an angle of 30° and their common optics with two apertures are used. More detail described in [2].

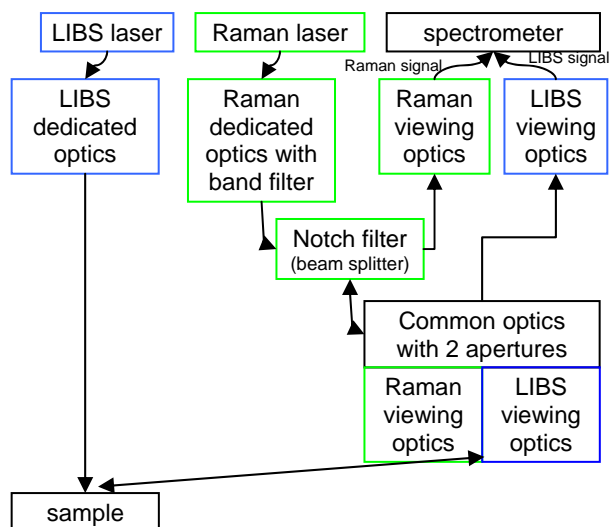


Fig. 8. Block diagram of optical head. The arrows indicate the light direction.

For the LIBS laser a Q-switched Nd:YAG has been developed with the laser head directly connected to the optical head connected via optical fibre optics to a pump diode. The excitation wavelength is 1064 nm with an output energy of about 1 mJ, pulse duration is 1.7 ns with a repetition rate of 100 Hz. For Raman spectroscopy a continuous wave laser diode with a volume Bragg grating is used at a wavelength of about 660 nm with an output power of 20 mW.

Table 3. Channel description of the optical head with the dedicated wavelength range

Channel description	Spectral (range) [nm]
LIBS illumination	1064
Raman illumination	658
Raman viewing	660 to 840
LIBS viewing	240 to 840

The optical head *Bread Board* (BB) is based on the design of a small optical head design, using components available commercially off the shelf as much as possible. By building this BB, flexibility of possible changes can still be implemented. For the FM the optical head design is transferred to Kayser-Threde in Germany who have implemented the knowledge from the optical head BB as far as possible.

3 TEST

Different calibration performance and functional tests defined for the project are carried out in ambient temperature and thermal-vacuum cycling conditions.

Measurements with neon (Ne) and mercury argon (HgAr) light sources and stainless steel (LIBS) are performed for wavelength calibration to assure sufficient lines in all diffraction orders. A white light source is used for detectable ranges in the spectrometer as well. With the help of these emission lines judgement over the line width (full width at half maximum) can also be done.

The clock waveforms required to operate the CCD and LIBS laser were generated using a *Digital Signal Processor* (DSP). Specific sequencer programs were developed for the Raman and LIBS modes of operation. In LIBS mode, the CCD imaging area was pre-flushed before the laser was repeatedly pulsed and then the acquired image was rapidly transferred into the store region of the device (so that the pixels could be accurately sampled and digitised). The CCD was operated in a similar manner for Raman mode, but the image acquisition time was significantly longer (a few seconds) and the laser was operated continuously throughout the image acquisition period. A background image was obtained for each sample dataset so that pixel by pixel background subtraction could be performed during post processing. Look-up tables containing the column and row positions of each pixel in a particular order were then used to extract the relevant spectra for each sample.

For ambient temperature and pressure testing, a dedicated test setup has been constructed with dry-nitrogen flushing to prevent the risk of contaminating the cooled detector in the EBB spectrometer [Fig. 9].



Fig. 9. Test setup in dry-nitrogen flushed climate chamber at TNO Science & Industry in Delft.

Table 4 and Table 5 state the SNR values retrieved by the radiometric model based on component level measurements (except grating efficiency, which is based on manufacturer values) for Raman and LIBS measurements respectively.

Table 4. Radiometric model retrieved SNR values for Raman spectroscopy with different integration times (IT).

SNR	Comments
490	For efficiency 10^{-6} , IT = 0.1 s
260	For efficiency 10^{-9} IT = 30s

Table 5. Modelled SNR for LIBS with different amounts of laser shots for major elements to be found in basalt.

SNR	Comments
280	20 shots – Al 394.4 nm (major element)
290	20 shots – Al 396.1 nm (major element)
116	20 shots – Ca 422.7 nm (major element)
155	20 shots – Si 390.5 nm (major element)

Stainless steel (type 1.4301) LIBS spectra measured with the EBB (50 pulses) in comparison to standard spectra is shown in Fig. 10 (note: the standard is not measured on the same stainless steel type).

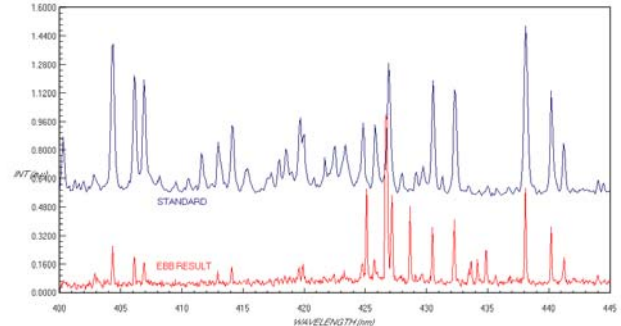
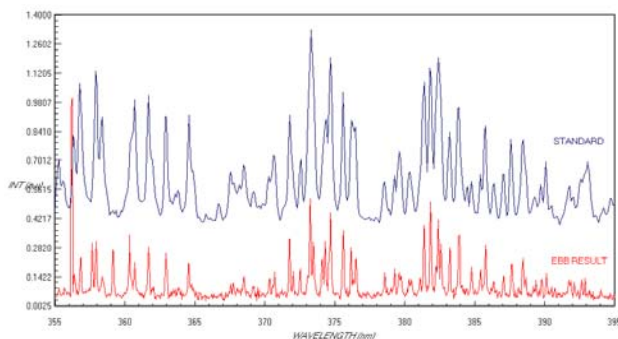


Fig. 10. Stainless steel (type 1.4301) LIBS spectra EBB (50 pulses) vs standard spectra. Selected spectral ranges from 355 to 445 nm.

Several emission lines around 375 nm from LIBS measurements on stainless steel with varying amounts of pulses are visualised in Fig. 11. While with 10 pulses, each 1.7 ns long with a repetition rate of 100 Hz, the peaks are hardly detectable, while with increasing amounts of pulses their intensity increases respectively.

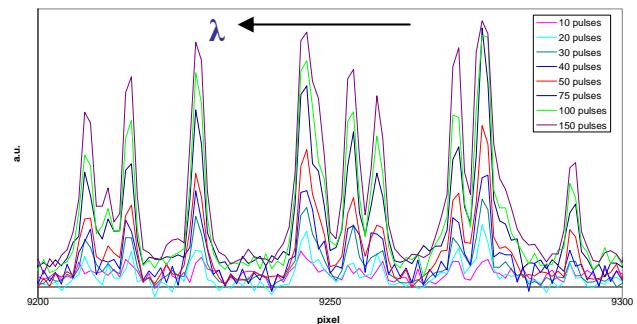


Fig. 11. Stainless steel (type 1.4301) LIBS results: zoom around 375 nm (diffraction order 6) with different amounts of pulses.

Significant Raman shifts are observed for gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) after a few seconds and averaging over several measurements increases the SNR. And it is anticipated that requirements will be met within five minutes acquisition period.

For thermal-cycling environmental testing under vacuum pressure conditions the spectrometer is placed in a dedicated chamber [Fig. 12].

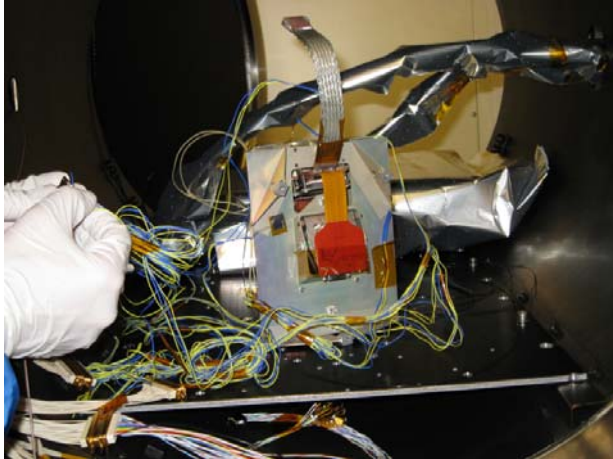


Fig. 12. Spectrometer placed on its side (put on -y surface) in the thermal vacuum chamber.

Via an optical fibre feed through, the spectrometer can be connected to external sources, i.e. direct connection to light sources or the optical head BB, allowing Raman and LIBS signals to be fed to the spectrometer. Comparison of measurements are performed during thermal cycling for repeatability of measurements to check for effects of temperature, vacuum, cycling and possible thermal settings. Three complete cycles have been realised [Fig. 13] covering the operational and non-operational temperature ranges [Table 6]. The results show that the repeatability of the line positions after thermal cycling is very good under the same environmental conditions (i.e. temperature and pressure). At ambient pressure and temperature the measurements recur very well at the same position on the detector before and after thermal cycling, i.e. no thermal setting effects are detected. Vacuum measurements taken at different stages at the same temperature are also very well reproduced at the same position on the detector independent of the thermal cycling.

Table 6. Operational and non-operational temperature definitions of EBB.

Temp [°C]	EBB specifications
70	Max non-operational temperature
30	Max operational temperature
-10	Nominal CCD temperature
-40	Min operational temperature
-70	Min non-operational temperature

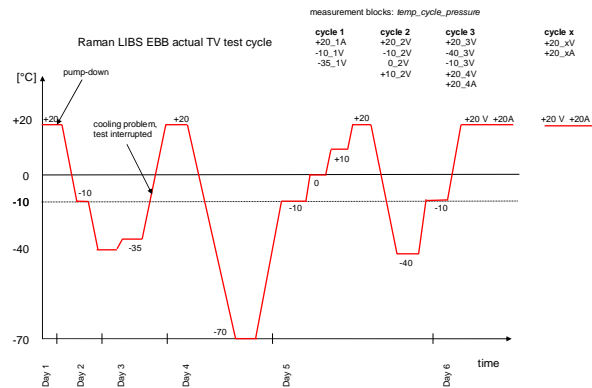


Fig. 13. Thermal vacuum cycling performed at TNO in Delft/NL.

A shift in spectral (dispersion) direction of about two pixels (i.e. 27 μm) is observed between the ambient and vacuum measurements, a so-called ambient-vacuum effect [Fig. 14]. In cross-dispersion, a shift is also observed. The shift is in line for the neon and mercury argon measurements as well as the white light source. These shifts can be accommodated with the software extraction of the diffraction order positions on the CCD and do not hamper the performance of the EBB.

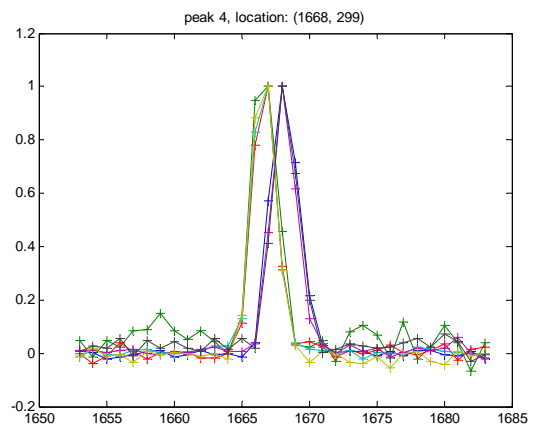


Fig. 14. Ambient-vacuum effect: Ne peak cross section under vacuum pressure (left) and ambient pressure (right) taken at room temperature during the different cycles as illustrated in Fig. 13.

Also at the low operational temperature, the peak positions are well reproduced [Fig. 15]. Within the accuracy of the measurement analysis, it can be stated that no thermal setting effect can be observed the repeatability is good. Thus the Ne measurements confirm / verify the findings of the HgAr lamp measurements.

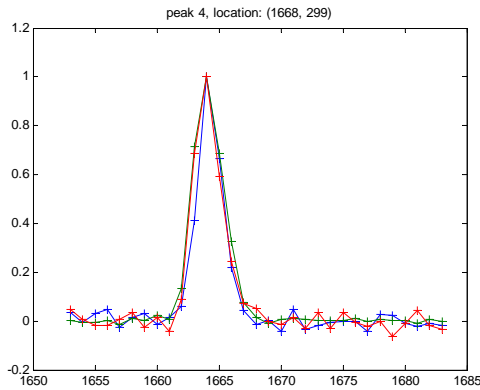


Fig. 15. Thermal cycling: Good repeatability in position of Ne peak cross section at min operational temperature taken during different cycles.

The spectral shift between the extreme operational temperatures, i.e. +20 and -40°C is about three pixels (in dispersion direction), i.e. about 40 μm [Fig. 16]. this is a very small value due to the a-thermal design of the spectrometer unit of the EBB.

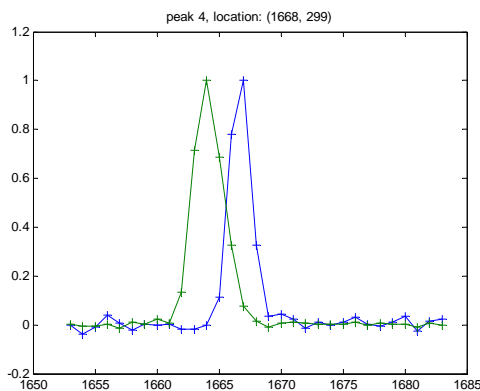


Fig. 16. Effect of temperature, vacuum pressure measurements at the extreme operational temperatures, -40°C left and 22°C right.

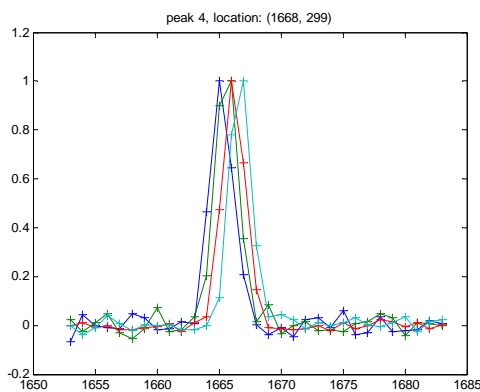


Fig. 17. Neon peak measured at -12° to 22°C within one cycle.

An image shift of the dispersion orders is observed from low to high temperature from the bottom left to upper right on the detector. The shift can partly be explained by the temperature influence on the grating. The grating substrate material is quartz. The temperature coefficients: $0.5 \cdot 10^{-6} /K$ quartz; $7 \cdot 10^{-6}/K$ glass (BK7); $\Delta T = 60 K \rightarrow 400 \text{ l/mm}$ $40.5 \mu\text{m}$ positioning change $\rightarrow \sim 5 \cdot 10^{-6}/K$ from calculation. The temperature influence can lead to a shift of the image of the dispersion orders. Another effect is the disturbance of the thermal centre by the clamping of the active cooling system of the detector for operation at -10°C, which makes mechanical shifts due to different CTE of materials possible.

With the white light source measurements the expected focus/ image of the slit height on the detector is checked and focus in cross-dispersion direction is very similar between the different pressure conditions. This verifies the design.

4 FLIGHT MODEL SPECTROMETER UNIT

The specifications for the FM have changed slightly. Amongst others the excitation wavelength for Raman spectroscopy is lowered to 532 nm (to the green instead of red for the EBB). Additionally, the change incorporates the possibility to use LIBS only on the external optical head, while Raman spectroscopy is used internally as well as externally. Due to instrument mass constraints the possibility to skip LIBS completely is included in the current studies. Since the technology development and the main interfaces as well as spectrometer unit specifications are driven by LIBS, several relaxations are implemented. The wavelength range is minimised to the Raman range, i.e. excitation wavelength at 532 nm to 670 nm in the red of the visible wavelength range. The spectral resolution of the Raman shift (depending on excitation wavelength) is ideally 8 cm^{-1} , which translates to 0.23 nm at 530 nm and 0.36 nm at 670 nm.

5 CONCLUSION AND OUTLOOK

An overview of the combined Raman and Laser Induced Breakdown Spectrometer EBB designed, built and tested at TNO Science & Industry in Delft including system retrieved budgets from requirements to verify the feasibility for such an instrument with the verification of the instrument's end-to-end functional performance for ESA's ExoMars mission (launch 2013). The subsystem design and justification with more detail outlines the optical and electronic assemblies. This is followed by the test results from the ambient pressure and thermal vacuum cycling

campaigns. This has been realised in a time frame of 2.5 years. The instrument based on a specifically designed extremely compact spectrometer with high resolution over a large wavelength range, suitable for both Raman spectroscopy and LIBS measurements, is successfully verified by the testing campaign including Raman and LIBS measurements. These measurements are comparable to existing scientific data. The combined Raman LIBS instrument is regarded as a fundamental, next generation instrument for organic, mineralogical and elemental characterisation of Martian soil and rock samples.

AKNOWLEDGEMENTS

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Note that the EBB realisation would not have been what it is without contributions from the complete industrial team lead by TNO. The following subcontractors have contributed to the EBB: Brunel University (UK) for the Focal Plane Assembly; CEA (F) for the LIBS plasma characterisation; cosine Research (NL) and MONOCROM (E) for the Raman and LIBS lasers; Swiss Space Technology (CH) for the *Command and Data Handling Unit* (CDHU) design and the University of Valladolid (E) for scientific support.

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