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MOBILE RAMAN SPECTROMETRY ON SCORPIO 7 ROVER

Keywords: *Martian rover, Raman spectrometry, OFF-ROAD Scientific Association, Scorpio 7, University Rover Challenge.*

This article describes the design of the mobile Raman spectrometer of the Scorpio 7 rover. It was constructed to study the organic content of soil samples taken during the Rover Challenge series of Mars rover competitions. The basic theoretical issues that are used in Raman spectroscopy are described. Design assumptions and requirements for the construction and control software of the spectrometer during its use on board the Scorpio 7 Mars rover, constructed by the OFF-ROAD Scientific Association at the Wroclaw University of Technology, are discussed. Measurements of Raman spectra carried out by the Raman spectrometer installed in the research module of the Scorpio 7 rover are presented.

1. INTRODUCTION

Raman spectroscopy (RS) is a spectral analysis technique that utilizes inelastic scattering to obtain information about the material being studied, specifically its vibrational states [3]. This is achieved by exposing the material to intense monochromatic light, typically a laser, and analyzing the resulting spectrum. RS has gained widespread application in various fields of science and everyday life due to its ability to examine solid samples without the need for prior purification and the potential for miniaturization for portable systems [1]. Modified Raman spectrometers are particularly used in biological research as they have minimal interference with water, allowing the study of biological samples in their natural state [9]. Additionally, RS techniques are employed as an analytical method in medicine, the pharmaceutical industry, environmental protection, archaeology, geology, customs protection, and quality control of food products [1].

The Raman spectrometer was constructed by students of the OFF-ROAD Unconventional Vehicles Scientific Circle operating at the Department of Fundamentals of Mechanical Engineering and Mechatronic Systems, Wroclaw University of Technology. The aim of building this analytical device was to increase

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the research capabilities of the Scorpio 7 Mars rover during its participation in the Rover Challenge series. The main task of the constructed Raman spectrometer is to examine soil samples collected by the Scorpio 7 rover for biomarkers. By identifying these organic compounds, it is possible to correctly determine whether active life forms are, or have been, present in the soil sample.

The solutions used during the construction of the Raman spectrometer adapted for operation on the Scorpio 7 rover can be used to conduct chemical analysis in hazardous conditions for humans. A potential avenue for the development of this technology is the modification of the spectrometer to a SORS-type system, which would allow remote chemical composition analysis of unidentified chemicals without the need to open their containers [13].

The currently constructed system could be used to conduct autonomous chemical composition studies of contaminated areas without the need for a large number of qualified personnel.

2. RAMAN SCATTERING [2]

Raman scattering involves the interaction of a photon of a specific energy with the electron density of a chemical bond present in the molecule under study. This

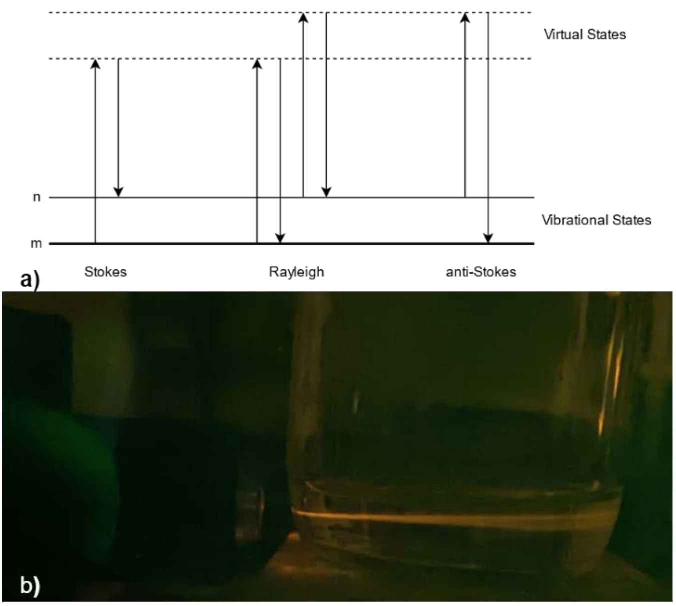

Fig. 1 Representation of Raman Scattering a) Simplified Jablonski diagram describing light scattering phenomena, b) Raman scattering from Tetrahydrofuran solution excited with laser light of 532nm, 50mW. Image acquired using 550nm long-pass filter.

interaction causes the electrons involved in the bond to be excited to a virtual state from which the electron returns to a lower excited vibrational level resulting in a Stokes band. If the electron was at an excited vibrational level (due to, for example, an elevated ambient temperature) before the interaction with the photon, the interaction results in the electron being excited to a higher virtual state, from which it returns to the ground state, resulting in Anti-Stokes scattering. These phenomena can be represented graphically in the simplified Jablonski diagram shown in Figure 1a.

As a result of the interaction of the photon with the electrons present in the chemical bonds of the analyzed compound, the photon undergoes an inelastic scattering from the tested material and loses part of its original energy. As a result of the loss of part of its energy, the photon, when reflected from the sample, decreases its frequency, which is observed as a change in the color of the scattered light, as can be seen in Figure 1b for the tested Tetrahydrofuran solution.

3. MATERIALS AND METHODS

3.1. DESCRIPTION OF THE RAMAN SPECTROMETER

The Raman spectrometer consists of two optical systems: the excitation system and the spectrometer (Figure 2). The first part is responsible for generating a Raman signal in the sample. This effect is achieved by focusing monochromatic light, such

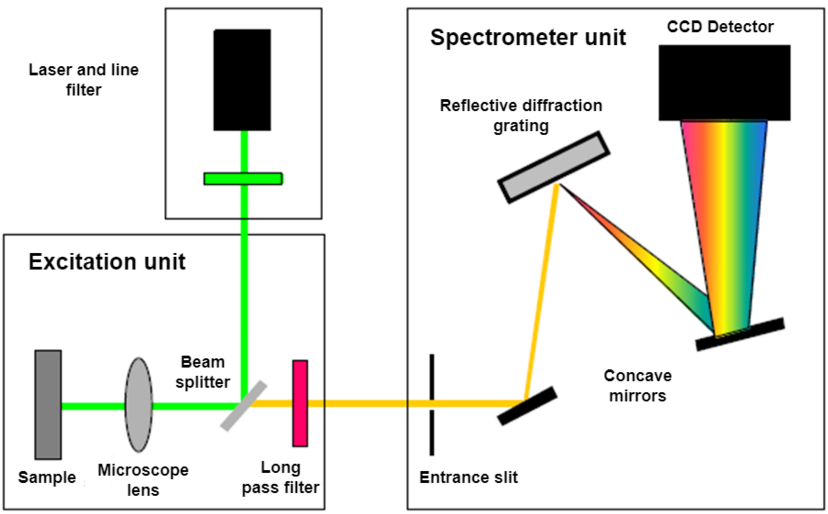

Fig. 2 Diagram of Raman spectrometer in a backscattering setup [8].

as a laser, on the surface of the tested material. The generated electromagnetic radiation is then filtered out of the Rayleigh scattering (excitation beam) using optical filters. The filtered radiation is then focused into the spectrometer using a set of focusing lenses. In the spectrometer, the signal is directed by a system of concave mirrors first to a reflective diffraction grating and then to a CCD array. On the surface of the diffraction grating, a single polychromatic beam is split into multiple monochromatic beams. The radiation is directed via another concave mirror to the surface of the CCD matrix, which converts the resulting spectral spectrum into digital information.

The design of the Raman spectrometer used on the Scorpio 7 rover was based on the basic assumptions outlined in the paragraph above. Due to the operating conditions of the spectrometer under construction, necessary modifications have been made to ensure optimal performance.

3.2. HOUSING

The housing for the Raman spectrometer used on the Scorpio 7 rover was made using additive manufacturing technology on 3D printers using FFF (Fused Filament Fabrication) technology, from PET-G type filament. This type of technology and material was chosen because of the low cost of fabricating customized structural components and the satisfactory strength-to-weight ratio.

3.3. EXCITATION UNIT

Due to the low intensity of Raman scattering obtained when testing solid samples, it was decided to use an excitation system in a backscattering-type setup. In this system, the excitation laser beam first is reflected from a dichroic mirror, which is positioned at an angle of 45 degrees to the laser beam (Figure 3b). This positioning of this mirror ensures that the excitation beam is directed directly at the tested sample. After the excitation beam reflects off the surface of the dichroic mirror, the excitation beam is focused by the microscope objective, which directs the excitation beam onto the sample.

This excitation system provides the least number of optical elements that are in the path of the generated Raman scattering, which returns via the same path as the excitation beam. Due to the dichroic properties of the mirror used to direct the excitation beam onto the sample, the generated Raman scattering passes through this optical element, where it is then directed into the spectrometer.

Due to the 50% efficiency of the selected dichroic mirror used in the constructed excitation system [5], it is necessary to use an additional optical filter to filter out residual Rayleigh scattering from the generated Raman scattering that has not been reflected by the dichroic mirror.

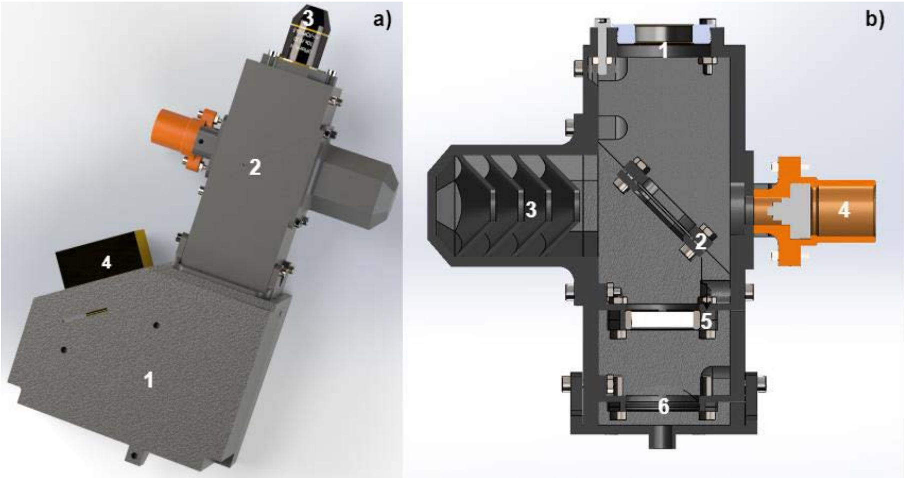

Fig. 3. 3D visualizations of constructed Raman Spectrometer
a) Scorpio's 7 Raman Spectrometer (1 – Spectrometer Unit, 2 – Excitation Unit,
3 – Microscope Objective, 4 – CCD array);
b) Cross-section of the Excitation Unit (1 – Objective Mount, 2 – Diffraction Mirror,
3 – Laser Light Trap, 4 – Laser Mount, 5 – Optical Filter, 6 – Focusing Lens).

3.4. SPECTROMETER UNIT

The optical system used in the Raman spectrometer under construction consists of five optical elements: an entrance slit, two focusing mirrors, a reflecting diffraction grating, and a CCD array (Figure 3a). Due to the focal lengths of the focusing mirrors used and the possible space for the Raman spectrometer inside the body of the Scorpio 7 rover, it was decided to use a modified optical distribution according to the Czerny-Turner layout [12]. In this arrangement, the analyzed radiation beam first passes through the entrance slit, which is located opposite the first of the focusing mirrors. This mirror directs the radiation beam from the slit to the reflecting surface of the diffraction grating. Once the beam is reflected and split on the surface of the grating, it falls on the surface of the second focusing mirror, which directs the split beam onto the surface of the CCD array.

The distances between the optical elements and their angular position concerning each other were first simulated and then optimized using numerical methods, to obtain the required resolution of the system for the observation of Raman spectra.

3.5. SCORPIO 7 ROVER

Scorpio 7 is a mobile research platform, modeled by its design on rovers that travel on the surfaces of Mars or the Moon. To move easily over rough terrain, the vehicle is equipped with a four-wheel differential suspension. The driving module of the Scorpio 7 rover is a modified version of the rocker-boogie suspension used in NASA's Mars rovers (Perseverance or Curiosity).

The rocker arms of the constructed rover are connected by a differential mechanism that allows it to overcome obstacles up to 30 cm high. In addition to the driving module, the Scorpio 7 platform has a manipulator module, which has 6 degrees of freedom. This means that this manipulator is capable of movement in 6 different axes. The manipulator on this research platform can perform precision operations (Figure 4a), such as typing on a keyboard, and can take soil samples for testing using an interchangeable tip in the form of a small excavator bucket (Figure 4b). In addition, the Scorpio 7 mobile research platform carries 5 digital cameras, needed for precise control of the ride or manipulator. To maintain sufficient communications with the Scorpio 7 rover, radio and antenna masts have been installed on board, with radio systems operating at frequencies from 2.4 to 5.8 GHz.

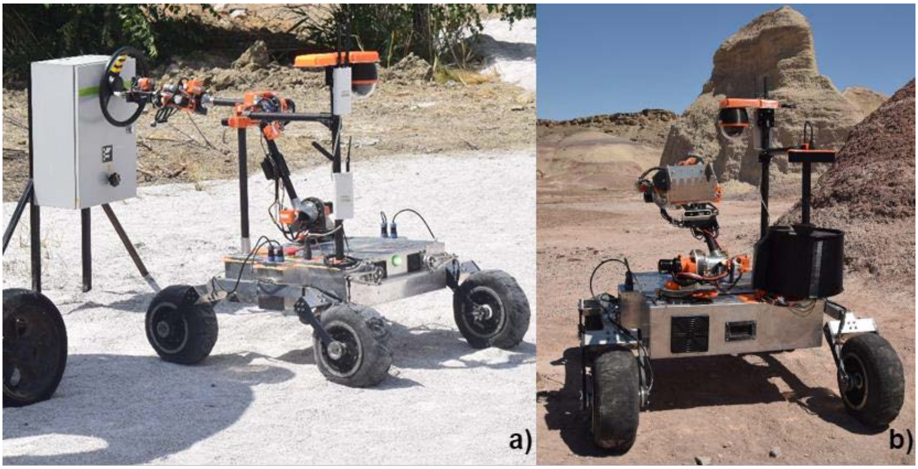

Fig. 4. Scorpio 7 Rover.
a) during the Anatolian Rover Challenge 2023 competition; b) with manipulator in digging configuration during the University Rover Challenge 2023 competition

3.6. RESEARCH MODULE DESCRIPTION

The research module located on the Scorpio 7 rover was prepared for the requirements of the 2023 University Rover Challenge, where it was required to detect the activity of living organisms in soil samples collected by the rover [6]. The module used consists of two main segments: analytical and storage. The main device of the analytical segment is a Raman spectrometer under construction, which allows the identification of organic compounds based on the Raman spectra obtained. A digital microscope has also been added to the segment for visual analysis of samples.

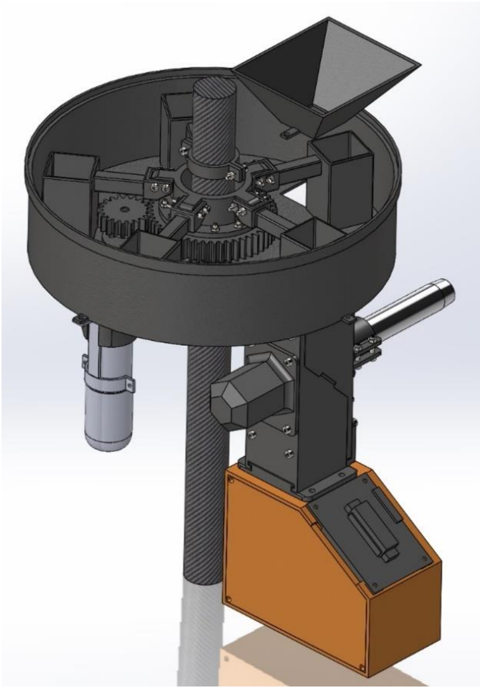

Fig. 5 Model of the storage segment of the Scorpio 7 rover's research module
with connected Raman spectrometer

To analyze the soil samples collected by the analysis segment of the Scorpio 7 rover's research module, it is first necessary to store them in the rover's controlled environment - the storage segment (Figure 5). A rotating mechanism has been constructed, with 5 chambers with external dimensions of 33x33x55mm. Using this mechanism, it is possible to move a given chamber to 3 different locations: for analysis with a Raman spectrometer, for visual analysis with a digital microscope, and under the reception area of the collected soil sample. The bottom of these chambers is made of polymethylmethacrylate, due to the possibility of analysis with a Raman spectrometer and a digital microscope - both of which are mounted under the storage segment so that the bottom of the sample chambers can be observed.

3.7. READING DATA FROM THE RAMAN SPECTROMETER

According to the rules of the 2023 University Rover Challenge [6], all analysis of the collected soil samples had to take place on board the rover being operated. Thus, it was necessary to configure a server to provide a USB interface from the rover's on-board computer to the IP network, since the software and libraries provided by the manufacturer of the CCD array support only Microsoft Windows family operating systems [4], which is not used in a mobile vehicle.

As a result, after connecting to the rover's Wi-Fi network and running the USB server client application, a computer at the base with Microsoft Windows installed was able to communicate with the array connected to the rover's onboard computer (Figure 6).

To read data from the CCD array, software was created using communication libraries provided by the manufacturer to retrieve data on the exposure intensity of each pixel of the array and visualize it in the form of graphs.

3.8. RAMAN SPECTROMETER SOFTWARE

To interpret the data, a software application was written in which the Raman spectra obtained during the spectrometer measurement are visualized. Basic functions were installed in the application to analyze Raman spectra, e.g.: modifying the signal integration time (the time the array collects the signal, increasing its intensity). In addition, an Asymmetric Least Squares (ALS) [11] measurement baseline estimation algorithm has been added to the application, which allows filtering out the fluorescence spectrum from the collected Raman spectrum (the resulting fluorescence spectrum has a much higher intensity than the Raman spectrum).

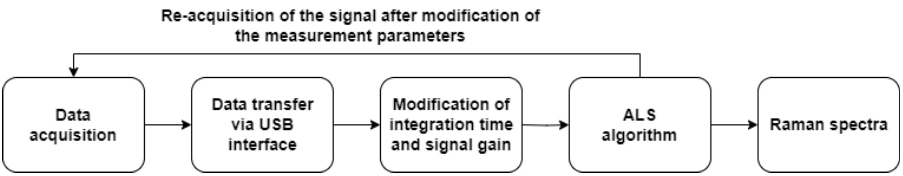

Fig. 6 Diagram of the process for obtaining a Raman spectrum from the Scorpio 7 rover's Raman spectrometer

4. RAMAN SPECTRUM MEASUREMENTS ON THE SCORPIO 7 ROVER

During the first test under the operating conditions of the Scorpio 7 rover, satisfactory Raman spectra were obtained from the constructed spectrometer. The measurements focused primarily on qualitative analysis of soil samples. Calibration and testing of the instrument were carried out using a pure THF solution (Figure 7) and soil samples with different percentages of spirulina (Figure 9), to simulate the presence of various organic substances in the soil sample under test.

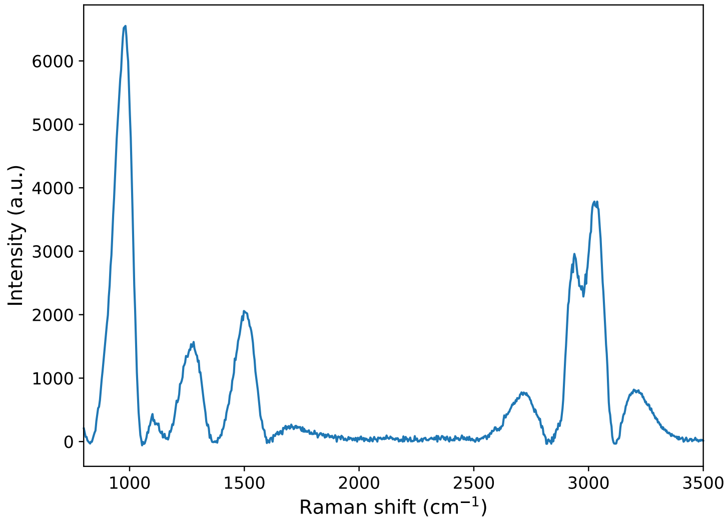

Fig. 7 Raman spectrum of THF solution obtained in the Raman spectrometer (532 nm; 50mW; Integration time: 0.4s)

The obtained Raman spectra were subjected to further data processing using an ALS-type algorithm. In the case of the study of solid samples, it was necessary to use this type of processing of the received data, because the received signal was characterized by very low intensity and there was a phenomenon of fluorescence of the sample, which prevented the analysis of the received data - the fluorescence spectrum "covered" the Raman spectrum of interest.

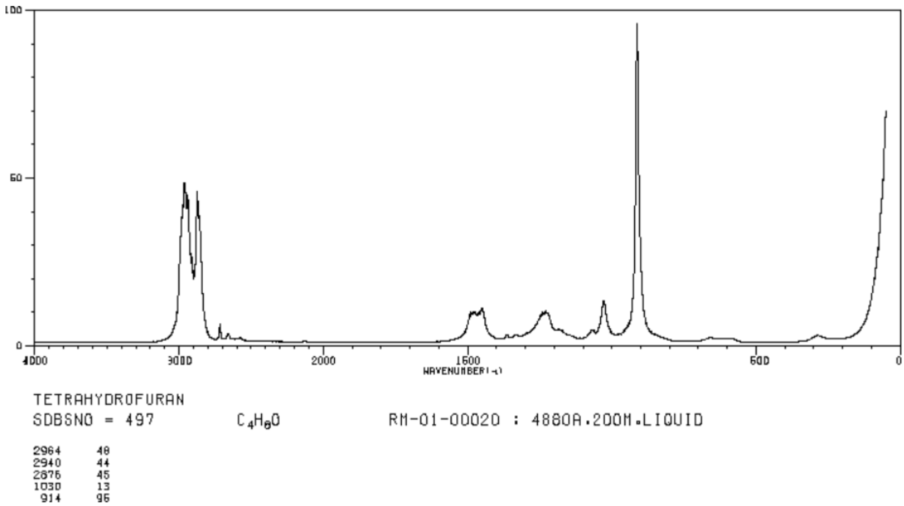

Fig. 8. Raman spectrum of THF solution obtained with 488 nm laser excitation [7].

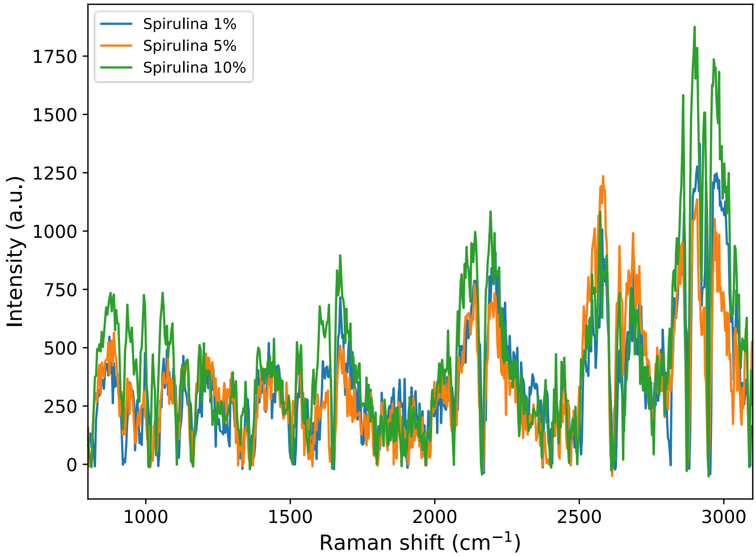

Fig. 9 Raman spectra obtained from soil samples containing spirulina at different weight concentrations (1%, 5%, and 10%) (532 nm; 50mW)

The main conclusions of the analyses were the presence of a wide range of organic substances contained in the sample with spirulina added. First of all, this is evidenced by the presence of intense peaks in the spectral region from 3150 - 3340 cm^{-1} [10]. Activity in this spectral region indicates the presence of the -NH bond, which is widely present in amino acids. In addition, the visible peaks of high intensity in the range from 700 - 1260 cm^{-1} testify to the presence of aliphatic and aromatic carbon bonds, which are widely present in organic compounds [10].

5. SUMMARY AND CONCLUSIONS

Implementing the Raman spectrometer under construction into the design of the Scorpio 7 rover made it possible to conduct chemical analysis of collected soil samples. Together with additional microscopic analysis in the research module of the Scorpio 7 rover, it significantly expanded the in-situ analysis capabilities of the unconventional vehicle of the OFF-ROAD Scientific Circle. After testing the operation of the spectrometer during the movement of the Scorpio 7 mobile research platform, the need to increase the stability of the Raman spectrometer in use was noted. The currently used system for recording Raman spectra requires a change in the used housing for optical components. The properties of the used 3D printing technology, which is characterized by anisotropic mechanical properties and the occurrence of material shrinkage, cause the used optics to be exposed to uncontrolled displacement during shocks caused by the movement of the Scorpio 7 rover. The result of these displacements is the decalibration of the spectrometer, which significantly affects the veracity of the recorded Raman spectra.

After conducting a series of measurements with the constructed Raman spectrometer, the need to replace the used excitation source (532 nm laser, 50 mW) with a source of higher power was recognized, since the currently recorded Raman spectra are characterized by very low signal intensity. Too low a power of the used excitation may cause organic compounds to generate a less intense Raman scattering phenomenon that will not be observed by the used recording system.

Conclusions from the work of the current system will be taken into account in the next version of the Raman spectrometer.

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