

Raman spectroscopy goes to Mars

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Introduction

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 capabilities, 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. As a consequence of these capabilities a great expansion in applications has been seen in the last 20 years across many fields ranging, *inter alia*, from chemistry to mineralogy and geology, art and archaeology, forensic sciences, polymers and biomaterials.

In spite of this expansion and the capabilities of Raman spectroscopy, it has been, and to a great extent still is, considered a laboratory technique. Nevertheless, in recent years several systems have been specifically developed for field applications. These systems have profited from recent technical advances in laser sources, optical elements and spectrometers and detectors, which have led to the possibility of developing robust, compact and miniaturised spectrometers, which have many of the spectral capabilities of laboratory-based systems.

These developments also paved the way for the potential use of Raman spectroscopy in planetary exploration as part of rover or lander instrumentation, in particular for the exploration of Mars.

At present, Raman spectroscopy, separately or in combination with LIBS (Laser induced breakdown spectroscopy) or fluorescence, is considered as a fundamental, next-generation instrument for the characterisation of mineralogical and organic material during exploration of Mars.

While instrumentation for robotic missions is probably the most important consideration for Mars exploration, it is also important to note that Raman applications adding to the knowledge of Mars also cover other important aspects, such as the study of Martian meteorites and potential terrestrial Mars analogues.

In the context of this general framework, we will, in this article, discuss some recent developments and applications of Raman spectroscopy for planetary exploration with particular interest on Mars.

Raman for Mars

Several attempts to develop miniaturised Raman spectrometers for analysis on planetary surfaces have been made in recent years. These instruments can be classified into two main groups, close-up or remote instruments.^{1,2} In both cases, the potential to measure spectra of organic and inorganic material has been demonstrated. For the remote case, spectra of samples have been recorded up to a distance of 100 metres!

Nevertheless, Raman spectroscopy suffers from some limitations, which are mainly those derived from the fluorescence emission induced in the samples by the laser excitation. In general, dark materials are low emitting while light materials are more fluorescent. The use of near infrared excitation and FT-Raman spectrometers suppresses the fluorescence to a great extent, but these spectrometers are more complex and have moving parts, which presents greater difficulties for space applications where miniaturised and robust spectrometers are desirable. Also excitation in the near infrared causes additional difficulties for the detection systems at high wave-numbers, where important bands such

as those of water stretching vibrations appear.

Raman scattering is a very weak effect and needs, in general, to be screened from stray light. This poses additional difficulties for daylight operations, which are, of course, the more convenient for rover operation on planetary surfaces.

Pulsed-Raman techniques offer important benefits to overcome these limitations. Appropriate use of a pulsed laser with gated detection allows for discrimination against unwanted daylight background and also against long-lived fluorescence emissions from the samples.

A Raman spectrometer ideal for surface mineral and organic analysis should, in principle, comprise a robust and miniaturised spectrometer capable of working remotely at a distance of up to several metres, which is excited by a pulsed laser and in which spectra are recorded by a gated detection mode. Figure 1 shows an artist's impression of such a system taken from the EXLIBRIS proposal to the ESA-Pasteur Call for Ideas.³ This instrument proposal is for a combined LIBS–Raman spectrometer. Excitation for Raman spectroscopy is in a pulsed mode using 533nm wavelength

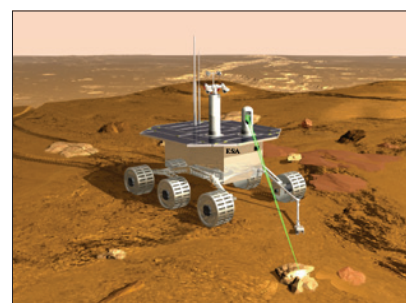


Figure 1. Artist's representation of the EXLIBRIS Raman–LIBS integrated instrument for chemical and structural mineral characterisation on planetary surfaces.

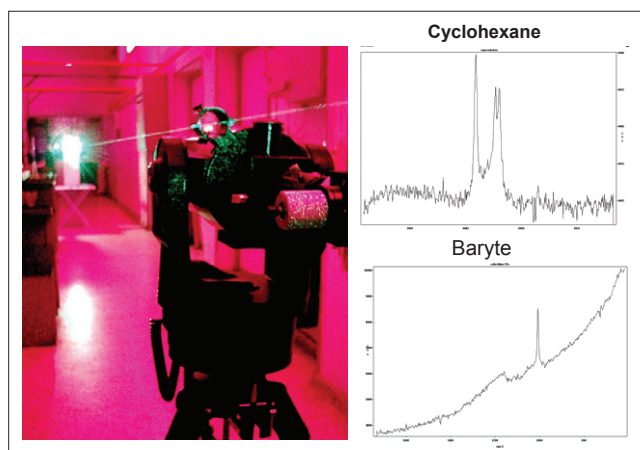


Figure 2. Remote Raman spectrometer taking spectra at a distance of 10 m. The CH and SO₄ stretching bands of cyclohexane and baryte recorded by this means are also shown.

radiation, and the system is able to take spectra over a range of about 10 m around the rover. In Figure 2, laboratory tests exciting in continuous mode over the range 10–20 m are shown.

Remote Raman systems are not actually envisaged for the next Mars missions. However, close-up and microscope Raman-LIBS systems and applications are included in the EXOMARS PASTEUR payload and programme, the first ESA mission of AURORA PROGRAM. This will be devoted mainly to characterising the biological environment on Mars in preparation for robotic missions and then human exploration. The close-up Raman probe will take spectra from surface samples guided by a robotic arm; while the Raman microscope will take spectra inside the rover laboratory on prepared samples. In Figure 3 details of the instrument breadboard proposed for the Pasteur payload by TNO industry in collaboration with our scientific group is presented.⁴ The mass of such a prototype is about 1.5 kg.

Martian meteorites

Analysis of Martian meteorites is an important source of information about the mineralogy of Mars and complementary to the development of the instruments mentioned above for Mars exploration. Micro-Raman spectroscopy is a very powerful technique for characterising materials at the microscopic level in a non-destructive way.

About 30 meteorites are at present recognised as Martian meteorites. Among these the SNC meteorites, named after the type specimens of the three original sub-groups (Shergotty, India, 25 August 1865; Nakhla, Egypt, 28 June 1911, and Chassigny, France, 3 October 1915), are of particular interest.

Nakhla is the signature meteorite for the nakhlite subgroup of the SNC meteorites. Nakhla can be described as an olivine-bearing, clinopyroxenite consisting mostly of augite with less abundant Fe-rich olivine, plagioclase, K-feldspars, Fe–Ti oxides, FeS, with several other minor minerals as oxides and carbonates.

Micro-Raman spectroscopy allows for the identification of all these minerals in a non-destructive way.⁵ In Figure 4, a Raman spectrum from an individual mineral grain in the Nakhla meteorite is shown as an example. By using only this technique and

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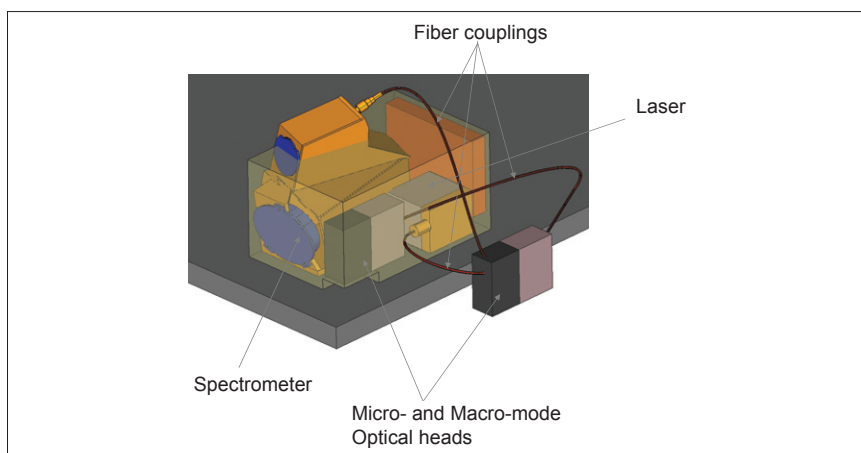


Figure 3. Overview of the combined Raman-LIBS elegant breadboard proposed for EXOMARS-PASTEUR payload by TNO Science & Industry.

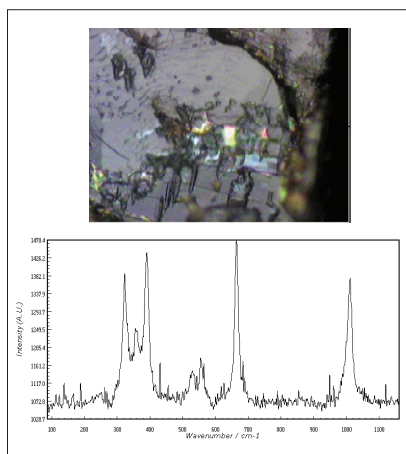


Figure 4. Raman spectrum of a clinopyroxene single micro-crystal identified in the Nakhla meteorite.

correlating the data against band parameters and chemical composition of refer-

ence materials, valuable mineralogical information can be obtained.

Mars analogues

Terrestrial analogues for Mars can be defined as settings on our planet where geological features, biological attributes or combinations thereof offer possibilities for comparisons with possible counterparts on Mars and for partial simulations of Martian conditions, where technologies for exploration can be tested and improved in these environments.

Two areas of Southern Spain are of special relevance in this context. Rio Tinto (Huelva province) is a modern model of the formation of sulphates, linked to significant acidophilic biogenic activity. Sulphates mainly come from aqueous alteration of iron-rich sulphide minerals

of the Iberian Pyrite Belt (SW Spain). It is an important analogue to searching for life in highly acidic liquid water. The Jaroso Ravine is an ancient model of formation of supergenic sulphates associated with polymetallic (Fe, Pb, Ag) sulphides and sulphosalts, which are genetically linked to the calc-alkaline shoshonitic volcanism (Upper Miocene) of the SE Mediterranean margin of Spain. The Jaroso Ravine is located at Sierra Almagrera, Almería province, which is the world type locality of jarosite.

Both these locations are good candidates from which to collect samples for Raman experiments in the laboratory or to undertake *in situ* measurements for mineralogical comparison of several mineral phases, which are mainly sulphate minerals and in particular those belonging to the jarosite-alunite groups.

Raman spectroscopy enabled the identification of a great variety of iron-bearing sulphates from both locations. Rio Tinto shows mainly rhomboclase, coquimbite, rozenite and copiapite minerals. In the Jaroso Ravine, alunite minerals are the most abundant. Jarosite and natrojarosite, kalinite, gypsum and baryte were also identified. Figures 5 and 6 illustrate some of the results obtained.

Raman spectroscopy has also proved its potential for *in situ* characterisation of the chemical speciation inside Rio Tinto acidic waters. Figure 7 shows a typical shallow puddle in the Rio Tinto source and spectra recorded from it. From the Raman data obtained *in situ*, chemical

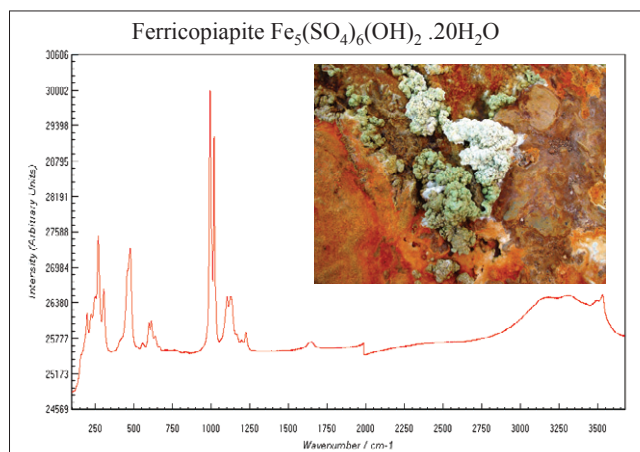


Figure 5. Raman spectrum in macro-mode of ferricopiapite mineral from Rio Tinto.

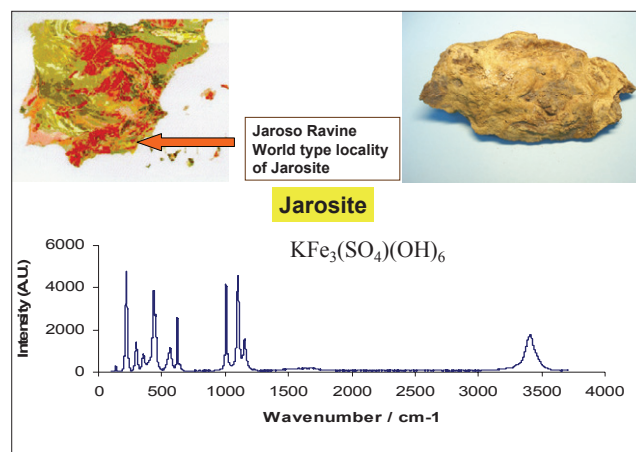


Figure 6. Raman spectrum in macro-mode of Jarosite from the Jaroso Ravine.

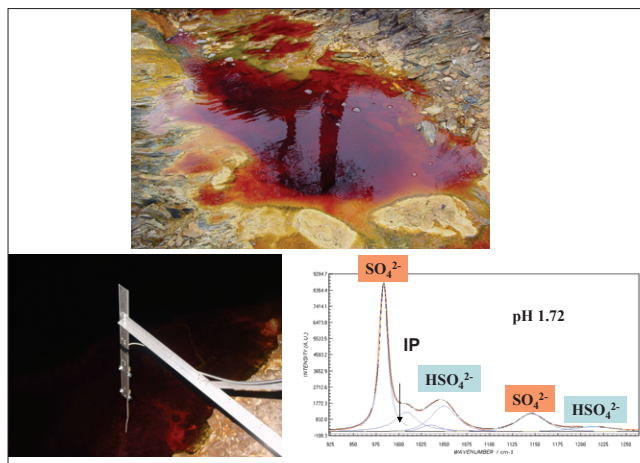


Figure 7. *In situ* Raman spectroscopy of acidic water in Rio Tinto puddles. In the bottom left, the Raman probe taking spectra at night is also shown. The bottom right show the S–O stretching vibrations of the different chemical species. IP is the Fe^{2+} – SO_4^{2-} ion pair.

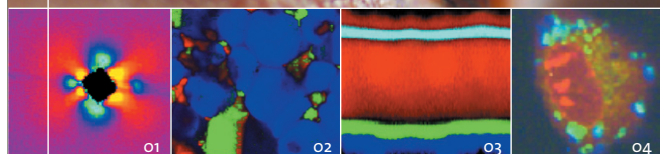
equilibrium and transport properties can be deduced on the river.

Finally, a novel application of Raman spectroscopy related also with the area of Rio Tinto is its use for the mineralogical characterisation of its subsurface as a part of the MARTE (Mars Analog Research and Technology Experiment) project.⁶ This project explores the subsurface anaerobic chemoautotrophic biosphere in this area of SW Spain, as a prelude test for a future astrobiological research on Mars. The Raman spectrometer forms part of the Borehole Inspection System (BHIS), which goes into the borehole after the drill is removed in order to remotely characterise the mineral composition of the rocks and detect possible bio-signatures.

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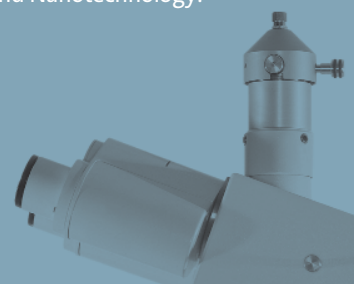
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