Spectrochimica Acta Part A 80 (2011) 148–155

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Analysis of Arctic ices by Remote Raman Spectroscopy

Fernando Rull[a,*], Alberto Vegas[b], Antonio Sansano[a], Pablo Sobron[c]

[a] Centro de Astrobiologia, Unidad Asociada UVa-CSIC. Ed.INDITI P.203 Parque Tecnologico de Boecillo, E47151 Boecillo (VA), Spain
[b] TCP Sistemas e Ingenieria, C/Fernández Caro, 7 E28027 Madrid, Spain
[c] Department of Earth & Planetary Sciences and the McDonnell Center for Space Sciences, Washington University in St. Louis, St. Louis, MO 63130, USA)

ARTICLE INFO

Article history:
Received 29 August 2010
Received in revised form 7 April 2011
Accepted 7 April 2011

Keywords:
Remote Raman Spectroscopy
Raman ice
Arctic ice
AMASE expedition
In situ analysis

ABSTRACT

A portable remote Raman instrument for field analysis has been developed. This instrument has been tested in the Arctic conditions during AMASE (Arctic Mars Analog Svalbard Expedition) campaigns 2007, 2008 and 2009. Besides its capability for mineral detection the remote system proved to be a very useful tool for ice structural analysis of icebergs and ice-wall in glaciers. For the first time at our knowledge Arctic ice has been analyzed in situ in different conditions and at distances ranging from 10 to 120 m. The spectra obtained have enough quality to be used for quantitative spectral analysis.

1. Introduction

Mineral phase identification, molecular detection and chemical composition at stand-off distances constitute a very important field of application of the spectroscopic techniques. Applications of remote detection using Raman and combination of Raman other complementary techniques as laser-induced breakdown spectroscopy (LIBS) or laser-induced fluorescence (LIF) are increasing in the last years. These techniques have proven to be very effective in areas such as planetary surface analysis, drugs and explosive detection and work in harsh and remote environments [1–5]. Among these techniques Remote Raman Spectroscopy (RRS) is the most used and the pioneering works of Sharma and collaborators showed its capabilities at different distances and with different instrument configurations [6–10]. These results are in many cases comparable with those obtained with handled spectrometers which have been used for mineralogical and bio- and geochemical detection at short distance [11–14].

In our group at the Unidad Asociada at the Centro de Astrobiologia several prototypes of RRS have been developed since 2004 and recently a LIBS-Raman combination at distances up to 15 m is also being used [15]. These instruments have been designed mainly for field applications and in particular for potential use in surface planetary missions. The instruments have been also designed for other applications including the study of art and cultural heritage working at the places where access is not possible using conventional contact instruments. There are additional applications that could benefit from the advantages of RSS, for instance, environmental sciences. We have successfully analyzed mine drainage-related products in the Rio Tinto (Spain) area at different distances showing the potential of RSS to analyze contaminated waters and efflorescent mineralogy in field sites where neither sampling nor using conventional environmental field tools such as hand-held X-ray fluorescence (XRF) and Raman spectrometers is possible.

Climate-related research based on the study ice in glaciers, icebergs and other natural ice formations could also benefit from RSS. For instance, analyzing ice at distances ranging 1 to 100–200 m could allow obtaining in situ structural information of ice formation and long and short-term transformations in big ice-walls which are in general quite difficult and in some cases dangerous for sampling.

In this context, we have tested a prototype of a field Remote Raman spectrometer in an Arctic environment that features a variety of ice-related formation such as icebergs and glaciers. We deployed our prototype during the Artic Mars Analog Svalbard Expedition (AMASE) campaigns in 2007, 2008 and 2009. AMASE is a NASA-funded scientific and technological expedition to the Svalbard Archipelago (Norway) in which the geophysical features and the mineralogy in selected sites, thought to be analogous to sites on ancient Mars, are investigated. Geological and mineralogical research aims to find biosignatures and possible life forms in volcanic areas, warm springs, and perennial rivers in connection with Astrobiology.

---

* Corresponding author. Tel.: +34 983140501.
E-mail address: rull@fmc.uva.es (F. Rull).

1386-1425/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2011.04.007

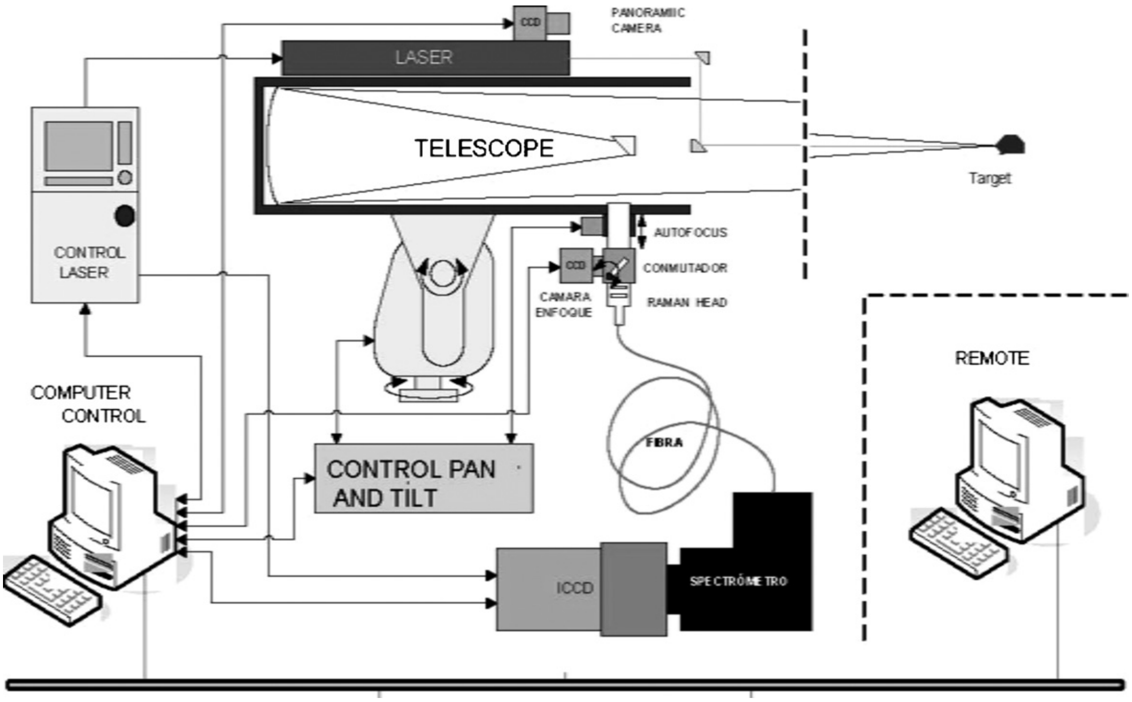

Fig. 1. Schematics of the remote Raman instrument configuration. The instrument can be totally computer controlled. This control includes the pan and tilt system, the laser head and the telescope collecting optics allowing mapping automatically the target through the digitized image of the panoramic camera.

2. Experimental

The remote Raman instrument consists on a laser used for excitation, a Raman spectrometer and the appropriate optics to focus the illuminated target on the spectrometer entrance. Fig. 1 shows the schematic of the system developed for working at distances up to 150 m and Fig. 2 shows the prototype used at the field in Artic conditions. The laser is an Nd–YAG pulsed laser emitting at 532 nm with a maximum rate of 40 Hz and with 32 mJ energy and 4 ns width pulses. The telescope is a reflective Maksutov-Cassegrain of 125 mm diameter from Meade (ETX-127 model) and the laser beam is coaxially aligned with the telescope optical path. The spectrometer is a transmission spectrograph built in our laboratory using a holographic transmission grating (Kaiser Optical) and coupled through optical fiber to the telescope. The detection is gated using an iCCD from Andor. The operation mode consist in a computer controlled sequence of operations starting with the telescope pointing to the sample using a panoramic camera and a pan and tilt system. This image is displayed on the computer screen and when a target is selected the system allow switching to a second vision camera coupled to the telescope to see in detail the target image. This operation is performed using an optomechanical device that also controls the autofocus and switches the image to the vision camera or to the spectrometer when the target is on focus (see Fig. 1 for details). Finally the laser is switched on at variable power to estimate the appropriate gate parameters for spectral acquisition (time delay and time width). The most critical parameter is the time delay which depends on the electronic response and the distance to the target and has to be estimated for each measurement.

Fig. 2. A general overview of the Remote Raman prototype deployed at the field in the Svalbard Islands (Arctic) during AMASE 2008 and 2009 expeditions.

A general view of the operation mode and the software interface control is depicted in Fig. 3. On top a view of both the panoramic and telescope coupled camera images can be seen with some samples placed a 25 m. In Fig. 3 the telescope camera image of a 25 mm diameter disk of pressed sulfur can be seen and the spectrum obtained with 1 s integration time is also shown at the bottom. For use at the field, the instrument is placed in a compact box with all the electronics integrated inside. The system can be controlled by a laptop connected by cable or a wireless system. In the particular case of Arctic conditions during AMASE campaigns (average temperature −5 to +2 °C) the instrument includes two small heaters that allow the temperature of the electronics and the laser cooling water be set at temperatures >10 °C prior to starting operation. At this moment the instrument is switched on and the dissipating heat maintain the system working for hours with an appropriate design of the box. The power supply of the whole system in these conditions is provided by a small portable electric generator.

3. Results and discussion

In situ analysis of ice walls in glaciers or icebergs is a well suited application of the remote Raman instrument. The structural information obtained from Raman spectra is quite useful and can be related with temperature and pressure effects on ice [20,21].