Enhancing Gas Detection Limits in Raman Spectroscopy: implications for the exploration of Mars and other Planetary Surfaces

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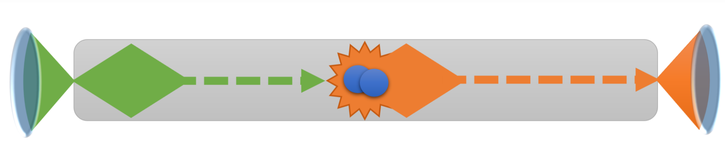
Introduction

Raman spectroscopy is a powerful technique capable of characterising the composition and structure of mineral targets. Its high specificity can also be used to measure gas composition and detect minor components in planetary atmospheres, including methane and other hydrocarbons.

However, the lower density of gases compared to mineral or liquid solutions results in a weaker Raman response, making the application of the technique challenging for volatiles in low concentrations. There is ongoing research on the use of *hollow core fibers* (HCF) in laboratory environments for liquid and gas solutions.

Here, we study the applicability of these HCF-based sensors in the context of planetary surface exploration, considering that such a lightweight concept could be easily integrated into any space exploration mission equipped with an RLS-like Raman spectrometer.



Sensor schematic. Light from laser (532 nm) is coupled into the fiber. Excitation light interacts with molecules along the whole path within the HCF, generating Raman scattered light, which is collected within the solid angle allowed by the numerical aperture (NA) of the fiber.

The HCF increases the total effective interaction volume of the excitation laser with the sample and improves the collection efficiency.

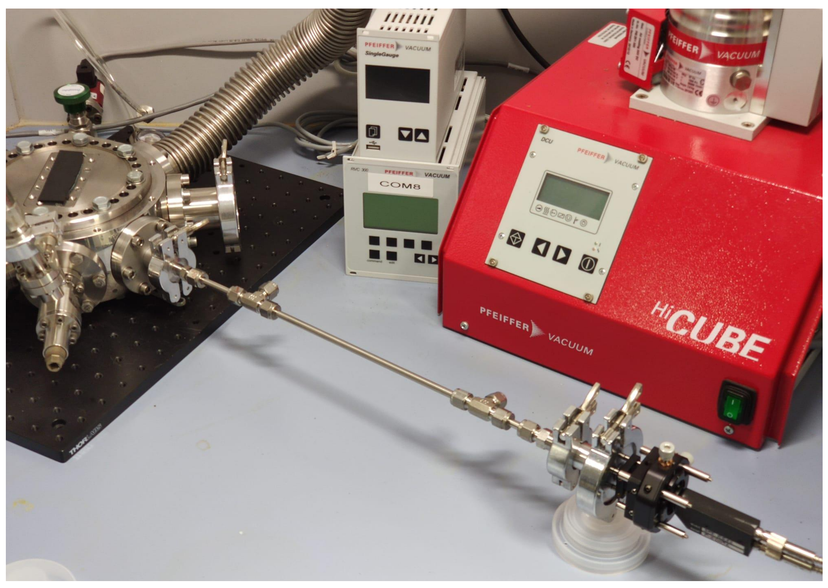
Tests performed

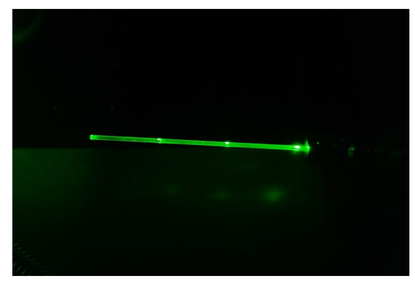
The sensor concept has been developed in atmospheric conditions, allowing fine tuning of the optical assembly such as fiber length.

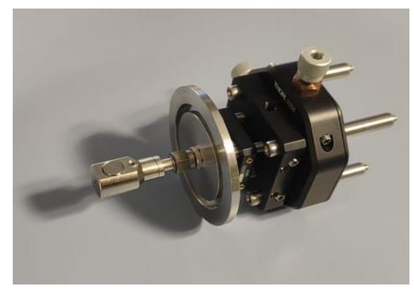
Afterwards, a vacuum chamber has been used to simulate relevant use environments and characterize the behavior of the fiber sensor under different conditions:

- Small amounts of oxygen and hydrogen in a vacuum environment.
- Same test gases in an inert nitrogen atmosphere at various pressures (0.5, 1 and 2 bar) and concentrations ranging from 0.5 % to 20 %.
- Methane and simple hydrocarbons (ongoing).

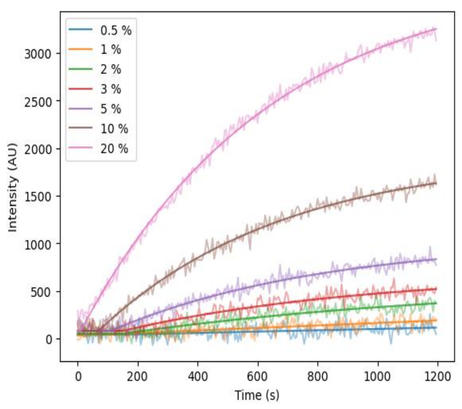
The mentioned sample gases were selected for several reasons. Oxygen and nitrogen are representative of the Earth atmosphere. Hydrogen has a Raman peak in 4161 cm^{-1}, broadening the wavenumber coverage of the experiments. It being a lighter molecule allows to understand the effect of molecular mass in sensor response time.

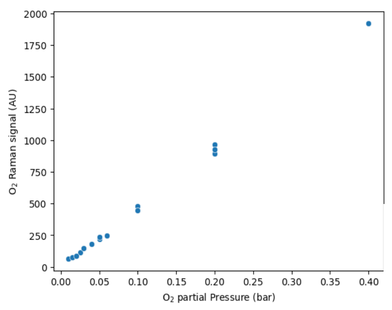






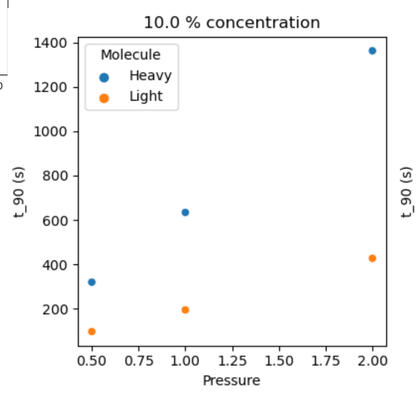
Signal of the analyte increases as it diffuses into the HCF.
Curves were fit to characterize diffusion speed.





Pressure and concentrations were registered during all the tests and correlated with the measured Raman intensity.

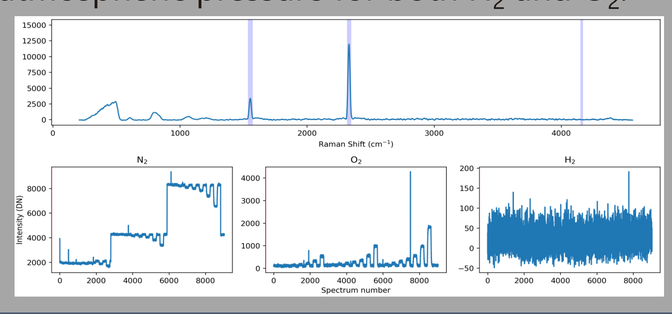
Diffusion time was faster at lower pressures and increased with molecular mass.



Data analysis and results

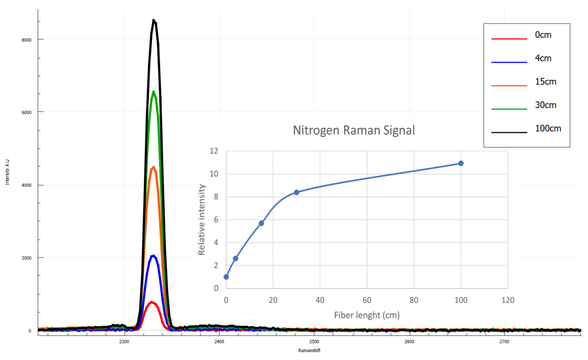
- Instrument reference correction, baseline subtraction and signal filtering are applied to each spectrum.
- Signal associated with each gas was measured performing peak area integration, although certain gases and more complex molecules could benefit from multivariate techniques.
- Curves of signal versus time are fit to determine detection time and sensitivity of the sensor.
- Limits of detection have been calculated both theoretically from the sensor sensitivity curve fits as well as from the SNR and signal intensity from each individual spectrum. The lowest tested concentration, 0.5 %, was determined to be detectable at atmospheric pressure for both H_2 and O_2.

Software developed for spectra measurement and processing.
Spectrum is shown on top, peak intensities can be seen for each gas.



Conclussions

- A clear **performance increase** has been obtained with respect to a bare Raman probe without HCF.
- High **specificity**: The concentration of each individual component in a mixture can simultaneously quantified.
- Signal has a **lineal dependence** on partial pressure and therefore amount of analyte.
- Limit of detection is as low as **0.5 %** at 1 bar with the current iteration of the sensor.



Dependance of Raman intensity scattered by atmospheric nitrogen with varying length of HCF.

Greater lengths provide better signal, but diminishing returns are observed.

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