High Sensitivity Planetary Composition Measurements Using Integrating Cavity Enhanced Spectroscopy.

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Introduction: The desire to understand planetary atmospheres, terrestrial chemistry, or search for potential biological markers on Ocean Worlds often involves some form of optical spectroscopy. Common spectroscopic methods include absorption, fluorescence, or Raman based measurements. We present a new approach to planetary spectrographic instruments based on a novel high reflectivity integrating cavity.

The exploration of planetary surfaces using Raman based spectroscopy techniques is relatively new, and promises to play an important role in NASA's future exploration of the Solar System. Similar to the spectral fingerprints available through infrared imaging spectroscopy the Raman excited emissions provide distinct signatures, including those of more complex molecules typically found in trace abundances.

In many ways the initial survey of the Solar System with Raman spectrographs is just beginning at Mars. Future missions including UV fluorescence measurements will have increasingly focused objectives related to biologically interesting species and related design requirements for highly sensitive (low abundance level) measurements in increasingly extreme environments. The need to better adapt UV Raman and fluorescence measurement techniques combined with IR Raman for the high sensitivity needed for life detections motivates us to develop a new instrument optimized for high sensitivity and with multiple excitation source wavelengths.

While many optical spectroscopy techniques have the capability to provide very sensitive measurements, many suffer from significant practical challenges such as scattering within the sample region, small sample volume interaction, weak excitation sources, or weak optical signals. For example, most optical absorption instruments do not measure absorption directly but measure attenuation where the presence of scattering will significantly degrade the measurement. Weak optical signals from Raman or fluorescence based instruments in a laboratory setting require sensitive low noise detectors and often long integration times.

Several techniques have been developed to address many of the issues commonly encountered with optical spectroscopy instruments. However, these techniques often come with an additional cost such as increased complexity.

Integrating Cavity Enhanced Spectroscopy (iCES): Integrating cavities are utilized extensively in optics from irradiance measurements, to detection systems, to the generation of uniform light sources.[1] However, until recently, commonly available integrating cavity materials generally did not have the optical characteristics to be used effectively for sensitive spectroscopy measurements and/or for space flight instrumentation.

Recently, our colleagues at Texas A&M University have developed a new process for fabricating a highly reflective Lambertian reflector from commercially available fumed silica powders. This disruptive advancement in the state-of-the-art integrating cavity material has resulted in significantly higher reflectance with very low absorption. In addition, the cavity has been shown to have excellent performance in the deep UV region of the spectrum.[2]

After fumed silica powder is pressed and sintered, it can be formed into any shape as shown in Figure 1. Cavity ring-down measurements have demonstrated reflectivity of 99.98% throughout the visible spectrum and into the near infrared, from 400 nm to 1.2 μm, and 99.96% into the deep UV, the highest reflectivity of any known Lambertian reflector.[3]

Figure 1. Integrating cavity formed from high purity fumed silica. This integrating cavity has the highest reflectivity of any known Lambertian reflector at 99.98% at 532 nm and 99.96% at 260 nm.

There are several benefits of such a highly reflective integrating cavity. The integrating cavity can be substituted into many instruments where a Fabry-Perot type cavity or Herriott cell is used with the advantage of not having to mode-match the coherent source to the cavity. Because light reflects incoherently within the cavity, it is possible to use incoherent light as a source as well. In addition, the new integrating cavity has been shown to be insensitive to scattering within the sample, which is a significant limitation to traditional cavity enhanced instruments.[4] The integrating cavity also results in increased sample volume interaction along with build up of the excitation source light within the cavity, providing demonstrated gains of 60 to 100 times. Finally, the cavity collects all of the light within the cavity where it eventually exits through the output port. The collection of light from all directions substantially enhances the optical output signal.

While the integrating cavity method does have many significant benefits there are two basic limitations. 1) The sample must me placed inside of the cavity, requiring one or more moving parts for its use in flight. 2) The cavity may is less appropriate for techniques relying on optical coherence, which is lost when reflected from the walls of the cavity.

Demonstration of ICES: Our collaborators at Texas A&M University have demonstrated the effectiveness of ICES using several different spectroscopy techniques. These techniques include integrating cavity ring-down absorption spectroscopy, fluorescence spectroscopy, Raman spectroscopy, and direct scattering measurements.

Integrating cavity enhanced fluorescence spectroscopy. Sensitive trace measurements of liquid contaminants using integrating cavity enhanced fluorescence spectroscopy to detect urobilin in water was demonstrated. The researchers were able to detect 100×10^{-15} mole (femto-moles) of urobilin with significant signal remaining.[5] The device consisted of a commercially available blue LED, the integrating cavity, and a commercial spectrometer.

Integrating cavity enhanced Raman spectroscopy (ICERS). Initial Raman spectroscopy sensitivity studies are extremely promising where Raman enhancement at 532 nm on the order of 10^5 has been observed (Figure 3). Background measurements show the Raman shift of nitrogen at 2331 cm^{-1} and oxygen at 1556 cm^{-1}. In addition, studies of liquids and bulk materials such as pyrene have shown the ability to measure down to $37x10^{-9}$ moles where the integrating cavity is providing substantial signal enhancement over typical Raman measurement techniques. These measurements can be substantially improved by utilizing UV resonance enhancement of the Raman signal which is now possible.

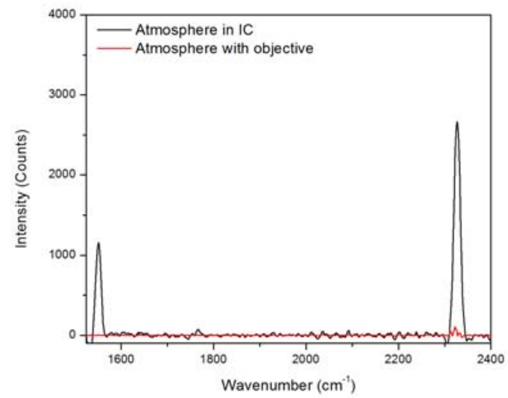

Figure 3. Raman spectrum of atmosphere collected with an integrating cavity (black trace) and with a 20x, 0.5 NA microscope objective. The spectrum collected with the microscope objective was taken over 1 hour while the spectrum taken inside the cavity was taken over 1.2 seconds. Raman spectroscopy of bulk pyrene demonstrated the ability to detect down to 37 nM with a 532 nm excitation source.[7]

Summary: iCES has been demonstrated to provide significant signal enhancement for fluorescence and Raman measurements. In addition, ICES instruments are insensitive to scattering within the sample making it possible to make sensitive absorption measurements. An iCERS instrument is currently under development at SwRI for trace gas analysis and UV resonance enhanced Raman spectroscopy of bulk samples.

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