

# Tandem Raman and IR spectroscopies for monitoring of soil gases in CO<sub>2</sub> sequestration

## Benefits at a glance

- Continuous online monitoring of underground CO<sub>2</sub> sequestration
- Simultaneous quantification of other soil gases, such as N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>
- Rapid detection of abnormalities at a sequestration site

## Introduction

A promising tactic for reducing anthropogenic release of atmospheric greenhouse gases is geologic storage of carbon in which Carbon Dioxide (CO<sub>2</sub>), or other greenhouse gas species, are sequestered in underground reservoirs rather than being released into the atmosphere where they could contribute to global climate change.

One of the challenges associated with CO<sub>2</sub> sequestration is that monitoring of soil gases at the sequestration site is necessary in order to ensure the continued integrity of the site. Vibrational-spectroscopic methods, such as mid-infrared (IR) absorption and Raman spectroscopies, offer a promising method for continuous monitoring of important species such as H<sub>2</sub>O vapor, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub>, and CH<sub>4</sub> in soil gas for comparison to ambient levels in order to assess the integrity of sequestration sites in real time.

The greatest challenge in gas monitoring at sequestration sites is distinguishing between variations in CO<sub>2</sub> levels that indicate a problem with the site and those caused by natural phenomena such as photosynthesis, respiration at plant roots, and the natural cycling of organic carbon in the soil. Typically the natural variation at the site is measured for one year or more to establish a baseline, and then future monitoring of the site involves comparative analysis of CO<sub>2</sub> within the borehole and in the local atmosphere.

The work described in this note demonstrates a viable means of comparing CO<sub>2</sub> concentrations at these sites.

## Experimental

Vibrational spectroscopy is well-suited for analysis of small homo- and heteronuclear soil gases. It gives sharp spectra that can be easily quantified, and it is able to collect spectra in real time using small sampling loops and other standard equipment.

The experimental configuration in this work consists of three compartments: a well completion (that is, the finished well equipped for injection), an external gas circulation module, and various sensors, including a Raman spectrometer, an IR analyzer, a pressure sensor, and temperature and moisture sensors. Figure 1 contains a synthetic diagram of the gas-analysis system.

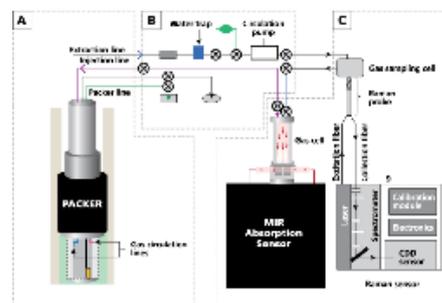


Figure 1: Schematic diagram of the gas-analysis system, showing (A) borehole and completion, (B) external module for gas circulation, and (C) IR and Raman analyzers. (Adapted with permission from Reference 1. © 2013 Elsevier.)

Raman spectra were collected with a Raman gas-phase analyzer, using 532 nm laser excitation, providing a usable range of 175 to 4325 cm<sup>-1</sup> for the Raman data. A Raman probe was installed in gas flow loop with a custom gas cell and connected to the spectrometer by optical fibers.

① All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

The custom gas cell was constructed to take advantage of multi-reflection scattering amplification by focusing the laser through a sapphire window and reflecting it with mirrors before collecting the Raman backscatter through the sapphire window and transmitting it through the probe head to the spectrometer.

## Results

Figure 2 shows a typical Raman spectrum of soil gas at the sequestration site in this study. Key peaks for H<sub>2</sub>O vapor, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> are labeled.

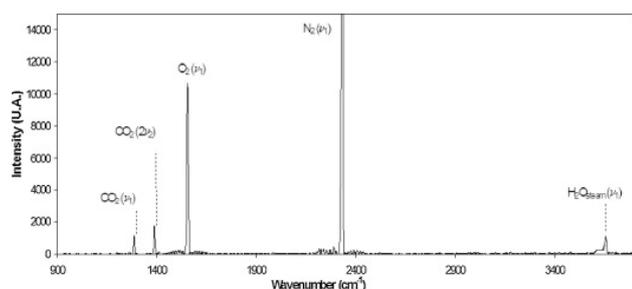


Figure 2: A typical Raman spectrum measured at the site in this study. Key peaks: H<sub>2</sub>O vapor (3657 cm<sup>-1</sup>), N<sub>2</sub> (2331 cm<sup>-1</sup>), O<sub>2</sub> (1555 cm<sup>-1</sup>), and CO<sub>2</sub> (Fermi dyad at 1388 and 1285 cm<sup>-1</sup>). (Reprinted with permission from Reference 1. © 2013 Elsevier.)

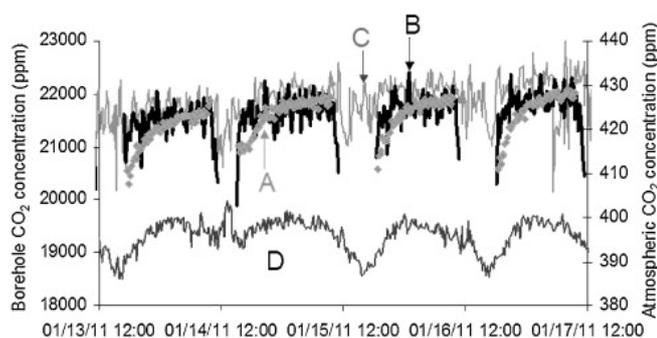


Figure 3: Diurnal variation of CO<sub>2</sub> at the site and in the atmosphere over four days in January 2011. A, B are borehole CO<sub>2</sub> concentrations calculated by IR, while C is the borehole CO<sub>2</sub> concentration calculated from the Raman spectrum using the Fermi dyad at 1388 and 1285 cm<sup>-1</sup>. D is the atmospheric CO<sub>2</sub> concentration measured by IR. (Reprinted with permission from Reference 1. © 2013 Elsevier.)

The sharp, distinctive peaks of the Raman spectrum enable fast, accurate quantification of these various soil gases. Figure 3 compares measurements of CO<sub>2</sub> variation over four days in January 2011, during the injection operation, showing that the Raman data compare well to those from spectral measurements. Data from other soil gases (H<sub>2</sub>O vapor, N<sub>2</sub>, and O<sub>2</sub>) can be found in reference 1.

## Conclusion

The results from this study suggest that Raman spectroscopy is a viable method for real-time monitoring of soil gases at CO<sub>2</sub> sequestration sites. A Raman spectrometer was coupled to a well completion and was used to successfully monitor concentrations of several important soil gases, including CO<sub>2</sub>, at a sequestration site. Because Raman spectroscopy is not sensitive to liquid water, it enables continuous monitoring regardless of wet or dry conditions, in contrast to mid-IR absorption spectroscopy, which is unusable in wet conditions due to its broad liquid-water spectrum. However, because IR is so sensitive in dry conditions, coupling of both IR and Raman enables each technique to be used under its own ideal conditions.

Furthermore, the use of fiber coupling enables the Raman probe head to be located within the completion while the spectrometer base unit remains accessible in a surface module. Also, for comparative analysis, several Raman probe heads can be installed at various locations at the site, such as in boreholes, near injection wells, near abandoned wells for which integrity is a concern, near underground gas pipes, and at natural sites such as aquifers and fault zones.

## Reference

1. Taquet, N., Pironon, J., De Donato, P., Lucas, H. and Barres, O. "Efficiency of combined FTIR and Raman spectrometry for online quantification of soil gases: Application to the monitoring of carbon dioxide storage sites" *International Journal of Greenhouse Gas Control*, January 2013, 12, 359–371.