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Monitoring CO$_2$ sequestration leakage via laser-based spectroscopy in the field
Los Gatos Research (LGR)

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Measurement made easy

Introduction

Efforts to minimize the heat trapping effects of greenhouse gases on climate include purifying, capturing, and storing (sequestering) carbon dioxide in geologic formations. These formations include oil and gas reservoirs, saline aquifers, and coal seams. It is critical that the stored carbon dioxide does not leak back into the atmosphere too rapidly, and carbon sequestration sites are equipped with sensors to detect carbon dioxide leaks.

Problem

However, these sensors are unable to distinguish between naturally-occurring (e.g. plant respiration) and leaked carbon dioxide. Thus, research is needed to identify analyzers that are better suited for carbon sequestration monitoring.

Carbon has a stable isotope with an extra neutron, represented as carbon-13 or $^{13}$C. The ratio of the carbon-13 isotope to the standard carbon-12 isotope is represented as $\delta^{13}$C. Simulations have shown that sequestration leaks resulting in an increase of only a few parts per million volume of CO$_2$ gas may be discerned by a shift in the presence of this isotope ratio.

Thus, researchers need field-deployable analyzers capable of accurately measuring the carbon isotope ratio of ambient CO$_2$. 
Solution

The Zero Emissions Research and Technology (ZERT) Center in Bozeman Montana facilitates studies of geological carbon sequestration in the field. The center can set up controlled subsurface carbon dioxide leaks for testing of CO₂ detection instrumentation. Researchers from the Institute of Marine Sciences and Los Gatos Research, a member of the ABB Group, conducted such studies at the ZERT Center in the summer of 2009 (reported in *Analytical Chemistry* 2011 Aug 15;83(16):6223-9).

In this study the researchers used a CO₂ isotope analyzer from Los Gatos Research. This analyzer utilizes a laser-based technique, called off-axis integrated cavity output spectroscopy (Off-Axis ICOS), that simultaneously measures both the CO₂ concentration and the carbon isotope ratio. The analyzer incorporates a temperature-controlled distributed feedback laser diode operating near 2.05 μm. The laser enters a 59-cm-long, high-finesse optical cavity and repeatedly reflects between two mirrors. The multiple reflections within the cavity result in an effective optical path length of three kilometers, greatly increasing the instrument’s sensitivity.

![Location of sample inlets during controlled CO₂ leak studies](image)

The analyzer’s tunable laser in these studies spanned over 20 GHz to include infrared absorption of both $^{12}$CO₂ and $^{13}$CO₂. The instrument determined the absolute concentration of these two isotopes in the gas sample by using the integrated peak areas, gas temperature, effective optical path length, and measurement pressure in accordance with Beer’s Law. The project included development of a comprehensive software package to control the instrument, save data, and autonomously sample multiple inlets and calibration gases.
Researchers interfaced the Off-Axis ICOS carbon dioxide isotope analyzer to a custom multiport inlet unit. This inlet unit provided ambient gas sampling from an array of multiple locations along the controlled leakage site, Fig. 1, page 2. The 13 inlet lines (Fig. 2) and two certified calibration cylinders connected with an array of solenoid valves, passed through a Nafion drying filter, and entered the LGR Off-Axis ICOS CO₂ isotope analyzer. The system automatically cycled through the inlets every 35.5 minutes.

**Results**

Two of the inlets located far from the controlled leak suggested a CO₂ source ($\delta^{13}C = 27.0$) consistent with local vegetation. Inlets near the leak showed large CO₂ mixing ratios (ranging from 388 ppm to greater than 40 000 ppm) whose predominant source was the released CO₂ (inferred $\delta^{13}C = -58.2$ per mil). Measurements three meters from the source showed daily CO₂ cycles (382-2400 ppm) influenced by the leaked CO₂. Combining data from all of the sampling inlets was used to spatially localize the leak.

Future work will focus on using the data with other collocated measurements such as wind speed and direction to estimate the CO₂ leak rate and better locate the leak position.