Application of Cavity-Ring-Down-Spectroscopy to Measure Local and Regional Methane Fugitive Emissions

Lahiru P. Gamage, Wilson K. Gichuhi
1. School of Environmental Sciences, Tennessee Tech University
2. Department of Chemistry, Tennessee Tech University

Introduction

Abstract

Rising concerns about the direct and indirect role of fugitive emissions on Earth's climate and their contributions to Carbon/Methane cycles has led to the need for improved and expanded measurement capabilities of critical greenhouse gases in the atmosphere. In this work, a high precision Cavity-Ring-Down Spectroscopy (CRDS) technique is used to simultaneously and continuously measure carbon dioxide (CO$_2$), methane (CH$_4$), carbon monoxide (CO), and water vapor (H$_2$O) in ambient air. High accuracy of the measurements is established by reference to calibration using standard reference gases. The precision and accuracy of the analyzer meet and exceed the compatibility targets set by the World Meteorological Organization—Global Atmosphere Watch for baseline measurements in the unpolluted troposphere for CO$_2$, CO, and CH$_4$, in the Northern Hemisphere. Preliminary results of indoor and outdoor ambient air measurements at Tennessee Tech University are presented as a testbed for deploying the CRDS analyzer in the field to detect and measure CH$_4$ fugitive emissions in various locations within Putnam County.

Methane cycle

- The methane cycle is the biogeochemical cycle where methane is exchanged among the biogeochemical cycles (atmosphere, hydrosphere, and biosphere, geosphere).
- Fugitive emissions are the sum of emissions from accidental discharges, equipment leaks, filling losses and etc.

Fugitive emissions

- Since the mirrors have slightly less than 100% reflectivity (99.999%), the light inside the cavity steadily leaks out and decays to zero.

Experimental set-up

- Laser based technique that can measure different gases in atmosphere.
- Very small amount of sample size is needed for the analysis.
- Three mirror cavity with a long path length of approximately 20 km, increases the sensitivity of the instrument.

Results and Discussion

Calibration:

Precise and accurate calibrations with factory calibration standards reveal the correct isotopic composition of the mixtures.

Table 1: Main isotopes and their abundance of CO$_2$, CH$_4$, and CO

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (%)</th>
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</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>99.999</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>28.0</td>
</tr>
<tr>
<td>CO</td>
<td>13.7</td>
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</tbody>
</table>

Table 2: Concentrations of CH$_4$ standards given by the CRDS analyzer and factory calibration standards

| Concentration (ppm) | CRDS Concentration (ppm) | Factory Calibration
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>2.2</td>
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<tr>
<td>2.5</td>
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<tr>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
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</tbody>
</table>

Figure 3: Instrumentation and basic technique of CRDS. Intensity of the light leak is the laser proportional to the concentration of the gaseous species.

- In CRDS, the beam from a single frequency laser enters a cavity defined by three high reflectivity mirrors.
- Since the mirrors have slightly less than 100% reflectivity (99.999%), the light intensity inside the cavity steadily leaks out and decays to zero.

Figure 5: The interfere given by cm$^{-1}$ histogram of the two main isotopes of methane from 6000 cm$^{-1}$ to 6400 cm$^{-1}$. Inset of the figure shows the line profile showing a single line of the second overtone spectra observed by CRDS analyzer for 1.9000 ppm CH$_4$.

Atmospheric simulations of CO$_2$, CO, CH$_4$, and H$_2$O at 140 torr, 20 km path length and 0.03 cm$^{-1}$ instrumental resolution

Main Isotopes of CH$_4$ ($^{12}$CH$_4$ and $^{13}$CH$_4$)

- CRDS has moved a step further to measure this
- Fugitive emissions are the sum of emissions from accidental discharges, equipment leaks, filling losses and etc.

Figure 6: Continuous measurements of CO, CO$_2$, CH$_4$, and H$_2$O and variations of wind speed, solar radiation and U/V index during that period. During night time CH$_4$ levels has increased since there is no wind speed to mix the gases in the atmosphere.

Application 1: Measurements of Methane emissions from enteric fermentation in ruminants

Methane production: CO$_2$ + 8H + 8e$^-$ $\rightarrow$ CH$_4$ + 2H$_2$O

Figure 7: Atmospheric simulations of CO, CO$_2$, CH$_4$, and H$_2$O at 140 torr, 20 km path length and 0.03 cm$^{-1}$ instrumental resolution

Conclusion and future directions

Fugitive emissions

- Fugitive emissions are the sum of emissions from accidental discharges, equipment leaks, filling losses and etc.
- Solid fuels and oil/natural gas systems are the main sources of fugitive emissions.
- Poor quality and incomplete data about fugitive emissions on solid fuels.
- Data on equipment leaks are often unavailable.
- CRDS technique can be applied to monitor fugitive emissions due to the very precise measurements.

References


Acknowledgement

Tennessee Tech University (Start-up grant)

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