



# Measurements of carbon-14 with cavity ring-down spectroscopy



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## ABSTRACT

Accelerator Mass Spectrometry (AMS) is the most sensitive method for quantitation of  $^{14}\text{C}$  in biological samples. This technology has been used in a variety of low dose, human health related studies over the last 20 years when very high sensitivity was needed. AMS helped pioneer these scientific methods, but its expensive facilities and requirements for highly trained technical staff have limited their proliferation. Quantification of  $^{14}\text{C}$  by cavity ring-down spectroscopy (CRDS) offers an approach that eliminates many of the shortcomings of an accelerator-based system and would supplement the use of AMS in biomedical research. Our initial prototype, using a non-ideal wavelength laser and under suboptimal experimental conditions, has a 3.5-modern, 1- $\sigma$  precision for detection of milligram-sized, carbon-14-elevated samples. These results demonstrate proof of principle and provided a starting point for the development of a spectrometer capable of biologically relevant sensitivities.

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## 1. Introduction

Upon the adoption of Accelerator Mass Spectrometry (AMS) to the measurement of carbon-14, scientists realized the possible implications to biomedical applications [1]. Since this time, AMS has facilitated biomedical studies where sensitive detection of carbon-14 is required. Many experiments, utilizing carbon-14 microdoses and microtracers, would not have been possible without AMS. However, AMS's complexity, cost, and limited throughput have become a bottle neck for biomedical studies. Together with other scientific applications of carbon-14, biomedical research has driven interest in the development of a laser based method to quantify concentrations of carbon-14. Starting with a paper by Labrie and Reid in 1981, several groups have explored the possibility of measuring carbon-14 with laser spectroscopy [2–5]. Of particular interest is the work by Galli et. al., which demonstrated a detection limit of .043 fraction modern [6]. This experimental setup leveraged a state-of-the-art laser system utilizing an optical frequency comb and a saturated-absorption cavity ring-down spectroscopy (SCAR) technique. While the milestone study by Galli et al. demonstrates the efficacy of laser based carbon-14 measurements, the complexity of the laser system used prohibits its ease of distribution to biomedical labs.

Our goal is to develop an instrument that balances complexity and sensitivity to enable biomedical studies. Using simple, robust

hardware the laser-based instrument would not replace but would supplement AMS in biomedical studies. Here we present the preliminary results of our initial cavity ring-down spectroscopy (CRDS) system. These initial experiments were conducted at non-ideal wavelengths and temperatures, and carbon-14 sensitivities necessary for biomedical work were not expected. However, this initial prototype elucidated many of the design hurdles needed for developing a biomedical CRDS carbon-14 spectrometer.

## 2. Method

This initial prototype used a quantum-cascade laser (QCL) to measure at the non-ideal P(40) transition wavelength of the  $^{14}\text{C}^{16}\text{O}_2$  antisymmetric stretch rovibrational band. The instrument consists of a heavily modified Picarro CRDS. These instruments utilize a tunable QCL laser (Hamamatsu), an etalon based wavelength monitor, a traveling-wave optical cavity, and an HgCdTe photodetector (Vigo). Modification were made to enable low-temperature experimental conditions. However, all measurements reported here were made near room temperature. Further details can be found in “Development of a low-temperature cavity ring-down spectrometer for the detection of carbon-14” McCartt et al. [7].

Glucose mixtures with 1-, 50-, and 100-modern levels of carbon-14 were prepared by diluting carbon-14 elevated glucose in contemporary glucose. These samples were later measured with AMS to determine the exact carbon-14 concentration, however for simplicity, they will be referred to as 1-, 50-, and 100-modern samples for the remainder of the paper. CRDS measurements of

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the combusted sugar samples were made for several breakpoint vials for each carbon-14 concentration. Breakpoint vials typically contained 5 mg of carbon, however only approximately .5 mg is necessary to make a measurement.

All tests gases measured with the CRDS system were cryogenically purified before measurement. The test gases first flow through an annular piping component which is partially submerged in a dry ice and isopropyl alcohol cooling bath. This cryogenic element freezes out any remaining H<sub>2</sub>O from the test samples [8]. The second cryogenic element is a liquid nitrogen cold finger. The carbon dioxide is frozen onto the cold finger, and the remaining gaseous components, such as carbon monoxide and nitrogen, are evacuated to vacuum. Unfortunately some species have phase transitions similar to carbon dioxide. These species cannot be filtered out cryogenically and must be accounted for spectroscopically.

The cavity temperature was maintained at 300 K, and a measurement pressure of 10 torr was selected based on HITRAN simulations of the spectroscopic region [9].

The details of the data acquisition routine are covered in “Model-based, closed-loop control of PZT creep for cavity ring-down spectroscopy” McCartt et al. [10].

### 3. Results

Fig. 1 below gives an overview of the carbon-14 measurement spectra.

The surrounding spectra is composed primarily of carbon dioxide isotopologues and some other interfering species. The inset shows the P(40) <sup>14</sup>CO<sub>2</sub> line location and the total loss for both the 1- and 100-modern samples. The 1- and 100-modern data represents the average of 30-min of measurements from a single break-point-vial. The error from both measurements amounts to a 5% error on the 1- to 100-modern sample peak signal (error bars were smaller than the data points in the inset of Fig. 1). Subtracting the 1-modern spectra loss from elevated samples provides a simple analysis method but cannot account for variations in the sample carbon matrix, interfering species concentrations, or measurement wavelength. Using a spectroscopic model to quantify the <sup>14</sup>C<sup>16</sup>O<sub>2</sub> concentration can account for these variations.

### 4. <sup>14</sup>CO<sub>2</sub> P(40) spectroscopic fit and comparison to AMS

Data was quantified using a spectroscopic model developed from HITRAN and measurements of surrounding interfering spectra. While beyond the scope of this short form paper, extensive characterization of the surrounding interfering species spectra

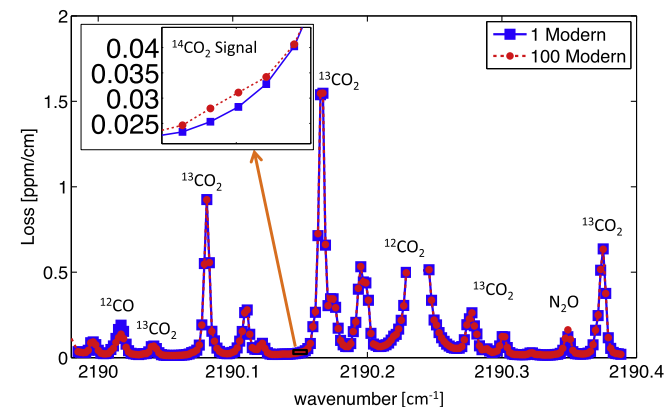


Fig. 1. Overview of carbon-14 measurement spectra. Inset shows loss from P(40) <sup>14</sup>CO<sub>2</sub> line for both contemporary and 100-modern carbon dioxide samples.

was conducted. A more detailed description can be found in the first authors thesis [7].

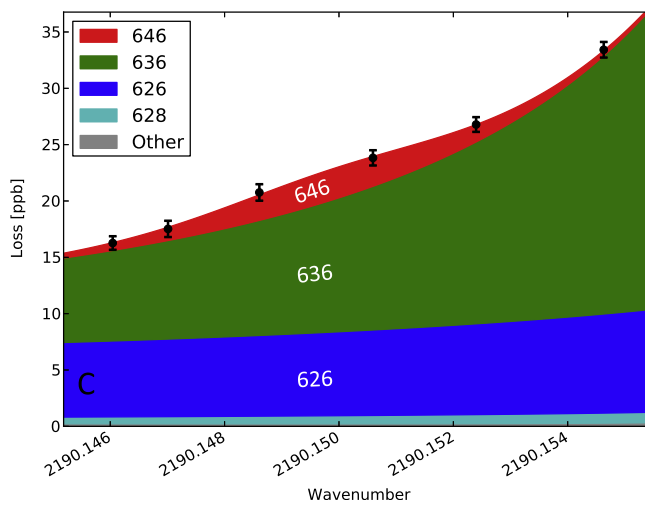
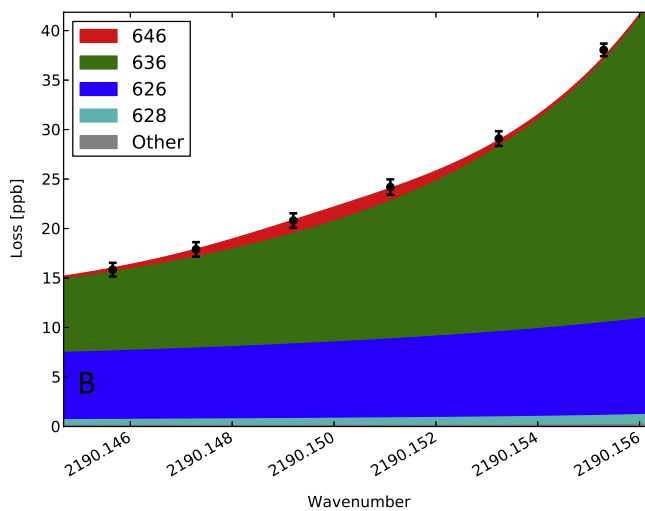
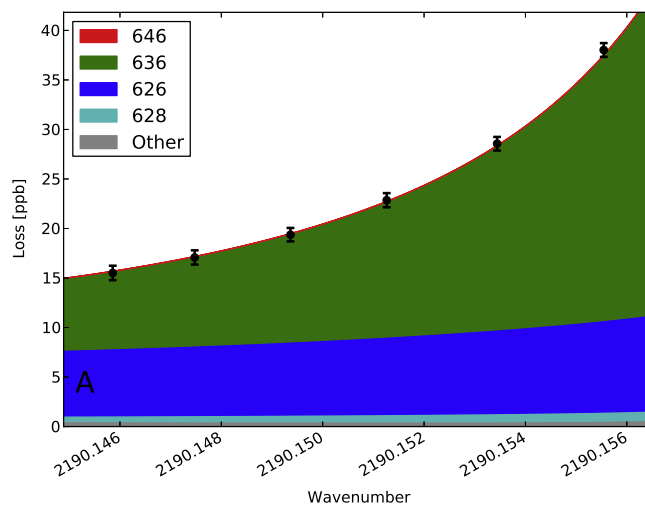


Fig. 2. Spectroscopic model fits of the <sup>14</sup>CO<sub>2</sub> P(40) line. Individual 1-, 50- and 100-modern fits are shown from top to bottom in Panels A, B, and C respectively. Error bars represent the 1-σ confidence from the ring-down events at each measurement wavelength. Shaded regions represent the species contribution to total loss at a given wavenumber.

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