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## Towards a semi-continuous dry extraction technique for CO<sub>2</sub> and $\delta^{13}\text{C}$ -CO<sub>2</sub> analysis using laser spectrometry

### Content

We face two major challenges in the ice core gas community: resolving centennial-scale changes in high-accumulation ice cores and extracting orbital-scale variability in highly thinned deep ice cores. Ice core measurements of the concentration and isotopic composition of CO<sub>2</sub> are historically costly, labour-intensive, and have a low throughput. A step change, similar to the advances made by continuous flow analysis of CH<sub>4</sub>, is needed.

We have focused on developing a new type of dry extraction technique capable of analysing ~3x3 cm ice sticks – akin to continuous flow analysis cross section. In vacuum, a grating surface supports the vertical ice stick and is translated back and forth using a bellows. Experiments with various grating surfaces, including microtome blades, and their impact on extraction efficiency will be discussed. The liberated air is first dried and then condensed in dip tubes (volume ~ 8 mL) using a closed-cycle cryogenic system.

The trapped air is analysed for the concentration and carbon isotopic composition of CO<sub>2</sub> by tuneable infrared laser direct absorption spectroscopy with a custom-built instrument package from Aerodyne Research. The instrument utilises a quantum cascade laser ranging between 2299.6 – 2299.9 cm<sup>-1</sup> with an optical cell of ~160 mL operating at pressures ranging between 1 and 5 torr – roughly equivalent to a sample size of 0.2 and 1 mL (STP). Sample and reference gas are introduced statically into the cell through critical orifice valves with very fast response times (<8 ms) such that pressure can be controlled to within ~0.001 torr. The instrument uses a fully automated referencing scheme that can interweave multiple references within a series of sample aliquots.

Preliminary tests with dry atmospheric reference gases at glacial levels in SilcoNert-coated dip tubes suggest the instrument is capable of high-precision measurements on at least 4 mL of air for CO<sub>2</sub> and  $\delta^{13}\text{C}$ -CO<sub>2</sub> (1-sigma s.d. of 0.2 ppm and 0.03 per mil, respectively).

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