

High precision measurements of greenhouse gases in small ice core samples

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1. Introduction

Since the industrial revolution, the concentrations of greenhouse gases such as CO₂, CH₄, and N₂O have increased¹⁾. To understand the interaction between these gases and climate, analyzing the evolution of their increased concentration is fundamental. It is equally important to investigate their natural variability on various timescales (10 to 10⁵ years). Therefore, improving the precision and resolution of measurements of these gases is a major target of paleo-climatic community.

To this aim, we have developed here a high precision system for measuring the concentrations of CO₂, CH₄ and N₂O (by gas chromatography), δ¹⁵N of N₂, δ¹⁸O of O₂, O₂/N₂, Ar/N₂ (by mass spectrometry), and air content (by manometric measurement), all from a single ice sample. This method is based on an existing Japanese air extraction and measurement systems^{2), 3)}, and provides higher resolution measurements with lower quantities of ice. In this presentation, we will describe the method concerning the CO₂, CH₄, and N₂O measurements and present the test results and preliminary results obtained from a Greenland ice core (NEEM).

2. Method

Air is extracted from an ice sample with a wet extraction technique (dry extraction method is under development). An ice sample (typically 70 - 80 g after trimming the surface) is melted in a vacuum chamber, and the released air is continuously transferred via a water trap into a sample tube at <10 K. The gas concentrations are measured with three detectors included in two gas chromatographs (7890A, Agilent Technologies, hereafter GCs). Inside the first GC, two separate flame ionization detectors measure CO₂ (after conversion to CH₄ by nickel catalyst) and CH₄, while an electron capture detector measures N₂O in the second GC. To measure the gas concentrations with high precision, the following daily procedure is applied. It is composed of a detector stability verification step, followed by calibration processes, once before and once after the sample injections. The detector stability is checked by measuring three standard gases injected at ambient pressure, in turns, three cycles. Once accepted, calibration points (on an area-pressure space) for ice-core measurements are established by measuring the same standard gases injected at three sub-ambient pressures injections (200 - 800 hPa). With quadratic fits, the calibration points produce three calibration curves. This allows a precise determination of ice-core gas concentrations with varying pressure. Ice-core air samples are injected through a low-volume inlet into evacuated sample loops at sub-ambient pressure, and measured in the same manner as the standard gases. Two measurements are typically made for each sample. After the sample measurements, the second set of low-pressure standard gas are made, allowing corrections for the drifts of detector responses through time. The gas concentrations of a sample are calculated by making quadratic fits through the standard-gas calibration points for the time and pressure of each sample. To increase the system's reproducibility, and to decreased time consumption, the all calibration processes have been automatized. The software for this system control and data acquisition has been coupled with an analyzer software, which provides a complete treatment of the datas. Both software have been developed on LabView 10.0 (National Instruments).

3. Results

We will present the following results:

- System's precision (1 sigma) using standard gases used as samples directly at the GCs inlet and through the extraction line.
- Preliminary results from the NEEM ice core (depth intervals 112-600m and 1285-1495m).

References

- 1) IPCC WG1 assessment report, 2007.
- 2) Nakazawa, T. et al., *J. Glaciol.*, **39**(132), 209-215, 1993.
- 3) Kawamura et al., 2007, *Nature*, **448**, 912-916, 2007.