# Continuous in-field measurements of gas concentration from ice cores

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**New techniques have revolutionized the way trace gases are measured from ice cores. What took decades to complete in the past now only takes a few months. We report about the recent development in measuring the methane concentration from ice cores.**

Ice cores provide a unique opportunity to access the past composition of the Earth's atmosphere. Up to now methane concentration measurements have been made on individual ice samples. Such work is laborious and it took two decades to obtain the methane data for the composite record shown in Figure 1A.

Initially chemical measurements were also obtained from individual ice samples. During the 1990s a methodology known as Continuous Flow Analyses was invented and has been further developed since (Bigler et al. 2011; Kaufmann et al. 2008). This method is based on the continuous melting of a section of the ice core. The meltwater is then split and diverted into detectors specific to the chemical ion species to be analyzed. In this way a large range of chemical components can be analyzed directly at the ice core drill site. Note that for these chemical measurements, a debubbler unit is required to remove the air from the ice (on the order of 10% by volume) since the air would hamper the chemical analysis. It has been a long-term ambition to measure the gas composition of ice cores using a similar methodology. The University of Bern, Switzerland, has developed such a system.

## First in-the-field methane concentration measurements

The system, developed in Bern, is based on a small portable Gas Chromatograph for methane concentrations (Schüpbach et al. 2009). The debubbler unit has been modified so that the expelled air is routed through a membrane unit to separate the air from the remaining water. The membrane unit consists of a hydrophobic membrane tube where the outside of the tube is flushed with ultrapure Helium. The air passes through the membrane and is taken up by the Helium stream. The Helium/air sample mixture is then dried and transferred through a column trap held at the temperature of liquid nitrogen to concentrate the air sample. Finally, this air sample is injected into the Gas Chromatograph. This new way of measuring ice core air composition has proven successful and produces a measurement at ~15 cm intervals along the core with a measurement uncertainty of 3%, i.e. sufficient to reveal the main features of atmospheric methane concentration changes (Schüpbach et al. 2009). Still, the resolution potentially achievable is limited by the requirement to (1) pre-concentrate the sample and (2) separate the trace gases chromatographically.

## Introduction of laser spectrometers to ice core works

The research teams at LGGE (Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France) and CIC (Centre for Ice and Climate, Copenhagen, Denmark) have independently developed the use of cavity enhanced laser spectrometry for obtaining methane concentration measurements. Whilst the LGGE group has made improvements to a prototype instrument (SARA) in collaboration with a laser physics research laboratory at Grenoble (LIPhy, http://www-lsp.ujf-grenoble.fr/SARA-Analyzer-laser-of-traces-of), the CIC group has adapted a commercially available Picarro instrument for the specific requirement of ice core analysis.

During the 2009 NEEM deep drilling campaign, the CIC scientists made the

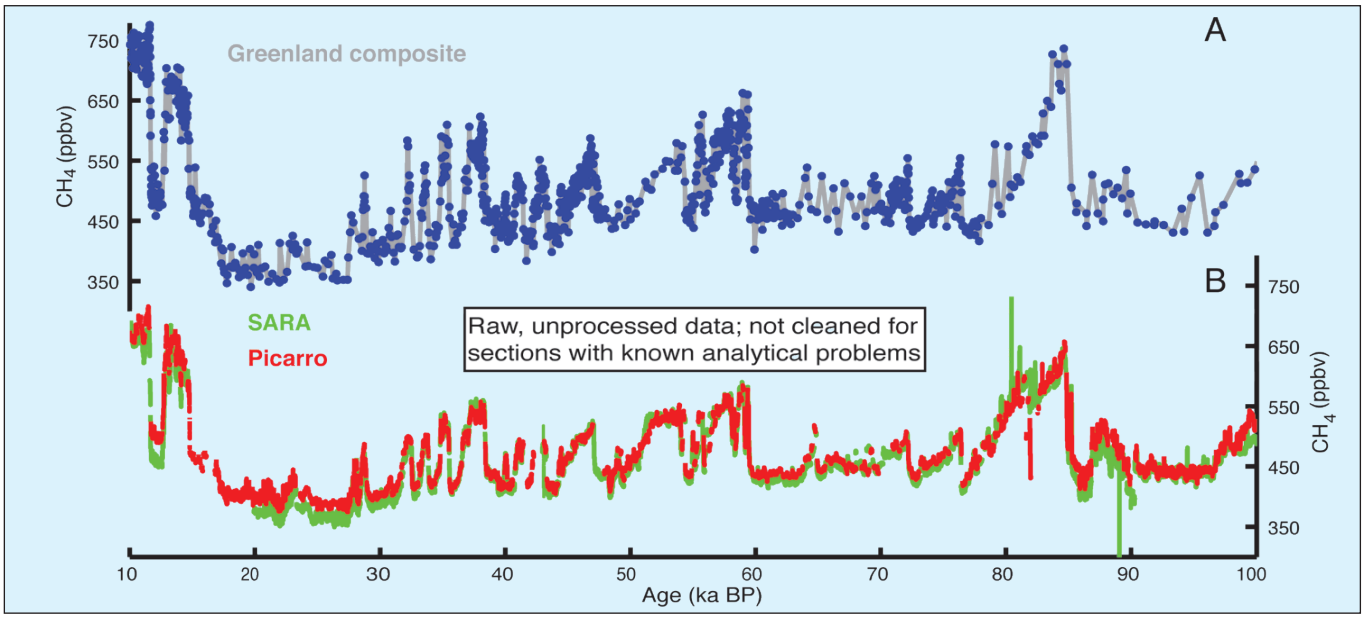


*Figure 1: Methane concentration variations over the last 100 ka.* ***A)*** *Composite record from several Greenland ice cores (Blunier et al. 2007),* ***(B)*** *Raw data obtained with the SARA (green curve) and Picarro laser spectrometers (red curve). This data is preliminary, uncalibrated, and for illustrative purposes only. It is known to contain sections with analytical issues.*

first attempt to couple a Picarro instrument to the existing Bern Continuous Flow Analyses setup. The instrument was connected to the outlet of the Gas Chromatograph gas trapping system in order to measure the sample diluted in Helium. This setup was initially unsuccessful due to the variable dilution of the sample but it demonstrated that laser instruments could be successfully used in the field. Furthermore, initial tests indicated that it would be possible to obtain reliable results if gas concentration measurements were made on the undiluted flow.

## Success during the NEEM 2010 field season

During the 2010 field season, the project was expanded and included two laser instruments backed up by the Gas Chromatograph system (Fig. 2). LGGE and CIC researchers developed a way of extracting the gas in the melt stream without diluting the sample using a Membrana MicroModule unit and the setup was modified such that the gas/water stream from the debubbler unit was routed directly through the membrane unit. On the gas side of the membrane the air extracted from the ice was pumped through a drier to remove water vapor and then successively through the SARA and Picarro analyzers (Fig. 2). Figure 1 shows the composite of several Greenland ice core methane concentration records obtained over the last 20 years (Fig. 1A) and the raw methane concentration data obtained from the respective laser spectrometers (Fig. 1B). In just two months of using the laser spectrometers the teams were able to obtain measurements that previously took two decades to perform.

Although the system was regularly calibrated with a standard gas, there are obvious differences and inconsistencies between the records. These arise from leaks in the setup and from incomplete gas extraction. For the 2010 records the only way to calibrate the data was to measure some individual samples. While, in principle, the measurements should be continuous, they were in fact broken up into sections of 1.1 m. At the beginning of each section the cavities of the spectrometers are filled with standard gas, which is then slowly replaced with sample gas. Over the course of time in places where sample and standard gas coexist in the cavity the methane concentration of the sample cannot be measured, and in the 2010 setup up to one third of the sample was lost, resulting in only some sections being continuously measured for their methane concentration.

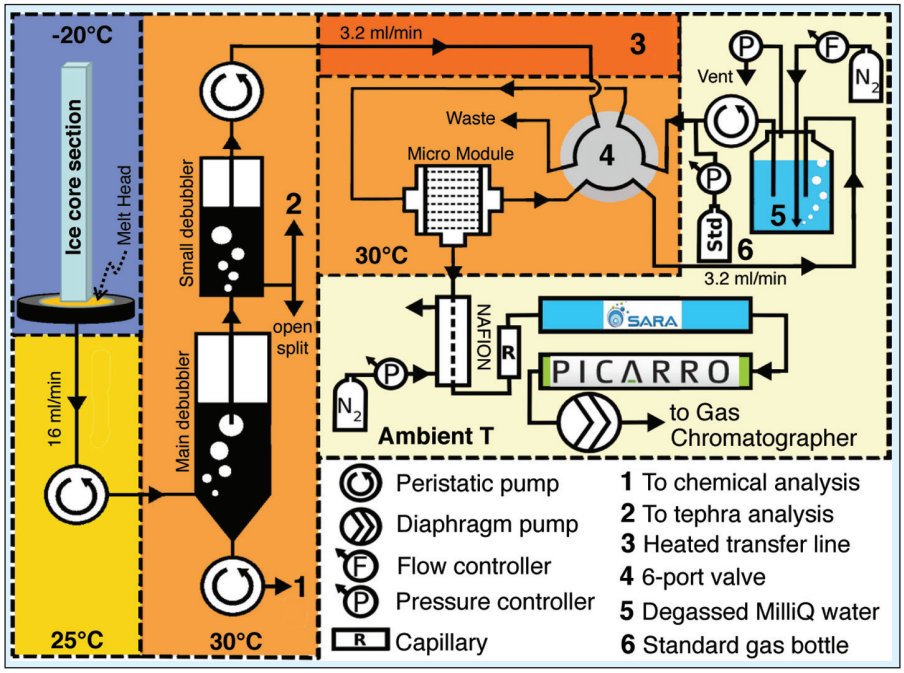


*Figure 2: Schematic of the NEEM 2010 field setup for measuring methane concentrations.*

Since 2010, there has been continuous development and improvement in the sample calibration procedure. We now receive good data getting the system into a dynamical steady state situation. In this way solubility correction and eventual leaks are constant and identical for calibration measurements and samples. The precision of the laser systems is significantly better than that of a Gas Chromatograph system with an uncertainty as small as 0.4%.

Stowasser et al. (2012) investigate to what degree the time resolution of methane records can be improved by continuous measurements. Atmospheric variations are smoothed by traveling through the open porous space (firn) in the top part of the ice sheet (the first ~60-100 m) before the gas becomes trapped permanently in the ice. To obtain the full resolution of the smoothed concentration record trapped in the ice, the dispersion by the measurement system has to be less than the smoothing that occurs in the firn layer. The CIC system obtains a spatial resolution of 5 cm, which is adequate to detect any climatically relevant fluctuations in methane back to at least 66 ka BP in the NEEM ice core.

The significant advantage of the online gas concentration measuring technique is the higher resolution that can be obtained in a very short amount of time. This is especially true for the last millennium and part of the Holocene where the system enables a sub-annual temporal resolution on the NEEM ice core to be obtained. At first glance this ability is meaningless, as the atmospheric variations (e.g. annual fluctuations) are completely smoothed out, but we also found indications of sub-annual methane signals in the NEEM ice core. These signals could point to either in-situ production of methane in the NEEM ice or, alternatively, an artifact of the trapping process of air in the firn layer (e.g. stratigraphic inversions due to firn layers trapping gases at different depths) (Rhodes et al. unpublished data). Future investigations are necessary to clarify these issues.

## Outlook

Laser spectrometer development has rapidly improved over the past few years. In the future it will be possible to analyze not only one atmospheric component such as the methane concentration described here, but a suite of atmospheric components simultaneously. This has already been achieved by the SARA instrument, which has measured both methane and carbon monoxide on a section of the NEEM ice core. Within the framework of the Past4Future project, online measurements of trace gases will be able to supply climate models with the most complete dataset to date.

## Selected references

Full reference list online under:

http://www.pages-igbp.org/products/newsletters/ref2013_1.pdf

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