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# A gas chromatography / pyrolysis / isotope ratio mass spectrometry system for high precision $\delta$D measurements of atmospheric methane extracted from ice cores

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Methane ($CH_4$) is the third most important greenhouse gas after water vapour and carbon dioxide ($CO_2$). Since the industrial revolution the mixing ratio of $CH_4$ in the atmosphere rose to $\sim$1800 ppbv, a value never reached within the last 800 000 years. Nowadays, $CH_4$ contributes $\sim$20% to the total radiative forcing from all of the long-lived greenhouse gases. This $CH_4$ increase can only be assessed compared to its natural changes in the past. Air enclosures in polar ice cores represent the only direct paleoatmospheric archive and show that atmospheric $CH_4$ concentrations changed in concert with northern hemisphere temperature during both glacial/interglacial transitions as well as rapid climate changes (Dansgaard-Oeschger events). With tropical and boreal wetlands, biomass burning, thermokarst lakes, ruminants, termites, living biomass and marine gas hydrates all contributing to the natural atmospheric $CH_4$ level, an unambiguous source attribution remains difficult. Stable hydrogen and carbon isotopic studies on methane ($\delta$D($CH_4$) and $\delta^{13}CH_4$) in ice cores allow to constrain individual $CH_4$ source/sink changes as the different sources exhibit distinct carbon and hydrogen isotopic composition.

Here we present a highly automated, high precision on line gas chromatography pyrolysis isotope ratio monitoring mass spectrometry technique (GC/P/irmMS) for analysis of $\delta$D($CH_4$). It includes gas extraction from ice, preconcentration, gas chromatographic separation and pyrolysis of methane from only 500 g of ice with $CH_4$ concentrations as low as 350 ppbv. Such ice samples containing only approximately 40 mL air and 1 nmol $CH_4$ can be measured with a precision of 3.4‰. Precision for 65 mL air samples with recent atmospheric concentration is 1.5‰. The accuracy of our method is estimated by lab intercomparison exercises to be 1.4‰. Methane concentration can be obtained along with isotope data which is crucial for reporting ice core data on matched time scales and enables us to detect flaws in the measurement procedure. Custom made script based processing of MS raw and peak data enhance the system performance with respect to stability, peak size dependency, hence precision and accuracy and last but not least time requirement.

The new method was applied on ice samples from the North Greenland Ice Core Project and we present the first $\delta$D($CH_4$) record covering Dansgaard Oeschger events 7 & 8 (i.e. 34 - 40 kilo years before present) in high resolution.