A gas chromatography/combustion/isotope ratio mass spectrometry system for high-precision δ^{13}C measurements of atmospheric methane extracted from ice core samples

Melanie Behrens¹, Jochen Schmitt¹, Klaus-Uwe Richter¹, Michael Bock¹, Ulrike C. Richter¹, Ingeborg Levin² and Hubertus Fischer¹

¹Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany
²Institut für Umweltphysik, University of Heidelberg, Heidelberg, Germany

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Past atmospheric composition can be reconstructed by the analysis of air enclosures in polar ice cores which archive ancient air in decadal to centennial resolution. Due to the different carbon isotopic signatures of different methane sources high-precision measurements of δ^{13}CH₄ in ice cores provide clues about the global methane cycle in the past. We developed a highly automated (continuous-flow) gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) technique for ice core samples of ~200 g. The methane is melt-extracted using a purge-and-trap method, then separated from the main air constituents, combusted and measured as CO₂ by a conventional isotope ratio mass spectrometer. One CO₂ working standard, one CH₄ and two air reference gases are used to identify potential sources of isotope fractionation within the entire sample preparation process and to enhance the stability, reproducibility and accuracy of the measurement. After correction for gravitational fractionation, pre-industrial air samples from Greenland ice (1831 ± 40 years) show a δ^{13}CVPDB of −49.54 ± 0.13‰ and Antarctic samples (1530 ± 25 years) show a δ^{13}CVPDB of −48.00 ± 0.12‰ in good agreement with published data. Copyright © 2008 John Wiley & Sons, Ltd.

Migeotte¹ first identified methane as a component of the earth’s atmosphere via its absorption bands in the infrared spectrum. Today methane is recognised as an important greenhouse gas that affects the earth’s temperature directly due to its strong absorption capacity and indirectly by producing water vapour through its oxidation in the stratosphere.²,³ Systematic atmospheric measurements of the methane mixing ratio became available in 1978.⁴ However, the atmospheric abundance of methane has been reconstructed back in time as far as ~800,000 years BP (before present, i.e. before 1950) with the aid of high-resolution measurements of air entrapped in polar ice and firn (compacted snow).⁵ It was shown that during the last glacial cycles measured methane mixing ratios never exceeded 770 ppb until the industrial period started and was as low as 350 ppb during the Last Glacial Maximum (LGM). From about 1750 the globally averaged atmospheric mixing ratio increased rapidly until the 1990s and then more slowly to modern values of 1774 ppb in the year 2005.⁵–⁸

Isotopic analysis allows us to estimate the contributions of different sources and sinks to the atmospheric CH₄ burden.⁹–¹² From a carbon isotope point of view three major 100 methane sources can be distinguished: (i) methane of biogenic origin which is most depleted in δ^{13}C with δ^{13}C of 102 about −60 ± 5‰, e.g. originating from wetlands, rice paddies, ruminants and termites; (ii) thermogenic methane like natural gas (δ^{13}C ≈ −40 ± 5‰); and (iii) pyrogenic methane generated e.g. by biomass burning (δ^{13}C ≈ −25 ± 3‰)¹¹,¹² and references cited in ¹³ Removal of methane mainly occurs in the troposphere through oxidation by the OH¹⁰ radical, and to a smaller extent by aerobic oxidation in ¹⁹ soils.¹⁴,¹⁵ Less than 10% of CH₄ is oxidised in the stratosphere ¹⁰ through reaction with OH¹⁰ and Cl¹⁰ radicals. Currently, a ¹¹¹ tropospheric Cl¹⁰ sink is also being discussed but it has not yet ¹¹² been included in global methane budgets.¹⁶ Due to kinetic ¹¹³ isotope fractionation¹⁷,¹⁸ the sink processes enrich the δ^{13}CH₄ ¹¹⁴ in the atmosphere which has a modern value of about −47‰ ¹¹⁵ compared with the average source signature of about −55‰.¹¹³ ¹¹⁶ Craig et al.¹⁹ were the first to determine δ^{13}CH₄ from air ¹¹⁷ entrapped in 25 kg of ice. Obviously, this large amount of ice ¹¹⁸ cannot be provided from multi-parameter ice core studies ¹¹⁹ where ice supply is strongly limited. The development of ¹²⁰ continuous-flow gas

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In this paper we describe a highly automated GC/C/IRMS system with melt-purge extraction for ice core analyses suitable for ice sample sizes of about 200 g (equivalent to about 20 mL STP) with methane mixing ratios as low as about 350 ppb. The system performance is demonstrated by blank, reproducibility and first ice core measurements. With the aid of four reference gases we developed correction procedures that substantially improved our precision and accuracy. Our final precision is 0.1% for 20 mL STP of air from pre-industrial ice (700 ppb) and better than 0.3% for glacial samples with a concentration of 350 ppb. Our absolute $\delta^{13}$CH$_4$ values of air from ice core samples were undistinguishable from published data and the overall accuracy is better than 0.3% compared with a recent air $\delta^{13}$CH$_4$ reference.

**EXPERIMENTAL**

**Instrumentation**

Our high-precision continuous-flow GC/C/IRMS system (Fig. 1) is based on a completely reconfigured pre-concentration device (PreCon) with combustion oven, GC-Box and an IRMS interface (GP-Interface) (all ThermoFinnigan, Bremen, Germany) coupled to an Isoprime mass spectrometer (GV Instruments, Manchester, UK) similar to the design of Merritt et al.\textsuperscript{21} and Rice et al.\textsuperscript{25} To adjust the original system for the extraction of very small amounts of CH$_4$ from ice cores, we added a helium (He) purification trap, an ultra-high vacuum sample vessel, an air sample loop, an adsorption trap for CH$_4$\textsuperscript{22} and a CH$_4$ reference gas insertion. The gas flow rates of our system are pressure regulated except where otherwise mentioned. All tubes are made from stainless steel or fused silica. V1, V2 and V3 are pneumatic six-port two-position valves (1/16" fittings, 0.4 mm port diameter, Valcon E rotor; Valco, VICI AG, Schenkon, Switzerland). The other valves are pneumatic on/off valves (MOVPT, Vespel seat and ferrules; SGE, Darmstadt, Germany). All valves except those on the sample vessel and all traps are automatically operated by the MassLynx mass spectrometer software (GV Instruments).

**Measurement procedures**

The equipment shown in the left box in Fig. 1 is used for the extraction and specific trapping of CH$_4$ from an air reference or an ice sample. Before the high-flow He carrier gas (99.999 vol.-% purity; Air Liquide, Düsseldorf, Germany) enters the pre-concentration device, it is pre-cleaned by a high-capacity gas purifier (not shown in Fig. 1; Supelco, Bellefonte, PA, USA) that removes H$_2$O, O$_2$, CO and CO$_2$. Our supplemental He purifier trap filled with Hayesep D 80/100 mesh (Supelco) and cooled to −196°C with liquid nitrogen (LN$_2$) is used to additionally remove CH$_4$ and higher hydrocarbons. Ice samples are prepared in a cold laboratory where about 230 g of pre-cut ice is trimmed with a blade to remove potential contaminants from the saw. The remaining piece of about 200 g is placed into the pre-cooled (approx. −20°C) air sample loop. The GC-Box is a 63 CF-flange (SEG-250; Caburn-MDC Europe Ltd., St. Leonards-on-Sea, UK) that is equipped with two manual valves (SS-DSVCR4, Swagelok, Solon, OH, USA). After sealing the vessel with a copper gasket, air in the

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Figure 1. Flow scheme of the GC/C/IRMS system for analysis of $\delta^{13}$CH$_4$ from air entrapped in ice cores. The valves and traps are shown in the state of extraction of air from a melted ice sample and pre-concentration of methane.

vessel and potentially adsorbed on the outer surface of the sample is removed by evacuation with an ultra-high-vacuum pump (Turbomac 50, Oerlikon Leybold GmbH, Köln, Germany) for 1 h. During evacuation the vessel is kept at approx. –10°C. After attaching the vessel to the extraction line using two 1/4” Ultra-Torr connectors (Swagelok), a Visual Basic script is started that controls all the following measurement operations. The connections to the manual valves of the vessel are purged with 10 mL/min He for 30 min by opening the purge valves while the ice is melted within a warm water bath (20–40°C) placed around the vessel. After the ice has melted, this bath is replaced by a cool bath to keep the temperature constant at 0°C. To bring the vessel to the operating pressure for CH4 trapping, V2 is switched and the inlet valve of the vessel is opened so that He fills the vessel. The inlet valve of the vessel is closed and V2 is toggled again to cool down the CO2 and the CH4 trap under He-flow. After switching V2, the manual valves of the vessel are opened to strip the sample air out of the vessel. The inflow capillary (1/16” o.d. stainless steel) reaches the bottom of the vessel so that He bubbles through the melt-water. The bulk of water vapour in the He stream is removed by a 60 cm Nafion membrane (0.07” o.d.; Perma Pure LLC, Toms River, NJ, USA) cooled to –25°C. CO2, N2O and residual water are held in a 1/8” stainless steel trap at –196°C (LN2). This trap is filled with Ni wires to ease the adsorption of ice particles by providing a higher surface area. Methane from the stripped air is pre-concentrated in a consecutive CH4 trap (1/8”, 50 cm stainless steel tube) filled with Hayesep D 80/100 mesh. This CH4 pre-concentration column is kept at –140°C. Temperature fluctuations measured by a thermocouple placed in the centre of the CH4 trap are limited to less than 1 K by a PID-heat controller (West 6400; West Instruments, Brighton, UK). The stripping and trapping of methane take 90 min. During this step the sample vessel headspace volume is exchanged about 15 times. Most of the non-methane atmospheric gases leave the system through the vent at V3.

For proper separation and combustion of CH4 the equipment shown in the middle box of Fig. 1 is used. To connect the CH4 trap to the gas chromatograph He flow of 1.1 mL/min V3 is switched. The CH4 trap is lifted out of the cooling bath while the cryofocus trap is still warm to allow residual N2 and O2 to leave the CH4 trap for 5.5 min before the CH4 is cryofocused on a 1 m 0.32 mm i.d. CP-PoraBond Q column (Varian, Darmstadt, Germany) immersed in LN2 for 10 min. The cryofocus is then warmed to inject the CH4 and residual air components into a 30 m 0.32 mm i.d. CarbonPLOT GC column (Agilent, Böblingen, Germany). After chromatographic separation at 30°C, methane and residual air components are combusted at 940°C in a microoxidation Al2O3 tube filled with CuO, NiO and Pt wires (ThermoFinnigan). Re-oxidation of the Cu and Ni wires is done weekly by introducing 0.5 mL/min O2 (99.998 vol.-% purity; Air Liquide) in a countercflow of He using the backflush valves for 2 h at the same temperature. Water from the combustion of CH4 is removed by a second Nafion membrane downstream of the oven and the CO2 produced from CH4 is transferred to the mass spectrometer via a conventional open split. The Isoprime mass spectrometer is equipped with three Faraday collectors for m/z 44, 45 and 46 as well as two additional collectors to monitor m/z 28 and 32 simultaneously, which is critical for optimising the system performance. To examine the performance of the different parts of our system we follow three referencing strategies.

(i) Fractionation processes can potentially occur during the pre-concentration steps due to partial CH4 trapping, loss of CH4 during the removal of other air components, or incomplete transfer of CH4 to the cryofocus trap. Reference air is inserted directly or through degassed melt-water via the sample loop on valve V1 to test the reproducibility of these processes.

(ii) To monitor the fractionation processes in the low-flow part of the system, i.e. mass discriminations due to the chromatographic isotope effect and chromatographic peak distortion, the combustion process and flow conditions at the open split,26 CH4 reference peaks are injected daily in separate acquisition runs. During ice sample and air reference acquisitions CH4 reference peaks are also injected before and after the peaks from the pre-concentrated sample to check the stability of the system.

(iii) A CO2 reference gas (ISO-TOP CO2, Air Liquide) is inserted via the reference gas port in each acquisition to correct for effects that appear in the source of the mass spectrometer. The isotope ratios of all peaks are calculated against this CO2 working standard that was calibrated in our laboratory on a MAT 252 dual-inlet mass spectrometer (ThermoFinnigan) against NIST 8563 (CO2-Light) gas standard. The δ13CO2 of our working standard is —49.35% versus Vienna PeeDee Belemnite (VPDB) (1σ = 0.02, n = 9). All measured m/z 45/44 ratios were corrected for 17O using the Craig algorithm.27

Chromatographic separation

In continuous-flow GC/IRMS analysis of air samples co-eluting sample peaks can distort the isotopic measurement100 due to isobaric contamination or changing conditions in the ion source of the mass spectrometer. In particular, N2 and O2 that elute only shortly before CH4 potentially interfere with the m/z 44 signal by peak tailing or reaction to N2O in the combustion oven or in the ion source. Baseline separation105 of CH4 from N2 and other contaminants is attained in our analysis, as shown in Fig. 2(a). The grey curve, representing the m/z 28 signal, displays small peaks that occur simultaneously with the m/z 44 signals. This is due to CO2 ions formed in the ion source when the CO2 working110 standard or CO2 from CH4 combustion or residual CO2 from the sample gets into the ion source of the mass spectrometer.112 Furthermore, there are m/z 28 peaks from contamination in the CH4 reference insertion, in each case slightly ahead of the m/z 44 peak of the sample. After the first CH4 reference peak115 there is a large m/z 28 signal from N2 that was released from our CH4 trap before the cryofocus was cooled. However, as117 presented in Fig. 2(b), residual N2, N2O (~2080 s), CO2 (~2210 s) and other contaminants are well separated from119 the CH4-derived m/z 44 sample peak, implying no interference of other gases in our δ13CH4 quantification.
CH₄ and synthetic air references

The CH₄ reference gas (99.9995 vol.-% purity; Air Liquide) allows us to test the performance of the combustion process rapidly, omitting the time-consuming CH₄ pre-concentration steps. This internal reference generates a peak similar in size and shape to a sample peak and therefore enables us to correct for effects that appear in the low-flow part of our system (see Instrumentation, Fig. 1). The CH₄ insertion consists of a 1/16" T-piece (Swagelok) where CH₄ enters a He stream from a mass flow controller (Analyt-MTC, Müllheim, Germany) so that a mixing ratio of roughly 1500 ppm CH₄ in He is achieved. By opening a pneumatic on/off valve about 7 nL CH₄ per second leaks into the GC flow via a 25 μm i.d. fused-silica capillary. In addition to the CH₄ reference injections in each sample acquisition, we usually measured six consecutive injections of CH₄ reference daily to determine the trends of the low-flow part of the system (see Measurement procedures).

In order to check long-term fractionation trends of the whole system we routinely admitted 20 mL STP synthetic air (with 1 ppm CH₄ (99.995 vol.-% purity), 250 ppm ISO-TOP CO₂ and 250 ppb N₂O (99.999 vol.-% purity); Air Liquide) from the loop on valve V1 (see Fig. 1) and analysed the δ¹³CH₄ using the ice sample measurement procedure. The time series of CH₄ reference and synthetic air reference measurements (Fig. 3) follow the same trend. The spline fits generated from these measurements run in parallel. Starting in August 2007 there is, however, a constant shift caused by changes in the overall system as explained in the following subsection. The correlation coefficients of the splines are 0.92 and 0.85 prior to and after August 2007, respectively. This implies that most of this systematic long-term variation is caused by the low-flow part of our system and we can be confident that the high-flow part causes only minor isotopic changes. From the CH₄ reference measurement time series we generated a spline curve to correct for this systematic error caused by the combustion process, as shown in Fig. 3. Methane reference, air reference, and ice sample measurements were corrected using this curve. This spline correction (in contrast to a day-to-day correction) allows us to remove the long-term systematic error without introducing the stochastic measurement error affecting each individual CH₄.
reference value. Table 1 shows the standard deviations (SDs) of the CH4 and air references before and after the trend correction.

**Neumayer air as absolute reference**

Since a CH4 reference introduced into the GC system cannot correct for any isotope effects that may occur during the extraction and pre-concentration of methane from an air sample, we used a conventionally calibrated air sample that was introduced via the sample loop to determine the accuracy of our method. The air used, obtained from the German Antarctic station Neumayer, has a δ13CH4 of −46.97% versus VPDB (1σ = 0.04, n = 2) determined by off-line sample preparation and dual-inlet IRMS on a MAT 252 mass spectrometer (ThermoFinnigan) at the Institut für Umweltpsychik, Heidelberg. Calibration of the Heidelberg δ13CH4 measurements is performed using pure CO2 IAEA Standard Reference Materials (RM 8562: δ13C = −3.72‰, RM 8564: δ13C = −10.45‰, RM 8563: δ13C = −41.59‰). The absolute agreement of the Heidelberg δ13CH4 measurements on the VPDB CO2 scale is estimated to be better than ±0.1‰.

An intercomparison with three air samples from the southern hemisphere between Heidelberg and NIWA (National Institute of Water and Atmospheric Research, Wellington, New Zealand) yielded a difference NIWA-Heidelberg δ13CH4 = 0.04‰ (1σ = 0.04‰). Extracting the Neumayer air standard directly from the sample loop led to a δ13C value of −46.78‰ (1σ = 0.10‰, n = 5), i.e. 0.19‰ more enriched in 13C. Due to the high reproducibility of this value we corrected all our samples by this offset, representing the net fractionation occurring in our whole system. Parts of our system had to be rebuilt after the detection of a leak. This led to a shift in the isotope values of the trend-corrected synthetic air measurements, as can be seen from Fig. 4. This means that

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Peak area (nAs)</th>
<th>SD δ13C-VTDB (%) uncorrected</th>
<th>Shot noise</th>
<th>SD after CH4 reference correction</th>
<th>SD after Neumayer correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2 working standard</td>
<td>92</td>
<td>0.02</td>
<td>0.02</td>
<td>−49.35</td>
<td>0.06</td>
</tr>
<tr>
<td>CH4 reference</td>
<td>12</td>
<td>0.11</td>
<td>0.05</td>
<td>−40.27</td>
<td>0.06</td>
</tr>
<tr>
<td>Air reference</td>
<td>10</td>
<td>0.13</td>
<td>0.05</td>
<td>−40.55</td>
<td>0.10</td>
</tr>
<tr>
<td>Air reference through melt-water</td>
<td>11</td>
<td>0.19</td>
<td>0.05</td>
<td>−40.73</td>
<td>0.15</td>
</tr>
<tr>
<td>Neumayer air standard</td>
<td>13</td>
<td>0.10</td>
<td>0.05</td>
<td>−46.78</td>
<td>0.10</td>
</tr>
<tr>
<td>B27, Greenland</td>
<td>8</td>
<td>0.13</td>
<td>0.06</td>
<td>−49.04</td>
<td>0.13</td>
</tr>
<tr>
<td>B37, Antarctica</td>
<td>6</td>
<td>0.13</td>
<td>0.07</td>
<td>−47.26</td>
<td>0.12</td>
</tr>
<tr>
<td>EPICA DML, Antarctica</td>
<td>4–7</td>
<td>0.09</td>
<td>0.06</td>
<td>−47.57</td>
<td>0.09</td>
</tr>
</tbody>
</table>

*Two replicates were measured in five depth intervals.
we assume a new net fractionation of 0.36% for sample measurements after August 2007. Two measurements of Neumayer air confirmed this new offset with a mean value of 

−46.47%. This is 0.50% more enriched than the approved value in line, within the error limits, with the offset of 0.37% that was determined by 82 measurements of synthetic air with a SD of 0.08%. In the following we corrected all samples after August 2007 by −0.37%.

Estimation of loss and contamination processes

By comparing measured and expected peak areas of air samples admitted to our system, loss and contamination processes can be estimated. The mean and SD of peak areas from long-term air reference measurements (20 mL (STP), 1000 ppb CH4) is 10.42 ± 0.83 nAs (equivalent to 80 ppb CH4) but this mainly reflects changes in the combustion process. Accordingly, for replicate measurements within single days, the SD was only 0.05 nAs (5 ppb CH4). A better indication for the small loss and contamination is provided by the introduction of 10–40 mL (STP) of reference air within single days which gave linear regression coefficients (R²) of 0.99 to 1 between measured and expected peak areas with extrapolated blank areas of only −0.06 nAs (6 ppb CH4) with a SD of 0.06 nAs. In addition, the introduction of gas mixtures with higher (3000 ppb) or lower methane mixing ratios (500 ppb) in N₂ or hydrocarbon-free air resulted in peak areas and isotope values statistically indistinguishable from the expected values, implying negligible influence of loss and contamination. These findings were confirmed by system blank measurements with peak areas of 0.06 nAs with an SD of 0.005 nAs which is equal to 5–7 ppb CH4. If one assumes the blank signal to be contamination from laboratory air, the isotopic effect can be calculated using a mass balance. With a broad δ13CH₄ range of −40 to −50% of our laboratory air (measured isotope values range only from −43.3 to −44.5%) this contamination would shift the measured isotope values of the air references by only 0.01 to −0.06% and the Neumayer air by only 0.03 to −0.02%. The effect on ice core sample values would be somewhat higher due to the lower methane mixing ratios, resulting in shifts of 0.02 to −0.18% for a sample with 350 ppb methane and −41% and of 0.06 to −0.03% for samples with 750 ppb methane and −47%. These variations are smaller than our specified measurement uncertainty and also one order of magnitude smaller than the observed variations in ice cores. Accordingly, any potential loss or contamination of CH₄ in the GC/C/IRMS system does not significantly affect our results.

Ice core samples

Ice sample measurements are additionally susceptible to contamination from gas leaks in the extraction vessel or gas desorption from sample vessel walls as well as isotope

Figure 4. Synthetic airQ1 reference measurements after the trend correction with the spline correction curve from CH₄ reference measurements (Fig. 3). The dashed line is the assigned true value according to the offset correction determined by the Neumayer air measurements.
fractionation due to incomplete extraction of CH₄. Blank measurements bypassing the sample vessel demonstrated a low contamination level, resulting in CH₄ peak areas below 1% of average sample peak areas which can be neglected for isotope measurements (see previous section). However, peak areas equivalent to 1–5% of sample peak areas were obtained from blank measurements including the dry and previously evacuated sample vessel. Depending on the isotope value of the contamination this may shift the isotope values of ice samples. Blank measurements are difficult to interpret because the pressure in a dry evacuated vessel is several orders of magnitude lower than during a sample measurement. In particular, the lack of water vapour in such a dry blank measurement probably leads to a higher amount of CH₄ remaining on the vessel wall after evacuation and this can affect the δ²CH₄ measurement. A clean gas-free ice could be used in a blank test but is very difficult to produce, so alternative tests for the extraction method had to be applied. Air reference measurements through completely degassed water in the sample vessel showed no deviation in peak size and isotope value, implying that the blank of the system including a wet sample vessel is not elevated compared with the direct sample loop injections.

In addition, the extraction efficiency represents a potential source of uncertainty. We therefore routinely introduced an air reference that was bubbled through the melt-water of the preceding ice sample. Since the sample vessel remains at about 2 bar overpressure after melting the ice, atmospheric contamination can be ruled out. Therefore, the CH₄ peak area and isotope value of these air reference measurements may only be influenced by remnant sample gas dissolved in the liquid or desorbing from vessel and tubing walls. The CH₄ peak areas from air references extracted directly after the ice sample were 6 ± 2% larger and 0.17 ± 0.16‰ more depleted than air reference measurements bypassing the melt-water. The depletion of air reference measurements through the melt-water of an extracted ice sample correlates significantly (correlation coefficient R = 0.48, n = 35) with the isotope value of that preceding sample. Based on an isotopic mass balance calculation assuming complete extraction of air reference together with the remaining sample gas we calculated an extraction efficiency of 95 ± 5%. Repeated extractions of air reference gas through the same melt-water produced declining depletion for the first two or three measurements. The following extractions were undistinguishable from air references without melt-water, i.e. the extraction process itself; without memory effect of the preceding sample causes no systematic fractionation. For ice sample measurements incomplete extraction may lead to a fractionation effect from solution of CH₄ in the melt-water. However, assuming equilibrium conditions the maximal isotopic effect was calculated using a Rayleigh distillation model described by Schaefer 31 and the fractionation coefficients given in Knox et al. 32 to be only −0.20‰ for an extraction efficiency of 90%. In order to quantify all possible variable influences on the isotope value of ice samples, replicate measurements of ice core samples were used. For this purposes we used three ice cores.

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(i) The B37 core was drilled in Antarctica at Kohnen station (75°00'0S, 00°04'E) close to the European Project for Ice Coring in Antarctica (EPICA) deep ice core drill site in Dronning Maud Land (DML). From the depth interval 121–121.6 m, seven samples were taken for reproducibility measurements. The air enclosed in the ice is subject to diffusion in the firn column and encountered slow occlusion of ice bubbles over an extended time period. This leads to a width of the gas age distribution in an ice core sample of 59 ± 5 years 33 for this site. Accordingly, the mixing ratio and isotope value of the trapped methane can be considered to be virtually constant for a depth interval of 1 m at the recent accumulation rate of 64 mm water equivalent per year. The mean gas age of these samples was calculated to be 420 years BP 76 (1530) using the EDM1.1 timescale 34 and assuming a gas age/ice age difference of 825 years. 37

(ii) A series of EPICA DML samples was measured over the entire last glacial/interglacial transition and was presented in Fischer et al. 36 The reproducibility of these samples was determined by analysing replicates at selected depth intervals.

(iii) The B27 core from Greenland (76°39’N, 46°29’W), from which we used two samples from 97 and 101 m depth, has a smaller gas age spread of about ±20 years (J. Frei, personal communication) due to the shallower and faster bubble close-off at this site than in the DML cores. Using high-resolution γ-density measurements to determine the depth of bubble close-off and a model for the firm diffusion and bubble enclosure process, 35 the mean age for the B27 gas samples was determined to be 119 years BP (1831).

Table 1 summarises the reproducibilities of our reference and standard gases and some first ice core measurements. All δ¹³C values except for the CO₂ working standard were corrected with the CH₄ reference correction curve (see Fig. 3) and then shifted by −0.19‰ (before August 2007) or −0.37‰ (after August 2007), according to the Neumayer air reference measurements.

The shot noise limit (σₖ) was described by Merritt and Hayes 36 as an absolute measure of system performance. By defining the ion counting statistics as the only source of noise, the standard deviation (SD) is given by:

\[
\sigma^2 = 2 \times 10^9 (1 + R)^2 q/44 i R
\]

with the characteristic ion current ratio R of m/z 45/44 (approximately R = 0.011), 44 the m/z 44 current, t the integration time and q, the elementary charge (1.6 × 10⁻¹⁹C). If the sample and standard signal areas are equal, for the integrated m/z 44 signal (A (nAs)) Eqn. (1) becomes:

\[
\sigma^2 = 0.02973/44 A
\]

In Table 1 the shot noise limits were calculated according to the given signal areas. The high reproducibility of our measurements in the range of only 1 to 2.5 times the shot noise (see Table 1) implies minor influences of blanks and/or fractionation during the gas extraction on our measurement precision. The highest measured SD was 0.25‰ for a double
replicate sample from the EDML core with a CH$_4$ concentration of about 380 ppb. We excluded a few measurements that were identified as outliers in the EDML $\delta^{13}$CH$_4$ record when the air reference introduced into and extracted from the melt-water of the previously extracted ice sample also differed by more than 0.4% from its expected value. Inspection of the system showed that these anomalous measurements occurred when liquid water from previous use was found in the tubing and valves from and to the extraction vessel. How this moisture influenced sample and subsequent air reference measurements remained unclear, but this was also observed by Schaefer and Whiticar$^{24}$ to influence $\delta^{13}$CH$_4$.\textsuperscript{10} Though the $\delta^{13}$CH$_4$ record determined a mean $\delta^{13}$CH$_4$ value of $-48.00\pm 0.12$% (1$\sigma$, n = 7) from our Antarctic ice core (B37), i.e. equal within the error limits compared with the Antarctic DSS core for the year 1536 ($-47.78\pm 0.13$) and for the year 1507 ($-48.08\pm 0.17$). In addition, the values for the year 1831 (±30 years) from the Greenland B27 core are equal within the error limits with the values from the Antarctic DSS core. The mean $\delta^{13}$CH$_4$ of the B27 ice sample is $-49.54\pm 0.13$% (1$\sigma$ = 0.13) and the closest value from the Antarctic ice core is $-49.40\pm 0.17$% (1$\sigma$ = 0.10, 1830). Especially, the excellent agreement between both Antarctic ice cores for the given time interval strongly supports the accuracy of our $\delta^{13}$CH$_4$ measurements and again points to minor systematic effects due to sample loss or contamination.

### SUMMARY AND CONCLUSIONS

We have demonstrated that our highly automated GC/C/IRMS system is an excellent technique to measure $\delta^{13}$CH$_4$ in multi-parameter ice core studies. Ice core samples from glacial and interglacial times with a gas content of about 20 mL STP and a methane mixing ratio down to 350 ppb can be measured with a precision of better than 0.3%. For methane mixing ratios of about 700 ppb a precision of 0.13% is reached.

With the aid of standard and reference gases we can ensure a trend correction for our laboratory procedure and are able to monitor the performance of the different parts of our system. In particular, the use of a methane reference gas allows us to monitor and correct for changing conditions in the low-flow part of the system comprising the combustion oven and the gas chromatograph which may significantly influence $\delta^{13}$C.
The absolute $\delta^{13}$CH$_4$ value is established by comparison with a known air reference which can be measured very similarly to an ice sample and has a $\delta^{13}$CH$_4$ value of modern atmospheric methane. Calibration to the VPDB scale is therefore based on one point and should be applicable to $\delta^{13}$CH$_4$ values around $-47\%$. This calibration is verified by measuring older atmospheric methane samples from $\sim$1530 and $\sim$1830 which are known to be more depleted in $^{13}$C relative to today. Accordingly, the accuracy of our data is confirmed by the very good match to the data presented by Ferratti et al.\textsuperscript{23} In the future, however, a second air standard will be introduced to cover a larger range of possible atmospheric $\delta^{13}$CH$_4$ values.

This very low uncertainty achieved in our analysis allows quantitative estimates of e.g. biomass burning and boreal wetland emission for the glacial/interglacial transition derived from the EDML core.\textsuperscript{30} Further enhancement of measurement precision would not permit us to improve the quantification of source and sink processes in the methane budget significantly but, for the determination of the interhemispheric gradient in $\delta^{13}$CH$_4$, higher precision and accuracy in the range of $<0.1\%$ are needed.

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