**COMPOUND-SPECIFIC RADIOCARBON ANALYSIS OF ATMOSPHERIC METHANE: A NEW PRECONCENTRATION AND PURIFICATION SETUP**

**C. Espic1,2, M. Liechti1, M. Battaglia1,2, D. Paul3, T. Röckmann3, S. Szidat1,2\***

1Departement of Chemistry and Biochemistry, University of Bern, Bern, Switzerland.

2Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland.

3Institute for Marine and Atmospheric Research (IMAU), Utrecht University, Utrecht, the Netherlands.

\*Corresponding author. Email: szidat@dcb.unibe.ch.

# appendix

The data presented here refer to the individual measurements used to assess the averaged performance parameters of the MPPS, which are summarized in Table 1.

## Constant contamination



Figure S1 Constant contamination of the MPPS (procedural blank). Black open squares: measured F14C values with 1σ uncertainties. Red lines: Statistical “drift” model, including 1σ confidence bands (dashed red lines). Blue crosses: corrected F14C values, using the drift model.

## Cross contamination

The contamination from the previous sample (φ), deduced from the successive 14C measurements of modern and fossil methane samples processed through the MPPS, is evaluated using a simple mass balance equation:

With (ms, Rs), (mb1, Rb1) and (mb2, Rb2) the carbon masses and F14C values of the modern sample, the first blank and the second blank, respectively.

Table S1 Determination of the MPPS cross contamination by successive preconcentration, purification and 14C measurement of modern and fossil methane samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample code | Sample type | Material | 14C measured (F14C) | Mass (µg C) |
| BE-9339.1.1 | Modern CH4 | Modern methane standard | 1.016 ± 0.008 | 59.2 |
| BE-9340.1.1 | Fossil CH4 | Standard gas mixture | 0.022 ± 0.004 | 19.5 |
| BE-9341.1.1 | Fossil CH4 | Standard gas mixture | 0.011 ± 0.004 | 18.7 |
| BE-9342.1.1 | Modern CH4 | Modern methane standard | 1.010 ± 0.008 | 59.2 |
| BE-9343.1.1 | Fossil CH4 | Standard gas mixture | 0.022 ± 0.004 | 20.3 |
| BE-9344.1.1 | Fossil CH4 | Standard gas mixture | 0.011 ± 0.003 | 18.7 |

## Repeatability and accuracy

Table S2 System repeatability and accuracy for the 14C measurements of atmospheric methane samples, which have been preconcentrated and purified using the MPPS.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample code | Sample type | Material | 14C measured (F14C) | Mass (µg C) |
| BE-9307.1.1 | Atmospheric CH4 | Pressurized air sample | 1.544 ± 0.014 | 66.6 |
| BE-9308.1.1 | Atmospheric CH4 | Pressurized air sample | 1.535 ± 0.012 | 70.5 |
| BE-9345.1.1 | Atmospheric CH4 | Pressurized air sample | 1.538 ± 0.012 | 69.3 |
| BE-9346.1.1 | Atmospheric CH4 | Pressurized air sample | 1.547 ± 0.011 | 70.5 |
| BE-9347.1.1 | Atmospheric CH4 | Pressurized air sample | 1.522 ± 0.011 | 70.5 |
| BE-9348.1.1 | Atmospheric CH4 | Pressurized air sample | 1.549 ± 0.011 | 71.7 |
| BE-9322.1.1 | Modern CH4 | Modern methane standard | 1.011 ± 0.008 | 64.7 |
| BE-9323.1.1 | Modern CH4 | Modern methane standard | 1.016 ± 0.008 | 64.7 |
| BE-9324.1.1 | Modern CH4 | Modern methane standard | 1.027 ± 0.008 | 63.9 |

## Yield

Table S3 Methane yield of individual air samples preconcentrated and purified using the MPPS. The samples were collected in 200 L Al bags at the Beromünster tall tower, Switzerland. During each sample collection, the CH4 mole fraction was measured with a PICARRO gas analyzer and used to infer the theoretical amount of CH4 injected into the MPPS. The CH4 yield of individual samples is finally calculated by comparing the amount of CH4-derived CO2 recovered into a glass ampoule to the original amount of CH4 processed through the setup.

|  |  |  |  |
| --- | --- | --- | --- |
| Sampling date | Original CH4 (µg C) | CH4-derived CO2 (µg C) | CH4 yield (%) |
| 07/26/2018 | 63.8 | 65.8 | 103.5 |
| 08/08/2018 | 63.9 | 63.9 | 100.3 |
| 08/23/2018 | 65.3 | 65.8 | 101.0 |
| 09/06/2018 | 67.0 | 66.6 | 99.8 |
| 09/20/2018 | 65.6 | 65.4 | 100.0 |
| 10/04/2018 | 66.4 | 67.8 | 102.5 |
| 10/18/2018 | 69.2 | 69.3 | 100.5 |
| 11/01/2018 | 64.4 | 65.8 | 102.5 |
| 11/15/2018 | 68.2 | 67.8 | 99.7 |
| 11/29/2018 | 63.0 | 64.7 | 103.1 |
| 12/27/2018 | 62.5 | 61.9 | 99.3 |
| 01/10/2019 | 66.4 | 66.6 | 100.6 |
| 02/07/2019 | 63.8 | 64.7 | 101.8 |
| 02/21/2019 | 62.8 | 63.9 | 102.2 |