

Supplementary information to: A combustion setup to precisely reference $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotope ratios of pure CH_4 to produce isotope reference gases of $\delta^{13}\text{C}-\text{CH}_4$ in synthetic air

Sperlich, P.^{1,*,**}, Guillevic, M.^{1,2,**}, Buizert, C.¹, Jenk, T.M.¹, Sapart, C.J.³, Schaefer, H.⁴, Popp, T.J.¹, and Blunier, T.¹

¹Centre for Ice and Climate, University of Copenhagen (CIC), Copenhagen, Denmark

²Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Gif sur Yvette, France

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

⁴National Institute for Water and Atmospheric Research (NIWA), Wellington, New Zealand

* now at: Max-Planck-Institute for Biogeochemistry (MPI-BGC), Jena, Germany

** These authors contributed equally to this work.

1 Purity of biogenic CH_4

1.1 Impurity quantification in biogenic CH_4

The biogenic CH_4 was sampled at a biogas power plant in northern Germany that uses agricultural crops to produce CH_4 which is pumped into the local gas grid. This requires a high purity level of the CH_4 which is achieved by coupling the biogas plant to an industrial purification reactor that increases the CH_4 content to about 95% by removing H_2S , H_2O and CO_2 . The remaining 5% comprise mostly N_2 , O_2 , CO_2 and traces of H_2S . For our purposes, the biogenic CH_4 needed further purification. Non- CH_4 carbon containing molecules that could impact on the isotope measurements were removed. H_2S , which possibly degrades the analytical systems was furthermore reduced.

To assess the composition and purity of the gases, mass abundance scans were performed by dual-inlet IRMS analysis for high purity fossil CH_4 , biogenic CH_4 as well as purified biogenic CH_4 . The mass abundance scans were then compared to analyze their content of non- CH_4 components. In general, mass abundance scans of a pure CH_4 show diverse spectra of masses because certain fractions of CH_4 molecules decompose and/or re-combine to secondary molecules within the ion source, as a result of the electron bombardment (Brunnée and Voshage, 1964). Ions producing these spectra can therefore be an artefact, suggesting the abundance of non existing gas species in the sample gas. Converting mass abundances to gas compositions therefore introduces an error. The mass abundance scans are thus not the most accurate method to quantify impurities within a CH_4 gas. However, we will show that comparing mass abundance scans of CH_4 with different purity level allows for a sufficient estimate.

Correspondence to: P. Sperlich
(psperl@bgc-jena.mpg.de)

1.2 Carbon containing impurities

The performed mass abundance scans were evaluated by ISODAT 3.0, the software used to control the mass spectrometer. The results for the purified biogenic CH_4 are shown in Table 1 and Figure 1, indicating very small signals on m/z 26, 29, 30 and 44 which are caused by non- CH_4 hydrocarbon ions. We allocated molecules with their chemical formulas to the peaks: C_2H_2^+ , C_2H_5^+ , C_2H_6^+ , C_3H_8^+ and CO_2^+ , thus containing one to three carbon atoms per molecule.

We assume that mass abundance signals on m/z 12, 13, 14, 15, 16 and 17 are caused by CH_4 -derived ions containing one carbon and variable numbers of hydrogen atoms. The sum of peak areas from mass abundances that derive from CH_4 molecules was compared to the sum of peak areas from mass abundances that possibly results of non- CH_4 hydrocarbons (m/z 26, 29, 30, 44) which were weighted for the maximum number of carbon atoms. This is based on the assumption that the entire signal on m/z 26, 29, 30 and 44 is derived from hydrocarbons and that all ions causing the peak on m/z 44 comprised of C_3H_8^+ with three carbon atoms instead of CO_2^+ . This is important because one molecule of C_3H_8 produces 3 molecules of CO_2 in the combusted sample. Therefore, one molecule of C_3H_8^+ contributes three times stronger to the signal on m/z 44 than one molecule of CO_2 . We also assume that non- CH_4 hydrocarbons are stable in the ionization chamber and do not contribute to signals m/z 12 to m/z 17.

In this most conservative scenario, a maximum of about 0.55% of the carbon that was detected in the ion source resulted from an ion containing more than one carbon atom. A similar analysis of our high purity fossil CH_4 reveals that about 0.67% of the detected ions were derived from ions containing at least two carbon atoms. The company providing the high purity fossil CH_4 specifies the purity level of its CH_4 N45 with 99.995% with a mixing ratio of non- CH_4 hydrocarbons ≤ 20 ppmv. Therefore, we conclude that

the scan procedure over-estimates the content of non-CH₄ hydrocarbons by two orders of magnitude due to processes inside the ion source. Based on the comparison of the mass abundance scans from purified biogenic CH₄ and fossil CH₄, we can assume a similar purity level.

A simple mass balance calculation based on the assumption of a 99.995 % purity level shows, that the average $\delta^{13}\text{C}$ isotope ratio of the impurities would have to be higher than 744 ‰ or lower than -856 ‰ to affect the determined carbon isotope ratios of the biogenic CH₄ by more than the given uncertainty. Because these extreme carbon isotope ratios are highly unlikely in naturally occurring gases, we conclude that our biogenic CH₄ is sufficiently purified from non-CH₄ hydrocarbons.

1.3 H₂S

The low H₂S content of both purified and unpurified biogenic CH₄ samples could only be detected by the most sensitive Faraday cup detector of the IRMS. Because this detector was saturated for the very abundant CH₄ ions, we related the H₂S signal on m/z 34 to the O₂ signal on m/z 32 which is constant in both the purified and un-purified biogenic CH₄. The purification step decreased the H₂S by 75%. However, this is at a very low concentration levels where the evaluation of the H₂S peaks is unreliable. Given that H₂S was reduced to prevent degradation of the analytical system and is not expected to alter the measurements on CH₄ isotope ratios we consider the observed reduction as sufficient.

2 Effect of system leakage

2.1 Monitoring Argon in the sample

Mass abundance scans using dual-inlet IRMS were performed on each combusted CH₄ sample. Any leakage of laboratory air into the offline combustion setup would increase the relative abundance of Argon (Ar) compared to the mass abundance of CO₂. We interpreted the ratio of the peak heights of Ar (m/z 40) to CO₂ (m/z 44) as indicator for laboratory air leakage into the offline combustion setup during a combustion process. To increase the sensitivity of this comparison, we used the Ar signal of a Faraday cup with a 100 times stronger. The resulting ratio is 0.006 +/- 0.0003 for the pure CO₂-40339. We found the same ratio in the combusted samples stemming from fossil CH₄. We found a ratio of 0.03 in the biogenic CH₄ which is higher due to the containing 5% of atmospheric air. We found these ratios to be stable for the respective CH₄ type. These measurements give us confidence that the measurements were not affected by leakage into the system during the aliquotation, the combustion or the sample transfer into the dual-inlet IRMS.

2.2 Sensitivity test for laboratory-air leakage

The effect of an undetected CO₂ blank can be estimated with the following sensitivity test. The offline combustion system was evacuated, closed off and tested for leaks in over-night test prior to each measurement. A sample would only be introduced if the pressure increase overnight stayed below the detection limit of our piezoelectric pressure gauge (1 mbar precision). We give a conservative estimate of the maximum effect an undetected leak would have as blank contribution. We assume a pressure increase of 1 mbar in the system of ~ 600 ml volume, which corresponds to a leakage of 0.6 ml. If we conservatively assume 1 part per thousand of the leakage is CO₂ with a $\delta^{13}\text{C}$ isotope ratio of -7 ‰ a small biogenic CH₄ sample with a $\delta^{13}\text{C}$ of -56 ‰ would be most affected. A mass balance calculation shows that the maximum possible blank contribution would affect a 120 ml sample of biogenic CH₄ with -56 ‰ by 0.0002 ‰ which is by two orders of magnitude lower than the precision of our method. We conclude that any undetected potential blank has no significant effect on our results. The blank contribution is most likely even lower because most of the combusted samples were about 50% larger than anticipated in the calculation. Also, the lab air contains more depleted CO₂ from human breath which is more depleted in ¹³C. Any additional CH₄ leakage would furthermore reduce this blank effect due to its lower isotopic leverage.

References

References

Brunnée, C. and Voshage, H.: Massenspektrometrie, Teil 1, Verlag Karl Thiernig KG, München, 12 edn., 1964.

Table 1. Table S1: Mass abundances in the purified biogenic CH₄ as evaluated by ISODAT 3.0. The evaluation parameters were extremely tuned to be able to capture very small abundances and therefore compromising the accuracy of the quantification. Hence, peak numbers 8 and 9 show opposing sizes in peak area and height. The CH₄-derived ions were identified following Brunnée and Voshage (1964).

number of identified peak	magnetic field [steps]	m/z	ion	peak height [mV]	peak area [mV * steps]
1	5385	12	C ⁺	648	1964
2	5665	13	CH ⁺	1842	5837
3	5935	14	CH ₂ ⁺	3855	12182
4	6190	15	CH ₃ ⁺	22075	74717
5	6450	16	CH ₄ ⁺	25370	78391
6	6690	17	CH ₅ ⁺ or ¹³ CH ₄ ⁺	485	1673
7	6920	18	H ₂ O ⁺	823	2760
8	7365	20	H ₂ ¹⁸ O ⁺	4	22
9	8630	26	C ₂ H ₂ ⁺	2	25
10	9020	28	N ₂ ⁺	795	3249
11	9210	29	C ₂ H ₅ ⁺	15	86
12	9400	30	C ₂ H ₆ ⁺	10	65
13	9765	32	O ₂ ⁺	221	995
14	10120	34	H ₂ S ⁺	not evaluated	not evaluated
15	11140	40	Ar ⁺	19	128
16	11795	44	C ₃ H ₈ ⁺ or CO ₂ ⁺	33	202

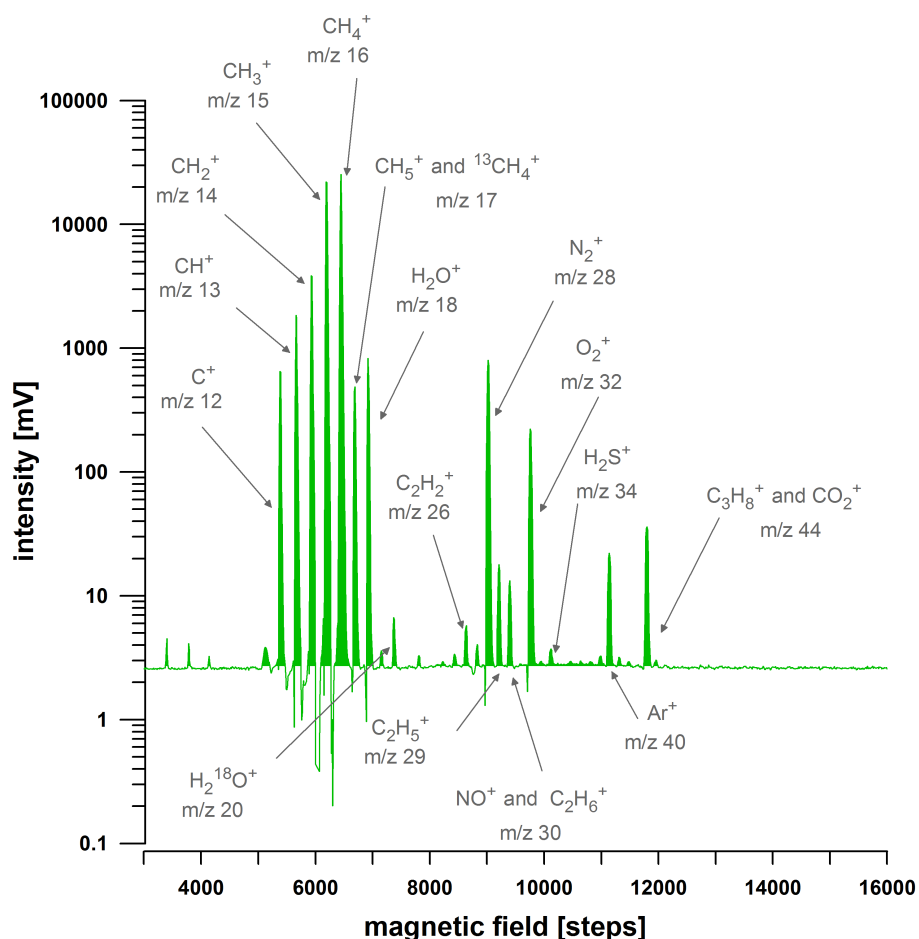


Fig. 1. Figure S1: Shown is a scan of mass abundances between m/z 5 and m/z 60 when purified bio-methane is introduced into the ion source of the dual inlet IRMS. The y-axis is set to logarithmic scale to better visualize the low abundances. Chemical formulas and m/z ratios identify the respective peaks, indicated by the arrows.