

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

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## 1 Purity of biogenic $\text{CH}_4$

### 1.1 Impurity quantification in biogenic $\text{CH}_4$

The biogenic  $\text{CH}_4$  was sampled at a biogas power plant in northern Germany that uses agricultural crops to produce  $\text{CH}_4$  which is pumped into the local gas grid. This requires a high purity level of the  $\text{CH}_4$  which is achieved by coupling the biogas plant to an industrial purification reactor that increases the  $\text{CH}_4$  content to about 95% by removing  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The remaining 5% comprise mostly  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and traces of  $\text{H}_2\text{S}$ . For our purposes, the biogenic  $\text{CH}_4$  needed further purification. Non- $\text{CH}_4$  carbon containing molecules that could impact on the isotope measurements were removed.  $\text{H}_2\text{S}$ , 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  $\text{CH}_4$ , biogenic  $\text{CH}_4$  as well as purified biogenic  $\text{CH}_4$ . The mass abundance scans were then compared to analyze their content of non- $\text{CH}_4$  components. In general, mass abundance scans of a pure  $\text{CH}_4$  show diverse spectra of masses because certain fractions of  $\text{CH}_4$  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  $\text{CH}_4$  gas. However, we will show that comparing mass abundance scans of  $\text{CH}_4$  with different purity level allows for a sufficient estimate.

### 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  $\text{CH}_4$  are shown in Table 1 and Figure ??, indicating very small signals on m/z 26, 29, 30 and 44 which are caused by non- $\text{CH}_4$  hydrocarbon ions. We allocated molecules with their chemical formulas to the peaks:  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_2\text{H}_5^+$ ,  $\text{C}_2\text{H}_6^+$ ,  $\text{C}_3\text{H}_8^+$  and  $\text{CO}_2^+$ , 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  $\text{CH}_4$ -derived ions containing one carbon and variable numbers of hydrogen atoms. The sum of peak areas from mass abundances that derive from  $\text{CH}_4$  molecules was compared to the sum of peak areas from mass abundances that possibly results of non- $\text{CH}_4$  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  $\text{C}_3\text{H}_8^+$  with three carbon atoms instead of  $\text{CO}_2^+$ . This is important because one molecule of  $\text{C}_3\text{H}_8$  produces 3 molecules of  $\text{CO}_2$  in the combusted sample. Therefore, one molecule of  $\text{C}_3\text{H}_8^+$  contributes three times stronger to the signal on m/z 44 than one molecule of  $\text{CO}_2$ . We also assume that non- $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  specifies the purity level of its  $\text{CH}_4$  N45 with 99.995% with a mixing ratio of non- $\text{CH}_4$  hydrocarbons  $\leq 20$  ppmv. Therefore, we conclude that

the scan procedure over-estimates the content of non-CH<sub>4</sub> 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 CH<sub>4</sub> and fossil CH<sub>4</sub>, 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 CH<sub>4</sub> by more than the given uncertainty. Because these extreme carbon isotope ratios are highly unlikely in naturally occurring gases, we conclude that our biogenic CH<sub>4</sub> is sufficiently purified from non-CH<sub>4</sub> hydrocarbons.

### 1.3 H<sub>2</sub>S

The low H<sub>2</sub>S content of both purified and unpurified biogenic CH<sub>4</sub> samples could only be detected by the most sensitive Faraday cup detector of the IRMS. Because this detector was saturated for the very abundant CH<sub>4</sub> ions, we related the H<sub>2</sub>S signal on m/z 34 to the O<sub>2</sub> signal on m/z 32 which is constant in both the purified and un-purified biogenic CH<sub>4</sub>. The purification step decreased the H<sub>2</sub>S by 75%. However, this is at a very low concentration levels where the evaluation of the H<sub>2</sub>S peaks is unreliable. Given that H<sub>2</sub>S was reduced to prevent degradation of the analytical system and is not expected to alter the measurements on CH<sub>4</sub> 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 CH<sub>4</sub> 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 CO<sub>2</sub>. We interpreted the ratio of the peak heights of Ar (m/z 40) to CO<sub>2</sub> (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 CO<sub>2</sub>-40339. We found the same ratio in the combusted samples stemming from fossil CH<sub>4</sub>. We found a ratio of 0.03 in the biogenic CH<sub>4</sub> which is higher due to the containing 5% of atmospheric air. We found these ratios to be stable for the respective CH<sub>4</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> with a  $\delta^{13}\text{C}$  isotope ratio of -7 ‰ a small biogenic CH<sub>4</sub> 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 CH<sub>4</sub> 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 CO<sub>2</sub> from human breath which is more depleted in <sup>13</sup>C. Any additional CH<sub>4</sub> leakage would furthermore reduce this blank effect due to its lower isotopic leverage.

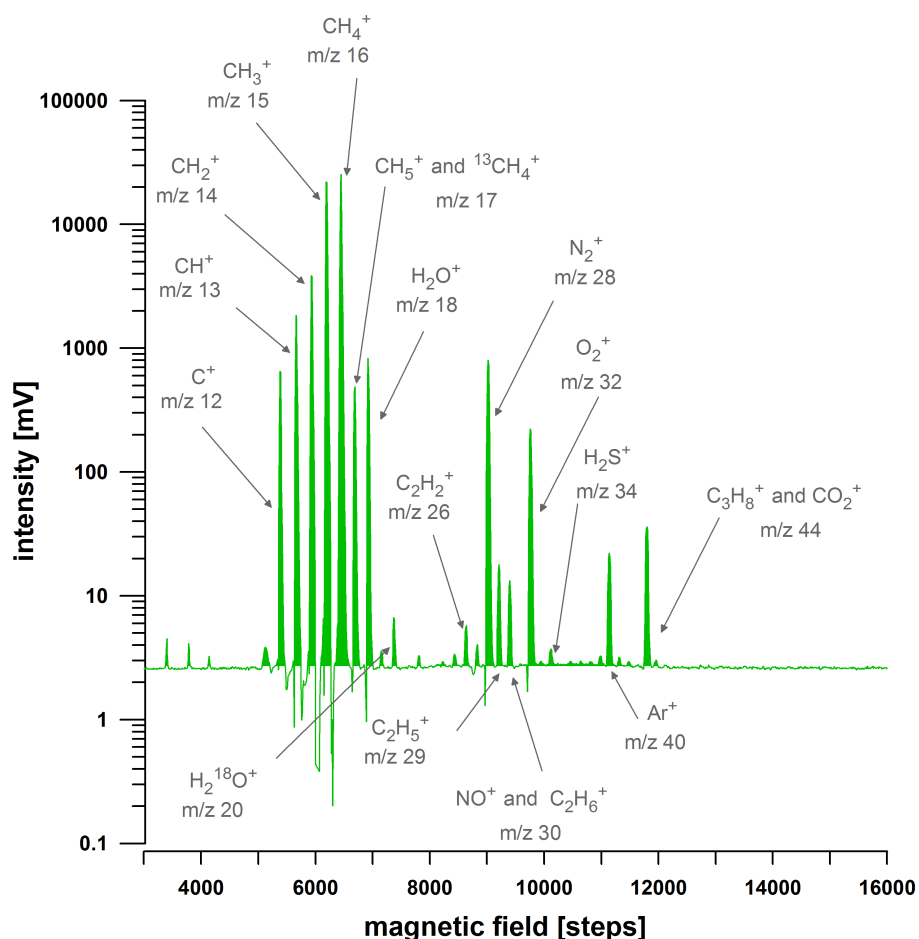
## References

### References

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

**Table 1.** Table S1: Mass abundances in the purified biogenic CH<sub>4</sub> 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 CH<sub>4</sub>-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 <sup>+</sup>   | 648              | 1964                   |
| 2                         | 5665                   | 13  | CH <sup>+</sup>  | 1842             | 5837                   |
| 3                         | 5935                   | 14  | CH <sub>2</sub> <sup>+</sup>   | 3855             | 12182                  |
| 4                         | 6190                   | 15  | CH <sub>3</sub> <sup>+</sup>   | 22075            | 74717                  |
| 5                         | 6450                   | 16  | CH <sub>4</sub> <sup>+</sup>   | 25370            | 78391                  |
| 6                         | 6690                   | 17  | CH <sub>5</sub> <sup>+</sup> or <sup>13</sup> CH <sub>4</sub> <sup>+</sup> | 485              | 1673                   |
| 7                         | 6920                   | 18  | H <sub>2</sub> O <sup>+</sup>  | 823              | 2760                   |
| 8                         | 7365                   | 20  | H <sub>2</sub> <sup>18</sup> O <sup>+</sup>                                | 4                | 22                     |
| 9                         | 8630                   | 26  | C <sub>2</sub> H <sub>2</sub> <sup>+</sup>                                 | 2                | 25                     |
| 10                        | 9020                   | 28  | N <sub>2</sub> <sup>+</sup>  | 795              | 3249                   |
| 11                        | 9210                   | 29  | C <sub>2</sub> H <sub>5</sub> <sup>+</sup>                                 | 15               | 86                     |
| 12                        | 9400                   | 30  | C <sub>2</sub> H <sub>6</sub> <sup>+</sup>                                 | 10               | 65                     |
| 13                        | 9765                   | 32  | O <sub>2</sub> <sup>+</sup>  | 221              | 995                    |
| 14                        | 10120                  | 34  | H <sub>2</sub> S <sup>+</sup>  | not evaluated    | not evaluated          |
| 15                        | 11140                  | 40  | Ar <sup>+</sup>  | 19               | 128                    |
| 16                        | 11795                  | 44  | C <sub>3</sub> H <sub>8</sub> <sup>+</sup> or CO <sub>2</sub> <sup>+</sup> | 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.