Calculation of methane production from manometric measurements

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1 BMP-methods

File version 2.4. This file is from the GitHub repository BMP-methods. For more information, visit BMP-methods at https://github.com/sashahafner/BMP-methods.

2 Description

This document describes calculations for manometric measurment of biogas. Two methods are commonly used and both are described here: one based on normalized CH_4 concentrations (method 1) and one that explicitly includes estimation of CH_4 in the bottle headspace (method 2). Expected results from the two methods are identical; differences are due only to error in measurement of biogas composition or headspace volume. Both methods are available through the `cumBg()` function in the biogas package [1] and through the web application OBA (https://biotransformers.shinyapps.io/oba1/) and can be easily added to, e.g., a spreadsheet template.

3 Standardization of measured gas volume

Both methods use the same approach for standardization of gas volume. Dry biogas volume in a bottle's headspace before and after venting is calculated by correcting for water vapor, temperature, and pressure. First the volume of headspace gas is converted to dry conditions at standard pressure:

$$V_{dry} = V_{headspace}(P_{meas} - P_{H_2O})/101.325\,\text{kPa} \tag{1}$$

where P_{meas} is the measured headspace pressure and P_{H_2O} the water vapor partial pressure (both in kPa). Eq. (1) is an expression of Boyle's law. The value of P_{H_2O} is assumed to be the saturation vapor pressure prior to venting, and can be calculated using, e.g., the Magnus-form equation given below (Eq. 21 in [2]):

$$P_{H_2O} = 0.61094e^{(17.625T/(243.04+T))} \quad (2)$$

where T is temperature in °C. Immediately after venting, when water vapor has been lost through venting but water evaporation has not yet led to equilibrium, it may be reasonable to assume that the mixing ratio of water is the same as it was prior to venting. Assuming saturation prior to venting and an insignificant change in temperature, this is equivalent to taking relative humidity as the ratio of post- to pre-venting absolute pressure (always < 1.0). Alternatively, it may be no less accurate to assume 100% relative humidity after venting as well, especially if more than a few minutes pass between venting and measurement of residual pressure. Althought the difference in resulting BMP estimates is not large (perhaps a few %), it is prudent to state which of these two assumptions was made when reporting BMP results.

Volume is then further standardized to 273.15 K by application of Charles's law:

$$V_{std} = V_{dry} 273.15\,\mathrm{K}/T_{meas} \quad (3)$$

where V_{std} is the standardized volume of gas within a bottle's headspace at the time of pressure measurement.

Interval biogas production is calculated as:

$$V_{biogas,i} = V_{std,pre,i} - V_{std,post,i-1} \quad (4)$$

where all V is standardized gas volume in a bottle's headspace, *pre* and *post* refer to before and after venting, respectively, i indicates the current interval and $i - 1$ the previous one.

4 Calculation of CH_4 production

4.1 Method 1

In the first method, biogas is assumed to consist of only CH_4 and CO_2 at the time of production (i.e., as produced by the microbial community) and CH_4 production is calculated from vented (removed) biogas only. This method is described in [3]. Coupled with the assumption that all gas production is biogas (Eq. 4), this provides the simplest approach for calculating CH_4 production.

First, concentrations of CH_4 and CO_2 are adjusted so they sum to 1.0:

$$x_{CH_4,n} = x_{CH_4}/(x_{CH_4} + x_{CO_2}) \quad (5)$$

where x_{CH_4} and x_{CO_2} are the measured CH_4 and CO_2 concentrations as volume (mole) fraction (possibly including a correction for water vapor–this has no effect here) and $x_{CH_4,n}$ is the normalized CH_4 volume fraction.

Methane production in an interval i is then calculated as

$$V_{CH_4,i} = x_{CH_4,n} V_{biogas,i} \tag{6}$$

Cumulative production is taken as the cumulative sum of interval values.

4.2 Method 2

Method 2 relies on fewer assumptions, but requires the true concentration of CH_4 (volume fraction) of CH_4 within the bottle headspace, with correction only for water vapor. Here, CH_4 production in an interval is determined from the change in bottle CH_4 content during an incubation interval.

$$V_{CH_4,i} = x_{CH_4,i} \cdot V_{std,pre,i} - x_{CH_4,i-1} \cdot V_{std,post,i-1} \tag{7}$$

Cumulative production is taken as the cumulative sum of interval values. Note that Eq. (7) reduces to Eq. (6) when $x_{CH_4,n} = x_{CH_4}$ and $x_{CH_4,i} = x_{CH_4,i-1}$, i.e., if all flusing gas has been removed from the bottle headspace, biogas production is indeed only CH_4 and CO_2, and biogas composition has not changed during an interval.

5 Calculation example

In the following example, CH_4 production is calculated from a single interval measurement made on a single bottle in a BMP trial. Calculations are made using both manometric calculation methods 1 and 2. Bottle headspace volume ($V_{headspace}$) was 81.3 mL and measured headspace pressure prior to venting was 101.8 kPa (gauge, or 203.1 kPa absolute). Bottle headspace temperature (T_{meas}) was assumed to be 30°C. Ambient pressure was 101.3 kPa. Measured biogas composition x_{CH_4} for the given interval was 0.656, and x_{CO_2} was 0.289. For the previous interval, x_{CH_4} was 0.587.

For both methods standardized gas volume is calculated before and after venting from Eq. (3) by correcting for water vapor, temperature, and pressure, in order to determine interval biogas production ($V_{biogas,i}$). First water vapor is calculated at the measured headspace temperature

$$P_{H_2O} = 0.61094 \cdot e^{\frac{17.625 \cdot 30^\circ C}{243.04 \cdot 30^\circ C}} = 4.237\,\mathrm{kPa}$$

Secondly, headspace volume is converted to dry conditions at standard pressure pre- and post-venting using Eq. (1).

$$V_{dry,pre} = \frac{81.3\,\mathrm{mL} \cdot (203.1\,\mathrm{kPa} - 4.237\,\mathrm{kPa})}{101.325\,\mathrm{kPa}} = 159.6\,\mathrm{mL}$$

Post headspace pressure (P_{post}) was assumed to be constant atmospheric pressure of 101.3 kPa.

$$V_{dry,post} = \frac{639\,\mathrm{mL} \cdot (101.3\,\mathrm{kPa} - 4.237\,\mathrm{kPa})}{101.325\,\mathrm{kPa}} = 77.88\,\mathrm{mL}$$

Then following Eq. (3), pre- and post-venting standardized gas volume is calculated for the current (*i*) and previous (*i-1*) intervals.

$$V_{std,pre,i} = \frac{159.6\,\text{mL} \cdot 273.15\,\text{K}}{303.15\,\text{K}} = 143.8\,\text{mL}$$

$$V_{std,post,i-1} = \frac{77.88\,\text{mL} \cdot 273.15\,\text{K}}{303.15\,\text{K}} = 70.17\,\text{mL}$$

With pre- and post-venting standardized volume, interval biogas production can be calculated from Eq. (4).

$$V_{biogas,i} = 143.8\,\text{mL} - 70.17\,\text{mL} = 73.63\,\text{mL}$$

5.1 Method 1

The mole fraction of CH_4 (x_{CH_4}, dimensionless) normalized for CH_4 and CO_2 can be calculated according Eq. (4).

$$x_{CH4,n} = \frac{0.656}{0.656 + 0.289} = 0.694$$

Then, following Eq. (6), CH_4 production in the interval is calculated.

$$V_{CH4,i} = 0.694 \cdot 73.63\,\text{mL} = 51.1\,\text{mL}$$

5.2 Method 2

CH_4 production in the interval is calculated following Eq. (7) using the true concentration of CH_4 within the bottle headspace.

References

[1] Hafner, S.D., Koch, K., Carrere, H., Astals, S., Weinrich, S., Rennuit, C. 2018 Software for biogas research: Tools for measurement and prediction of methane production. SoftwareX 7: 205-210

[2] Alduchov, O.A., Eskridge, R.E. 1996 Improved Magnus form approximation of saturation vapor pressure. Journal of Applied Meteorology 35: 601-609

[3] Richards, B.K., Cummings, R.J., White, T.E., Jewell, W.J. 1991 Methods for kinetic-analysis of methane fermentation in high solids biomass digesters. Biomass and Bioenergy 1: 65-73