

# Calculation of methane production from volumetric measurements

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## 1 BMP-methods

File version 1.4. 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 volumetric measurement of biogas. As with manometric methods, two methods are commonly used and both are described here: one based on normalized CH<sub>4</sub> concentrations (method 1) and one that explicitly includes estimation of CH<sub>4</sub> 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 measured gas volume (e.g., in a syringe or hanging water column) is converted to dry conditions at standard pressure:

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

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, 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  $^{\circ}\text{C}$ . Volume is then further standardized to 273.15 K by application of Charles's law:

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

where  $V_{std}$  is the standardized volume of gas within a bottle's headspace at the time of pressure measurement. Interval biogas production  $V_{biogas,i}$  is taken as this standardized volume  $v_{std}$ . Cumulative production is taken as the cumulative sum of interval values.

## 4 Calculation of $\text{CH}_4$ production

### 4.1 Method 1

In the first method, biogas is assumed to consist of only  $\text{CH}_4$  and  $\text{CO}_2$  at the time of production (i.e., as produced by the microbial community) and  $\text{CH}_4$  production is calculated from vented (removed) biogas only. This method is described in [3]. Coupled with the assumption that all gas production is biogas, this provides the simplest approach for calculating  $\text{CH}_4$  production.

First, concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  are adjusted so they sum to 1.0:

$$x_{CH_4,n} = x_{CH_4}/(x_{CH_4} + x_{CO_2}) \quad (4)$$

where  $x_{CH_4}$  and  $x_{CO_2}$  are the measured  $\text{CH}_4$  and  $\text{CO}_2$  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  $\text{CH}_4$  volume fraction.

Methane production in an interval  $i$  is then calculated as

$$V_{CH_4,i} = x_{CH_4,n}V_{biogas,i} \quad (5)$$

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  $\text{CH}_4$  (volume fraction) of  $\text{CH}_4$  within the bottle headspace, with correction only for water vapor. Here,  $\text{CH}_4$  production in an interval has two components: a vented part that is naturally interval, and a residual headspace part, that is naturally cumulative:

$$V_{CH_4,i} = V_{CH_4,v,i} + (V_{CH_4,HSR,i} - V_{CH_4,HSR,i-1}) \quad (6)$$

where the subscript  $v$  indicates vented volume and  $HSR$  = residual headspace volume (post-venting).

Vented  $\text{CH}_4$  is calculated from:

$$V_{CH_4,v,i} = x_{CH_4,i} V_{biogas,i} \quad (7)$$

Headspace  $\text{CH}_4$  is calculated from:

$$V_{CH_4,HSR,i} = x_{CH_4,i} V_{post,i} \quad (8)$$

where  $V_{post}$  is the post-venting standardized volume of gas in the bottle headspace. Cumulative production is taken as the cumulative sum of interval values.

## 5 Example Calculations

In the following example,  $\text{CH}_4$  production is calculated from a single interval measurement made on a single bottle in a BMP trial. Calculations are made using both volumetric method 1 and 2. For both methods standardized gas volume is calculated from Eq. (3) by correcting for water vapor, temperature, and pressure.

Measured biogas volume ( $V_{biogas,i}$ ) was 73.6 mL at a temperature ( $T_{meas}$ ) of 30°C. Measured headspace pressure ( $P_{meas}$ ) prior to venting was 101.8 kPa (gauge, or 203.1 kPa absolute) Ambient pressure was 101.325 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.

First water vapor pressure is calculated at the measured headspace temperature using Eq (2).

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

Secondly, the measured volume is converted to dry conditions at standard pressure using Eq. (1).

$$V_{dry} = \frac{73.6 \text{ mL} \cdot (203.1 \text{ kPa} - 4.237 \text{ kPa})}{101.325 \text{ kPa}} = 144.5 \text{ mL}$$

Then, volume is further standardized following Eq. (3).

$$V_{std} = \frac{144.5 \text{ mL} \cdot 273.15 \text{ K}}{303.15 \text{ K}} = 130.2 \text{ mL}$$

$V_{biogas,i}$  is taken as this  $V_{std}$ . Cumulative production is taken as the cumulative sum of interval values.

For method 2 additional calculation of standardized gas volume post venting is required in order to determine interval biogas production. Post-venting pressure in the current ( $P_{post,i}$ ) and previous ( $P_{post,i-1}$ ) intervals was assumed to be constant atmospheric pressure of 101.325 kPa.

$$V_{dry,post,i-1} = V_{dry,post,i} = \frac{73.6 \text{ mL} \cdot (101.325 \text{ kPa} - 4.237 \text{ kPa})}{101.325 \text{ kPa}} = 70.53 \text{ mL}$$

Then, following Eq. (3) post-venting standardized gas volume is calculated.

$$V_{post,i} = \frac{70.53 \text{ mL} \cdot 273.15 \text{ K}}{303.15 \text{ K}} = 63.55 \text{ mL}$$

## 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).

$$x_{CH_4,n} = \frac{0.656}{0.656 + 0.289} = 0.694$$

Then, following Eq. (5),  $CH_4$  production in the interval is calculated.

$$V_{CH_4,i} = 0.694 \cdot 130.2 \text{ mL} = 90.39 \text{ mL}$$

## 5.2 Method 2

$V_{dry,post,i}$  =  $CH_4$  production in the interval is calculated following Eq. (6) using the true concentration of  $CH_4$  within the bottle headspace. First vented  $CH_4$  volume ( $V_{CH_4,v,i}$ ) is obtained from the interval biogas production and the mole fraction of  $CH_4$  using Eq. (7).

$$V_{CH_4,v,i} = 0.656 \cdot 130.2 \text{ mL} = 85.42 \text{ mL}$$

Secondly, post-venting residual headspace pressure in the current and previous interval are calculated following Eq. (8).

$$V_{CH_4,HSR,i} = 0.656 \cdot 63.55 \text{ mL} = 41.69 \text{ mL}$$

$$V_{CH_4,HSR,i-1} = 0.587 \cdot 63.55 \text{ mL} = 37.31 \text{ mL}$$

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

$$V_{CH_4,i} = 85.42 \text{ mL} + (41.69 \text{ mL} - 37.31 \text{ mL}) = 89.80 \text{ mL}$$

## 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