# Calculation of methane production from volumetric measurements


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## 1 BMP-methods

File version 1.2. 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 measurment of biogas. As with manometric methods, 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 measured gas volume (e.g., in a syringe or hanging water column) is converted to dry conditions at standard pressure:

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

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

# 4 Calculation of $CH_4$ 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, 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:

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

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

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

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 $CH_4$ (volume fraction) of $CH_4$ within the bottle headspace, with correction only for water vapor. Here, $CH_4$ 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 $CH_4$ is calculated from:

$$V_{CH_4,v,i} = x_{CH_4,n,i} V_{biogas,i} \tag{7}$$

Headspace $CH_4$ is calculated from:

$$V_{CH_4,HSR,i} = x_{CH_4,n,i} V_{post,i} \tag{8}$$

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, $CH_4$ 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 618 mL at a temperature ($T_{meas}$) of 20C and atmospheric pressure ($P_{meas}$) of 101.325 kPa. First water vapor pressure is calculated at the measured headspace temperature using Eq (2).

$$P_{H_2O} = 0.61094 \cdot e^{\frac{17.625 \cdot 20C}{243.04+20C}} = 2.333\ kPa$$

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

$$V_{dry} = \frac{618\ mL \cdot (101.325\ kPa - 2.333\ kPa)}{101.325\ kPa} = 592.158\ mL$$

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

$$V_{std} = \frac{592.158\ mL \cdot 273.15\ K}{293.15\ K} = 551.758\ mL$$

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

## 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), but was given as 0.627. Then, following Eq. (5), $CH_4$ production in the interval is calculated from interval biogas production.

$$V_{CH_4,i} = 0.672 \cdot 551.758\ mL = 345.952\ mL$$

### 5.2 Method 2

Post-venting dry and standardized volume for current interval ($i$) and the previous interval ($i$-$1$) is required for method 2 and can be calculated following Eq. (1) and (3), respectively. Post headspace pressure ($P_{post}$) was assumed to be constant at 1.01 bar throughout the BMP trial.

Assuming constant biogas composition, $CH_4$ production in the interval can be calculated following Eq. (6). Under the assumptions of constant post headspace pressure and gas composition, Eq. (6) reduces to Eq. (7). Meaning that $CH_4$ production in the interval is equal to vented $CH_4$ volume and hence, method 2 equals method 1:

$$V_{CH_4,i} = V_{CH_4,v,i} = 345.952\ mL$$

## 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