Calculation of Methane Production from Volumetric Measurements*

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1 Introduction

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 [Hafner et al., 2018] and through the web application OBA (https://biotransformers.shinyapps.io/oba1/) and can be easily added to, e.g., a spreadsheet template.

2 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

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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:

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

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 Alduchov and Eskridge [1996]):

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

where T is temperature in °C. Volume is then further standardized to 273.15 K by application of Charles's law:

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

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.

3 Calculation of methane production

3.1 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 Richards et al. [1991]. 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:

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

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

$$V_{CH_4,i} = x_{CH_4,n}V_{biogas,i} \tag{5}$$

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

3.2 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:

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

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

Vented CH_4 is calculated from:

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

Headspace CH_4 is calculated from:

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

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.

4 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 73.6 mL at a temperature (T_{meas}) of 30°C and a pressure (P_{meas}) of 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).

$$V_{dry} = \frac{73.6\,\text{mL} \cdot (101.325\,\text{kPa} - 4.237\,\text{kPa})}{101.325\,\text{kPa}} = 124.8\,\text{mL}$$

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

$$V_{std} = \frac{124.8\,\text{mL} \cdot 273.15\,\text{K}}{303.15\,\text{K}} = 112.4\,\text{mL}$$

$V_{biogas,i}$ 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. Bottle headspace volume was 81.3 mL.

$$V_{dry,post,i-1} = V_{dry,post,i} = \frac{81.3\,\mathrm{mL} \cdot (101.325\,\mathrm{kPa} - 4.237\,\mathrm{kPa})}{101.325\,\mathrm{kPa}} = 77.88\,\mathrm{mL}$$

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

$$V_{post,i} = \frac{77.88\,\mathrm{mL} \cdot 273.15\,\mathrm{K}}{303.15\,\mathrm{K}} = 70.17\,\mathrm{mL}$$

4.1 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. (5), CH_4 production in the interval is calculated.

$$V_{CH_4,i} = 0.694 \cdot 112.4\,\mathrm{mL} = 78.04\,\mathrm{mL}$$

4.2 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).

$$V_{CH_4,v,i} = 0.656 \cdot 112.4\,\mathrm{mL} = 73.74\,\mathrm{mL}$$

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

$$V_{CH_4,HSR,i} = 0.656 \cdot 70.17\,\mathrm{mL} = 46.03\,\mathrm{mL}$$

$$V_{CH_4,HSR,i-1} = 0.587 \cdot 70.17\,\mathrm{mL} = 41.19\,\mathrm{mL}$$

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

$$V_{CH_4,i} = 73.74\,\mathrm{mL} + (46.033\,\mathrm{mL} - 41.19\,\mathrm{mL}) = 78.59\,\mathrm{mL}$$

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