Calculation of Methane Production from Volumetric Measurements*

Sasha D. Hafner, Nanna Løjborg,
Sergi Astals, Christof Holliger,
Konrad Koch, and Sören Weinrich

sasha.hafner@eng.au.dk

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1 Introduction

This document describes calculations for volumetric measurement of biogas. As with manometric methods, two methods are commonly used to address the problem of biogas dilution with flushing gas, 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 effectively identical; differences in cumulative CH_4 production are due only to error in measurement of biogas composition or headspace volume, in addition to small effects of changes in biogas composition over time.

2 Standardization of measured gas volume

Both methods use the same approach for standardization of gas volume. Standard gas volume is calculated by correcting the measured volume V_{meas} for

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water vapor, temperature, and pressure.

$$V_{std} = \frac{V_{meas}(p_{meas} - p_{\mathrm{H_2O}})}{101.325\,\mathrm{kPa}} \cdot \frac{273.15\,\mathrm{K}}{(T_{meas} + 273.15)} \tag{1}$$

where p_{meas} is the gas pressure, T_{meas} is the gas temperature at the time of volume measurement in °C, $p_{\mathrm{H_2O}}$ the water vapor partial pressure, 273.15 K (0°C) is the standard temperature, 101.325 kPa is the standard pressure, and V_{std} is the standardized gas volume. Eq. (1) combines Boyle's and Charles's laws. Other units can, of course, be used, but standard temperature and pressure must be equivalent (e.g., 1.01325 bar, 1.0 atm) and Eq. (1) is based on absolute temperature (note the conversion within the equation by + 273.15).

The value of $p_{\mathrm{H_2O}}$ 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])[1]:

$$p_{\mathrm{H_2O}} = 0.61094 e^{(17.625 \cdot T_{meas}/(243.04 + T_{meas}))} \tag{2}$$

3 Calculation of methane production

With volumetric methods, biogas is typically allowed to accumulate during individual measurement intervals. Biogas volume and composition are then measured for each interval. When biogas accumulates in sealed bottles, measured biogas volume is taken as the measured vented (removed) volume. In other cases, biogas might accumulate in a separate vessel also used to measure volume (e.g., a eudiometer). Regardless of the method used, standardized biogas volume ($V_{b,std}$) is calculated from the measured biogas volume using Eq. (1).

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. With this method, each measurement interval is completely independent of the others; CH_4 production for each interval is determined from $V_{b,std}$ and normalized biogas composition for that interval. This method is described in Richards et al. [1991] (Section 3) and VDI [2016] (Eq. (7)). Coupled with the assumption that all gas production is biogas, this provides the simplest approach for calculating CH_4 production.

Concentrations of CH_4 and CO_2 are normalized so they sum to 1.0:

$$x_{\mathrm{CH_4},\,n} = x_{\mathrm{CH_4}}/(x_{\mathrm{CH_4}} + x_{\mathrm{CO_2}}) \tag{3}$$

where $x_{\mathrm{CH_4}}$ and $x_{\mathrm{CO_2}}$ 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 $x_{\mathrm{CH_4},\,n}$ is the normalized CH_4 volume fraction.

[1] Other options exist, and will provide nearly identical values.

Methane production in an individual measurement interval is then calculated from the standardized biogas volume measured in that interval $V_{b,std}$ with:

$$V_{\mathrm{CH_4}} = x_{\mathrm{CH_4},n} \cdot V_{b,std} \tag{4}$$

Cumulative CH_4 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. Because determination of CH_4 production in an individual interval depends on both, a subscript i for measurement interval is introduced here.

Vented CH_4 for interval i $\mathrm{V}_{\mathrm{CH_4},\,v,\,i}$ is calculated simply as the product of standardized vented (removed) biogas volume and CH_4 mole fraction for that interval:

$$V_{\mathrm{CH_4},\,v,\,i} = x_{\mathrm{CH_4},i} \cdot V_{b,std,i} \tag{5}$$

And headspace CH_4 produced in interval i is given by:

$$V_{\mathrm{CH_4},\,h,\,i} = (x_{\mathrm{CH_4},i} \cdot V_{h,std,i}) - (x_{\mathrm{CH_4},i\,-\,1} \cdot V_{h,std,i-1}) \tag{6}$$

where $V_{h,std,i}$ is the post-venting total standardized volume of gas in the bottle headspace (calculated using Eq. (1)).

Total production in interval i is the sum of the two components.

$$V_{\mathrm{CH_4},\,i} = V_{\mathrm{CH_4},\,v,\,i} + V_{\mathrm{CH_4},\,h,\,i} \tag{7}$$

As with method 1, the cumulative sum of these values gives cumulative CH_4 production. Alternatively (and equivalently), cumulative CH_4 production at the end of interval i can be calculated from the following.

$$V_{\mathrm{CH_4},\,cum,\,i} = \sum_{j=1}^{i} V_{\mathrm{CH_4},\,v,\,i} + x_{\mathrm{CH_4},i} \cdot V_{h,std,i} \tag{8}$$

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