Calculation of Methane Production from Gravimetric Measurements*

Sasha D. Hafner, Brian K. Richards,
Sergi Astals, Christof Holliger,
Konrad Koch, and Sören Weinrich
`sasha.hafner@eng.au.dk`

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1 Introduction

In the gravimetric BMP method, bottles are weighed after venting biogas that accumulated during each measurement interval, and a subsample is analyzed for composition [3]. With mass loss and biogas composition, CH_4 production can accurately be determined. The standardised volume of CH_4 produced and released by venting is calculated separately for each bottle and for each incubation interval, based on the observed mass loss and an estimate of biogas density and water vapour content. Biogas density is calculated from composition, using one of two possible approaches, called "method 1" and "method 2" here. In method 1, vented biogas is assumed to consist of only CH_4 and CO_2. When flushing gas density differs from biogas density, this assumption introduces systematic error (generally small), but a correction can be applied as long as virtually all of the initial headspace gas is removed from the bottle by the end of the test. Alternatively, method 2 assumes vented biogas is a mixture of CH_4, CO_2, and N_2, to account for common flushing gases (or mixtures, e.g., pure N_2 or a mix of N_2 and CO_2). Here, two components must be considered in order to account for

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total CH_4 production: 1) CH_4 removed in vented biogas, and 2) CH_4 remaining in the bottle headspace. This method may be slightly more accurate. In the original publication describing the gravimetric method [3] only method 1 was presented.

2 Calculation of CH_4 production

2.1 Method 1

The mole fraction of CH_4 normalized for CH_4 and CO_2 can be calculated according Eq. (1).

$$x_{CH4,n} = \frac{x_{CH_4}}{x_{CH_4} + x_{CO_2}} \tag{1}$$

Biogas density (g mL^{-1}) at standard conditions (dry at 101.325 kPa, 0°C) is calculated from this value, assuming that biogas (as produced) contains only CH_4 and CO_2.

$$\rho_b = \rho_{CH_4,n} x_{CH_4,n} + \rho_{CO_2}(1 - x_{CH_4,n}) \tag{2}$$

In Eq. (1) d_{CH_4} and d_{CO_2} are pure gas densities at standard conditions, which are 0.0007174 and 0.001977 g mL^{-1} for CH_4 and CO_2, respectively. This value of ρ_b can be used to calculate biogas volume from mass loss, but a small correction for water vapor is needed. Water vapor pressure (p_{H_2O}, kPa) is assumed to be at saturation, and can be calculated using a Magnus-form equation from Alduchov and Eskridge (1996) as with other BMP methods [1].

$$p_{H_2O} = 0.61094 \cdot e^{\frac{17.625T}{243.04+T}} \tag{3}$$

From this value the water concentration in biogas (g mL^{-1}) can be calculated.

$$c_{H_2O} = M_{H_2O} \cdot \frac{p_{H_2O}}{p_{hs} - p_{H_2O}} \cdot \frac{1}{v_b} \tag{4}$$

Here, M_{H_2O} is the molar mass of water (18.02 g mol^{-1}) and v_b is biogas molar volume, which varies slightly with composition (ca. 0.3%) but can be taken as 22300 mL g^{-1} [3]. The standardized volume of vented biogas (assumed to equal produced biogas volume) is given by the following equation.

$$V_b = \frac{\Delta m_b}{\rho_b - c_{H_2O}} \tag{5}$$

Here, Δm_b is the measured mass loss over a measurement interval (g). Finally, the volume of CH_4 produced is given by:

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

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

2.2 Method 2

As in method 1, vented CH_4 is the product of vented volume and CH_4 mole fraction. But biogas density is calculated from the mole fraction of all significant biogas components.

$$\rho_b = \rho_{CH_4} x_{CH_4} + \rho_{CO_2} x_{CO_2} + \rho_{N_2} x_{N_2} \tag{7}$$

Density of N_2 under standard conditions is 0.001250 g mL^{-1}. This estimate of ρ_b is used in Eq. (5), as in method 1, to calculate vented biogas volume. And the volume of vented CH_4 in a single interval is then given by:

$$V_{CH_4,vt} = x_{CH_4} V_b \tag{8}$$

Cumulative vented CH_4 is taken as the cumulative sum of interval values. Total cumulative CH_4 production is the sum of vented CH_4 and CH_4 in the bottle headspace. The latter is calculated from the dry standardized biogas volume within the bottle headspace after venting, which is determined from headspace volume as shown below (as with other BMP methods [1]).

$$V_{hs,std} = (V_{hs}(p_{hs} - p_{H_2O})/101.325\,\text{kPa}) \cdot 273.15\,\text{K}/T_{hs} \tag{9}$$

Here T_{hs} is headspace temperature, p_{hs} is the measured (total) headspace pressure, and p_{H_2O} the water vapor partial pressure (both in kPa). Eq. (9) is based on Boyle's and Charles' laws. The value of p_{H_2O} is assumed to be the saturation vapor pressure, and can be calculated using Eq. (3). Residual headspace pressure is not typically measured in the gravimetric method, but if venting is done carefully, it is identical to ambient pressure. With this value of standardized headspace volume, CH_4 within the bottle headspace can be calculated using the following equation.

$$V_{CH_4,hs} = x_{CH_4} V_{hs,std} \tag{10}$$

Total CH_4 production at measurement interval i is the sum of vented CH_4 (Eq. (8)) for all previous intervals and CH_4 in the bottle headspace (Eq. (10)) at the end of the interval, as shown below.

$$V_{CH_4,c,tot,i} = V_{CH_4,hs,i} + \sum_{j=1}^{j=i} V_{CH_4,vt,i} \tag{11}$$

References

[1] Hafner, S.D., 2019, Calculation of methane production from volumetric measurements, part of the BMP-methods repository, `https://github.com/sashahafner/BMP-methods`

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

[3] Hafner, S.D., Rennuit, C., Triolo, J.M., Richards, B.K., 2015, Validation of a simple gravimetric method for measuring biogas production in laboratory experiments., Biomass and Bioenergy 83: 297-301