

Calculation of Methane Production from Gas Density-Based Measurements*

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1 Introduction

Biochemical methane potential (BMP) can be measured using several different methods. In the gas density BMP (GD-BMP) method, bottle mass loss and vented biogas volume from one or more time intervals are used to determine biogas density, and from that, composition. With this information, CH₄ production can be calculated from either biogas volume or bottle mass loss. Development and validation of the method is described in Justesen et al. [2019]. This document describes calculations for the GD-BMP method and provides an example calculation. Note that all these calculations can be carried out easily using the web application OBA (<https://biotransformers.shinyapps.io/oba1/>) or the biogas package (<https://CRAN.R-project.org/package=biogas>) [Hafner et al., 2018a]. For a detailed measurement protocol, see document 304 from the Standard BMP Methods website [Hafner et al., 2020a].

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[†]For more information and other documents, visit <https://www.dbfz.de/en/BMP>. For document version history or to propose changes, visit <https://github.com/sashahafner/BMP-methods>.

2 GD-BMP algorithms

There are two algorithms that can be used for GD-BMP calculations, which differ only in the way mass loss is calculated. The general and recommended approach is referred to as GD_t (t for total). For GD_t , mass loss for each individual bottle (Δm_b) is taken as the sum of mass loss across all individual incubation intervals, which is exactly identical to the difference between initial and final mass. The alternative is referred to as GD_v , and should be used only when bottle leakage is significant. With GD_v , Δm_b is taken as the sum of the difference between pre- and post-venting mass over the entire BMP test. For both GD_t and GD_v , biogas volume V_b is taken as the sum of standardized volume across all measurement intervals.

These algorithms are described in detail in [Justesen et al. \[2019\]](#) (see Fig. 2, Section 2.1.3, and Table S1).

3 Calculation of bottle leakage

For an individual bottle over a single incubation interval, bottle leakage is calculated as the difference between the pre- and post-venting bottle mass.¹ The sum of these values across all measurement intervals is an estimate of total leakage for an individual bottle.

Leakage detection limit can be estimated from the standard deviation in measured mass of sealed bottles with water only (“water controls”) over all measurements, s_{wc} . From this value a standard deviation in the sum of k values can be determined, and the limit of detection (LOD) may be taken as 3 (or more) times this value.

$$LOD = 3s_{wc}\sqrt{k} \quad (1)$$

In Eq. (1) k is the total number of measurement intervals, and s_{wc} is the standard deviation in the measured mass of a water control bottle over all measurement intervals. With two or more water control bottles, s_{wc} can be taken as the mean of values calculated separately for each bottle. Measured leakage larger than the detection limit is strong evidence that leakage occurred. In this case, the GD_v algorithm may be used (Section 2). However, precision is higher with GD_t and a more prudent approach is to repeat the test taking care to avoid leakage. For large leaks (e.g., perhaps > 20% of total mass loss) the test should always be repeated.

More details on leakage calculations can be found in [Hafner et al. \[2018b\]](#).

4 Calculation of methane production

Using Eq. (2), biogas density (ρ_b , g/mL) is determined by mass loss (Δm_b , g) and standardized biogas volume (V_b , mL), corrected for water vapor content

¹For details on making these measurements see document 304 [\[Hafner et al., 2020a\]](#).

($c_{\text{H}_2\text{O}}$, g/mL) in the gas.

$$\rho_b = \frac{\Delta m_b}{V_b} - c_{\text{H}_2\text{O}} \quad (2)$$

Standardized biogas volume is determined from measured vented biogas volume by correcting for moisture, temperature, and pressure, as described in the BMP-methods document 201, on volumetric calculations [Hafner et al., 2020b]. Water vapor pressure ($p_{\text{H}_2\text{O}}$, kPa) is assumed to be at saturation, and can be calculated using a Magnus-form equation from Alduchov and Eskridge [1996]².

$$p_{\text{H}_2\text{O}} = 0.61094 \cdot e^{\frac{17.625T_{hs}}{243.04+T_{hs}}} \quad (3)$$

T_{hs} in Eq. (3) indicates the bottle headspace temperature at the time of venting ($^{\circ}\text{C}$). The concentration of the water vapor present in the vented biogas ($c_{\text{H}_2\text{O}}$) is then calculated from the molar mass of water ($M_{\text{H}_2\text{O}} = 18.02$ g/mol), the partial pressure ($p_{\text{H}_2\text{O}}$, kPa), the pressure of biogas in the bottle headspace just prior to venting (p_{hs} , kPa), and the molar volume of biogas at standard conditions (here, dry, 101.325 kPa, and 0°C).

$$c_{\text{H}_2\text{O}} = M_{\text{H}_2\text{O}} \cdot \frac{p_{\text{H}_2\text{O}}}{p_{hs} - p_{\text{H}_2\text{O}}} \cdot \frac{1}{v_b} \quad (4)$$

The molar volume of biogas (v_b) at standard conditions is approximated as 22300 mL/mol [Hafner et al., 2015].

Finally, the mole fraction of CH_4 in biogas (x_{CH_4} , dimensionless) normalized for CH_4 and CO_2 ($x_{\text{CH}_4} + x_{\text{CO}_2} = \text{unity}$) is calculated from the normalized difference in density of CO_2 and biogas³.

$$x_{\text{CH}_4} = \frac{\rho_{\text{CO}_2} - \rho_b}{\rho_{\text{CO}_2} - \rho_{\text{CH}_4}} \quad (5)$$

In Eq. (5) ρ_{CH_4} and ρ_{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. From Eq. (5), the content of CH_4 in the biogas is known and can be used for calculation of BMP as with gravimetric or volumetric methods [Hafner et al., 2015]. Eq. (5) is based on the assumption that biogas contains only CH_4 and CO_2 . Over a complete BMP incubation, this is generally a reasonable approximation, but a correction is available [Justesen et al., 2019].

5 Example calculation

In the following example, CH_4 production is calculated from measurements made on a single bottle in a BMP trial. For a complete BMP trial, the standardized biogas volume⁴ was 779.2 mL, and the complete total mass loss was

²Other options exist, and will provide nearly identical values.

³In the original work [Justesen et al., 2019] molar mass was calculated as an intermediate step, but this is not needed.

⁴See document 201 [Hafner et al., 2020b] for information on calculation of standardized biogas volume.

1.070 g. Total leakage mass loss was only 0.003 g, much smaller than the detection limit of 0.04 g, so the GD_t approach is appropriate. Data are from Justesen et al. [2019] (Experiment 2, cellulose bottle).

To find the biogas density (ρ_b) with Eq. (2), water vapor partial pressure is first calculated using Eq. (3). The bottle headspace temperature (T_{hs}) is assumed to be 30°C.

$$p_{\text{H}_2\text{O}} = 0.61094 \cdot e^{\frac{17.625 - 30}{243.04 + 30}} = 4.237 \text{ kPa}$$

Then, following Eq. (4), the concentration of the water vapor ($c_{\text{H}_2\text{O}}$) is calculated.

$$c_{\text{H}_2\text{O}} = 18.016 \text{ g mol}^{-1} \cdot \frac{4.237 \text{ kPa}}{150 \text{ kPa} - 4.237 \text{ kPa}} \cdot \frac{1 \text{ mol}}{22300 \text{ mL}} = 2.348 \cdot 10^{-5} \text{ g mL}^{-1}$$

With $c_{\text{H}_2\text{O}}$ and measured biogas volume and bottle mass loss, biogas density can be calculated from Eq. (2).

$$\rho_b = \frac{1.070 \text{ g}}{779.2 \text{ mL}} - 2.348 \cdot 10^{-5} \text{ g mL}^{-1} = 1.349 \cdot 10^{-3} \text{ g mL}^{-1}$$

The mole fraction of CH_4 (x_{CH_4} , dimensionless) is calculated from the density of the biogas components using Eq. (5).

$$x_{\text{CH}_4} = \frac{1.977 \cdot 10^{-3} \text{ g mL}^{-1} - 1.349 \cdot 10^{-3} \text{ g mL}^{-1}}{1.977 \cdot 10^{-3} \text{ g mL}^{-1} - 7.174 \cdot 10^{-4} \text{ g mL}^{-1}} = 0.498$$

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