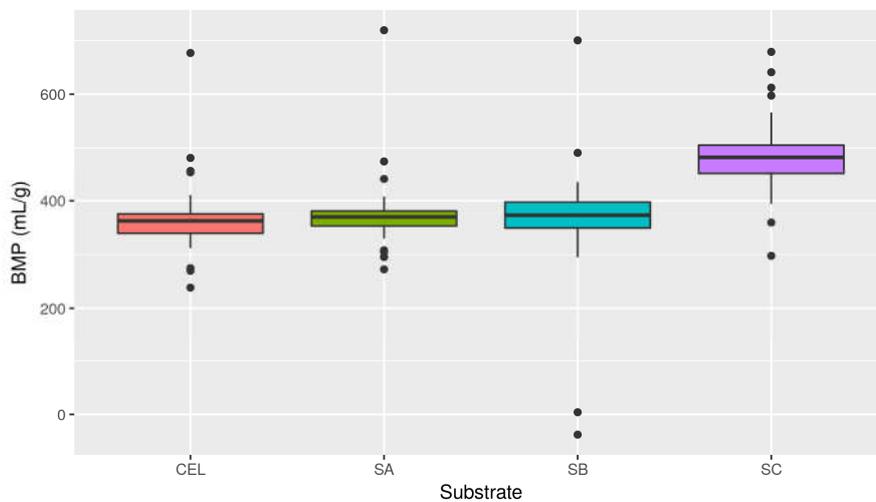


Improving BMP determination with mass-based measurements

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Error in measurement of biochemical methane potential (BMP) is a major problem



Gravimetric biogas methods can help

- To those who are getting started with biochemical methane potential (BMP) measurement: **Gravimetric methods can be cheaper, easier, and more accurate than alternatives.**
- To those who already use manual volumetric or manometric methods: **Gravimetric measurements can reduce error and save time, consider them as an addition or replacement.**

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Three ways that a simple laboratory scale can be used to improve BMP measurements

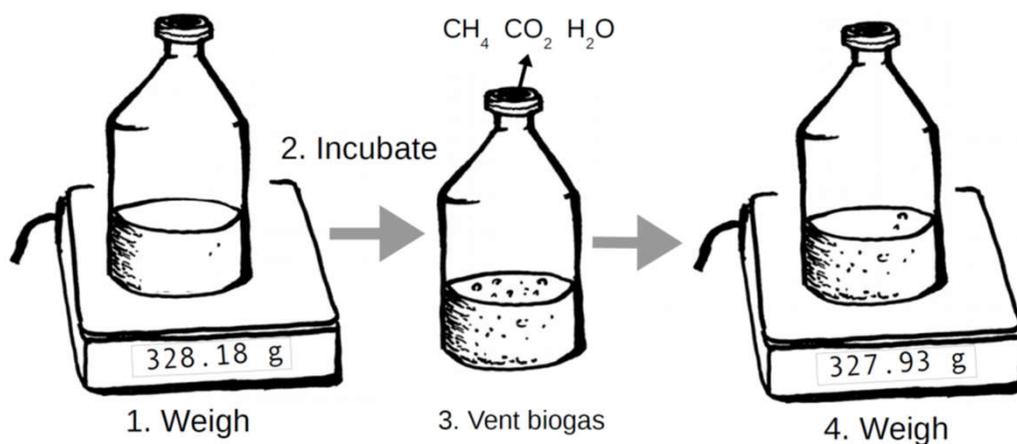
1. Gravimetric BMP measurement
2. Leak detection and quantification by mass loss
3. Gas density (GD) BMP measurement

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1. The gravimetric BMP method

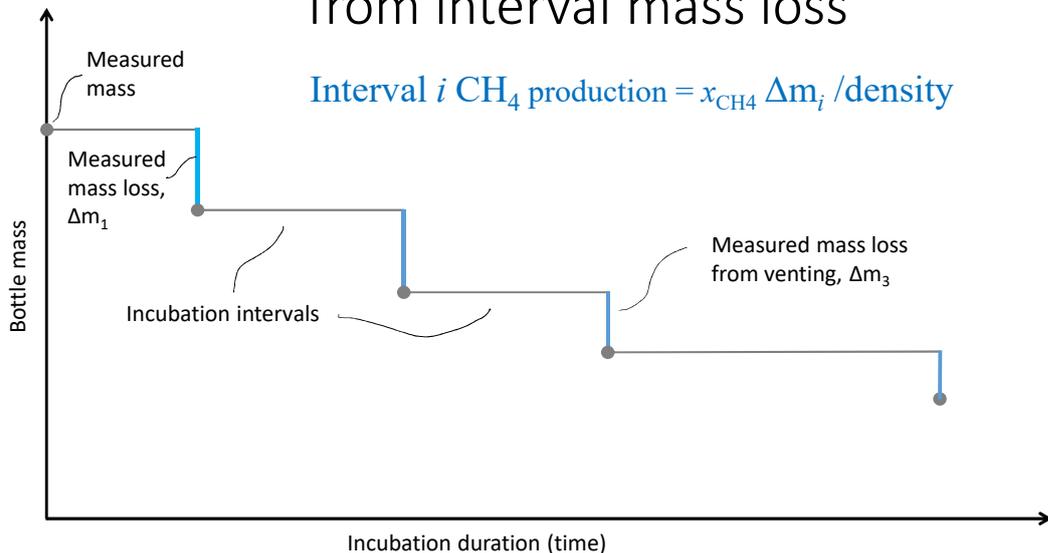
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Gravimetric BMP measurement is based on mass loss from BMP bottles due to venting



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Biogas and CH₄ production are determined from interval mass loss



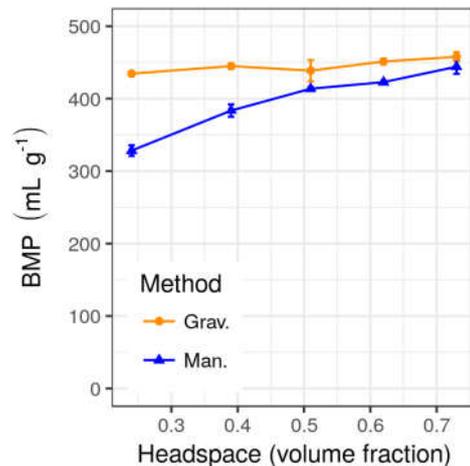
The gravimetric approach was originally described nearly 30 years ago

- Bill Jewell's group at Cornell University developed the original method:
 - Richards, B.K. et al. 1991. Methods for kinetic analysis of methane fermentation in high solids biomass digesters. *Biomass and Bioenergy* 1: 65-73.
- We have recently extended and further tested the general approach:
 - Hafner, S.D., et al. 2015. Validation of a simple gravimetric method for measuring biogas production in laboratory experiments. *Biomass and Bioenergy* 83, 297-301.
 - Hafner, S.D., Astals, S. Under review. Systematic error in manometric measurement of biochemical methane potential: sources and solutions. *Waste Management*

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Gravimetric measurement has some advantages over other methods

- Direct method: measurement of vented biogas
- Not sensitive to:
 - Headspace volume or pressure (see plot)
 - Headspace temperature
 - Biogas leakage
- Error does not accumulate
- Mass contains the history, missing values not fatal
- Quick and easy



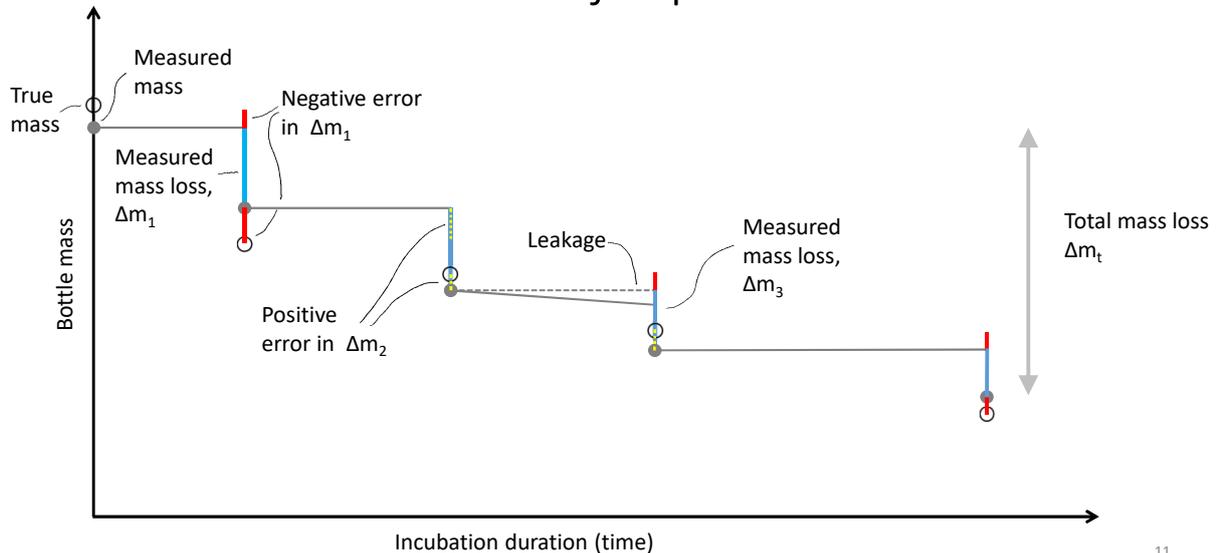
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But the gravimetric method has some limitations too

- Requires an accurate biogas density estimate
 - Depends on composition because of molar mass difference (44 vs. 16 g/mol)
 - Small error in composition makes for large error in CH₄ volume: ± 0.03 mol/mol (e.g., 65 ± 3% volume) → ± 8% in CH₄ volume
- Sensitivity may be low
 - With scale readability of 0.1 g → resolution ca. 100 mL
 - Practical accuracy limit ca. 5 mL CH₄ with 0.1 mg readability and careful work
- Loss of non-biogas mass will cause errors
 - Watch out for loss of reacting mass!
 - Shaking bottles not advised, will contaminate septum, swirl instead

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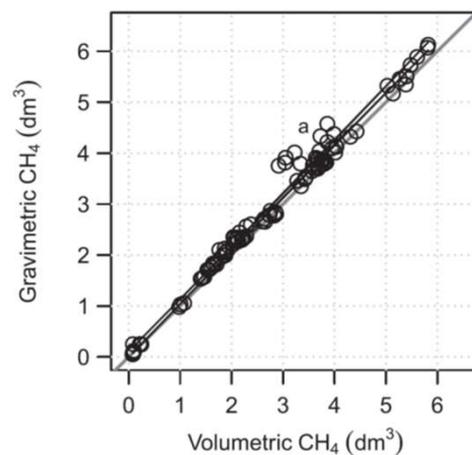
Low resolution in interval measurements is not a major problem



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Multiple lines of evidence show that the gravimetric BMP method works

1. Compared to volumetric measurement in reactors from 100 mL to 12 L, generally < 10% difference
2. Inclusion in large inter-laboratory study, gravimetric BMP of 4 substrates were within 5% of overall mean values
3. Measured ethanol BMP 96-101% of theoretical maximum
4. Measured cellulose BMP 86-87% of theoretical maximum



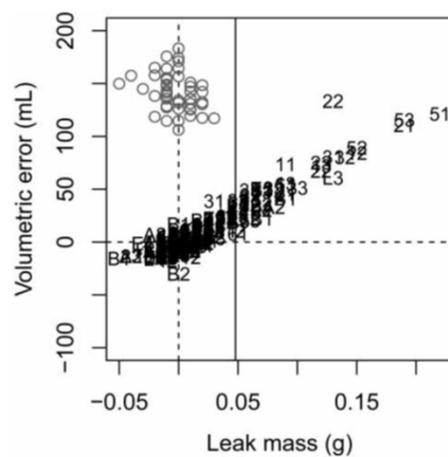
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2. Biogas leakage

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Are you sure your BMP bottles don't leak?

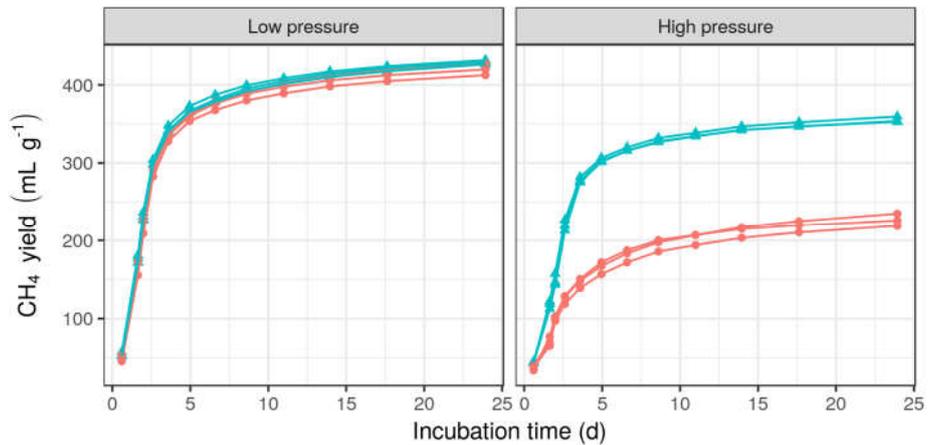
- Have you checked?
- We have detected leakage in recent BMP trials, although typically only in a few bottles
- Leaks are difficult to detect without direct measurement
- Leaks may be small or large
- Leakage can be eliminated with good septa



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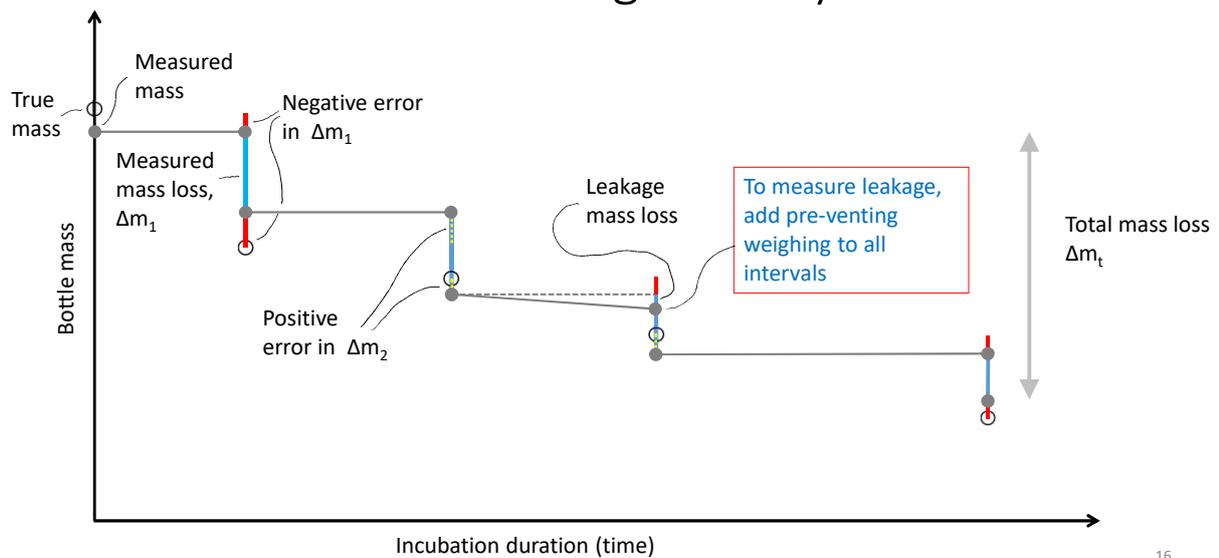
Any leaks here? How can you tell?

Simultaneous manometric measurements of CH₄ yield from a single batch of wastewater sludge



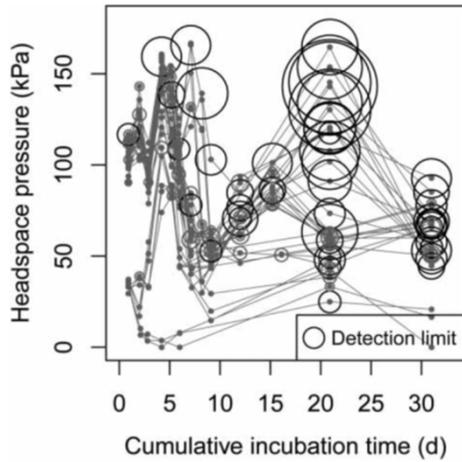
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Measurement of leakage is easy



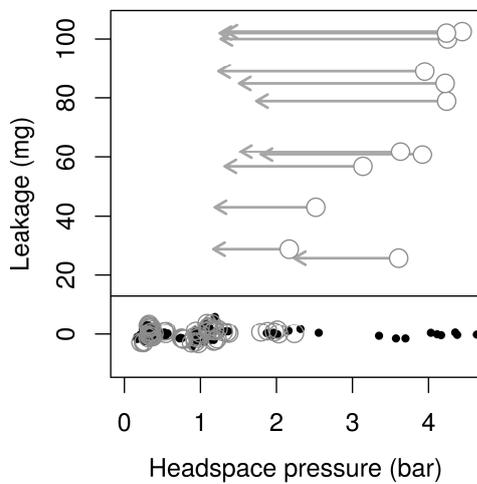
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Leakage is related to septum characteristics, including the number of punctures



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Leakage can be completely eliminated by using thick septa



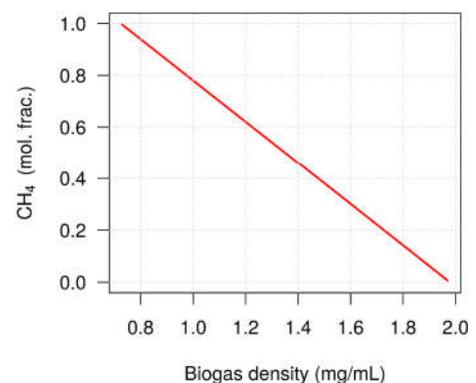
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The gas density BMP method (GD BMP)

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A new BMP method based on gas density

- Biogas density varies with composition
- GD method is based on measurement of both biogas volume and mass loss
 - Only syringes, a scale, and a simple manometer needed (e.g., u-tube)
 - Density is calculated after correcting for temperature, pressure, and water vapor
 - Composition is determined from calculated density
 - CH_4 production then determined using gravimetric or volumetric methods



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How does GD BMP stack up?

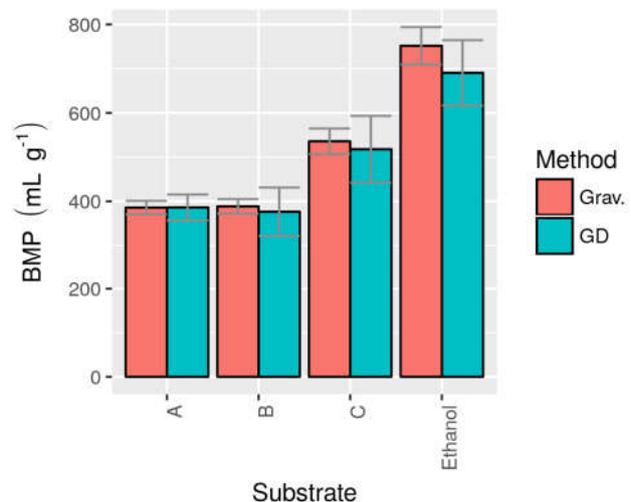
- With careful measurements (scale with 0.1 mg readability, no leakage): indistinguishable (< 2% difference) from gravimetric reference
- Low labor requirement: 1-3 minute per bottle per interval (including leak measurements)

Substrate	Gravimetric BMP (mL/g)	GD BMP (mL/g)
Feed ingredient C	502 ± 6.3	510 ± 9.5
Cellulose	368 ± 8.6	365 ± 5.0

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GD BMP accurate even with less precise measurements

- Scale with only 100 mg readability
- GD BMP within 11% of both gravimetric and volumetric results
- But with larger random error



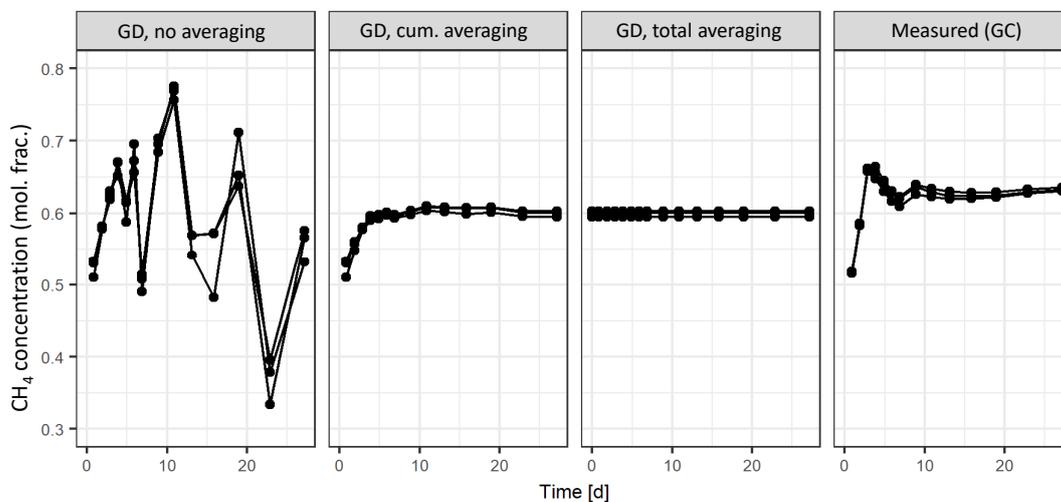
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The GD BMP method has some limitations

- Resolution in mass measurement may be low
 - Problem can be addressed by using total mass loss and total volume instead of interval values
 - Kinetic results will be biased for substrates with significant changes in biogas composition
- Initial headspace density contributes error
 - N_2 density 1.25 mg/mL, similar to 55% CH_4 in biogas
 - Could be significant when biogas production is low
 - Can be addressed through calculations
- Leakage can inflate density, underestimate CH_4 production
 - Can be addressed through use of venting mass loss in calculations

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Interval error in mass can significantly affect biogas composition estimates



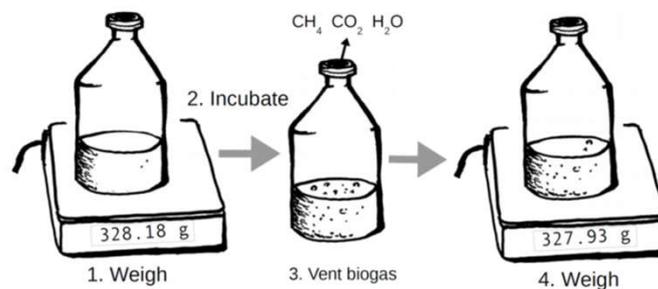
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Conclusions

1. Gravimetric BMP measurement is less error-prone than other manual methods. Should it become the standard for evaluation of others?
2. Biogas leakage in BMP trials may not be rare, but it is easy to measure, and measurements should be included in manual BMP tests.
3. Gas density BMP (GD BMP) provides a means to accurately measure BMP with simple, inexpensive equipment and little effort.

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Thank you for your attention! Questions?



Feel free to contact me by email:

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Application of anaerobic batch tests – gravimetric measurements

State of the art and future perspectives

Possibilities Pros

- ✓ Accuracy
- ✓ Low sensitivity to systematic sources of error
- ✓ Simple equipment
- ✓ Quick, easy measurements

Need for research

- Evaluation of the methods in other labs

Challenges Cons

- ✗ May have low resolution and high random error (depends on equipment)
- ✗ Need for accurate determination of biogas composition (or careful mass and volume measurements)

Application of anaerobic batch tests – BMP tests in general

State of the art and future perspectives

Possibilities Pros

- ✓ Possibility for accurate assessment of substrate quality
- ✓ Need not be time-consuming or expensive

Need for research (some topics being explored in IIS-BMP project, led by Christof Holliger)

- Comparison of measurement methods
- Quantification of sources of error
- Standardization of data processing
- Simple inoculum assessment

Challenges Cons

- ✗ Systematic errors in measurement methods
- ✗ Differences in “custom” methods/equipment
- ✗ Lack of standardization in data processing
- ✗ Inoculum effects, especially on kinetics