**Determination of the Ripley ratio (VFA/alkalinity)**

**Alkalinity**

* Alkalinity can be defined as alkalizing or buffering capacity and is often expressed as calcium carbonate (CaCO3) equivalents. Buffering capacity maintains a stable and neutral pH even as acid or base are added to digester slurry. Feeding rich, high-energy feedstock materials increases the production of volatile fatty acids (VFAs) that are the precursor of methane. VFAs are indeed acids and lower pH so they must be buffered in digester slurry. Manure has low energy content, but possesses great buffering capacity and is therefore valuable feedstock (Callaghan et al., 2002; Hartmann & Ahring, 2005). When feedstock contains sufficient manure its buffering capacity maintains a steady neutral pH and stable AD process even as high-energy feedstock material is added to the mix.

The Ripley ratio titration measures the ratio of IA:PA and approximates the ratio of VFA : alkalinity. This ratio is one of the simplest and most useful indicators of AD process stability. In Germany the Ripley ratio is called ‘FOS/TAC’. Titration is a laboratory method used to find the concentration of a solution when that solution is reacted with a second solution of known molarity. The two solutions must react with a known stoichiometry. To determine the Ripley ratio, a solution of sodium hydroxide with known molarity is used to titrate set volumes of the anaerobic digester slurries, dropping their pH values from roughly neutral through pH values of 5.7, 4.3 and 4.0. The volume of base required to reach each pH value, or combination of pH values, is used to determine an alkalinity.

* Total alkalinity is a measured by titration through pH 4.0. Partial alkalinity is determined by titration to pH 5.7 and is a measure of the bicarbonate alkalinity – or buffering capacity – of the slurry. Bicarbonates deprotonate between pH 4.5 and 8.3Intermediate alkalinity is determined by titration to pH 4.3 and approximates the amount of volatile fatty acids; VFAs are half-protonated at pH 4.3.

Generally, digester slurry (aka digestate) should have Ripley ratio values of 0.2 to 0.4. Drosg (2013) cites 0.5 as a crisis value, but notes that healthy Ripley ratios must be determined empirically for each digester facility with its specific technology, diet and operational parameters. When Ripley ratios climb above their healthy range of 0.2 to 0.4 they indicate that the digestion process is in danger of becoming unstable. This instability can result from a number of causes: 1) an overabundance of VFAs; 2) a lack of buffering capacity; or 3) some combination of the two. As the Ripley ratio rises, digester pH will fall, also indicative of this instability commonly referred to as a ‘sour’ digester. However, changes in Ripley ratios occur more rapidly than changes in pH and are therefore a better warning of instability.

VTCAD’s Solid Waste Management Facility Certification Plan requires weekly determination of Ripley ratios. The assay requires use of a laboratory fume hood and takes 2-4 hours to complete.

* **Equipment:**
* an automatic titration system; or
* burettes and stands,
* a pH probe and pH standards
* a magnetic stir plate
* beakers & graduated cylinders
* a laboratory fume hood and a sink

**Reagents:**

* pH standards: 4.0 & 7.0
* sulfuric acid titrant, 0.1 N: Make by diluting 2.72 mL of concentrated H2SO4 to 1 L with distilled, deionized H2O (ddH2O)

**Calibration of pH probe:**

1. Plug the GLX into an electrical outlet for power and turn it on.
2. Plug the probe into the GLX if its not already secured. Set up a probe rinse beaker and squirt bottle.
3. Press ‘home’ on the GLX;
4. Go to ‘digits’ and hit the center ‘check’ button twice;
5. At ‘data properties’ go to ‘number of digits’;
6. Hit the ‘check’ button to increase to 2 digits;
7. Hit ‘F1’ for OK;
8. You should see a pH reading with hundreths (2 digits after the decimal); but
9. If this is not the case, start over; then
10. Press ‘home’;
11. Hit F4 to get to ‘sensors’;
12. Select 5 samples per second, smooth off, visible;
13. Hit F4 for ‘sensors’;
14. Choose ‘calibrate’ with 2-point calibration;
15. Remove the probe from the storage solution and rinse with ddH2O.
16. Place the probe into the pH 4.0 solution and wait for the number shown at the bottom right of the GLX screen to stabilize and then press pt1.
17. Rinse and repeat the calibration with the pH 10.0 standard solution, hitting pt2 when the reading stabilizes.
18. When calibration is complete, hit F1 (=OK).

**Ripley titration protocol:**

1. Set up a 50-mL buret in a buret stand, close the stopcock and fill with 0.1 N H2SO4 solution. Bleed down to the 0.0 mL line, or any easy starting volume.
2. Place a stir plate below the buret and adjust the buret so that a small beaker will fit beneath it.
3. Arrange the pH probe so that its cord will drape over the buret clamp.
4. Gently invert the sample bottles of digester slurry and pour 50 mL into a graduated cylinder. Transfer the sample into a beaker with a stir bar.   
   [NB: For easiest titration the sample must be homogeneous; use a blender stick or centrifuge. Otherwise, use tweezers or a scoopula to remove big chunks or fibers that float to the top and would lodge in the pH probe.]
5. Place the beaker on a stir plate and stir the sample at moderate speed.
6. Insert the pH probe until the lower third is covered and is away from and not being hit by the stir bar. Clamp the probe wire to keep the probe’s position stable.
7. Record the initial pH value of the slurry.
8. Titrate the slurry to pH 5.7 with 0.1 N H2SO4 and record the volume used exactly as ‘V5.7’. Note that it’s worth going slowly during the first trial to avoid missing the endpoint. The second and third trials will go more quickly as the first 80% of required acid volume can be added quickly without fear of overshooting the pH target.
9. Titrate the slurry to pH 4.3 with 0.1 N H2SO4 and record the volume used exactly as ‘V4.3’.
10. Titrate to the sample to pH 4.0 with 0.1 N H2SO4 and record the volume of acid exactly as ‘V4.0’.
11. Remove the pH probe and rinse well with ddH2O. Store as directed in fresh storage solution.

**Calculations:**

* Total alkalinity (TA) = (V4.0 + V4.3 + V5.7) x N x 50,000 [CaCO3 mg/L]

V

* Partial alkalinity (PA) = V5.7 X N X 50,000 [CaCO3 mg/L]

V

* Intermediate alkalinity (IA) = V4.3 X N X 50,000 [CaCO3 mg/L]

V

*Where: N = acid normality; V = volume of sample (mL)*

Units of measurement: mg/L CaCO3 = (mL)(eq/L)(mg/eq)/mL = mg/L

* **Note:** The relationship between parts per million (ppm) and mg/L is given by:  
   (ppm)(solution density) = mg/L

So for dilute aqueous solutions (with a density very close to 1 g/mL): ppm = mg/L

**Type the data into the spreadsheet posted on the R: drive:**

R: > anaerobic digester > data

**Derivation of calculations for expressing alkalinity as CaCO3:**

1. Calculate the molecular weight (molar mass) of CaCO3:  
    40.08 + 12.01 + (3 x 15.99) = 100.06 g/mol
2. Divide this molar mass by the ionic charge or oxidation number to calculate equivalents of CaCO3:  
    100.06 g/mol = 50.03 ~ 50 g/equivalent = 50,000 mg/equivalent CaCO3  
    2 equiv./mol

**References:**

Callaghan, F.J., Wase, D.A.J., Thayanithy, K., Forster, C.F. (2002) Continuous co-digestion of cattle slurry with fruit and vegetable wastes and chicken manure. Biomass and Bioenergy, 22: 71- 77

Drosg, B. (2013) Biogas process monitoring – techniques and recommendations, IEA

Frear, C., Liao, W., Ewing, T., Chen, S. (2010) Baseline performance monitoring of commercial dairy anaerobic digester, CSANR Research Report, 2010-001, Climate Friendly Farming

Hartmann, H. and Ahring, B.K. (2005) Anaerobic digestion of the organic fraction of municipal solid waste: influence of co-digestion with manure, Water Research, 39: 1543 - 1552

Jenkins, R.S., Morgan, J.M., Zhang, X. (1991) Measuring the usable carbonate alkalinity of operating anaerobic digesters, Research Journal WPCF, 63(1): 28 -34

Ripley, L.E., Boyle, W.C., Converse, J.C. (1986) Improved alkalimetric monitoring for anaerobic digestion of high-strength wastes. Journal – Water Pollution Control Federation, 58: 406-11.

Snoeyink, V. and Jenkins, D. (1980) Water Chemistry, John Wiley and Sons, NY, ISBN: 0-471-05196-9

[www.ehow.com/how\_5328969\_calculate-alkalinity-caco.html](http://www.ehow.com/how_5328969_calculate-alkalinity-caco.html)