

## EXECUTIVE SUMMARY

Successful operation of anaerobic systems depends on, amongst others, maintenance of a near neutral pH in the reactor liquid. The pH established in an anaerobic system is a result of the interaction between the weak acid/bases present. In the desired operating pH range ( $6,6 < \text{pH} < 7,4$ ), the main weak acid/base buffering against pH change is the carbonate [characterized by  $\text{H}_2\text{CO}_3^*$ alkalinity and pH, or, total species concentration ( $C_T$ ) and pH] and the main weak acid/bases causing pH decline are the short-chain fatty acids [characterized by total species concentration ( $A_T$ ) and pH]. For pH control in anaerobic systems, monitoring these weak acid/bases is essential. However, the numerous difficulties with existing methods for measurement of these weak acid/bases preclude their widespread use: For direct measurement of total species concentrations ( $C_T$  and  $A_T$ ), there is a lack of the necessary expensive sophisticated equipment at most full-scale installations in South Africa; for the existing indirect titration techniques, the methods are cumbersome and provide only approximations of the parameters of interest.

To overcome these problems, with this manual two simple titration procedures are presented: A 4 pH point titration for determining the carbonate weak acid/base and a 5 pH point titration for determining both the carbonate and short-chain fatty acid (SCFA) weak acid/bases in aqueous solutions. Besides the carbonate and SCFA weak acid/bases, the most common additional weak acid/bases in anaerobic digestion are phosphate, ammonium and sulphide. These can be accounted for in the titration procedures if their total species concentrations are known. Where these are not available, guidance is given on their influence on the accuracy of the results.

The titration methods require only an acid titration over the middle range of pH (initial pH to pH 6,7; 5,9; 5,2 for 4 pH point titration and to additional pH 4,3 for 5 pH point titration). If the initial pH is below 6,7, strong base addition is required to reach pH 6,7 before the strong acid titration can be commenced; however, the requirement is only to increase the pH to 6,7, i.e. there is no need to standardize the strong base. These features of the titration methods provide decided advantages over existing methods in testing time required and simplicity of testing procedure, and overcome criticisms levelled at previous titration methods, of difficulties in adequate pH probe calibration due to large pH ranges and precipitation.

Algorithms for calculating the carbonate  $C_T$  and  $\text{H}_2\text{CO}_3^*$ alkalinity from the 4 pH point titration data, or the carbonate  $\text{H}_2\text{CO}_3^*$ alkalinity and short-chain fatty acid  $A_T$  from the 5 pH point titration data, have been encoded into two computer programs, TITRA4 and TITRA5 respectively, which are included with the manual. Besides quantifying the carbonate or carbonate plus SCFA, the computer programs allow a check on the pH probe by providing an estimate of a systematic pH error where this may be present, due to poor calibration, residual liquid junction effect or any other influences on the glass electrode. The systematic pH error is taken into account automatically by the computer programs in the calculations. This increases the accuracy of data derived from the titration procedures.

The titration procedures presented with this manual should find wide use for routine monitoring of anaerobic digestion systems, and for a range of other applications.