

Use of a simple titration procedure to determine H_2CO_3^* alkalinity and volatile fatty acids for process control in waste-water treatment

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Abstract

A simple 5-pH point titrimetric method developed elsewhere was tested for measurement of bicarbonate (oc H_2CO_3^*) alkalinity and volatile fatty acids (VFA) in primary sludge, fermented primary sludge or its supernatant, settled sewage and anaerobic digester sludge (under process failure conditions). The titrimetric method incorporates a computer program to calculate the necessary results from a modified Gran titration in the presence of known concentrations of phosphate and ammonia. Comparisons were made between the titrimetric method, a colorimetric method and an HPLC method for VFA determination. The value of the titrimetric H_2CO_3^* alkalinity result compared to that of conventional methods for anaerobic digester samples was also investigated. The results indicated good overall agreement between the three methods of VFA determination. From statistical analysis, the titrimetric method was found to over-predict the VFA content of failed anaerobic digester samples by approximately 15%, relative to the colorimetric method. Statistical agreement between the titrimetric and HPLC methods for these samples was good, provided the high frequency of outliers (ca. 20% of the data pairs rejected) was taken into account. No immediate explanation for the deviations between the methods for failed anaerobic digester samples could be found. However, from the point of view of method simplicity, and avoidance of inherent pitfalls in other methods of H_2CO_3^* alkalinity estimation, the titrimetric method gave very useful results in process control and chemical dosing during start-up of two full-scale anaerobic digesters. The potential value of the titrimetric method for process control of primary sludge fermentation in biological nutrient removal plants was also highlighted. Although problems were encountered with reaching the lower detection limits of all three methods, the results for settled sewage suggest that the titrimetric method can give a fairly reliable estimate of VFA, even at low concentrations. Using the titrimetric method, good recovery of VFA from spiked samples of settled sewage in the range 40 to 80 mg/l as acetic acid was obtained. Using pure solutions of carbonate and acetate, the detection limits for the titrimetric method were found to be approximately 10 mg/l as CaCO_3 and 5 mg/l as acetic acid. Scrupulous attention to pH probe maintenance and calibration was found to be an essential requirement for use of the titrimetric method, particularly at low concentrations when the systematic pH error estimate by the computer program cannot be relied upon.

Introduction

In waste-water treatment, measurement of volatile fatty acid (VFA) concentration and carbonate subsystem alkalinity are important in the control of a number of unit processes. For example, successful operation of anaerobic digesters depends heavily on maintaining a stable neutral pH. Since large masses of organic material are converted to methane, carbon dioxide and water via volatile fatty acid intermediates, for process stability it is recommended that a VFA: Alkalinity ratio of <0.3 be maintained in anaerobic digesters (Ross et al., 1992). On the other hand, biological nutrient removal (BNR) activated sludge plants often require the generation of VFA-rich primary sludge supernatant by fermentation either in the primary settling tanks or in side-stream processes (Barnard, 1984; Osborne et al., 1986; Pitman et al., 1992). The VFA generated may be mixed with the settled sewage or pumped as primary sludge supernatant directly to the activated sludge anaerobic or anoxic reactors to enhance biological P (and/or N) removal. In such cases the higher the VFA conversion from primary sludge, the greater the P and N removal potential (Wentzel et al., 1990). In such cases, process control requires the VFA content of settled sewage and primary sludge (or fermented primary sludge supernatant) to be measured.

The conventional method for measurement of alkalinity involves titration to an endpoint pH of around 4.5 which is usually detected using a mixed methyl red - bromocresol green indicator, and the result is reported as methyl red or total alkalinity (Loewenthal and Marais, 1976). Apart from the carbonate subsystem, total alkalinity includes contributions from phosphates, ammonia, VFA and other weak acid subsystems typically present in waste water. Borates and silicates may be significant in clean water analyses but less so in waste water. Bicarbonate alkalinity may be estimated using nomographs or by difference between the total alkalinity and phenolphthalein (carbonate) alkalinity (*Standard Methods*, 1985). However, in neither of these methods is the carbonate/bicarbonate subsystem alkalinity distinguished from that of the other subsystems which may be very significant in waste water, notably phosphate and VFA. For VFA determination by titration, a preliminary steam distillation step is required (*Standard Methods*, 1985) but this is tedious and poor recovery commonly occurs due to undetected leaks in the distillation system.

DiLallo and Albertson (1961) proposed a titrimetric method for differentiating between carbonate species and "volatile acid alkalinity". The sample is first titrated from its initial pH to pH 4.0 thereby determining the total alkalinity. The pH is then lowered to 3.3 to convert all the carbonate species to carbonic acid and dissolved CO_2 . Since the equilibrium is such that dissolved CO_2 predominates, the carbonate species can be very largely expelled by light boiling of the sample for 3 min. The sample is back-titrated with strong base and the amount of base added between pH 4.0 and 7.0 forms an estimate of the "volatile acid alkalinity". In effect, the

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