

# Evaluating 5 and 8 pH-point titrations for measuring VFA in full-scale primary sludge hydrolysate

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## Abstract

An evaluation of 5 and 8 pH-point titrimetric methods for determining volatile fatty acids (VFAs) was conducted, and the results were compared for tap water and primary treated wastewater at the laboratory scale. These techniques were then applied to full-scale primary sludge hydrolysate, and the results were compared with those obtained via gas chromatography. The comparison showed that the VFA concentrations measured with the two titration methods were higher than those obtained via gas chromatography, differing by 9 and 13 mg COD·ℓ<sup>-1</sup> for the hydrolysate and by 5 and 6 mg COD·ℓ<sup>-1</sup> for the ordinary primary settler effluent. No improvement in the accuracy of VFA concentration measurement was obtained from applying the 8 pH-point titration method instead of the 5 point method. The 5 pH-point method was successfully applied to determine VFA in full-scale primary sludge hydrolysate and was shown to be equally efficient to the methods that are routinely-used for this purpose.

**Keywords:** Multiple pH-point titration, volatile fatty acids, wastewater, full-scale, primary sludge hydrolysis

## Introduction

At wastewater treatment plants (WWTPs), the addition of various external carbon sources to serve as energy source for the denitrifying heterotrophic bacteria, such as ethanol, methanol and acetic acid (AcOH), is used for extended nitrogen removal (Henze et al., 2002). The main advantages of external carbon sources are low sludge production and on-demand accessibility. Despite these advantages, full-scale applications of sludge hydrolysis for the internal production of volatile fatty acids (VFAs), functioning as an alternative carbon and energy source, is of interest, and has been implemented at several WWTPs (Andreasen et al., 1997; Canziani et al., 1995; Johansson et al., 1996; Jönsson et al., 1996; Ucisik et al., 2008). In wastewater terminology, sludge hydrolysis comprises all mechanisms that make slowly biodegradable substrates available for bacterial growth (Gujer et al., 1999).

The production of endogenous carbon sources by the application of sludge hydrolysis is motivated by sound arguments, e.g., independence from fluctuating market prices and the avoidance of transport costs. Furthermore, internally-produced VFAs are natural constituents in wastewater, and, therefore, no microbiological adaptation is required (Nyberg, 1996). Interestingly, Jönsson et al. (2008) calculated a possible decrease of 50% in the amount of external carbon source needed for denitrification resulting from the addition of hydrolysate; this was later confirmed by Hey et al. (2012) through simulations.

The major challenges associated with internal carbon source production are the optimal monitoring, control and distribution of the carbon produced. An overload of produced VFA from the hydrolysate generates increased oxygen demand

in the biological process, increased sludge production and, if anaerobic digestion is used, possibly decreased gas production. In contrast, a lack of carbon prevents sufficient nitrogen removal and may cause poor biological phosphorus removal.

Monitoring alkalinity and VFAs has long been considered a key indicator in evaluating the operation of anaerobic systems, because sudden changes in either parameter can signal process disturbances or even failure (Ahring et al., 1995). Therefore, significant efforts have been directed towards the development of analytical methods for the off- and on-line measurements of VFAs. Among other techniques, gas chromatography (GC), high-pressure liquid chromatography (HPLC), and Fourier transform-infra red spectroscopy (FT-IR) have been reported (Zumbusch et al., 1994; Banister and Pretorius, 1998; Steyer et al., 2002). However, the multiple pH-point titrimetric technique has attracted considerable attention, mainly because of its robustness, wide range of application, cost efficiency and user-friendliness (Moosbrugger et al., 1993; Buchauer, 1998; Lahav et al., 2000, 2002, 2004; Feitkenhauer et al., 2002; Vanrolleghem et al., 2003). Another pronounced advantage of titrations is the potential of simultaneously measuring alkalinity and VFA concentrations. The 5 pH-point method, first proposed by Moosbrugger et al. (1993), was based on choosing the initial pH of the sample in addition to 2 pairs of pH points symmetrically distributed around the dissociation points (pKa) of the carbonate and acetate systems. The 8 and 9 pH-point titration methods were subsequently developed based on the 5 pH-point method but included additional pH points for increased accuracy and precision (Lahav et al., 2002; Ai et al., 2011).

The present study aimed to evaluate the accuracy of the 5 and 8 pH-point titrimetric methods by determining the recovery of VFA in both tap water and primary settler effluent. Furthermore, the precision and applicability of the two selected methods were assessed by measuring the VFA content in hydrolysate obtained from a full-scale hydrolysis of primary sludge. The results from the latter experiment were compared with those obtained via gas chromatography (GC) analysis.

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