A comparison of two simple titration procedures to determine volatile fatty acids in influents to waste-water and sludge treatment processes

K Buchauer
Unterbergerstrasse 1, A-6020 Innsbruck, Austria
c/o Consulting Engineers Bennat, Völser Strasse 11, A-6020 Innsbruck, Austria

Abstract

Science knows quite a number of possibilities to determine volatile fatty acids in waste water and sludges. The simplest and cheapest method, however, developed so far is titration with acid and base. Different suggestions on how to apply this principle abound. This paper compares a method developed in South Africa with a German approach. Both methods were developed for effluents of treatment processes, i.e. for the control of anaerobic fermentation processes. Nevertheless these procedures are increasingly being applied to influents, too, e.g. for the control and optimisation of enhanced biological phosphorus removal from waste water. In order to promote the advantages of titration, it is crucial to find a procedure which provides both optimum accuracy and simplicity. Taking into account a minimal modification of the original German method, it shows that the accuracy of both methods is equivalent for all media investigated in this study (waste water, primary sludge, high- and low-load activated sludge). Hence it is simplicity that becomes decisive for method selection in most cases. In this respect the German method is regarded as superior because it only requires acid, uses one pH point less and enables S_a calculation by a simple explicit equation. But whenever there is additional interest in the specification of carbonate alkalinity, the South African procedure is recommended.

Nomenclature

Ac^- = acetate CH_3COO^-
Alk_{HCO3} = alkalinity (mmol/ℓ) due to HCO_3^-/CO_2 buffer
Alk_{meas} = measured alkalinity (mmol/ℓ)
Alk_{sa} = alkalinity (mmol/ℓ) due to S_a buffer
BNR = biological nutrient removal
CH_3COOH = acetic acid
CO_2 = carbon dioxide (mg/ℓ)
$[CO_2]$ = concentration of CO_2 (mol/ℓ)
$[CO_3^{2-}]$ = concentration of carbonate (mol/ℓ)
C_T = carbonate total species concentration (mol/ℓ)
= $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$
GC = gas chromatograph
HAc = acetic acid (mg/ℓ)
HCO_3^- = bicarbonate (mg/ℓ)
$[HCO_3^-]$ = concentration of HCO_3^- (mol/ℓ)
H_2CO_3 = carbonic acid (mg/ℓ)
$[H_2CO_3]$ = concentration of H_2CO_3 (mol/ℓ)
$[H_2CO_3^*]$ = $[CO_2$ dissolved$] + [H_2CO_3]$ (mol/ℓ)
HPLC = high performance liquid chromatograph
$H_2PO_4^-$ = first dissociation step of phosphoric acid
HPO_4^{2-} = second dissociation step of phosphoric acid
n = number of observations
N = normality (mmol/ℓ)
NH_3 = ammonia (mg/ℓ)
NH_4^+-N = ammonium nitrogen (mg/ℓ)
$[NH_4^+$-N$]$ = concentration of NH_4^+-N (mmol/ℓ)
pK_a = dissociation constant
PO_4^{3-}-P = phosphate phosphorus (mg/ℓ)
r = correlation coefficient
S = standard deviation
S_a = volatile fatty acids (mg/ℓ), considered to be acetic acid
SCFA = short-chain fatty acids
TDS = total dissolved solids (mg/ℓ)
UASB = upflow anaerobic sludge blanket
$VA_{5\text{-}4,HCO3}$ = volume of acid (mℓ) required to titrate a sample from pH 5.0 to pH 4.0 due to HCO_3^-/CO_2 buffer
$VA_{4,3,meas}$ = measured volume of acid (mℓ) required to titrate a sample from initial pH to pH 4.3
$VA_{5\text{-}4,meas}$ = measured volume of acid (ml) required to titrate a sample from pH 5.0 to pH 4.0
$VA_{5\text{-}4,\ sa}$ = volume of acid (ml) required to titrate a sample from pH 5.0 to pH 4.0 due to S_a buffer
VFA = volatile fatty acids
VS = volume of a titrated sample (mℓ)
WWTP = waste-water treatment plant
X = mean

Introduction

The term volatile fatty acids is a lumped parameter of different acids, with acetic acid, propionic acid, butyric acid and valeric acid being the most common forms. The dominant volatile fatty acid species in waste water and sludges from waste-water treatment is acetic acid (CH_3COOH). In the literature, the terms volatile fatty acids (VFA), short chain fatty acids (SCFA) or S_a (according to IAWQ Activated Sludge Model No. 2 - Henze et al., 1995a) are synonymous.

VFA play a crucial role in denitrification (Van Haandel and Marais, 1981), enhanced biological phosphorus removal, bio-P (Henze et al., 1995b; Wentzel et al., 1986), and they can be used effectively for the control of mesophilic sludge digesters (Kapp, 1984).

☎ (++0512) 274715; fax (++0512) 285511
Received 4 April 1997; accepted in revised form 14 October 1997.

Methods available so far for the analysis of S_a are:

- *Steam distillation* (Deutsche Einheitsverfahren, 1971): Requires certain specialised equipment plus experience, and it is time-consuming.
- *Colorimetric method* according to Montgomery et al. (1962): Simple procedure, which is said to be of poor accuracy at low S_a-concentrations (Scheer, 1995) and which is rather sensitive towards residual colour (Moosbrugger et al., 1993).
- *Chromatographic methods* (HPLC, GC): Require high investment in technical equipment which is not commonly available at a WWTP.
- *Titrimetric methods:* Mostly very simple procedures, which can be conducted with minimum of time and effort. Often this group is said to be not fit for low S_a concentrations as e.g. present in domestic wastewater (Scheer, 1994; Scheer, 1995). The titration procedures developed so far are quite different. Amongst others there are methods by: DiLallo and Albertson (1961), McGhee (1968), Nordmann (1977), Colin (1984), Kapp (1984), Ripley et al. (1986), Powell and Archer (1989), Moosbrugger et al. (1992; 1993). A detailed survey of these procedures (Buchauer, 1997) proved especially the method of Kapp (1984) and the method of Moosbrugger et al. (1992; 1993) to be worthy of a closer comparison. The former method is widely used in the German-speaking countries like Germany, Switzerland and Austria. The latter method, from the author‘s point of view, seems to be the only current approach with a real potential for accuracy improvement.

This paper tries to point out differences, advantages and shortcomings of both methods in order to be able to offer a sound recommendation for the optimum procedure.

Titration procedures

Method according to Kapp (1984)

Principle

Kapp founded his procedure on a principle suggested by McGhee (1968). The basic idea is that the acid required to titrate a sample from pH 5.0 to pH 4.0 can be considered proportional to the content of S_a present in the sample. This applies because between pH 5.0 and pH 4.0 there is usually no weak acid/base subsystem present that strongly effects acid consumption apart from the acetate subsystem. Moreover, the pK_a values of acetic acid, propionic acid, butyric acid and valeric acid are all close to 4.75. Thus they show very similar buffering characteristics and can indeed be lumped together as one parameter. The only additional buffer considered in the S_a calculation procedure of Kapp (1984) is the carbonate subsystem of HCO_3^-/CO_2 which has a pK_a of approximately 6.3. Other buffer systems are assumed to be negligible. Kapp (1984) argues that the ammonia subsystem (NH_3/NH_4^+) has its pK_a at ca. 8.95 which is far removed from the pH range under discussion. Similarly $H_2PO_4^-/HPO_4^{2-}$ (pK_a at ca. 7.2) influences the alkalinity only to a minimal extent (ca. 0.03 mmol/mg P).

The method according to Kapp (1984) was originally developed for the control of mesophilic sludge digesters. It proved, however, to be suitable for other applications, too (see under **Control of the method**), provided special attention was paid to acid standardisation, sample filtration, acid dosage, constant mixing and pH probe calibration.

The recorded results of the Kapp titration procedure are evaluated by an iteration scheme which is based on a combined empirical theoretical approach (Kapp, 1984).

Analysis description (Kapp, 1984; Kapp, 1992)

- Before analysis the sample is filtered through a 0.45 µm membrane filter. In the case of online application an ultrafiltration unit is used.
- Filtered sample (20 mℓ) is put into a titration vessel, the size of which is determined by the basic requirement to guarantee that the tip of the pH electrode is always immersed below the liquid surface.
- Initial pH is recorded.
- The sample is titrated slowly with 0.1 N sulphuric acid until pH 5.0 is reached. The added volume of the titrant is recorded.
- More acid is slowly added until pH 4.3 is reached. The total volume of the added titrant is again recorded.
- The latter step is repeated until pH 4.0 is reached, and the volume of added titrant recorded once more.
- A constant mixing of sample and added titrant is required right from the start to minimise exchange of CO_2 with the atmosphere during titration. Depending on the system in use this is done via a small impeller or via a magnetic stirrer.

Derivation of the S_a calculation scheme

The calculation scheme according to Kapp (1984) is an iteration procedure which is rather impractical to handle. The recommended algorithm (Kapp, 1984) includes the repeated use of various figures. However, Kapp (1984) also gives regression equations which can be used alternatively to the figures. These equations are included in the following derivation. Hence, a suggestion is presented here to transfer Kapp's iteration scheme (1984) into a simple explicit equation (Buchauer, 1996), through which the details of the method are dealt with.

First S_a approximation (= first iteration step according to Kapp (1984))

The measured acid consumption between pH 5.0 and pH 4.0 is regarded by Kapp (1984) to be due to two buffers only: S_a and HCO_3^-/CO_2 buffer. Thus it is possible to write:

$$VA_{5\text{-}4,\,sa} = VA_{5\text{-}4,meas} - VA_{5\text{-}4,HCO3} \qquad (1)$$

For an estimation of $VA_{5\text{-}4,sa}$, Kapp (1984) conducted titration experiments using different sample concentrations of acetic acid (volume of the sample, VS = 20 mℓ). S_a varied between ca. 0 and 70 mmol/ℓ. The following regression equation between volume of 0.1 N titrant (sulfuric acid) required for titration, and concentration of the respective S_a was found by Kapp (1984) (r = 0.9999):

$$VA_{5\text{-}4,\,sa} = -0{,}0283 + 0{,}09418 \cdot S_a / 60 \qquad (2)$$

When using propionic, butyric or valeric acid instead of acetic acid, Kapp (1984) obtained regression results, which were almost identical with Eq. (2). Since acetic acid is usually the dominant fraction of S_a, he concluded that using Eq. (2) for his method is sufficiently accurate in any case.

Eq. (2) can be rewritten in a more general form for variable acid normality N and variable sample volume VS as follows (Buchauer, 1996):

$$VA_{5\text{-}4,\,sa} = 0.1 / N \cdot (-0.0283 + 0.09418 \cdot S_a/60) \cdot VS/20 \qquad (4)$$

For an estimation of $VA_{5\text{-}4,HCO3}$, Kapp (1984) titrated 20 mℓ of an NH_4HCO_3 solution at different concentrations (NH_4^+-N varied between ca. 400 and 10 000 mg/ℓ) with 0.1 N strong acid and found (r = 0.9969):

$$VA_{5\text{-}4,HCO3} = 0.044875 + 0.000335 \cdot NH_4^+\text{-}N \qquad (5)$$

Generally this can be rewritten for variable acid normality N and variable sample volume VS as (Buchauer, 1996):

$$VA_{5\text{-}4,HCO3} = 0.1/N \cdot (0.044875 + 0.000335 \cdot NH_4^+\text{-}N) \cdot VS/20 \qquad (6)$$

Using theoretical considerations concerning the anaerobic degradation of proteins, Kapp (1984) postulated the following general relationship, which he also proved to be true experimentally for filtrate of digested sludge with NH_4^+-N varying between ca. 300 and 3 600 mg/ℓ (r = 0.997):

$$[HCO_3^-] = [NH_4^+\text{-}N] = NH_4^+\text{-}N/14 \qquad (7)$$

Eq. (7) → Eq. (6) yields:

$$VA_{5\text{-}4,HCO3} = 0.1/N \cdot (0.044875 + 0.000335 \cdot 14 \cdot [HCO_3^-]) \cdot VS/20 \qquad (8)$$

$$= 0.005 \cdot (0.044875 + 0.00469 \cdot [HCO_3^-]) \cdot VS / N \qquad (9)$$

For the first S_a approximation Kapp (1984) assumes that the measured alkalinity of a sample is only caused by the HCO_3^-/CO_2 buffer. Mathematically this means:

$$Alk_{HCO3} = Alk_{meas} = [HCO_3^-] \qquad (10)$$

where:

$$Alk_{meas} = VA_{4,3,meas} \cdot N \cdot 1000 / VS \qquad (11)$$

Eq. (10) → Eq. (9) yields:

$$VA_{5\text{-}4,HCO3} = 0.005 \cdot (0.044875 + 0.00469 \cdot Alk_{HCO3}) \cdot VS / N \qquad (12)$$

Introduction of Eq. (12) and Eq. (4) into Eq. (1) delivers:

$$0.1 / N \cdot (-0.0283 + 0.09418 \cdot S_a / 60) \cdot VS / 20 =$$
$$= VA_{5\text{-}4.meas} - 0.005 \cdot (0.044875 + 0.00469 \cdot Alk_{HCO3}) \cdot VS / N \qquad (13)$$

Rearranging Eq. (13):

$$-0.0001415 \cdot VS / N + 0.0000078483 \cdot S_a \cdot VS / N =$$
$$= VA_{5\text{-}4.meas} - 0.000224375 \cdot VS / N - 0.00002345 \cdot Alk_{HCO3} \cdot VS / N \qquad (14)$$

$$0.0000078483 \cdot S_a =$$
$$= N \cdot VA_{5\text{-}4.meas} / VS - 0.00002345 \cdot Alk_{HCO3} - 0.000082875 \qquad (15)$$

$$S_a = 127416 \cdot N \cdot VA_{5\text{-}4.meas} / VS - 2.99 \cdot Alk_{HCO3} - 10.6 \qquad (16)$$

By using Eq. (10), Eq. (16) can be rewritten to give the first S_a approximation:

$$S_a = 127416 \cdot N \cdot VA_{5\text{-}4,meas} / VS - 2.99 \cdot Alk_{meas} - 10.6 \qquad (17)$$

Second S_a approximation (= second iteration step according to Kapp (1984))

By having a first estimate of S_a, it now becomes possible to consider the influence of S_a upon alkalinity:

$$Alk_{HCO3} = Alk_{meas} - Alk_{sa} \qquad (18)$$

To quantify Alk_{sa} Kapp (1984) considered that by titration to pH 4.3 ca. 60% of acetate CH_3COO^- is present as CH_3COOH. Thus:

$$Alk_{sa} = 0.6 \cdot S_a / 60 = 0.01 \cdot S_a \qquad (19)$$

With Eq. (17), Eq. (18) and Eq. (19) it becomes possible to derive a second approximation for Alk_{HCO3}:

Eq. (19) → Eq. (18) yields:

$$Alk_{HCO3} = Alk_{meas} - 0.01 \cdot S_a \qquad (20)$$

Eq. (17) → Eq. (20) yields:

$$Alk_{HCO3} = Alk_{meas} - 1274.16 \cdot N \cdot VA_{5\text{-}4.meas} / VS + 0.03 \cdot Alk_{meas} + 0.11 \qquad (21)$$

$$= -1274.16 \cdot N \cdot VA_{5\text{-}4.meas} / VS + 1.03 \cdot Alk_{meas} + 0.11 \qquad (22)$$

Eq. (22) → Eq. (16) delivers the second approximation for S_a:

$$S_a = 127416 \cdot N \cdot VA_{5\text{-}4.meas} / VS - 2.99 \cdot (-1274.16 \cdot N \cdot VA_{5\text{-}4.meas} / VS + 1.03 \cdot Alk_{meas} + 0.11) - 10.6 \qquad (23)$$

$$= 131226 \cdot N \cdot VA_{5\text{-}4.meas} / VS - 3.08 \cdot Alk_{meas} - 10.9 \qquad (24)$$

Third S_a approximation (= third iteration step according to Kapp (1984))

Similar to the second S_a approximation a third S_a approximation is conducted. First an improved approximation of Alk_{HCO3} is derived, which is used to further improve the approximation of S_a.

Eq. (24) → Eq. (20) yields:

$$Alk_{HCO3} = Alk_{meas} - 1312.26 \cdot N \cdot VA_{5\text{-}4.meas} / VS + 0.03 \cdot Alk_{meas} + 0.11 \qquad (25)$$

$$= -1312.26 \cdot N \cdot VA_{5\text{-}4.meas} / VS + 1.03 \cdot Alk_{meas} + 0.11 \qquad (26)$$

Eq. (26) → Eq. (16) delivers the third approximation for S_a:

$$S_a = 127416 \cdot N \cdot VA_{5\text{-}4.meas} / VS - 2.99 \cdot (-1312.26 \cdot N \cdot VA_{5\text{-}4.meas} / VS + 1.03 \cdot Alk_{meas} + 0.11) - 10.6 \qquad (27)$$

$$= 131340 \cdot N \cdot VA_{5\text{-}4.meas} / VS - 3.08 \cdot Alk_{meas} - 10.9 \qquad (28)$$

Further iterations are considered unnecessary by Kapp (1984), because they only supply marginally different S_a results. Consequently Eq. (28) represents the complete iterative calculation scheme according to Kapp (1984), expressed in one explicit equation.

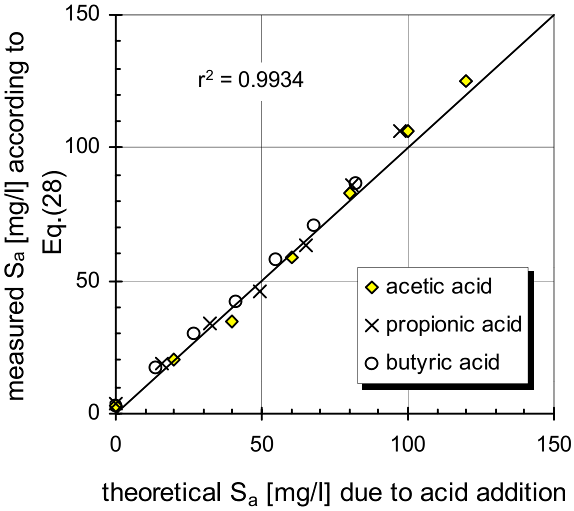

Figure 1
Control of Eq. (28) by dosing known amounts of acetic acid, propionic acid and butyric acid to tap water

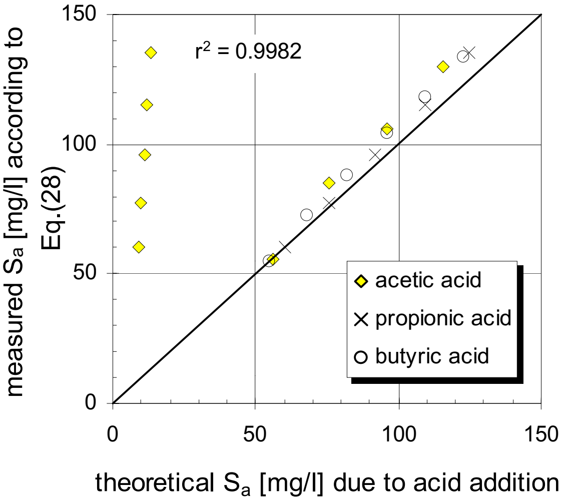

Figure 2
Control of Eq. (28) by dosing known amounts of acetic acid, propionic acid and butyric acid to crude waste water (S_a of the original sample: 56 mg/ℓ)

Control of the method

The method of Kapp was tested by himself using samples of digested sludge, which were analysed by titration and steam distillation (Kapp, 1984). S_a concentrations obtained by titration were on an average 3.5% above the results of distillation. Correlation coefficient was r = 0.9965.

Later on he also confirmed the suitability of his procedure for online S_a measurement in the influent to waste-water treatment plants (Kapp, 1992). Accuracy he claimed to be ± 5 mg/ℓ or ± 10% for $S_a \geq 20$ mg/ℓ.

Brückner (1995) conducted experiments with domestic waste water and landfill leachate. By comparing the titration according to Kapp (1984) to steam distillation she found very good correlation, without giving detailed statistical parameters. In addition she pointed out that a high concentration of lipids could give rise to S_a titration results of up to + 40%.

In this study numerous experiments were conducted to investigate Eq. (28). First samples of both tap water and deionised water were titrated after adding known amounts of acetic acid, propionic acid or butyric acid (up to 200 mg/ℓ as S_a). Eq. (28) proved to deliver S_a concentrations minimally above the theoretical values (mean: + 2 mg/ℓ). The same kinds of experiments were done using different sources of crude waste water as original sample. By comparing theoretical S_a concentrations in these mixtures, varying between 0 mg/ℓ and maximum 200 mg/ℓ, with measured ones, Eq. (28) was found to deliver slightly too high values, again. Deviations amounted to a mean + 14 mg/ℓ. Figures 1 and 2 show two arbitrary examples of these experiments.

Two reasons for this increasing deviation seem possible. Either it can be seen as a consequence of statistical imperfections of the regression equations included in the derivation of Eq. (28), or it can be caused by the influence of buffer subsystems not considered in Kapp's method. The different findings, as described before and depicted in Figs. 1 and 2, lead to the assumption that the latter prevails.

Consequently the method of Moosbrugger et al. (1992; 1993) was used to analyse the same samples. This method is superior to the method of Kapp (1984) because it takes into account the influence of ammonium, phosphate and sulphide weak acid/bases, too. Taking the ammonium and phosphate subsystem into account, the outcome of Moosbrugger's approach was virtually the same as for Kapp's method. Both methods delivered slightly too high S_a concentrations, even though S_a concentrations according to Moosbrugger's method were mostly somewhat lower than those according to Eq. (28).

This means that both methods can yield S_a concentrations which are actually too high. This confirms the observation of Brückner (1995) that subsystems which are neither considered by Kapp (1984) nor by Moosbrugger et al. (1992; 1993) have the potential to affect S_a results, too, e.g. lipids.

This study did not go deeper into that subject, but confined itself to question the results of Kapp's method (1984) in comparison to Moosbrugger's method (1992; 1993).

Summing up, one has to take note of the fact that Eq. (28) usually delivers slightly too high S_a concentrations for all media discussed so far, i.e. anaerobic digested sludge and waste-water influent. Thus, in order to optimise the evaluation accuracy, an empirical correction of Eq. (28) either by a constant factor or by changing the equation slope was considered.

The latter is regarded as unsuitable because an extrapolation of the required correction, as found necessary for low S_a concentrations in waste-water influent, resulted in the calculation of increasingly too low S_a values the more those were rising. And this widening gap by far exceeded the quoted 3% deviation for samples of anaerobically digested sludge.

Hence it was decided to introduce an empirical correction of Eq. (28) by a constant factor of minus 14 mg/ℓ which supposedly benefits the accuracy of Kapp's method in any case. This leads to the following suggestion for an improved S_a calculation (Buchauer, 1996):

$$S_a = 131340 \cdot N \cdot VA_{5\text{-}4,meas} / VS - 3.08 \cdot Alk_{meas} - 25 \qquad (29)$$

Nevertheless one has to keep in mind that this correction of Kapp's original method (1984) is merely an empirical manoeuvre, suggested due to experiments with limited experimental systems. The question of how it affects the outcome of other sample systems can only be answered by a systematic comparison with a different analytical method. For this purpose, in this paper, the method of Moosbrugger et al. (1992; 1993) was used.

5 pH point method according to Moosbrugger et al. (1992; 1993)

Principle

The method according to Moosbrugger et al. (1992; 1993) is based on the theory of weak acid/base chemistry. In order to optimise its accuracy the procedure provides an estimate of systematic pH error which may be due to residual liquid junction potential, poor pH probe calibration or other influences. pH points are selected as pairs symmetrical to pK_a of HCO_3^-/CO_2 system (= 6.3) and to pK_a of HAc/ Ac^- system (= 4.75) in such a way that the pH correction is still applicable and avoids increasing the first pH too much. Thus pH 6.7, pH 5.9, pH 5.2 and pH 4.3 are selected. An empirical condition $C_T/S_a > 2$ is introduced to guarantee proper functioning of the pH correction. However, no reason was found to theoretically underline this requisite. The method also offers a possibility to consider the influence of known concentrations of other weak acid/bases (in addition to the carbonate and S_a system). Consequently the ammonium, phosphate and sulphide concentrations are included in the algorithm and thus their effect upon S_a is eliminated. Besides the S_a analysis the procedure enables the determination of $H_2CO_3^*$ alkalinity, too. The calculation of both S_a concentration and $H_2CO_3^*$ alkalinity is elaborate and hence it is recommended to use a computer program, as e.g. available in Moosbrugger et al. (1992).

Analysis description

Detailed descriptions of the very method are available in Moosbrugger et al. (1992; 1993). Hence it is considered unnecessary to repeat the complete instruction. Basically acid is added stepwise in order to reach the four pH values cited above. It is not compulsory yet to reach each of those pH values exactly, an approach within ± 0.1 of the respective pH is sufficient. In case the initial pH is below 6.7 a base is required for the initial titration. Amounts of titrant and corresponding pH are recorded. Ideally, in order to ensure optimum accuracy, temperature (°C), total dissolved solids TDS (mg/l) or specific conductivity (mS/m) and concentration of free and saline ammonia (mg/l as N), inorganic phosphate (mg/l as P) and sulphide (mg/l as S) are determined, too, and entered into the S_a calculation program.

Control of the method

In Moosbrugger et al. (1993) the method is tested with effluents from UASB reactors treating brewery (lauter tun) and wine distillery wastes. The UASB reactor was operated both under high-load and low-load conditions. Hence S_a ranged from 10 mg/l to 1 200 mg/l. Additionally these samples were augmented with different concentrations of acetic acid, thus obtaining S_a concentrations stepwise increasing from 100 mg/l to maxima around 1 000 mg/l. Comparison with the colorimetric method of Montgomery et al. (1962) yielded close correlation.

De Haas and Adam (1995) undertook a detailed study into S_a determination via titration, colorimetric method and HPLC analysis. Both waste water, primary sludge and digested sludge samples were analysed. The best correlation between these three methods was found for primary sludge, with titration slightly tending to overpredict S_a concentrations. Using anaerobically digested sludge under process failure and start-up conditions (pH < 6.0; S_a > 1 500 mg/l) titration delivered 15% higher S_a than either of the other methods. Approximately 20% of the results were considered outliers. Generally these deviations only occured where S_a exceeded 2 000 mg/l. It was speculated that interference from partially hydrolysed proteins or peptides may have contributed to such deviations. The analysis of waste water again resulted in a close correlation between titration and colorimetric methods, both, however, ca. 10 mg/l above HPLC concentrations. HPLC measurement comprised acetic acid, propionic acid and butyric acid. The detection limit for S_a was found to be 5 mg/l, even in the case of $C_T/S_a < 2$.

Experimental

For analysis of S_a by means of titration, both the recommendations of Kapp (1984) and Moosbrugger et al. (1992; 1993) were adhered to, respectively. In order to guarantee optimal accuracy of acid dosage a titroprocessor, Mettler DL40GP, was used. This allowed dosage of minute amounts of acid as small as 0.005 ml. The original volume of any sample analysed was generally 50 ml. In the case of waste water and activated sludge the filtered samples remained undiluted. In the case of primary sludge, 25 ml filtrate was diluted with 25 ml deionised water. The titrants were 0.1 N HCl acid and 0.1 N NaOH. For filtration Whatman glass filters were used. Samples of primary sludge were centrifuged for 3 min before filtration. NH_4-N and PO_4-P were determined photometrically (Dr. Lange test no. LCK 303, LCK 350, respectively), TDS (Deutsche Einheitsverfahren, 1987) and temperature were measured and all these parameters considered for the 5 pH point titration procedure according to Moosbrugger et al. (1992; 1993). Sulphide was generally neglected.

The samples comprised all typical influent media usually present at WWTPs. Waste-water samples were always taken downstream of the influent screen; primary sludge samples were withdrawn directly from the collecting hopper of primary sedimentation tanks; activated sludge samples were drawn from the return sludge of aerobic stages of BNR activated sludge plants. High-load activated sludge samples were taken out of the return sludge from the first stage of 2-stage plants. The sludge age of high-load sludge samples varied between 0.3 d and 1.5 d, and for low-load sludge samples it varied between 7 d and 35 d.

A total of eleven different domestic WWTPs was selected, samples drawn over the period of about one year, conveyed to the laboratory and analysed. At the time of first analysis most initial S_a concentrations of activated sludge samples were near zero, initial S_a of waste water was in the range of ca. 20 to 40 mg/l, and initial S_a of primary sludge was highest (mean ca. 1 000 mg/l). After the first analysis samples were often stored anaerobically for up to 14 d at constant temperature, varying, however, for different experiments between 5°C and 20°C, and analysed again. This explains the high S_a concentrations in some of the waste water and sludge samples depicted hereafter. Further special handling of the samples during storage seemed unnecessary because a change in the quality of the samples was highly desired. Thus it was possible to analyse samples characterised by a wide range of distinctive concentrations of S_a, CO_2, etc..

TABLE 1
RESULTS FOR S_A DETERMINATIONS ACCORDING TO EQ. (29) AND THE 5 pH POINT PROCEDURE. X = MEAN; S = STANDARD DEVIATION; n = NUMBER OF OBSERVATIONS

Medium		Kapp (1984) Eq. (29)	Moosbrugger (1992; 1993) 5 pH point procedure	Correlation r^2
Waste water	X	51	52	0.9502
	S	43	37	
	n	22	22	
Primary sludge	X	1241	1221	0.9980
	S	954	923	
	n	24	24	
High-load activated sludge with sludge age 0.3 d - 1.5 d	X	210	210	0.9979
	S	317	332	
	n	26	26	
Low-load activated sludge with sludge age 7 d - 35 d	X	76	77	0.9930
	S	109	102	
	n	33	33	

TABLE 2
CHARACTERISTICS OF THE TITRATED SAMPLES. X = MEAN; S = STANDARD DEVIATION; n = NUMBER OF OBSERVATIONS

Medium		Temperature °C	NH_4^+-N mg/ℓ	PO_4^{3-}-P mg/ℓ
Waste water	X	15.5	48.6	5.3
	S	1.6	19.0	3.6
	n	22	22	22
Primary sludge	X	12.6	145.7	19.6
	S	4.4	130.0	13.6
	n	24	24	24
High-load activated sludge with sludge age 0.3 d - 1.5 d	X	14.0	40.3	11.7
	S	2.7	37.9	15.8
	n	26	26	26
Low-load activated sludge with sludge age 7 d - 35 d	X	15.6	18.6	21.4
	S	1.8	18.1	28.2
	n	33	33	33

Results and discussion

Comparison of method handling

Some general requisites proved to be indispensable for both procedures to obtain reliable results:

- Very accurate handling of titrant dosage: It is recommended not to exceed titrant increments of 0.01 mℓ. Furthermore automatic titroprocessors can improve accuracy simply because they avoid overdosage, when a certain target pH point is required. Sometimes this can be very difficult and time-consuming by manual titration.
- Exact calibration of the pH probe.
- Exact determination of the titrant normality.
- If possible, avoidance of storage, agitation or stirring of the sample before analysis, since this usually results in S_a losses due to stripping effects.
- Constant mixing of sample and added titrant to minimise exchange of CO_2 with the atmosphere once the titration proceeds.

If the analysis is conducted manually the method according to Moosbrugger et al. (1992; 1993) is regarded somewhat easier, because it does not require reaching target pH points exactly, but allows a tolerance of ± 0.1 pH units. On the other hand this procedure involves titration to 4 pH points whereas the method of Kapp (1984) involves 3 pH points only, which is one reason why the latter analysis can be done somewhat faster. However, should the titration be conducted automatically, these aspects become irrelevant.

A more decisive disadvantage of the method according to Moosbrugger et al. (1992; 1993) is its necessity to handle both a strong base and a strong acid. The initial pH of the samples is frequently below pH 6.7 (= first target pH point in the 5 pH point procedure); thus the procedure requires a pH increase to begin with. The method according to Kapp (1984) has its first target pH point at 5.0 which is so low that a base is actually never in demand. A strong acid is generally sufficient for the needs of waste water and sludge analysis.

It should be noted that the method of Kapp (1984) is aimed only at determination of S_a; the Moosbrugger method, however, is aimed at measurement of carbonate alkalinity, too.

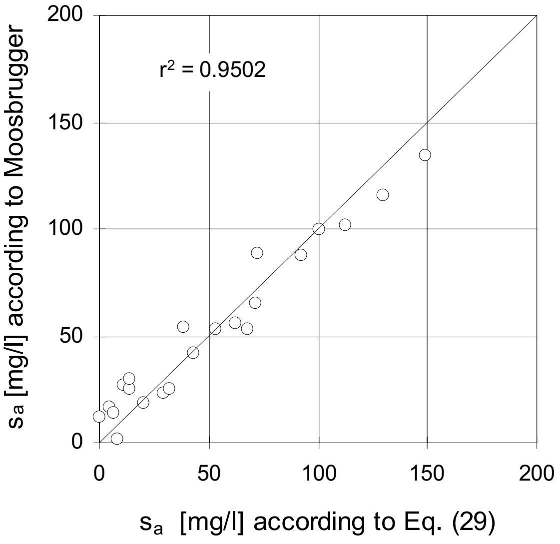

Figure 3

S_a concentrations in wastewater - plot of results for

- *method according to Kapp (1984), Eq. (29), and*
- *method according to Moosbrugger et al. (1992; 1993)*

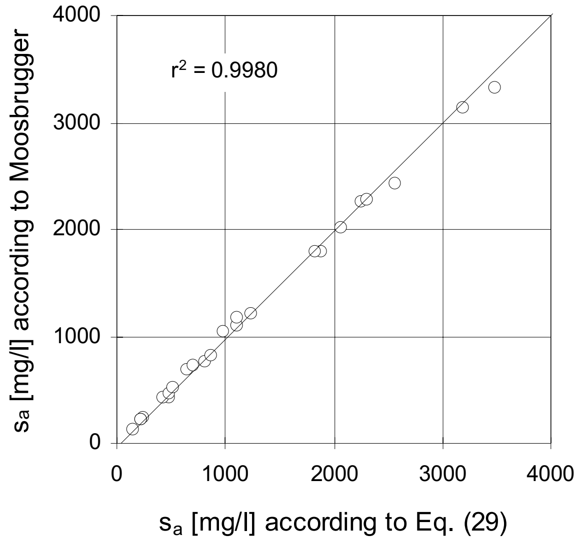

Figure 4

S_a concentrations in primary sludge - plot of results for

- *method according to Kapp (1984), Eq. (29), and*
- *method according to Moosbrugger et al. (1992; 1993)*

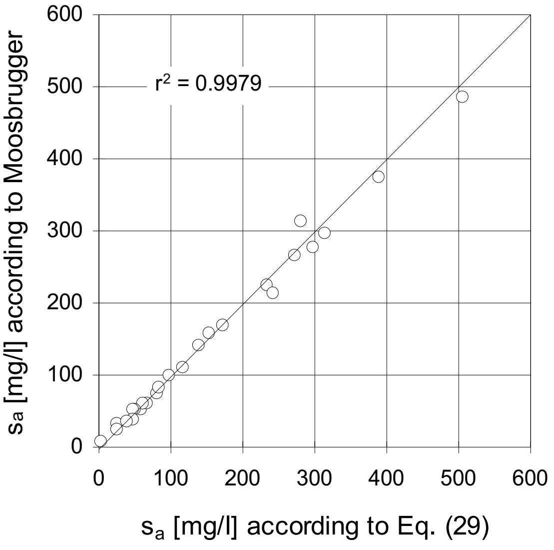

Figure 5

S_a concentrations in high-load activated sludge - plot of results for

- *method according to Kapp (1984), Eq. (29), and*
- *method according to Moosbrugger et al. (1992; 1993)*

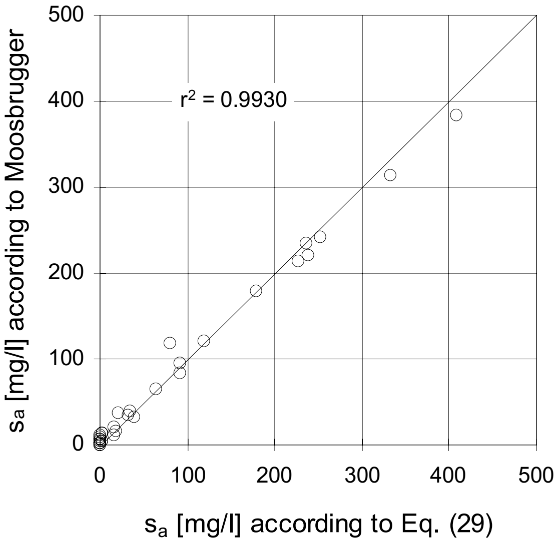

Figure 6

S_a concentrations in low-load activated sludge - plot of results for

- *method according to Kapp (1984), Eq. (29), and*
- *method according to Moosbrugger et al. (1992; 1993)*

Comparison of method correlation between the procedure of Kapp (1984) and the procedure of Moosbrugger et al. (1992; 1993)

The general suitability of both methods to determine S_a was not a major focus of this work. As described before, both procedures have been tested extensively and compared to steam distillation, colorimetric methods and HPLC analysis by various other authors. Thus this paper confines itself to correlating the two methods with one another.

The results of Kapp's S_a analysis via Eq. (29) vs. the 5 pH point titration according to Moosbrugger et al. (1992; 1993) are summarised in Table 1, Fig. 3, Fig. 4, Fig. 5 and Fig. 6. Characteristics of the titrated samples are compiled in Table 2.

In case of waste water there is a minimal tendency of Eq. (29) to underestimate S_a by 1 mg/l. Even though correlation for this medium is lowest, $r^2 = 0.95$ still is high. Moreover, an error as small as 1 mg/l is considered irrelevant for ordinary purposes. For primary sludge Eq. (29) delivers a mean S_a of 1241 mg/l. The method of Moosbrugger (1992; 1993) delivers a mean S_a of 1221 mg/l. This deviation of 1.6% is minimal again. The correlation between the two methods of $r^2 = 0.9980$ is higher than for any other type of sample.

Both high- and low-load biological sludge proved almost equivalent to the high correlation yielded with primary sludge. Virtually no deviations between the two methods were found, even though mean concentrations were as high as 76 mg/ℓ and 210 mg/ℓ, respectively.

Conclusions

The 4 pH point titration procedure according to Kapp (1984) and the 5 pH point titration procedure according to Moosbrugger et al. (1992; 1993) are considered to be equivalent in terms of accuracy to determine S_a concentrations in influents to waste-water treatment processes, i.e. waste water, primary sludge, high- and low-load activated sludge.

Handling of both methods is rather simple but requires carefulness. It seems advantageous that the method according to Kapp (1984) firstly does not need a base and secondly enables S_a calculation by a simple explicit equation (Eq. (29)). The method of Moosbrugger et al. (1992; 1993) is superior if not only S_a but carbonate alkalinity, too, is required.

Generally it was observed that for all media under investigation results are virtually identical as long as S_a is below ca. 200 mg/ℓ. If S_a rises higher there is a minimal tendency of the method according to Kapp to predict slightly higher S_a concentrations, e.g. for primary sludge with a mean S_a = 1 230 mg/ℓ average deviations amount to + 20 mg/ℓ. Sensitivity investigations using the procedure of Moosbrugger et al. (1992; 1993), varying ammonium, phosphate, temperature and TDS within possible ranges, could in no case explain these small differences. Hence the reason for S_a differences between the two methods seems to be system-endemic. Moreover, one can indirectly conclude for the media investigated in this paper that there is obviously no need to consider these additional parameters in calculating S_a.

A literature review indicates that both methods tend to minimally overpredict S_a. Why this is the case is not yet clear, but it should be kept in mind when considering titration results.

Acknowledgement

This work was partially developed in the course of a Ph.D. thesis, which was financially supported by a grant from the Vereinigung Österreichischer Industrieller, Landesgruppe Tirol. Additionally thanks are due to Prof Dr Ingerle of the University of Innsbruck, Department of Civil Engineering, Institute of Environmental Engineering, for giving me the opportunity to conduct the necessary laboratory work at his institute.

References

BRÜCKNER H (1995) Vergleich verschiedener Abwasseranalysenmethoden. *Das Gas- und Wasserfach (gwf) Wasser - Abwasser* **136** (9) 474-477.

BUCHAUER K (1996) Biologische Hydrolyse zur Optimierung von Bio-P (Biological Hydrolysis for the Optimization of Bio-P). Ph.D. thesis, University of Innsbruck, Dept. of Civil Engineering, Institute of Environmental Engineering, 297 pp.

BUCHAUER K (1997) Titrationsverfahren in der Abwasser- und Schlammanalytik zur Bestimmung von flüchtigen organischen Säuren. *Das Gas- und Wasserfach (gwf) Wasser - Abwasser* **138** (6) 313-320.

COLIN F (1984) *Anaerobic Digestion and Carbohydrate Hydrolysis of Waste.* Elsevier Applied Science Publishers.

DE HAAS DW and ADAM N (1995) Use of a simple titration procedure to determine $H_2CO_3^*$ alkalinity and volatile fatty acids for process control in waste-water treatment. *Water SA* **21** (4) 307-318.

DEUTSCHE EINHEITSVERFAHREN (1971) *Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung.* DEV H21, Bestimmung der mit Wasserdampf flüchtigen organischen Säuren, 1-2.

DEUTSCHE EINHEITSVERFAHREN (1987) *Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung.* DEV H1, Bestimmung des Gesamttrockenrückstandes, des Filtrattrockenrückstandes und des Glührückstandes, 1-8.

DILALLO R and ALBERTSON DE (1961) Volatile acids by direct titration. *JWPCF* **33** (4) 356-365.

HENZE M, GUJER W, MINO T, MATSUO T, WENTZEL MC and MARAIS GvR (1995a) Wastewater and biomass characterization for the activated sludge model No. 2: Biological phosphorus removal. *Water Sci. Technol.* **31** (2) 13-23.

HENZE M, GUJER W, MINO T, MATSUO T, WENTZEL MC and MARAIS GvR (1995b) *Activated Sludge Model No. 2.* IAWQ Scientific and Technical reports, No. 3, IAWQ, London.

KAPP H (1984) *Schlammfaulung mit hohem Feststoffgehalt.* Stuttgarter Berichte zur Siedlungswasserwirtschaft, Band 86, Oldenbourg Verlag, München, 300 pp.

KAPP H (1992) On-line-Messung der organischen Säuren. *Korrespondenz Abwasser* **39** (7) 999-1004.

MC GHEE TJ (1968) A method for approximation of the volatile acid concentrations in anaerobic digesters. *Water and Sewage Works* **115** 162-166.

MONTGOMERY HAC, DYMOCK JF and THOM NS (1962) The rapid colorimetric determination of organic acids and their salts in sewage sludge liquor. *The Analyst* **87** 947-952.

MOOSBRUGGER RE, WENTZEL MC, EKAMA GA and MARAIS GvR (1992) Simple Titration Procedures To Determine $H_2CO_3^*$ Alkalinity And Short-chain Fatty Acids In Aqueous Solutions Containing Known Concentrations Of Ammonium, Phosphate And Sulphide Weak Acid/Bases. WRC Report No. TT 57/92, UCT Research Report W 74.

MOOSBRUGGER RE, WENTZEL MC, LOEWENTHAL RE, EKAMA GE and MARAIS GvR (1993) Alkalinity measurement: Part 3 - A 5 pH point titration method to determine the carbonate and SCFA weak acid/bases in aqueous solution containing also known concentrations of other weak acid/bases. *Water SA* **19** (1) 29-40.

NORDMANN W (1977) Die Überwachung der Schlammfaulung. *KA-Informationen für das Betriebspersonal,* Beilage zur *Korrespondenz Abwasser* 3/77.

POWELL GE and ARCHER DB (1989) On-line titration method for monitoring buffer capacity and total volatile fatty acid levels in anaerobic digesters. *Biotechnol. and Bioeng.* **33** 570 - 577.

RIPLEY LE, BOYLE JC and CONVERSE JC (1986) Improved alkalimetric monitoring for anaerobic digestion of high-strength wastes. *JWPCF* **58** (5) 406-411.

SCHEER H (1994) Vermehrte biologische Phosphorelimination - Bemessung und Modellierung in Theorie und Praxis. Veröffentlichungen des Institutes für Siedlungswasserwirtschaft und Abfalltechnik der Universität Hannover, Heft 88, 276 pp.

SCHEER H (1995) *Vermehrte biologische Phosphorelimination in der Abwasserreinigung.* Abschlußbericht eines Erfahrungsaustausches deutschsprachiger Hochschulen, Mitteilungen der Oswald-Schulze-Stiftung, Heft 19, 174 pp.

VAN HAANDEL AC and MARAIS GvR (1981) Nitrification And Denitrification In The Activated Sludge Process. Research Report No. W 39, Dept. of Civil Eng., Univ. of Cape Town.

WENTZEL MC, LÖTTER LH, LOEWENTHAL RE and MARAIS GvR (1986) Metabolic behaviour of *Acinetobacter spp.* in enhanced biological phosphorus removal - a biochemical model. *Water SA* **12** (4) 209-224.