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

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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 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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Ac⁻</td>
<td>acetate CH₃ COO⁻</td>
</tr>
<tr>
<td>Alk_{HCO₃}</td>
<td>alkalinity (mmol/l) due to HCO₃⁻/CO₂ buffer</td>
</tr>
<tr>
<td>Alk_{meas}</td>
<td>measured alkalinity (mmol/l)</td>
</tr>
<tr>
<td>Alk₀</td>
<td>alkalinity (mmol/l) due to S₀ buffer</td>
</tr>
<tr>
<td>BNR</td>
<td>biological nutrient removal</td>
</tr>
<tr>
<td>CH₃ COOH</td>
<td>acetic acid</td>
</tr>
<tr>
<td>CO₂⁻</td>
<td>concentration of CO₂ (mol/l)</td>
</tr>
<tr>
<td>[CO₂⁻]</td>
<td>concentration of carbonate (mol/l)</td>
</tr>
<tr>
<td>C_r</td>
<td>carbon dioxide (mg/l)</td>
</tr>
<tr>
<td>CO₂</td>
<td>carbon dioxide (mg/l)</td>
</tr>
<tr>
<td>[H₂ CO₃⁺]</td>
<td>[H₂ CO₃⁻] + [HCO₃⁻] + [CO₃²⁻]</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>HAc</td>
<td>acetic acid (mg/l)</td>
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<tr>
<td>HCO₃⁻</td>
<td>bicarbonate (mg/l)</td>
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<td>[HCO₃⁻]</td>
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<td>concentration of CO₂⁻ (mol/l)</td>
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<tr>
<td>[H₂ CO₃⁺]</td>
<td>[CO₂ dissolved] + [H₂ CO₃⁻] (mol/l)</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatograph</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>first dissociation step of phosphoric acid</td>
</tr>
<tr>
<td>n</td>
<td>number of observations</td>
</tr>
<tr>
<td>N</td>
<td>normality (mmol/l)</td>
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<tr>
<td>NH₄⁺</td>
<td>ammonia (mg/l)</td>
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<tr>
<td>NH₄⁻⁻</td>
<td>ammonium nitrogen (mg/l)</td>
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<td>[NH₄⁺]</td>
<td>concentration of NH₄⁺ (mmol/l)</td>
</tr>
<tr>
<td>pH₀⁺</td>
<td>dissociation constant</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>phosphate phosphorus (mg/l)</td>
</tr>
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r = correlation coefficient
S = standard deviation
S₀ = 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_{5-4,HCO₃} = volume of acid (ml) required to titrate a sample from pH 5.0 to pH 4.0 due to HCO₃⁻/CO₂ buffer
VA_{4,3,meas} = measured volume of acid (ml) required to titrate a sample from initial pH to pH 4.3
VA_{4,3,meas} = measured volume of acid (ml) required to titrate a sample from pH 5.0 to pH 4.0
VA_{5-4,meas} = measured volume of acid (ml) required to titrate a sample from pH 5.0 to pH 4.0 due to S₀ 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 (CH₃ COOH). In the literature, the terms volatile fatty acids (VFA), short chain fatty acids (SCFA) or S₀ (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).
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**: Most 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 affects acid consumption apart from the acetate subsystem. Moreover, the pK 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 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 at ca. 8.95 which is far removed from the pH range under discussion. Similarly HPO\(_4\)/HPO\(_4^{2-}\) (pK 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 \( \mu \)m 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:

\[
VA_{5-4,s} = VA_{5-4,meas} - VA_{5-4,HCO3} \quad (1)
\]

For an estimation of \( VA_{5-4,s} \), 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) \((r = 0.9999):\)

\[
VA_{5-4,s} = -0.0283 + 0.09418 \cdot S_a / 60 \quad (2)
\]

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):
For an estimation of $VA_{\text{NH}_4\text{HCO}_3}$, Kapp (1984) titrated 20 ml of an NH$_4$HCO$_3$ solution at different concentrations (NH$_4^+$-N varied between ca. 400 and 10 000 mg/l) with 0.1 N strong acid and found $(r = 0.9969)$:

$$VA_{\text{NH}_4\text{HCO}_3} = 0.044875 + 0.000335 \cdot \text{NH}_4^+\text{-N} \quad (5)$$

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

$$VA_{\text{NH}_4\text{HCO}_3} = 0.1/N \cdot (0.044875 + 0.000335 \cdot \text{NH}_4^+\text{-N}) \cdot VS/20 \quad (6)$$

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 $(r = 0.997)$:

$$[\text{HCO}_3^-] = [\text{NH}_4^+\text{-N}] = \text{NH}_4^+\text{-N}/14 \quad (7)$$

Eq. (7) $\rightarrow$ Eq. (6) yields:

$$VA_{\text{NH}_4\text{HCO}_3} = 0.1/N \cdot (0.044875 + 0.000335 \cdot [\text{HCO}_3^-]) \cdot VS/N \quad (8)$$

For the first $S_a$ approximation Kapp (1984) assumes that the measured alkalinity of a sample is only caused by the HCO$_3^-/\text{CO}_2^-$ buffer. Mathematically this means:

$$\text{Alk}_{\text{HCO}_3} = \text{Alk}_{\text{meas}} = [\text{HCO}_3^-] \quad (10)$$

where:

$$\text{Alk}_{\text{meas}} = VA_{\text{HCO}_3\text{meas}} \cdot N \cdot 1000 / VS \quad (11)$$

Eq. (10) $\rightarrow$ Eq. (9) yields:

$$VA_{\text{HCO}_3\text{meas}} = 0.05 \cdot (0.044875 + 0.000469 \cdot [\text{HCO}_3^-]) \cdot VS/N \quad (12)$$

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

$$-0.0001415 \cdot VS/N + 0.00002345 \cdot VS/N = \text{VA}_{\text{HCO}_3\text{meas}} = 0.0283 + 0.09418 \cdot S_a/60 \cdot VS/20 \quad (14)$$

Rearranging Eq. (13):

$$-0.000078483 \cdot S_a = \text{VA}_{\text{HCO}_3\text{meas}} \cdot 0.00002345 - \text{Alk}_{\text{HCO}_3} \cdot VS/N \quad (15)$$

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

$$S_a = 127416 \cdot N \cdot VA_{\text{HCO}_3\text{meas}} / VS - 2.99 - \text{Alk}_{\text{HCO}_3} - 10.6 \quad (17)$$

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:

$$\text{Alk}_{\text{HCO}_3} = \text{Alk}_{\text{meas}} - \text{Alk}_{\text{HCO}_3} \quad (18)$$

To quantify Alk$_{\text{HCO}_3}$ Kapp (1984) considered that by titration to pH 4.3 ca. 60% of acetate CH$_3$COO$^-$ is present as CH$_3$COOH. Thus:

$$\text{Alk}_{\text{HCO}_3} = 0.6 \cdot S_a/60 = 0.01 \cdot S_a \quad (19)$$

With Eq. (17), Eq. (18) and Eq. (19) it becomes possible to derive a second approximation for Alk$_{\text{HCO}_3}$:

$$\text{Alk}_{\text{HCO}_3} = \text{Alk}_{\text{meas}} - 0.01 \cdot S_a \quad (20)$$

Eq. (17) $\rightarrow$ Eq. (20) yields:

$$\text{Alk}_{\text{HCO}_3} = \text{Alk}_{\text{meas}} - 1274.16 \cdot N \cdot VA_{\text{HCO}_3\text{meas}} / VS + 0.03 \cdot \text{Alk}_{\text{meas}} + 0.11 \quad (21)$$

Eq. (22) $\rightarrow$ Eq. (16) delivers the second approximation for $S_a$:

$$S_a = \frac{127416 \cdot N \cdot VA_{\text{HCO}_3\text{meas}} / VS + 1.03 \cdot \text{Alk}_{\text{meas}} + 0.11}{2.99} \quad (23)$$

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$_{\text{HCO}_3}$ is derived, which is used to further improve the approximation of $S_a$.

Eq. (24) $\rightarrow$ Eq. (20) yields:

$$\text{Alk}_{\text{HCO}_3} = \frac{131226 \cdot N \cdot VA_{\text{HCO}_3\text{meas}} / VS - 3.08 \cdot \text{Alk}_{\text{meas}} - 10.9}{2.99} \quad (28)$$

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.
proved to deliver $S_a$ concentrations minimally above the theoretical ones (Kapp, 1992). Accuracy he claimed to be ± 5 mg/l distillation (Kapp, 1984). $S_a$ concentrations obtained by titration digested sludge, which were analysed by titration and steam distillation, without giving detailed statistical parameters. In addition she found very good correlation coefficient was $r = 0.9965$.

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):

$$S_a = 131340 \cdot N \cdot VA_{s,\text{meas}} / VS - 3.08 \cdot \text{Alk}_{\text{meas}} - 25 \quad (29)$$

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 errors 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 \( \text{HCO}_3^-/\text{CO}_2^- \) system (= 6.3) and to \( pK_a \) of \( \text{HAc}/\text{Ac}^- \) 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 \( C_i/S_i > 2 \) 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 \( \text{H}_2\text{CO}_3^- \) alkalinity, too. The calculation of both \( S_a \) concentration and \( \text{H}_2\text{CO}_3^- \) 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 \( \pm 0.1 \) 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 occurred 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 \( C_i/S_i < 2 \).

**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 titrtprocessor 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. \( \text{NH}_4^-\text{N} \) and \( \text{PO}_4^-\text{P} \) 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 \( S_a \), \( \text{CO}_2^- \), etc..
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 m\(^\text{l}\). Furthermore automatic titroprocessors can improve accuracy simply because they avoid overdose, 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 \(S_e\) 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 \(S_e\); the Moosbrugger method, however, is aimed at measurement of carbonate alkalinity, too.

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

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water</td>
<td>X 51</td>
<td>52</td>
<td>0.9502</td>
</tr>
<tr>
<td></td>
<td>S 43</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n 22</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Primary sludge</td>
<td>X 1241</td>
<td>1221</td>
<td>0.9980</td>
</tr>
<tr>
<td></td>
<td>S 954</td>
<td>923</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n 24</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>High-load activated sludge</td>
<td>X 210</td>
<td>210</td>
<td>0.9979</td>
</tr>
<tr>
<td>with sludge age 0.3 d - 1.5 d</td>
<td>S 317</td>
<td>332</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n 26</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Low-load activated sludge</td>
<td>X 76</td>
<td>77</td>
<td>0.9930</td>
</tr>
<tr>
<td>with sludge age 7 d - 35 d</td>
<td>S 109</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n 33</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2
CHARACTERISTICS OF THE TITRATED SAMPLES. \(X = \text{MEAN}; S = \text{STANDARD DEVIATION}; n = \text{NUMBER OF OBSERVATIONS}

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

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 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 Sₐ 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 Sₐ calculation by a simple explicit equation (Eq. (29)). The method of Moosbrugger et al. (1992; 1993) is superior if not only Sₐ but carbonate alkalinity, too, is required.

Generally it was observed that for all media under investigation results are virtually identical as long as Sₐ is below ca. 200 mg/l. If Sₐ rises higher there is a minimal tendency of the method according to Kapp to predict slightly higher Sₐ concentrations, e.g. for primary sludge with a mean Sₐ = 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 Sₐ 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 Sₐ.

A literature review indicates that both methods tend to minimally overpredict Sₐ. 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.

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