Accurate on-site volatile fatty acids (VFA) measurement in anaerobic digestion – verification of a new titrative method

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Abstract
This paper reports on the development and verification of a new simple, rapid and accurate titration method suitable for on-site measurement of volatile fatty acids (VFA) and carbonate alkalinity in anaerobic reactors. The method takes into account the effects of the phosphate, ammonium, sulfate, and sulfide weak acid subsystems on titration results. The method involves eight pH observations and typically the full procedure takes 15 minutes. To evaluate the accuracy of the method three industrial anaerobic digesters effluents were tested. The technique was verified by adding known aliquots of acetic acid to effluents previously measured for VFA and carbonate alkalinity using the method. After the addition, the VFA concentration was re-measured and the difference between the two results was compared with the amount of acetic acid added. Very high accuracy for VFA measurements (> 97%) plus very good repetition was obtained with all three effluent types. Generally, VFA measurement accuracy increased with VFA concentration. In the typical case of low VFA concentrations accompanied by very high carbonate alkalinity, the raw sample should be “spiked” with a known amount of acetic acid in order to increase measurement accuracy.

Keywords
VFA measurement, titration method, anaerobic reactors, alkalinity measurement

INTRODUCTION
Typical control strategy in methanogenic anaerobic reactors is to maintain a relatively low concentration of volatile fatty acids (VFA) and a pH range of 6.6 < pH < 7.4. Normally in such reactors the carbonate system forms the main weak-acid system responsible for maintaining the pH around neutrality, while the VFA systems (acetic, propionic, and butyric acids) are the major cause for pH decline. Under stable operating conditions, the H₂ and acetic acid formed by acidogenic and acetogenic bacterial activity are utilized immediately by the methanogens and converted to methane. Consequently, the VFA concentration is typically very low, carbonate alkalinity is not consumed and the pH is stable. Conversely, under overload conditions or in the presence of toxins or inhibitory substances, the activity of the methanogenic and acetogenic populations is reduced causing an accumulation of VFA which in turn increases the total acidity in the water, reducing pH. The extent of the pH drop depends on the \( \text{H}_2\text{CO}_3^+ \) alkalinity concentration. In medium and well-buffered waters (typically the case in anaerobic digestion), high concentrations of VFA would have to form in order to cause a detectable pH drop, by which time reactor failure would have occurred. Therefore, pH measurement cannot form the sole control means, and direct measurement of either (or both) VFA or \( \text{H}_2\text{CO}_3^+ \) alkalinity concentration is necessary.

Measurement of \( \text{H}_2\text{CO}_3^+ \) alkalinity in a mixture of weak acid subsystems cannot be executed via direct titration to the \( \text{H}_2\text{CO}_3^+ \) equivalence point (around pH 4.5) because no clear end point can be defined. Characterization of the carbonate subsystem can be carried out using an inorganic carbon analyzer, however this instrument apart from not being generally available on-site, is prone to gross inaccuracy due to CO₂ loss. Therefore, VFA concentration is the most practical measurement for
monitoring any indication of stress in an anaerobic treatment system. If the system is not rectified at an early stage, failure is likely.

Currently, VFA can be measured by straight distillation, steam distillation, a colorimetric technique or using gas chromatography. However, all these methods are time consuming, and except for the latter, not very accurate. Gas chromatography requires specialized equipment and a dedicated operator and is generally not available on-site. In terms of simplicity, speed and cost-effectiveness it is generally accepted that titrative methods are superior for the purpose of routine monitoring and control. During the last 4 decades, a considerable number of quantitative and semi-quantitative titrimetric methods have been proposed for the measurement of either VFA or \( \text{H}_2\text{CO}_3^* \) concentrations or both. Most of these methods are reviewed elsewhere, and found to be either too complicated to execute or too approximate to serve for accurate control (Lahav, submitted). A new method was recently developed requiring eight pH observations used within a mathematical model to determine VFA and \( \text{H}_2\text{CO}_3^* \) alkalinity (Lahav et al., 2002). In contrast to previous titrative methods, the new method can be applied generally (irrespective of the VFA / carbonate species ratio) and possesses both self-assessment and self-rectification mechanisms of the output data for quality control purposes.

Initial verification of the model using both various laboratory made solutions and an effluent from an operating industrial treatment plant can be found elsewhere (Lahav et al., 2002). In this paper, the feasibility and accuracy of the method was further assessed by applying the method to three industrial anaerobic reactors. In order to test the method at various VFA and carbonate alkalinity compositions, increasing aliquots of acetic acid were added to all waters and the samples were measured again. The difference between this measurement (from which the known aliquot concentration is subtracted) and the VFA concentration in the original sample was used to determine the accuracy of the analysis. Detailed guidelines for correct execution of the method can be found elsewhere (Lahav et al., 2002).

**MODEL DERIVATION**

The model is an extension of the “5 - point method”, an approach proposed by Moosbrugger et al. (1993). The basic model involves equating a mass balance for alkalinity in terms of the volume of standard strong acid titrant added (equation 1) to a mass balance of alkalinity in terms of all proton accepting species likely to be present in an anaerobic reactor (equation 2).

\[
M_{\text{total alk}}(x) = V_e \cdot C_a - V_x \cdot C_a
\]

Where: \( M_{\text{total alk}}(x) = \) total mass of alkalinity after the addition of \( V_x \) ml of standard strong acid (mol), \( V_e = \) the unknown volume of standard strong acid to be added to the alakilimetric end point (l), \( V_x = \) the volume of standard strong acid added to a point \( x \) with pH equal to \( \text{pH}_x \) (l), and \( C_a = \) concentration of standard strong acid titrant (mol/l).

\[
M_{\text{total alk}}(x) = \{[\text{HCO}_3^-]_x + 2[\text{CO}_3^{2-}]_x + [\text{A}^-]_x + [\text{HS}^-]_x + 2[S^{2-}]_x + [\text{NH}_3]_x + 3[\text{PO}_4^{3-}]_x + 2[\text{HPO}_4^{2-}]_x + [\text{H}_2\text{PO}_4^-]_x + [\text{OH}^-]_x - [\text{H}^+]_x\} \cdot (V_x + V_s)
\]

Where \([y]_x\) indicates molar concentration of species \( y \) after addition of \( x \) ml of standard acid (mol/l), \([\text{A}^-]\) = dissociated short chain VFA species concentration (mol/l) and \( V_s = \) volume of sample (l).

Equation 2 can be reformulated in terms of total weak acid species concentrations using equilibrium equations for the weak acid subsystems and mass balance equations for each of the weak acid
subsystems (equations 3 to 7 below). For brevity, only the VFA and carbonate subsystems are given as the other subsystems follow the same approach. For the carbonate subsystem:

\[ (H^+)_x \cdot [HCO_3^-]_x / [H_2CO_3]_x = K'_C1 \]  
(3)

\[ (H^+)_x \cdot [CO_3^{2-}]_x / [HCO_3^-]_x = K'_C2 \]  
(4)

\[ C_T \cdot V_s/(V_x + V_s) = [H_2CO_3^+]_x + [HCO_3^-]_x + [CO_3^{2-}]_x \]  
(5)

Where \( (\cdot) \) denotes activity, \([ \cdot ]\) denotes molarity and \( K' \) equals apparent equilibrium constant after adjustment for Debye–Huckel effects.

For the VFA subsystem (all the VFA are considered to constitute a single weak acid system with an equilibrium constant \( K_a \) because they all have pK values that are very close to each other):

\[ (H^+)_x \cdot [A^-]_x / [HA]_x = K'_a \]  
(6)

\[ A_T \cdot V_s/(V_x + V_s) = [HA]_x + [A^-]_x \]  
(7)

Solving for \( C_T \) from equations 3, 4 and 5 and for \( A_T \) from equations 6 and 7 respectively gives the desired equations:

\[ [HCO_3^-]_x = C_T \cdot V_s/(V_x + V_s) / \{1 + K'_C2 / (H^+)_x + (H^+)_x / K'_C1\} \]  
(8)

\[ [CO_3^{2-}]_x = C_T \cdot V_s/(V_x + V_s) \cdot K'_C2 / \{(H^+)_x + K'_C2 + ((H^+)_x)^2 / K'_C1\} \]  
(9)

\[ [A^-]_x = A_T \cdot V_s/(V_x + V_s) \cdot K'_a / \{(H^+)_x + K'_a\} \]  
(10)

Similar equations are developed for the phosphate, sulfate, sulfide and ammonium proton accepting species. Substituting the equations for each of the species concentration into equation 2 (for example as given in equations 8 to 10 for the carbonate and VFA subsystems) gives an equation for total mass of alkalinity in terms of \( A_T, C_T, P_T, N_T, S_T, SO_4^{2-}, \) and \( pH_x:\)

\[ M_{\text{total alk (x)}} = \{C_T \cdot V_s/(V_x + V_s) \cdot F_{n1}(pH)_x + A_T \cdot V_s/(V_x + V_s) \cdot F_{n2}(pH)_x + P_T \cdot V_s/(V_x + V_s) \cdot F_{n3}(pH)_x + S_T \cdot V_s/(V_x + V_s) \cdot F_{n4}(pH)_x + SO_4^{2-} \cdot V_s/(V_x + V_s) \cdot F_{n5}(pH)_x + N_T \cdot V_s/(V_x + V_s) \cdot F_{n6}(pH)_x + 10^{(14 - pH_x)/f_m - 10\cdot pH_x/f_m} \} \cdot (V_s + V_x) \]  
(11)

Where: \( P_T, S_T, \) and \( N_T \) represent the total phosphate, sulfate and ammonium concentrations, \( f_m=\) monovalent activity coefficient, and \( F_{n1} \) to \( F_{n6} \) are functions of \( pH_x \) and equilibrium constants for the carbonate, acetate, phosphate, sulfide, sulfate and ammonium subsystems.

Equating equations 1 and 11 gives the desired equation linking the mass of alkalinity based on acid added to the mass of alkalinity based on species concentrations:

\[ (V_e - V_x) \cdot C_a = \{C_T \cdot V_s/(V_x + V_s) \cdot F_{n1}(pH)_x + A_T \cdot V_s/(V_x + V_s) \cdot F_{n2}(pH)_x + P_T \cdot V_s/(V_x + V_s) \cdot F_{n3}(pH)_x + S_T \cdot V_s/(V_x + V_s) \cdot F_{n4}(pH)_x + SO_4^{2-} \cdot V_s/(V_x + V_s) \cdot F_{n5}(pH)_x + N_T \cdot V_s/(V_x + V_s) \cdot F_{n6}(pH)_x + 10^{(14 - pH_x)/f_m - 10\cdot pH_x/f_m} \} \cdot (V_s + V_x) \]  
(12)
At each point in the titration (i.e. for each $V_x$ and corresponding $pH_x$), equation 12 includes 3 unknowns: $V_e$, $A_T$ and $C_T$, provided that the phosphate, sulfate, sulfide and ammonium concentrations are measured and temperature and TDS (or EC) are known. Thus, to solve for $V_e$, $A_T$ and $C_T$ only 3 sets of data ($V_x$ and $pH_x$) need to be known. This however leads to poor prediction.

Moosbrugger et al. (1993) developed a titration method for measuring VFA based on making a “first estimate” of $A_T$ and $C_T$. The “first estimate” was obtained by using two pairs of data points recorded symmetrically about $pK_{C_1}$ and $pK_a$ (approximately half a pH unit on either side of the respective $pK$ values). When inserted into equation 12, the data from the four titration points give four equations. Subtracting the equation formed from the fourth data point from that derived from the third, gives an equation in terms of $C_T$ and $A_T$ in which the VFA alkalinity term dominates. Similarly, subtracting the equation formed from the second data point from that derived from the first, gives an equation in terms of $C_T$ and $A_T$ in which the $H_2CO_3^-$ alkalinity term, significantly dominates. Therefore, an error in the first two pH observations would be mainly “absorbed” by the carbonate subsystem minimizing the effect on the VFA calculation. The two new equations are solved to produce the first estimate of $A_T$ and $C_T$.

In the “5-point” approach, assessment and correction of the first estimate was carried out by adding a constant value to all pH observations, using a numerical method. In the new method an improved approach is developed by accurately measuring total alkalinity by a Gran titration and using this value in addition to the first estimate of $A_T$ and $C_T$, to give the final result. The Gran titration requires a further 3 sets ($V_s$, $pH_s$) of points taken at the pH range of 2.4 < $pH$ < 2.7. In this pH region, the species $CO_3^{2-}$, $HCO_3^-$, $A^-$, $PO_4^{3-}$, $HPO_4^{2-}$, $NH_3$, $HS^-$, $S^{2-}$ and $OH^-$ are negligible and equation 11 reduces to:

\[
\text{Total alkalinity}_x = V_e \cdot C_a - V_x \cdot C_a = \{[SO_4^{2-}]_x + [H_2PO_4^-]_x - [H^+]_x\} \cdot (V_x + V_s) \tag{13}
\]

Expressing $SO_4^{2-}$ and $H_2PO_4^-$ as a function of $P_T$, $SO_{4T}$ and equilibrium constants and rearranging terms gives:

\[
C_a \cdot (V_e - V_s) = (SO_{4T} \cdot V_s/(V_s+V_x)) / \{1 + (H^+)_x / K'_{SO4} \} + P_T \cdot V_s/(V_s+V_x) / \{1 + (H^+)_x / K'_{P1} + K'_{P2} / (H^+)_x + K'_{P3} \cdot K'_{P2} / ((H^+)_x)^2\} - 10^{-pHs} \cdot (V_s + V_x) \tag{14}
\]

The left-hand side of equation 14, for which all variables are known is now defined as $F_x$. Plotting $F_x$ vs. $V_x$ gives a linear relationship where the y intercept gives the value of $V_e$.

The assessment of the first estimate of $A_T$ and $C_T$ is effected as follows: $A_T$ and $C_T$ (determined from the first estimate) and $V_e$ (determined from the Gran function analysis) are inserted in equation 12 together with the initial $pH$ value (i.e. where $V_x = 0$). Furthermore, both $A_T$ and $C_T$ are now multiplied by a proportional term ‘x’, to account for inconsistencies in pH observations yielding:

\[
V_e \cdot C_a = \{x \cdot C_T \cdot F_{n1}(pH_0) + x \cdot A_T \cdot F_{n2}(pH_0) + \text{Const}\} \cdot V_s \tag{15}
\]

Where: Const = a constant representing the proton accepting term for the phosphate, sulfide, ammonium and water subsystems at the initial pH ($pH_0$).

The value of $x$ gives an assessment of the first estimate for $A_T$ and $C_T$. The closer $x$ is to unity, the better the first estimate conforms to the accurately measured $V_e$. An acceptable value for $x$ is a relative error ($|x-1| \cdot 100$) of less than 5%. Higher relative error indicates an unacceptable execution of the method, or a gross error in one of the parameters used. The improved values for $A_T$ and $C_T$ are then obtained by multiplying each of the two parameters by $x$ to conform to the
accurately measured $V_e$ using the initial pH. For the final output of the algorithm, the improved $A_T$ gives the final value for VFA concentration and the improved $C_T$ is used to calculate the final value for $H_2CO_3^*$ alkalinity using the initial pH.

It should be noted that when the initial pH is lower than about 6.85, a known volume of standard base should be added to the sample to allow acid titration to the prescribed pH points. In such case the algorithm is changed as follows: (i) $V_x$ is modified by the volume of NaOH addition; (ii) $V_e$ is derived as before and then modified giving:

$$V_e^{(\text{final})} = (Ve^{(\text{Gran Function})} \cdot C_a - V_{NaOH} \cdot C_{NaOH}) / C_a \quad (16)$$

Where: $V_{NaOH}$ = volume of standard NaOH solution added to lift pH above 6.85 (l) and $C_{NaOH}$ = concentration of standard NaOH solution (mol/l).

**MATERIALS AND METHODS**

**Sample origin.** Three industrial effluents were tested: the effluent of a biochemical factory (citric acid manufacturing) UASB reactor (Gadot industries, Haifa, Israel), effluent of a juice-industry UASB reactor (Kibbutz Givat-Haim, Israel), and waters from a municipal sludge digester (Hadera, Israel), each characterized by a different water composition as presented in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$SO_4^{2-}$-S (mg/l)</th>
<th>$PO_4^{3-}$-P (mg/l)</th>
<th>$NH_4^+$-N (mg/l)</th>
<th>EC (mS/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gadot Industries (Haifa)</td>
<td>8.3 – 185.5</td>
<td>4.4 – 12.3</td>
<td>420 – 700</td>
<td>479 - 594</td>
</tr>
<tr>
<td>Gat industries (Givat Haim)</td>
<td>6.9 – 13.0</td>
<td>12.3 – 15.4</td>
<td>10.5 – 17.1</td>
<td>330 - 354</td>
</tr>
<tr>
<td>Sludge digester (Hadera)</td>
<td>12</td>
<td>90</td>
<td>878</td>
<td>795</td>
</tr>
</tbody>
</table>

**Computation:** All calculations were carried out using a computer program (available from the authors). Input consisted of the initial pH, seven sets of $V_x$ and $pH_x$ values, sample TDS and temperature, and the total concentrations of dissolved sulfate, ammonium, phosphate and sulfide. Data output included $C_T$, VFA, total alkalinity (as determined by the Gran function), and carbonate alkalinity concentrations. Also, the relative error and accuracy of the Gran function linear regression computation were given for quality assessment purposes.

**Analysis:** Dissolved ammonium, phosphate, and sulfate were measured using a Metrohm IC analyzer. pH was measured by a Metrohm combined electrode. Titrations were carried out using an automatic titrator (Metrohm Titrino 702) in the temperature range of 23 °C – 28 °C. All results presented are the average and standard deviation of at least three replicates.

**RESULTS AND DISCUSSION**

Since the VFA concentration in well controlled anaerobic treatment systems is relatively low, the experimental approach adopted was to add known increasing concentrations of acetic acid to the effluents and determine whether the algorithm’s solution reflected the increase in VFA. In this way, the samples simulated a typical build-up of VFA in anaerobic reactors. Results are presented in Tables 2 to 4.

Results of measurements carried out on samples from the Hadera treatment plant are listed in Table 2. Sludge anaerobic digesters are typically characterized by high ammonium and phosphate concentrations, and very high carbonate alkalinity. Such waters are perceived difficult to measure.
accurately by titrative methods because of the large difference in concentration between the low VFA and the typically high carbonate alkalinity concentrations. This difference results in a substantial buffering capacity of the carbonate subsystem in the pH region normally dominated by the VFA subsystem \((4.0 < \text{pH} < 5.0)\). Consequently, any small error in determination of \(\text{H}_2\text{CO}_3^*\) alkalinity might yield a corresponding large error in the VFA value.

Referring to Table 2, the following can be inferred: (i) The measured average VFA concentrations were always within 5% of the expected values and on average a recovery of 97.8% of the acetic acid aliquot added was attained. It was noted that the greater the acetic acid aliquot added, the higher the measurement accuracy and repetition attained. This trend repeated itself also with the other effluent types tested. It would appear that for the purpose of obtaining high accuracy, an addition of a known acetic acid “spike” to the raw sample is advantageous; (ii) The accuracy of the total alkalinity measurement (via the Gran titration) was greater than 99.9% with very good repetition for all the samples, substantiating the assumption that it can serve to assess and improve the first VFA and \(\text{H}_2\text{CO}_3^*\) alkalinity estimate; (iii) For a particular experiment, the standard deviation of the measured VFA alkalinity data varied from 2.5 mg/l as HAc for the low concentration samples to 19.6 mg/l as HAc for the high concentration samples. The average standard deviation (in percentage) for all samples above 100 mg/l as HAc was 3.8% and the only sample with high average standard deviation was the raw water (STDV = 2.5 mg/l or 20.5%). This high value is mainly attributed to the very low VFA concentration of the sample (12.5 mg/l) and the very large difference between carbonate and VFA buffering capacities as outlined above. For the much higher measured concentration of \(\text{H}_2\text{CO}_3^*\) alkalinity, the standard deviation was very low for all measurements (average = 0.97%); and (iv) The proportional error column, representing a comparison between \(V_e\) as measured by the Gran Function and the \(V_e\) value derived from the first four data points used to determine the first estimate of \(A_T\) and \(C_T\), show that these two independent measurements were closely equal, a finding that gives credence to the method.

Table 2. Average measurements of municipal sewage digester effluents (Hadera) to which increasing aliquots of acetic acid were added.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetic acid aliquot (mg/l as HAc)</th>
<th>Measured VFA (mg/l as HAc)</th>
<th>Measured (\text{H}_2\text{CO}_3^*) alkalinity (mg/l as CaCO(_3))</th>
<th>Measured total alkalinity (mg/l as CaCO(_3))</th>
<th>Prop. error in first estimate (%)</th>
<th>Recovered aliquot (mg/l as HAc)</th>
<th>Accuracy of aliquot recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>0</td>
<td>12.5±2.6</td>
<td>3311±7.5</td>
<td>3718±7.9</td>
<td>2.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+100</td>
<td>100</td>
<td>115.7±7.2</td>
<td>3325±94.4</td>
<td>3785±97.9</td>
<td>3.51</td>
<td>103.2</td>
<td>96.8</td>
</tr>
<tr>
<td>R+200</td>
<td>200</td>
<td>222.2±5.5</td>
<td>3195±20.2</td>
<td>3716±12.7</td>
<td>1.71</td>
<td>209.7</td>
<td>95.2</td>
</tr>
<tr>
<td>R+300</td>
<td>300</td>
<td>317.6±12.6</td>
<td>3130±20.4</td>
<td>3726±16.3</td>
<td>1.83</td>
<td>305.1</td>
<td>98.3</td>
</tr>
<tr>
<td>R+400</td>
<td>400</td>
<td>415.8±19.6</td>
<td>3058±38.4</td>
<td>3718±23.3</td>
<td>1.79</td>
<td>403.3</td>
<td>99.2</td>
</tr>
<tr>
<td>R+500</td>
<td>500</td>
<td>510.8±9.8</td>
<td>2941±6.3</td>
<td>3675±11.6</td>
<td>1.59</td>
<td>498.3</td>
<td>99.7</td>
</tr>
</tbody>
</table>

Figure 1 shows the measured values for VFA, \(\text{H}_2\text{CO}_3^*\) alkalinity, and total alkalinity (as determined via the Gran approach), vs. the VFA (acetic acid aliquot) added to the Hadera samples. As expected, since no alkalinity and carbonate species were added, no changes in total alkalinity were found. With regard to VFA, the change in concentration measured closely equaled the amount of acetic acid added as shown by the data’s linearity. Similarly, for \(\text{H}_2\text{CO}_3^*\) alkalinity, the measured values decreased proportionally with HAc added. \(\text{H}_2\text{CO}_3^*\) destruction is to be expected because the HAc added to the sample is fully converted to the dissociated form in the initial pH range of the samples \((6.65 < \text{pH} < 8.2)\). Total alkalinity remained unchanged with acetic acid addition, since the \(\text{H}_2\text{CO}_3^*\) alkalinity decreased by the same concentration that the VFA alkalinity increased.
Results of samples drawn from the juice industry UASB reactor in Givat-Haim are listed in Table 3. These samples were relatively simple to measure due to process stability and relatively low carbonate alkalinity concentration.

Table 3. Average measurements of juice industry UASB effluents (Gat industries) to which increasing aliquots of acetic acid were added. (a samples to which NaOH was added)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetic acid aliquot (mg/l as HAc)</th>
<th>Measured VFA (mg/l as HAc)</th>
<th>Measured H₂CO₃⁺ alkalinity (mg/l as CaCO₃)</th>
<th>Measured Total alkalinity (mg/l as CaCO₃)</th>
<th>Prop. error in first estimate (%)</th>
<th>Recovered aliquot (mg/l as HAc)</th>
<th>Accuracy of aliquot recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw1</td>
<td>0</td>
<td>17.4±4.5</td>
<td>1261±17.9</td>
<td>1336±16.3</td>
<td>1.33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+ 100</td>
<td>100</td>
<td>113.2±5.8</td>
<td>1168±12.7</td>
<td>1320±16.9</td>
<td>1.39</td>
<td>96.0</td>
<td>96.0</td>
</tr>
<tr>
<td>R+200</td>
<td>200</td>
<td>226.3±4.4</td>
<td>1067±18.8</td>
<td>1310±20.9</td>
<td>1.14</td>
<td>208.9</td>
<td>95.5</td>
</tr>
<tr>
<td>R+300</td>
<td>300</td>
<td>306.8±12.6</td>
<td>1047±7.4</td>
<td>1352±13.2</td>
<td>1.10</td>
<td>289.4</td>
<td>96.5</td>
</tr>
<tr>
<td>Raw2</td>
<td>0</td>
<td>12.2±2.8</td>
<td>1495±25.9</td>
<td>1550±28.5</td>
<td>1.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+400</td>
<td>400ᵃ</td>
<td>415.5±8.7</td>
<td>1150±14.0</td>
<td>1531±11.3</td>
<td>1.93</td>
<td>396.7</td>
<td>99.2</td>
</tr>
<tr>
<td>R+500</td>
<td>500ᵃ</td>
<td>507.8±1.4</td>
<td>1089±22.3</td>
<td>1544±22.1</td>
<td>1.78</td>
<td>495.6</td>
<td>99.1</td>
</tr>
</tbody>
</table>

Referring to Table 3, all parameters show high accuracy both with respect to VFA determination (average accuracy in recovery of acetic acid = 97.3%) and is repetition (average standard deviation of 2.26%, 1.43% and 1.30% for VFA - excluding the raw measurements, H₂CO₃⁺ alkalinity and total alkalinity respectively). As with the other effluents measured, a high standard deviation was obtained in measuring the low VFA concentrations in the raw samples. Both the accuracy and the repetition of the VFA results improved noticeably for higher VFA concentrations.

Results of samples from the biochemical industry UASB reactor in Haifa (Gadot industries) are listed in Table 4. These samples were relatively difficult to measure due to the relative instability of the process with regard to both VFA and other species concentrations (mainly NH₄⁺ and PO₄³⁻) in addition to high carbonate alkalinity and Ca²⁺ concentrations. It was found that CaCO₃ precipitation occurred directly after filtration resulting in interference in the test procedure. The degree of precipitation depended on the amount of time between filtration and test initiation. If the test is applied immediately, no observable interference is encountered. Therefore, to determine the
recovery of acetic acid aliquots added, the raw sample concentration had to be measured together with the measurement of the modified samples. As for the previous waters, results showed both high accuracy in acetic acid recovery, and good repetition.

Table 4. Average measurements of a biochemical industry UASB effluents (Gadot industries) to which increasing aliquots of acetic acid were added.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetic acid aliquot (mg/l as HAc)</th>
<th>Measured VFA (mg/l as HAc)</th>
<th>Measured H$_2$CO$_3$* alkalinity (mg/l as CaCO$_3$)</th>
<th>Measured total alkalinity (mg/l as CaCO$_3$)</th>
<th>Prop. error in first estimate (%)</th>
<th>Recovered aliquot (mg/l as HAc)</th>
<th>Accuracy of aliquot recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw1</td>
<td>0</td>
<td>91.9±25.6</td>
<td>3421±96.6</td>
<td>3736±58.6</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+100</td>
<td>100</td>
<td>193.2±26.9</td>
<td>3321±47.7</td>
<td>3681±41.9</td>
<td>1.34</td>
<td>101.3</td>
<td>98.7</td>
</tr>
<tr>
<td>Raw2</td>
<td>0</td>
<td>81.1±3.8</td>
<td>3375±56.4</td>
<td>3706±40.1</td>
<td>1.14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+200</td>
<td>200</td>
<td>294.2±15.1</td>
<td>3323±19.4</td>
<td>3753±18.5</td>
<td>0.68</td>
<td>205.7</td>
<td>97.2</td>
</tr>
<tr>
<td>Raw3</td>
<td>0</td>
<td>104.4±7.6</td>
<td>3451±85.1</td>
<td>3789±114</td>
<td>0.73</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+300</td>
<td>300</td>
<td>401.8±21.2</td>
<td>3245±46.6</td>
<td>3741±46.1</td>
<td>0.62</td>
<td>297.4</td>
<td>99.1</td>
</tr>
<tr>
<td>Raw4</td>
<td>0</td>
<td>132.3±10.9</td>
<td>3271±104.5</td>
<td>3675±51.9</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R+400</td>
<td>400</td>
<td>520.6±12.9</td>
<td>3102±55.6</td>
<td>3706±58.6</td>
<td>0.96</td>
<td>388.3</td>
<td>97.1</td>
</tr>
<tr>
<td>R+500</td>
<td>500</td>
<td>616.9±16.1</td>
<td>2978±21.1</td>
<td>3647±32.2</td>
<td>0.59</td>
<td>484.6</td>
<td>96.9</td>
</tr>
</tbody>
</table>

CONCLUSIONS

- Results verify the feasibility and accuracy of a novel on-site method for VFA and alkalinity measurements as means of control of industrial anaerobic reactors. VFA concentration is typically determined with an accuracy of greater than 95%. For concentrations above 200 mg/l as HAc typical accuracy is within ±98%, with very good repetition in results.
- The results show that when executed properly, the method gives very accurate and repetitive results, using a relatively simple procedure that can be easily implemented in field laboratories.
- In order to increase the measurement accuracy of samples containing VFA concentrations lower than 100 mg/l as HAc, it is recommended to spike the sample with a known concentration of acetic acid.

REFERENCES

