ACIDIFICATION OF WATER USED IN GLASSHOUSES

Abstract: The pH of water used for irrigating and feeding tomatoes in glasshouses should be lowered to 5.5-6.0 in order to reduce the incidence of blocked trickle-irrigation nozzles and to prevent a high pH developing in the growing medium as the season progresses. This pH range is also suitable for nutrient solutions used in nutrient-film and rockwool growing systems.

Results of acidification tests showed that 68, 205 and 268 ml of 72% HNO₃ were sufficient to reduce the pH of 1000 l of water to 6.0 in three samples with initial pH values of 7.30, 7.35 and 8.30, respectively. This shows that acid must be added carefully by the grower as relatively small amounts have a large effect on the pH of the water.

The pH of acidified water samples rose only slightly up to 48 h after acidification, but after 6 days the increase was more considerable. This suggests that the target pH should be reduced by 0.5 of a pH unit to allow for this change.

Introduction
The water supplies used by many glasshouse growers in Ireland are hard (1), especially if the supply comes from a well. This is caused mainly by the presence of calcium and magnesium bicarbonates in the water. These compounds may cause blockage of trickle-irrigation systems (2, 3). In addition, it has been found that growers using hard water end up with high pH values in their peat modules towards the end of the season, i.e., far above the recommended range 5.5 to 6.5. It is desirable, therefore, that the pH of hard waters be modified using nitric or phosphoric acid, or both, and some recommendations to this effect have been made in The Netherlands (4, 5, 6). The advent of growing tomatoes in rockwool medium and by the nutrient-film technique (NFT) also requires that the pH of hard water be reduced by acidification as there is no buffering capacity in the absence of a peat or soil medium.

The present study was carried out to investigate the use of nitric acid or phosphoric acid, or both, for acidifying waters containing different amounts of calcium/magnesium salts. The work embraced modifying the pH of water samples with dilute acid at laboratory level and studying the shape of the titration curves. The implications of extension to large-scale acidification with concentrated acids at commercial level were also considered. Results of the study formed the basis for setting up an analytical service for water acidification testing, and for making recommendations to growers on the precautions and procedures necessary for water acidification at commercial level.

Procedure
Acidification tests were carried out on water from two wells (sources A and B) and a mains supply (source C). The pH, electrical conductivity (EC) and alkalinity values for the waters are shown in Table 1. Samples (1 litre) in beakers with mechanical stirrers were acidified using either 0.1M HNO₃ or 0.1M H₃PO₄ to pH 4 (measured on pH meter) and the titration curves were drawn.
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TABLE 1: Volume (ml) of 72% nitric acid required to reduce the pH of 1000 l of water to 6.0

<table>
<thead>
<tr>
<th>Source</th>
<th>A (Well)</th>
<th>B (Well)</th>
<th>C (Mains)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid required</td>
<td>265</td>
<td>205</td>
<td>68</td>
</tr>
<tr>
<td>pH before acidification</td>
<td>8.30</td>
<td>7.35</td>
<td>7.30</td>
</tr>
<tr>
<td>Alkalinity (CaCO₃, mg/l) before acidification</td>
<td>318</td>
<td>309</td>
<td>114</td>
</tr>
<tr>
<td>EC³ (µS) before acidification</td>
<td>660</td>
<td>520</td>
<td>210</td>
</tr>
<tr>
<td>EC³ (µS) after acidification</td>
<td>725</td>
<td>580</td>
<td>250</td>
</tr>
</tbody>
</table>

*Electrical conductivity

A mathematical formula was derived based on the 0.1M HNO₃ titration figure (for 1 litre of water) which enabled the calculation of the amount of concentrated nitric acid required per 1000 l of water to reduce the pH to 6, or to any other desired value.

Tests were carried out on water which had been acidified to see if the pH changed with time. Twelve 250-ml samples in conical flasks (four for each water source) were assembled and nutrients (0.75 g KN0₃ + 0.155 g NH₂CONH₂ + 0.095 g NH₄H₂PO₄ per litre) were added to half of them. This was done to see if this level of nutrients (levels recommended commercially) in the acidified water caused a change in pH over time. Six of the samples were then acidified to pH 5.5 with HNO₃ and the other six to pH 6.0 resulting in a 3 water sources x 2 final pH values x 2 nutrient levels (+) combination.

Results and discussion

Titration curves: The titration curves obtained with 0.1M HNO₃ on water from the three sources are shown in Figure 1. As expected, they follow the classical pattern for monobasic acid x base curves. Similarly shaped curves were obtained with 0.1M H₃PO₄. The steepness of the curve for the source C sample shows that there is little flexibility for the over-addition of acid, i.e., a small miscalculation of the amount of concentrated acid to add will result in a pH value well below the target figure. Table 1 shows that only 68 ml of 72% HNO₃ are required to reduce the pH of 1000 l of water (source C) from pH 7.3 to pH 6.0. The addition of acid also raised the EC of the water slightly. It should be noted (7) that EC is a good indicator of alkalinity in natural waters, as shown by the data in Table 1. However, the pH of the water may not be a good indicator of alkalinity as water from sources B and C had similar pH values but quite different alkalinitities (Table 1).

Volume of acid required: The volume of nitric acid required to reduce the pH of 1000 l of water to the target pH value can be calculated from the formula:

\[ \text{ml of } Y \% \text{ HNO}_3 \text{ required} = \frac{(M \times T \times 6302)}{(Y \times v)} \]
where \( Y \) = % strength (by weight) of the HNO\(_3\) being used for acidification

\( M \) = molarity of the HNO\(_3\) being used to titrate a 1-litre sample of the water in the laboratory

\( T \) = titration figure (ml) found to reach the target pH using HNO\(_3\) with strength \( M \)

\( \varrho \) = density of HNO\(_3\) corresponding to \( Y \).

Normally \( Y \) would be 72%, \( M \) would equal 0.1 and \( \varrho \) would be 1.422. The procedure used on receipt of a sample is to titrate a 1-litre portion with 0.1M HNO\(_3\) to the target figure of, say, 6.0. This gives the value for \( T \) in the equation. The grower must give details of the percentage strength of the HNO\(_3\) he wishes to use for bulk acidification; the values for \( Y \) and \( \varrho \) can be entered in the equation which gives the number of ml of HNO\(_3\) required per 1000 l of water.

Phosphorus is usually included in NFT solutions at a rate of 45-60 mg/l (8). The source of P used is often H\(_3\)PO\(_4\), especially in hard waters, as it has a dual function in supplying P and reducing pH. In very soft waters, H\(_3\)PO\(_4\) cannot be used as the amount required to give 45-60 mg/l may drop the pH to an undesirably low level. In waters where H\(_3\)PO\(_4\) is used as the source of P, and which then require the addition of HNO\(_3\) to achieve the target pH, the required amount of H\(_3\)PO\(_4\) must first be added to the 1-litre sample; the sample is then titrated to the target pH with HNO\(_3\),
and the values are entered into the equation above as before. The HNO₃ also contributes N to the nutrient solution and so replaces some, but not all, of the urea.

Growers who are acidifying water should send samples of the water for testing to a recognised laboratory at least once a year; obviously if the EC of the water changes by more than 10% during the season, a sample should be sent for testing immediately. Changes in water EC can often occur through variations in mains supply and also when growers mix water from different sources.

Change in pH of acidified water: The data (Table 2) show that the pH of the acidified samples rose only slightly up to 48 h after acidification. However, after 6 days the increase was more considerable and this finding suggests that the target pH should be reduced by 0.5 of a pH unit to allow for this change. Presumably these changes are due to slow-acting natural buffering systems in the water.

Acidified samples containing nutrients showed a smaller change in pH after 6 days than those containing no nutrients; the pH of the samples acidified to a 5.5 target value showed a greater percentage change in pH after 6 days than those acidified to pH 6.0, while acidified samples from water source B showed a smaller pH change after 6 days than did source A or C samples. These data suggest that the presence or absence of nutrients, the target pH value, and the source of the water itself can have a small modifying effect on the pH of acidified water over time. Similar small changes in pH were found in 500-l tanks of acidified water which contained a range of nutrients (8); the changes were sufficiently small as to be considered insignificant.

Acidifying water in bulk: For reasons of cost it is desirable that the acidification be carried out on a batch basis in a tank rather than by a continuous bleed of acid from a diluter. Having acidified a batch of water it is desirable to use all of it rather than to carry out a topping-up operation with fresh water which in turn requires

<table>
<thead>
<tr>
<th>Sample identity</th>
<th>No. of samples</th>
<th>Immediate</th>
<th>0.75 h</th>
<th>48 h</th>
<th>6 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>X (overall)</td>
<td>12</td>
<td>5.75</td>
<td>6.00</td>
<td>5.98</td>
<td>6.50</td>
</tr>
<tr>
<td>X (+)³</td>
<td>6</td>
<td>5.75</td>
<td>5.99</td>
<td>5.97</td>
<td>6.34</td>
</tr>
<tr>
<td>X (−)</td>
<td>6</td>
<td>5.75</td>
<td>6.00</td>
<td>6.01</td>
<td>6.68</td>
</tr>
<tr>
<td>X (5.5)b</td>
<td>6</td>
<td>5.50</td>
<td>5.79</td>
<td>5.79</td>
<td>6.41</td>
</tr>
<tr>
<td>X (6.0)</td>
<td>6</td>
<td>6.00</td>
<td>6.20</td>
<td>6.18</td>
<td>6.61</td>
</tr>
<tr>
<td>X Source A²</td>
<td>4</td>
<td>5.75</td>
<td>5.98</td>
<td>6.04</td>
<td>6.59</td>
</tr>
<tr>
<td>X Source B</td>
<td>4</td>
<td>5.75</td>
<td>6.01</td>
<td>5.99</td>
<td>6.33</td>
</tr>
<tr>
<td>X Source C</td>
<td>4</td>
<td>5.75</td>
<td>6.00</td>
<td>5.94</td>
<td>6.61</td>
</tr>
</tbody>
</table>

³Samples with (+) and without (−) added nutrients — see procedure

²Samples acidified to pH 5.5 or 6.0

³Three water sources
acidification. A topping-up procedure may necessitate another laboratory analysis of the water in the topped-up tank before further acidification can be carried out. Alternatively, the grower could meter the additional water (V litres) into his tank and calculate the amount of acid required as per the formula above but with an extra term as multiplier, namely \( V/1000 \). The water in the tank would be already at the target pH.

Tanks or reservoirs in which water is acidified and held must be such that they do not react with the acidified water. For example, an unprotected galvanized tank would probably be attacked by water of pH 6, thereby resulting in an excessively high zinc content in the water.

It is desirable that the acid be added at different points around the tank as this facilitates mixing. Growers can test for the correct target pH and adequate mixing by dipping the tank at various points with Universal Indicator Paper or by using a pH meter. Obviously, this is an essential quality control procedure that the grower must carry out to his satisfaction before using the water. The dangers of concentrated acids and the necessary precautions for their handling must be stressed at all times to growers.

**Conclusions:** Acidification of water used for nutrient solutions to a target pH of 5.5 or 6.0 requires relatively small amounts of concentrated acid and the addition must, therefore, be carried out carefully and accurately. Changes in the pH of acidified water over a 6-day period were generally fairly small and were not considered a problem in commercial practice.

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**References**

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