

## Acidifying a sample to a specific pH before analysis

If we want to test for ammonium concentration in an aqueous sample, the sample pH must be low enough to convert the ammonia ( $\text{NH}_3$ , volatile) to ammonium ( $\text{NH}_4^+$ ). The ionic form will stay in solution rather than leaving as a gas.

For Lachat analysis, the solution can be acidified to a pH of 2 using HCl. This solution can be analyzed for ammonium and nitrate.

A sample of millipore water should have a pH = 7. It may be slightly lower if  $\text{CO}_2$  has been absorbed from the atmosphere and formed carbonic acid. Assuming a pH of 7 and a sample size of 5 mL, how much HCl do I need to add to get to pH = 2?

Concentrated HCl is 35-37wt% or 10-12M. Assume a 10M HCl solution (reasonable for a bottle of HCl that has not been fresh/unopened).

At pH=7 (start),  $[\text{H}_3\text{O}^+] = 10^{-7}\text{M}$ . At pH=2 (end),  $[\text{H}_3\text{O}^+] = 10^{-2}\text{M}$ .

At start I have  $5\text{mL water} \times \left(10^{-7} \frac{\text{mol H}^+}{\text{l}}\right) = 5 \times 10^{-7} \text{mol H}^+$

At the end I want  $(5\text{mL water} + x\text{mL HCl}) \times \left(10^{-2} \frac{\text{mol H}^+}{\text{l}}\right) = (5 + x) \times 10^{-2} \text{mol H}^+$

The amount of acid that I need to add will be the volume of 10M HCl required to increase the hydronium ion ( $\text{H}_3\text{O}^+$  or (short-hand  $\text{H}^+$ )) concentration by  $[(5 + x) \times 10^{-2} \text{mol H}^+] - [5 \times 10^{-7} \text{mol H}^+]$  (end concentration - start concentration) where x is the volume of the added acid.

This expression must be equal to the volume  $x \times$  acid concentration, thus

$$[(5 + x) \times 10^{-2} \text{mol H}^+] - [5 \times 10^{-7} \text{mol H}^+] = x \times 10 \frac{\text{mol}}{\text{l}}$$

For a 5mL sample you will need 5 $\mu\text{l}$  of concentrated HCl.

If your sample is buffered at a higher pH then you either need to know the concentration of the buffer and calculate the volume of acid needed OR you can start with the above amount of acid (absolute minimum that you will need) and test with pH paper until you reach a pH of 2. You can add 50 $\mu\text{l}$  of acid before the change in volume results in a concentration change (of the original sample) of 1%.