## Principles of titration for $CO_2$ determination

Carbon dioxide acts as an acid when it dissolves in water, because of the reaction:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The resulting carbonic acid can be neutralized by a strong base such as sodium hydroxide:

$$H_2CO_3 + 2Na^+ + 2OH^- \rightarrow 2Na^+ + CO_3^{2-} + 2H_2O$$

If there is a lot of sodium hydroxide (as in a 1 M NaOH trap), then the reaction will be driven to completion, and any $CO_2$ that dissolves in the solution will stay captured as $CO_3^{2-}$.

The quantification of the captured $CO_2$ is actually a back-titration. That is, we are actually measuring how much NaOH is left after the $H_2CO_3$ has been neutralized. Because 2 moles of NaOH are required for each mole of $H_2CO_3$:

Trapped $CO_2$ = (original NaOH – final NaOH)/2

NaOH and HCl react in a 1:1 ratio, and essentially all the NaOH has reacted when the phenolpthanlein indicator changes colour. That means at the end-point:

$CO_2^{3-}$ = (original NaOH – added HCl)/2

In practice, we are more certain of the original concentration of the NaOH solution (which comes from a laboratory-grade standard solution) than about our own mixed HCl solution. Therefore, it is better to titrate a few aliquots of fresh NaOH standard solution with your acid, and correct the samples for these blank values.

From here on, square brackets [x] mean concentration of x. Let us say that you measured out an aliquot of $V$ mL of fresh NaOH, and this blank requires $T_b$ mL of HCl solution to reach the end-point. That means that the concentration of your acid solution is actually:

$$[\mathbf{HCl}] = [\mathbf{NaOH}] \cdot \frac{V}{T_b}$$

If an aliquot of $V$ mL of a sample requires $T_s$ mL of acid to reach the end-point, then the *concentration* of $CO_3^{2-}$ in the sample (which is the concentration of trapped $CO_2$) is

$$[\mathbf{CO_3^{2-}}] = \frac{[\mathbf{NaOH}] * V - [\mathbf{HCl}] * T_s}{2 * V}$$

$$= \frac{[\mathbf{NaOH}] \cdot V - [\mathbf{NaOH}] \cdot \frac{V}{T_b} \cdot T_s}{2 * V}$$

$$= \frac{[\mathbf{NaOH}] \cdot \left(1 - \frac{T_s}{T_b}\right)}{2}$$

Note that this assumes that the same NaOH concentration was used for the traps and for the blank aliquots, and also that the same aliquot volume was used for titration of the blanks as for the samples.

Now, if the traps had a total volume $V_t$, then the total amount of $CO_2$ trapped, in µg C, is:

$$m_{CO_2} = \frac{1000\mu g}{mg} * \frac{12.01 mg}{mmol} * V_t * [CO_3^{2-}]$$

and so

$$m_{CO_2} = \frac{1000 * 12.01 * V_t * [NaOH] * \left(1 - \frac{T_s}{T_b}\right)}{2}$$

where:

$m_{CO2}$ = mass of total carbon dioxide absorbed in the trap, in µg C

$V_t$ = volume of trap, in mL

[NaOH] = concentration of NaOH solution used for trap and blanks (1 M)

$T_s$, $T_b$ = volume of HCl required to titrate sample and blanks, respectively

# Titration Protocol

See also the *Principles of titration* info sheet for a basic introduction and calculations.

**Health, safety & environment**
Phenolphthalein is a potential carcinogen: avoid skin contact, be careful not to splash droplets around the lab, and wipe down the workspace thoroughly when you are finished.

The acids and bases are relatively dilute, but are still dangerous, especially to eyes.

If $^{14}C$ labelling has been used in your experiment, your NaOH traps will be radioactive. Take the necessary safety precautions and dispose of the radioactive waste appropriately.

If you have **any** doubts about what is required to work with these hazards, ask the lab manager and consult the relevant MSDS.

**Equipment required:**

- small and large volumetric flasks
- beakers
- plastic basin with water
- pipette for samples
- $BaCl_2$ solution (1 M) - usually already prepared, next to titrator (also SrCl2 possible)
- phenolphthalein solution (phph) – usually next to titrator, can refill from bottle under fumehood
- droppers or pipettes for $BaCl_2$ and phph
- 20 mL scinti vial with lid

**Volumes and concentrations**
This protocol does not give recommended volumes or concentrations of solutions, because these should be optimised for each experiment, depending on expected $CO_2$ generation, trap size, sampling interval, and the required sensitivity, amongst other things. However, there are two things to think about when deciding on these parameters:

(i) At least half of the NaOH should remain unneutralized to ensure effective $CO_2$ trapping. This means not more than 0.25 mmol $CO_2$ trapped per mL of trap solution, with 1M NaOH used in the trap.
(ii) The titration method itself has its own variability, with a standard deviation of about 0.05 mL in the volume of acid.

**Procedure**

| Task | Comment |
|---|---|
| Prepare HCl at the required concentration by diluting the standard 1 M solution available in the boxes, using deionized water | |
| Fill a 20 mL scinti vial with fresh NaOH, seal it, and label the vial | |
| Switch on the titrator (power switch at the back) | |
| Unscrew and empty the titrator's solution bottle and rinse it out with a small amount of the new HCl solution, then pour in the new solution | Lay out some paper to avoid contamination of the tubing inside the bottle. |
| Drain and refill the titrator reservoir at least three times (more if you are changing the concentration) | During this process, tap lightly on the tubing of the titrator to flush out bubbles<br><br>Put a note on the bottle to show what concentration is inside |
| Prepare a tray of small beakers with small stirrer bars | Make sure the beakers and stirrer bars are clean |

| | |
|---|---|
| Calibrate a pipette to the right volume for the samples, and check that the volume is stable | Calibrate on a balance using water at room temperature: 1 mL = 1 g |
| Have pipettes or droppers ready for $BaCl_2$ and phph<br><br>Do not leave pipettes lying flat on the table when in use – drops could run back into the device and damage it! | $BaCl_2$ should be added in excess to the $CO_2$ trapped in the sample, but this does not have to be extremely exact. One or two drops of phph are needed, which also doesn't have to be exact. However, pipetting 10 uL gives a more consistent colour, which can be helpful. |
| Before starting with actual samples, titrate at least four aliquots of NaOH to ensure the system is operating properly. Record these values as blanks for the calculation. | The NaOH blanks should titrate near to the expected value (10.00 mL for the recommended parameters), and most values should not differ from each other by more than +/- 0.05 mL.<br><br>Do not breath directly on the blank (NaOH standard solution), and keep it sealed when not using. |
| Titration procedure:<br>(i) pipette sample amount into beaker<br>(ii) add $BaCl_2$ and phph<br>(ii) put under titrator nozzle and turn up stirrer speed<br>(iii) add HCl using the right button of the titrator control until the exact point at which the pink colour disappears – this volume is your result. Avoid having a last drop hanging on the titrator tip.<br>(iv) turn off the stirrer<br>(v) empty beaker into $^{14}C$ waste container (if labelled)<br>(vi) put beaker into basin of water<br>(vii) refill titrator reservoir by holding down the left button or zero the counter by pushing it twice | Take care not to breath directly onto the samples ($CO_2$)<br><br>The titrator has three speed levels controlled by one button. Use the lowest speed when nearing the endpoint.<br><br>It is also possible to prepare some beakers with $BaCl_2$ and phph beforehand, and then just pipette the sample immediately before titration.<br><br>Deionized water can be added to the samples to increase their volume or wash down the sides of the beaker. This will not affect the result.<br><br>The reservoir contains 20 mL. Avoid refilling it in the middle of a titration. |
| At frequent occasions during the sample run, and also after the last sample, titrate the NaOH standard to ensure that this still matches the values from the beginning. Also record these values for the calculations. | |
| When the beakers are all dirty, rinse out twice with deionized water in the basin. Do not use soap! | It is not necessary to dry the beakers before reuse. |
| When you are finished, wipe down the table and titrator with a wet paper towel. | |