

Water Hardness Measurements

1 The investigation

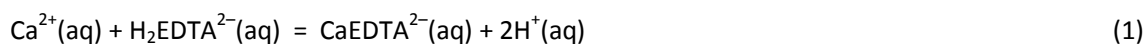
Hard water is caused by the presence of naturally occurring calcium and magnesium salts in water.

In this online experiment you will measure the total hardness of a water sample by following the chemical reaction of Ca^{2+} and Mg^{2+} ions with ethylene-di-amine-tetra-acetic acid (EDTA).

First, you will determine the concentration of the EDTA solution by reaction with a calcium solution of known concentration; this process is called standardisation. You will then analyse a river water sample using the standardised EDTA solution and calculate its total hardness.

2 Analytical method

To determine the hardness of the water sample you will react the Ca^{2+} and Mg^{2+} ions in the water sample with ethylene-di-amine-tetra-acetic acid (EDTA, a 'chelating' agent) according to the equation:



EDTA has the ability to capture or 'chelate' metal ions (e.g. Ca^{2+} and Mg^{2+}) by forming several bonds to a single metal ion. Structure **1** shows the metal–EDTA chelate complex, illustrated here with Ca^{2+} .

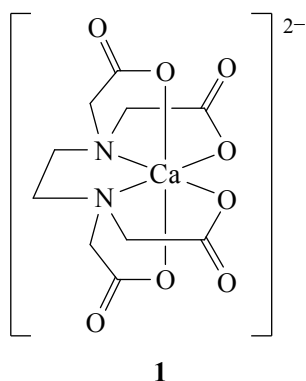


Figure 1 Metal (M)–EDTA complex

- According to Equation 1, how many moles of Ca^{2+} ions will react with one mole of EDTA ions?
- One mole of Ca^{2+} ions will react with one mole of EDTA ions.

The complex is particularly stable and its formation takes place in a controlled 1:1 ratio, according to Equation 1).

The end point of the titration can be determined using an indicator; in this case, a dye called Eriochrome Black T (ErioT). When this indicator is added to a solution at pH 10, it forms a complex with any calcium and magnesium ions present and the solution will turn pink to wine-red in colour (Figure 2a); the intensity depending on the concentration of metal ions in the solution. The dye–metal ion complex is less stable than the EDTA–metal ion complex. On titrating with EDTA, the solution will turn blue when sufficient EDTA has been added to react with all the calcium and

magnesium ions present (Figures 2b and 2c). At this point EDTA will be of sufficient concentration to displace all the metal ions from the indicator complex (the end point of the titration).

The indicator reaction and the different stages of the reaction are depicted in the following equation and in Figure 2.

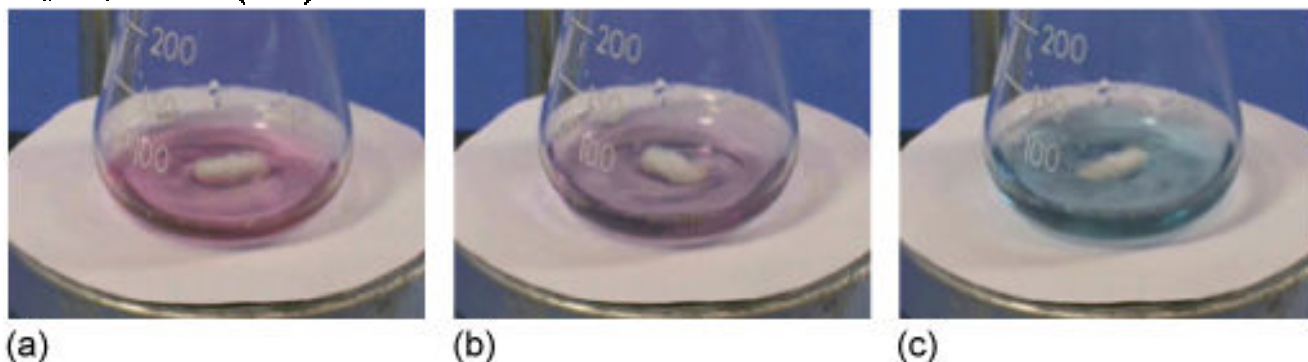
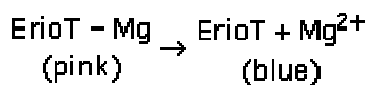


Figure 2 Colour changes for EDTA titration using ErioT indicator: (a) pink colour well before endpoint; (b) solution just before endpoint, (c) blue colour at end point.

Since ErioT is most effective as an indicator in a solution at pH 10, a 'buffer' solution is also added to the water sample to keep the pH constant.

3 The tasks

3.1 Task 1: standardisation of EDTA

The first task is the precise calculation of the concentration of the EDTA solution you will be using to determine the water hardness. The approximate concentration of this solution is 0.01 molar (mol l^{-1}).

To carry out the EDTA standardisation, you will be using a solution of calcium carbonate of a concentration of 0.010 mol l^{-1} as the primary standard to check the precise concentration of the EDTA solution.

You will now complete an interactive screen experiment to determine the precise concentration of the EDTA solution that you will later use to determine water hardness of your water sample. Detailed instructions are provided within the experiment, but the details below provide a summary of the steps that you need to take.

1. Access the interactive screen experiment.
2. Fill your burette with EDTA solution.
3. Measure 10.00 ml of the standard calcium solution using a volumetric pipette and transfer into a conical flask.
4. Add deionised water and dilute to 50 ml.
5. Add 2.00 ml ammonia buffer solution using a measuring pipette.
6. Add one or two drops of ErioT indicator. The solution will turn pink.
7. Record the initial burette reading.

8. Titrate immediately with the EDTA solution until the colour of the mixture turns from pink, through purple, to blue. While adding EDTA, make sure the solution in the conical flask is thoroughly mixed using a magnetic stirrer. As the end point approaches and the solution turns purple, the EDTA should be added very slowly – drop by drop. At the end point the last of the pinkish tinge disappears and a pure blue colour is left.
9. Record the volume of EDTA added.

Note: it is good practice to do a ‘rough’ titration first to estimate the approximate volume of EDTA required and then do the titration more carefully adding drop-by-drop as you approach the estimated end-point. You should repeat this standardisation procedure at least twice. You may need a third replicate measurement if your analytical results lack precision. Although you should include the value of your ‘rough’ standardisation in your records, you should not use it in any subsequent calculations.

A template of a table that you could use to record your experimental data is shown below (and available from the link below).

Table 1 Volumetric data for the standardisation titration of EDTA solution

	Rough	Trial 1	Trial 2	Trial 3 (if needed)
Volume of 0.010M Ca ²⁺ solution/cm ³				
no. of moles of Ca ²⁺ ions				
no. of moles of EDTA ions				
initial burette reading/cm ³				
final burette reading/cm ³				
volume of EDTA solution used/cm ³				
average volume of EDTA solution used /cm ³				

A .doc version of this table is provided for you to download from the ‘Water hardness determination’ application page of The OpenScience Lab.

Once you have determined the values you should calculate the concentration of the EDTA solution supplied in this investigation using the average volume of EDTA used.

3.2 Task 2: determining the hardness of water

You will now select a river water sample for determination of hardness from a selection of different rivers across the world. You will titrate this with your standardised EDTA solution.

The instructions below guide you through how to use the equipment to determine the hardness of a number of water samples.

1. Access the interactive titration experiment and fill your burette with EDTA.
2. Choose a river-water sample from the list of possible locations.
3. Measure 50.00 ml of the water sample using a volumetric pipette and transfer into a clean conical flask.

4. Add 2.00 ml ammonia buffer solution using a measuring pipette.
5. Add one or two drops of ErioT indicator. The solution will turn pink.
6. Record the initial burette reading.
7. Titrate immediately with the EDTA solution until the colour of the mixture turns from pink, through purple, to blue. While adding EDTA, make sure the solution in the conical flask is thoroughly mixed using a magnetic stirrer. As the end point approaches and the solution turns purple, the EDTA should be added very slowly – drop by drop. At the end point the last of the pinkish tinge disappears and a pure blue colour is left.
8. Record the volume of EDTA added.

Judging the exact end point can be difficult and the volume of EDTA required cannot be predicted. You may like to do a 'rough' titration first to estimate the approximate volume and then repeat, adding drop by drop as you approach the estimated end point. You should not include the value of your 'rough' titration in your calculation. Repeat the titration using the water sample at least twice.

A template of a table that you could use to record your experimental data is shown below and is available from the link below.

Table 2 Volumetric data for the titration of a water sample with EDTA solution.

	Rough	Trial 1	Trial 2	Trial 3 (if needed)
volume of water sample/cm ³				
initial burette reading/cm ³				
final burette reading/cm ³				
volume of EDTA solution used/cm ³				
average volume of EDTA solution used /cm ³				

A .doc version of this table is provided for you to download from the 'Water hardness determination' application page of The OpenScience Lab.

Use the data that you have accumulated during this investigation to calculate the total hardness of your chosen river water sample. When you have completed your calculation consider whether you would describe your water sample as soft, intermediate or hard. Water with less than 50 mg l⁻¹ of calcium carbonate is regarded as soft, with quantities between 50 and 200 mg l⁻¹ as intermediate, and with quantities greater than 200 mg l⁻¹ as hard.