4.3 Primary standard solutions

To be able to accurately determine the concentration of an unknown solution, it is titrated against a solution with an accurately known concentration. Accuracy is the number of significant figures to which a quantity is known. Some mass balances measure to the nearest gram, while others measure to the nearest milligram (0.001 gram). The mass balance that can measure to the nearest milligram is a more accurate measuring device than the mass balance that measures to the nearest gram. Accuracy is determined by the measuring instrument that is used.

Accuracy is the number of significant figures to which a quantity is known. It is determined by the measuring instrument that is used.

A chemical that can be made up into a solution of accurately known concentration is called a **primary standard**. A primary standard must be stable over a long time and under common laboratory conditions. A primary standard must:

- have a large molar mass so that a reasonable mass is measured; hence, there is a smaller percentage error.
- be cheap so that it is affordable for use
- be of high purity so that no side reactions occur
- be stable in the presence of air, so that no reaction with air occurs
- not have any water of hydration, which may change due to atmospheric conditions such as humidity
- dissolve readily in solvent, generally water, to form a stable solution.

Anhydrous sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) are frequently used as primary standards in school science laboratories since they meet all of these criteria.

EXPERIMENT 4.2

MAKING A PRIMARY STANDARD SOLUTION

Primary standard solutions have an accurately known concentration and are stable over a period of time in common laboratory conditions.

Aim

To make a primary standard solution

Materials

- 250 mL volumetric flask with lid
- Electronic balance
- Clean, dry 150 mL beaker
- Spatula
- Approximately 1.5 g anhydrous sodium carbonate
- 300 mL distilled water
- Wash bottle filled with distilled water
- Filter funnel

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Solid sodium carbonate can irritate skin and eyes.	Wear safety glasses and wash your hands at the end of the experiment.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1 Rinse the volumetric flask with a small volume of distilled water.
2 Place a clean, dry 150 mL beaker on the electronic balance and tare the balance.
3 Accurately measure out, to the nearest 0.001 g, about 1.4 g of anhydrous sodium carbonate into the beaker.
4 Add about 80 mL of distilled water to the beaker and stir until the sodium carbonate has completely dissolved.
5 Place the filter funnel into the neck of the volumetric flask.
6 Pour the sodium carbonate solution into the volumetric flask.
7 Pour a small volume of distilled water into the beaker, swirl and pour into the volumetric flask.
8 Rinse the filter funnel by pouring some distilled water from the wash bottle into the volumetric flask.
9 Remove the filter funnel.
10 Fill the volumetric flask with distilled water until the bottom of the meniscus is just touching the line on the volumetric flask.
11 Place a lid on the volumetric flask, hold the lid in place, invert and swirl the contents of the flask so that mixing occurs.
12 Label your solution and keep it for use in Experiment 4.3.

Results

Accurately record the mass of anhydrous sodium carbonate that was measured out.

Analysis of results

Calculate the concentration of the sodium carbonate solution. Your answer should be given to four significant figures.

Discussion

1 Justify why the beaker and filter funnel were rinsed after use.
2 Evaluate the accuracy of this technique for preparing a primary standard.
3 Sodium carbonate decahydrate is readily available, has a higher molar mass and is cheaper than anhydrous sodium carbonate. Justify why anhydrous sodium carbonate is used as a primary standard while sodium carbonate decahydrate is not.

QUESTION SET 4.2

Remembering

1 Identify three criteria that must be met for a substance to be used as a primary standard.

Understanding

2 What is the purpose of a primary standard?
3 Explain why sodium hydroxide is not appropriate for use as a primary standard.
4 Use your knowledge of the nature of hydrochloric acid to explain why it should not be used as a primary standard.

Applying

5 A student was making the following primary standard – 250 mL of a 0.135 mol L^{-1} solution of sodium hydrogen carbonate.
  a Calculate the mass of sodium hydrogen carbonate that must be used to make this solution.
  b Describe the method used to make this primary standard.

Evaluating

6 A student wanted to measure 90 mL of a solution. Justify whether a 100 mL measuring cylinder or a 100 mL volumetric flask is a more accurate piece of equipment for this task.

4.4 Performing volumetric analysis

The solution in the burette is called the **titrant**. The solution to be analysed – the solution with the unknown concentration – is called the **analyte**.

The most common titration conducted in a school science laboratory is the acid–base titration. The basic technique for performing a titration is as follows:

- One of the solutions will have an accurately known concentration.
- Place one of the solutions in the burette. The acid is generally placed in the burette as bases have the capacity to etch the glass and, over time, change the volume of the burette.
- Use a pipette to transfer a known volume of the other solution to a conical flask that has been rinsed with water.
- Add two drops of an appropriate acid–base indicator (see page 236) to the solution in the conical flask.
- Slowly add the solution from the burette to the conical flask until the indicator just shows the first permanent colour change.
- Record the volume of solution added from the burette.
- Repeat the experiment several times until the volume of solution added from the burette is consistent to within about one-third of a division (0.03 mL). The second and subsequent titrations should involve slowing the rate of flow of solution from the burette to dropwise and parts of drops when near the endpoint. Use the average titre for the most accurately known titrations for your calculations.
- Write a balanced chemical equation and use mole calculations to determine the concentration of the unknown solution.

WORKED EXAMPLE 4.1

Potassium hydrogen phthalate, $KH(C_8H_4O_4)$, is a good primary standard for standardising alkali solutions. It contains one acidic hydrogen per formula unit. Potassium hydrogen phthalate (0.917 g) was dissolved in water and titrated with approximately 0.2 mol L^{-1} sodium hydroxide solution; 27.2 mL hydroxide solution was needed to reach the endpoint. Calculate the accurate molarity of the hydroxide solution.

Answer

$M = 0.165 \text{ mol L}^{-1}$

Logic

1 Write a balanced chemical equation for the reaction.

$$KH(C_8H_4O_4)(aq) + NaOH(aq) \rightarrow Na^+(aq) + K(C_8H_4O_4)^-(aq) + H_2O(l)$$

2 Calculate the number of moles of potassium hydrogen phthalate that reacted with the sodium hydroxide.

$$n_{KH(C_8H_4O_4)} = \frac{m_{KH(C_8H_4O_4)}}{M_{KH(C_8H_4O_4)}} = \frac{0.917}{204.22} = 0.00449 \text{ mol}$$

3 Calculate the number of moles of sodium hydroxide that reacted with the potassium hydrogen phthalate.

Using equation $n_{NaOH} = n_{KH(C_8H_4O_4)} = 0.00449$ mol

4 Calculate the molarity of the sodium hydroxide solution.

$$c_{NaOH} = \frac{n_{NaOH}}{V_{NaOH}} = \frac{0.00449}{0.0272} = 0.165 \text{ mol L}^{-1}$$

WORKED EXAMPLE 4.2

The acidity of a particular white wine was determined by titrating 25.0 mL of the wine with 0.0511 mol L^{-1} sodium hydroxide solution; 8.70 mL was required. Calculate the molarity of hydrogen ions in the wine. Assume that the hydrogen ions come entirely from diprotic tartaric acid, $H_2C_4H_4O_6$, and calculate the concentration of tartaric acid in the wine in grams per 100 mL.

Answer

Concentration = 0.133 g/100 mL

Logic

1 Write a balanced chemical equation for the reaction.

$$H_2C_4H_4O_6(aq) + 2NaOH\,(aq) \rightarrow 2Na^+(aq) + C_4H_4O_6^{2-}(aq) + 2H_2O(l)$$

2 Calculate the number of moles of sodium hydroxide that reacts with tartaric acid.

$$n_{NaOH} = C_{NaOH} \times V_{NaOH} = 0.0511 \times 0.00870 = 0.000445\,\text{mol}$$

3 Calculate the number of moles of hydrogen ions that react with the sodium hydroxide. Using the equation and data in the question: $n_{H^+} = n_{NaOH} = 0.000445\,\text{mol}$

Tartaric acid is diprotic; that is, each molecule of tartaric acid contains 2 hydrogen ions.

4 Calculate the molarity of hydrogen ions in tartaric acid.

$$C_{H^+} = \frac{n_{H^+}}{V_{H_2C_4H_4O_6}} = \frac{0.000445}{0.0250} = 0.0178\text{ mol L}^{-1}$$

5 Calculate the concentration of tartaric acid in g/100 mL, using equation:

$$n_{H_2C_4H_4O_6} = \frac{1}{2}n_{NaOH} = 0.000222\text{ mol}$$

$$m_{H_2C_4H_4O_6} = n_{H_2C_4H_4O_6} \times M_{H_2C_4H_4O_6} = 0.000222 \times 150.088 = 0.0334\text{ g}$$

$$[H_2C_4H_4O_6] = \frac{m_{H_2C_4H_4O_6}}{V_{H_2C_4H_4O_6}} = \frac{0.0334}{0.0250} = 1.33\text{g L}^{-1} = 0.133\text{ g/100 mL}$$

Try these yourself

a Oxalic acid dihydrate, $(COOH)_2.2H_2O$, can be used as a primary standard for standardising alkali solutions. 0.291 g diprotic oxalic acid required 18.2 mL of a potassium hydroxide solution for exact neutralisation. Calculate the molarity of the hydroxide solution.

b 5.267 g anhydrous sodium carbonate was dissolved in water in a volumetric flask and the volume made up to 250 mL. 10 mL of this solution was pipetted into a conical flask and titrated with hydrochloric acid. 21.3 mL was needed to reach the equivalence point. Calculate the molarity of the hydrochloric acid solution. This solution was then used to determine the concentration of an unknown barium hydroxide solution. 25 mL of the barium hydroxide solution required 27.1 mL hydrochloric acid solution for exact neutralisation. Calculate the molarity of the barium hydroxide solution. In addition, calculate its concentration in grams per litre.

Choice of indicators

It is important that the indicator chosen is appropriate for the pH of the equivalence point. Different acids and bases have different strengths – they have different degrees of ionisation. Hydrochloric acid, sulfuric acid and nitric acid are classified as strong acids because all molecules completely ionise in solution. Other acids are classified as weak acids because only some molecules ionise in solution. Similarly, hydroxide salts and oxide salts are classified as strong bases while most other bases, including carbonates, are classified as weak bases.

As you learnt in *Nelson Chemistry Units 1 & 2 for the Australian Curriculum* Chapter 7, a reaction between an acid and a base, a neutralisation reaction, is essentially a reaction between the hydronium ions and hydroxide ions to form water:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$

or

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

However, during neutralisation reactions, a salt is also formed. When determining which indicator to use, you must:

- identify the salt that is formed
- determine whether either ion in the salt is a weak acid or a weak base or neither
- decide whether the resultant solution will have a pH greater than 7, less than 7 or equal to 7.

In light of this, it is important to choose the most appropriate indicator, the indicator that will change colour at the expected pH of the equivalence point.

Table C4.2 Indicators used for different types of titrations

Type of titration	Example	Predicted equivalence point	Indicator
Strong acid–strong base	Hydrochloric acid and sodium hydroxide	Neutral	Bromothymol blue
Strong acid–weak base	Hydrochloric acid and sodium carbonate	Acidic region	Methyl orange
Weak acid–strong base	Acetic acid and sodium hydroxide	Basic region	Phenolphthalein
Weak acid–weak base	Acetic acid and sodium carbonate	Generally don't use direct titration	

TITRATION – DETERMINING THE ENDPOINT

Visit this website for descriptions, photos and short videos related to performing a titration, especially detecting the endpoint.

WOW

History of volumetric analysis

The French chemist François Antoine Henri Descroizilles made the first burette in 1791. It was further refined by another Frenchman, Joseph Louis Gay-Lussac, who also came up with the names 'pipette' and 'burette' in 1824. In 1855, the German chemist Karl Friedrich Mohr wrote the first book on volumetric analysis titled *Lehrbuch der chemisch-analytischen Titrir-methode* (Instructional Book of Titration Methods in Analytical Chemistry).

Performing the titration

It is now time to put all of this information together and perform a titration.

EXPERIMENT 4.3

PERFORMING A TITRATION

In this titration, you will be using the primary standard that you made in Experiment 4.2 to determine the unknown concentration of a solution of hydrochloric acid. Hydrochloric acid is a strong acid and sodium carbonate is a weak base so the equivalence point will be in the acidic region. Methyl orange is a suitable indicator for this titration.

Aim

To determine the concentration of a hydrochloric acid solution using volumetric analysis

▶

Materials

- 250 mL of an accurately known concentration of sodium carbonate (from Experiment 4.2)
- 50 mL burette
- Retort stand and burette clamp
- 25 mL pipette and pipette filler
- 2 × 150 mL beakers
- 250 mL conical flask
- Dropper bottle containing methyl orange indicator
- 200 mL of hydrochloric acid of unknown concentration
- 2 small labels to label the 150 mL beakers
- Wash bottle with distilled water

What are the risks in doing this experiment?	How can you manage these risks to stay safe?
Dilute solutions of hydrochloric acid, sodium carbonate and methyl orange indicator may splash onto your skin or into your eyes.	Wear safety glasses and wash your hands at the end of the experiment.
Glassware could break and cut your hands.	Keep glassware away from the edge of the bench. When the pipette is not in use, leave the pipette filler on the pipette to prevent it rolling off the bench. If glassware does break, inform your teacher immediately.

In your write-up, add any more risks you can think of, as well as ways to manage them.

Procedure

1 Rinse one of the 150 mL beakers with a small amount of the hydrochloric acid solution, empty it, label it and fill it with about 100 mL of the hydrochloric acid solution.
2 Prepare the burette, then fill it with the hydrochloric acid solution.
3 Rinse the other 150 mL beaker with a small amount of the sodium carbonate solution, empty it, label it and fill with about 100 mL of the sodium carbonate solution.
4 Rinse the conical flask with water.
5 Prepare the pipette, then use the pipette to transfer 25.00 mL of the sodium carbonate solution to the conical flask.
6 Add 2 drops of methyl orange indicator to the conical flask and swirl to mix.
7 Place the conical flask under the burette and begin the titration.
8 When the first permanent colour change has occurred, record all results.
9 Repeat the titration several more times until the titrant added is within 0.03 mL.

Results

Record the:

- concentration of sodium carbonate solution
- volume of sodium carbonate used
- volume of hydrochloric acid used.

Analysis of results

1 Calculate the average volume of hydrochloric acid used.
2 Write a balanced chemical equation for the reaction between hydrochloric acid and sodium carbonate.
3 Calculate the number of moles of sodium carbonate placed in the reaction vessel (conical flask).
4 Use the mole ratio from your balanced chemical equation to determine the number of moles of hydrochloric acid that was titrated.
5 Calculate the concentration of hydrochloric acid that was titrated.

Discussion

1 Compare your value for the concentration of the hydrochloric acid with that of other students and with the value provided by your teacher.
2 Discuss any variations in the value and suggest how to improve the accuracy of your results.
3 Justify why the conical flask was rinsed with water and not the solutions that were placed in it.

pg 235 solns

a) $n(C_2O_4K_2.2H_2O) = \frac{m}{M}$

$M = 110.07.$

$= \frac{0.291}{110.07}$

$= 0.0026437$ mol

$C_2O_4K_2 + 2NaOH \rightarrow C_2O_4Na_2 + 2H_2O.$

$n(C_2O_4K_2.2H_2O) \times 2 = n(NaOH)$

$= 0.0052875.$

$n(NaOH) = CV.$

$0.0052875 = C \times (18.12 \times 10^{-3})$

$C(NaOH) = 0.290524$ M.

whilst data sheet is to 2DP, normally titre are to 2DP

i.e. if 18.20 ml then 0.29 M.

but as 18.2 ml then 0.3 M

b) i) $n(Na_2CO_3) = \frac{m}{M_r}$

$M(Na_2CO_3) = 105.99$ $\qquad = \frac{5.267}{105.99}$

$n(Na_2CO_3)_{250mL} = 0.0496933$ mols

$n(Na_2CO_3)_{10mL} = n(Na_2CO_3)_{250} \times \frac{10}{250}$

$n(Na_2CO_3)_{10mL} = 0.0019877$ mols

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO$

$n(Na_2CO_3) \times 2 = n(HCl)$

$= 0.0039754$

$n(HCl) = cV$

$0.0039754 = c \times (21.3 \times 10^{-3})$

$c(HCl) = 0.1866417M$.

ii) $n(HCl) = cV$

$= 0.1866417 \times (27.1 \times 10^{-3})$

$= 0.0050579$ mols

$2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O$.

$n(HCl) \times \frac{1}{2} = n(Ba(OH)_2)$

$= 0.0025289$ mols

$n(Ba(OH)_2) = cV$

$0.0025289 = c \times (25 \times 10^{-3})$

$c(Ba(OH)_2) = 0.1011598M$ to 2sf $\underline{0.10M}$

$c(Ba(OH)_2) = 0.10M$ or $0.10\ mol\ L^{-1}$

Molar mass of $Ba(OH)_2 = 171.316$ per L^{-1} ÷ 10 = 17.13 g per litre