

## Evaluation

Prepare for a short test based on **Experiment 3-1**. Access videos from the electronic version of this experiment on the NCHE 121 eFundi website.

## Experiment 3-1: Quantitative analysis of benzoic acid

## 3.1.1. Background

## 3.1.1.1. Analytical chemistry

Analytical chemistry offers a toolbox of methods with which we can investigate the composition of matter. The aim of all types of chemical analysis is to determine the quantity of a substance (**quantitative analysis**) or the identity of a substance (**qualitative analysis**). The material being investigated during a chemical analysis is called a **sample**. The specific substance in the sample of which the identity or amount needs to be determined is known as the **analyte**. The oldest analysis techniques are classified as **wet chemical analysis** – also known as classical analysis. These methods are found at school level as volumetric analysis, gravimetric analysis, and tests for anions. Wet chemical analysis uses chemical reactions and stoichiometry, but no electronic instrumentation other than a balance. **Instrumental analysis** involves modern sophisticated electronic instrumentation and computer software. Analytical instruments measure physical quantities such as the absorption of electromagnetic radiation, potential difference, current, resistance and thermal conductivity which can be linked to the identities or quantities of a chemical substances.

## 3.1.1.2. Titrations

A **titration** is an example of a volumetric analysis. It is a quantitative classical analysis method.

Some titration apparatuses are shown in **Figure 3-1**. During a **titration**, a solution containing the analyte is placed in a conical flask. The mass and concentration of the analyte is unknown. A suitable reagent, which will completely react with the analyte, is chosen. A standard solution of the suitable reagent is added from the burette into the conical flask. The volume of this reagent required to completely react with all the analyte is determined. An indicator is usually added to indicate the point at which all the analyte has reacted. The **indicator** is a colouring agent (dye) that changes colour at the point where the reaction is complete. Using stoichiometric calculations, the unknown concentration of the analyte in the solution can be calculated.

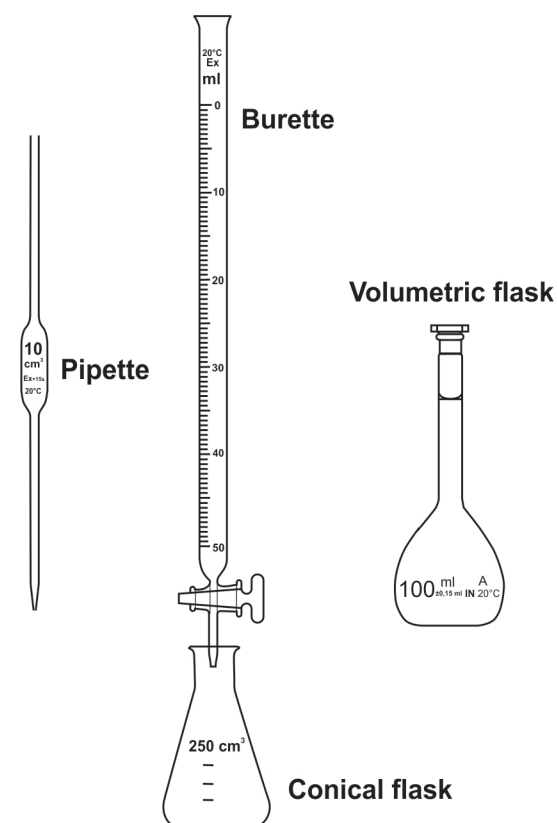
## 3.1.1.3. Titration calculations

You need to revisit calculations related to preparing solutions and titrations.

## 3.1.1.4. Molar concentration

When a solid dissolves in a liquid the molecules or ions are spread homogeneously throughout the liquid. The concentration of the solute is generally expressed as the amount of the dissolved substance in a standard amount of solvent or solution. To ease stoichiometric calculations, chemists prefer to use molar concentration:

Molar concentration is the number of moles of dissolved substance present per cubic decimetre ( $\text{dm}^3$ ) or litre (L) of solution.



**Figure 3-1:** Apparatus used when doing a titration.

$$c \text{ (mol}\cdot\text{dm}^{-3}\text{)} = \frac{n \text{ (mol)}}{V \text{ (dm}^3\text{)}}$$

Note that the definition refers to the volume of the solution and not the volume of the solvent. The molar concentration is also called the **molarity** of the solution. The concentration of substance A can be denoted as [A] or  $c_A$ . The units  $\text{mol}\cdot\text{dm}^{-3}$ ,  $\text{mol}\cdot\text{L}^{-1}$  and M (molar) are the same.

### 3.1.1.5. Preparing a solution from a weighed mass of substance

The equation below is extremely useful. It shows the relationship between the mass of a substance and its concentration in a given volume of solution.

$$\frac{m \text{ (g)}}{M \text{ (g}\cdot\text{mol}^{-1}\text{)}} = c \text{ (mol}\cdot\text{dm}^{-3}\text{)} \times V \text{ (dm}^3\text{)}$$

Using this equation, you'll be able to calculate the mass of substance required to prepare a solution with a desired concentration and volume. Remember that the unit for volume used here is litre or cubic decimetre and that  $1 \text{ dm}^3 = 1 \text{ L} = 1000 \text{ cm}^3 = 1000 \text{ ml}$ .

#### Example: Preparation of a standard sodium chloride solution

Calculate the mass of sodium chloride required to prepare a  $0.100 \text{ mol}\cdot\text{dm}^{-3}$  solution in a  $100 \text{ cm}^3$  volumetric flask.

## Solution

The following equation connects mass to concentration: 
$$\frac{m_{\text{NaCl}}}{M_{\text{NaCl}}} = c_{\text{NaCl}} \times V_{\text{NaCl}}$$

1. Calculate the molar mass of sodium chloride.
2. Convert the required volume of solution to litre or cubic decimetre ( $\text{dm}^3$ ) if necessary.
3. Calculate the mass required:

$$m_{\text{NaCl}} = M_{\text{NaCl}} \times c_{\text{NaCl}} \times V_{\text{NaCl}} = (58.442 \text{ g} \cdot \text{mol}^{-1})(0.100 \text{ mol} \cdot \text{dm}^{-3})(0.100 \text{ dm}^3) = 0.584 \text{ g}$$

According to this calculation, **0.584 g** of NaCl is required to prepare the desired solution.

## Practical skill: Preparation of a standard solution

The diagrams below show how to prepare a solution of known concentration.

<b>Step 1</b>	The sodium chloride (0.584 g) is placed in a volumetric flask.
<b>Step 2</b>	Some distilled water is added, and the flask is swirled to dissolve the sodium chloride. The flask is not filled completely at this point.
<b>Step 3</b>	When the sodium chloride has dissolved, more distilled water is poured into the volumetric flask to bring the volume almost to the mark. The last bit of distilled water can be added with a dropper to avoid overfilling of the volumetric flask. (This is a useful tip if you do not make solutions regularly.)
<b>Step 4</b>	The flask now contains $100.0 \text{ cm}^3$ ( $0.100 \text{ dm}^3$ ) solution with concentration of $0.100 \text{ mol} \cdot \text{dm}^{-3}$ . (Volumetric flasks with different capacities are available, including 10 mL, 25 mL, 50 mL, 100 mL, 250 mL, 500 mL, 1000 mL, 2000 mL and 5000 mL.)

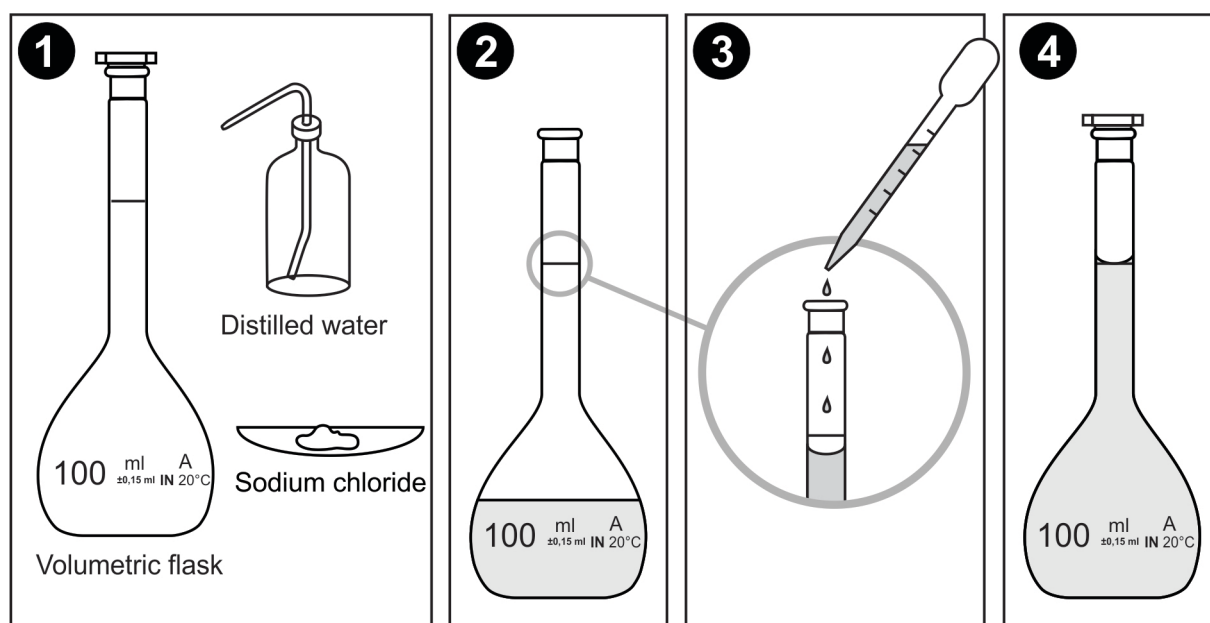


Figure 3-2: Preparing a solution of known concentration

### 3.1.1.6. Determination of the concentration of the analyte

If we are only concerned with the concentration of the analyte in the solution, the following relationship between concentration, volume and the stoichiometric coefficients of the analysis reaction may be used as a shortcut to the answer.

$$\frac{n_A}{n_B} = \frac{c_A \times V_A}{c_B \times V_B}$$

In this equation  $n_A$  and  $n_B$  are the stoichiometric coefficients of the reagents in the **balanced** reaction.



#### Example: Determination of the concentration of sodium hydroxide

The concentration of a 10.0 cm<sup>3</sup> sample of sodium hydroxide is determined by with a standard solution of oxalic acid. The concentration of the oxalic acid is 0.201 mol.dm<sup>-3</sup> and the titration volume obtained is 28.15 cm<sup>3</sup>. Calculate the concentration of sodium hydroxide solution.



#### Solution

The required equation is:

$$\frac{n_A}{n_B} = \frac{c_A \times V_A}{c_B \times V_B}$$

Then

$$c_B = \frac{c_A \times V_A \times n_B}{n_A \times V_B} = \frac{0,201 \times 28,15 \times 2}{1 \times 10} = 1,13\text{M}$$

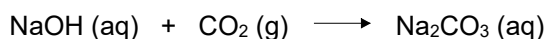
You can also find the solution with normal stoichiometric calculations. The number of moles of oxalic acid is related to the number of moles of sodium hydroxide. The latter may then be converted to concentration.

### 3.1.1.7. Standardisation of a reagent using a titration

Recall that a standard solution is a solution of known concentration. There are two ways to prepare these standard solutions:

#### (a) Use a solution of a primary standard as a reagent

A **primary standard** is a substance of which the exact concentration in a solution can be calculated from the mass of the substance and the volume of the solution. Not all substances are primary standards. The concentration of these substances can only be estimated by using the mass of the substance and the volume of the solution. Sodium hydroxide, for example, absorbs water vapour and carbon dioxide from the atmosphere.



This results in the lowering of the sodium hydroxide concentration over time. It is thus a good practice to determine the exact concentration of sodium hydroxide just before the analysis is carried out.

### (b) Use a reagent that has been standardised against a primary standard

Primary standards can be used to determine the exact concentration of substances that are not primary standards.

**Standardisation is the determination of the true concentration of a reagent that that is not a primary standard.**

### Conceptual example of standardisation

Suppose you want to determine the concentration of an unknown solution of hydrochloric acid using a titration. You decide to titrate 10.0 mL samples of the hydrochloric acid with 0.100 M sodium hydroxide solution. The sodium hydroxide solution is prepared by dissolving 0.400 g of the solid in water and filling the 100.0 mL volumetric flask to the mark. **However, sodium hydroxide is not a primary standard.** Consequently, the concentration of the solution will not be exactly 0.100 M. To determine the real concentration of the sodium hydroxide you should perform a standardisation. A convenient primary standard is oxalic acid dihydrate,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ . One way to standardise the sodium hydroxide is to make a solution of oxalic acid. This solution has a known concentration. (The concentration can be calculated from the mass of the acid and the volume of the solution.) Samples of the oxalic acid solution can then be titrated with the sodium hydroxide solution and the exact concentration of the sodium hydroxide solution can be calculated. You may use the familiar equation below to calculate the concentration of sodium hydroxide.

$$\frac{n_A}{n_B} = \frac{c_A \times V_A}{c_B \times V_B}$$

The concentration obtained by standardisation will differ from 0.100 M in most cases, but not very much. It will frequently be between 0.099 M and 0.110 M. This calculated concentration should now be used in further calculations.

### 3.1.2. Purities of chemical substances

The price of a given chemical depends on the degree of difficulty of its preparation, on whether it needs to be imported, and on its degree of purity. The percentage purity of a substance is defined as

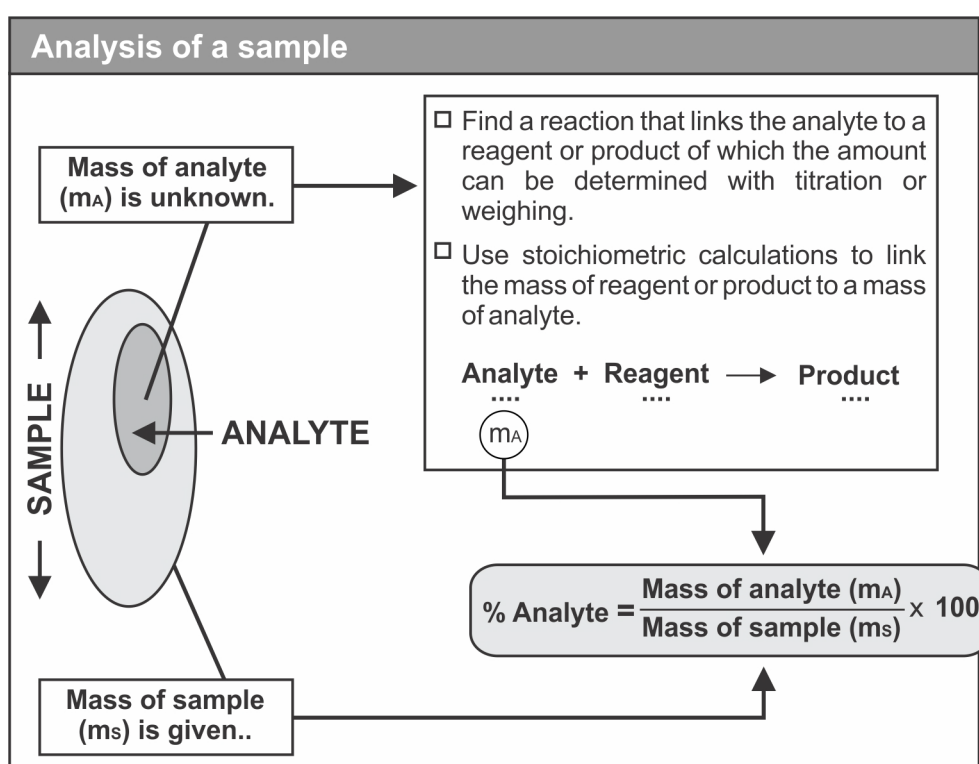
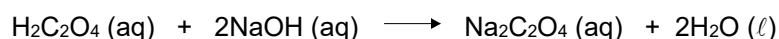
$$\% \text{ Purity} = \frac{\text{mass of pure substance}}{\text{mass of sample}} \times 100 .$$

The degree of purity required for a specific application should be considered when ordering chemicals for a laboratory. Using chemicals with a higher purity than necessary can have a significant cost implication. The purest grade of chemicals is the most expensive and is usually reserved for analytical work [quantitative and qualitative analysis]. In contrast chemicals of lower purities are frequently still suitable for preparing chemical substances. This is observed because the purity of a prepared product is usually more dependent on the purification techniques used during its preparation than on the purity of the reagents. The purity of a chemical substance is determined by the techniques of analytical chemistry.

**Figure 3-3** shows the principle on which all qualitative chemical analyses are based. The sample contains the analyte of which the amount is to be determined. A chemical reaction is selected that is specific for the analyte. The amount of the analyte is calculated from the stoichiometry of the reaction used for analysis. The percentage of the analyte is the ratio of the mass of the analyte and the mass of the sample multiplied by 100.

### Example

An impure sample of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) with a mass of 2,034 g is dissolved in  $100 \text{ cm}^3$  distilled water in a volumetric flask. Samples of  $10.0 \text{ cm}^3$  of the solution are titrated with standardised sodium hydroxide solution with concentration  $0.25 \text{ mol}\cdot\text{dm}^{-3}$ . The average titration value is  $16.50 \text{ cm}^3$ . Calculate the percentage of oxalic acid in the sample.



**Figure 3-3:** Quantitative analysis of a sample



### Explanation of the general analysis technique

### Solution

- The number of moles of NaOH required to react completely with the oxalic acid is

$$n_{\text{NaOH}} = c_{\text{NaOH}} \times V_{\text{tit}} = (0.25) \left( \frac{16.50}{1000} \right) = 4.125 \times 10^{-3} \text{ mol}$$

By using the stoichiometry of the reaction, the number of moles of sodium hydroxide used may be related to the number of moles of oxalic acid present in the sample. The number of moles of oxalic acid is half the number of moles of sodium hydroxide:

$$n_{\text{Oxalic acid}} = \frac{1}{2} \times 4.125 \times 10^{-3} = 2.061 \times 10^{-3} \text{ mol}$$

The mass of oxalic acid in 10.0 cm<sup>3</sup> of the sample solution is

$$m_{\text{Oxalic acid}} = nM = (2.061 \times 10^{-3} \text{ mol})(90.035 \text{ g}\cdot\text{mol}^{-1}) = 0.186 \text{ g.}$$

The mass of oxalic acid calculated in the last step represents only 10.0 cm<sup>3</sup> of the original 100 cm<sup>3</sup> sample solution. We have to multiply the calculated mass of oxalic acid by 10 before substituting into the equation. {We used 10.00 cm<sup>3</sup> of the available 100 cm<sup>3</sup>, so we used 10/100 = 1/10 of the sample in each titration.} The mass of the oxalic acid in the 100 cm<sup>3</sup> original solution is 10 × 0.186 g = 1.860 g.

$$\% \text{ Analyte} = \frac{m_{\text{Oxalic acid}}}{m_{\text{Sample}}} \times 100 = \frac{1.860}{2.034} \times 100 = 91.4\%$$

### 3.1.3. Experimental method

#### Additional apparatus and consumables

- 50 cm<sup>3</sup> Burette
- 10 cm<sup>3</sup> Pipette
- Pipette pump
- Propette

#### Chemicals

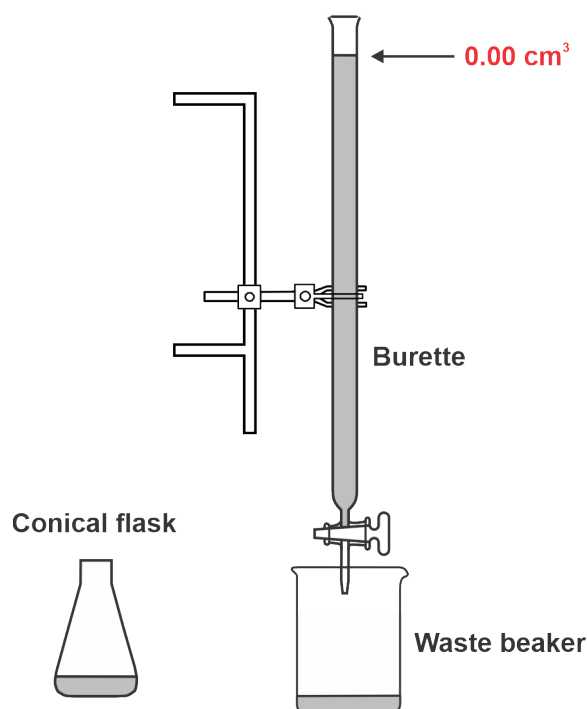
- Acetic acid solutions
- Benzoic acid from previous experiment (~0.5 g)
- Phenolphthalein indicator solution
- Sodium hydroxide solution (~0.035 M)



#### Titration technique and colour change

##### 3.1.3.1. Determining the concentrations of an acetic acid solution

1. Set up the apparatus as shown in the **Figure 3-4**.
2. Use a funnel to add approximately 15 cm<sup>3</sup> of sodium hydroxide solution to the burette.
3. There may be no air bubbles in the tip and tap sections of the burette. Open the tap of the burette wide so that sodium hydroxide solution flows into the waste beaker until the air bubbles flush out. You can help the process by tapping the burette with your fingernail where the air bubbles are present.
4. Use a funnel to add approximately 50 cm<sup>3</sup> of sodium hydroxide solution to the burette. [Fill the burette approximately to the 0.00 cm<sup>3</sup> mark at the top.] **Remove the funnel before you start the titration.**



**Figure 3-4:** A typical titration setup

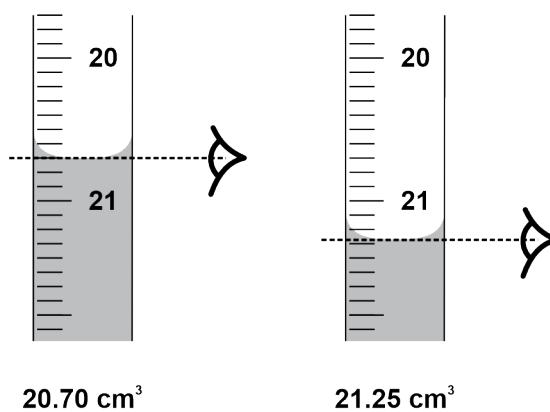
- Place  $10.0 \text{ cm}^3$  of acetic acid solution ( $V_A$ ) into the conical flask with a pipette and a pipette pump.



#### How to safely fit the pipette to the pipette pump

- Add 2 – 3 drops of phenolphthalein indicator to the acetic acid solution and put a white paper underneath the flask. The white paper makes it easier to see colour changes in the solution.

Burette readings are always noted to two decimals. You are using a Class B pipette that was mass produced and less accurate than a Class A pipette. Therefore, the second decimal is estimated as 0 or 5 [Figure 3-4].



**Figure 3-5:** Taking a burette reading



7. **Do a rough titration to determine the approximate titration volume:** Note the initial volume ( $V_1$ ) on the burette on the report sheet. Add  $1\text{ cm}^3$  amounts of sodium hydroxide solution from the burette into the conical flask until the indicator changes to any shade of pink. Note the end volume ( $V_2$ ) on the burette on the report sheet. The exact concentration of the sodium hydroxide solution will be provided in the laboratory.
8. The titration volume ( $V_B$ ) is obtained by subtracting the initial reading ( $V_1$ ) on the burette from the end reading ( $V_2$ ) on the burette:  $V_B = V_2 - V_1$ .
9. Clean the conical flask and then put  $10.0\text{ cm}^3$  of acetic acid solution ( $V_A$ ) into the conical flask using a pipette and a pipette pump. Add indicator solution to the conical flask.
10. Note the initial volume reading on the burette before starting the following titration.
11. Add sodium hydroxide solution from the burette into the conical flask until the added volume is approximately  $1,5\text{ cm}^3$  **less** than the estimated titration volume obtained from the rough titration.
12. Then add sodium hydroxide solution drop-by-drop while swirling to determine the titration volume to the nearest drop. **Stop the titration when a drop sodium hydroxide solution changes the colour of the indicator to a light, almost invisible shade of pink.** Note the end reading.
13. Repeat the titration with a fresh samples of acetic acid solution by repeating steps 9,10, 11 and 12. **You need at least three titration values that do not differ by more than  $0.10\text{ cm}^3$  from one-another.**

### 3.1.3.2. Determination of the purity of a benzoic acid sample

Use the benzoic acid that you prepared in **Experiment 2-1** for this determination.

1. Make a solution of benzoic acid in a  $100.0\text{ cm}^3$  volumetric flask [**Figure 3-2**]. Weigh out approximately  $0.5\text{ g}$  of your benzoic acid. Note the exact mass to three decimals. Place a funnel on top of the volumetric flask and then wash the benzoic acid into the flask with  $50\text{ cm}^3$  ethanol. Shake to dissolve the benzoic acid and then fill the flask to the  $100\text{ cm}^3$  mark with distilled water. Take care not to overfill the volumetric flask– use a propette to add the last bit of solvent. Use samples of this solution to determine the purity of your benzoic acid.
2. **Rough titration:** Do a rough titration following the procedure that was used in the determination of the acetic acid concentration. Use a  $10.0\text{ cm}^3$  sample of the benzoic acid solution that contains 3 drops of phenolphthalein indicator. Add standardised  $0.035\text{ mol}\cdot\text{dm}^{-3}$  sodium hydroxide solution during the rough titration. {The exact concentration of the sodium hydroxide solution will be provided in the laboratory.}



**NaOH-solution is corrosive. Avoid skin contact. Wash the affected area thoroughly with lots of water in case of accidental contact.**

3. **Accurate titrations:** Do an accurate titration following the procedure that was used in the determination of the acetic acid concentration. Titrate a  $10\text{ cm}^3$  sample of the benzoic acid solution containing three drops of phenolphthalein indicator solution with the standardised  $0.035\text{ mol}\cdot\text{dm}^{-3}$  sodium hydroxide solution.
4. Repeat the accurate titration until you have three values that do not differ by more than  $0.10\text{ cm}^3$  from one-another.
5. Calculate the percentage purity of your benzoic acid using the average titration value.

### **3.1.4. Waste disposal and clean-up**

- Chemical substances that were used or produced in this experiment should be discarded into the indicated waste containers.
- Wash and pack away all your apparatus. Ensure that your workspace is clean and dry and that all water and gas taps are closed.

### **3.1.5. Experimental report**

Complete the report and submit it to your student assistant before you leave the laboratory.