## Theory

When chlorine compounds are used to sterilise swimming-pool water, the active agent is usually chloric (I) acid, HOCl . It kills micro-organisms by oxidation. Chloric (I) acid and its conjugate base, the chlorate(I) ion, $\mathrm{ClO}^{-}$, together make up what is called "free chlorine". These species react with a solution of iodide ions in the same way as chlorine itself does. When chlorine reacts with potassium iodide in an acidic solution it liberates iodine:

$$
\mathrm{Cl}_{2}+2 \mathrm{KI} \rightarrow \mathrm{I}_{2}+2 \mathrm{KCl}
$$

The intensity of the colour of the iodine solution formed is a measure of the concentration of the oxidising chlorine in water. The concentration of chlorine in a sample of swimming pool water or diluted bleach is obtained by comparing the colour obtained on reaction with potassium iodide solution with those colours obtained by the similar reactions of some standard solutions of chlorine. This comparison can be done very accurately using a colorimeter (Fig. 1).


Fig. 1

## Procedure

NB: Wear your safety glasses.
Add $2.5 \mathrm{~cm}^{3}$ of Milton Sterilising fluid to a $250 \mathrm{~cm}^{3}$ volumetric flask and dilute to the mark with deionised water. To a series of five $50 \mathrm{~cm}^{3}$ volumetric flasks add $5 \mathrm{~cm}^{3}$ of $5 \%$ ethanoic acid solution.

Transfer the diluted Milton solution to a burette. To the first $50 \mathrm{~cm}^{3}$ flask add nothing at this stage; to the second $50 \mathrm{~cm}^{3}$ flask add $1.0 \mathrm{~cm}^{3}$ of this solution. To the third, fourth and fifth flasks, add $2.0 \mathrm{~cm}^{3}, 4.0 \mathrm{~cm}^{3}$ and 8.0 $\mathrm{cm}^{3}$ of the solution respectively.

Using a burette, transfer $5.0 \mathrm{~cm}^{3}$ of $2 \%$ potassium iodide solution to each flask and dilute to the mark with deionised water. Stopper each flask, mix thoroughly, and allow about five minutes for the colour to develop. These solutions are now the working standards. Label the flasks (Fig. 2) as A, B, C, D and E respectively.


Fig. 2

| Chemical | Flask A | Flask <br> B | Flask C | Flask D | Flask E |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 5\% Ethanoic acid | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ |
| 2\% Potassium <br> iodide | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ | $5 \mathrm{~cm}^{3}$ |
| Diluted Milton | $0 \mathrm{~cm}^{3}$ | $1 \mathrm{~cm}^{3}$ | $2 \mathrm{~cm}^{3}$ | $4 \mathrm{~cm}^{3}$ | $8 \mathrm{~cm}^{3}$ |
| Concentration of <br> NaOCl in p.p.m. | 0 | 4 | 8 | 16 | 32 |
| Total volume in <br> flask | $50 \mathrm{~cm}^{3}$ | 50 <br> $\mathrm{~cm}^{3}$ | $50 \mathrm{~cm}^{3}$ | $50 \mathrm{~cm}^{3}$ | $50 \mathrm{~cm}^{3}$ |

Switch on the colorimeter and place a 440 nm wavelength filter in the filter slot. Pour each working standard into a cuvette, rinsing each cuvette first with the solution it is to contain.

Using the operating procedure for the colorimeter, as per the manufacturer's instruction book, zero the instrument. Obtain the absorbance for each standard, starting with the most dilute. Rinse the sample cells with deionised water after each sample has been used.

Plot a graph of absorbance versus concentration (in terms of chlorine) for the series of standards.

To a $50 \mathrm{~cm}^{3}$ volumetric flask add $5 \mathrm{~cm}^{3}$ of $5 \%$ ethanoic acid solution, and then $5.0 \mathrm{~cm}^{3}$ of $5 \%$ potassium iodide solution. Fill the flask up to the mark with the swimming pool water or diluted bleach. Allow about five minutes for the colour to develop. Label this flask as flask F.

Obtain the absorbance for the solution in flask F.

From the graph, obtain the concentration of NaOCl in the sample. Multiply by 71 / 74.5 to calculate the concentration of free chlorine in the sample

## Table of results

Copy this table into your practical report book
Absorbance of solution in flask A
Absorbance of solution in flask B
Absorbance of solution in flask C
Absorbance of solution in flask D
Absorbance of solution in flask E
Absorbance of solution in flask F
Concentration of NaOCl in the sample
Concentration of free chlorine in the sample
=
$=$
$=$
$=$
$=$
$=$
$=$
$=$
=
$=$

Specimen results and calculations

| Absorbance of solution in flask A | $=0.00$ |
| :--- | :--- |
| Absorbance of solution in flask B | $=0.06$ |
| Absorbance of solution in flask C | $=0.12$ |
| Absorbance of solution in flask D | $=0.24$ |
| Absorbance of solution in flask E | $=0.43$ |



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Absorbance of solution in flask F =0.18
Concentration of NaOCl in the sample =12.6 p.p.m}
Concentration of free chlorine in the sample =12.6 X 51.5/74.5 p.p.m
= 8.71 p.p.m
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## student questions

Why is potassium iodide used in this experiment?
Potassium iodide is readily oxidised to iodine by chlorine. Chlorine solutions do not themselves have sufficient colour to be analysed using a colorimeter, whereas the iodine solutions formed do.

## Why is ethanoic acid used in this experiment?

Acidic conditions are necessary to ensure complete reaction of chlorine with potassium iodide.

Why is excess potassium iodide used in this experiment?
To ensure that all of the chlorine reacts, and that all of the iodine formed dissolves.

The amount of chlorine in a water sample can also be determined by titrating the iodine solution formed (on reaction with potassium iodide) with standard sodium thiosulfate solution. What advantage is there in using a colorimeter for determining chlorine?
The colorimeter reading can be taken very quickly. Once the calibration curve is available, the concentration of chlorine can then be very quickly found. The colorimetric method would be particularly useful where a number of different water samples have to be analysed. The alternative would be to carry out a number of titrations for each sample, which would be very time-consuming.

