SPECTROSCOPY

Spectroscopy is any type of chemical analysis that involves the use of the electromagnetic spectrum (light). Samples are exposed to light of different energies, and the amount of radiation that is absorbed or emitted is recorded. This type of analysis can be used with water samples.

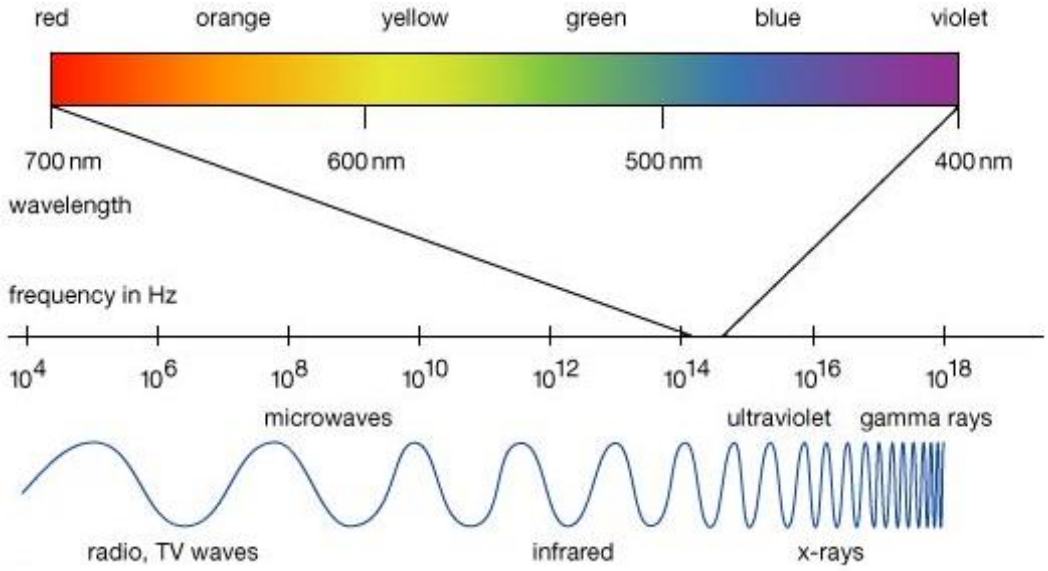
Spectroscopic analysis is used to:

1. Determine the components of a sample (qualitative analysis).

2. Determine the concentration of one particular component of a sample (quantitative analysis).

THE ELECTROMAGNETIC SPECTRUM

The electromagnetic spectrum describes the range of all possible electromagnetic radiation frequencies.



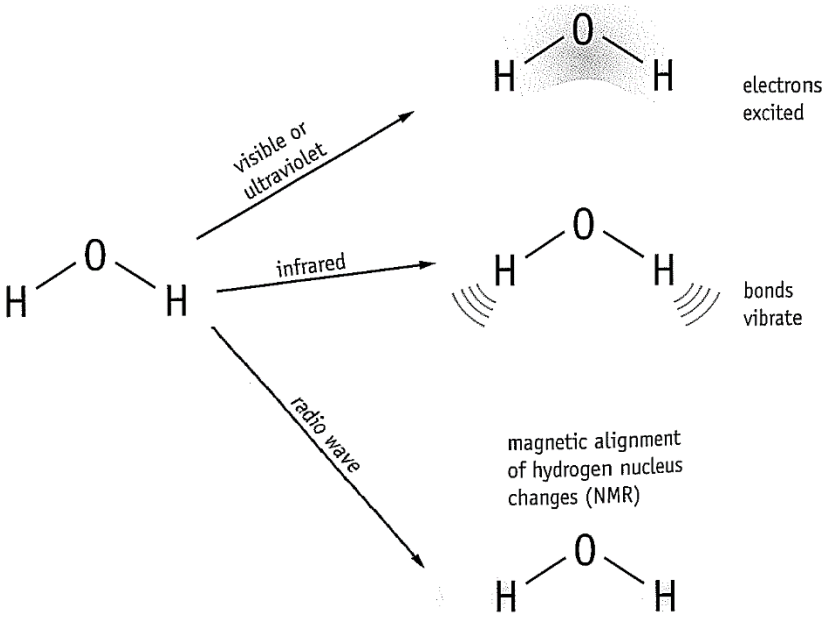
Radiation from each portion of the electromagnetic spectrum has a specific frequency, wavelength and energy associated with it. Since there are so many different types of electromagnetic energy, there are also many different types of spectroscopic analyses.

Energy of Light	Type of Light	Type of Spectroscopy
High ↓ Low	UV-Visible	UV-Visible Atomic Absorption
	Visible	Colorimetry Atomic Absorption Flame Tests
	Infrared	Infrared
	Radio-waves	NMR

USING RADIATION IN SPECTROSCOPY

Radiation interacts with atoms and molecules in different ways. Which part of an atom or molecule is affected and what changes occur simply depends upon the wavelengths or energies involved.

For example:

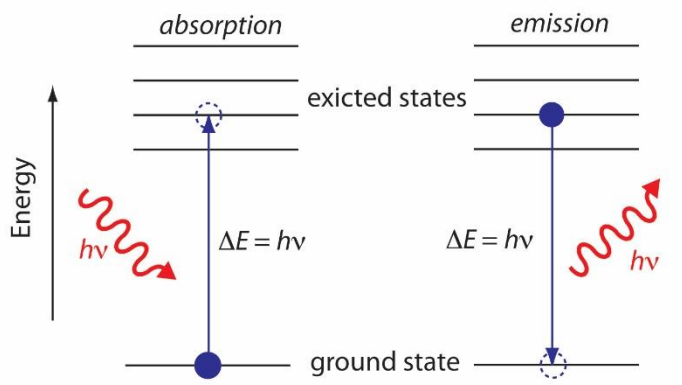


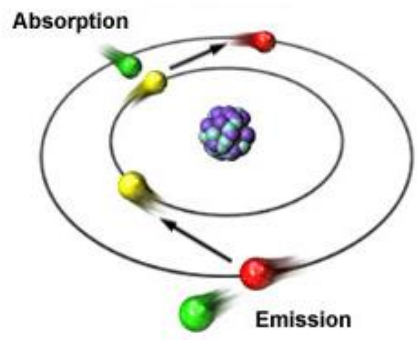
The type of spectroscopy chosen for an analysis depends on:

- The type of energy that is best absorbed/emitted by a sample.
- The information that is required from the analysis.

THE EFFECTS OF RADIATION ON ATOMS

Light in the visible and UV section of the electromagnetic spectrum has just the right amount of energy to be absorbed by valence electrons.





When an **atom** is excited by light, its **valence electrons** can absorb a photon and move to a higher energy level. The energy of the absorbed photon must be exactly equal to the difference between the final and initial energy levels. When an electron is in a higher-energy shell it is said to be in an **excited state**.

- The absorbed energy is used to overcome the forces of attraction between the valence electrons and the positively charged nucleus.
- Depending on how much energy is absorbed, a valence electron may move up one, two or many energy levels.
- When an electron is in an excited state, it is very unstable. The excited electrons almost instantly return to a lower and more stable energy level.
- As excited electrons return to a lower energy level or their ground state, they emit the difference in energy levels as radiation of specific wavelengths.

There are two distinct processes occurring when UV or visible light is used to analyse a sample.

1. UV or visible **light is absorbed** by the sample causing electrons to move to an excited energy level.
2. UV or visible **light is emitted** as the excited electrons fall to a lower energy level.

These two processes are the basis of a number of different spectroscopic techniques.

Light absorbed/emitted	Type of Spectroscopy
Emitted	Flame Tests (covered in Unit 1)
Absorbed	UV-Visible Spectroscopy Colorimetry Atomic Absorption Spectroscopy

QUANTITATIVE ANALYSIS

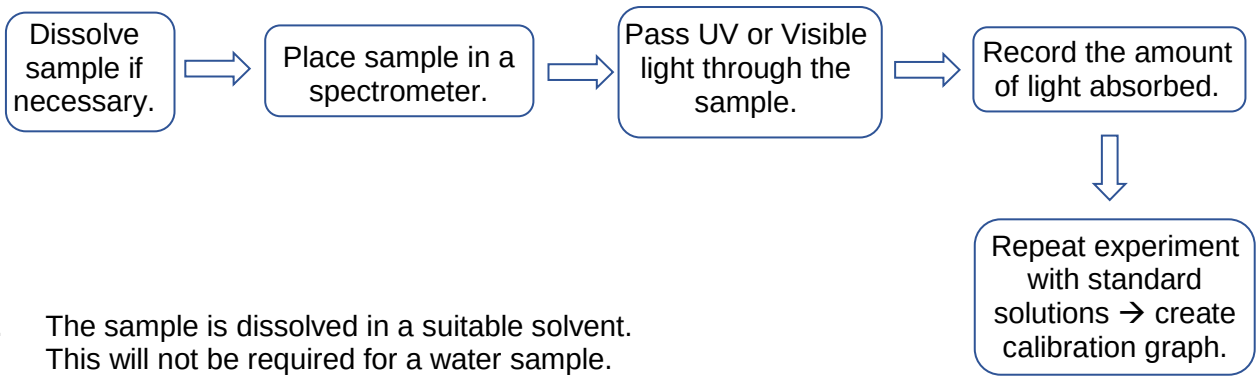
Quantitative analysis of samples is done by measuring the amount of light absorbed by a sample. Examples of these types of spectroscopy are:

- Colorimetry
- UV-Vis Spectroscopy
- Atomic Absorption Spectroscopy

These types of spectroscopy can be used to determine the concentration of a component in a sample. For example:

- The concentration of $NaCl$ in sea water.
- The amount of dissolved metals in ground water.
- The concentration of pesticides in a river.

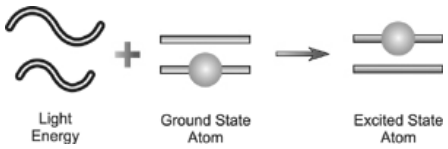
STEPS INVOLVED IN QUANTITATIVE ANALYSIS VIA SPECTROSCOPY



1. The sample is dissolved in a suitable solvent.
   This will not be required for a water sample.

2. The sample is placed into a spectrometer. A spectrometer is an instrument that measures the amount of radiation absorbed by a sample.

3. Radiation of a **specific frequency** is passed through the sample by the spectrometer. Some of this radiation is absorbed by the sample and some is transmitted.



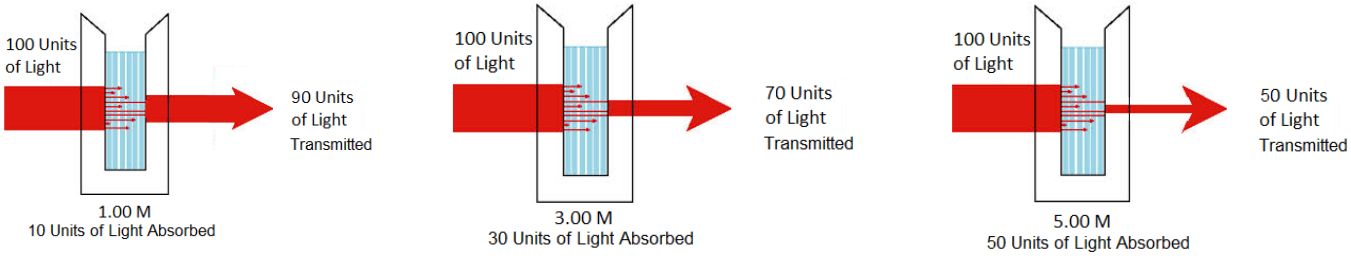
4. The radiation that is not absorbed by the sample reaches a detector.

   The detector compares the amount of radiation that initially passed through the sample to the amount of radiation that makes it to the detector. The difference is recorded as an absorbance reading.

   Amount of light absorbed by the sample = Initial amount of light – the amount of light hitting the detector.

The amount of light absorbed is proportional to the concentration of the sample.

Absorbance $\propto$ Concentration ***(At low concentrations only)***



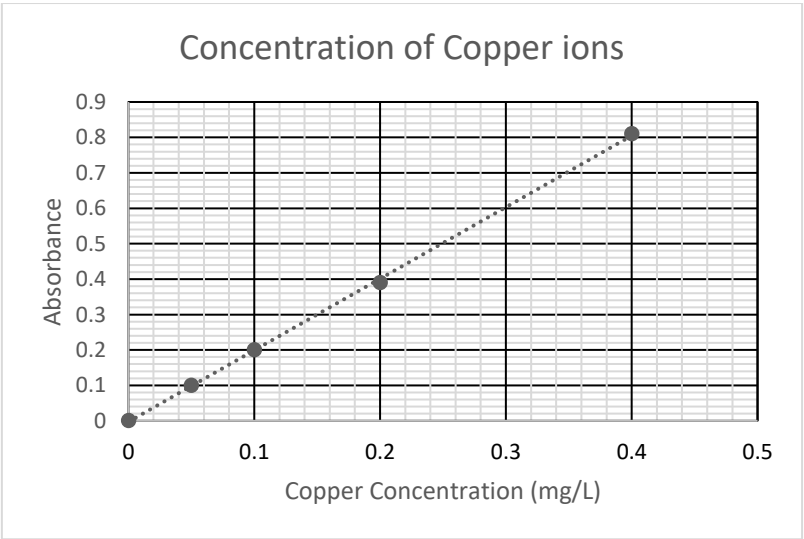
5. The concentration of a species is determined by comparing the amount of radiation absorbed or with the results obtained from samples of known concentrations (standard solutions).

For example: Analysis of Cu^{2+} ion concentration in a sample of water.

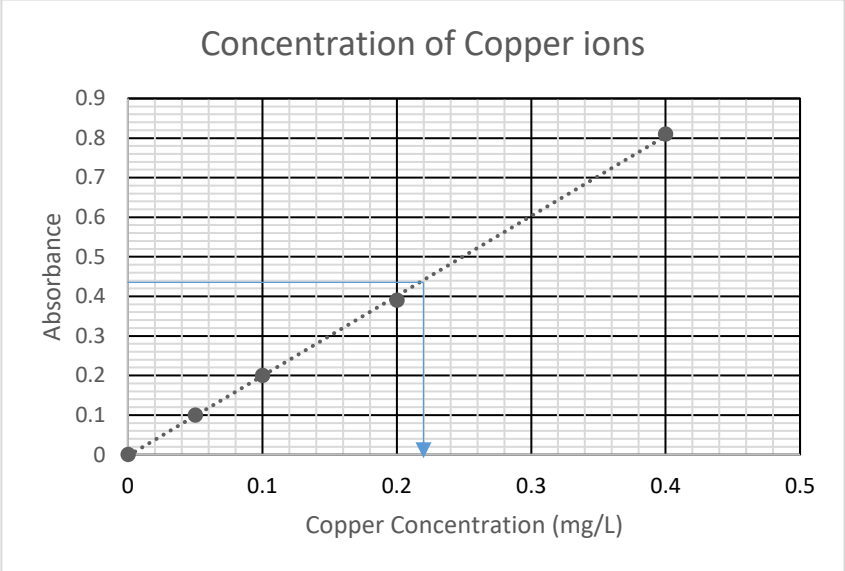
i. Standard solutions of Cu^{2+} ions, and the water sample, are analysed using a spectrometer:

Concentration of Cu^{2+} ions (mg/L)	Absorbance
0.00	0.00
0.050	0.10
0.100	0.20
0.200	0.39
0.400	0.81
Sample	0.42

ii. A calibration curve is drawn from the data (use a line of best fit).

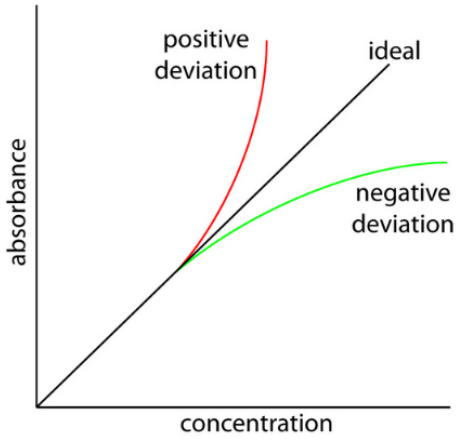


iii. The concentration of the sample is determined from the calibration graph.



The concentration of Cu^{2+} in the sample is 0.220 mg/L.

CALIBRATION CURVES

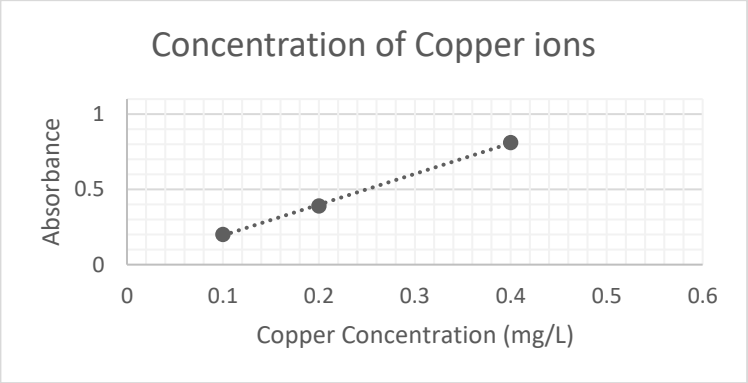


At higher levels of concentration, the absorbance-concentration relationship may become non linear. Therefore, **do not extrapolate at high concentrations**.

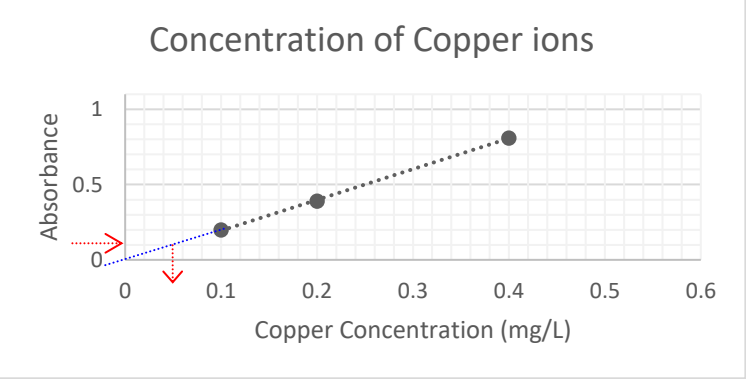
At low concentrations, the relationship between concentration and absorbance is constant and predictable, therefore, extrapolation can be performed.

For example:

Determine the concentration of Cu^{2+} ions when the absorbance is 0.10, 0.60 and 1.0.

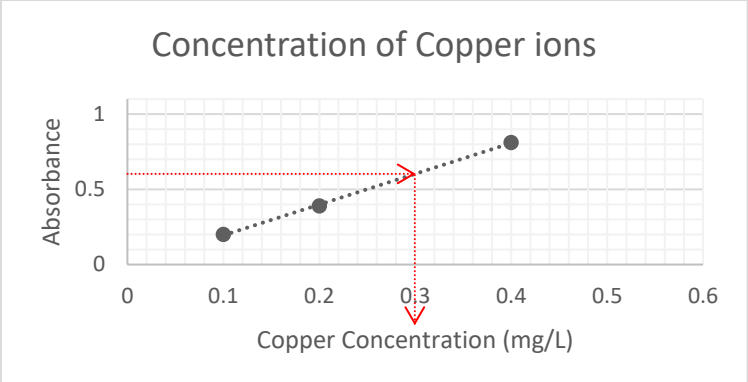


At an absorbance of 0.10, the graph can be extrapolated downwards.
$\therefore c(Cu^{2+}) = 0.050\, mg/L$

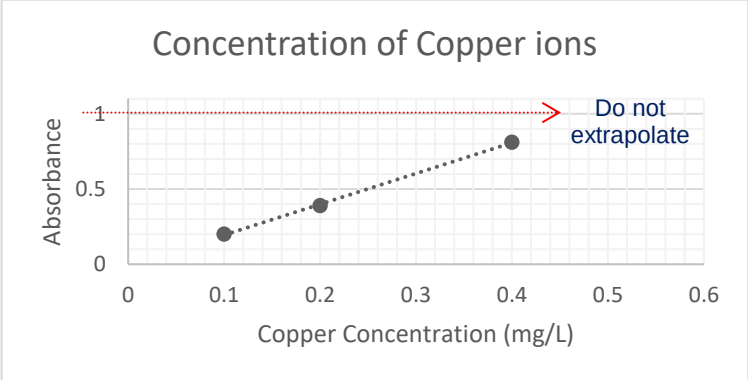


An absorbance of 0.60 falls within the date of the given calibration curve → read concentration off the graph.

$\therefore c(Cu^{2+}) = 0.30\, mg/L$



An absorbance of 1.0 does not fit within the data of the given calibration curve. Since the graph cannot be extrapolated at high concentrations, the sample will need to be diluted so that its absorbance falls within the calibration data.



Note:

- Standards are chosen so that a linear plot is obtained.
- If plotted points are slightly scattered, we draw the line of best fit.

  A line of best fit by eye is drawn through the scatterplot so that an equal number of points lie on either side of the line and/or the sum of the distances of the points above the line are roughly equal to the sum of the distances below the line.
- Never force a curve to pass through the origin – draw the line of best fit instead.

CALIBRATING THE SPECTROMETER

Calibration curves are constructed every time a spectrometer is used. This is because the amount of absorbance by the standard solutions and the sample will change depending on the exact conditions under which the analysis was conducted.

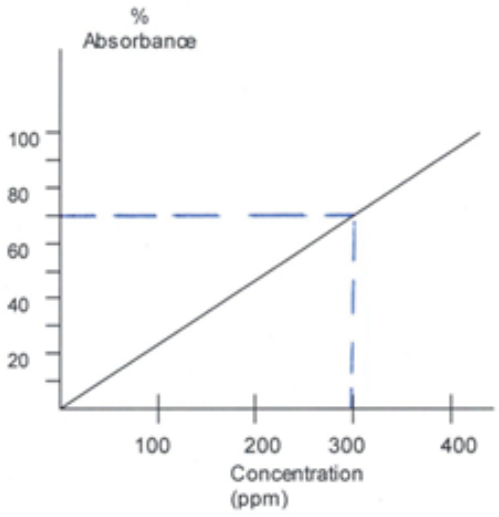
For example: The amount of absorbance measured can be affected by:

- The temperature of the sample.
- Absorbance by the solvent.
- Absorbance by the sample container (cuvette).

Calibration curves correct for these variables since the conditions under which the sample is analysed are identical to those used for the standard solutions. That is, any absorbance due to the solvent or the cuvette will be identical in all solutions that are tested.

For example: How temperature effects absorbance readings.

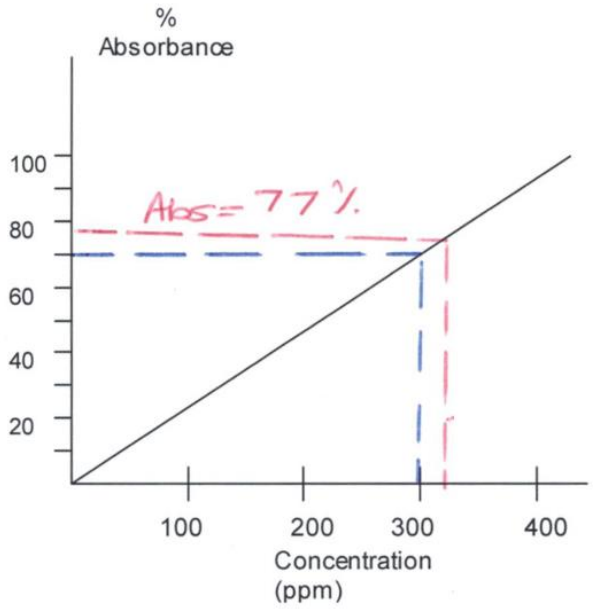
The calibration curve for the concentration of copper ions in solution is shown below.
The data for the calibration curve was collected at a temperature of 20°C.



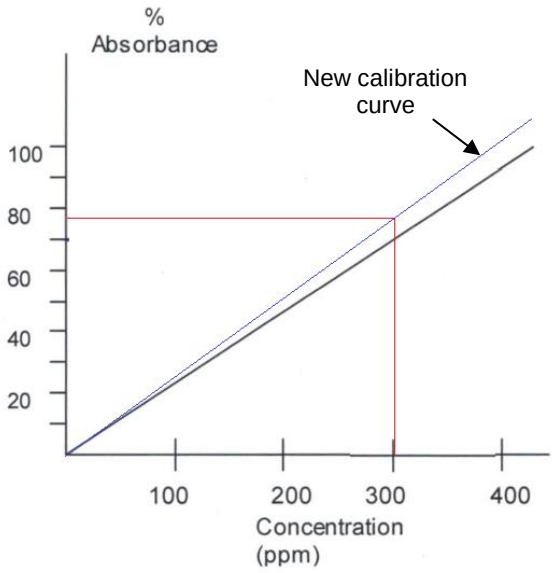
A water sample was tested at 20°C and had an absorbance of 70%.
This indicates that the copper ion concentration was 300 ppm.

The next day, the same water sample was tested again. This time the temperature was 25°C and the absorbance reading was 77%, so the increase in temperature caused a 10% increase in absorbance.

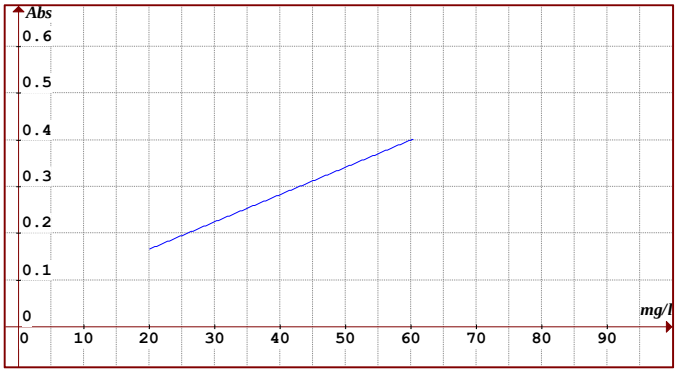
If the same calibration graph is used to determine the concentration of copper ions, then an erroneous concentration of 330 ppm will be calculated.



However, if data for a new calibration graph is collected at 25°C, then all of these absorbances will also be 10% higher than they were at the lower temperature. Now when the absorbance of 77% is used, the correct concentration of 300 ppm is obtained!!



QUESTION 48
The following standard curve was produced using a spectrometer.



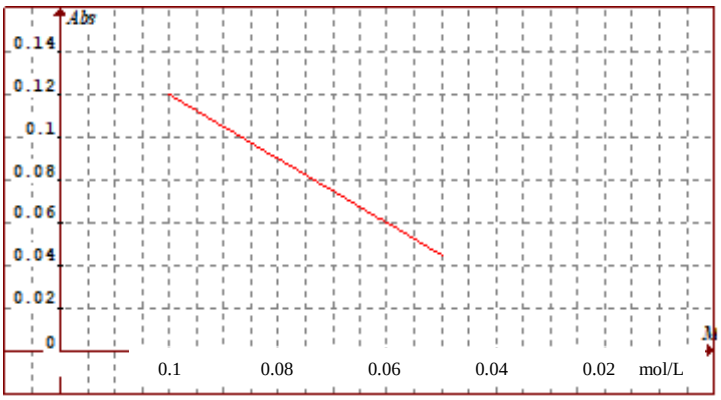
Can this curve be used to determine the concentration of a solution that produces an absorbance reading of:

(a) 0.1?
(b) 0.5?

If yes, state the concentration. Otherwise, give a reason why a concentration cannot be determined.

Solution

QUESTION 49
The following standard curve was produced using a spectrometer.



Can this curve be used to determine the concentration of a solution that produces an absorbance reading of:

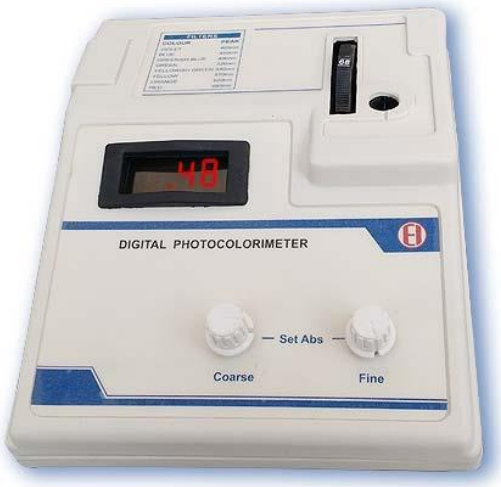
(a) 0.14?
(b) 0?

If yes, state the concentration. Otherwise, give a reason why a concentration cannot be determined.

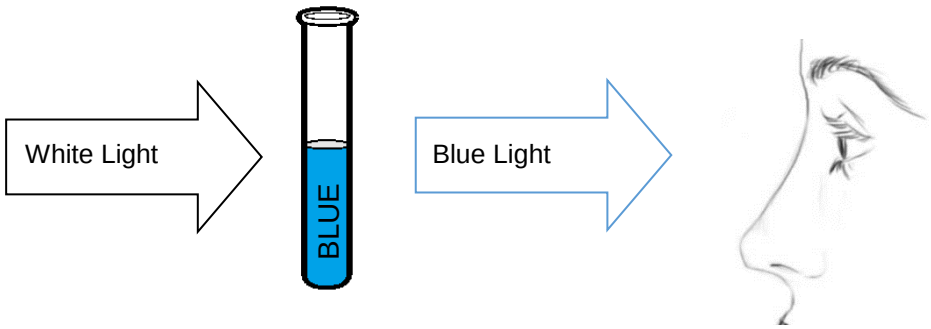
Solution

COLORIMETRY
(VISIBLE SPECTROSCOPY)

Colorimetry is a quantitative tool that measures the concentration of substances in **coloured** solutions.



Solutions seem coloured since they absorb some of the colours from white light and transmit others.

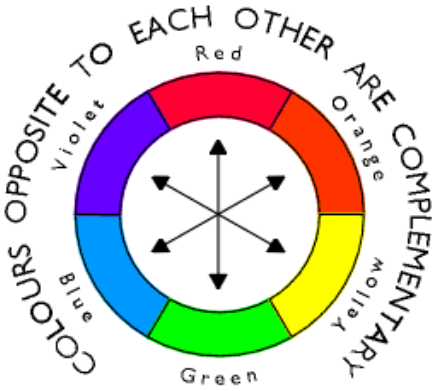


Orange Light Absorbed

Blue light is not absorbed.
Orange light is absorbed.

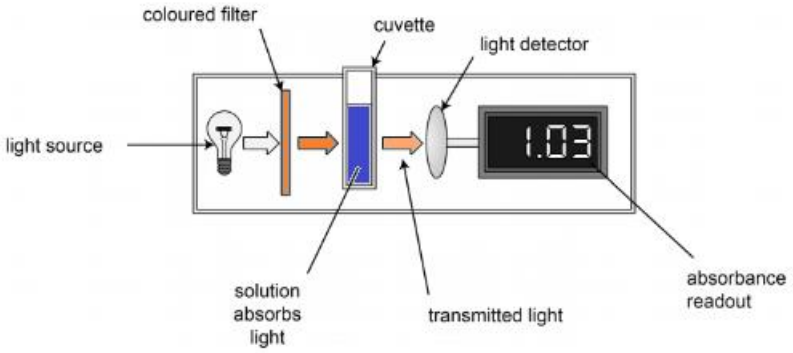
Since orange is absorbed by a blue solution, orange is known as the complementary colour of blue. If a blue solution is to be analysed, orange light must be used since it will be absorbed whereas blue light will not.

COMPLEMENTARY COLOURS



Colour circle showing complementary pairs of colours

THE COMPONENTS OF A COLORIMETER



- The coloured sample solution is placed into a glass or quartz vessel (a cuvette), which is inserted into the colorimeter.
- The light source produces white light which is a mixture of all of the coloured forms of electromagnetic radiation.
- The light passes through a coloured filter so that only light that is complementary in colour to that displayed by the sample solution is selected.
  (E.g. An orange filter is selected for blue solutions.)
- Light of the selected wavelength is passed through the sample.
- The sample being tested absorbs this light.

  Valence electrons in the sample become excited as they absorb light from the light source.

The amount of light absorbed is directly proportional to the concentration of sample in the solution.

The greater the concentration of the component being analysed, the greater the amount of light absorbed.

Absorbance $\propto$ Concentration

- The remaining light reaches the detector.
- The amount of light absorbed is displayed on the recorder.
- A calibration curve is drawn by measuring the absorbance of a set of standard solutions. The concentration of the unknown solution can then be determined.

ADVANTAGES OF COLORIMETRY

- Simple technique.
- Equipment and reagents are relatively inexpensive.
- Can be used to analyse a variety of chemical species e.g. most metal cations and some simple anions.

DISADVANTAGES OF COLORIMETRY

- Not capable of detecting very low concentrations of chemical species.
- Results obtained are not as accurate as Atomic Absorption Spectroscopy.
- Technique is restricted to samples that can absorb **visible** light. (Solutions must be coloured or able to be coloured.)
- More than one substance may absorb at the chosen wavelength and therefore, this technique is only suitable for use with samples that are pure.

QUESTION 50

An aqueous solution containing MnO_4^- is a clear violet colour. The concentration of this solution is to be measured using visible spectroscopy. An aqueous MnO_4^- solution will:

A Absorb mainly yellow light and therefore allow yellow light to pass through the solution.

B Absorb mainly yellow light and therefore allow violet light to pass through the solution.

C Absorb mainly violet light and therefore allow yellow light to pass through the solution.

D Absorb mainly violet light and therefore allow violet light to pass through the solution.

QUESTION 51

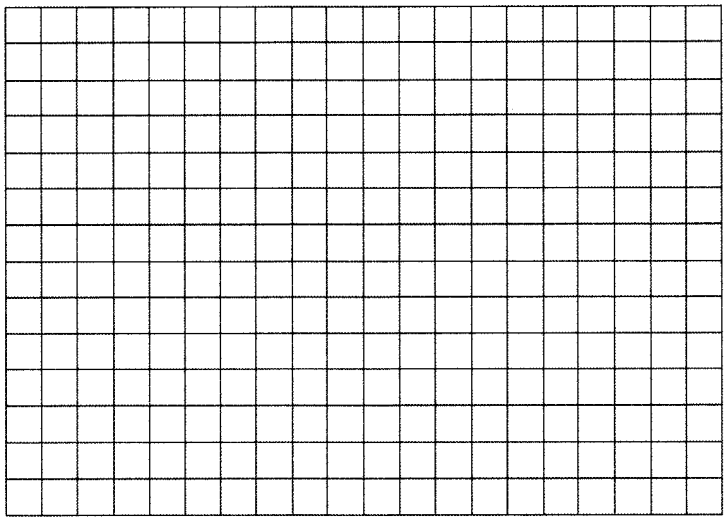
(a) Can the concentration of opaque solutions be accurately determined in visible spectroscopy? Give a reason for your answer.

(b) If a sample was opaque, would the calculated concentration be equal to, higher than or lower than the true value?

QUESTION 52
The absorbance of varying concentrations of a copper sulfate solution was determined using visible spectroscopy and given below.

Standard	Concentration ($mmol/L$)	Absorbance
1	0	0.00
2	10	0.10
3	20	0.18
4	30	0.30
5	40	0.42
6	50	0.50

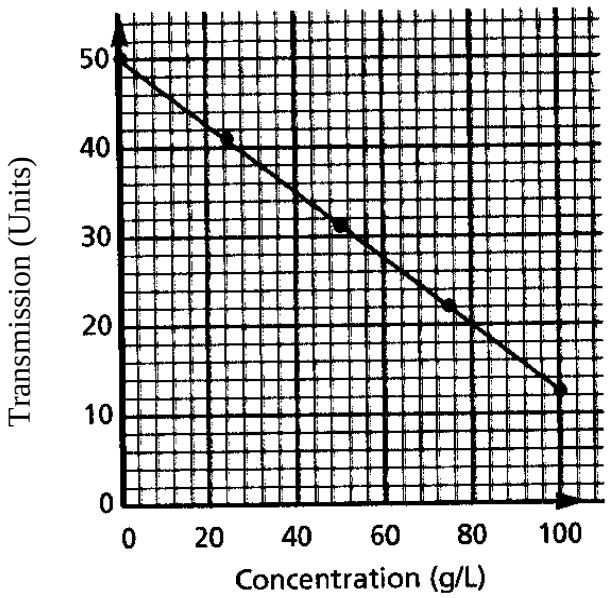
(a) Plot the corresponding calibration curve on the grid below.



(b) A sample of copper sulfate solution was placed in the colorimeter and an absorbance reading of 0.35 units was obtained. Estimate the concentration of the solution.

(c) What light intensity reading would you expect a solution with concentration 25 mmol/L to have?

QUESTION 53
A colorimeter is used to measure the concentration of copper sulfate in a pure solution. The following calibration graph is obtained.



(a) What happens to the intensity of light transmitted as the concentration increases? Give a reason for your answer.

(b) A sample of copper sulfate solution was placed in the colorimeter and a light intensity reading of 26 units was obtained. Estimate the concentration of the solution.

(c) What light intensity reading would you expect a solution with concentration 20 g/L to display?

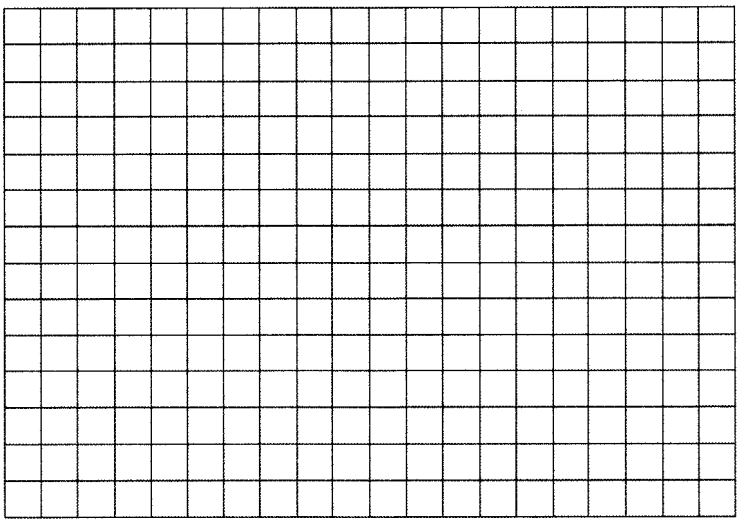
QUESTION 54

A student wishes to determine the concentration of permanganate in a solution of unknown concentration of potassium permanganate, which is purple in colour. The student prepares a set of standard solutions of permanganate concentration between 1 and 10 ppm. These solutions as well as the unknown are analysed using a colorimeter, the results of which are given below.

[*Permanganate*] **(** *ppm* **)**	**Absorbance**
0	0.000
1.0	0.064
3.0	0.193
5.0	0.321
7.0	0.448
10.0	0.641
Unknown	0.535

(a) Which light source, purple or green, you would choose for this analysis? Give a reason for your choice.

(b) Construct a calibration curve and determine the concentration of permanganate (in ppm) in the sample.

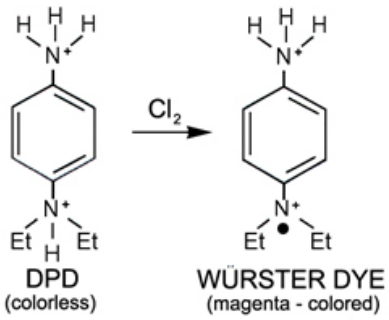


(c) (i) Determine the mass of permanganate (in μg) in 100 ml of the unknown solution.

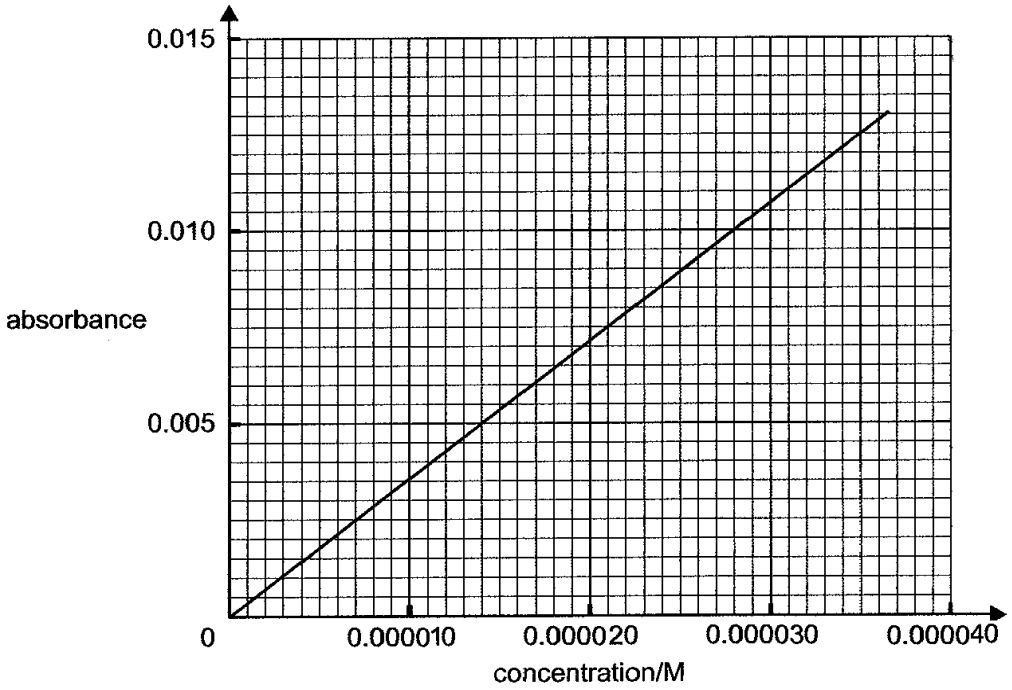
(ii) Express this concentration in M.

QUESTION 55

The water in pools and spas should have a free chlorine content of 1.00 – 3.00 ppm.
One method of testing for free chlorine concentration is to treat the water sample with DPD.
This reagent is colourless but is converted to magenta when reacted with chlorine.

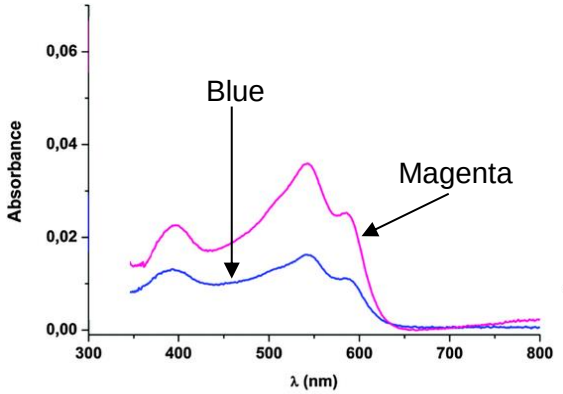


One such test involved reacting a 100.00 ml sample of pool water with excess DPD.
This procedure was also followed for five standard solutions of chlorine. The results were converted into a calibration graph as shown below:



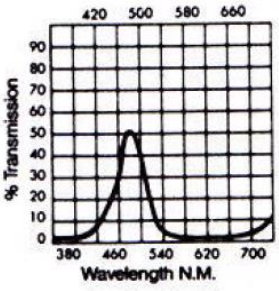
(a) Determine if the levels of chlorine are within the exceptable range if the absorbance of the sample was 0.10.

(b) The graph below shows the absorbtion spectra of blue and magenta solutions.

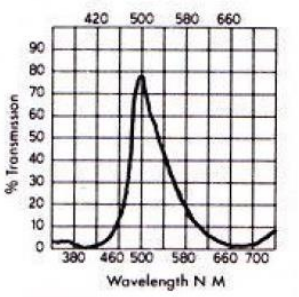


i. Which wavelength is best absorbed by magneta?

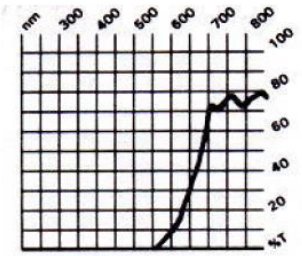
ii. The graphs below show which wavelenths of light are transmitted by different filters. Use the graphs to determine which filter would be the best to use for this experiment.



Blue Filter



Green Filter



Red Filter

iii. The green filter lets through a range of wavelengths. How could this affect the experimental results?

iv. Copper ions are a common contaminant of water samples since some water supply pipes can be made of this metal. Copper ions turn water blue. How would the presence of copper ions affect the calculated concentration of chlorine. (Look at the graph in part 'i' for a hint!)