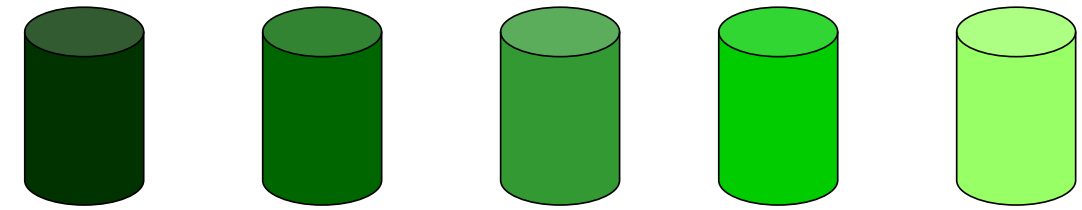
COLORIMETRY

Colorimetry is a mainly quantitative technique that is used to determine the concentration of solute particles in a solution. **This method determines the concentration of a coloured solute in an unknown solution by comparing the intensity of light it absorbs with that of a series of standard solutions**. It is mainly used for analysing cations but it can also be used for analysing anions. It can only be used to analyse coloured solutions. Colourless solutions can be analysed if the solute particles are made to react with a substance in order to produce a coloured ionic complex.

BACK GROUND INFORMATION

When white light passes through a coloured solution, the solute particles will interact with the light. Recall that white light contains all the wavelengths or colours of light that make up the visible spectrum. The solute particles will mainly absorb a particular colour of light but this colour is not responsible for the colour of the solution. The colour of the solution is complimentary to the colour absorbed. For example, a solution that appears orange will contain solute particles that absorb blue light and transmit orange light and a solution that appears blue will contain solute particles that absorb orange light and transmit blue light. **Transmitted light is responsible for the colour of a solution.**

Consider 5 glasses of lime cordial.

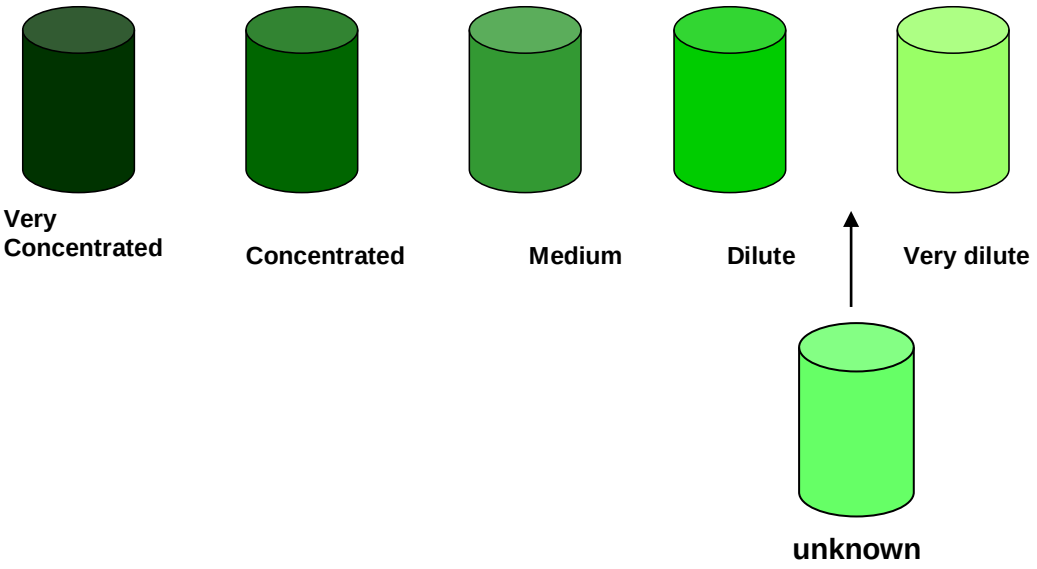


Very Concentrated | **Concentrated** | **Medium** | **Dilute** | **Very dilute**

Lime cordial looks green because the solute particles in the cordial absorb purple light but transmit the complimentary green colour. The “Very Concentrated” lime cordial solution contains a large number of solute particles, therefore the solution is absorbing most of the purple light that is falling on it resulting in its dark green appearance. As the solutions become less concentrated, less purple light is absorbed and the shade of green observed becomes lighter.

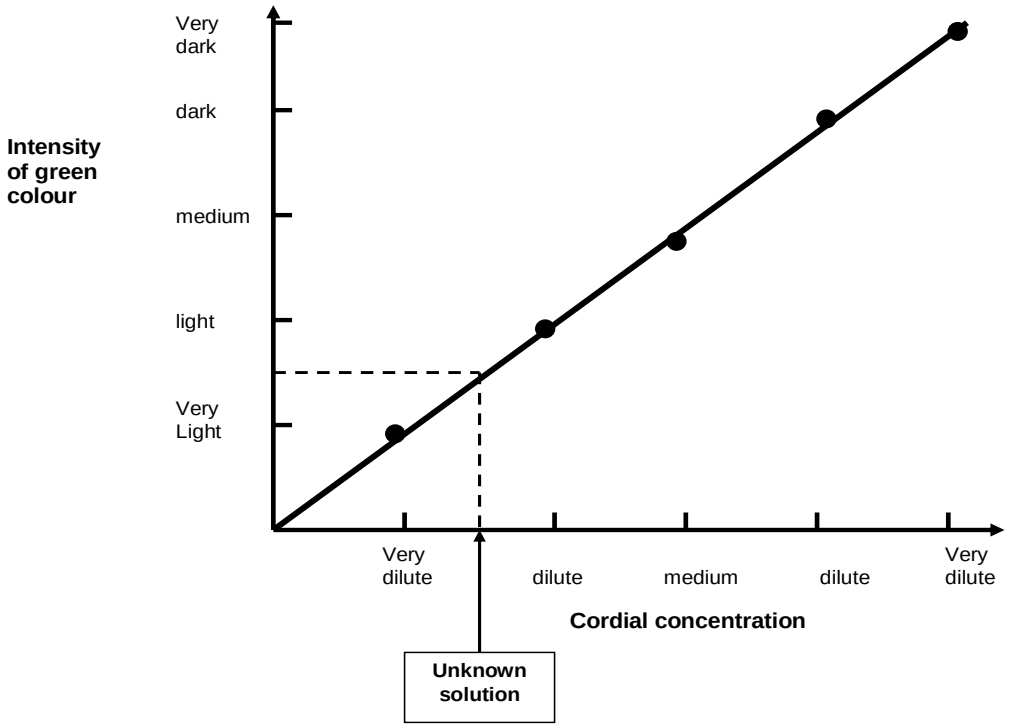
These 5 solutions can be considered to be **standard solutions** because they all have a known concentration, even though their concentrations have been described using very simple terms instead of precise numerical measurements such as molarity, ppm etc.

We can use these standard solutions to determine the concentration of an unknown cordial solution. There is a direct relationship between the darkness of the green colour of the solutions and their concentrations. To analyse a lime cordial solution of unknown concentration, it is necessary to compare the colour of the standards with the unknown solution.



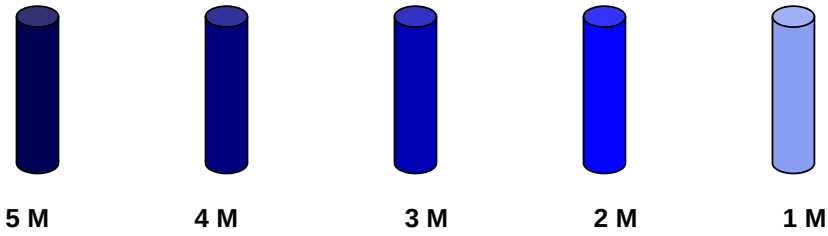
The shade of green of the unknown is somewhere between the “dilute and “very dilute” standard solutions. Therefore we can conclude that the unknown cordial solution has a concentration of **“Dilute to Very Dilute”.**

This simple example of quantitative analysis can be represented by a graph known as a **standard curve** or **calibration graph.** In this case the standard curve will graph the concentration of the standard solutions against the darkness of their green colour.

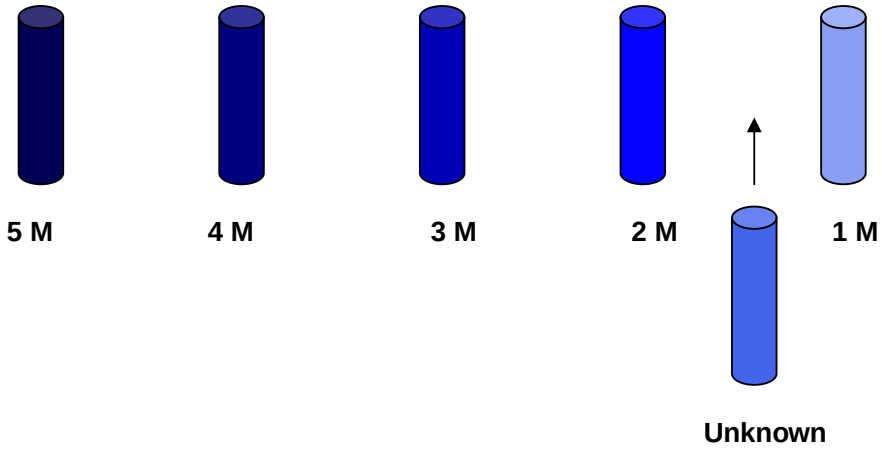


This analysis of cordial is very trivial but the principles involved can be applied to the analysis of solutions that have a much greater scientific importance.

This time, let's consider 5 test tubes of $CuSO_4$ solution.

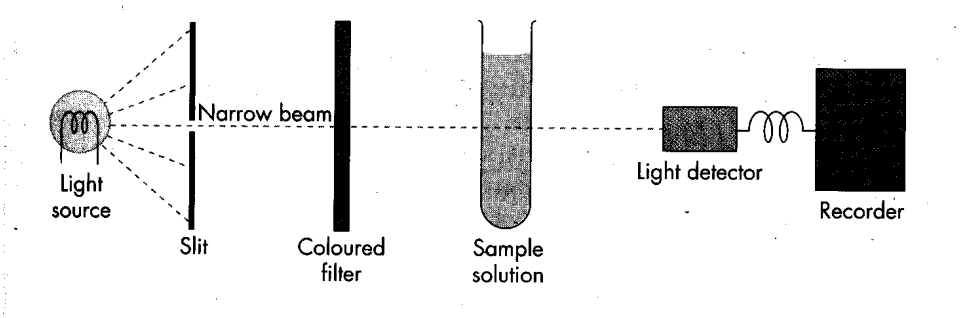


$CuSO_4$ solutions are blue because the Cu^{2+} ion absorbs orange light and the transmitted complimentary colour of blue is observed. The more concentrated the solution the darker the shade of the blue colour. This time we have measured the concentration much more precisiely using molarity (M). Once again the above solutions are known as standard solutions because their concentrations are known. An unknown solution of $CuSO_4$ can have its concentration determined by comparing the intensity of its colour with those of the standard solutions.



When matched up against the standard solutions, the unknown has a concentration that is somewhere between 1 and 2 M. Since we are just using our eyes to compare the colour of the unknown with the standard solutions, a more precise determination of the unknown's concentration is not possible. The terms used to describe the colour of the cordial solutions such as "dark", "very dark" etc. need to be replaced with a numerical scale. This can be achieved by finding the **ABSORBANCE** of the solutions using a quantitative technique known as **COLORIMETRY.**

The instrument used in colorimetry is a **COLORIMETER** or **SPECTROPHOTOMETER.** A cross-section of such an instrument is shown below:



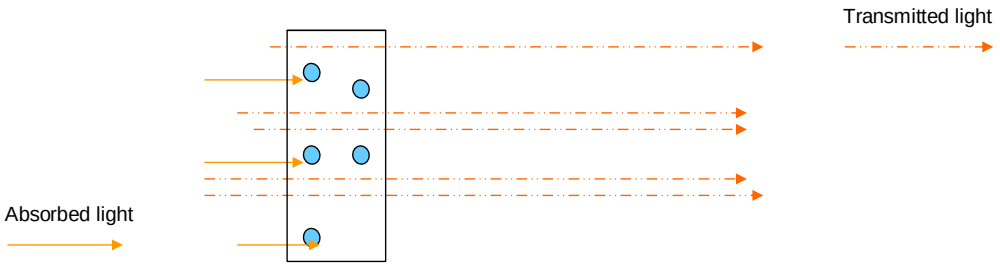
The main design features are the:

- **Light source:** Emits white light containing all wavelengths of the visible spectrum
- **Slit:** Blocks out light that is travelling on an angle. Selects light that is travelling at a horizontal angle only and in the one direction.
- **Coloured filter:** Usually a thin piece of coloured glass or plastic that allows light of only one wavelength (colour) to pass through.
- **Sample solution:** A test tube that contains the sample solution to be analysed.
- **Light detector:** Detects light that has passed through (transmitted) the solution.
- **Recorder:** This displays the amount of transmitted/absorbed light.

HOW DOES A COLORIMETER WORK?

The functioning of the colorimeter will be shown through the analysis of the unknown copper sulfate solution.

A sample of one of the standard solutions (1 M) is placed in a test tube and put into the sample solution position. Since copper sulfate is blue, it will mainly absorb orange light. So an orange filter is used in the colorimeter. Light from the lamp contains all wavelengths of visible light. Only light from the orange part of the spectrum will pass through the filter and into the sample solution of $CuSO_4$. Since the 1 M standard is quite dilute, a relatively small proportion of orange light will be absorbed by the solution. A large proportion of light will pass through the spaces between the solute particles.

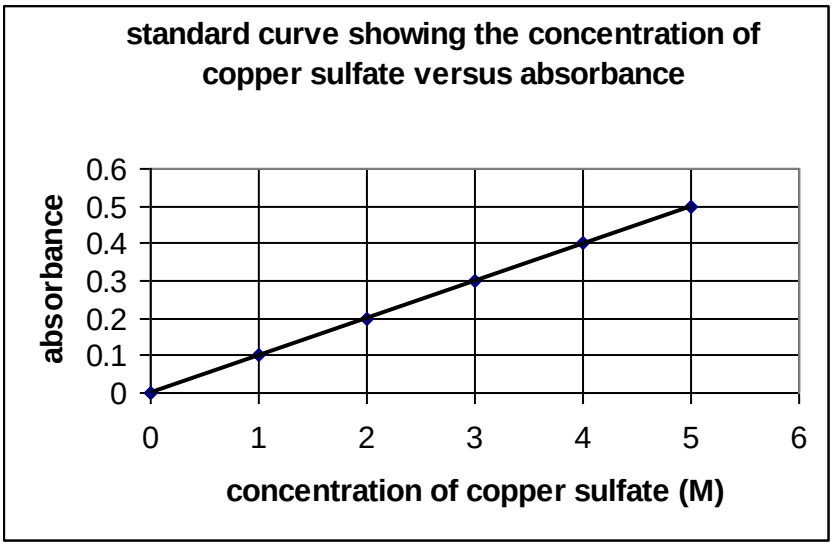


Note: In this context, transmitted light is referring to the wavelength of light that is known to be absorbed by the solution that passed between the solute particles

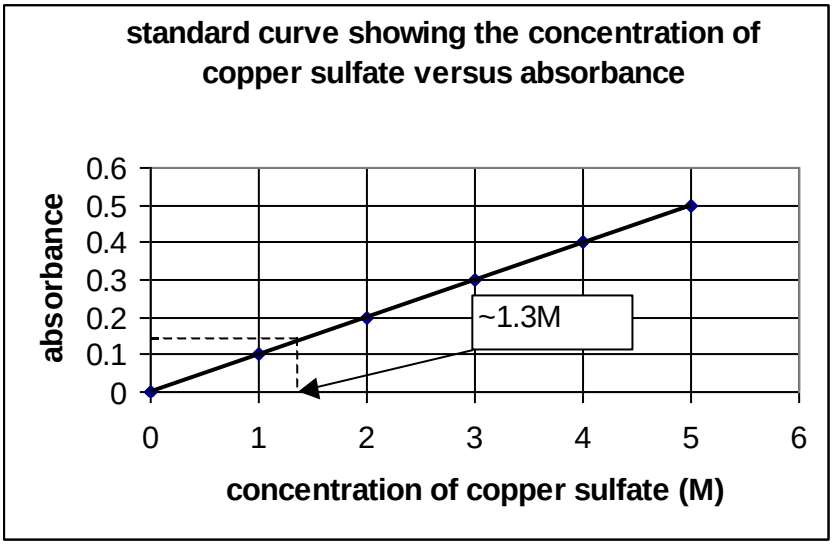
This light (transmitted) will reach the detector. The recorder will display this information as either a **transmission reading** or an **absorbance reading.** Transmission and absorbance readings are complimentary. Eg. If a solution has a transmission reading of 75%, its absorbance reading will be 25%. A colorimeter will usually display the absorbance reading using **arbitrary figures** between **0** and **1**, where **0** indicates that no light has been absorbed (100% transmission) and **1** indicates that all of the light has been absorbed (0% transmission). For the purposes of this demonstration, the 1 M standard will be given an absorbance reading of **0.1**. The 2 M, 3 M, 4 M and 5 M standards will have absorbance readings in proportion to the I M standard.

[Standard $CuSO_4$] (M)	Absorbance reading
1	0.1
2	0.2
3	0.3
4	0.4
5	0.5

A standard curve showing the relationship between the concentration of the standards and their absorbance can be constructed. The table shows that as the concentration of solute increases so does the absorbance as there are more solute particles present to absorb the orange light.



The unknown copper sulfate solution can now be analysed in the colorimeter. For the purposes of this demonstration let's give it an absorbance of **0.13**. Its concentration can now be determined by comparing its absorbance with those of the standard solutions.



APPLICATIONS OF COLORIMETRY

- Limited as this technique has been superseded by UV-Visible Spectroscopy.
- Can be used to detect most simple anions and cations accurate to **ppm.**

EXAMPLE 1

An environmental scientist wished to test water from a creek sample for phosphorous content. Excess phosphorous from fertilizer run off can lead to the poisoning of waterways known as eutrophication. To perform this test, she generates a calibration curve by making up a series of 4 solutions of known phosphorous concentration. These solutions are reacted with ammonium molybdate, ammonium vanadate and concentrated nitric acid to generate a yellow molybdenum vanadatophosphoric acid complex. The scientist tested an unknown solution of the creek water sample for phosphorous content. The results are as follows:

Solution number	Concentration of Phosphorous (ppm)	Spectrophotometer reading
Blank	0	0.001
1	2.0	0.175
2	4.0	0.345
3	6.0	0.517
4	8.0	0.691
Unknown creek water	?	0.466

(a) Construct a calibration curve for the 4 standard solutions

(b) The “blank” sample contained distilled water only. Why did this sample produce an absorbance reading?

(c) What was the concentration of the unknown sample of creek water in ppm?

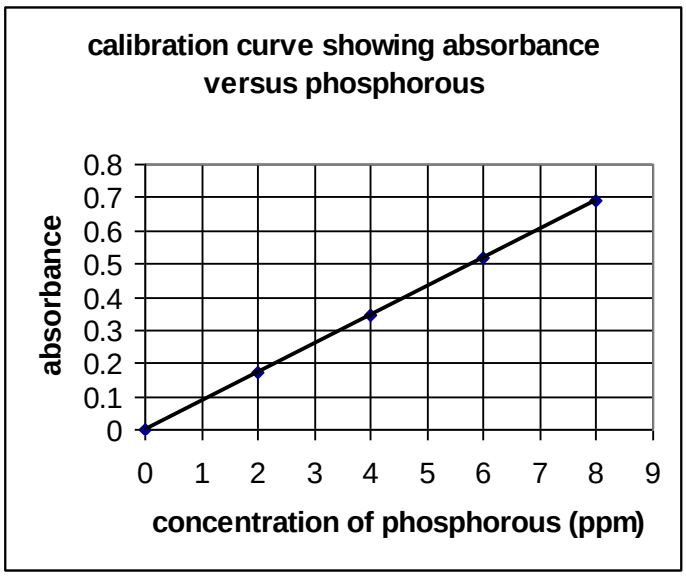
(d) What was the concentration of creek water in molarity (M). Assume that the density of the creek water is 1 gmL^{-1}

(e) What mass of phosphorous would you consume if you drank some creek water from a full 250 mL glass? Assume that the density of the creek water is 1 gmL^{-1}

(f) Why was each sample reacted with concentrated nitric acid, ammonium molybdate and ammonium vanadate before analysis in the colorimeter?

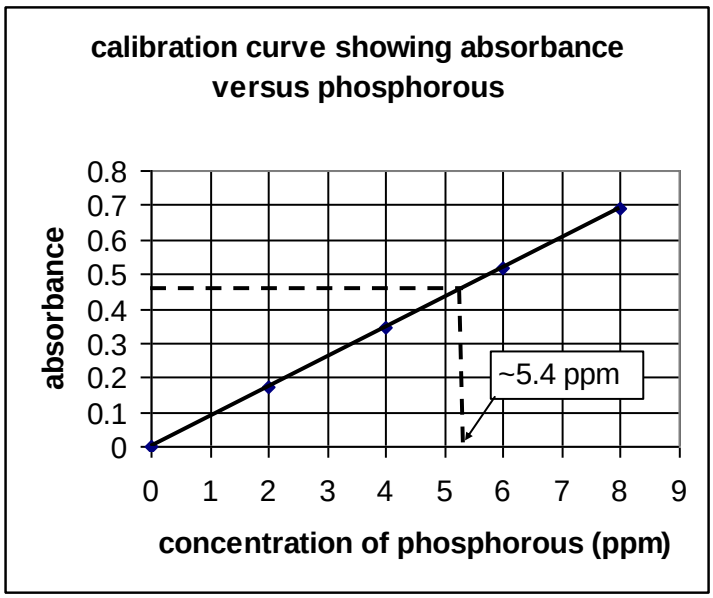
Solution

(a)



(b) There are several reasons why the "blank solution" produced a small absorbance reading. The water molecules or the test tube may have absorbed a small amount of light. The water may have been contaminated with ions that absorbed the wavelength of light used for this analysis.

(c) The concentration of the unknown creek water is approximately 5.4 ppm.



The density of the creek water is 1 g mL^{-1} so 10^6 grams of the creek water will have a volume of 10^6 mL. 5.4 ppm means that 10^6 mL of creek water will contain 5.4 grams of P. To calculate the molarity of the creek water we need to firstly calculate the mass of P in 1000 mL of creek water and then convert the mass into moles.

10^6 mL of creek water $\rightarrow$ 5.4 grams of P
1000 mL of creek water $\rightarrow$ x grams of P

$$x = 5.4 \times \frac{1000}{10^6} = 5.4 \times 10^{-3} \text{ grams}$$

$$n(P) = \frac{\text{mass (P)}}{\text{molar mass (P)}}$$

$$\frac{5.4 \times 10^{-3}}{31} = 1.4 \times 10^{-4} \text{ mole}$$

therefore molarity = 1.4×10^{-4} M

(d) Since the concentration of the creek water is 5.4 ppm, we know that 10^6 mL of creek water will contain 5.4 grams of P. So, 250 mL of the same creek water will have to contain much less:

10^6 mL of creek water $\rightarrow$ 5.4 grams
250 mL of creek water $\rightarrow$ x grams

$$x = 5.4 \times \frac{250}{10^6} = 1.4 \times 10^{-3} \text{ grams of phosphorous}$$

(e) Colorimetry can only be used to analyse coloured solutions. Solutions containing phosphorous particles are colourless so the concentrated nitric acid, ammonium molybdate and ammonium vanadate were added to change the phosphorous particles into a yellow coloured vanadatophosphoric acid complex. Anaysis of this coloured complex would therefore enable the analysis of P.