

Chemistry 12

Tutorial 12

Determining the Concentration of a Specific Ion Using Precipitation Titrations

In Tutorial 12 , you will be shown:

1. How titrations involving precipitation reactions can be used to determine the concentration of an ion in solution.
2. How to perform the necessary calculations involving precipitation titrations.
3. How some of the indicators used in precipitation titrations work.

Review of Titrations

First of all, let's look at some of the terminology used in talking about titrations.

A good one to start with might be the definition of "titration" itself.

Titration - The process of adding a measured amount of a *standard solution* to a specified amount of *sample solution* in order to find the concentration of a certain ion in the sample solution. (*Don't try to memorize this or even fully understand it yet. It will be quite clear later on.*)

Standard Solution - A solution of *known* concentration used in a titration.

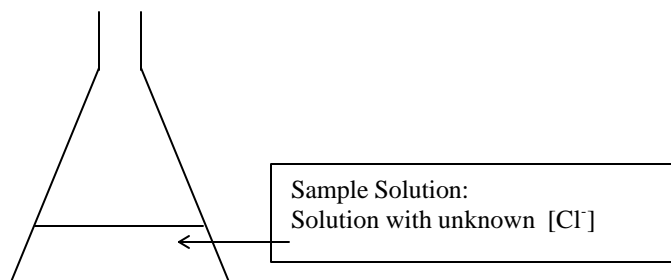
Sample Solution - A solution of *unknown* concentration. The concentration of this solution will be found using the process of titration.

Indicator - A substance which will change colour or do something else to show that the titration is complete.

An Example of a Titration

The best way to understand what is taking place during a titration is to go through an example and have every miniscule (tiny) point explained. Make sure you ask someone if you come to something you don't understand. Start on the next page...

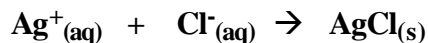
O.K. Let's say you had a solution that contains chloride (Cl^-) ions and you really want to know the molar concentration of chloride ions ($[\text{Cl}^-]$) in the solution. By the way, this solution will now be called the "**sample** solution".



What we could do is find something that forms a precipitate with Cl^- ions.

Looking at the old faithful **solubility table**, a good ion is silver (Ag^+).

The **net-ionic equation** for the **precipitation** reaction would be:



You'll notice that the coefficient on Ag^+ is the same as the coefficient on Cl^- (1).

This means that when the reaction is just complete:

$$\text{moles of Ag}^+ = \text{moles of Cl}^-$$

This will become important when we do the calculations.

The concentration of $[\text{Ag}^+]$ in the solution that we add must be known very precisely. This solution is called the **standard solution**.

Now, we all know that it's impossible to have a solution of JUST Ag^+ . There must be a negative ion present also. In order to keep things as simple as possible, it's best if the negative ion doesn't form precipitates with anything. A good choice would be the **nitrate** ion (NO_3^-).

If you look this up on the solubility chart, you'll see that it doesn't form precipitates with any positive ion.

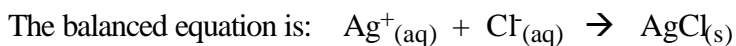
So our standard solution could be silver nitrate ($\text{AgNO}_3(\text{aq})$). As we said before, the concentration of this solution should be known precisely. Let's go to the stockroom and find some 0.100 M AgNO_3 solution. Notice, the concentration is known to the nearest 0.001 M, so this is very precise.

Basically, in a titration, we have to find out what volume of the 0.100 M AgNO₃ is needed to just precipitate all the Cl⁻ ions in the sample solution.

We must also put a precisely measured volume of the sample solution into the flask.

Here is the main “game plan” in a titration of this kind. The details of how we do each step will be looked at later.

1. Standard solution (ie. 0.100 M AgNO₃) is added to the sample solution until all the Cl⁻ ions are precipitated.
2. The volume of this standard solution needed to do this is recorded.
3. Now the *moles* of the Ag⁺ ions used can be calculated. Since we know the *concentration* of the Ag⁺ (0.100 M) (*Remember that each AgNO₃ gives one Ag⁺.*), and we now know the *volume* (Litres) of the Ag⁺ solution, we can use the equation: ***moles = M x Litres***
4. Once we know the moles of Ag⁺ used, we can use the coefficients in the balanced equation to find the moles of Cl⁻ that were present in the sample.



In this case the coefficients on Ag⁺ and Cl⁻ are the same so

$$\text{moles of Ag}^+ = \text{moles of Cl}^-$$

(Note: The coefficients are equal here but don't assume they will be equal with every titration!)

5. Now we know the moles of Cl⁻ that were present in the sample. Since we measured the volume of the sample solution precisely, we can now calculate the concentration of Cl⁻ ([Cl⁻]). We can use the formula:

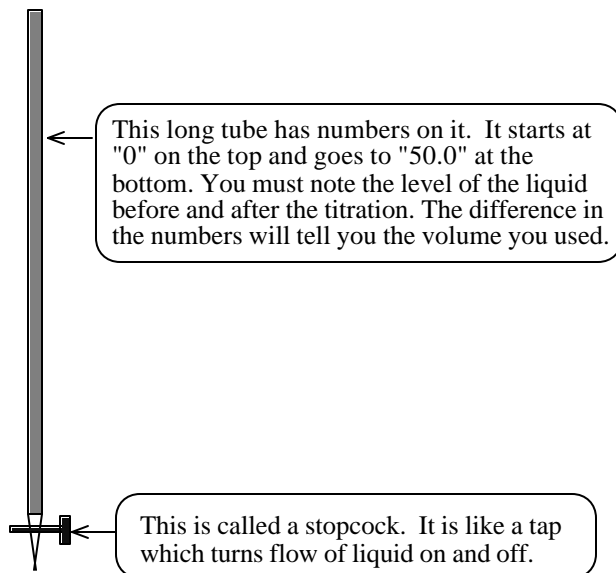
$$M = \frac{\text{moles (of Cl}^-)}{L \text{ (of sample solution)}}$$

Read these 5 steps over a couple of times. Remember that the volume of the standard solution (what we add) and the volume of the sample solution (what is in the flask) are two different things, so don't get them confused.

Before we can carry out the actual titration, a couple more points have to be understood: (*Will this never end, you ask?*)

- a) A device called a **burette** is used to add the standard solution (0.100 M AgNO_3)
This device tells us what volume of AgNO_3 solution has been added. (see diagram...)

A Burette



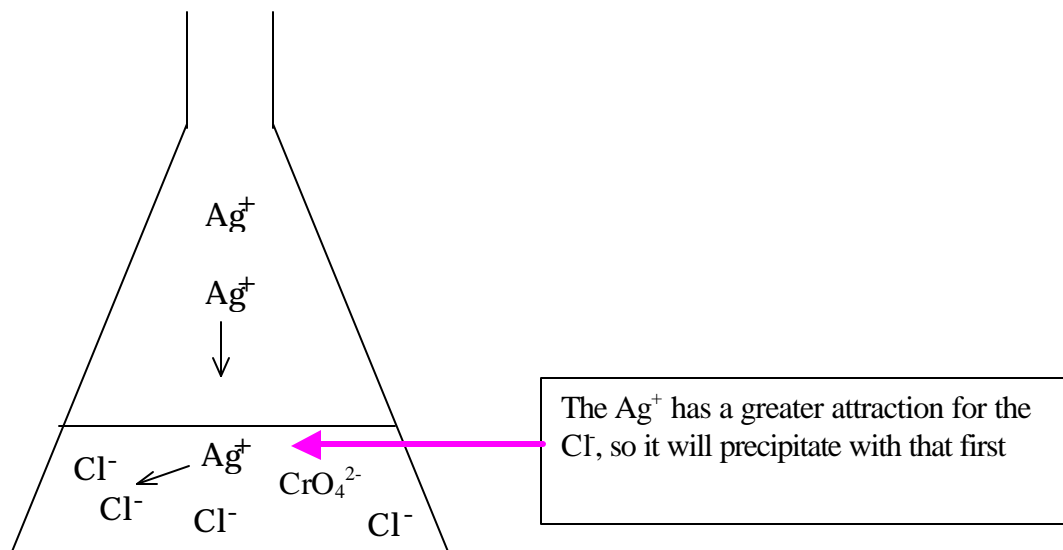
- b) We need something to tell us when all the Cl^- ions are used up. Imagine adding the Ag^+ ions to the Cl^- ions to form a precipitate. The solution would gradually get cloudier as the precipitate formed. But it would be really hard to know precisely when it stopped getting cloudier (all the Cl^- is used up) without actually going past that point.

But there is a way! And as usual, to understand how it works takes a little bit of explanation. (*But that's why you like Chemistry, isn't it?*) You really have to be able to visualize what is going on in the flask. It will take some concentration, so it would be better to read this without Blink 182 or Limp Bizkit in the background.

What we can do is put a few drops of an indicator called Na_2CrO_4 solution.
It is the CrO_4^{2-} ion that does the job here.

The precipitate AgCl is **white**.
The precipitate Ag_2CrO_4 is a **brick red** colour.

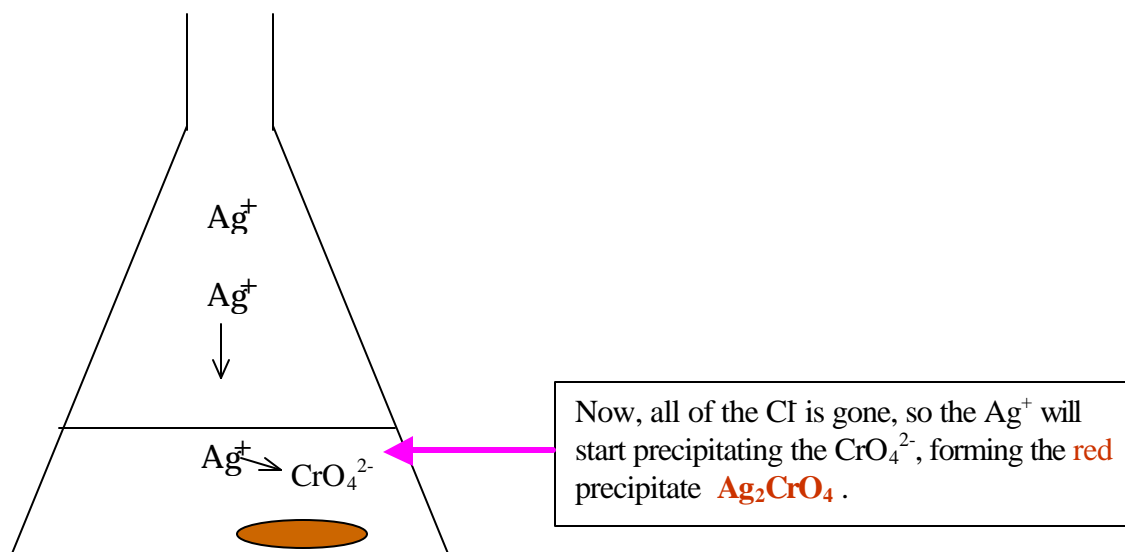
It is known that AgCl is **less soluble** than Ag_2CrO_4 . What this means is that if Ag^+ ions are added to a solution containing BOTH Cl^- ions and CrO_4^{2-} ions, the added Ag^+ ions will have a greater attraction for the Cl^- ions, so the precipitate of AgCl will form first. See the diagram on the top of the next page....



The Ag^+ ions will keep bonding with the Cl^- ions forming the white precipitate AgCl *as long as there are Cl^- ions present.*

As soon as all the Cl^- ions are used up, the Ag^+ will then start precipitating with the CrO_4^{2-} ions, forming the precipitate Ag_2CrO_4 . But recall that the colour of Ag_2CrO_4 is **brick red**.

Thus, as you can see, *as soon as all the Cl^- ions are used up, the next drop of Ag^+ solution will turn the solution red.*



So, as soon as all the Cl^- is consumed, and a small amount of Ag_2CrO_4 forms, a faint brick red colour will be noticed. At this point, we would STOP the titration.

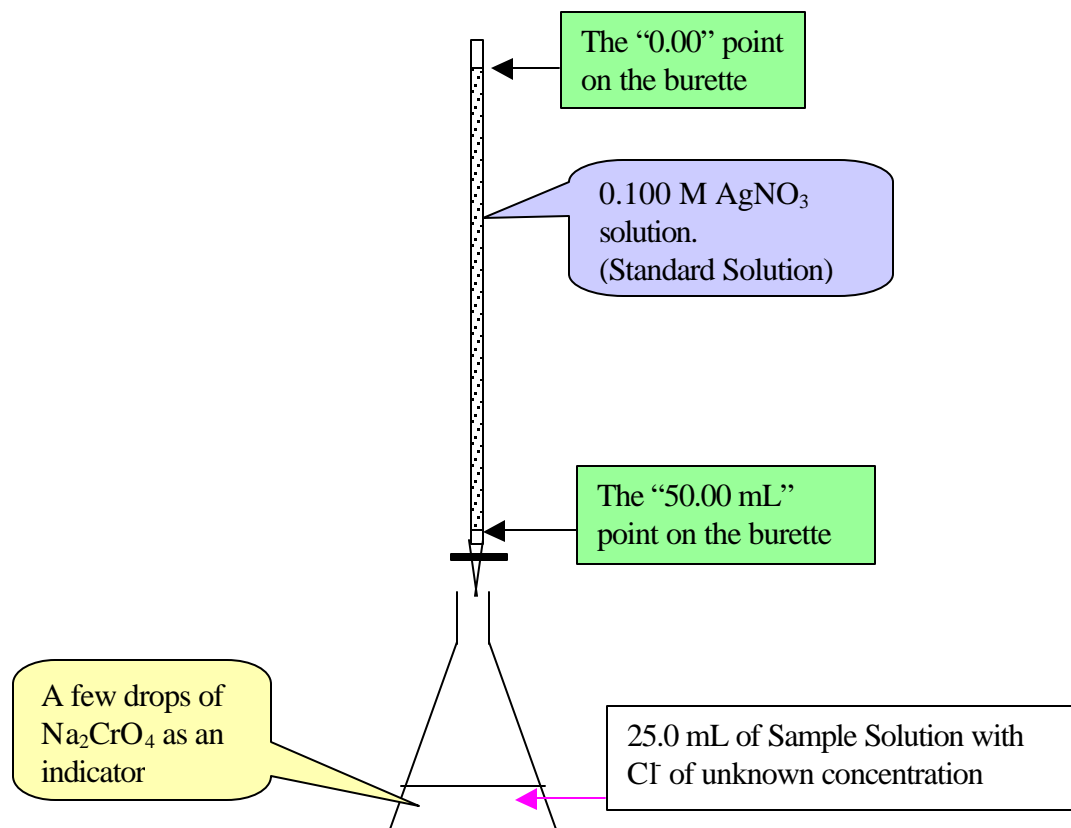
This is the point where we have added the exact amount of Ag^+ ions necessary to precipitate all the Cl^- ions in solution. (Don't worry about the extra drop or two, titrations always have a certain margin of error.) This point is called the ***equivalence point*** or ***stoichiometric point***.

So, let's look at an actual titration:

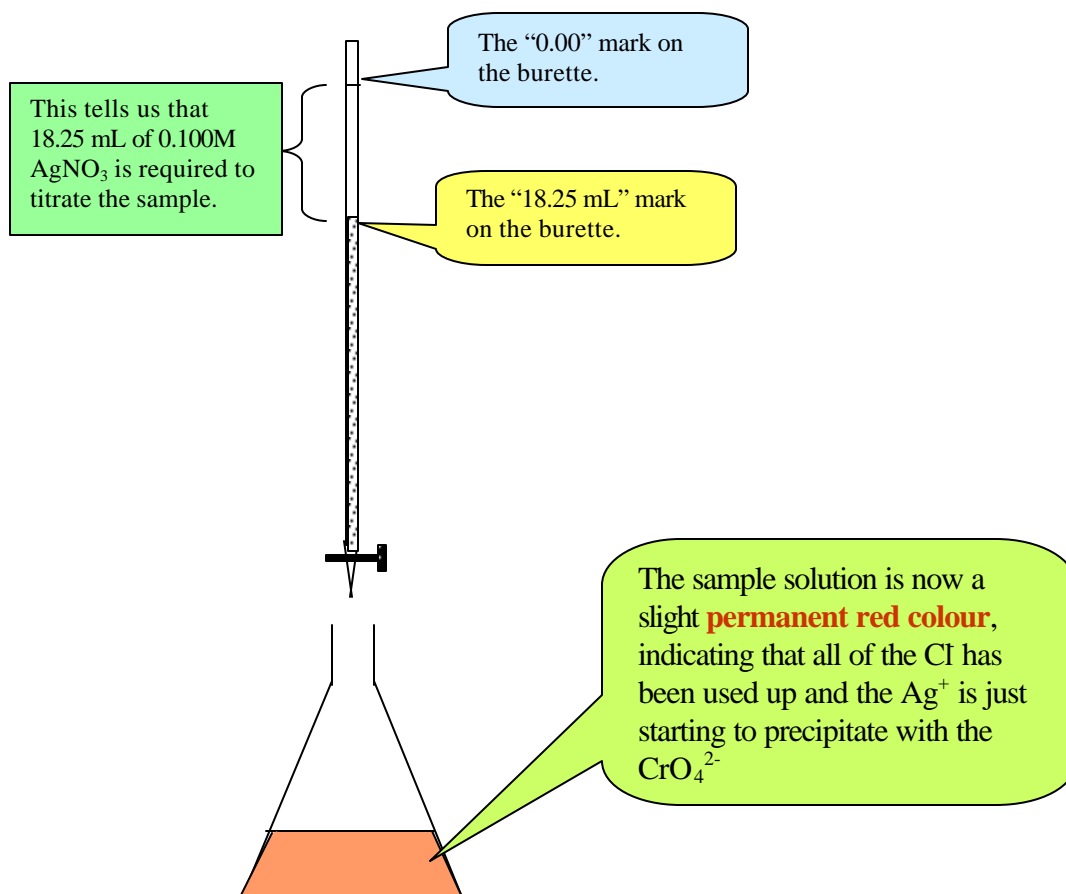
We have 25.0 mL of a solution containing Cl^- ions of unknown concentration. We want to titrate it and determine its concentration.

Here's what we would do:

1. Add exactly 25.00 mL of the Cl^- solution to an erlenmeyer flask. This is the **sample** solution.
2. Add a few drops of 0.1 M Na_2CrO_4 (aq) to the flask as an **indicator**.
(The exact concentration is not critical.)
3. Fill the burette to the "0.00" mark with 0.100 M AgNO_3 solution. This is the **standard** solution.



- Open the stopcock on the burette to slowly add the AgNO_3 solution to the flask. The white precipitate AgCl starts to form making the solution in the flask a cloudy white.
- Keep swirling the flask and adding AgNO_3 until there is a *permanent, very pale reddish colour*. Close the stopcock. This is called the **endpoint** or the **transition point** of the titration. If the red colour is too dark, it means you've gone too far!
- Note the reading on the burette at this point. In this example, let's pretend the final reading is 18.25 mL.



- Repeat this procedure two or three times, each time starting with a new sample of the Cl^- solution with indicator. The burette doesn't have to be refilled each time, as long as the difference in the readings before and after the titration is calculated. This would give the volume of AgNO_3 solution used for each titration.

Let's pretend the following readings were obtained in four titrations:

<i>Titration Trial</i>	<i>Volume of AgNO₃ used (mL)</i>
Trial 1	18.25
Trial 2	17.86
Trial 3	17.91
Trial 4	17.88

Calculations

The following are typical calculation steps which would use the data obtained to determine the [Cl⁻] in the sample solution.

1. Calculate the best average value for the volume of AgNO₃ used.

You'll notice that the volume in Trial 1 is significantly higher than in the other 3 trials. This can often happen in a titration on the first trial because the experimenter doesn't know where the endpoint is going to be. He or she may add a little too much standard solution before he or she notices that the pink colour is permanent. The first trial in any titration is really just to get a rough idea of where the endpoint is going to be.

You have to use your judgment a bit with this, but in this case it would be better to leave the first volume (18.25 mL) out when calculating the average since it is probably not as accurate as the other three.

$$\text{The best average then is: } \frac{17.86 + 17.91 + 17.88}{3} = \underline{\underline{17.88 \text{ mL}}}$$

2. Calculate the moles of AgNO₃ (or Ag⁺) (standard solution) used in the titration using the **best average volume** from the data.

The best average volume in this case is 17.88 mL = 0.01788 L. (Don't round off at any point during the calculations, just on the last calculation of the series.)

If you will glance at "Step 3" on page 6, you will see that the Molar Concentration of AgNO₃ [AgNO₃] = 0.100 M.

Hopefully, you will also recall from your vast Chemistry experience that:

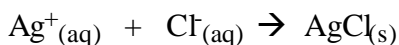
$$\text{moles} = M \times \text{Litres}$$

This equation can be used to find the moles of AgNO₃ used:

$$\text{moles} = M \times \text{Litres}$$

$$\text{moles} = 0.100 \text{ M} \times 0.01788 \text{ L} = \underline{0.001788 \text{ moles AgNO}_3 (\text{Ag}^+)}$$

3. Write the balanced net ionic equation for the reaction taking place in the titration. In this case it is just the Ag⁺ from the AgNO₃ that is reacting with the Cl⁻ in the sample solution. The NO₃⁻ is a spectator ion so it is left out in the net ionic equation.



4. Use the balanced net ionic equation to find the moles of Cl⁻ in the sample.

Looking at the net ionic equation, you can see that the coefficients on Ag⁺ and Cl⁻ are equal. (They are both "1"). At the equivalence point of the titration you can generally assume that the moles of reactants present will be in the same ratio as their coefficients in the balanced equation. (In this case 1:1) so:

$$\text{moles of Cl}^- = \text{moles of Ag}^+$$

$$\text{so moles of Cl}^- = \underline{0.001788 \text{ moles}}$$

5. Calculate the [Cl⁻] in the sample solution.

Glancing at "Step 1" on page 6, you will notice that we used 25.00 mL of the sample solution (with unknown [Cl⁻]). So the volume of the Cl⁻ solution is 25.00 mL or 0.02500 Litres.

We know the moles of Cl⁻ from calculation 4 are 0.001788 moles

Again, from Chemistry 11, to find Molar Concentration we use:

$$M = \frac{\text{moles}}{L}$$

So

$$[\text{Cl}^-] = \frac{0.001788 \text{ moles}}{0.02500 \text{ L}} = \underline{0.07152 \text{ M}}$$

Now is the time to look at **significant digits**. In the original data given on pages 6, 7 and 8, you will see that the **lowest number** of significant digits is 3. (The concentration of Na_2CrO_4 is not used in any of the calculations so its significant digits are not counted.) The final answer, then should be rounded off to **3 significant digits**. (Remember “0”s at the beginning of a number are not significant!)

The final answer would be:

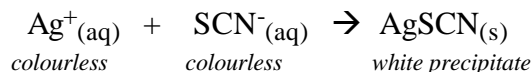
$$[\text{Cl}^-] = \underline{0.0715 \text{ M}} \text{ or if you wish, } \underline{7.15 \times 10^{-2} \text{ M}}$$

Warning! The most common mistake with titration calculations is getting volumes and concentrations mixed up. Always ask yourself, “This is the volume of what?” or “This is the concentration of what?” etc. For example in the last step, since you are calculating the $[\text{Cl}^-]$, make sure you have the moles of Cl^- and the volume of Cl^- , not something else. It’s worth double checking!

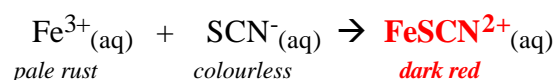
Titration for Ag^+ Ion Concentration

A common method of titrating a solution with unknown $[\text{Ag}^+]$ is shown by the following:

1. The burette is filled with a solution of potassium thiocyanate (KSCN) of a known concentration (eg. 0.100 M). This is the **standard** solution. The thiocyanate ion (SCN^-) is the active ion here. The K^+ ion is a spectator.
2. A known volume of the silver (Ag^+) solution is added to an erlenmeyer flask. This is the **sample** solution.
3. This time the indicator added to the flask is a solution containing the Fe^{3+} ion. (eg. $\text{Fe}(\text{NO}_3)_3$ (aq)).
4. The main reaction for the titration is a precipitation of Ag^+ and SCN^- ions to form a precipitate of $\text{AgSCN}_{(s)}$:



5. Once just enough SCN^- solution has been added to react with all the Ag^+ ions, (the ***stoichiometric point***), any excess SCN^- ions added will react with the indicator, Fe^{3+} ions and form a complex ion (a larger ion made up of smaller ones) called FeSCN^{2+} . This ion, called the ferrothiocyanate ion, is NOT a precipitate, BUT IS a **very intense red colour**. You may recall seeing it when you did Experiment 19-A on equilibrium. The reaction is:



A slight **permanent red** would appear at the *endpoint* of the titration. This would indicate that the ***stoichiometric point*** (the point where there is just enough SCN^- to react with all the Ag^+ in the sample) has been reached.

NOTE: At this point you may be confused between the two terms, *stoichiometric point* and *endpoint*.

Stoichiometric Point -

The point in a titration where there is precisely enough of the standard solution to react with all of the sample solution. The ratio of moles of the two reactants are the same as the ratio of coefficients in the balanced equation. (eg. in $\text{Ag}^+_{(\text{aq})} + \text{SCN}^{-}_{(\text{aq})} \rightarrow \text{AgSCN}_{(\text{s})}$, that ratio is 1:1.)

Endpoint-

The point in a titration where the indicator changes colour.

Ideally, the *endpoint* would occur at the same time as the *stoichiometric point*, so they would basically mean almost the same thing. In Unit 4, we will visit these two terms again.

6. By measuring the *volume* of SCN^- solution used (standard solution), knowing its *concentration*, and by knowing the *volume* of Ag^+ solution (sample solution) used, the $[\text{Ag}^+]$ can be determined using the same series of calculations shown in the previous example.

Self-Test on Tutorial 12

1. In order to find the concentration of chloride ion in a sample of pool water, a 50.0 mL sample of the pool water was titrated with 0.500 M AgNO_3 solution, using sodium chromate solution ($\text{Na}_2\text{CrO}_4(\text{aq})$) as an indicator. At the stoichiometric point, it was found that 53.4 mL of AgNO_3 solution had been added.
 - a) Calculate the **moles of Ag^+** used.

 - b) Write the **balanced net-ionic equation** for the titration.

 - c) Determine the **moles of Cl^-** ions in the sample.

 - d) Calculate the **$[\text{Cl}^-]$** in the sample of pool water.

Check **page 1** of **Tutorial 12 Solutions** for the answers.

2. A solution containing silver ions (Ag^+) is titrated with 0.200 M KSCN solution to find the $[\text{Ag}^+]$ in the sample. The indicator $\text{Fe}(\text{NO}_3)_3$ (aq) is used to signal when the stoichiometric point is reached. It is found that 15.6 mL of 0.200 M KSCN is needed to titrate a 25.0 mL sample of Ag^+ solution. Determine the $[\text{Ag}^+]$ in the sample. Show all steps in a clear concise manner. (Use question 1 as a guide.)

Check **page 2** of Tutorial 12 Solutions for the answer.

3. Explain how the indicator Na_2CrO_4 works in titrations for chloride (Cl^-) ion concentration using Ag^+ as a standard solution.

Check **page 3** of Tutorial 12 Solutions for the answers.

4. Explain how the indicator $\text{Fe}(\text{NO}_3)_3$ works in titrations for silver (Ag^+) ion concentration using SCN^- as a standard solution.

Check **page 4** of Tutorial 12 Solutions for the answers.

