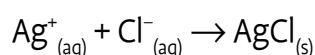


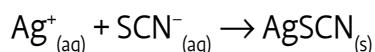
Determination of Chloride Ion Concentration by Titration (Volhard's Method)

Introduction

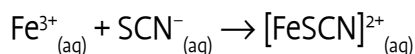
This method uses a back titration with potassium thiocyanate to determine the concentration of chloride ions in a solution. Before the titration an excess volume of a silver nitrate solution is added to the solution containing chloride ions, forming a precipitate of silver chloride. The term 'excess' is used as the moles of silver nitrate added are known to exceed the moles of sodium chloride present in the sample so that all the chloride ions present will react.



The indicator Fe^{3+} (ferric ion) is then added and the solution is titrated with the potassium thiocyanate solution. The titrate remains pale yellow as the excess (unreacted) silver ions react with the thiocyanate ions to form a silver thiocyanate precipitate.



Once all the silver ions have reacted, the slightest excess of thiocyanate reacts with Fe^{3+} to form a dark red complex.



The concentration of chloride ions is determined by subtracting the titration findings of the moles of silver ions that reacted with the thiocyanate from the total moles of silver nitrate added to the solution.

This method is used when the pH of the solution after the sample has been prepared is acidic. If the pH is neutral or basic, Mohr's method or the gravimetric method should be used. The method is illustrated below by using the procedure to determine the concentration of chloride (from sodium chloride) in cheese.

Equipment Needed

boiling chips

500 mL volumetric flask

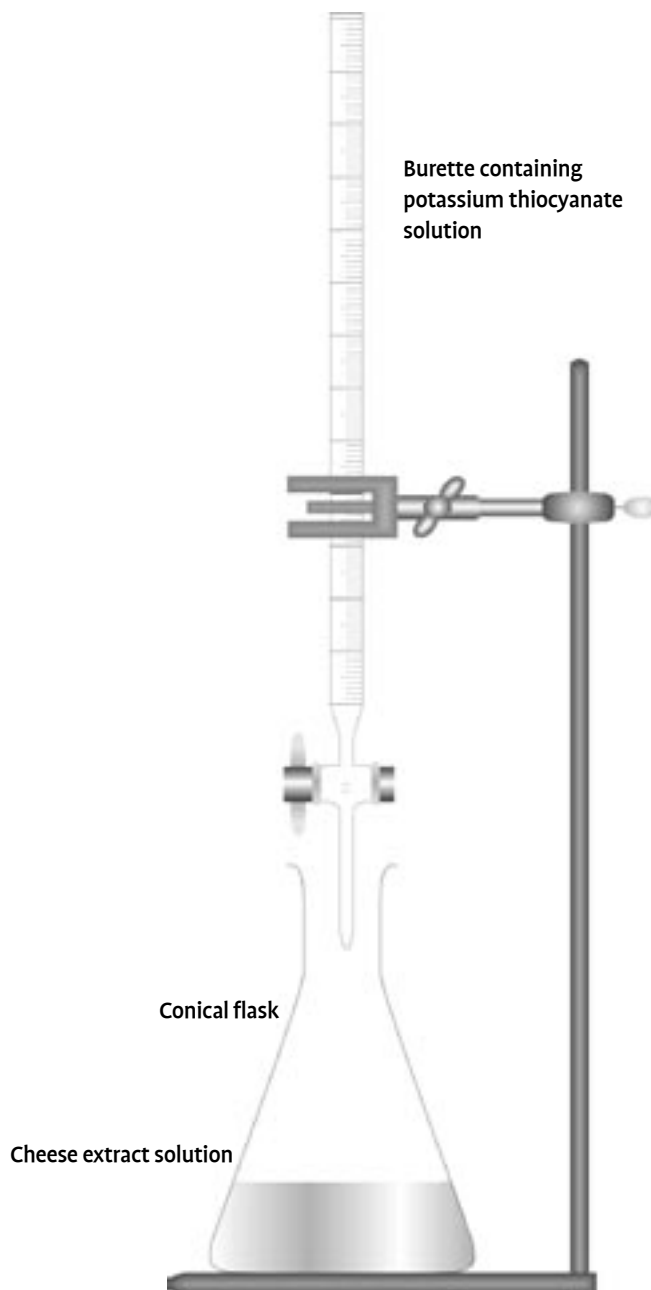
10 mL and 100 mL measuring cylinders

conical flasks

Bunsen burner, tripod and gauze

burette and stand

50 mL pipette (if possible)



Solutions Needed

Concentrated nitric acid (see safety notes): (6 mol L⁻¹)

Silver nitrate solution: (0.1 mol L⁻¹). If possible, dry 5 g of AgNO₃ for 2 hours at 100°C and allow to cool. Accurately weigh about 4.25 g of solid AgNO₃ and dissolve it in 250 mL of distilled water in a conical flask. Store the solution in a brown bottle.

Potassium thiocyanate solution: (0.1 mol L⁻¹). Weigh 2.43 g of solid KSCN and dissolve it in 250 mL of distilled water in a volumetric flask.

Potassium permanganate solution: (5%) Add 1.5 g KMnO₄ to 30 mL of distilled water.

Ferric ammonium sulfate solution: (saturated) Add 8 g of NH₄Fe(SO₄)₂·12H₂O to 20 mL of distilled water and add a few drops of concentrated nitric acid.

Method

Sample Preparation

The salt sodium chloride is added during the manufacture of cheddar cheese. In this method, the cheese is 'digested' to release this salt to obtain the concentration of chloride ions. To carry out this digestion, the cheese is reacted with nitric acid and potassium permanganate. The chloride ions are then 'free' to form a precipitate with the added silver ions.

1. Cut or grate the cheese into fine pieces and accurately weigh about 6 g into a 500 mL conical flask.
2. Precisely add 50 mL of 0.1 mol L⁻¹ silver nitrate solution (by pipette if possible), 20 mL of concentrated nitric acid, (**very carefully – see safety notes**), 100 mL of distilled water and a few boiling chips, and heat the solution to boiling.
3. As the solution boils add 5 mL of 5% potassium permanganate solution. This addition will cause a very smelly reaction and should be done in a fumehood. Keep boiling until the purple colour disappears, then add another 5 mL of potassium permanganate solution. Continue this process until 30 mL of potassium permanganate solution has been added and the cheese particles are completely digested (or as close as possible). To find out when digestion is complete, remove the flask from heat and allow it to stand for a few moments. Undigested cheese particles will float upon the surface of the clear liquid, while the white precipitate of silver chloride will sink to the bottom. If there is still too much undigested cheese, the boiling and addition of 5 mL of potassium permanganate should be continued, checking each time until there is a satisfactory level of digestion.

4. Cool the solution and filter it. Wash the solid residue with a few mL of distilled water.

5. Make the filtrate up to 500 mL in a volumetric flask.

Titration

1. Use a volumetric cylinder to measure 100 mL of the cheese extract solution (be as precise as possible) and pour it into a conical flask.
2. Add 1 mL of saturated ferric ammonium sulfate solution as indicator.
3. Titrate the unreacted silver ions with the 0.1 mol L⁻¹ potassium thiocyanate solution. The end point is the first appearance of a dark red colour due to the ferric thiocyanate complex (figure 1).
4. Repeat the titration with 100 mL samples of the cheese extract solution until you obtain concordant results (titres agreeing within 0.1 mL).

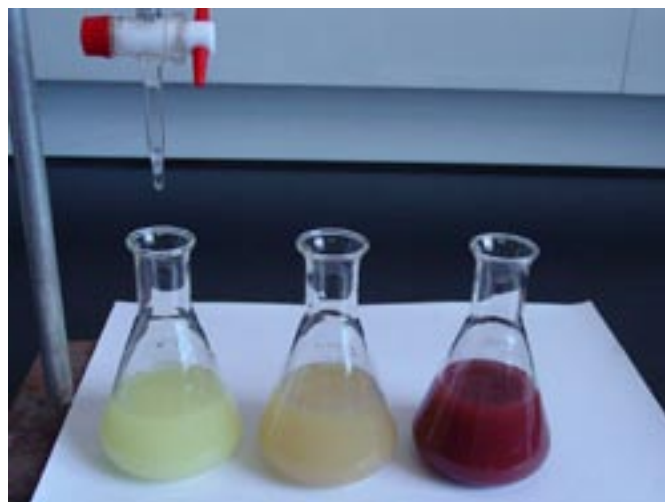
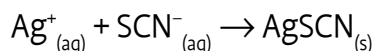


Figure 1 Left flask: before the titration endpoint, addition of SCN⁻ ions leads to formation of silver thiocyanate precipitate, making the solution cloudy. Here the solution also takes a faint yellow colour due to the colour of the cheese extract. Centre flask: at the endpoint all the free silver ions have been precipitated by SCN⁻. The slightest excess of SCN⁻ forms a dark red coloured complex with the Fe³⁺ ions from the ferric ammonium sulfate indicator, giving the solution a slight orange/red colouration. Right flask: If addition of SCN⁻ is continued past the endpoint, further ferric thiocyanate complex is formed and a stronger dark red colour results. NB: The titration should be stopped when the first trace of dark red colour is observed. Using an incompletely titrated reference flask for comparison is a helpful way to identify the first appearance of red colouration.

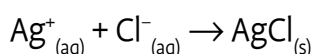
Result Calculations

1. Determine the average volume of potassium thiocyanate used from your concordant titres.
2. Calculate the moles of potassium thiocyanate used.
3. Use the equation of the reaction between silver ions and thiocyanate ions



to calculate the moles of unreacted silver nitrate in 100 mL of cheese extract, and multiply the figure by five to determine the total moles of unreacted silver nitrate (the excess) in the 500 mL volumetric flask.

4. Calculate the moles of silver nitrate in the 50 mL of solution that was added during the sample preparation to the cheese.
5. Calculate the total moles of silver nitrate that reacted with the salt from the cheese by subtracting the moles of unreacted silver nitrate (the excess) from the total moles of silver nitrate added to the cheese.
6. Use the equation of the reaction between the silver ions and the chloride ions to calculate the moles of sodium chloride in the sample of cheese.



7. Calculate the concentration of sodium chloride in the cheese as grams of salt per 100 g cheese (% salt).

Safety

Concentrated nitric acid is very corrosive. Wear safety glasses and take great care handling the concentrated acid.

Safety glasses should be worn throughout the method, especially during the sample preparation.

Additional Notes:

1. Silver nitrate solution will stain clothes and skin. Any spills should be rinsed with water immediately.
2. Residues containing silver ions and precipitate are usually saved for later recovery of silver metal. Check this with your teacher.
3. A 'blank' titration substituting sucrose (sugar) for the cheese should be carried out to see if there are any 'contaminating' chloride ions present in the reagent solutions used. If any are found, the figure should be subtracted from the titration results.
4. For greatest accuracy it is a good idea to standardise your thiocyanate solution by titrating

several samples against your standardised silver nitrate solution (once again using ferric ammonium sulfate indicator). The concentration of SCN^- determined by this titration should then be used in all calculations.

Contact Us

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