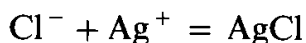


11.57 CHLORIDE

Determination of chloride as silver chloride: Discussion. The aqueous solution of the chloride is acidified with dilute nitric acid in order to prevent the precipitation of other silver salts, such as the phosphate and carbonate, which might form in neutral solution, and also to produce a more readily filterable precipitate. A slight excess of silver nitrate solution is added, whereupon silver chloride is precipitated:

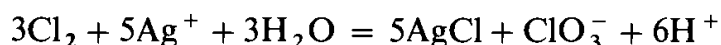


The precipitate, which is initially colloidal, is coagulated into curds by heating the solution and stirring the suspension vigorously; the supernatant liquid becomes almost clear. The precipitate is collected in a filtering crucible, washed with very dilute nitric acid, in order to prevent it from becoming colloidal (Section 11.8), dried at 130–150 °C, and finally weighed as AgCl.

Silver chloride has a solubility in water of 1.4 mg L⁻¹ at 20 °C, and 21.7 mg L⁻¹ at 100 °C. The solubility is less in the presence of very dilute nitric acid (up to 1 per cent), and is very much less in the presence of moderate concentrations of silver nitrate (see Section 2.7; the optimum concentration of silver nitrate is 0.05 g L⁻¹, but the solubility is negligibly small up to about 1.7 g L⁻¹). The solubility is increased by the presence of ammonium and of alkali-metal salts, and by large concentrations of acids. Under the conditions of the precipitation, very little occlusion occurs. If silver chloride is washed with pure water, it may become colloidal and run through the filter. For this reason the wash solution should contain an electrolyte (compare Sections 11.3 and 11.8). Nitric acid is generally employed because it is without action on the precipitate and is readily volatile; its concentration need not be greater than 0.01M. Completeness of washing of the precipitate is tested for by determining whether the excess of the precipitating agent, silver nitrate, has been removed. This may be done by adding one or two drops of 0.1M hydrochloric acid to 3–5 mL of the washings collected after the washing process has been continued for some time; if the solution remains clear or exhibits only a very slight opalescence, all the silver nitrate has been removed.

Silver chloride is light-sensitive; decomposition occurs into silver and chlorine, and the silver remains colloiddally dispersed in the silver chloride and thereby imparts a purple colour to it. The decomposition by light is only superficial, and is negligible unless the precipitate is exposed to direct sunlight and is stirred frequently. Hence the determination must be carried out in as subdued a light as possible, and when the solution containing the precipitate is set aside, it should be placed in the dark (e.g. in a locker), or the vessel containing it should be covered with thick brown paper.

It has been found that in a solution containing silver chloride and 1–2 per cent excess of 0.2M silver nitrate, exposure to direct sunlight for 5 hours with occasional stirring leads to a positive error of about 2.1 per cent whilst exposure in a bright laboratory, with no direct or reflected sunlight and occasional stirring, gives a positive error of about 0.2 per cent. This positive error is due to the liberation of chlorine during exposure to light: the chlorine is largely changed back to chloride ions, which cause further precipitation of silver chloride. A possible reaction is:



On the other hand, in the determination of silver by precipitation with a slight excess of 0.2M hydrochloric acid (Section 11.40), the error is negative, e.g. 0.4 per cent after 2 hours' exposure in direct sunlight with no stirring, and 0.1 per cent after 2 hours' exposure in a bright laboratory, with no direct or reflected sunlight and occasional stirring. This arises from the loss of chlorine which escapes from the precipitate. The weight of the precipitate may be brought to the correct value by treatment with nitric acid, followed by hydrochloric acid.

Procedure. Weigh out accurately about 0.2 g of the solid chloride (or an amount containing approximately 0.1 g of chlorine)* into a 250 mL beaker provided with a stirring rod and covered with a clockglass. Add about 150 mL of water, stir until the solid has dissolved, and add 0.5 mL of concentrated nitric acid. To the cold solution add 0.1M silver nitrate slowly and with constant stirring. Only a slight excess should be added; this is readily detected by allowing the precipitate to settle and adding a few drops of silver nitrate solution, when no further precipitate should be obtained. **Carry out the determination in subdued light.** Heat the suspension nearly to boiling, while stirring constantly, and maintain it at this temperature until the precipitate coagulates and the supernatant liquid is clear (2–3 minutes). Make certain that precipitation is complete by adding a few drops of silver nitrate solution to the supernatant liquid. If no further precipitate appears, set the beaker aside in the dark, and allow the solution to stand for about 1 hour before filtration. In the meantime prepare a sintered-glass filtering crucible; the crucible must be dried at the same temperature as is employed in heating the precipitate (130–150 °C) and allowed to cool in a desiccator. Collect the precipitate in the weighed filtering crucible. Wash the precipitate two or three times by decantation with about 10 mL of cold very dilute nitric acid (say, 0.5 mL of the concentrated acid added to 200 mL of water) before transferring the precipitate to the crucible. Remove the last small particles of silver chloride adhering to the beaker with a 'policeman' (Section 3.23). Wash the precipitate in the crucible with very dilute nitric acid added in small portions until 3–5 mL of the washings, collected in a test-tube, give no turbidity with one or two drops of 0.1M hydrochloric acid. Place the crucible and contents in an oven at 130–150 °C for 1 hour, allow to cool in a desiccator, and weigh. Repeat the heating and cooling until constant weight is attained.

Calculate the percentage of chlorine in the sample.

Note on the gravimetric standardisation of hydrochloric acid. The gravimetric standardisation of hydrochloric acid by precipitation as silver chloride is a convenient and accurate method, which has the additional advantage of being independent of the purity of any primary standard (compare Section 10.38). Measure out from a burette 30–40 mL of the, say, 0.1M hydrochloric acid which is to be standardised. Dilute to 150 mL, precipitate (but omit the addition of nitric acid), and weigh the silver chloride. From the weight of the precipitate, calculate the chloride concentration of the solution, and thence the concentration of the hydrochloric acid.

11.58 CYANIDE

Note. Great care must be taken in the use and determination of cyanides owing to their highly poisonous nature.

* Analytical grade potassium chloride or sodium chloride, dried at 110–120 °C, is suitable.