Forensic Science (M.Sc. II semester)

Paper: FS-201 (Forensic Chemistry)

Topic: Determination of chloride as silver chloride, sulphate as barium sulphate & gravimetric determination of iron as Fe_2O_3

by

Dr. M. K. Bharty
Asstt. Professor
Department of Chemistry
Institute of Science
Banaras Hindu University

Determination of chloride as silver chloride:

The aqueous solution of the chloride is acidified with dilute nitric acid in order to prevent 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.

$$Cl^- + Ag^+ = AgCl \qquad \text{(wash with dil. } HNO_3 \text{ acid solution)}$$

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, dried at 130-150 °C and finally weighed as AgCl. If silver chloride is washed with pure water, it become colloidal and run through the filter. Silver chloride is light sensitive, decomposition occurs into silver and chloride and the silver remains colloidially dispersed in the silver chloride and thereby imparts a purple color to it. It should be placed in the dark or the vessel containing it should be covered with thick brown paper.

Procedure: Weigh out accurately about 0.2 gm of the solid chloride into a 250 mL beaker. Add about 150 mL of water, stir until the solid has dissolved and then add 0.5 mL concentrated nitric acid. To the cold solution add 0.1M silver nitrate slowly and with constant stirring. Carried out the determination in subdued light (dark).

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 min.). 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 1h before filtration. In the meantime, prepare a sintered glass filtering crucible, the crucible must be dried at about 130-150 °C and allow to cool in a desiccators. Collect the precipitate in weighed crucible, wash the precipitate two or three times by 10 mL of cold very dilute nitric acid solution before transferring the precipitate to the crucible. Wash the precipitate in the crucible with very dilute nitric acid solution. Place the crucible and contents in an oven at 130-150 °C for 1h, allow to cool in a desiccator and weigh. Repeat the heating and cooling until constant wet is attained. Calculate the percentage of chloride in the sample.

Determination of sulphate as barium sulphate

The method consists in slowly adding a dilute solution of barium chloride to a hot solution of the sulphate slightly acidified with hydrochloric acid.

$$\mathrm{Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4}$$

The precipitate is filtered off, washed with water, carefully ignited at a red heat and weight as $BaSO_4$. It is customary to carry out the precipitation in weakly acid solution in order to prevent the possible formation of the barium salts of such anions as chromate, carbonate and phosphate, which are insoluble in neutral solutions; moreover the precipitate so obtained consists of large crystals and is therefore more easily filtered.

Barium sulphate exhibits a marked tendency to carry down other salts. Whether the results will be low or high will depend upon the nature of the co-precipitated salt. Thus barium chloride and barium nitrate are readily co-precipitated. These salts will be an addition to the true weight of the barium sulphate, hence the results will be high. Since the chloride is unchanged upon ignition and the nitrate will yield barium oxide. Pure barium sulphate is not decomposed when heated in dry air until a temperature of about 1400°C is reduced.

$$\mathrm{BaSO_4 = BaO + SO_3}$$

But the precipitate is easily reduced to sulphide at temperatures above 600°C by the carbon of the filter paper.

$$\mathrm{BaSO_4 + 4C = BaS + 4CO}$$

The reduction is avoided by first charring the paper without inflaming and then burning off the carbon slowly at a low temperature with free access of air. If a reduced precipitate is obtained, it may be reoxidised by treatment with sulphuric acid followed by volatilization of the acid and reheating. The final ignition of the barium sulphate need not be made at a higher temperature than 600-800°C (dull red heat).

Procedure: Weigh out accurately about 0.3 gm of solid (or a sufficient amount to contain 0.05-0.06 gm of sulpher) into a 400 mL beaker provided with a stirring rod and clock-glass cover. Dissolve the solid in about 20 mL of water, add 0.3-0.6 mL of concentrated HCl acid and dilute to 200-250 mL. Heat the solution to boiling add drop wise from a burette or pipette 10-12 mL of warm 2% $BaCl_2$ solution (5 gm $BaCl_2.2H_2O$ in 100 mL of water ~ 0.2M).

Stir the solution constantly during the addition. Allow the precipitate to settle for a minute or two. Then test the supernatant liquid for complete precipitation by adding a few drops of barium chloride solution. If a precipitate is formed add slowly a further 3 mL of the reagent, allow the precipitate to settle as before and test again. Repeat this operation until an excess of barium chloride is present. When an excess of the precipitating agent has been added, keep the covered solution hot, but not boiling, for an hour in order to allow time for complete precipitation. The volume of the solution should not be allowed to fall below 150 mL. The precipitate should settle readily and a clear supernatant liquid should be obtained. Filter the precipitate ($BaSO_4$).

Clean, ignite and weigh either a porcelain filtering crucible or a vitreosil filtering crucible. Carry out the ignition either upon a crucible ignition dish or by placing the crucible inside a nickel crucible at red heat (600-800 °C). Allow to cool in a desiccator and weigh.

After digestion of the precipitate, filter the supernatant liquid through the weighed crucible using gentle suction. Reject the filtrate, after testing for complete precipitation with a little barium chloride solution. Transfer the precipitate to the crucible and wash with warm water until 3.5 mL of the filtrate give no precipitate with a few drops of silver nitrate solution. Dry the crucible and precipitate in an oven at 100-110 °C and then ignite in a manner similar to that used for the empty crucible for periods of 15 minutes until constant weight is attained.

Gravimetric determination of iron as Fe_2O_3

$$\mathrm{Fe(II,III)O_n.yH_2O(s)[rust]} \xrightarrow{\mathrm{HCl}} \mathrm{Fe^{2+}_{aq.}} + \mathrm{Fe^{3+}_{aq.}} + \mathrm{Cl^{-}_{aq.}}$$

$$\mathrm{Fe^{2+}_{aq.}} \xrightarrow{\text{oxidation with HNO}_3} \mathrm{Fe^{3+}_{aq.}}$$

$$\mathrm{Fe^{3+}_{aq.}} + 3\mathrm{OH^-}[\text{from NH}_{3\ \mathrm{aq.}}] + (x-1)\mathrm{H_2O} \xrightarrow{\text{isolation/ filteration}} \mathrm{FeO(OH).xH_2O(gel)}\downarrow$$

$$\mathrm{FeO(OH).xH_2O(gel)} \xrightarrow{\Delta,900^\circ\mathrm{C}} \mathrm{Fe_2O_3}\ [\text{Hematite, red} - \text{brown and steel grey}]$$

Procedure:

1. Dry the unknown in a 110 °C oven for 1h.
2. Bring three porcelain crucibles and caps to constant weight by heating to redness for 15 minutes over a burner. Cool in a desiccator and weigh each crucible.
3. Accurately weigh three (0.4-0.5 gm) samples of unknown containing enough Fe to produce 0.3 gm of Fe_2O_3. Dissolve each sample in 15-20 mL of 6M HCl (by heating for about 20 minutes in the fume hood). Add 5 mL of 6M HNO_3 to the filtrate and boil for a few minutes to ensure that all iron is oxidized to Fe(III).
4. Dilute the sample to 200 mL with distilled water and add 3M NH_4OH with constant stirring until the solution is basic. Digest the precipitate by boiling for 5 minutes and allow it to settle.
5. Decant the supernatant liquid through ashless filter paper. Try to retain most of the precipitate in the beaker. Test the filtrate for completeness precipitation by adding a little 3M ammonia to it.
6. Add 25-30 mL of 1% NH_4NO_3 to the beaker containing the precipitate. Heat and decant the hot solution through the same filter. Wash with NH_4NO_3 once again.
7. Carefully remove the filter paper from the funnel, taking care that no precipitate is lost and put it in the beaker containing the rest of the precipitate.
8. Add 30 mL of 3M HCl and warm the beaker to dissolve the iron.
9. Add 3M ammonia with stirring to reprecipitate the iron oxide. Decant through a funnel fitted with a fresh ashless filter paper. Wash the precipitate twice with water and decant supernatant liquid into filter.
10. Wash the precipitate with 1% NH_4OH until little or no Cl^- is detected in the filtered supernatant. Test the filtrate for chloride by acidifying with dilute HNO_3 and adding a few drops of $AgNO_3$ solution. Allow the filter to drain overnight, protect from dust.
11. Transfer the precipitate to porcelain crucible.
12. Dry the crucible with a small flame. Avoid spattering. After it is dry, char the filter paper by increasing the flame temperature. Finally, ignite the product for 15 minutes with the full heat of the burner.
13. Cool the crucible in air and then in a desiccator. Weigh the crucible, reignite and bring to constant weight (0.3 gm) with repeated heating.
14. Calculate the weight percent of iron in each sample, average, the standard deviation and the relative standard deviation.