

Precipitation Titrations

Determination of Chloride by the Mohr Method

A silver nitrate solution is standardized using primary-standard sodium chloride. An unknown chloride is then determined using this solution. The Mohr method uses CrO_4^{2-} as an indicator. A precipitate of Ag_2CrO_4 forms in the presence of a slight excess of Ag^+ and signals the end point. The color goes from a yellow to a brownish-yellow. The change can be detected most precisely when the color in the titration flask is compared to a reference color. A mixture containing CrO_4^{2-} indicator in a suspension of CaCO_3 , simulating AgCl precipitate, is used for this purpose. An indicator blank is prepared using a portion of this mixture. The blank provides a correction for the slight difference between the end point and the equivalence point, a systematic error.

Preparation:

- Read section 35H (pp 798-805) *The Measurement of Volume* in your text, especially the material on measurement of an aliquot and directions for use of a buret. Precipitation titrimetry is covered in Chapter 13.
- Oven-dry about 2.0 gram of standard NaCl and your unknown for one hour or more at 120-130 °C. Place these materials in a dessicator to cool before weighing.
- Titrant: Prepare 500 mL of approximately 0.1 M AgNO_3 by diluting 100 mL of the 0.5 M stock solution. Store this light-sensitive solution in a dark bottle and keep it in your locker when it is not in use.
- Reference and blank: Add 4 mL of indicator (0.1 M K_2CrO_4) and 0.5 g of CaCO_3 to 200 mL of water. Use half of this mixture for the color reference and to determine the indicator blank.

Procedure for Standardization of Silver Nitrate Solution:

- Aliquots: Transfer a 1.0 g (analytical balance) sample of standard sodium chloride into a small funnel placed in the neck of a 100 mL volumetric flask. Carefully rinse the sample into the flask. The sample should be dissolved completely before filling to the mark. Volumetric flasks are not well designed for mixing. After filling to the mark, invert the flask repeatedly and let the air bubble do the mixing. Reagents which are not thoroughly mixed together will form inhomogeneous solutions and lead to serious errors. Since 1.0 g of NaCl is about 16 mmol, each 25 mL aliquot will contain exactly 1/4 of the total or 4 mmol of Cl^- . This will require approximately 40 mL of the 0.1 M silver nitrate solution.
- Titrate the blank mixture first. It will help you visualize the end point.

- Titration: Pipet a 25 mL aliquot into a 250 mL Erlenmeyer flask, add about 25 mL of water, 2 mL of indicator and titrate. Repeat with a second aliquot.
- Charges: Weigh two individual samples of 220 to 250 mg directly into 250 mL Erlenmeyer flasks. These “charges” correspond to about 4 mmoles Cl⁻. Dissolve these in about 50 mL of water, add 2 mL of indicator and titrate.

Determination of % Chloride in the unknown: Weigh out three charges into 250 mL Erlenmeyer flasks. A sample size of 250 mg is probably appropriate, but it is good practice to do a preliminary determination first. Then the sample size can be adjusted so that the titration requires about 40 mL. Titrate the unknowns in the same way as the standards.

Housekeeping: Dispose of AgCl from titrations and excess AgNO₃ in containers provided in the sinks. Save dried NaCl for flame photometry experiment. Return stock solution bottles.

Report: On a large index card, report the average percent chloride, the percent chloride found with each determination and the standard deviation. Raw data and calculations should be in your notebook for inspection upon request.