

CHLORIDE

PRINCIPLE

Inorganic chloride is precipitated by titration with standard silver nitrate solution and the end point is detected potentiometrically using a silver-silver chloride indicator electrode (Note 1).

SCOPE

The method is applicable to corn syrups, finished sugars and other clarified starch hydrolyzates.

SPECIAL APPARATUS

1. Potentiometer: Beckman pH indicator, ZEROMATIC IV, or equivalent
2. Electrode: Beckman silver billet combination electrode, VWR, Catalog No. BA39261, supplied with a length of silver wire (Note 2).

Coating the electrode with silver chloride: Lightly burnish the metal tip of the electrode with mild detergent and scouring powder. Rinse in purified water. Connect the silver billet electrode to the anode (+) of a 1.5 volt dry cell, and connect the silver wire to the cathode (-). Coat the electrode by immersing it and the silver wire in 4 *M* potassium chloride solution until the electrode color becomes dark. Reverse the battery connections until the electrode color is discharged. Repeat this cycle again. Finally, coat the electrode again and remove from the solution. The electrode may be stored for several days after immersing the tip in purified water. When the coating color visibly lightens, it should be recoated.

REAGENTS

1. Silver Nitrate Solution, 0.05 *N*: Standard. Dissolve 8.495 g of reagent grade silver nitrate (AgNO_3) in purified water. Dilute to 1 L volume and mix thoroughly.

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2. Silver Nitrate Solution, 0.01 *N*: Standard. Transfer 200.0 mL of standard 0.05 *N* silver nitrate solution to a 1 L volumetric flask, dilute to volume and mix thoroughly.
3. Silver Chloride - Saturated Potassium Chloride Solution, 4 *M*: Dissolve 298 g of reagent grade potassium chloride (KCl) in purified water, add a few drops of 0.05 *N* silver nitrate solution, dilute to 1 L volume and mix thoroughly.
4. Ammonium Nitrate Solution, 10%: Dissolve 10 g of reagent grade ammonium nitrate (NH₄NO₃) in 100 mL of purified water.
5. Nitric Acid, Concentrated: Reagent grade (70% HNO₃; sp g 1.42)

PROCEDURE

Visually inspect the silver-silver chloride electrode coating, recoat if necessary and connect the main electrode lead to the glass electrode jack of the pH indicator. Connect the small electrode lead to the reference electrode jack of the pH indicator. Turn on the pH indicator and turn the selector switch to measure emf. Refill the reference electrode compartment with silver chloride-saturated 4 *M* potassium chloride solution, if necessary. Refill the bridge compartment with fresh 10% ammonium nitrate solution daily or as necessary (Note 3).

Weigh 15-50 g (± 0.1 g) of sample (Note 4) in a 250 mL beaker, add 100 mL of warm purified water and mix well. Place the beaker on a magnetic stirrer, add a stirring bar, 1 mL of concentrated nitric acid and immerse the electrode in the sample solution. While stirring, titrate the sample with standard silver nitrate solution (Note 4) adding in increments of 1 mL. Record the potential and titer after each addition of titrant. When the potential begins to change, add titrant in increments of 0.2 mL. When the potential "break" has been passed, resume titrating in 1 mL increments for three more additions.

CHLORIDE — continued**CALCULATION**

Plot the titration curve of emf vs. titrant volume. Read the volume of titrant corresponding to the equivalence point (point of maximum inflection) from the curve.

$$\% \text{ Chloride, as is} = \frac{(\text{mL AgNO}_3)(\text{AgNO}_3 \text{ Norm.})(0.0355)(100)}{\text{Sample Wt., g}}$$

NOTES AND PRECAUTIONS

1. Results of equivalent precision and accuracy are obtained with automatic analyzers which generate silver ion coulometrically and detect the end point amperometrically.
2. A silver and calomel electrode system may be used for end point detection. Contact between the calomel reference electrode and the sample solution must be made through a chloride-free potassium nitrate bridge.
3. It is recommended that the bridge solution be replaced with fresh (free of chloride ions) solution once a day or as necessary to prevent chloride contamination of the sample solution. It is necessary to replace the bridge solution following coating of the electrode.
4. Optimum sample size depends on chloride content. Materials containing more than 0.03% chloride are conveniently analyzed using 15 g and 0.05 *N* silver nitrate titrant. Materials containing less than 0.03% chloride are conveniently analyzed using 50 g and 0.01 *N* silver nitrate titrant.