2. Any of the following catalyze the digestion: a crystal of CuSO₄, 0.1 g of selenium, 0.2 g of CuSeO₃. The catalyst can be omitted, if desired.

3. A modification of this procedure uses about 50 mL of 4% boric acid solution instead of the standard HCl in the receiver flask. After distillation is complete, the ammonium borate produced is titrated with standard 0.1 M HCl, with 2 to 3 drops of bromocresol green as indicator.

4. If any sodium hydroxide solution comes into contact with your skin, wash the affected area immediately with copious amounts of water.

5. Granulated zinc (10 to 20 mesh) is added to minimize bumping during the distillation; it reacts slowly with the base to produce small bubbles of hydrogen that prevent superheating of the liquid.

6. The percentage of protein in the unknown is calculated by multiplying the % N by an appropriate factor: 5.70 for cereals, 6.25 for meats, and 6.38 for dairy products.

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### 37D Precipitation Titrations

As noted in Section 13F, most precipitation titrations make use of a standard silver nitrate solution as titrant. Directions follow for the volumetric titration of chloride ion using an adsorption indicator.

#### 37D-1 Preparing a Standard Silver Nitrate Solution

**PROCEDURE**

Use a top-loading balance to transfer the approximate mass of AgNO₃ to a weighing bottle (Note 1). Dry at 110°C for about 1 hr but not much longer (Note 2), and then cool to room temperature in a desiccator. Weigh the bottle and contents (to the nearest 0.1 mg). Transfer the bulk of the AgNO₃ to a volumetric flask using a powder funnel. Cap the weighing bottle, and reweigh it and any solid that remains. Rinse the powder funnel thoroughly. Dissolve the AgNO₃, dilute to the mark with water, and mix well (Note 3). Calculate the molar concentration of this solution.

**Notes**

1. Consult with the instructor concerning the volume and concentration of AgNO₃ to be prepared. The mass of AgNO₃ to be taken is as follows:

<table>
<thead>
<tr>
<th>Silver Ion Concentration, M</th>
<th>Approximate Mass (g) of AgNO₃ Needed to Prepare</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>16.9</td>
</tr>
<tr>
<td>0.05</td>
<td>8.5</td>
</tr>
<tr>
<td>0.02</td>
<td>3.4</td>
</tr>
<tr>
<td>1000 mL</td>
<td>8.5</td>
</tr>
<tr>
<td>500 mL</td>
<td>4.2</td>
</tr>
<tr>
<td>250 mL</td>
<td>1.8</td>
</tr>
</tbody>
</table>

2. Prolonged heating causes partial decomposition of AgNO₃. Some discoloration may occur, even after only 1 hr at 110°C; the effect of this decomposition on the purity of the reagent is ordinarily imperceptible.

3. Silver nitrate solutions should be stored in a dark place when not in use.
37D-2 The Determination of Chloride by Titration with an Adsorption Indicator

Discussion

In this titration, the anionic adsorption indicator dichlorofluorescein is used to locate the end point. With the first excess of titrant, the indicator is incorporated into the counter-ion layer surrounding the silver chloride and imparts color to the solid (page 360). To obtain a satisfactory color change, it is desirable to maintain the particles of silver chloride in the colloidal state. Dextrin is added to the solution to stabilize the colloid and prevent its coagulation.

PREPARATION OF SOLUTIONS

Dichlorofluorescein indicator (sufficient for several hundred titrations). Dissolve 0.2 g of dichlorofluorescein in a solution prepared by mixing 75 mL of ethanol and 25 mL of water.

PROCEDURE

Dry the unknown at 110°C for about 1 hr; allow it to return to room temperature in a desiccator. Weigh individual samples (to the nearest 0.1 mg) into individual conical flasks, and dissolve them in appropriate volumes of distilled water (Note 1). To each, add about 0.1 g of dextrin and 5 drops of indicator. Titrate (Note 2) with AgNO₃ to the first permanent pink color of silver dichlorofluoresceinate. Report the percentage of Cl⁻ in the unknown.

Notes

1. Use 0.25-g samples for 0.1 M AgNO₃ and about half that amount for 0.05 M reagent. Dissolve the former in about 200 mL of distilled water and the latter in about 100 mL. If 0.02 M AgNO₃ is to be used, weigh a 0.4-g sample into a 500-mL volumetric flask, and take 50-mL aliquots for titration.
2. Colloidal AgCl is sensitive to photodecomposition, particularly in the presence of the indicator; attempts to perform the titration in direct sunlight will fail. If photodecomposition appears to be a problem, establish the approximate end point with a rough preliminary titration, and use this information to estimate the volumes of AgNO₃ needed for the other samples. For each subsequent sample, add the indicator and dextrin only after most of the AgNO₃ has been added, and then complete the titration without delay.

37D-3 The Determination of Chloride by a Weight Titration

Discussion

The Mohr method uses CrO₄²⁻ ion as an indicator in the titration of chloride ion with silver nitrate. The first excess of titrant results in the formation of a red silver chromate precipitate, which signals the end point.

Instead of a buret, a balance is employed in this procedure to determine the mass of silver nitrate solution needed to reach the end point. The concentration of the silver nitrate is most conveniently determined by standardization against primary-
standard sodium chloride, although direct preparation by mass is also feasible. The reagent concentration is expressed as weight (mass) molarity (mmol AgNO₃/g of solution). See Section 13D-1 for additional details.

### PREPARATION OF SOLUTIONS

(a) Silver nitrate, approximately 0.1 mmol/g of solution (sufficient for about 10 titrations). Dissolve about 4.5 g of AgNO₃ in about 500 mL of distilled water. Standardize the solution against weighed quantities of reagent-grade NaCl as directed in Note 1 of the procedure. Express the concentration as weight (mass) molarity (mmol AgNO₃/g of solution). When not in use, store the solution in a dark place.

(b) Potassium chromate, 5% (sufficient for about 10 titrations). Dissolve about 1.0 g of K₂CrO₄ in about 20 mL of distilled water.

**Note**
Alternatively, standard AgNO₃ can be prepared directly by weight. To do so, follow the directions in Section 37D-1 for weighing out a known amount of primary-standard AgNO₃. Use a powder funnel to transfer the weighed AgNO₃ to a 500-mL polyethylene bottle that has been previously weighed to the nearest 10 mg. Add about 500 mL of water and weigh again. Calculate the weight molarity.

### DIRECTIONS FOR PERFORMING A WEIGHT TITRATION

Prepare a reagent dispenser from a 60-mL polyethylene bottle with a screw cap equipped with a fine delivery tip. The tip can be prepared by constricting the opening of an ordinary medicine dropper in a flame. With a cork borer, make a hole in the cap that is slightly smaller than the outside diameter of the tip. Carefully force the tip through the hole; apply a bead of epoxy cement to seal the tip to the cap. Label the bottle.

Fill the reagent dispenser with a quantity of the standard titrant, and tighten the screw cap firmly. Weigh the bottle and its contents to the nearest milligram. Introduce a suitable indicator into the solution of the analyte. Grasp the dispenser so that its tip is below the lip of the flask and deliver several increments of the reagent by squeezing the bottle while rotating the flask with your other hand. When it is judged that only a few more drops of reagent are needed, ease the pressure on the bottle so that the flow stops; then touch the tip to the inside of the flask and further reduce the pressure on the dispenser so that the liquid in the tip is drawn back into the bottle as the tip is removed from the flask. Set the dispenser on a piece of clean, dry glazed paper and rinse down the inner walls of the flask with a stream of distilled or deionized water. Add reagent a drop at a time until the end point is reached (Note). Weigh the dispenser and record the data.

**Note**
Increments smaller than an ordinary drop can be added by forming a partial drop on the tip and then touching the tip to the wall. Rinse the walls with wash water to combine the partial drop with the bulk of solution.
PROCEDURE

Dry the unknown at 110°C for at least 1 hr (Note). Cool in a desiccator. Consult with your instructor for a suitable sample size. Weigh (to the nearest 0.1 mg) individual samples into 250-mL conical flasks, and dissolve in about 100 mL of distilled water. Add small quantities of NaHCO₃ until effervescence ceases. Introduce about 2 mL of K₂CrO₄ solution, and titrate to the first permanent appearance of red Ag₂CrO₄.

Determine an indicator blank by suspending a small amount of chloride-free CaCO₃ in 100 mL of distilled water containing 2 mL of K₂CrO₄. Correct reagent masses for the blank. Report the percentage of Cl⁻ in the unknown. Dispose of AgCl and reagents as directed by the instructor.

Note
The AgNO₃ is conveniently standardized concurrently with the analysis. Dry reagent-grade NaCl for about 1 h. Cool; then weigh (to the nearest 0.1 mg) 0.25-g portions into conical flasks and titrate as previously.

COMPLEX-FORMATION TITRATIONS WITH EDTA

37E

See Section 17D for a discussion of the analytical uses of EDTA as a chelating reagent. Directions follow for direct titration of magnesium and determination of the hardness of natural water.

37E-1 Preparation of Solutions

PROCEDURE

A pH-10 buffer and an indicator solution are needed for these titrations.

1. Buffer solution, pH 10 (sufficient for 80 to 100 titrations). Dilute 57 mL of concentrated NH₃ and 7 g of NH₄Cl in sufficient distilled water to give 100 mL of solution.
2. Eriochrome Black T indicator (sufficient for about 100 titrations). Dissolve 100 mg of the solid in a solution containing 15 mL of ethanolamine and 5 mL of absolute ethanol. This solution should be freshly prepared every 2 weeks; refrigeration slows its deterioration.

37E-2 Preparation of Standard 0.01 M EDTA Solution

Discussion

See Section 17D-1 for a description of the properties of reagent-grade Na₂H₂Y · 2H₂O and its use in the direct preparation of standard EDTA solutions.

PROCEDURE

Dry about 4 g of the purified dihydrate Na₂H₂Y · 2H₂O (Note 1) at 80°C to remove superficial moisture. Cool to room temperature in a desiccator. Weigh (to the