tare and the mass measurement itself. The standard deviations in mass and volume can be taken, as shown in Table 37-1.

The final calculation of the sampling variance is done by subtracting the variances due to sample preparation and final measurement from the overall variance. Taking the square root gives the sampling standard deviation (Note 2). Finally, the sampling constant is obtained by multiplying the % relative standard deviation (RSD) squared and the average mass of the sample (see Equation 8-7).

Notes
1. Unknowns should contain 0.40 to 0.64 g of solid KH₂PO₄ added to about 80 g of solid NaCl.
2. The sampling standard deviation will usually be the largest component of the overall variance.

### 37B GRAVIMETRIC METHODS OF ANALYSIS

General aspects, calculations, and typical applications of gravimetric analysis are discussed in Chapter 12.

#### 37B-1 The Gravimetric Determination of Chloride in a Soluble Sample

**Discussion**

The chloride content of a soluble salt can be determined by precipitation as silver chloride.

\[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl(s)} \]

The precipitate is collected in a weighed filtering crucible and is washed. After the precipitate has been dried to a constant mass at 110°C, its mass is determined.

The solution containing the sample is kept slightly acidic during the precipitation to eliminate possible interference from anions of weak acids (such as CO₃²⁻) that form sparingly soluble silver salts in a neutral environment. A moderate excess of silver ion is needed to diminish the solubility of silver chloride, but a large excess is avoided to minimize coprecipitation of silver nitrate.

Silver chloride forms first as a colloid and is subsequently coagulated with heat. Nitric acid and the small excess of silver nitrate promote coagulation by providing a moderately high electrolyte concentration. Nitric acid in the wash solution maintains the electrolyte concentration and eliminates the possibility of peptization during the washing step; the acid subsequently decomposes to give volatile products when the precipitate is dried. See Section 12A-2 for additional information concerning the properties and treatment of colloidal precipitates.
In common with other silver halides, finely divided silver chloride undergoes photodecomposition:

\[ 2\text{AgCl}(s) \xrightarrow{h\nu} 2\text{Ag}(s) + \text{Cl}_2(g) \]

The elemental silver produced in this reaction is responsible for the violet color that develops in the precipitate. In principle, this reaction leads to low results for chloride ion. In practice, however, its effect is negligible provided that direct and prolonged exposure of the precipitate to sunlight is avoided.

If photodecomposition of silver chloride occurs before filtration, the additional reaction

\[ 3\text{Cl}_2(aq) + 3\text{H}_2\text{O} + 5\text{Ag}^+ \rightarrow 5\text{AgCl}(s) + \text{ClO}_3^- + 6\text{H}^+ \]

tends to cause high results.

In the usual procedure, some photodecomposition of silver chloride is inevitable. It is worthwhile to minimize exposure of the solid to intense sources of light as much as possible.

Because silver nitrate is expensive, any unused reagent should be collected in a storage container; similarly, precipitated silver chloride should be retained after the analysis is complete.\(^3\)

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**PROCEDURE**

Clean three medium-porosity sintered-glass or porcelain filtering crucibles by allowing about 5 mL of concentrated HNO\(_3\) to stand in each for about 5 min. Use a vacuum (see Figure 2-16) to draw the acid through the crucible. Rinse each crucible with three portions of tap water, and then discontinue the vacuum. Next, add about 5 mL of 6 M NH\(_3\) and wait for about 5 min before drawing it through the filter. Finally, rinse each crucible with six to eight portions of distilled or deionized water. Provide each crucible with an identifying mark. Dry the crucibles to constant mass by heating at 110°C while the other steps in the analysis are being carried out. The first drying should be for at least 1 hr; subsequent heating periods can be somewhat shorter (30 to 40 min). This process of heating and drying should be repeated until the mass becomes constant to within 0.2 to 0.3 mg.

Transfer the unknown to a weighing bottle and dry it at 110°C (see Figure 2-9) for 1 to 2 hr; allow the bottle and contents to cool to room temperature in a desiccator. Weigh (to the nearest 0.1 mg) individual samples by difference into 400-mL beakers (Note 1). Dissolve each sample in about 100 mL of distilled water to which 2 to 3 mL of 6 M HNO\(_3\) have been added.

Slowly, and with good stirring, add 0.2 M AgNO\(_3\) to each of the cold sample solutions until AgCl is observed to coagulate (Notes 2 and 3), and then introduce an additional 3 to 5 mL. Heat almost to boiling, and digest the solids for about 10 min. Add a few drops of AgNO\(_3\) to confirm that precipitation is complete. If more precipitate forms, add about 3 mL of AgNO\(_3\), digest, and again test for

complete precipitation. Pour any unused AgNO₃ into a waste container (not into the original reagent bottle). Cover each beaker, and store in a dark place for at least 2 hr (preferably until the next laboratory period).

Read the instructions for filtration in Section 2F. Decant the supernatant liquids through weighed filtering crucibles. Wash the precipitates several times (while they are still in the beaker) with a solution consisting of 2 to 5 mL of 6 M HNO₃ per liter of distilled water; decant these washings through the filters. Quantitatively transfer the AgCl from the beakers to the individual crucibles with fine streams of wash solution; use rubber policemen to dislodge any particles that adhere to the walls of the beakers. Continue washing until the filtrates are essentially free of Ag⁺ ion (Note 4).

Dry the precipitate at 110°C for at least 1 hr. Store the crucibles in a desiccator while they cool. Determine the mass of the crucibles and their contents. Repeat the cycle of heating, cooling, and weighing until consecutive weighings agree to within 0.2 mg. Calculate the percentage of Cl⁻ in the sample.

When the analysis is complete, remove the precipitates by gently tapping the crucibles over a piece of glazed paper. Transfer the collected AgCl to a container for silver wastes. Remove the last traces of AgCl by filling the crucibles with 6 M NH₃ and allowing them to stand.

Notes
1. Consult with the instructor concerning an appropriate sample size.
2. Determine the approximate amount of AgNO₃ needed by calculating the volume that would be required if the unknown were pure NaCl.
3. Use a separate stirring rod for each sample and leave it in its beaker throughout the determination.
4. To test the washings for Ag⁺, collect a small volume in a test tube and add a few drops of HCl. Washing is judged complete when little or no turbidity develops.

37B-2 The Gravimetric Determination of Tin in Brass

Discussion
Brasses are important alloys. Copper is ordinarily the principal constituent, with lesser amounts of lead, zinc, tin, and possibly other elements as well. Treatment of a brass with nitric acid results in the formation of the sparingly soluble “metastannic acid” H₂SnO₃·xH₂O; all other constituents are dissolved. The solid is filtered, washed, and ignited to SnO₂.

The gravimetric determination of tin provides experience in the use of ashless filter paper and is frequently performed in conjunction with a more inclusive analysis of a brass sample.

PROCEDURE

Provide identifying marks on three porcelain crucibles and their covers. During waiting periods in the experiment, bring each set of crucibles and covers to constant mass by ignition at 900°C in a muffle furnace.

Do not dry the unknown. If so instructed, rinse it with acetone to remove any oil or grease. Weigh (to the nearest 0.1 mg) approximately 1-g samples of the unknown into 250-mL beakers. Cover the beakers with watch glasses.
beakers in the hood, and cautiously introduce a mixture containing about 15 mL of concentrated HNO₃ and 10 mL of H₂O. Digest the samples for at least 30 min; add more HNO₃ if necessary. Rinse the watch glasses, then evaporate the solutions to about 5 mL, but not to dryness (Note 1).

Add about 5 mL of 3 M HNO₃, 25 mL of distilled water, and one quarter of a tablet of filter paper pulp to each sample; heat without boiling for about 45 min. Collect the precipitated H₂SnO₃·xH₂O on fine-porosity ashless filter papers (see Section 2F-3 and Notes 2 and 3). Use many small volumes of hot 0.3 M HNO₃ to wash the last traces of copper from the precipitate. Test for completeness of washing with a drop of NH₃(aq) on the top of the precipitate; wash further if the precipitate turns blue.

Remove the filter paper and its contents from the funnels, fold, and place in crucibles that (with their covers) have been brought to constant mass (see Figure 2-14). Ash the filter paper at as low a temperature as possible. There must be free access of air throughout the charring (see Section 2F-3 and Figure 2-15). Gradually increase the temperature until all the carbon has been removed. Then bring the covered crucibles and their contents to constant mass in a 900°C furnace (Note 4).

Calculate the percentage of tin in the unknown.

Notes
1. It is often time-consuming and difficult to redissolve the soluble components of the residue after a sample has been evaporated to dryness.
2. The filtration step can be quite time-consuming and once started cannot be interrupted.
3. If the unknown is to be analyzed electrolytically for its lead and copper content (see Section 37K-1), collect the filtrates in tall-form beakers. The final volume should be about 125 mL; evaporate to that volume if necessary. If the analysis is for tin only, the volume of washings is not important.
4. Partial reduction of SnO₂ may cause the ignited precipitate to appear gray. In this case, add a drop of nitric acid, cautiously evaporate, and ignite again.

37B-3 The Gravimetric Determination of Nickel in Steel

Discussion

The nickel in a steel sample can be precipitated from a slightly alkaline medium with an alcoholic solution of dimethylglyoxime (see Section 12D-3). Interference from iron(III) is eliminated by masking with tartaric acid. The product is freed of moisture by drying at 110°C.

The bulky character of nickel dimethylglyoxime limits the mass of nickel that can be accommodated conveniently and thus the sample mass. Care must be taken to control the excess of alcoholic dimethylglyoxime used. If too much is added, the alcohol concentration becomes sufficient to dissolve appreciable amounts of the nickel dimethylglyoxime, which leads to low results. If the alcohol concentration becomes too low, however, some of the reagent may precipitate and cause a positive error.

PREPARATION OF SOLUTIONS

1. Dimethylglyoxime, 1% (w/v). Dissolve 10 g of dimethylglyoxime in 1 L of ethanol. (This solution is sufficient for about 50 precipitations.)
2. **Tartaric acid, 15% (w/v).** Dissolve 225 g of tartaric acid in sufficient water to give 1500 mL of solution. Filter before use if the solution is not clear. (This solution is sufficient for about 50 precipitations.)

**PROCEDURE**

Clean and mark three medium-porosity sintered-glass crucibles (Note 1); bring them to constant mass by drying at 110°C for at least 1 hr.

Weigh (to the nearest 0.1 mg) samples containing 30 to 35 mg of nickel into individual 400-mL beakers (Note 2). In the hood, dissolve each sample in about 50 mL of 6 M HCl with gentle warming. Carefully add approximately 15 mL of 6 M HNO₃, and boil gently to expel any oxides of nitrogen that may have been produced. Dilute to about 200 mL and heat to boiling. Introduce about 30 mL of 15% tartaric acid and sufficient concentrated NH₃\(_{(aq)}\) to produce a faint odor of NH₃ in the vapors over the solutions (Note 3); then add another 1 to 2 mL of NH₃\(_{(aq)}\). If the solutions are not clear at this stage, proceed as directed in Note 4. Make the solutions acidic with HCl (no odor of NH₃), heat to 60° to 80°C, and add about 20 mL of the 1% dimethylglyoxime solution. With good stirring, add 6 M NH₃ until a slight excess exists (faint odor of NH₃) plus an additional 1 to 2 mL. Digest the precipitates for 30 to 60 min, cool for at least 1 hr, and filter.

Wash the solids with water until the washings are free of Cl\(^{-}\)/H\(_{11002}\) (Note 5). Bring the crucibles and their contents to constant mass at 110°C. Report the percentage of nickel in the sample. The dried precipitate has the composition Ni(C₄H₇O₂N₂)₂ (288.92 g/mol).

**Notes**

1. Medium-porosity porcelain filtering crucibles or Gooch crucibles with glass pads can be substituted for sintered-glass crucibles in this determination.
2. Use a separate stirring rod for each sample and leave it in the beaker throughout.
3. The presence or absence of excess NH₃ is readily established by odor; use a waving motion with your hand to waft the vapors toward your nose.
4. If Fe₂O₃·ₓH₂O forms on addition of NH₃, acidify the solution with HCl, introduce additional tartaric acid, and neutralize again. Alternatively, remove the solid by filtration. Thorough washing with a hot NH₃/NH₄Cl solution is required; the washings are combined with the solution containing the bulk of the sample.
5. Test the washings for Cl\(^{-}\) by collecting a small portion in a test tube, acidifying with HNO₃, and adding a drop or two of 0.1 M AgNO₃. Washing is judged complete when little or no turbidity develops.

**37C NEUTRALIZATION TITRATIONS**

**Discussion**

Neutralization titrations are performed with standard solutions of strong acids or bases. While a single solution (of either acid or base) is sufficient for the titration of a given type of analyte, it is convenient to have standard solutions of both acid and base available in case back-titration is needed to locate the end point more exactly. The concentration of one solution is established by titration against a primary standard; the concentration of the other is then determined from the acid/base ratio (that is, the volume of acid needed to neutralize 1.000 mL of the base).