37H-4 The Determination of Copper in Brass

Discussion

The standardization procedure described in Section 37H-3 is readily adapted to the determination of copper in brass, an alloy that also contains appreciable amounts of tin, lead, and zinc (and perhaps minor amounts of nickel and iron). The method is relatively simple and applicable to brasses with less than 2% iron. A weighed sample is treated with nitric acid, which causes the tin to precipitate as a hydrated oxide of uncertain composition. Evaporation with sulfuric acid to the appearance of sulfur trioxide eliminates the excess nitrate, redissolves the tin compound, and possibly causes the formation of lead sulfate. The pH is adjusted through the addition of ammonia, followed by acidification with a measured amount of phosphoric acid. An excess of potassium iodide is added, and the liberated iodine is titrated with standard thiosulfate. See Section 37H-3 for additional discussion.

PROCEDURE

If so directed, free the metal of oils by treatment with an organic solvent; briefly heat in an oven to drive off the solvent. Weigh (to the nearest 0.1 mg) 0.3-g samples into 250-mL conical flasks, and introduce 5 mL of 6 M HNO₃ into each; warm (use the hood) until solution is complete. Add 10 mL of concentrated H₂SO₄, and evaporate (use the hood) until copious white fumes of SO₃ are given off. Allow the mixture to cool. Cautiously add 30 mL of distilled water, boil for 1 to 2 min, and again cool.

Follow the instructions in the third and fourth paragraphs of the procedure in Section 37H-3.

Report the percentage of Cu in the sample.

37I TITRATIONS WITH POTASSIUM BROMATE

Applications of standard bromate solutions to the determination of organic functional groups are described in Section 20C-4. Directions follow for the determination of ascorbic acid in vitamin C tablets.

37I-1 Preparation of Solutions

PROCEDURE

1. Potassium bromate, 0.015 M. Transfer about 1.5 g of reagent-grade potassium bromate to a weighing bottle, and dry at 110°C for at least 1 hr. Cool in a desiccator. Weigh approximately 1.3 g (to the nearest 0.1 mg) into a 500-mL volumetric flask; use a powder funnel to ensure quantitative transfer of the solid. Rinse the funnel well, and dissolve the KBrO₃ in about 200 mL of distilled water. Dilute to the mark, and mix thoroughly.

   Solid potassium bromate can cause a fire if it comes into contact with damp organic material (such as paper towels in a waste container). Consult with the instructor concerning the disposal of any excess.

2. Sodium thiosulfate, 0.05 M. Follow the directions in Section 37G-1; use about 12.5 g of Na₂S₂O₃ · 5H₂O per liter of solution.

3. Starch indicator. See Section 37G-1(b).
37I-2 Standardization of Sodium Thiosulfate against Potassium Bromate

Discussion

Iodine is generated by the reaction between a known volume of standard potassium bromate and an unmeasured excess of potassium iodide:

\[
\text{BrO}_3^- + 6I^- + 6H^+ \rightarrow \text{Br}^- + 3I_2 + 3H_2O
\]

The iodine produced is titrated with the sodium thiosulfate solution.

PROCEDURE

Pipet 25.00-mL aliquots of the KBrO₃ solution into 250-mL conical flasks and rinse the interior walls with distilled water. Treat each sample individually beyond this point. Introduce 2 to 3 g of KI and about 5 mL of 3 M H₂SO₄. Immediately titrate with Na₂S₂O₃ until the solution is pale yellow. Add 5 mL of starch indicator, and titrate to the disappearance of the blue color.

Calculate the concentration of the thiosulfate solution.

37I-3 The Determination of Ascorbic Acid in Vitamin C Tablets by Titration with Potassium Bromate

Discussion

Ascorbic acid, C₆H₈O₆, is cleanly oxidized to dehydroascorbic acid by bromine:

\[
\text{O} = \text{C} \quad \text{O} \quad \text{H} \quad \text{H} \\
\text{C} = \text{C} \quad \text{C} \quad \text{C} \quad \text{H} + \text{Br}_2 \rightarrow \\
\text{H} \quad \text{H} \quad \text{H} \\
\text{O} = \text{C} \quad \text{O} \quad \text{H} \quad \text{H} \\
\text{C} = \text{C} \quad \text{C} \quad \text{C} \quad \text{H} + 2\text{Br}^- + 2\text{H}^+
\]

Ascorbic acid oxidation by bromine.

An unmeasured excess of potassium bromide is added to an acidified solution of the sample. The solution is titrated with standard potassium bromate to the first permanent appearance of excess bromine; this excess is then determined iodometrically with standard sodium thiosulfate. The entire titration must be performed without delay to prevent air oxidation of the ascorbic acid.

PROCEDURE

Weigh (to the nearest milligram) 3 to 5 vitamin C tablets (Note 1). Pulverize them thoroughly in a mortar, and transfer the powder to a dry weighing bottle. Weigh
individual 0.40-g to 0.50-g samples (to the nearest 0.1 mg) into dry 250-mL conical
flasks. Treat each sample individually beyond this point. Dissolve the sample (Note
2) in 50 mL of 1.5 M \( \text{H}_2\text{SO}_4 \); then add about 5 g of KBr. Titrate immediately with
standard KBrO\(_3\) to the first faint yellow due to excess Br\(_2\). Record the volume of
KBrO\(_3\) used. Add 3 g of KI and 5 mL of starch indicator; back-titrate (Note 3) with
standard 0.05 M Na\(_2\)S\(_2\)O\(_3\).

Calculate the average mass (in milligrams) of ascorbic acid (176.12 g/mol) in
each tablet.

Notes
1. This method is not applicable to chewable vitamin C tablets.
2. The binder in many vitamin C tablets remains in suspension throughout the
analysis. If the binder is starch, the characteristic color of the complex with
iodine appears on addition of KI.
3. The volume of thiosulfate needed for the back-titration seldom exceeds a few
milliliters.

### 37J POTENTIOMETRIC METHODS

Potentiometric measurements provide a highly selective method for the quantitative
determination of numerous cations and anions. A discussion of the principles
and applications of potentiometric measurements is found in Chapter 21. Detailed
instructions are given in this section on the use of potentiometric measurements to
locate end points in volumetric titrations. In addition, a procedure for the direct
potentiometric determination of fluoride ion in drinking water and in toothpaste is
described.

#### 37J-1 General Directions for Performing a
Potentiometric Titration

The procedure that follows is applicable to the titrimetric methods described in this
section. With the proper choice of indicator electrode, it can also be applied to most
of the volumetric methods given in Sections 37B through 37H.

#### PROCEDURE

1. Dissolve the sample in 50 to 250 mL of water. Rinse a suitable pair of electrodes with deionized water, and immerse them in the sample solution. Provide magnetic (or mechanical) stirring. Position the buret so that reagent can be delivered without splashing.
2. Connect the electrodes to the meter, commence stirring, and record the initial buret volume and the initial potential (or pH).
3. Record the meter reading and buret volume after each addition of titrant. Introduce fairly large volumes (about 5 mL) at the beginning. Withhold a succeeding addition until the meter reading remains constant within 1 to 2 mV (or 0.05 pH unit) for at least 30 s (Note). Judge the volume of reagent to be added by estimating a value for \( \Delta E/\Delta V \) after each addition. In the immediate vicinity of the equivalence point, introduce the reagent in 0.1-mL increments. Continue the