⟨261⟩ MERCURY

Method I

NOTE—Mercuric dithizonate is light-sensitive. Perform this test in subdued light.

Reagents—

DITHIZONE STOCK SOLUTION—Dissolve 40 mg of dithizone in 1000 mL of chloroform.

DITHIZONE TITRANT—Dilute 30.0 mL of *Dithizone Stock Solution* with chloroform to 100.0 mL. This solution contains approximately 12 mg of dithizone per L.

MERCURY STOCK SOLUTION—Transfer 135.4 mg of mercuric chloride to a 100-mL volumetric flask, and dilute with 1 N sulfuric acid to volume. This solution contains the equivalent of 100 mg of Hg in 100 mL.

MERCURY SOLUTION FOR STANDARDIZING DITHIZONE TITRANT—Transfer 2.0 mL of *Mercury Stock Solution* to a 100-mL volumetric flask, and dilute with 1 N sulfuric acid to volume. Each mL of this solution contains the equivalent of 20 μg of Hg.

The following solutions are called for in the limit test for mercury that is specified in the monographs on Ferrous Fumarate, Ferrous Sulfate, and Dried Ferrous Sulfate.

HYDROXYLAMINE HYDROCHLORIDE SOLUTION—Prepare as directed in the test for *Lead* ⟨251⟩.

STANDARD MERCURY SOLUTION—On the day of use, quantitatively dilute 1.0 mL of *Mercury Stock Solution* with 1 N sulfuric acid to 1000 mL. Each mL of the resulting solution contains the equivalent of 1 μg of mercury.

DITHIZONE EXTRACTION SOLUTION—Prepare as directed in the test for *Lead* ⟨251⟩.

DILUTED DITHIZONE EXTRACTION SOLUTION—Just prior to use, dilute 5 mL of *Dithizone Extraction Solution* with 25 mL of chloroform.

Standardization of Dithizone Titrant—Transfer 1.0 mL of *Mercury Solution for Standardizing Dithizone Titrant* to a 250-mL separator, and add 100 mL of 1 N sulfuric acid, 90 mL of water, 1 mL of glacial acetic acid, and 10 mL of hydroxylamine hydrochloride solution (1 in 5). Titrate the solution with *Dithizone Titrant* from a 10-mL microburet, shaking the mixture 20 times after each addition and allowing the chloroform layer to separate, then discarding the chloroform layer. Continue until a final addition of *Dithizone Titrant* is green in color after shaking. Calculate the quantity, in μg, of Hg equivalent to each mL of *Dithizone Titrant* by the formula:

$$20/V$$

in which V is the volume, in mL, of *Dithizone Titrant* added.

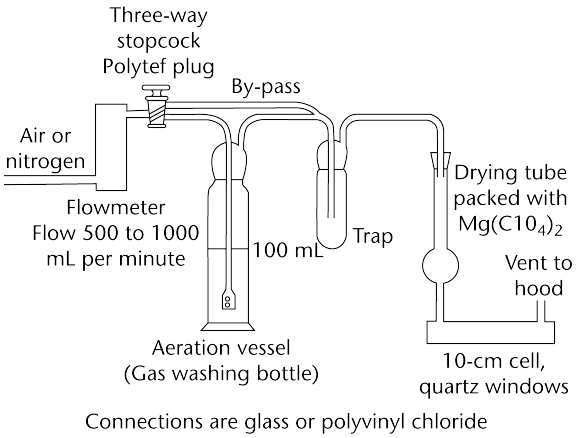
Test Preparation—Transfer about 2 g of the substance under test, accurately weighed, to a glass-stoppered, 250-mL conical flask, add 20 mL of a mixture of equal volumes of nitric acid and sulfuric acid, attach a suitable condenser, reflux the mixture for 1 hour, cool, cautiously dilute with water, and boil until fumes of nitrous acid no longer are noticeable. Cool the solution, cautiously dilute with water, transfer to a 200-mL volumetric flask, dilute with water to volume, mix, and filter.

Procedure—Transfer 50.0 mL of *Test Preparation* to a 250-mL separator, and extract with successive small portions of chloroform until the last chloroform extract remains colorless. Discard the chloroform extract, and add to the extracted *Test Preparation* 50 mL of 1 N sulfuric acid, 90 mL of water, 1 mL of glacial acetic acid, and 10 mL of hydroxylamine hydrochloride solution (1 in 5). Proceed as directed under *Standardization of Dithizone Titrant*, beginning with "Titrate the solution." Calculate the amount of mercury.

Method IIa and Method IIb

Mercury Detection Instrument—Use any suitable atomic absorption spectrophotometer equipped with a fast-response recorder and capable of measuring the radiation absorbed by mercury vapors at the mercury resonance line of 253.6 nm. [NOTE—Wash all glassware associated with the test with nitric acid, and rinse thoroughly with water before use.]

Aeration Apparatus—The apparatus (see *accompanying diagram*) consists of a flowmeter capable of measuring flow rates from 500 to 1000 mL per minute, connected via a three-way stopcock fitted with a polytef plug to an aeration vessel (250-mL gas washing bottle), followed by a trap, a drying tube packed with magnesium perchlorate, a 10-cm × 25-mm flow-through cell with quartz windows, and terminating with a vent to a fume hood.



Mercury Aeration Apparatus

Reagents—

Potassium Permanganate Solution—Dissolve 5 g of potassium permanganate in 100 mL of water.

Hydroxylamine Hydrochloride Solution—Dissolve 10 g of hydroxylamine hydrochloride in 100 mL of water.

Stannous Chloride Solution—Dissolve 10 g of $SnCl_2 \cdot 2H_2O$ in 20 mL of warm hydrochloric acid, and add 80 mL of water. Prepare fresh each week.

Standard Mercury Solution—Prepare from *Mercury Stock Solution* as directed under *Method I*. Each mL of the *Standard Mercury Solution* contains the equivalent of 1 μg of mercury.

Test Preparation—Unless otherwise directed in the individual monograph, use the quantity, in g, of the test substance calculated by the formula:

$$2.0/L$$

in which L is the mercury limit, in ppm.

Method IIa

Standard Preparation—Pipet 2.0 mL of *Standard Mercury Solution* into a 100-mL beaker, and add 35 mL of water, 3 mL of sulfuric acid, and 1 mL of potassium permanganate solution. Cover the beaker with a watch glass, boil for a few seconds, and cool.

Test Preparation—Transfer the calculated amount of the test substance to a 100-mL beaker, and add 35 mL of water. Stir, and warm to assist solution, if necessary. Add 2 drops of phenolphthalein TS, and, as necessary, slowly neutralize with constant stirring, using 1 N sodium hydroxide or 1 N sulfuric acid. Add 3 mL of sulfuric acid and 1 mL of *Potassium Permanganate Solution*. Cover the beaker with a watch glass, boil for a few seconds, and cool.

Procedure—Assemble the *Aeration Apparatus* as shown in the accompanying diagram, with the aeration vessel and the trap empty, and the stopcock in the bypass position. Connect the apparatus to the absorption cell, and adjust the air or nitrogen flow rate so that, in the following procedure, maximum absorption and reproducibility are obtained without excessive foaming in the test solution. Obtain a smooth baseline reading at 253.6 nm, following the manufacturer's instructions for operating the instrument.

Treat the *Standard Preparation* and the *Test Preparation* similarly, as follows. Destroy the excess permanganate by adding *Hydroxylamine Hydrochloride Solution*, dropwise, until the solution is colorless. Immediately wash the solution into the aeration vessel with water, and dilute with water to 100 mL. Add 2 mL of *Stannous Chloride Solution*, and immediately reconnect the aeration vessel to the aeration apparatus. Turn the stopcock from the bypass position to the aerating position, and continue the aeration until the absorption peak has been passed and the recorder pen returns to the baseline. Disconnect the aeration vessel from the apparatus, and wash with water after each use. After correcting for any reagent blank, any absorbance produced by the *Test Preparation* does not exceed that produced by the *Standard Preparation*.

Method IIb

Caution—Some substances may react with explosive violence when digested with hydrogen peroxide. Exercise safety precautions at all times.

Standard Preparation—Pipet 2.0 mL of *Standard Mercury Solution* into a 125-mL conical flask, add 3 mL each of nitric acid and sulfuric acid, mix, and add an amount of 30 percent hydrogen peroxide equal to the total amount used in preparing the *Test Preparation*. Attach a suitable water-cooled condenser with a standard-taper joint to fit the flask, and reflux the mixture in a fume hood for 1 hour. Turn off the water circulating through the condenser, and heat until white fumes appear in the flask. Cool, and cautiously add 10 mL of water through the condenser, while swirling the flask. Again heat until white fumes appear,

cool, and add an additional 15 mL of water. Remove the condenser, and rinse the sides of the flask to obtain a volume of 35 mL. Add 1 mL of *Potassium Permanganate Solution*, boil for a few seconds, and cool.

Test Preparation—Transfer the calculated amount of the test substance to a 125-mL conical flask. Add 5 mL each of nitric acid and sulfuric acid and a few glass beads. Attach a suitable water-cooled condenser with a standard-taper joint to fit the flask, and digest in a fume hood, preferably on a hot plate, and at a temperature not exceeding 120°, until charring begins. (If additional sulfuric acid is necessary to wet the specimen completely, add it carefully through the condenser, but do not allow the total volume added to exceed 10 mL.) After the test substance has been decomposed by the acid, cautiously add, dropwise through the condenser, 30 percent hydrogen peroxide, allowing the reaction to subside and again heating between drops (add the first few drops very slowly with sufficient mixing, in order to prevent a rapid reaction; discontinue heating if foaming becomes excessive). When the reaction has abated, heat cautiously, rotating the flask occasionally to prevent the specimen from caking on glass exposed to the heating unit. Maintain oxidizing conditions at all times during the digestion by adding small quantities of the hydrogen peroxide solution whenever the mixture turns brown or darkens. Continue the digestion until the organic matter is destroyed, and then reflux the mixture for 1 hour. Turn off the water circulating through the condenser, and heat until fumes of sulfur trioxide are copiously evolved and the solution becomes colorless or retains only a light straw color. Cool, and cautiously add 10 mL of water through the condenser, while swirling the flask. Again heat until white fumes appear. Cool, and cautiously add 15 mL of water. Remove the condenser, and rinse the sides of the flask with a few mL of water to obtain a volume of 35 mL. Add 1 mL of *Potassium Permanganate Solution*, boil for a few seconds, and cool.

Procedure—Proceed as directed for *Procedure* under *Method IIa*.