

SULFUR DIOXIDE (Monier-Williams)

PRINCIPLE

Sulfur dioxide is released by boiling an acidic sample dispersion, and it is removed by sweeping with a stream of nitrogen. The gas stream is passed through dilute hydrogen peroxide solution where sulfur dioxide is oxidized to sulfuric acid. The acid is titrated with standard alkali. (Note 1)

SCOPE

The method applies to all corn starches, and with modifications, to water-soluble starches and dextrans, corn sugars and corn syrups.

SPECIAL APPARATUS

1. The FDA modified "Monier-Williams" apparatus (Figure 1) is available from Fisher Scientific, 91/92 Cat. No. K513800 (Kontes 513800), Pittsburgh, PA, and affiliates worldwide. It or some of its parts are also available from other laboratory supply houses. (Note 2)
2. Heating mantle, for a 1000 mL boiling flask, controlled by a variable transformer.
3. Flow controlling valve, with flow indicator, capable of controlling nitrogen gas flow to 200 mL/min.
4. Refrigerated circulating bath, capable of maintaining chilled cooling fluid, at 5-10 °C flow through condenser (Note 3)
5. Vortex mixer
6. Buret, class A, 10 mL
7. Pipet bulb

REAGENTS

Analytical Methods of the Member Companies of the
Corn Refiners Association, Inc.

SULFUR DIOXIDE — continued

1. Hydrogen Peroxide Solution, 3%: Dilute 10 mL of C.P. neutral 30% hydrogen peroxide (H_2O_2) with purified water to 100 mL. Prepare daily.
2. Sodium Hydroxide Solution, 0.01 *N*: Dilute 10 mL of 0.100 *N* NaOH solution to 100 mL. Standardize using methyl red indicator with standard potassium hydrogen phthalate.
3. Pyrogallol Solution: Place 4.5 g of analytical reagent grade pyrogallol into a gas washing bottle (H, Figure 1). Place top on bottle and purge with nitrogen for 3-5 minutes. Remove the top and through a long-stem funnel, add a solution of 65 g potassium hydroxide in about 85 mL of purified water. Replace top and resume nitrogen flow. (This is usually done in connection with the set-up of the apparatus.)
4. Hydrochloric Acid, 4 *N*: Mix one volume of 36.5% HCl (sp g 1.19) hydrochloric acid with two volumes of purified water.
5. Methyl Red Indicator
6. Nitrogen Gas, high purity
7. Ethanol, 5%: Dilute 1 part ethanol with 19 parts purified water

PROCEDURE

With the nitrogen source attached to the gas washing bottle, begin flow of nitrogen at 200 mL/min. Prepare pyrogallol solution as indicated in REAGENTS section. Place the boiling flask in the heating mantle and clamp in place. Place 200 mL of purified water into the boiling flask. Grease the bottom joint of the Allihn condenser with silicon grease and place it into a side neck of the boiling flask. Place the dropping funnel, WITHOUT the bottom joint greased, into the other side neck and close the stopcock. Grease the joint of the funnel adaptor and place it on the top of the funnel. Grease the joint of the peroxide trap bubbler and place it on the top of the condenser. Slip the test tube under the tip of the bubbler and clamp it so that the tip of the bubbler is about 2 cm from the bottom of the tube. Add 30 mL of 3% hydrogen peroxide solution to the test tube. Grease the flask glass inlet and insert it into the center neck of the boiling flask. Check that the nitrogen is

SULFUR DIOXIDE — continued

bubbling through the hydrogen peroxide solution in the test tube. Start condenser coolant flow, and let nitrogen bubble through the assembled system for 15 minutes.

Into a clean, tared beaker weigh about 50 g of the sample (Notes 4 and 5); record the weight to the nearest 0.01 g. Add about 200 mL of 5% ethanol for starch samples or 200 mL of purified water for syrup or sugar samples and stir to suspend. With minimum delay (Note 6), remove the dropping funnel and quantitatively transfer the suspension to the boiling flask through the opening (using a funnel), using an additional 100 mL of 5% ethanol for the transfer. Replace the dropping funnel and verify that the nitrogen resumes bubbling through the hydrogen peroxide solution in the test tube. Remove the adaptor from the top of the dropping funnel, add 90 mL of 4 *N* hydrochloric acid to the funnel, and replace the adaptor. Attach a pipet bulb to the adaptor tube, open the stopcock on the adaptor, squeeze the bulb to pressurize the funnel, close the stopcock and remove the bulb (Note 7). Open the stopcock on the funnel, allow to drain until about 5 mL of the acid remains in the funnel and close the stopcock. If necessary, repeat the pressurizing and draining until about 5 mL remains in the funnel. Then, with the funnel stopcock closed, open the adaptor stopcock to relieve pressure. Turn on the power to the heating mantle and adjust so that about 80-90 drops per minute drip from the condenser into the flask. Allow to reflux for 105 minutes.

After the heating time, with the nitrogen still bubbling, remove the test tube from the bubbler tube. Add 5 drops of methyl red indicator and mix the contents of the test tube using a vortex mixer, so that the solution washes the sides of the tube to within 3 cm of the top. As quickly as possible, using a 10 mL buret, titrate the distillate with 0.01 *N* NaOH to an absence-of-pink end point. Turn off the nitrogen, disassemble and clean the apparatus.

Determine a blank on reagents.

SULFUR DIOXIDE — continued**CALCULATION (Note 8)**

$$\text{Sulfur Dioxide, ppm (as is)} = \frac{(0.01 \text{ N NaOH} - \text{Blank}) \times 32 \times .01 \times 100}{\text{Sample Wt. (g)}}$$

NOTES AND PRECAUTIONS

1. Reference: Monier-Williams Procedure (with Modifications) for Sulfites in Food, Center for Food Safety and Applied Nutrition, FDA, November, 1985. *51 Fed. Reg.* 25012, July 9, 1986.
2. Most components are available from lab supply houses, except for the bubbler tube, which is available from O'Brien's Scientific Glassblowing, P.O. Box 495, Monticello, IL 61856.
3. The cooling fluid must be maintained at 5-10 °C. At this temperature, most volatile organic acids that could interfere with the determination will condense and will not carry over into the peroxide trap.
4. The sample size is chosen to allow verification that the equivalent SO₂ content is <10 ppm.
5. For cold-water soluble or swellable starches, the procedure is modified to the following:

With the gas-delivery head removed from the center neck of the boiling flask, and a powder funnel inserted, add about 50 g of the sample to the flask, weighing by difference to the nearest 0.01 g. Wash the residue through the funnel with 300 mL of 5% ethanol. Replace the gas delivery head, and check for gas bubbles in the hydrogen peroxide solution in the test tube. Then continue with the addition of acid to the dropping funnel.
6. Minimum exposure of the sample solution to air is necessary to prevent the premature oxidation of any sulfur dioxide present to sulfate, preventing distillation into the peroxide trap.
7. The pressure must be enough to discharge the acid against the pressure of the nitrogen. However, it must not be high enough to force all the acid out,

SULFUR DIOXIDE — continued

as this would allow some of the nitrogen stream, including possibly sulfur dioxide, to back up into the funnel.

8. If there are known interferences from volatile acidic components, it may be necessary to do an alternate determination of the sulfate.

METHOD HISTORY

Combined the Sulfur Dioxide methods for Corn Starch (Unmodified) (B-58), Corn Syrup (E-66) and Corn Sugar (F-54) on 4-15-2010.

Corn Starch (Unmodified), Sulfur Dioxide (B-58), Date of Acceptance 5-07-1956, Revised 4-09-1991.

Corn Syrup, Sulfur Dioxide (E-66), Date of Acceptance 8-25-1952, Revised 4-09-1991.

Corn Sugar, Sulfur Dioxide (F-54), Date of Acceptance 11-13-1961, Revised 4-09-1991.

SULFUR DIOXIDE — continued

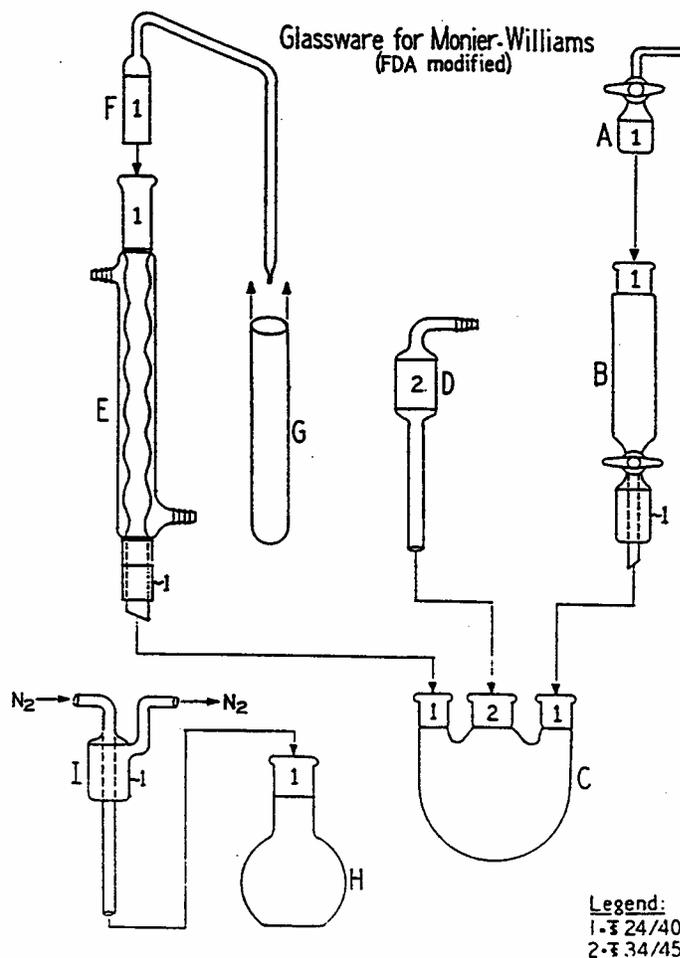


Figure 1 - Apparatus

Description

- A. Adaptor: 24/40 male joint, 2 mm Teflon stopcock, medium hose connection
- B. Dropping funnel: 24/40 female joint on top, 41 mm O. D. tubing, 4 mm Teflon stopcock, 24/40 male joint with inner seal
- C. Boiling flask: 1000 mL, 3 neck, with 34/45 center and 24/40 side necks
- D. Flask gas inlet: 34/40 male joint with extension to bottom of flask, medium hose connector at top
- E. Allihn condenser: six bulb type, 300 mm jacket, 24/40 joints
- F. Peroxide trap bubbler: As specified in FDA modification, with 24/40 joint
- G. Test Tube, 25 mm diameter, 150 mm long
- H. Glass washing bottle: 250 mL round flask with flat bottom, 24/40 joint
- I. Gas washing bottle top: 24/40 male joint, with inner seal and two side arms