

SULFATE IN ALUMINA OR SILICA-ALUMINA BASE CATALYSTS — TURBIDIMETRIC METHOD

UOP Method 320-86

SCOPE

This method is for determining sulfate in alumina or silica-alumina base catalysts in the range of 0.01 to 0.1 mass-percent. Catalysts containing higher amounts of sulfate can be analyzed by UOP Method 742.

OUTLINE OF METHOD

An exact amount of sample is dissolved in a controlled amount of hydrochloric acid. Barium chloride is added in a regulated manner in the presence of a colloid stabilizer. The resulting turbidity of the solution is measured spectrophotometrically, and the amount of sulfate present is read from a previously prepared calibration curve.

APPARATUS

Balance, readability 0.1-mg

Balance, top-loading, readability 0.01-g

Beakers, cup type, polypropylene, Sargent-Welch Scientific, Cat. No. S-4694-91, or equivalent

Beakers, electrolytic, extra high form, 250-mL capacity, Sargent-Welch Scientific, Cat. No. S-4715-B, or equivalent. Modify with nitrogen inlet tube as shown in Fig. 1

Beakers, Griffin, low form, 100-mL capacity, Sargent-Welch Scientific, Cat. No. S-4675-H, or equivalent

Cells, spectrophotometric, 50-mm path length, Beckman Instruments, Inc., Cat. No. 886510, or equivalent

Clamp, extension, round jaw, Sargent-Welch Scientific, Cat. No. S-19225, or equivalent

Clamp holder, fixed, iron, Sargent-Welch Scientific, Cat. No. S-19320, or equivalent

Condenser, acorn-type to fit electrolytic beaker, see Fig. 1, UOP Inc., or equivalent

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
--

Flask, Erlenmeyer, 125-mL, Sargent-Welch Scientific, Cat. No. S-34125D, or equivalent

Flasks, volumetric, 100- and 200-mL, Sargent-Welch Scientific, Cat. Nos. S-34855-20G and S-34855-20H, or equivalent

Funnels, analytical, 60°, Sargent-Welch Scientific, Cat. No. S-635345-E, or equivalent

Hot plate

Manifold, gas, glass, Fig. 2, Ace Glass (special order), Cat. No. 7416-10, or equivalent. The manifold allows the processing of up to 6 samples simultaneously.

Mortar, heavy porcelain, Coors, 275-mL capacity, Sargent-Welch Scientific, Cat. No. S-62250-50E, or equivalent

Pencil, tungsten carbide, glass-marking, Sargent-Welch Scientific, Cat. No. S-65755, or equivalent

Pestle, for heavy mortars, porcelain, Coors, Sargent-Welch Scientific, Cat. No. S-62251-E, or equivalent

Pipets, 1-, 3-, 5-, 7-, 10-, 20-, 25-, 40- and 50-mL, Fisher Scientific, Cat. Nos. 13-650 B, D, F, H, L, N, P, R, and S, or equivalent

Pipet, Mohr, 5-mL, Fisher Scientific, Cat. No. 13-665K, or equivalent

Policeman, rubber, diagonal, with glass rod, Sargent-Welch Scientific, Cat. No. S-73215-B, or equivalent

Regulator, nitrogen, two-stage, Matheson, Cat. No. 3104-580, or equivalent

Relief valve, back pressure regulator type, Matheson, Cat. No. 6341, or equivalent

Rubber expander, tubing and bulb, Sargent-Welch Scientific, Cat. No. S-73756, or equivalent

Spectrophotometer, minimum of $\pm 0.5\%$ photometric accuracy, double-beam, Perkin-Elmer, Cat. No. C688-0003, or equivalent

Stirring apparatus, magnetic, variable speed, Sargent-Welch Scientific, Cat. No. S-76506-90, or equivalent

Stirring bar, magnetic, octagonal, Teflon-coated, 22.2-mm long, 7.9-mm diameter, Sargent-Welch Scientific, Cat. No. S-76507-40D, or equivalent

Stopwatch/Timer, digital, Sargent-Welch Scientific, Cat. No. S-77510-50, or equivalent

Support, rectangular base, steel rod, 45-cm height, Sargent-Welch Scientific, Cat. No. S-78306-A, or equivalent

Tubing, Tygon, 7.9-mm ID, Sargent-Welch Scientific, Cat. No. S-73650-KE, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water.

Alcohol, Formula 30. Mix together 1000 mL of ethyl alcohol and 100 mL of methanol.

Alcohol-glycerol solution. Mix 2 parts of the Formula 30 alcohol and 1 part of glycerol.

Alumina stock solution. Weigh $4.00 \text{ g} \pm 2 \text{ mg}$ of ground alumina catalyst base into a 250-mL electrolytic beaker. Add by pipet 40 mL of concentrated hydrochloric acid, several boiling chips and 40 mL of water. Dissolve the catalyst base under reflux using the apparatus shown in Fig. 2. Allow to cool and then transfer to a 200-mL volumetric flask with water. Dilute to volume.

Alumina-silica stock solution. Weigh $4.0 \text{ g} \pm 2 \text{ mg}$ of ground silica-alumina catalyst base into a 250-mL electrolytic beaker. Add by pipet 40 mL of concentrated hydrochloric acid, several boiling chips and 40 mL of water. Reflux the catalyst base for 4 hours using the apparatus shown in Fig. 2. Allow to cool and then transfer to a 200-mL volumetric flask through Whatman No. 42 filter paper, rinsing the filter thoroughly with water. Dilute to volume.

Barium chloride, granular, Sargent-Welch Scientific, Cat. No. SC10925, or equivalent

Boiling chips, carborundum, Thomas Scientific, Cat. No. 1509-D30, or equivalent

Catalyst base, alumina and silica-alumina

Ethyl alcohol, 95%, denatured, Sargent-Welch Scientific, Cat. No. SC-12096, or equivalent

Filter paper, Whatman No. 42, Sargent-Welch Scientific, Cat. No. S-33175-F, or equivalent

Glycerol, reagent, Sargent-Welch Scientific, Cat. No. SC12377, or equivalent

Hydrochloric acid, concentrated

Methanol, absolute, reagent, Sargent-Welch Scientific, Cat. No. SC-13510, or equivalent

Methyl purple, indicator solution, Sargent-Welch Scientific, Cat. No. SC13597, or equivalent

Nitrogen, oxygen free

Sulfuric acid solution, 0.05-M, Sargent-Welch Scientific, Cat. No. SC15131, or equivalent. Standardize against tris(hydroxymethyl)aminomethane (THAM[®]). Weigh 0.30-g THAM to the nearest 0.1 mg, place in a 125-mL Erlenmeyer flask and add about 50 mL of water. Add 5 drops of methyl purple and titrate with the 0.05-M sulfuric acid to a violet color.

Sulfur standard. Pipet 61.9 mL of standardized 0.05-M sulfuric acid into a 100-mL volumetric flask and dilute to volume with water to prepare a working standard containing 0.1 mg sulfur/mL.

Tris(hydroxymethyl)aminomethane (THAM), Certified, Fisher Scientific, Cat. No. T395-100, or equivalent

PROCEDURE

Calibration of Beakers

Into 12 separate 100-mL beakers pipet 60 mL of water. Mark each of the beakers with the tungsten carbide pencil at the 60-mL level. These beakers should be reserved for the sulfate determination only.

Preparation of Standard Calibration Curve

Pipet 1, 3, 5, 7 and 10 mL of the sulfur standard solution into 5 separate calibrated beakers. Reserve a sixth beaker for a reagent blank. Pipet into each of the 6 beakers 25 mL of the alumina or silica-alumina stock solution, depending on the sample to be analyzed, and 10 mL of the alcohol-glycerine solution. Dilute with water to the 60-mL mark.

Weigh 0.29 ± 0.01 g of barium chloride crystals into one of the polypropylene beakers. The following sequence should be followed for one sample, standard or blank at a time. Quantitatively transfer the barium chloride to one of the 100-mL beakers. Add a stirring bar and stir for three minutes $\pm$ 5 seconds on a stirring apparatus. Allow four minutes for the turbidity to develop, and immediately read the absorbance of each standard and the blank in a 50-mm cell against water as a reference, at a wavelength of 420 nm. Plot a graph of the net absorbance versus sulfur concentration in milligrams for use in the calculations.

Sample Analysis

Weigh $2.00 \text{ g} \pm 2 \text{ mg}$ of ground sample to the nearest 0.1 mg into a 250-mL electrolytic beaker. Add a few boiling chips and 20 mL of water. Pipet 20 mL of concentrated hydrochloric acid into the beaker. Place the beaker on the hot plate, place an acorn reflux condenser in the top of the beaker and turn on the water. Connect the nitrogen line (see Figs. 1 and 2), and set the nitrogen pressure to 14-28 kPa (2-4 psig) to produce a bubble rate of approximately one bubble/second. Reflux the contents while maintaining the nitrogen flow for 4 hours.

After 4 hours, allow the solution to cool. Disconnect the nitrogen line and rinse the acorn condenser with water, collecting the washings in the beaker. Filter the contents of the beaker into a 100-mL volumetric flask using Whatman 42 filter paper. Wash the filter paper thoroughly with water. Dilute the solution to volume and shake to mix.

Pipet 10 to 50 mL of the above solution, depending on the sulfate content, into a clean, dry 100-mL beaker. Prepare a reagent blank with each set of samples. Pipet 10 mL of the alcohol-glycerol solution into each of the beakers and dilute to the 60-mL mark with water. Develop turbidity and read absorbance by the procedure described under *Preparation of Standard Calibration Curve* beginning with, "Weigh 0.29 g of barium chloride ... wavelength of 420 nm," except that the samples are read instead of the standards.

Also, transfer a portion of the original sample from the volumetric flask directly to a 50-mm cell. Read the absorbance against the water reference as described previously and record this value. This is a correction for the color of the original solution.

CALCULATIONS

Standards

Determine the net absorbance of the standards as follows:

$$\text{Net absorbance} = X - Y$$

where:

X = absorbance of standard, with developed turbidity

Y = absorbance of reagent blank, with developed turbidity

Samples

Determine the net absorbance of the samples as follows:

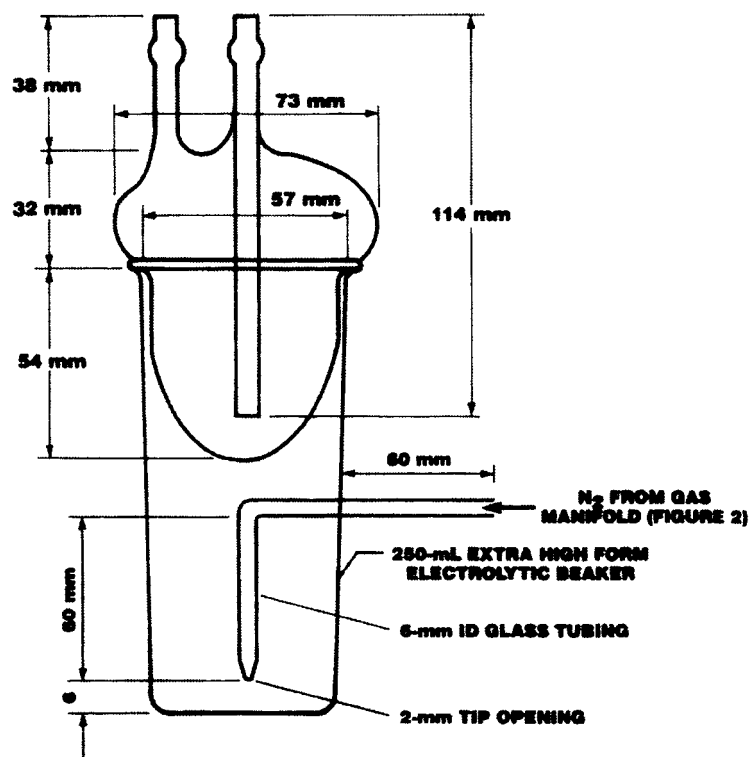


Figure 1

Reflux Vessel

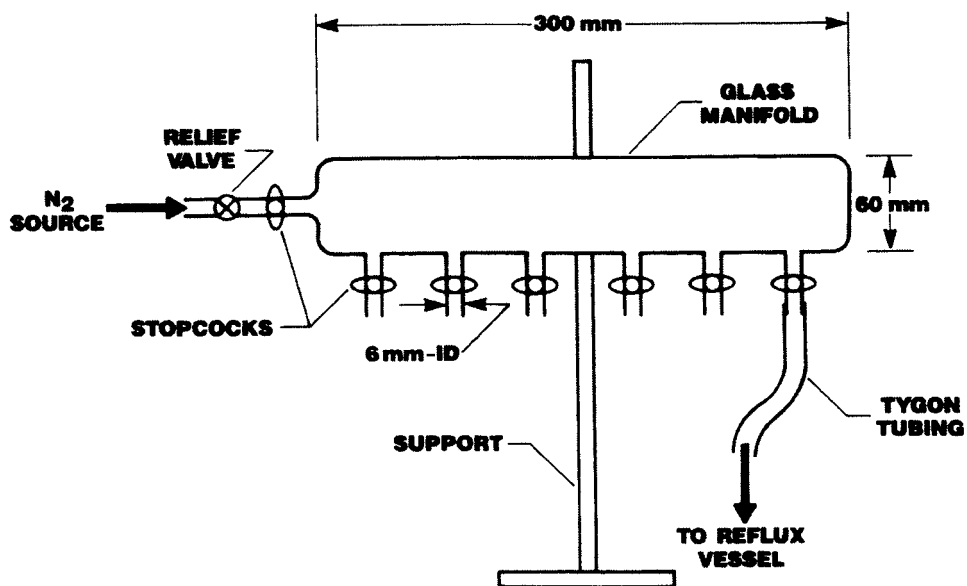


Figure 2

Gas Manifold System

$$\text{Net absorbance} = A - B - \frac{HC}{60}$$

where:

- A** = absorbance of the aliquoted sample, with developed turbidity
- B** = absorbance of the reagent blank, with developed turbidity
- C** = absorbance of the original sample solution in the volumetric flask
- H** = volume of sample pipeted for analysis, mL
- 60** = final solution volume, mL

Calculate the mass-% sulfate as follows:

$$\text{Sulfate, mass-\%} = \frac{(2.996)(100)KF}{1000GV}$$

where:

- F** = final volume to which sample solution was diluted, mL
- G** = mass of sample, g
- K** = milligrams of sulfur obtained from the graph using the calculated net absorbance
- V** = volume of sample pipeted for analysis, mL
- 2.996** = conversion factor from sulfur to sulfate
- 100** = conversion factor to calculate mass-%
- 1000** = conversion factor from milligrams to grams

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) for sulfate at the 0.03 mass-% level was calculated to be 0.0009%. Duplicate results by the same operator should not differ by more than 0.0033 mass-% (95% probability) at the stated level.

TIME FOR ANALYSIS

The labor requirement is 0.75 hour for a single determination. The elapsed time is 7 hours.

REFERENCE

UOP Method 742

SUGGESTED SUPPLIERS

Ace Glass Inc., P.O. Box 688, Vineland, NJ 08360
 Beckman Instruments, Inc., Scientific Instruments Division, 2500 Harbor Blvd., Fullerton, CA 92634
 Fisher Scientific, 1600 W. Glenlake Avenue, Itasca, IL 60143
 Matheson, P.O. Box 96, Joliet, IL 60434
 Perkin-Elmer Corp., Main Ave., (MS-12) Norwalk, CT 06856
 Sargent-Welch Scientific Co., 7300 N. Linder, Skokie, IL 60077
 Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0090
 UOP Inc., Box 5017, Des Plaines, IL 60017-5017