

SILICA IN CATALYSTS BY GRAVIMETRIC PROCEDURE

UOP Method 436-87

SCOPE

This method is for determining silica over the full range of levels typically encountered in the formulation of silica-alumina catalysts and catalysts bases. The lower limit of detection is approximately 0.5 mass-%.

OUTLINE OF METHOD

A weighed sample is dehydrated by treatment with concentrated sulfuric acid, and then further treated with concentrated hydrochloric and nitric acids to dissolve any remaining metals. The residue, consisting of silica and impurities, is filtered, washed, ignited and weighed. The impure silica is treated with hydrofluoric and sulfuric acids to volatilize the silica and thereby allow the gravimetric determination of the silica content by difference.

APPARATUS

Balance, readability 0.1-mg

Beaker, Griffin, low form, 400-mL, Sargent-Welch Scientific, Cat. No. S-4675-L, or equivalent

Bottle, washing, polyethylene, 500-mL, Sargent-Welch Scientific, Cat. No. S-9487-C, or equivalent

Crucible, high form, platinum, 30-mL, Engelhard Industries, Figure 202, or equivalent

Crucible cover, Coors, Sargent-Welch Scientific, Cat. No. S-23720-G, or equivalent

Cylinder, graduated, polypropylene, 25-mL, Sargent-Welch Scientific, Cat. No. S-24640-C, or equivalent

Cylinders, graduated, glass, 10- and 250-mL

Desiccator, bowl form, large, with external sleeve type stopcock, Sargent-Welch Scientific, Cat. No. S-25125-E, or equivalent

Disk, ceramic, 10-cm (4-inch) diameter, 4.76-mm (3/16-inch) thick, McDaniel Refractory Co., Cat. No. AAC13862, or equivalent

Furnace, box with controller, electric, capable of maintaining 1500 ± 10 C, Sargent-Welch Scientific, Cat. Nos. S-37005-BZ and S-37105, respectively, 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).

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Funnel, analytical, 60°, fluted, long stem, Sargent-Welch Scientific, Cat. No. S-3545-E, or equivalent

Hot plate, Lindberg, Sargent-Welch Scientific, Cat. No. S-41220-C, or equivalent

Mortar and pestle, heavy, porcelain, 50-mL, Sargent-Welch Scientific, Cat. Nos. S-62250-50B and S-62251-B, respectively, or equivalent

Pipet, 0.5-mL, volumetric transfer, Class A, Sargent-Welch Scientific, Cat. No. S-69514-AA, or equivalent

Rubber policeman, diagonal, without rods, Sargent-Welch Scientific, Cat. No. S-73225, or equivalent

Stirring rod, glass, 200-mm length, Sargent-Welch Scientific, Cat. No. S-40097-C, or equivalent

Support, rectangular base, steel rod, 51-cm height, Sargent-Welch Scientific, Cat. No. S-78306-B, or equivalent

Support, funnel, wood, 4 place, with clamp, Sargent-Welch Scientific, Cat. No. S-78815, or equivalent

Tongs, crucible, stainless steel, lock joint, platinum shoes, Sargent-Welch Scientific, Cat. No. S-82246, or equivalent

Watch glass, 90-mm OD, Sargent-Welch Scientific, Cat. No. S-83605-F, 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, except where noted.

Bromine water, Sargent-Welch Scientific, Cat. No. SC-11136, or equivalent

Calcium sulfate, anhydrous, indicating, Drierite, 8-mesh, Sargent-Welch Scientific, Cat. No. SC-11989, or equivalent

Filter paper, Whatman No. 42, 12.5-cm diameter, Sargent-Welch Scientific, Cat. No. S-33175-F, or equivalent

Gloves, disposable, polyethylene

Hydrochloric acid, concentrated, 37-38%

Hydrofluoric acid, concentrated, 48%

Nitric acid, concentrated, 70-71%

Sulfuric acid, concentrated, 95-96%

PROCEDURE

Grind a representative portion of the sample with a mortar to a fine powder. Weigh approximately 0.5 g of the ground sample, to the nearest 0.1 mg, into an unetched 400-mL beaker. With a graduated cylinder, slowly add 15 mL of water down the side of the beaker. Then cautiously add 7 mL of concentrated sulfuric acid, also down the side of beaker to prevent spattering, and swirl the beaker to mix the contents.

Cover the beaker with a watch glass and place it on a hot plate covered with a ceramic disk to allow slow heating. Allow the beaker to heat until copious white sulfuric fumes evolve and fill the void of the beaker. Remove the beaker from the hot plate and allow it to cool. Rinse the watch-glass with a minimal amount of water, collecting the washings in the beaker. Then wash down the sides of the beaker, again using a minimum amount of water.

With a graduated cylinder add 10 mL of concentrated hydrochloric acid and 2 mL of concentrated nitric acid to the beaker. Using a glass rod, stir the contents. Place the beaker on the hot plate covered with the ceramic disk, leaving the glass rod in the beaker. Heat the beaker until copious white sulfuric fumes evolve, then remove the beaker and allow it to cool. Repeat the addition of concentrated hydrochloric and nitric acids several times, as necessary, until the remaining residue in the beaker after cooling is a white-opaque color.

To the cool beaker, add 200 mL of water and 5 mL of bromine water with a graduated cylinder. Place the beaker on the ceramic disk covered hot plate. Stir the contents with the glass rod until the solution comes to a slow boil. (*CAUTION:* Failure to constantly stir until boiling begins can result in a violent reaction with sample losses.) Leave the stirring rod in the uncovered beaker and boil the contents slowly until the volume has been reduced to approximately 125 mL. Remove the beaker from the hot plate and allow it to cool.

When the beaker is warm to the touch, filter the contents through a Whatman No. 42 filter paper. Quantitatively transfer the beaker contents, liquid and solids, with the aid of a rubber policeman and water from a wash bottle onto the filter paper. Wash the filter paper and contents with successive aliquots of hot water using a total volume of approximately 200 mL.

Place the filter paper containing the impure silica in the crucible. Transfer the crucible to the hot plate and dry and char the paper containing the residue. Place the crucible in the furnace maintained at 1000 C and ignite for one hour.

After ignition is complete, remove the crucible, cover it with a crucible cover and place it in a desiccator. Allow it to cool and then weigh the uncovered crucible and residue to the nearest 0.1 mg. With a graduated cylinder add 2 mL of water, 0.5 mL of concentrated sulfuric acid by pipet, and 15 mL of hydrofluoric acid with a polypropylene graduated cylinder. Place the crucible on the hot plate covered with the ceramic disk and evaporate the crucible contents until dense white fumes no longer evolve. Remove the crucible from the hot plate and allow it to cool, then add an additional 15 mL of a hydrofluoric acid. Evaporate the contents on the ceramic disk covered hot plate until dense white fumes no longer evolve. Remove the ceramic disk and place the crucible directly on the hot plate. Heat the crucible until the contents appear dry.

Place the crucible in the furnace at 1000 C for one hour. Remove the crucible from the furnace, cover and place it in a desiccator to cool. When cool to the touch, obtain the mass of the uncovered crucible. The observed weight loss represents the silica content of the sample.

CALCULATIONS

Calculate the mass-% silica as follows:

$$\text{SiO}_2 \text{ mass - \%} = \frac{100 (A - B)}{C}$$

where:

A = mass of crucible and contents before treatment with hydrofluoric acid, g

B = mass of crucible and contents after treatment with hydrofluoric acid, g

C = mass of sample, g

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) was calculated for silica at the concentrations listed in the table below. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Sample Type	Level, mass-%	esd, mass-%	Allowable Difference, mass-%
Equilibrium FCC Catalyst	56	0.19	0.67
Fresh FCC Catalyst	57	0.06	0.24

TIME FOR ANALYSIS

The elapsed time for one analysis is 12 hours. The labor requirement is 1.5 hours.

SUGGESTED SUPPLIERS

Engelhard Industries, 700 Blair Rd., Carteret, NJ 07008
 McDaniel Refractory Co., P.O. Box 560, Beaver Falls, PA 15010
 Sargent-Welch Scientific, 7300 N. Linder Ave., Skokie, IL 60077