

SILICONES IN PETROLEUM DISTILLATES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

UOP Method 787-78

SCOPE

This method is applicable to the determination of silicones as hydrocarbon soluble silicon in light petroleum distillates. It is primarily intended to be used to analyze Platforming® charge stocks for silicones. The lower limit of detection is approximately 0.1 wt-ppm silicon.

OUTLINE OF METHOD

The sample is evaporated to effect a ten-fold concentration step. The residue is solubilized with xylene and brought to a specific volume. Evaporation can be effected by using an ordinary steam bath, but the more rapid and preferred technique is jet evaporation using nitrogen gas instead of air as described in ASTM Method D 381. The xylene diluted concentrate is aspirated into the nitrous oxide/acetylene flame of an atomic absorption spectrophotometer (AAS) and compared to a similarly aspirated organic silicon standard. Silicone then can be derived from the appropriate calculation, which is dependent upon the percent of silicon in the silicone standard used. This method is based upon an antifoam agent containing 39 wt-% of silicon. Also an alternative procedure for silicone determination by AAS is included for “cracked” naphtha samples which create insoluble gum-like residue after evaporation.

APPARATUS

Balance, capable of weighing to nearest 0.1 g

Balance, analytical, capable of weighing to nearest 0.1 mg

Beakers, 400- and 100-ml, electrolytic, lipless

Cooling vessel, desiccator or equivalent type, necessary if jet evaporation technique is used.

Flasks, volumetric, 10- and 100-ml

Hot plate, any laboratory type is suitable

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Jet evaporation bath, either solid metal block bath or liquid bath, electrically heated

Lamp, silicon, hollow cathode, high spectral output, Westinghouse, available from Perkin-Elmer, Cat. No. 303-6063, or equivalent

Pipets, 5- and 10-ml

Spectrophotometer, atomic absorption, commercial type equipped with a 5 cm single slot, nitrous oxide burner head, auxiliary oxidant supply and a readout device or recorder capable of 5x signal expansion

Steam bath, any commercial laboratory type is suitable; not necessary if jet evaporation bath is used

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 exist, unless otherwise specified. References to water mean distilled or deionized water. All references to ppm mean micrograms per milliliter.

Acetylene, compressed, cylinder commercial welding type

Nitrous oxide, compressed, cylinder technical grade

Silicon standard, 10,000-ppm ($\mu\text{g/ml}$), weigh 2.564 of GE No. 7 antifoam and silicone into a clean 100-ml flask and dilute to volume with xylene; mix and label as *Stock Silicon Standard at 10,000 $\mu\text{g/ml}$* .

Silicon standard, 1,000-ppm, pipet 10 ml of 10,000-ppm silicon standard into a 100-ml volumetric flask and dilute to mark with xylene. Mix and label.

Silicon standard 100-ppm, pipet 10 ml of 1,000-ppm silicon standard into a 100-ml volumetric flask and dilute to mark with xylene. Mix and label.

Silicon standard, "regular", 10-ppm, pipet 10 ml of 100-ppm standard into a 100-ml volumetric flask. Dilute to mark with xylene. Mix and label.

Silicone, GE antifoam No. 7 (ca. 39.0% Si), or equivalent

Xylene, reagent grade, available from J. T. Baker Chemical Company, or equivalent

PROCEDURE

Sample Concentration by Evaporation

Weigh 100 to 200 g of sample into a tared 400-ml beaker. Then, in a tared 100-ml beaker, evaporate 25-50 g increments of sample from the larger beaker. Continue the evaporation until the total sample has been added. Record the weight of the sample to the nearest 0.1 g. (See *Standard Addition Technique*.)

A steam bath may be used, but the more rapid procedure, ASTM D 381 modified to use nitrogen, is preferred.

Straight run naphthas and Platformer charge stocks should be evaporated to approximately 1 ml. Cracked naphthas which form gum-like residues should be concentrated only to 3.0 ± 0.5 g to allow complete solution of the sample.

Standard Addition Technique

When analyzing naphthas, which form gum-like residues, two equal but separate 100-200 g portions are taken and treated as described in *Sample Concentration by Evaporation* section. To one, immediately before the last incremental addition of sample, pipet 10 ml of 10 $\mu\text{g/ml}$ xylene silicon standard into the beaker. Thus, there will be two sample portions of equal weight evaporated for each sample; one will be the sample as received, the second, the sample plus an addition of 100 μg of silicon. Proceed as for Platformer charge stocks.

Instrument Calibration and Alignment

Silicon is determined using a fuel-rich nitrous oxide-acetylene flame. Periodic removal of carbon from the burner will be required using this flame. Set the wavelength to 251.61nm.

Alignment of the lamp and burner and adjustment of the fuel will be required to obtain maximum absorbance. Make these changes while aspirating the 100 $\mu\text{g/ml}$ silicon standard. Aspiration of the 10 $\mu\text{g/ml}$ silicon standard yields 53-55 chart units on a 100 unit full scale chart paper, or a 13 cm peak. This response is attained at 5x expansion.

ANALYSIS OF SAMPLE

Dilute the prepared concentrates in the evaporation beaker with 5 ml of xylene. Rinse down the sides of the beaker during the addition of xylene. Warm on a steam bath several minutes and quantitatively transfer to a 10-ml volumetric flask. Rinse the beaker several times with 1-2 ml increments of xylene. Transfer each washing to the 10-ml volumetric flask. Finally, dilute to volume with xylene.

Aspirate naphthas that form no gum-like resins using the 10 $\mu\text{g/ml}$ standard as a reference. Record chart units or peak height in centimeters for sample and standard.

For cracked naphthas or naphthas that form gum-like residues under the conditions of the evaporation, compare the sample against a second portion of equal weight, evaporated under the same conditions, but containing 10 $\mu\text{g/ml}$ of added silicon. Record peak height in chart units or centimeters.

CALCULATIONS

$$\text{Silicon, wt-ppm} = \frac{100A}{B-W}$$

where:

A = peak height of sample in chart units or centimeters

B = peak height in chart units or centimeters of standard 10 μg silicon/ml in xylene; or in the case of cracked naphthas, the response resulting from the added 10 $\mu\text{g/ml}$ (total peak height of sample + standard) minus (sample peak height)

W = weight of sample, g

NOTES

1. The calculation assumes a final volume of 10 ml and the reference standards to be 10 $\mu\text{g/ml}$, in the xylene or added to a separate portion of the sample.

2. In most cases, the conversion to silicone from silicon is:

$$\text{Silicone, wt-ppm} = \frac{\text{Silicon, wt-ppm}}{0.39}$$

PRECISION

Insufficient data are available to calculate an estimated standard deviation with at least 3.7 degrees of freedom. Based on limited experience, duplicates should agree within 0.1 wt-ppm.

TIME FOR ANALYSIS

The labor requirement for a single sample is 3 man-hours. In a group of three samples, 1-1/2 man-hours is required per sample.

SUGGESTED SUPPLIERS

J. T. Baker Chemical Company, 799 Roosevelt Road, Glen Ellyn, IL 60137

General Electric, 840 S. Canal Street, Chicago, IL 60607

Perkin-Elmer Corp., 328 Eisenhower Lane, Lombard, IL 60148