



Standard Test Method for Silicon Content of Silicone Polymers and Silicone-Modified Alkyds by Atomic Absorption¹

This standard is issued under the fixed designation D 3733; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the silicon content of silicone polymers and silicone modified alkyds when present in the nonvolatile portion of polymers, resins, or liquid coatings to the extent of 1 % or more.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- D 1153 Specification for Methyl Isobutyl Ketone²
- D 1193 Specification for Reagent Water³
- D 2372 Practice for Separation of Vehicle from Solvent-Reducible Paints⁴
- D 2698 Test Method for Determination of the Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging⁴
- D 2832 Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings⁴

3. Significance and Use

3.1 The silicon content of silicone modified alkyds has a direct relationship to the cost and performance characteristics, especially heat resistance of coatings prepared from them.

4. Summary of Test Method

4.1 The polymer solution or separated coating vehicle is diluted with methyl isobutyl ketone, and the silicon content is determined by atomic absorption spectroscopy.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, consisting of an atomizer and a single-slot burner; gas pressure-regulating and

-metering devices for nitrous oxide (N_2O) and acetylene; a silicon hollow-cathode lamp with a regulated constant current supply; a monochromator and associated optics; a photosensitive detector connected to an electronic amplifier; and a read-out device.

5.2 *Centrifuge*.

5.3 *Pipets*, 5, 10, 15, and 20-mL capacity.

5.4 *Volumetric Flasks*, 25, 50, 100, and 1000-mL.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

6.3 *Octaphenylcyclotetrasiloxane*.⁶

6.4 *Methyl Isobutyl Ketone* (MIBK), complying with Specification D 1153.

6.5 *Silicon, Standard Stock Solution* (100 μ g/mL)—Weigh exactly 0.709 g of octaphenylcyclotetrasiloxane and quantitatively transfer to a 1-L flask. Dilute to volume with MIBK.

7. Calibration and Standardization

7.1 Prepare the following standard solutions from the 100 μ g/mL silicon standard stock solution, diluting to the indicated volumes with MIBK:

| Stock Solution, mL | Dilute to, mL | Concentration, μ g/mL |
|--------------------|---------------|---------------------------|
| 20 | 25 | 80 |

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² *Annual Book of ASTM Standards*, Vol 06.04.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 06.01.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁶ Available as Standard Reference Material No. 1066a from Office of Standard Reference Materials, Room B-314, Chemistry Building, National Institute of Standards and Technology, Washington, DC 20234.

| | | |
|----|-----|----|
| 15 | 25 | 60 |
| 10 | 25 | 40 |
| 5 | 25 | 20 |
| 5 | 50 | 10 |
| 5 | 100 | 5 |

7.2 Operational instructions for atomic absorption spectrophotometers vary with different models. Consult the manufacturer's literature for establishing optimum conditions for the specific instrument used.

7.3 Turn the instrument on and set the wavelength to the 251.6-nm silicon line. Apply the recommended current to the silicon hollow-cathode lamp. Allow the instrument to warm up for about 15 min and set the slit width. Adjust the nitrous oxide and acetylene pressures and ignite the burner in accordance with instructions.

NOTE 1—An acetylene pressure of 7 psi (48 kPa) and a nitrous oxide pressure of 30 psi (207 kPa) have been found to be satisfactory for most instruments.

7.4 While aspirating MIBK, carefully adjust fuel and oxidant flow rates as well as aspiration rate, until a clean, steady flame is obtained and *no* detectable carbonization occurs on the burner head. Aspirate the 5 µg/mL standard solution and make any necessary readjustments in instrument parameters to obtain maximum absorption. Record optimized fuel and oxidant flow rates for future reference and use for calibration and sample analyses.

7.5 Aspirate MIBK. When the recorder, meter, or other read-out device reaches a constant value, adjust it to zero immediately.

7.6 Aspirate each of the appropriate standard solutions in ascending silicon concentrations, ending with the 100 µg/mL standard. Record the corresponding instrument readings. Aspirate MIBK between each standard, and after the last standard.

7.7 Construct a calibration curve on linear graph paper by plotting the absorbance versus concentration (micrograms per millilitre) for each standard solution.

NOTE 2—Complete calibration and standardization (7.3-7.7) immediately prior to sample analysis.

8. Procedure

8.1 If the sample is a pigmented coating, remove all traces of pigment by centrifuging in accordance with Practice D 2372 or Test Method D 2698. Determine the nonvolatile content of the vehicle or polymer solution in accordance with Guide D 2832.

8.2 Prepare at least two replicate specimens by weighing by difference from a dropping bottle or syringe, a quantity of the vehicle or polymer solution equivalent to 60 to 240 mg (see Note 3) of solids directly into 100-mL volumetric flasks. Dilute to volume with MIBK and mix thoroughly.

NOTE 3—If the approximate silicon content is known, use the following specimen weights to optimize analytical results:

| Expected Silicon Content, % | Optimum Weight of Solids, mg |
|-----------------------------|------------------------------|
| 8 | 70 |
| 4 | 150 |
| 2 | 300 |
| 1 | 600 |

8.3 Aspirate each specimen solution and determine the

absorbance in the same manner in which the instrument was calibrated. Determine the concentration of silicon in micrograms per millilitre from the calibration curve. If the absorbance is above the range covered by the calibration curve, dilute an aliquot of the sample solution to a suitable volume with MIBK. If the absorbance is below the range covered by the calibration curve, repeat the analysis using a larger specimen size.

NOTE 4—The method of standard additions may be used to improve the accuracy of the analysis. This method is particularly recommended for use with unknown samples where matrix effects may be potentially significant. For a detailed description of the procedure and calculations used in the method of standard additions, consult a standard text on atomic absorption spectroscopy or the instruction manual provided by the instrument manufacturer.

9. Calculation

9.1 Calculate the mean concentration of silicon in the nonvolatile portion of the material under test as follows:

$$\text{Silicon, \% in nonvolatile} = \frac{C \times F}{NV \times S} \quad (1)$$

where:

- C* = concentration of silicon in the aspirated test solution, µg/mL.
- F* = dilution factor from 8.3 (volume diluted to volume of aliquot),
- NV* = percent nonvolatile of material under test, and
- S* = specimen weight, g.

9.2 To calculate the equivalent amount of silicon dioxide in the sample, multiply the percent silicon found by 2.139.

9.3 If the type of silicone polymer present in a varnish or coating vehicle is known, separate analysis of the silicone polymer allows the determination of a conversion factor that may then be used to calculate the percent of silicone polymer present in the vehicle.

10. Report

10.1 Report the percent of silicon, silicon dioxide equivalent, or silicone polymer present in the nonvolatile content of the material under test.

11. Precision and Bias

11.1 In an interlaboratory study of the method⁷, the withinlaboratory coefficient of variation was found to be 4.11 % relative at 21 degrees of freedom and between laboratories coefficient of variation was 5.27 % relative at 6 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days, should be considered suspect if they differ by more than 12.1 % relative.

11.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different

⁷ Supporting data are available on loan from ASTM Headquarters. Request RR: D01 - 1009.

laboratories, should be considered suspect if they differ by more than 18.2 % relative.

11.2 *Bias*—No bias has been determined for this test method.

12. Keywords

12.1 atomic absorption—AA; silicon content

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