



A Honeywell Company

Silicon in Petroleum Liquids by ICP-OES

UOP Method 796-09

Scope

This method is for the determination of silicon (Si) in petroleum liquids using an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). Silicon (Si) is typically present in petroleum liquids as soluble organic silicones, but the method will also detect other forms of silicon (Si) such as the generally insoluble inorganic silicon (Si) salts and silica. The method is primarily used to analyze reformer charge stocks for silicones, but may also be used for refinery charge stocks as heavy as vacuum gas oil (VGO). The lower limit of quantitation is approximately 1.0 mg/kg (mass-ppm) as silicon (Si). Standard addition, as described in the *Appendix*, may be used to verify the results.

Reference

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample is mixed with an internal standard and diluted in an organic solvent. The sample is then analyzed directly by ICP-OES.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, analytical, capable of weighing to nearest 0.01 g

Bath, ultrasonic, VWR, Cat. No. 21811-820

Centrifuge, if needed, see *Procedure, Sample Preparation*

Gloves, thermal protection, VWR, Cat. No. 32932-270, if needed, see *Procedure, Sample Preparation*

Oven, laboratory, capable of operation at 100°C

Spatula, VWR, Cat. No. 57952-253, if needed, see *Procedure, Sample Preparation*

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).

© COPYRIGHT 2009 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. The UOP 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.

Spectrometer, ICP-OES, computer controlled, having sufficient resolving power and dispersion to separate the analytical lines in the 160 to 800 nm region. The computer shall be capable of performing background corrections, blank corrections, mass/volume corrections and dilution corrections. A commercial grating spectrometer with a band pass of 0.018 nm or less in the first order is satisfactory. PerkinElmer Optima 5300 V.

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Bottles, 240 mL, amber, with conical polyseal caps, VWR, Cat. No. 14234-032

Dry ice, if needed, see *Procedure, Sample Preparation*

Hexane, VWR, Cat. No. BJ216-1

Pipets, dropper, glass, Fisher, Cat. No. 13-700

Scandium standard, 1000 µg/g, in organic media, SPEX, Cat. No. ORG-SC8-2Z, used as an internal standard, see *Notes 1 and 2*

Silicon standard, 1000 µg/g, in organic media, SPEX, Cat. No. ORG-SI8-2Z, see *Notes 1, 2, and 3*

Silicone, 100% polydimethylsiloxane (37.87% silicon), Dow Corning, 200 Fluid, 10 cSt, see *Note 3*

Solvent, kerosene, VWR, Cat. No. AA36447-K7 or SPEX, Cat. No. KER-BLK-G

Vials, 20-mL, with conical polyseal caps, VWR, Cat. No. 16087-068

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of ICP-OES, and the equipment being used.

Preparation of Standards

Because the response of the ICP is linear, two-point standards (calibration standard and blank) approximating the concentration of silicon expected in the samples are used. See *Note 3*.

Preparation of Stock Silicon Standards

Prepare a nominally 1,000-mg/kg silicon standard from polydimethylsiloxane as follows (see *Note 3*). If a purchased Si standard is to be used in place of polydimethylsiloxane, skip this part and proceed with the preparation of the nominally 100- and 10-mg/kg silicon calibration standards below.

1. Weigh 2.64 ± 0.05 g of 100% polydimethylsiloxane (37.87% silicon) into a clean 240-mL bottle and record the weight to the nearest 0.01 g. Add 97.36 ± 0.05 g of kerosene and record the weight to the nearest 0.01 g. Mix by shaking and in an ultrasonic bath. Label as "Stock Silicon Standard A." It will contain approximately 10,000-mg/kg Si.
2. Weigh 10.00 ± 0.05 g of Stock Silicon Standard A into a clean 240-mL bottle and record the weight to the nearest 0.01 g. Add 90.00 ± 0.05 g of kerosene and record the weight to the nearest 0.01 g. Mix by shaking and in an ultrasonic bath. Label as "Stock Silicon Standard B." It will contain approximately 1000-mg/kg Si.
3. Calculate the concentration of silicon (Si) in Stock Silicon Standards A and B using Equations 1 and 2:

$$\text{Concentration of silicon (Si), Stock Silicon Standard A, mg/kg} = 378700 \frac{A}{A + B} \quad (1)$$

where:

A = weight of polydimethylsiloxane from Step 1, g

B = weight of kerosene from Step 1, g

$$378700 = 37.87 \times 10000$$

where:

37.87 = concentration of Si in polydimethylsiloxane, mass-%

10000 = factor to convert mass-% to mg/kg

$$\text{Concentration of silicon (Si), Stock Silicon Standard B, mg/kg} = C \frac{D}{D + E} \quad (2)$$

where:

C = concentration of Si in Stock Silicon Standard A, from Equation 1, mg/kg

D = weight of Stock Silicon Standard A in Step 2, g

E = weight of kerosene in Step 2, g

Preparation of Silicon Calibration Standards

Prepare nominally 100- and 10-mg/kg Silicon Calibration Standards as follows:

1. Tare a vial to the nearest 0.01 g and add 1.0 ± 0.05 g of the Stock Silicon Standard B or the purchased 1000- $\mu\text{g/g}$ silicon standard. Record the weight to the nearest 0.01 g.
2. Add 9.0 ± 0.05 g of kerosene and record the weight to the nearest 0.01 g.
3. Label the vial as Silicon Calibration Standard, first dilution.
4. Tare another vial to the nearest 0.01 g and add 1.0 ± 0.05 g of the first dilution standard. Record the weight to the nearest 0.01 g.
5. Add 9.0 ± 0.05 g of kerosene and record the weight to the nearest 0.01 g.
 - For ICP analysis, the composition of the calibration standard should match the sample as closely as possible, particularly when measuring silicon below 10 mg/kg. If the sample is a light naphtha or gasoline, it may change the characteristics of the plasma, even when diluted. For such samples, prepare the nominally 10-mg/kg silicon calibration standard by first adding 1.0 g of hexane, and then adding 8.0 g of kerosene.
6. Label the vial as Silicon Calibration Standard, second dilution.
7. Fill an additional vial with kerosene and label it as Solvent Blank.
 - For ICP analysis the composition of the calibration standard should match the sample as closely as possible, particularly when measuring silicon below 10 mg/kg. If the sample is a light naphtha or gasoline, it may change the characteristics of the plasma, even when diluted. For such samples, prepare the blank by first adding 1.0 g of hexane, and then adding 9.0 g of kerosene.

Calculate the concentration of silicon (Si) in the first and second dilutions using Equations 3 and 4:

$$\text{Concentration of silicon, Silicon Calibration Standard, first dilution, mg/kg} = F \frac{G}{G + H} \quad (3)$$

where:

F = concentration of Si in Stock Silicon Standard B (or purchased 1000- $\mu\text{g/g}$ Si standard), mg/kg

G = weight of the Stock Silicon Standard B in vial, g

H = weight of kerosene in vial, g

$$\text{Concentration of silicon, Silicon Calibration Standard, second dilution, mg/kg} = J \frac{K}{K + L} \quad (4)$$

where:

J = concentration of Si in the Silicon Calibration Standard, first dilution, from Equation 3, mg/kg

K = weight of Silicon Calibration Standard, first dilution, in vial, g

L = weight of kerosene (or kerosene plus hexane) in vial, g

Relabel the vials with the calculated concentration (to three significant figures) of silicon (Si) in each. For the low concentration silicon samples typically analyzed, the nominally 10-mg/kg Silicon Calibration Standard is used. Higher concentration samples may either be analyzed using the 100-mg/kg standard, or the sample may be diluted to a concentration to fit the 10-mg/kg standard.

Preparation of Scandium Internal Standard Solutions

A known concentration of scandium is added to sample solutions prior to ICP analyses, which is used as an internal standard for the calculation of silicon concentration. Prepare the nominally 100- and 10-mg/kg Internal Standard Solutions as follows:

1. Tare a vial to the nearest 0.01 g. Weigh in 1.0 ± 0.05 g of the 1,000 $\mu\text{g/g}$ scandium standard and record the weight to the nearest 0.01 g.
2. Add 9.0 ± 0.05 g kerosene and record the weight to the nearest 0.01 g.
3. Label the vial as Internal Standard Solution, first dilution.
4. Tare another vial and add 1.0 ± 0.05 g of the Internal Standard Solution, first dilution, and record the weight to the nearest 0.01 g.
5. Add 9.0 ± 0.05 g kerosene and record the weight to the nearest 0.01 g.
6. Label the vial as Internal Standard Solution, second dilution.

Calculate the concentration of scandium in the Internal Standard Solution, first and second dilutions using Equations 5 and 6:

$$\text{Concentration of scandium, Internal Standard Solution, first dilution, mg/kg} = 1000 \frac{M}{M + N} \quad (5)$$

where:

M = weight of the 1,000- $\mu\text{g/g}$ scandium standard in the Internal Standard Solution, first dilution vial, g

N = weight of kerosene in the Internal Standard Solution, first dilution vial, g

1000 = concentration of scandium in the 1,000 $\mu\text{g/g}$ standard

$$\text{Concentration of scandium, Internal Standard Solution, second dilution, mg/kg} = P \frac{Q}{Q + R} \quad (6)$$

where:

P = concentration of scandium in Internal Standard Solution, first dilution vial, from Equation 5, mg/kg

Q = weight of Internal Standard Solution, first dilution vial, g

R = weight of kerosene in Internal Standard Solution, second dilution vial, g

Relabel the vials with the calculated concentration (to three significant figures) of scandium in each.

Preparation of Spectrometer

Start up the ICP-OES, ignite the plasma according to the manufacturer's recommendations, and allow a minimum of 30 minutes for the instrument to stabilize before starting the analysis. When recommended by the manufacturer, perform a wavelength calibration prior to the start of the analysis. The recommended wavelengths to use for this analysis are listed in Table 1.

Table 1
Recommended Wavelengths

<u>Element</u>	<u>λ, nm</u>	
Sc	424.689	
Si	212.412 or 251.611* or 288.158	*Use 251.611 as the primary wavelength for silicon. The other wavelengths listed may be used to verify that there is no background interference at the primary wavelength.

Sample Preparation

Samples must be diluted with kerosene prior to analysis. The minimum dilution is a 9:1 ratio of diluent to sample. If aspirating the 9:1 diluted sample is problematic or the silicon is present at higher concentrations, increase the dilution factor. The lower limit of detection will be impacted with increased dilution.

Liquids

For samples that are liquid at room temperature and are miscible with the solvent:

1. Obtain a tare weight, to the nearest 0.01 g, of a vial with cap.
2. Shake the sample bottle and, using a disposable dropping pipet, weigh 1.0 ± 0.05 g of the sample; record the weight to the nearest 0.01 g.
 - If the 9:1 diluted sample is problematic, increase the dilution factor. For example, weigh only 0.5 g or less of the sample. Make up the weight difference by adding more solvent kerosene.
3. Add 8.0 ± 0.05 g of kerosene. Record the weight to the nearest 0.01 g.
4. Add 1.0 ± 0.05 g of the nominally 10-mg/kg Scandium Internal Standard Solution; record the weight to the nearest 0.01 g.
 - For high volume analyses, it may save time to pipet the Scandium Internal Standard Solution into the standard and samples. An automated pipettor (not listed in *Apparatus*) may be set up to dispense a repeatable volume corresponding to 1.00 g of scandium internal standard solution, which will then not need to be weighed.
5. Cap the vial and shake to mix the contents.
6. If insoluble matter is present, centrifuge the solution prior to analysis, and note the presence of insolubles in the report.
7. Prepare a calibration standard in the same manner as Steps 1 through 5 above, substituting the nominally 10-mg/kg Silicon Calibration Standard for the sample.
8. Prepare a Sample Blank in the same manner as Steps 1 through 5 above, except do not add sample in Step 2, and add 9.0 ± 0.05 g of solvent blank in Step 3.
9. Analyze the calibration standard, the sample blank, and the samples as described under *Sample Analysis*.

Viscous Liquids or Meltable Solids

If the sample is a solid or a very viscous liquid at room temperature and cannot be readily dissolved in the solvent:

1. Loosen the sample bottle cap and heat the sample in an oven at 100°C for approximately 30 minutes. Also place a glass dropper pipet in the oven.
 - Heating the sample above 100°C is not recommended as it may result in the loss of volatile silicone compounds.
2. Place a vial and cap (removed from vial) on the balance and obtain a tare weight.
3. Using thermal gloves or other protection, remove the pipet and sample bottle from the oven, tighten the cap on the sample bottle and shake to mix.
4. Using the hot pipet, transfer 1.0 ± 0.1 g of the hot sample into the tared sample vial. Record the weight to the nearest 0.01 g and continue with Steps 3 through 5 for liquid samples.
 - If the 9:1 diluted sample is problematic or the silicon is present at higher concentrations increase the dilution factor. For example, weigh only 0.5 g or less of the sample. Make up the weight difference by adding more solvent kerosene.
5. Place the vial in an ultrasonic bath for 10 minutes (or as needed for complete dissolution).
6. Analyze the calibration standard, the sample blank (both prepared as described under *Sample Preparation, Liquids*, Steps 7 and 8), and the sample as described under *Sample Analysis*.
 - The sample must be analyzed within 5 minutes after sonication. If not analyzed within 5 minutes, phase separation may occur, and the results may be suspect.

Non-meltable Solids

If the sample does not melt at 100°C:

1. Obtain dry ice and break it up so that optimum contact with the sample bottle is achieved
2. Place the sample bottle in the dry ice to cool for about 30 min.
3. Place a vial and cap (removed from vial) on the balance and obtain a tare weight to the nearest 0.01 g.
4. Using thermal protection, remove the sample bottle from the dry ice and use a spatula to break/homogenize the sample
5. Transfer 1.0 ± 0.1 g of the chilled sample into the tared sample vial. Record the weight to the nearest 0.01 g and continue with Steps 3 through 5 for liquid samples.
 - If the 9:1 diluted sample is problematic or the silicon is present at higher concentrations increase the dilution factor. For example, weigh only 0.5 g or less of the sample. Make up the weight difference by adding more solvent kerosene.
6. Place the vial in an ultrasonic bath for 10 minutes (or as needed for complete dissolution).
7. Analyze the calibration standard, the sample blank (both prepared as described under *Sample Preparation, Liquids*, Steps 7 and 8), and the sample as described under *Sample Analysis*.
 - The sample must be analyzed within 5 minutes after sonication. If not analyzed within 5 minutes, phase separation may occur, and the results may be suspect.

Sample Analysis

Follow the spectrometric procedure as described under *Preparation of Spectrophotometer*. Enter the appropriate weights for the sample and internal standard into the data system. Aspirate the

796-09

calibration standard, the sample blank, and the samples. Rerun the calibration standard at the end of the sample analyses to confirm the calibration. The final standard reading should be within 2% relative of its first reading. If it is not, check for problems and reanalyze the entire series. Aspirate the blank initially and between each standard or sample until the instrument returns to a baseline condition. The data system will calculate the mg/kg silicon (Si) in the sample and print the result. Standard addition may be used to verify the results, see *Appendix*.

Calculations

The calculations are performed by the data system after the analyst enters the appropriate values for weights of the sample and internal standard. Report results below 10 mg/kg to the nearest 0.1 mg/kg. Report results at 10 mg/kg or greater to the nearest 1 mg/kg.

Notes

1. Do not use purchased standards or dilutions made therefrom beyond the expiration date on the bottles of the purchased standards.
2. The terms $\mu\text{g/g}$ and mg/kg are mathematically the same. The term $\mu\text{g/g}$ is used by the vendor of the purchased standards. However, in the standard preparation, sample preparation, and reporting, mg/kg is used as it is the common reporting unit for trace analyses.
3. It is preferable to prepare silicon standards from polydimethylsiloxane as it has an almost unlimited shelf life. If 100% polydimethylsiloxane cannot be obtained locally, it is acceptable to prepare standards from a purchased 1000- $\mu\text{g/g}$ silicon standard.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining silicon (Si) in two samples with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests on each sample each day. The total number of tests was 16. The precision data are summarized in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 2 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Table 2
Repeatability and Site Precision, Silicon (Si), mg/kg

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
A	2.5	0.032	0.12	0.033	0.13
B	7.7	0.049	0.19	0.056	0.22

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

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

Suggested Suppliers

Dow Corning, see www.dowcorning.com for a local distributor

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

PerkinElmer Analytical Instruments, 710 Bridgeport Ave., Shelton, CT 06484-4794 (203-925-4600) www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com

Appendix

Standard Addition Technique

Scope

If verification of the result determined using the calibration and analysis techniques described in the body of the method is desired, a standard addition technique may be used. The technique as described is applicable over the range of approximately 1 to 50 mg/kg for an undiluted sample.

Outline of Method

The sample is spiked at two different levels with a silicon (Si) standard solution. The original sample and the spiked samples are analyzed. The concentrations of silicon in the sample are calculated from the results of the three analyses. Differences in the results determined by the three equations used give an indication of non-linearity of response.

Procedure

The procedure is written for a 9:1 solvent to sample dilution. If a greater dilution is needed, reduce the sample weight. For example, weigh only 0.5 g or less of the sample. Make up the weight difference by adding more solvent kerosene.

Prepare the two standard addition mixtures as follows:

1. Label three vials as A, B, and C respectively. Weigh 1.0 ± 0.05 g of the sample into each vial. Record each weight to the nearest 0.01 g.
2. Weigh 9.0 ± 0.05 g of kerosene, to the nearest 0.01 g, into Vial A and record the weight to the nearest 0.01 g.
3. Weigh 1.0 ± 0.05 g of the nominally 10-mg/kg Stock Silicon Standard, to the nearest 0.01 g, into Vial B. Weigh approximately 8.0 g of kerosene, to the nearest 0.01 g, into Vial B. Record the weights to the nearest 0.01 g.
4. Weigh 2.0 ± 0.05 g of the nominally 10-mg/kg Stock Silicon Standard, to the nearest 0.01 g, into Vial C. Weigh 7.0 ± 0.05 g of kerosene, to the nearest 0.01 g, into Vial C and record the weight.
5. Analyze each vial as described in the body of the method. A precise calibration of the instrument is not necessary when using the standard addition technique, as only the ratios of the three results will be used in the calculation.

Calculations

Calculate the concentrations of the added silicon (Si) to Vials B and C using Equations A1 and A2:

$$\text{Silicon (Si) added to Vial B, mg/kg} = S \frac{T}{U} \quad (\text{A1})$$

$$\text{Silicon (Si) added to Vial C, mg/kg} = S \frac{V}{W} \quad (\text{A2})$$

where:

S = concentration of silicon (Si) in the nominally 10-mg/kg silicon standard, from Equation 4 in the body of the method, mg/kg

T = weight of nominally 10-mg/kg silicon standard added to Vial B, g

U = total weight of liquid in Vial B (sample + silicon standard + kerosene), g

V = weight of nominally 10-mg/kg silicon standard added to Vial C, g

W = total weight of liquid in Vial C (sample + silicon standard + kerosene), g

Calculate the concentrations of silicon in the sample by the standard addition technique using Equations A3 through A5:

$$\text{Silicon (Si), from 1-g standard addition, mg/kg} = \frac{S_B X}{Y - X} \quad (\text{A3})$$

$$\text{Silicon (Si), from 2-g standard addition, mg/kg} = \frac{S_C X}{Z - X} \quad (\text{A4})$$

$$\text{Silicon (Si), from 1- and 2-g standard additions, mg/kg} = \frac{(S_C - S_B) X}{Z - Y} \quad (\text{A5})$$

where:

X = analyzed value for silicon in Vial A

Y = analyzed value for silicon in Vial B

Z = analyzed value for silicon in Vial C

S_B = silicon (Si) added to Vial B, from Equation A1, mg/kg

S_C = silicon (Si) added to Vial C, from Equation A2, mg/kg

If any of the results deviate by more than 10% from another (or 1 mg/kg below 10 mg/kg), that is an indication of non-linearity. Check procedures and techniques for possible causes of the non-linearity. If the deviations are less than 10%, report, to the nearest 0.1 mg/kg, the median value as the concentration of silicon in the sample.