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 quantition 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 100ºC

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).

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 x 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-µg/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-µg/g Si standard), mg/kg
G = weight of the Stock Silicon Standard B in vial, g
H = weight of kerosene in vial, g