

## 15

## Silicon

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## 15-1 INTRODUCTION

## 15-1.1 Forms and Amounts of Silicon in Soils

Silicon, which comprises 27.6% of the earth's crust (Jackson, 1964), occurs in a wide variety of forms and stabilities. In a simplistic model (Mitchell, 1975), Si occurs at every intermediate stage in a gradual transition between molecular solubility (silicic acid), homogeneously dispersed colloids (Hydrosols), nonrigid gels (Hydrogels), and rigid gels (Xerogels). The boundaries of this continuum are not sharp, and the entities are only arbitrarily definable. Silicon forms may also be defined in terms of *total*, *extractable*, and *soluble*. As the name implies, total Si comprises all forms of Si that may be present and can be solubilized by strong alkali fusion or acid digestion bomb methods. Extractable Si represents those forms removed by less severe dissolution agents, such as sodium dithionite, ammonium oxalate, weak alkalis, and sodium pyrophosphate. These extractants remove Si of intermediate stability commonly representing Si from poorly crystalline or amorphous soil components. Soluble Si represents the most labile form in soils and consists primarily of monomeric silicic acid; soluble Si occurs in interstitial soil solutions, soil leachates, and ground water and is generally extracted with water or dilute salt solutions when determination is desired. Quantity of extractable and soluble Si must be defined in terms of operational modes since it is commonly a function of methodology and extractants used.

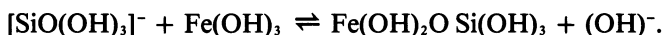
The quantity and distribution of Si in soils are influenced by parent material, climate, vegetation, texture, pedogenesis, and intensity of weathering. In soils of temperate and cold regions subject to little desilication, Si is concentrated in stable silicate minerals; more labile components of the weathered upper horizons have been removed through dissolution

and leaching. It is commonly concentrated as quartz, feldspars, layer silicates, and accessory minerals (zircon, beryl, tourmaline, etc.) in sand and silt fractions. Similar pedogenic conditions occur in many soils of tropical regions; however, in environments that favor desilication, sesquioxides (oxides, oxyhydroxides, and hydroxides of Fe and Al) concentrate preferentially to Si. Through the weathering of primary and secondary minerals, soluble Si is either leached from the system, precipitated on silicate templates, chemisorbed to sesquioxides, or incorporated into amorphous silicates. High quantities of both extractable and soluble Si are commonly observed in soils developing from pyroclastics, volcanic ejecta, or mafic bedrocks.

### 15-1.2 Dynamics of Silicon Dissolution in Soils

Dissolution and concentration of Si in soils are controlled by dynamic processes where equilibrium conditions are the exception rather than the rule. Soluble Si concentrations are a function of mineralogy, pH, sesquioxide content, reactivity of mineral surfaces, organic acids, and water content (Wilding et al., 1977). Organic acids, such as adenosine triphosphate (ATP), alginic acids, and amino acids have been shown to greatly enhance dissolution of silica (Evans, 1965; Crook, 1968), whereas cations such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Hg}^{2+}$  chemisorbed to Si surfaces are reported to inhibit dissolution due to formation of relatively insoluble silicate coatings (Krauskopf, 1959; Jones & Handreck, 1963; Beckwith & Reeve, 1963; Lidstrom, 1968). Disrupted (amorphous or microcrystalline) surface layers on quartz grains commonly yield abnormally high Si solubilities (Siffert, 1967; Lidstrom, 1968; Ribault, 1971).

In systems containing particulate sesquioxides, the adsorption of monosilicic acid by sesquioxides is greatest between pH 8 and 10. The pH dependency of the Si sorption is illustrated in the following equations:



In such systems, it is suggested that sesquioxides act as a soluble Si sink and increase dissolution of silica.

The concentration of soluble Si in ground water generally ranges from 5 to 30 mg of Si/liter (Krauskopf, 1967), whereas in soils, it ranges from 1 to 40 mg of Si/liter (McKeague & Cline, 1963; Jones & Handreck, 1963, 1967; Beckwith & Reeve, 1964; Crook, 1968; Elgawhary & Lindsay, 1972), with 15 or 20 mg of Si/liter most commonly present in soils at field capacity. The low concentration of monosilicic acid in natural waters is attributed to the slow kinetics of dissolution combined with dilution by rainwater (Krauskopf, 1959). Perturbation of soluble Si contents in soils is commonly noted from fluxes in water content, which creates a dilemma in determining in situ soluble Si concentrations at moisture contents below saturation since desic-

cation and subsequent rewetting of soils continually shift precipitation-dissolution dynamics. Thus, every attempt should be made to determine soluble Si content of soils within the natural moisture range. This would normally preclude air-drying of the soils before soluble Si extraction and analysis.

The concentration of soluble Si in soils lies approximately halfway between the equilibrium solubility of amorphous silica (50–60 mg of Si/liter) and quartz (3–7 mg of Si/liter). Thermodynamically, amorphous Si should dissolve and quartz precipitate yielding equilibrium concentrations of about 3 to 7 mg of Si/liter. However, quartz does not control the concentration of monosilicic acid in soils because of its very slow dissolution rate and negligible precipitation rate. Elgawhary and Lindsay (1972) conclude that a solid phase less soluble than amorphous Si and more soluble than quartz supports soluble Si concentrations found in soils; Kittrick (1969) has suggested kaolinite and montmorillonite, and Wilding et al. (1977) postulate that opal might serve that function. Later work by Wilding et al. (1979) suggests that biogenic opal of forest and grass origin has much slower dissolution rates than earlier suspected. The fate and stability of biogenic opal in soil systems are dependent on vegetative origin, specific surface area, Al content, hydration state, age, and rate of organic biodegradation of encasing tissues (Bartoli & Wilding, 1980). Biogenic opal solubilities under natural conditions approach geological opal and quartz and support Si solubilities of about 0.5 to 3 mg/liter. It is more probable that kinetics rather than thermodynamics control soluble Si levels in soils. Sorption-desorption reactions of sesquioxides and clay minerals result in faster Si equilibrium than dissolution-precipitation phenomena (McKeague & Cline, 1963; Beckwith & Reeve, 1963, 1964; Jones & Handreck, 1963).

## 15-2 PRINCIPLES

Analysis of Si by atomic absorption spectrometry (AAS) or colorimetric techniques requires that Si be in solution. When analysis of soluble or extractable forms of Si is performed, this requirement is easily met; however, when total Si analysis is desired, dissolution is made difficult by the presence of silicates and aluminates.

Traditionally, silicates are dissolved by fusion at high temperatures with a flux, followed by dissolution of the resulting melt in either water or acid. Fluxes may vary depending on procedures, desired analyses, and personal preference of the investigator, but generally, hydroxides, carbonates, or borates of alkali metals are used (Govett, 1961; Jackson, 1958; Ingamells, 1970). Govett (1961) and Katz (1968) indicate that  $\text{Na}_2\text{CO}_3$  fusion may yield low results for total Si. Sodium hydroxide has several advantages as the flux for dissolution of silicate minerals. Sample decomposition is relatively rapid and can be performed in inexpensive Ni crucibles at relatively low temperatures (Kilmer, 1965). It should be noted that Pt crucibles should not be used with NaOH (Jackson, 1958).

Teflon-lined acid digestion vessels have recently been utilized in dissolving silicates (Price & Whiteside, 1977; Buckley & Cranston, 1971; Bernas, 1968; Bigham et al., 1978). Silicate samples placed in such sealed vessels can be solubilized in HF in a relatively short period of time (1 hour or less) with heat provided by an ordinary drying oven. Precipitation of fluoride salts and loss of Si as  $\text{SiF}_4$  are overcome by the addition of  $\text{H}_3\text{BO}_3$  to the solution immediately following decomposition of the sample. Advantages of this method include reduced contamination and splattering problems, which are common to fusion techniques.

In many soil studies, the content of more labile forms of silica is of interest. Extractions using oxalate (Hallmark & Smeck, 1979; Gamble & Daniels, 1972), citrate-bicarbonate-dithionite (Harlan et al., 1977; Norton & Franzmeier, 1978; Gamble & Daniels, 1972), NaOH (Whittig et al., 1957; Yassoglou & Whiteside, 1960),  $\text{Na}_2\text{CO}_3$  (Follett et al., 1965),  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  in dilute acetic acid (Khalid et al., 1978), dilute salt solutions (Gallez et al., 1977; Weaver & Bloom, 1977; Elgawhary & Lindsay, 1972), and water have been employed.

Kilmer (1965) notes that the gravimetric procedure is the classical method for determination of silica. Although gravimetry has been extensively used historically, most workers today prefer the rapidity and convenience of either AAS or colorimetry.

Principles concerning AAS are covered in Chapter 2. Until the introduction of the  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  flame, Si could not be adequately determined by atomic absorption (Bowman & Wills, 1967). However, today such analysis is common, but care must be exercised to reduce matrix influences and ionization interferences. These can be minimized by near matching sample and standard and by maintaining readily ionizable components such as  $\text{K}^+$  and  $\text{Na}^+$  in moderate concentration (near 2,000 mg/liter) in the solution. However, determination of Si by atomic absorption has been noted to be difficult in high concentrations of dissolved solids due to continuous emission background and scattering effects of the flame (Price & Whiteside, 1977).

The colorimetric determination of Si involves the reaction of silicic acid with molybdic acid to form silicomolybdic acid, a yellow complex with the formula  $\text{H}_4(\text{SiMo}_{12}\text{O}_{40})$ . Formation of the silicomolybdic acid complex is maximum between pH 1.0 and 2.0. Strickland (1952a, b) demonstrated that two forms of silicomolybdic acid exist,  $\alpha$ -silicomolybdic acid forms at low acidities and  $\beta$ -silicomolybdic acid at high acidities, with the absorbance of the  $\beta$ -form being nearly twice that of the  $\alpha$ -form. The  $\beta$ -form, which is an unstable polymer of the  $\alpha$ -form, will spontaneously change into the  $\alpha$ -form by a first-order transformation. This reaction is hastened by heating, raising the pH above 2.5, or in an excess of electrolyte. However, most early colorimetric Si methods did not consider the form of silicomolybdic acid present; thus, absorbance decreased as a function of time due to  $\beta$  to  $\alpha$  conversion. Ringbom et al. (1959) favor the use of  $\alpha$ -acid in colorimetric determinations due to its greater stability and published a method in which

$\alpha$ -acid is formed by heating the solution and buffering the pH between 3.0 and 3.7 with monochloroacetic acid and ammonium monochloroacetate. But most recent methods employ the  $\beta$ -acid due to its greater sensitivity. Both methods presented herein (Govett, 1961; Weaver et al., 1968) employ molybdate in excess of that required to react with silica, which, according to Strickland (1952b), retards the formation of  $\alpha$ -silicomolybdic acid. Furthermore, both procedures use  $\text{H}_2\text{SO}_4$  as the acidifying agent, which appears to stabilize the  $\beta$ -silicomolybdic acid formed (Govett, 1961).

Either the yellow silicomolybdic acid complex or the blue silicomolybdous acid complex can be employed for colorimetric determination of Si. As with silicomolybdic acid, both  $\alpha$ - and  $\beta$ -forms of silicomolybdous acid exist: the  $\alpha$ -acid is greenish blue, whereas the  $\beta$ -acid, which exhibits the higher absorbance, is royal blue (Strickland, 1952b). Most methods reported in the literature favor the reduced blue complex due to its greater sensitivity (Bunting, 1944; Boltz & Mellon, 1947; Jeffery & Wilson, 1960; Morrison & Wilson, 1963; Weaver et al., 1968); however, if sensitivity is not critical, the reduction steps can be eliminated by using the yellow complex (Schwartz, 1942; Corey & Jackson, 1953; Ringbom et al., 1959; Govett, 1961). Following the work of Lindsay and Bielenberg (1940), in nearly all procedures utilizing silicomolybdous blue, reduction is accomplished with sodium bisulfite and 1-amino-2-naphthol-4-sulphonic acid.

The primary source of interferences for the colorimetric determination of Si in soils is Fe and P. The latter reacts with molybdate to form a phosphomolybdate complex that absorbs in the same wavelength ranges as silicomolybdic acid. Tartaric acid (Bunting, 1944; Ringbom et al., 1959; Weaver et al., 1968), sodium citrate (Lindsay & Bielenberg, 1940), and oxalic acid (Schwartz, 1942) have been used to suppress P interference; tartaric acid addition is the most widely accepted technique. Additions of tartaric acid (Bunting, 1944; Weaver et al., 1968) and oxalic acid (Jeffery & Wilson, 1960) have also been used to suppress Fe interference. Iron can interfere with formation of the yellow silicomolybdate complex by precipitating molybdate but is more troublesome in the blue silicomolybdous procedure, where  $\text{Fe}^{3+}$  consumes the reducing agent or  $\text{Fe}^{2+}$  causes premature reduction of silicomolybdic acid (Weaver et al., 1968). Jeffrey and Wilson (1960) indicate that Fe interference can be eliminated in the blue silicomolybdous procedure by measuring absorbance at 650 nm rather than at the absorption maximum of 810 to 820 nm.

In citrate-bicarbonate-dithionite extracts, both citrate and dithionite can cause interference with the colorimetric determination of silica. Weaver et al. (1968) suggest bubbling air through the extract for 4 hours to oxidize any unoxidized dithionite, which will cause premature reduction of silicomolybdic acid or turbidity. Nakai and Yoshinaga (1976) use  $\text{H}_2\text{O}_2$  to remove unreacted dithionite before determination of Si. Citrate interference, due to the complexing of molybdate by citrate, can be eliminated by using an excess of molybdate (Weaver et al., 1968; Nakai & Yoshinaga, 1976).

### 15-3 PROCEDURES

#### 15-3.1 Decomposition with Acid Digestion Vessel (Bernas, 1968)

##### 15-3.1.1 REAGENTS

1. Aqua regia: Mix 1 part conc nitric acid ( $\text{HNO}_3$ ) with 3 parts of conc hydrochloric acid ( $\text{HCl}$ ). Prepare fresh daily.
2. Hydrofluoric acid ( $\text{HF}$ ), 48%.
3. Boric acid ( $\text{H}_3\text{BO}_3$ ), solid.
4. Potassium chloride ( $\text{KCl}$ ) or cesium chloride ( $\text{CsCl}$ ), 2% in water: Bring 2 g of  $\text{KCl}$  or  $\text{CsCl}$  to a volume of 100 ml in a volumetric flask.

##### 15-3.1.2 PROCEDURE

Place 50 mg of sample ground to pass through a 200-mesh sieve into an acid digestion vessel (available from Parr Instrument Co.). Add 0.5 ml of aqua regia and 3 ml of  $\text{HF}$ . Close the vessel, and heat for 30 to 40 min at  $110^\circ\text{C}$ . Cool, open the vessel, and transfer the decomposed sample with the aid of 4 to 6 ml of water from a wash bottle into a 100-ml plastic beaker. The volume should not exceed 10 ml. Quickly add 2.8 g of  $\text{H}_3\text{BO}_3$ , and stir for 15 min with a Teflon stirring rod or bar on a magnetic stirrer. Slowly add about 40 ml of water. The precipitated metal fluorides and the  $\text{H}_3\text{BO}_3$  should completely dissolve, giving a clear homogeneous sample solution. Add 5 ml of  $\text{KCl}$  (if K analysis is desired on the sample, 2%  $\text{CsCl}$  may be substituted for  $\text{KCl}$ ). Dilute to volume in 100-ml volumetric flask, and store in plastic for analysis.

##### 15-3.1.3 COMMENTS

Boric acid reacts with silicon fluoride compounds to minimize loss of Si as  $\text{SiF}_4$  (section 1-2.1). Following addition of  $\text{H}_3\text{BO}_3$ , glassware can be used for dilutions; however, prolonged contact ( $>2$  hours) with glass is not recommended (Bernas, 1968). If Si is to be determined colorimetrically, addition of either  $\text{KCl}$  or  $\text{CsCl}$  may be omitted. Organic matter should be destroyed in samples containing more than 1% organic matter before decomposition in an acid digestion vessel. Occasionally sample decomposition is incomplete; it is suggested in such cases to increase the heating time rather than the temperature because the life of the Teflon vessels is shortened at higher temperatures. See section 1-5 for a similar alternative procedure.

#### 15-3.2 Decomposition by Sodium Hydroxide Fusion (Govett, 1961)

##### 15-3.2.1 REAGENTS

1. Sodium hydroxide ( $\text{NaOH}$ ), solid.
2. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), 1N.

### 15-3.2.2 PROCEDURE

Add 50 mg of 100-mesh sample that has been weighed to the nearest 0.1 mg to a Ni crucible containing 2 g of solid NaOH. Cover the crucible and heat to a dull redness for at least 10 min. After the melt is cooled, dissolve it in water by adding 50 ml of water and allowing it to stand overnight. Quantitatively transfer the dissolved melt to a plastic beaker, and acidify it with sufficient 1N H<sub>2</sub>SO<sub>4</sub> to yield a pH of about 1.5 in the final solution. Then quantitatively transfer the solution to a 1-liter volumetric flask, and dilute to volume.

## 15-3.3 Silicon Determination by Atomic Absorption Spectrometry

### 15-3.3.1 REAGENTS

1. Aqua regia: Mix 1 part conc nitric acid (HNO<sub>3</sub>) with 3 parts of conc hydrochloric acid (HCl). Prepare fresh daily.
2. Hydrofluoric acid (HF), 48%.
3. Boric acid (H<sub>3</sub>BO<sub>3</sub>), solid.
4. Potassium chloride (KCl) or cesium chloride (CsCl), 2% in water: Dissolve 2 g of KCl or CsCl in water, and bring to volume in 100-ml volumetric flask.
5. Solution A:<sup>1</sup> Combine 0.5 ml of aqua regia, 3 ml of HF, 2.8 g of H<sub>3</sub>BO<sub>3</sub>, 5 ml of 2% KCl or CsCl diluted to 100 ml with water.
6. Silicon standard, 1,000 mg of Si/liter. Store in a plastic bottle.
7. Silicon standard, 100 mg of Si/liter: Dilute 1,000 mg of Si/liter standard 10-fold with water. Store in a plastic bottle.

### 15-3.3.2 PROCEDURE

Prepare Si standards of 0, 20, 50, and 100 mg of Si/liter by pipetting 0 and 20 ml of 100 mg of Si/liter standard solution and 5 and 10 ml of 1,000 mg of Si/liter standard solution, respectively, into 100-ml volumetric flasks containing 20 ml of solution A. Dilute to volume, and store in plastic containers.

Dilute samples in 100-ml volumetric flasks by bringing 20 ml of sample to volume with water.

Determine Si by atomic absorption using N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub> with a fuel-rich flame at a wavelength of 251.6 nm. Standard operating conditions for atomic absorption units vary slightly among manufacturers and should be followed throughout the analysis.

<sup>1</sup> Composition of solution A may vary. In this procedure, it is assumed that the sample was decomposed by the method in section 15-3.1. Solution A should contain all reagents in like concentration as the sample and should be diluted by the same factor as the sample.

### 15-3.3.3 COMMENTS

Fuel-rich flames of  $\text{N}_2\text{O}-\text{C}_2\text{H}_2$  may cause build-up of C residues around the burner slot. Care must be exercised to remove these build-ups so that error in results is minimized. Usually 10 or more samples can be analyzed before build-up becomes a problem.

Sensitivity and detection limits of Si by atomic absorption are reported to be 2 and 0.2 mg/liter, respectively (Kriege et al., 1975). The digestion bomb procedure using a fluoro-borate matrix yields results within 1.3% relative error with established values from other methods (Bernas, 1968). Either KCl or CsCl is added to the fluoro-borate matrix as an ionization buffer; within this matrix, interference interactions between Si and Al appear to be negligible (Price & Whiteside, 1977).

Silicon extracted in ammonium oxalate,  $\text{NH}_4\text{OAc}$  (pH 4.8), HCl, NaOH, sodium dithionite, and water can also be determined by atomic absorption (Yuan & Breland, 1969; Searle & Daly, 1977; Wilding et al., 1979). However, care should be exercised to ensure a matrix match between samples and standards.

## 15-3.4 Colorimetric Determination of Silicon

### 15-3.4.1 REAGENTS

1. Ammonium paramolybdate tetrahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]^2$  solution (0.3M molybdate): Dissolve 54 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in approximately 800 ml of water, adjust the pH to 7 with 5N sodium hydroxide (NaOH), make to 1 liter volume, and store in a plastic bottle.
2. Tartaric acid solution, 20%: Dissolve 100 g of tartaric acid in 500 ml of water, and store in a plastic bottle. A fresh solution should be prepared when appreciable sediment forms.
3. Reducing solution: Dissolve 25 g of sodium bisulfite ( $\text{NaHSO}_3$ ) in 200 ml of water, and combine with a solution containing 2 g of anhydrous sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and 0.4 g of 1-amino-2-naphthol-4-sulfonic acid in 25 ml of water. Dilute the combined solution to 250 ml, and store in a plastic bottle in a refrigerator.
4. Standard Si solution, 50 mg of Si/liter: Digest clear quartz crystals in conc hydrochloric acid (HCl) for 1 hour, then rinse in water, dry, and grind in an agate mortar until quartz will pass through a 100-mesh screen. Heat the ground quartz to redness in a crucible for a brief period, cool, and store in a screw-cap vial. Fuse a 0.1070-g sample of ground quartz with NaOH in a Ni crucible in the same manner given in section 15-3.2. Dissolve the resulting melt in water, acidify with 1N  $\text{H}_2\text{SO}_4$  to yield a final pH of approximately 1.5, and dilute to a volume of 1 liter (primary Si standard). A secondary standard (1 mg of Si/liter) can be prepared by diluting 10 ml of primary standard to 500 ml. All standard

<sup>2</sup> Ammonium paramolybdate tetrahydrate is commonly sold under the name of ammonium molybdate or ammonium heptamolybdate tetrahydrate.



solutions should be stored in plastic bottles. A standard curve can be prepared by treating appropriate aliquots of the standard solution in the same manner as the unknown samples.

#### 15-3.4.2 YELLOW SILICOMOLYBDIC ACID PROCEDURE (Govett, 1961)

Add an aliquot of sample solution containing 100 to 400  $\mu\text{g}$  of Si to a 50-ml volumetric flask, and acidify with 10 ml of 1N  $\text{H}_2\text{SO}_4$ . Then add 10 ml of 0.3M ammonium paramolybdate tetrahydrate solution, and dilute to volume with distilled water. Mix the solution well, and measure the absorbance at 400 nm not sooner than 2 min or later than 10 min after adding the ammonium paramolybdate tetrahydrate. Prepare a standard curve by treating 0-, 2-, 4-, 6-, and 8-ml aliquots of the primary standard (50 mg of Si/liter) in the same fashion as the sample aliquot. Best results are obtained if the same period of time is allowed for color development in the standards and samples; 5 min is generally a suitable choice.

Thoroughly clean the glassware with cleaning solution, wash it, clean with 1:1 HCl, and then wash with distilled water. It is desirable to leave the 50-ml volumetric flasks standing in an acid bath of 1:1 HCl and wash well with distilled water just before use. Phosphorus interferences can be suppressed by the addition of tartaric acid. Replicate determinations yield a maximum standard deviation of 0.002 absorbance units.

#### 15-3.4.3 BLUE SILICOMOLYBDOUS ACID PROCEDURE (Weaver et al., 1968).

Add an aliquot of sample solution containing 5 to 25  $\mu\text{g}$  of Si to a 50-ml volumetric flask, add 10 ml of 1N  $\text{H}_2\text{SO}_4$ , and then add 10 ml of 0.3M ammonium paramolybdate tetrahydrate solution. After 2 min, add 5 ml of 20% tartaric acid, followed by 1 ml of 1-amino-2-naphthol-4-sulfonic acid reducing agent. Dilute the solution to volume with distilled water, mix well, and measure the absorbance at 820 nm after 30 min. A standard curve is prepared by treating 0-, 5-, 10-, 15-, and 20-ml aliquots of the secondary Si standard (1 mg of Si/liter) in the same manner as the sample aliquots.

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