Silicon in Agriculture
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Chapter 11

Methods for silicon analysis in plants, soils, and fertilizers

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The classical method for determining total silicon (Si) content of various materials has been conversion of insoluble silicates into sodium silicate through high temperature fusion with sodium hydroxide, or other sodic bases. The Si can then be determined by a variety of methods, including gravimetric, colorimetric, and absorption/emission spectrometry. Silicon also has been determined gravimetrically in plant tissue as the residue after acid digestion. We have developed a simple, inexpensive, and rapid method for solublizing Si in plant tissue that facilitates analysis of a large number of samples. When analyzing soils and fertilizers, a method for gauging the plant-available Si, rather than total Si, generally is desired. A number of soil-test methods have been developed. Some require extended incubation periods, field-moist soil, or other procedures that inhibit adoption by routine soil-testing laboratories. Silicon extracted by acetic acid has been correlated to Si uptake by rice (*Oryza sativa* L.) and rice grain yield. Using this method, the Everglades Soil Testing Laboratory analyses nearly five thousand samples annually. Since Si fertilizer sources differ in Si content and Si solubility, analytical methods have been developed for predicting their relative ability to provide plant-available Si. We use a column leaching method based on Si elution in Tris buffer (pH 7) for the evaluation of potential Si soil amendments. However, greenhouse and field evaluations are essential for making final determinations.

11.1. INTRODUCTION

Although the compound SiO_2 was isolated from various plant tissues in the late 18^{th} century, the pure element Si was first isolated by Berzelius in 1823. He obtained it by combining potassium fluorosilicate with potassium (Urry, 1983), i.e., $K_2SiF_6 + 4K_{metal} = 6KF + Si_{metal}$. Many procedures for determining the Si content of a wide variety of materials have been developed since that time. Nevertheless, although there are a few compendia of methods for examining mineral silicates, i.e., Jackson et al. (1986), there are virtually none that also review methods for chemically and physically analyzing plant materials for Si, and for determining total as well as plant-available Si in soils and fertilizers. An attempt is made to provide such comprehensive information on Si analysis in this paper. However, procedures are not presented in detail when they can be referenced in English-language journal publications that are widely available.

11.2. TOTAL ANALYSIS

11.2.1. Gravimetric methods.

The earliest procedures used to analyze various materials for Si were based on gravimetric methods utilizing chemistry that produced either losses or increases in weight. Typical weight loss methods utilize HF to evolve Si as SiF_4 gas. Robinson (1945) used this principle to analyze for Si in soils, after first bringing Si into solution by fusion. For determining Si in an organic matrix, such as plant tissue, the organic matter can be removed by oxidation at 550 C. After solubilizing non-Si elements in 6M HCl, the sample is filtered through ashless paper that retains the Si precipitate. The paper is ignited and weighed. Then HF is used to evolve the Si, so that the weight loss is assumed to be Si.

Yoshida et al. (1976) determined Si gravimetrically in rice straw in conjunction with the analysis of other elements. After chemical oxidation of the organic matter and acid dissolution of all remaining components of the straw except for Si, the remaining residue was assumed to be SiO_2 (termed "crude silica"), which was removed by filtration. The dried precipitate was transferred to a weighing vessel, and the increase in weight was assumed to be SiO_2.

Although requiring only relatively common and simple laboratory equipment, the gravimetric methods for determining Si in plant tissue, nevertheless, are time consuming and laborious, especially if only an analysis for Si is required. Elliott et al. (1988) described a "rapid" gravimetric procedure for the determination of Si in plant tissue that reduced analysis time and handling of individual samples through the use of fritted glass Gooche crucibles. The plant material is destroyed by heat and chemical additions, and the SiO_2 residue is weighed directly in the crucible as the increase in weight over the crucible alone.

11.2.2. Spectrometric methods

The development of modern spectrographic techniques has led to the general replacement of gravimetric methods in favor of more rapid techniques that are suitable for handling large numbers of samples. Solubilization of Si-containing materials is a prerequisite for using most of these methods.

11.2.2.1. Silicon solubilization for spectrometric analysis

Silicon, in a wide variety of substances, can be solubilized by fusion with such strongly-alkaline chemicals as Na_2CO_3, NaOH, $LiBO_2$, or LiB_4O_7. Sodium hydroxide is a good choice because sample decomposition is relatively rapid and can be performed in inexpensive Ni crucibles at relatively low temperatures (Kilmer, 1965). After cooling, the flux is dissolved in acid, and Si in the resulting solution can be determined by a variety of spectrometric procedures.

Silicon, in a wide variety of substances, can also be solubilized by closed system digestion (CSD) techniques that require less attention to individual samples than fusion methods, and therefore, are well-suited to the processing of large numbers of samples. For a typical CSD dissolution technique, the sample is digested with aqua regia (HNO_3/HCl) in a sealed TFE-fluorocarbon-lined digestion vessel (sometimes termed a "digestion bomb") that is heated in an ordinary drying oven at 100 to 110 C for two hours (Jones and Dreher, 1996). After cooling, H_3BO_3 is added and the sample is reheated below the boiling point for 10 to 15 min. to aid in the dissolution of any resulting precipitate.

Elliott and Snyder (1991) developed an autoclave induced digestion (AID) procedure for solubilizing Si in rice straw, which only requires NaOH and H_2O_2 as reagents, unsealed

polyethylene tubes, and an autoclave as specialized equipment. The AID procedure is well adapted to handling batches of 40 or more samples at a time. The procedure uses the autoclave to develop pressure, rather than developing pressure in sealed digestion vessels. Bell and Simmons (1997) found no significant difference between Si analyses of a National Institutes Standards Technology (NIST) pine needle standard (no. 1575) by a variety of methods and that by the AID procedure. Recognizing the unavailability of NIST standards for Si, they used the AID procedure to determine Si in several other NIST plant sample standards as well.

Nonozamsky et al. (1984) also described a "rapid" technique for extracting Si from plant tissue. By their method, ground plant material was shaken overnight at room temperature in a solution of HCl and HF, and remaining plant debris was removed by filtration. Methods for preventing formation of less soluble fluorosilicates were discussed.

11.2.2.2. Spectrometric analysis of dissolved silicon

Although dissolved Si can be determined by atomic absorption spectrometry (AAS) using a nitrous oxide-acetylene flame (Eaton et al., 1995) or by inductively coupled atomic plasma spectrometry (ICP, ICAP) (Jones and Dreher, 1996), it is probably most often determined by either manual or automated colorimetry because of the lower cost of the instrumentation, and the lower detection limits.

Silicon is determined colorimetrically (light absorption spectrometry) either by the yellow silicomolybdic acid procedure or by the blue silicomolybdous acid procedure. The latter generally is preferred because of its greater sensitivity. The two methods are similar, except that the blue color is developed through the addition of a reducing solution. The sample containing dissolved Si is reacted with ammonium molybdate (Kilmer, 1965; Hallmark et al., 1982). Tartaric acid is added to minimize interference by P in the form of a phosphomolybdate complex. After reduction with a solution containing sodium sulfite, sodium bisulfite, and 1-amino-2-naphthol-4-sulfonic acid, the intensity of the blue color that develops is measured at 650 mμ. This method will detect as little as 0.02 mg Si L^{-1} (Bunting, 1944). Both the yellow silicomolybdic acid method and the blue silicomolybdous acid procedure are presented in Standard Methods (Eaton et al., 1995) as method 4500-Si D and 4500-Si E, respectively. The latter can be conducted with automated colorimetry analytical instruments (Method 4500-Si F in Eaton et al., 1995), which is useful for large sample numbers.

11.2.2.3. Non-destructive spectrometric methods for determining total silicon

Several modern techniques have been used to determine the total Si content of soils, plants, and fertilizers without pre-analysis solubilization of the matrix. X-ray fluorescence spectroscopy (XRFS), which also is known as X-ray emission spectrography or X-ray spectrochemical analysis, assesses the presence and concentration of Si in soil and plant materials by measuring the characteristic secondary radiation emitted from a sample that has been excited with an x-ray source (Karathanasis and Hajek, 1996). Although certain limitations exist, excellent equipment has been developed in recent years, making it possible to rapidly analyze a great variety of samples.

Near infra-red spectroscopy (NIRS) also has been used to non-destructively determine Si in various materials. There is a sound chemistry basis for using this method for determining the content of water and nitrogen in samples, but for other elements and constituents the basis is less clear. Statistical associations between NIRS spectra of standard samples and unknowns can be constructed when a large data base exists for the matrix, but the correlations between

standards and the content of constituents in unknowns that have been analyzed by classical methods generally are lower than would be accepted in classical analytical chemistry. Nevertheless, because of the rapidity and simplicity of the analysis, and the relatively low cost of the equipment and improvements in the ease of operation, NIRS is becoming widely adapted for many analytical purposes, and such expansion in usage can be expected to continue. J. H. Meyer of the South African Sugar Experiment Station has been a leader in the use of both XRFS and NIRS for the analysis of Si in sugarcane leaves (Wood et al., 1985; Meyer, 1998).

11.3. CHEMICAL FORMS OF SILICON

11.3.1. Silicon in solution

Silicon can exist both as monosilicic acid and as polysilicic acid in soil solutions and soil extracts. The ammonium molybdate procedure reacts only with monosilicic acid, and therefore does not determine Si in the polysilicic acid form. Since plants are only able to absorb Si in the monosilicic acid form, it often is preferable that only this specie be measured in soil solutions and extracts. Atomic absorption spectropy and ICAP measure total Si, including monosilicic acid, polysilicic acid, and soluble organosilicon compounds. Alternatively, polysilicic acid polymers can be broken up with ultrasonification, or over time (weeks) with NaOH, and then can be determined colorimetrically. Monosilicic acid may be present both as orthosilicic acid and as metasilicic acid, but the former probably dominates in aqueous solutions. Metasilicate is more prevalent in crystalline minerals, such as wollastinite (calcium metasilicate). It should be possible to use IR spectrometry to differentiate between the two Si forms, since metasilicic acid has an oxygen-silicon double bond, whereas with orthosilicic acid all oxygens have a single bond to Si.

11.3.2. Silicon in organic compounds

Inanaga et al. (1995) provided evidence that Si in rice can exist in association with organic compounds. After suitable preparation, plant tissue was extracted with dimethylsulfoxide, and lignin-carbohydrate complexes that were analyzed for Si were precipitated with ethanol.

Organosilicon compounds can be isolated from soil solutions and extracts by selective adsorption on activated charcoal, which does not adsorb mono and polysilicic acids (Panov et al., 1989). The adsorbed organosilicon compounds then can be isolated by filtration, and the Si released by treating with NaOH and ultrasonification (Matychenkov and Snyder, 1996). ^{29}Si nuclear magnetic resonance (NMR) spectroscopy has been used to examine the structure of organosilicate coordination complexes (Kinrade et al., 1999).

11.4. PHYSICAL FORMS OF SILICON

A number of researchers have been interested in elucidating the physical forms of Si, particularly in plant tissue epidermal cells and in cell walls, but also in soils. Analysis of phytoliths, which are microscopic mineral particles, often containing Si, that are deposited within and around the cells of certain plants (Rovner, 1983), has been used to study paleosols, paleovegetation, for paleoenvironmental reconstruction, and for archaeological interpretation.

Analysis of the physical form of Si-containing phytoliths (silicophytoliths, opal phytoliths) can be used for plant identification (Ollendorf et al., 1988). A variety of silicon depositional patterns have been observed in plants, which are closely related to certain epidermal structures (Lanning and Eleuterius, 1987).

The petrological microscope has been used to examine silicified cells (Parry and Smithson, 1958; Lanning et al., 1980). Microscopic examination is made easier by partially or totally destroying the plant tissue, either with heat or chemically (Jones and Milne, 1963), or by a combination of both. The scanning electron microscope (SEM) also is used to observe Si deposits in plants after ashing tissue by heat, or chemically. Backscattered SEM images of silica bodies in leaf epidermal cells have been obtained after sonicating tissue in hexane-chloroform to remove epicuticular wax and sputter coating with gold (Whang et al., 1998). Bright dot maps of the distribution of Si in plant tissue can be obtained by combining SEM with energy-dispersive X-ray (EDX) analysis (Lanning and Eleuterius, 1987; Terrell and Wergin, 1981). Combinations of light microscopy of thin sections and SEM/EDX have been used to locate Si deposits in various ultrastructures of plants (Hodson and Parry, 1982).

Other physical analyses that have been conducted to study Si in plants include differential thermal analysis, specific gravity, refractive index, and measurement of surface area (Jones and Milne, 1963).

11.5. ASSESSMENT OF PLANT-AVAILABLE SILICON IN SOILS

Sufficient reports of improved crop yields and other benefits to Si applications have been documented in the scientific literature to suggest that Si fertilization should be considered for commercial production of rice, sugarcane (*Saccharum* sp.), and perhaps other crops. However, because of the expenses associated with Si fertilization, soil tests are needed to identify soils containing insufficient plant-available Si for optimum production. A number of Si soil tests have been investigated, with varying degrees of reliability, practicality, and commercial acceptance.

Khalid and Silva (1978) used a modified Neubauer (Stewart, 1932) biological extraction procedure to gauge the Si-supplying capacity of soils. One hundred rice seedlings were grown in 50 g of soil for 10 weeks, and Si was determined in the top growth plant tissue. Obviously, this procedure is not suitable for routine soil testing because of, among other things, the time required to complete the analysis.

Almost all soil test methods that have gained acceptance for routine use by laboratories that service commercial growers utilize an extracting solution to remove the nutrients of interest from the soil in some proportion that can be correlated with plant uptake and/or crop yield. After evaluating a variety of chemicals as extractants for Si, Imaizumi and Yoshida (1958) proposed the use of a M sodium acetate buffer (pH 4.0) for gauging plant-available Si in soils. The paper, which was written in Japanese and published in bulletin form, has been widely cited, but the details of the method are almost never given and, therefore, will be presented here. The buffer is made by diluting 49.2 ml acetic acid and 14.8 g anhydrous sodium acetate to 1 liter, and adjusting to pH 4.0 with acetic acid or sodium acetate (K. Nonaka, personal communication). Ten g of air-dried soil are placed in a 200 ml flask with 100 ml of the sodium acetate buffer. The flask is placed in a water bath for 5 hours at 40 C and shaken "occasionally". After filtering, Si in the filtrate is determined by the silicomolybdate blue

method, sometimes with modifications, has been used in Japan, Taiwan, and Korea (Lian, 1976), in China (Liang et al., 1994), India (Nayer et al., 1977), Malaysia and Thailand (Kawaguchi, 1966), and in Sri Lanka (Takijima et al., 1970). No doubt, it has been used in other countries as well, especially in conjunction with rice production. Nevertheless, in several reports (Takahashi, 1981; Takahashi and Nonaka, 1986; Nonaka and Takahashi, 1990), it was concluded that for soils previously fertilized with calcium silicate, the acetate buffer method is "too strong", i.e., it dissolves some nonavailable Si from the residual calcium silicate fertilizer. To overcome this problem, Nonaka and Takahashi (1988, 1990) developed a method for measuring water-soluble Si in rice soil that involves flooded soil incubation. By this method, a 10 g dry soil sample (air-dried and < 2 mm) is submerged in a 100 m. cylindrical bottle (about 4.5 cm i.d.) with 60 ml water and incubated at 40 C for a week, after which time the supernatant is analyzed for Si content. However, the researchers considered the 2-week period between sampling and reporting of results to be a serious disadvantage for commercial use.

Sumida (1992) developed two additional incubation methods. One requires 4 weeks of incubation at 30 C, and the other requires an unstated period of incubation of soil in a series of Si solutions of varying concentration. Because of the time requirement and complexity of these methods, neither appear suitable for use in a routine soil testing laboratory.

A number of extractants other than acetate buffer have been used in procedures that are suitable for routine soil testing. Hesse (1971) reported that H. F. Birch in East Africa found that soil fertility, as shown by yield, was significantly related to the water-soluble Si content of soils, and suggested that determinations of water-soluble Si would be very valuable in soil fertility investigations. However, no specific procedure for a Si soil test utilizing a water extract was given, which is unfortunate because Hesse also reported that J. A. McKeague found that the concentration of Si in water extracts varied with the contact time, pH, and temperature. Khalid et al. (1978) used a water extract (3 g soil, 30 ml water, 4 hours shaking) and a phosphate extract to gauge plant-available Si. For the latter test, 3 g soil was shaken for 4 hours with 30 ml 0.1 M acetic acid containing 50 mg P L^{-1} as $Ca(H_2PO_4)_2$ and adjusted to pH 3.5 with NH_4OH. It was assumed that the water extract measured the "intensity factor", and the phosphate buffer measured the "capacity factor". Multiple extractions were employed with the latter extract.

Naoto Kato (National Institute Agro-Environmental Sci., Tsukuba, Japan, 1999, personal communication) also has proposed a phosphate buffer method for measuring plant-available Si in which 5 g soil is shaken for 24 hours at 40 C with 50 ml of 0.04 M phosphate buffer (pH 6.2) solution (made by titrating 0.04M Na_2HPO_4 with 0.04 M NaH_2PO_4 to pH 6.2). After centrifugation and filtration, the Si concentration in the supernatant is measured colorimetrically. Kato reports that his proposed method is better for evaluating the Si availability to rice in paddy soils than the traditional acetate buffer method because the proposed method does not overestimate Si availability in soils that have been fertilized with Si. Apparently the buffer does not excessively solubilize residual calcium silicate, but the PO_4^{-2} displaces adsorbed SiO_3^{-2}.

Haysom and Chapman proposed the use of 0.01 M $CaCl_2$ for extracting plant-available Si from soils. Two g soil is shaken for 16 hours with 20 ml extractant in a 50 ml Nalgene tube using an end-over-end shaker. After centrifuging at 2000 rpm for 10 minutes, the supernatant is analyzed for Si. Values of 10 mg Si 100 g^{-1} soil or less are considered to have insufficient Si for maximum sugarcane production. They also evaluated 0.5 M NH_4OAc and 0.005 M H_2SO_4

as extractants for Si. These reagents were well correlated with cane yield, but Si extracted with $CaCl_2$ had the best correlation (r=0.903).

Citric acid has been used by Acquaye and Tinsley (1964) as an extractant for Si. One g soil was shaken with 50 ml extractant for 2 hours. After standing overnight, the sample was shaken for another hour, and Si determined in the supernatant.

It has been proposed that Si availability in soils can be determined on the basis of examining the ratio of Si to Al in acetic acid-ammonium acetate buffer solutions, or in 0.2 M HCl extracts, with additional consideration of Si/Fe and Al/(Si+Al+Fe) ratios, but not solely by the amount of Si extracted (Kawaguchi and Matsuo, 1958; Kawaguchi et al., 1958). However, this method does not appear to have gained much acceptance.

The University of Florida Everglades Research and Education Center, Belle Glade, provides a Si soil test for farmers growing rice on organic and sand soils in South Florida. Although developed and calibrated for rice, sugarcane growers also use the analysis. In this test, 25 ml 0.5 M acetic acid is added to 10 ml soil in a 75 ml test tube. After standing overnight, the mixture is tumbled for 2 hours on an end-over-end shaker. Following filtration, the filtrate is analyzed for Si colorimetrically, and expressed as mg Si L^{-1} soil. In a recent (presently unpublished) paper, Korndorfer and Snyder established Si soil test ranges of low (< 7 mg Si), medium (7 - 24 mg) and high (> 24). Nearly 6,000 soil samples were analyzed in 1999 by the soil test laboratory to determine the need for Si fertilization on rice and sugarcane, and requests for this analysis have grown nearly exponentially since 1994.

The fact that many extracts have been used for determining plant-available Si suggests that no one extract has been found that works equally well on all soils. Research is warranted when using any of the established extracts in a new soil area for which correlations with plant response have not been conducted. Furthermore, since air drying soil reduces the content of monosilicic acid, the plant-available Si form, because of adsorption to mineral surfaces, polymerization, and dehydration (Matychenkov and Snyder, 1996), that common precursor to soil analysis deserves examination.

11.6. ASSESSMENT OF PLANT-AVAILABLE SILICON IN FERTILIZERS

Although plant residues can be used for Si fertilization, most Si fertilization, both experimentally and commercially, is done with mineral Si sources, and most of these are calcium silicates. The calcium silicates range from fairly pure, naturally-occurring minerals, such as wollastinite, to industrial by-products from steel making or from the electric furnace production of phosphorus. Products from both processes commonly are termed "slag", although the term has been applied to a variety of materials and therefore, provides little information about the chemistry and physical properties of the material other than that it is inorganic.

The earliest wide-spread commercial fertilization of a crop, rice, with Si occurred in Japan. In that country, Si extraction with 0.5 M HCl at 30 C for 1 hour is the "official" method of gauging Si availability in slags (NIAES, 1987). However, many researchers in Japan have expressed the opinion that this method is of little value for predicting Si uptake by rice (K. Nonaka, H. Sumida, and N. Kato, personal communication), and several research reports support this contention (Takahashi, 1981; Kato and Owa, 1997). The pH 4.0 acetate buffer method of Imaizumi and Yoshida (1958) also has been proposed for gauging Si availability in slags (NIAES, 1987), even though, as has been previously stated, the method has been found

unsuitable for evaluating plant-available Si in soils that have been fertilized with calcium silicate slags, and Kato and Owa (1997) demonstrated that this method is poor.

Simple water extraction of Si in slags also has been used for estimating plant-availability. However, Kato and Owa (1997), after investigating the dissolution process of slags in flooded rice soils, modified the water extraction method to account for their findings. They pointed out that flooded rice soils generally are in the pH range of 6 - 7, and dissolved Ca is adsorbed by the rice. In the laboratory, dissolution of calcium silicate in water increases both pH and Ca concentration of the solution phase, both of which repress further calcium silicate dissolution. Therefore, these researchers developed a procedure using a weakly acidic cation exchange H-resin in the water to both moderate pH and adsorb Ca. Their procedure also is designed to prevent polymerized Si from forming. To do this, they keep the concentration of monosilicic acid below 100 mg Si L^{-1} by selecting an appropriate ratio of slag to water. Specifically, by their procedure, 0.2 g slag and 0.5 g of weakly acidic cation exchange resin (Amberlite IRC-50) in the H form are put into a 500 ml plastic bottle. After adding 400 ml distilled water, the bottle is immediately shaken for a while by hand and then by a reciprocal shaker (100 rpm) at 25 C for 96 hours. After filtration, the Si concentration in the solution is measured colorimetrically.

The author (Snyder), C. L. Elliott, and their colleagues utilized the dissolution principles elucidated by Kato and Owa (1997) in developing a "column" technique to rank mineral Si sources for plant availability. This method maintains neutral solution pH and low Ca concentration in the vicinity of the Si source, and sufficiently low dissolved Si concentration to minimize polymerization. Three g of Si source are mixed with 5.0 g medium density polyethylene and placed in a 20 ml plastic syringe. Glass wool above and below the mix is used to retain the mixture in the center of the syringe. A stopper fitted with a glass tube is inserted in place of the syringe plunger. A peristaltic pump is used to pass 0.1 M TRIS buffer (pH 7) upward through the syringe (the "column") at the rate of 1 ml min^{-1}. The total quantity of water passed through the column in each of 2 successive 24 h periods is analyzed for Si. The data are presented as Si dissolved g^{-1} Si source in each 24 hour period. A similar analysis of finely ground wollastinite is included with each analysis of candidate Si sources to serve as a reference.

We use laboratory analysis to identify promising mineral Si sources, and to reject those that appear unsuitable. However, greenhouse and field studies ultimately are required to provide absolute confidence about the Si supplying ability of the sources. For the greenhouse studies, rice is grown in pots containing a low-Si organic soil amended with various rates of candidate Si sources, including a wollastinite standard material and/or a calcium silicate slag that has been used commercially for about 10 years in south Florida. The rice is grown to maturity. The grain is harvested, but the most reliable criteria of Si availability is considered to be the concentration of Si in the "straw", which in this case is all of the top growth other than the grain. In field trials utilizing rice, both grain yield and the Si concentration of true straw, i.e., that cut by a combine, are used to evaluate the Si-supplying ability of the Si sources.

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