Chapter 2
Analysis of Silicon in Soil, Plant and Fertilizer

Abstract The first soil testing of plant-available silicon (Si) was not conducted until 1898 on Hawaiian soils. However, numerous procedures have since been developed for determination of Si content in a wide variety of materials including soils, plants and fertilizers. This chapter reviews current analytical procedures that are widely used for analysis of both total Si in soils, plants and fertilizers and plant-available Si in soils and fertilizers.

Keywords Plant available • Silicon fertilizer • Silicon analysis • Soil • Total silicon

2.1 General

Although silica bodies were isolated from various plant species in the early nineteenth century (Davy 1819; Struve 1835), the first soil test for plant-available Si was not conducted until 1898 on Hawaiian soils (Maxwell 1898). Since then, numerous procedures for determination of Si content in a wide variety of materials including soils, plants and fertilizers have been developed (Snyder 2001; Sauer et al. 2006). However, apart from the review articles by Snyder (2001) and Sauer et al. (2006), no reviews have been published with focus on comparing the published extraction techniques or methodologies for chemically and physically analysing plant materials for Si and for determining total as well as plant-available Si in soils and fertilizers. The classical methods for determining total Si content of various materials involve conversion of insoluble silicates into sodium silicate through high-temperature fusion with sodium carbonate or hydroxide or other sodic bases (Snyder 2001) followed by determination of Si by a variety of methods including gravimetry, colorimetry and absorption/emission spectroscopy. In general, all the analytical methods involve two major steps; the first one is to dissolve Si contained in the insoluble silicates and extract or isolate Si from the materials, and the second one is to gauge Si based on gravimetric methods, spectrometric methods or microscopic observation. X-ray fluorescence spectrometry (XRF) as a nondestructive technique for multielemental analysis of soil and plant materials showed even higher measurement accuracy for Si over the destructive methods based on alkaline fusion or acid

Y. Liang et al., *Silicon in Agriculture*, DOI 10.1007/978-94-017-9978-2_2

digestion (e.g. Ramsey et al. 1995; Reidinger et al. 2012); this technique, however, has not been routinely used so far. In this chapter, current methods that can be widely used are reviewed.

2.2 Analysis of Total Silicon in Soil

2.2.1 Gravimetric Methods

Gravimetric methods are classic accurate methods that are suitable for determination of total Si in a wide variety of solid materials including soils, waste materials, sewage sludge, plants, organic manures and fertilizers, etc. They require basic common and simple laboratory equipment except for the expensive platinum wares. On the other hand, they are time consuming and tedious and thus not suitable for routine analysis of a large number of samples especially if only an analysis of Si is required (Snyder 2001). Therefore, rapid and robust methods suitable for routine analyses are needed in modern laboratories. The principle and detailed procedure are listed in Table 2.1.

2.2.2 Spectroscopic Methods

The rapid development of modern spectroscopic techniques has made it possible to use more rapid and robust techniques suitable for routine analysis of large samples. However, conversion of the silicates contained in the solid samples into a soluble form of Si by using sodium carbonate (Na_2CO_3), lithium metaborate ($LiBO_2$) or sodium hydroxide (NaOH) is needed before using such spectrometric techniques (Snyder 2001). The principle and detailed procedure are listed in Table 2.2.

2.3 Analysis of Total Si in Plant Material

2.3.1 Gravimetric Methods

To analyse Si in an organic matrix, such as plant material, the organic matter should be first removed by oxidation at a high temperature (550 °C), and then the non-Si elements are solubilized by 6 M HCl followed by filtration through ashless filter paper that retains the Si precipitates. The paper is then ignited and weighed. Afterwards, HF is used to evolve Si so that the weight loss is assumed to be Si (Snyder 2001). Yoshida et al. (1976) used a gravimetric method to determine Si and other mineral elements in rice straw following the removal of organic matter by acid digestion.

Table 2.1 The principle and procedure for gravimetric methods

Principle	Procedure
Total Si includes all Si forms existing in soil, which can be dissolved by strong alkali fusion or acid digestion methods (Snyder 2001). The earliest procedures for gravimetric analysis of soil Si are based on chemical reactions that produce either losses or gains in weight. The classical Si analyses like those carried out early in the twentieth century by the Bureau of Chemistry and Soils of the US Department of Agriculture were done gravimetrically by fusing the soil samples with sodium carbonate (Na_2CO_3). The SiO_2 was then dissolved with HCl and precipitated, dehydrated and weighed (Robinson 1930). The typical weight loss methods as used by Robinson (1945) utilize HF to evolve Si contained in soils as SiF_4 gas to gauge Si in soils. Silicon is determined by dissolving the sample in diluted acid and subsequently dehydrating it to precipitate SiO_2. Because a variety of other insoluble oxides are also formed in this process, the precipitate weight is not a direct measure of the amount of Si in the sample. The treatment of the solid residue with HF results in the formation of volatile SiF_4. The decrease in weight following the loss of SiF_4 provides an indirect measure of the amount of Si in the original sample	1. Transfer exactly 1.0 g of air-dried, finely powdered soil sample to a platinum crucible, add approximately 5.0 g of anhydrous Na_2CO_3, and mix thoroughly to a uniform colour
	2. Cover additional 1.0 g of Na_2CO_3 evenly on the surface of the mixture and transfer the crucible to a muffle furnace
	3. Heat the muffle furnace to gradually raise the temperature to 950 °C for about 30 min until a tranquil melt forms
	4. Take out the crucible, swirl it gently and return it to the furnace for another 5 min
	5. Take out the crucible again and keep it on a porcelain plate on the bench
	6. After cooling, dissolve the residue in dilute HCl (1:1), add enough distilled water to completely immerse the crucible and then transfer the crucible to a large casserole
	7. Cover a watch glass on the crucible and leave it overnight on a steam bath
	8. Evaporate the solution to dryness on the steam bath and heat the residue, which contains SiO_2 and other solids, in an oven at 110 °C for 1 h
	9. Moisten the residue with HCl and repeat the dehydration. Remove any acid-soluble materials from the residue by adding 50 mL of distilled water and 5 mL of concentrated HCl
	10. Bring the solution to a boil and filter through ashless filter paper (Whatman No. 40). Wash the residue with hot 2 % (v/v) HCl followed by hot water
	11. Evaporate the filtrate to dryness twice and, following the same procedure, treat to remove any acid-soluble materials
	12. Combine the two precipitates, and dry and ignite to a constant weight at 1,200 °C
	13. After cooling in a desiccator, add 2 drops of 50 % (v/v) H_2SO_4 and 30 mL of 6 M HF. Remove the volatile SiF_4 by evaporating to dryness on a hot plate
	14. Finally, bring the residue to constant weight by igniting it at 1,200 °C
	15. Calculate the Si content based on the weight loss

According to Young (1971)

Table 2.2 The principle and procedure for spectroscopic methods

Principle	Procedures and reagents
Silicon in soil and also in a wide variety of other solid materials can be dissolved by fusion with strongly alkaline chemicals such as Na_2CO_3, NaOH, lithium metaborate ($LiBO_2$) or lithium tetraborate (LiB_4O_7). Because the fusion of samples with Na_2CO_3 involves the use of very expensive platinum crucibles at a high temperature (1,000 °C), relatively rapid fusion of soil samples with NaOH, another alkaline flux, was later recommended in inexpensive Ni crucibles at a relatively low temperature (Kilmer 1965). After cooling, the flux can be dissolved by acid (HCl or H_2SO_4), and Si in the solution can be quantified by a variety of spectroscopic techniques such as AAS or ICP (Snyder 2001). Both $LiBO_2$ and $Li_2B_4O_7$ are also used to dissolve Si compounds in soils because both of these chemicals are acidic compounds that can easily fuse silicates in soil. In either case, the finely ground soil is intimately mixed with the Li and Na fluxes with the mixture fused in a platinum or graphite crucible over a burner or in a muffle furnace. Clear glasses are formed with the Li fluxes and the opaque light-coloured fusion cakes are formed with the sodium fluxes. The fused material is dissolved to form a clear solution for subsequent analysis (Jones and Dreher 1996; Meyer and Bloom 1993)	(a) Sample preparation by NaOH fusion method
	1. Transfer 5 mL portions of 30 % NaOH solution to a series of 75-mL nickel crucibles cleaned with diluted HCl prior to use
	2. Evaporate the solutions to dryness over gas burners or electric heaters. Slight spattering can be ignored
	3. Accurately weigh (to the nearest 0.1 mg) 50 mg of each sample of silicate powder and two 50 mg portions of standard sample (feldspar). As each portion is weighed, transfer them to a crucible containing the fused NaOH
	4. Cover and heat the crucibles to dull redness for about 5 min. Remove each crucible from the heat and swirl the melt around the sides. Allow the melts to cool
	5. Transfer the crucibles plus contents to a series of 1-L plastic beakers
	6. Add about 980 mL of distillate water to each beaker (the exact amount is not important except that the same amount must go into each beaker). Allow to stand for at least 1 h
	7. Stir the contents of each beaker using a plastic stirring rod
	8. Add 20 mL of diluted HCl (1:1) to each beaker, stirring each at the time of addition
	9. Use nichrome tongs to lift each nickel crucible out and examine it; there should be no adhering melt. If any melt remains, allow some more time for dissolution with frequent stirring. When all the melts are dissolved, remove the crucibles and set them aside for washing with HCl before storing them. When the crucibles are removed, the solutions are ready to be used for spectroscopic determination of Si
	(b) Determination of Si by molybdenum blue method
	1. Transfer 8 mL of the reagent blank solution, 8 mL of each standard solution and 8 mL of each sample solution to 150-mL plastic beakers
	2. Add 25 mL of acidified water to each beaker
	3. Add 25 mL of the molybdate reagent to each beaker and leave it for 10 min
	4. Add 23 mL of the tartaric acid solution to each beaker
	5. Add 25 mL of the reducing solution to each beaker and leave it for at least 45 min
	6. Determine the percent transmission for each solution at 640 nm using the reagent blank as the reference, or read calculated Si concentration using an automated spectrophotometer

	Reagents[a]:
	1. Ammonium molybdate solution: dissolve 6.0 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 1,000 mL of distilled water
	2. Tartaric acid solution: dissolve 16 g of $H_2C_2H_4O_6$ in 1,000 mL of distilled water
	3. Acidified water: add 5 mL of 1:1 H_2SO_4 to 950 mL of distilled water
	4. Reducing solution: place 0.28 g of sodium sulphite, 3.6 g of sodium bisulphite and 0.06 g of 1-amino-2 napthol-4-sulphonic acid into a 1,000-mL bottle, add approximately 950 mL of distilled water, stir to dissolve, and fill the bottle up to the mark with distilled water

[a] Note: Highly consistent results are readily obtained when these solutions are prepared fresh, not more than 48 h before use

2.3.2 *Spectrometric Methods*

Spectrometric methods used widely for Si determination normally include colorimetric, atomic absorption spectrometric (AAS) and inductively coupled plasma spectrometric (ICP) assays of Si following alkaline- or acid-based digestion of plant materials. More recently, XRF, particularly portable X-ray fluorescence spectrometry (P-XRF), has been reported to be a much faster, safer, nonconsumptive and potentially more accurate method to determine Si concentrations in plant material (Reidinger et al. 2012). XRF works on the principle of excitation of inner orbital electrons by an X-ray radiation source. As the excited electrons relax to the ground state, they fluoresce, thereby ejecting photons of energy and wavelength characteristic of the atoms present. Despite several advantages of XRF over digestion-based techniques, such as its nonconsumptive nature and its higher measurement accuracy, XRF is still not routinely used for measurement of Si in plants partly due to the higher purchasing price of XRF instruments than that for equipment typically used in digestion-based techniques such as AAS or ICP (Reidinger et al. 2012).

2.3.2.1 Procedures for Sample Preparation (Table 2.3)

Table 2.3 Selected procedures for sample preparation

Method	Procedures for sample preparation
(a) Lithium metaborate fusion method (Meyer and Bloom 1993)	1. Tare 10-ml graphite crucibles and weigh 300 mg of $LiBO_2$
	2. Add 100 mg of plant tissues carefully to ensure that the sample is not in contact with the wall of the crucible
	3. Place the crucibles into a muffle furnace and heat slowly up to 485 °C over a period of 5 h to ash the plant tissues and continue to heat for 24 h at 485 °C
	4. Remove the crucibles from the oven and raise oven temperature to 950 °C
	5. Carefully mix plant ash with $LiBO_2$ with a small clean spatula
	6. Transfer the crucibles into the furnace for approximately 15 min or until the temperature returned to 950 °C using large long-handled tongs and leather gloves
	7. Remove the crucibles and place them on a heat-resistant slab to cool. At this time, the fused $LiBO_2$ and plant ash will form a small solid spherical bead
	9. Transfer the solid spherical bead into a high-density polyethylene plastic bottle containing 50 mL or 100 mL of 2 M HCl. Larger volumes of acid can be used if the sample is expected to contain larger amounts of silica
	10. Cap the bottles and place them on a shaker for 2 h
	11. Make appropriate dilutions and determine the Si content by the molybdenum blue method

(continued)

Table 2.3 (continued)

Method	Procedures for sample preparation
(b) Autoclave-induced digestion (AID) method (Elliott and Snyder 1991)	1. Place 100 mg of straw samples milled to pass a 20-mesh screen and dried to a moisture content of <10 % into a 250-mL polyethylene tube
	2. Add 2 mL 50 % H_2O_2 and 4.5 mL 50 % (w/w) NaOH
	3. Digest the resulting suspension in an autoclave at 138 kPa for 1 h
	4. Dilute the digested sample to 50 mL with deionized/distilled water
	5. Determine Si content colorimetrically
(c) Acid digestion and alkaline dissolution method (Nayar et al. 1975)	1. Prepare 50-mL Corning glass conical flasks which are thoroughly cleaned with hot alkali followed by acids and distilled water
	2. Weigh 100 mg finely ground, oven-dried (70 °C) plant samples into the flask containing 5 mL concentrated HNO_3 or a mixture of 5 mL concentrated HNO_3, 1 mL 70 % $HClO_4$ and 0.5 mL concentrated H_2SO_4
	3. Place the flask on a hot plate for acid digestion
	4. Wait for about 30 min till the brown fumes ceases and the volume of the acid is reduced to about 2 mL (overheating and drying should be avoided)
	5. Transfer the resultant solutions carefully with repeated washings into tall stainless-steel beakers containing 1–1.5 g of anhydrous Na_2CO_3 in suspension so that there is sufficient alkali in excess after neutralization of the acid
	6. Boil the alkali suspension in the stainless-steel beaker for 3–5 min to ensure complete dissolution of silica
	7. After cooling make up the resultant solution to 250 mL for colorimetric analysis of the dissolved Si
(d) Oven-induced digestion (OID) method (Kraska and Breitenbeck 2010)	1. Weigh 100 mg of dry and ground tissue samples into a 50-mL polyethylene screw-cap centrifuge tube previously washed with 0.1 M NaOH, rinsed with distilled water and dried
	2. Add 5 drops of octyl alcohol to reduce foaming prior to adding H_2O_2 and NaOH
	3. Add 2 mL of 30 % H_2O_2 to the samples
	4. Place the tightly capped tube in a convection oven at 95 °C
	5. Remove the tube and add 4 mL of 50 % NaOH to the hot samples after 30 min
	6. Gently vortex the sample tube and tightly cap, and then return to the oven (95 °C)
	7. Remove the sample tube after 4 h and add 1 mL of 5 mM NH_4F to facilitate the formation of monosilicic acid prior to quantitative transfer to 50-mL volumetric flask
	8. Dilute to final volume with distilled water for determination of the dissolved Si

(continued)

Table 2.3 (continued)

Method	Procedures for sample preparation
(e) Tiron extraction method (Guntzer et al. 2010)	1. Weigh 0.5 g of plant sample milled to pass a 20-mesh screen into a polypropylene tube
	2. Add 30 mL of a 0.1 M Tiron (4,5-dihydroxy-1,3-benzene-disulfonic acid disodium salt, $C_6H_4Na_2O_8S_2$) solution buffered at pH 10.5 to the plant sample in the tube
	3. Place the tube in a water bath at 85 °C and horizontally shake for 1 h with the cap loosely closed to prevent evaporation
	4. Cool the tube
	5. Take 10 mL of the extraction solution and add 10 mL of 30 % H_2O_2 to destroy Tiron to reduce the matrix effect during ICP-OES analysis
	6. Shake the new solution at 85 °C in the water bath for one more hour until it was colourless
	7. Cool and filter the solution at a 0.2-μm cellulose nitrate membrane before ICP-OES analysis
(f) Hydrofluoric acid extraction method (Saito et al. 2005)	1. Weigh 500 mg of dried and milled plant samples into a 50-mL polypropylene or polyethylene bottle
	2. Add 10 mL of the extraction solution (1.5 M HF + 0.6 M HCl)
	3. Stopper the bottle, stir the content of the bottle to immerse the plant tissues in the HF solution, and let it stand for 30 min at 30 °C (1 h at 18 °C) with occasional stirring (roughly every 10 min)
	4. Add 40 mL of distilled water, stir to homogenize the content, and let plant materials settle for 20 min
	5. Take the aliquot (0.1 mL) of the clear supernatant for determination of the dissolved Si

2.3.2.2 Procedures for Si Determination

Colorimetric Methods

Silicon (Si) can be determined colorimetrically, using light absorption spectrometer either by the blue Si molybdenum method at lower Si concentrations or by the yellow Si molybdenum method at higher Si concentrations. Si in solution reacts with ammonium molybdate forming a yellow silicomolybdate complex. Silicomolybdate complex can be finally converted into a reduced silicomolybdate complex which is blue, using a reducing solution such as ammonia ferrous sulphate, ascorbic acid or a mixture of sodium sulphite, sodium bisulphite and 1-amino-2-naphthol-4-sulfonic acid. Oxalic acid or tartaric acid is added to remove phosphate interferences. These two methods are similar in principle; however, the blue molybdenum method is more popular because of its higher sensitivity (Table 2.4).

Table 2.4 Procedures and reagent preparation for colorimetric determination of Si using molybdenum blue method

Reagents	Procedure
1. Si standard solution of 50 mg L^{-1} Si by diluting 1,000 mg L^{-1} Si standard with addition of 2.5 mM HCl to adjust the pH of the solution in the range between 2 and 4	(1) Transfer 1 mL sample solution to a 50-mL volumetric flask
2. 0.5 M B solution and 0.1 M B solution form H_3BO_3 (store in plastic bottles)	(2) Add 30 mL 20 % acetic acid
3. Stock 0.5 M Mo solution from $Na_2MoO_4 \cdot 2H_2O$ (store in a polypropylene bottle)	(3) Add 10 mL ammonium molybdate solution (54 g L^{-1}, pH 7.0)
4. Stock H_2SO_4 solution (0.8 M H_2SO_4 + 0.5 M B) from concentrated H_2SO_4 and H_3BO_3	(4) Shake up to mix thoroughly and keep for 5 min
5. Working Mo solution (0.25 M Mo + 0.4 M H_2SO_4 + 0.25 M B) freshly prepared before use by combining 1 volume of the stock H_2SO_4 solution, and 1 volume of the stock Mo solution (stable for about 1 month at 5 °C)	(5) Immediately add 5 mL 20 % tartaric acid and 1 mL reducing solution containing 8 g L^{-1} Na_2SO_3, 1.6 g L^{-1} 1-amino-2-naphthol-4-sulfonic acid and 100 g L^{-1} $NaHSO_3$
6. 0.5 M citric acid (stock citric) solution with addition of 250 mg L^{-1} of benzoic acid as antiseptic	(6) Adjust to 50 mL with 20 % acetic acid and wait for 30 min
7. 0.1 M citric acid (working citric) solution from 0.5 M citric acid	(7) Measure the absorbance at 650 nm
8. 1 M tartaric acid	

According to Kilmer (1965) and Hallmark et al. (1982)

AAS and ICP Methods

In addition to colorimetric determination of Si using a light absorption spectrometer, dissolved Si can also be determined by AAS using a nitrous oxide–acetylene flame (Eaton et al. 1995) or by ICP (Jones and Dreher 1996).

2.4 Analysis of Soluble Silicon in Soil

As the total Si content is not related to the concentration of soluble Si in soils and can provide little information on soil Si availability to plants, various chemical extractants (Table 2.5; Berthelsen and Korndörfer 2005) are developed to assess Si-supplying power or plant-available Si. Currently, the chemical extracts reported to be useful in assaying plant-available Si are water (at varying soil: water ratios), sodium acetate buffer (pH 4.0), ammonium acetate (pH 4.8), dilute HCl or H_2SO_4, ammonium oxalate (pH 3.0), dilute citric acid or acetic acid, dilute $CaCl_2$, dilute phosphate plus acetate (pH 3.5), sodium phosphate buffer (pH 6.2), dilute Na_2CO_3, etc. (Gillman and Bell 1978; Fox et al. 1967; Fox and Silva 1978; Haysom and Chapman 1975; Imaizumi and Yoshidai 1958; Haysom and Kingston 2001; Kato

Table 2.5 Methods used to determine soluble and extractable soil Si

Extractant	Soil–solution ratio (or recommended weights and volumes)	Method	Suggested critical level	Reference
H_2O	Pre-wet air-dry soil at a matric suction of 0.1 bar	Incubate at 25 °C for 1 day and centrifuge at 900 g (RCF) for 1 h		Gillman and Bell (1978); Menzies and Bell (1988)
H_2O	Saturated paste		2 mg kg^{-1}	Fox and Silva (1978)
H_2O	10 g:100 mL	Continuous shaking for 4 h and centrifuge at 24,000 g (RCF)	<0.9 mg kg^{-1} (deficient)	Fox et al. (1967); Elawad et al. (1982)
			<2.0 mg kg^{-1} (marginal)	
			8.0 mg kg^{-1}	
H_2O	10 g:60 mL	'Incubation method' – shake, degas, seal bottle, incubate at 40 °C for 1 week without shaking		Takahashi and Nonaka (1986); Nonaka and Takahashi (1988, 1990)
H_2O	1:4	Supernatant method – shake, degas, fill to replace all air space, seal bottle, incubate at 30 °C for 4 weeks		Sumida (1992)
Phosphate acetate (pH 3.5) [500 mg L^{-1} P as Ca $(H_2PO_4)_2$ and 0.1 M NH_4OAC]	10 g:100 mL	Continuous shaking for 4 h and centrifuge	<50 mg kg^{-1} (deficient)	Fox et al. (1967)
			50–150 mg kg^{-1} (marginal – adequate)	
0.04 M sodium phosphate buffer (pH 6.2)	1 g:10 mL	Continuous shaking for 24 h at 40 °C		Kato and Sumida (2000)
Modified Truog [0.01 M H_2SO_4 containing 3 g L^{-1} $(NH_4)_2SO_4$]	1 g:100 mL	Continuous shaking for 30 min	<40 mg kg^{-1} (deficient)	Fox et al. (1967)
			40–100 mg kg^{-1} (marginal – adequate)	
0.1 M HCl		Intermittent shaking over 5 h at 40 °C		Nayer et al. (1977)

0.5 M NH_4OAC (pH 4.5–4.8)	5 g:100 mL	Continuous shaking for 1 h	<20 mg kg^{-1} (deficient) 20–40 mg kg^{-1} (marginal – adequate)	Fox et al. (1967), Wong et al. (1970), Ayres (1966)
			<50 mg kg^{-1} (deficient)	
0.5 M NH_4OAC (pH 4.5–4.8)	2.5 g:50 mL	2.5 g soil leached with 10 * 5 mL aliquots of extractant		Bishop (1967)
1.0 M acetate buffer, pH 4.0	10 g:100 mL	Intermittent shaking over 5 h at 40 °C		Imaizumi and Yoshidai (1958)
0.01 M $CaCl_2$	1:10	Continuous shaking for 16 h and centrifuged	<20 mg kg^{-1} (deficient – marginal)	Haysom and Chapman (1975)
0.01 M $CaCl_2$	1:25	Shaking for 7 days, with a few drops of chloroform on a reciprocal shaker at 25 °C		Wickramasinghe (1994)
0.005 M H_2SO_4	1:200	Continuous shaking for 16 h and centrifuged	<100 mg kg^{-1} (deficient – marginal)	Hurney (1973)
0.5 M acetic acid	10:25 (v/v)	2 h shaking following standing overnight	<24 mg mL^{-1} (deficient)	Barbosa et al. (2001), Snyder (2001)
0.025 M Citric acid	1:10	Intermittent shaking over 5 h at 30 °C		Ueda and Yamaoka (1959)
0.1 M Citric acid	1:50	2 h shake, rest O/N, 1 h shake, centrifuge		Acquaye and Tinsley (1965)
KH_2PO_4–KOH pH 6.5	1:10	Incubation at 40 °C without shaking 24 h		Liu (2002)

and Sumida 2000; Korndörfer et al. 2001; Nayer et al. 1977; Nonaka and Takahashi 1988, 1990). In general, the most successful extractants are acid rather than neutral or alkaline solutions (Imaizumi and Yoshidai 1958), and dissolution is further increased by chelating agents due to decreased Si sorption resulting from the lower concentration of Al and Fe in solution (Berthelsen and Korndörfer 2005). Other factors such as the method of equilibration, soil–solution ratio, temperature and pH of extractant solution are also important.

2.4.1 Acetate Buffer Method

The acetate buffer method proposed by Imaizumi and Yoshida (1958) is one of the most widely used analytical methods to assay the Si-supplying capacity in soils (Table 2.6).

By comparing various chemicals including hot hydrochloric acid, ammonium oxalate buffer at pH 3.0, 2 % sodium carbonate, 0.002 N sulphuric acid at pH 3.0, saturated carbonic acid water at pH 3.8 and sodium acetate buffer at pH 4.0 as extractants, Imaizumi and Yoshida (1958) found that more soil Si was extracted by acid than by alkaline chemicals. They further concluded that CO_2-saturated water (pH 3.8) was best suited for estimating the Si uptake by rice plants followed by the acetate buffer, and the amount of SiO_2 extracted by CO_2-saturated water was correlated nicely with that extracted by acetate buffer (pH 4.0). Considering that preparing the acetate buffer is easier, and a more stable pH can be reached during extraction, and that the acetate-extractable SiO_2 is well correlated with the amount of Si taken up by rice, Imaizumi and Yoshida (1958) suggested the use of acetate buffer as an extractant to estimate Si-supplying power in soil. Up to now, this acetate buffer extractant has been used to assess the Si-supplying capacity in soils in Japan, Chinese Taiwan (Lian 1976), China (Qin 1979; He et al. 1980; Zang et al. 1982; Ma et al. 1985; Liang et al. 1994), South Korea (Park 2001), Korea (Lian 1976), Malaysia and Thailand (Kawaguchi 1966), Ceylon (Takijima et al. 1970), India

Table 2.6 The procedure of acetate buffer method

Extractant	Procedure
1.0 M acetate buffer (pH 4.0)	(1) Put 10 g of air-dried soils (<2 mm) into a 200-mL flask
	(2) Add 100 mL 1.0 M sodium acetate buffer which is prepared by diluting 49.2 mL acetic acid and 14.8 g anhydrous sodium acetate to 1 L and adjusting to pH 4.0 with acetic acid or sodium acetate
	(3) Put the flask into a water bath at 40 °C for incubation for 5 h with intermittent shaking (once every hour)
	(4) Filtrate
	(5) Measure Si colorimetrically at 650 nm

According to Imaizumi and Yoshidai (1958)

(Nayer et al. 1977), Australia (Haysom and Kingston 2001) and Brazil (Korndörfer et al. 2001).

As the acetate buffer method involves extracting Si in soil for 5 h at 40 °C and is thus time consuming and laborious, the modified procedure in Korea involves extracting Si for 90 min at 60 °C, which is reported to be more feasible for routine analysis of soil-available Si in laboratories (Park 2001).

However, it is also reported that the acetate buffer method overestimated the Si-supplying power in soils previously fertilized with slag-based calcium silicate fertilizers (Takahashi 1981; Takahashi and Nonaka 1986; Nonaka and Takahashi 1990) and in calcareous soils (Liang et al. 1994), because this acetate buffer is strong enough to dissolve some non-available Si from the residual calcium silicate fertilizers, and it extracts additional portions of Si which may be carbonate bound but not plant available in the calcareous soils (Liang et al. 1994).

2.4.2 Water Extraction Method

To overcome overestimation problems, Nonaka and Takahashi (1988, 1990) proposed a method for measuring water-soluble Si in rice paddy soils (Table 2.7).

For soils previously fertilized with slag-based calcium silicate fertilizers, Si extracted by this new method was generally correlated better with Si in rice straw than the Si extracted by the acetate buffer method. However, this method has not been widely used for routine lab testing or for commercial use since the 2-week period between soil sampling, and reporting of results is a serious disadvantage (Savant et al. 1997; Snyder 2001). Sumida (1992) developed two additional soil incubation methods. One involves incubation of soil under flooded conditions for 4 weeks at 30 °C using a soil–water ratio of 1:4. The other method requires 5 days of incubation of soil with the addition of external silicic acid in a range from 0 to 100 mg SiO_2 kg^{-1} at 30 °C using soil–water ratio of 1:10. They serve the purpose to investigate the impacts of silicate fertilizer management on the characteristics of Si dissolution and adsorption of various paddy soils. Although these methods provide

Table 2.7 The procedure of water extraction method

Extractant	Procedure
Distilled water	(1) Put 10 g of air-dried soil sample (<2 mm) into a 100-mL polyethylene cylindrical bottle
	(2) Add 60 mL distilled water to the bottle
	(3) Shake and degas
	(4) Put the bottle in an incubator at 40 °C for 1 week without further shaking
	(5) Filtrate
	(6) Measure Si in the supernatant colorimetrically at 650 nm

According to Nonaka and Takahashi (1988, 1990) the most suitable the Si-supplying capacity indices in paddy soils previously amended with calcium silicate or organic manure and in the soils with varying clay minerals and textures, they are not suitable for use in a routine soil testing laboratory because of their longer time requirement and/or complexity (Savant et al. 1997; Snyder 2001).

2.4.3 $CaCl_2$ Extraction Method

Water extracts have often been used to assay water-soluble or readily soluble Si (Elawad et al. 1982; Fox et al. 1967; Fox and Silva 1978; Gillman and Bell 1978; Menzies and Bell 1988; Nonaka and Takahashi 1988, 1990; Takahashi and Nonaka 1986). It is reported that the water-extractable Si was significantly correlated with Si uptake by plants (Fox et al. 1967; Medina-Gonzales et al. 1988; Takahashi and Nonaka 1986). However, some researchers find that the incubation method is generally not a suitable method since the low ionic strength of the solution may cause dispersion (Elgawhary and Lindsay 1972; Lindsay 1979). Generally, as drying of soil samples results in changes in equilibrium between soluble and solid Si compounds, and as soluble Si compounds (mainly monosilicic acids) adsorbed on soil particles are dehydrated during soil drying, extracting Si with water as an extractant requires a longer period of time (Table 2.5).

Considering the resulting dispersion effect caused by the low ionic strength in the water incubation solution, Elgawhary and Lindsay (1972) recommended the use of 0.02 M $CaCl_2$ as the reactive media to equalize ionic strengths and facilitate ready flocculation of colloidal Si. According to the soil chemical equilibrium principle, Si extracted with diluted $CaCl_2$ may correspond more closely to the levels of $Si(OH)_4$ expected from solubility predictions (Lindsay 1979). Accordingly, a diluted $CaCl_2$ solution was recommended by Haysom and Chapman (1975) as an extractant to assess Si-supplying power in soils under sugarcane (Table 2.8).

The critical value is 100 mg Si kg^{-1} soil, below which Si deficiency for sugarcane is expected. They concluded that although Si extracted with either 0.5 M NH_4OAC or 0.005 M H_2SO_4 was well correlated with cane yield, 0.01 M $CaCl_2$ was the best

Table 2.8 The procedure of water extraction method

Extractant	Procedure
0.01 M $CaCl_2$	(1) Put 2 g of air-dried soil sample (<2 mm) into a 50-mL polyethylene tube
	(2) Add 20 mL 0.01 M $CaCl_2$ to the tube
	(3) Shake for 16 h
	(4) Centrifuge at 2,000 rpm for 10 min
	(5) Measure Si in the supernatant colorimetrically at 650 nm

According to Nonaka and Takahashi (1988, 1990) extractant. This method was also adopted by Wickramasinghe (1994) with some modifications. After having compared a number of extraction methods over a wide range of soil types from north Queensland in Australia, Berthelsen (2000) concluded that 0.01 M $CaCl_2$-extractable Si provided a measure of the readily available Si present in the soil solution, while NH_4OAC- and acetic acid-extractable Si fractions were likely to contain rather simple polymers affected by changes in pH, CEC and the ratio of soluble Si–Al in the soil solution. Berthelsen et al. (2003) also reported that the Si contents in sugarcane were significantly related to readily soluble soil Si extracted by 0.01 M $CaCl_2$ but were not correlated with the level of soil Si extracted by a stronger acid extractant (e.g. 0.005 M H_2SO_4).

2.4.4 *Citric Acid Extraction Method*

Ueda and Yamaoka (1959) measured soil Si-supplying capacity in degraded paddy soils where nutrients such as bases, Fe, Mn and Si were leached out by using 0.025 M citric acid, 2 % Na_2CO_3, oxalic acid and oxalate buffer and 1 M acetate buffer to extract plant-available Si. Their results showed that the straw Si was significantly correlated with citric acid-extractable Si and with acetate buffer-extractable Si, but was not well correlated to the Si extracted by other extractants. They thus proposed using citric acid as an extractant to assess the soil Si-supplying power. Later, numerous researches all over the world confirmed that 0.025 M citric acid was the most suitable extractant to assay the plant-available Si in soils. For example, by comparing 1.0 M acetate buffer extractant with three other extractants, i.e. distilled water, 0.2 M HCl and 0.025 M citric acid, Nayer et al. (1977) reported that the extracting power was in the order of 0.2 M HCl > 0.025 M citric acid > 1.0 M acetate buffer at pH 4 > distilled water, with only some exceptions in some soils. They further found that citric acid-extractable Si had the strongest correlation with the Si taken up by rice plants. Zhang and Zang (1982) also compared the differences and similarities in the analytical methods for determining plant-available Si in 28 Si-fertilized paddy soils derived from coastal marine deposits, granite, basalt, red sandstone, quaternary red earth and alluvial deposits in Guangdong, Jiangxi, Zhejiang and Jiangsu provinces of South China. They used acetate buffer, 0.01 M H_2SO_4, 0.2 M HCl and 0.025 M citric acid with intermittent shaking at 30 °C for 5 h or 1 h and at 15 °C for 15 min to extract the plant-available Si in all the soils used. The results showed that the Si amounts extracted by these extractants were all significantly correlated with the straw Si content and with the relative increase of rice yield in Si-fertilized plots. However, it was roughly calculated that the amount of Si extracted by the acetate buffer and 0.01 M H_2SO_4 was less and by 0.2 M HCl was more than the amount of Si removed by rice during the growing season and that the amount of Si extracted by citric acid was approximately equal to that removed by rice.

2.4.5 Sulphuric Acid-Extractable Method

More recently, Hong et al. (2011) also studied the effect of five extracting methods (0.025 M citric acid with continuous shaking at 30 °C for 2 h, 1 % citric acid with intermittent shaking at 30 °C for 5 h, 1 M acetate buffer with intermittent shaking at 40 °C for 5 h, 0.01 M H_2SO_4 with continuous shaking at 20 °C for 30 min and 0.2 M HCl without shaking at 40 °C for 16 h) on extraction of Si in neutral and alkaline paddy soils sampled from Heilongjiang province, Northeast China. They found that, on the average, the concentration of Si measured by 0.2 M HCl extraction was 39-fold higher than by the other methods, and the concentration of Si determined by 0.01 M H_2SO_4 extraction was almost equal to that by 0.025 M citric acid extraction. They concluded that both 0.01 M H_2SO_4 and 0.025 M citric acid were the most suitable extractants to assess the Si-supplying power in neutral and especially in alkaline soils and argued that the 'too strong' acidity and 'too long' incubation period might be the major reasons for the unexpectedly higher content of Si solubilized by the 0.2 M HCl extractant.

Kanamugire et al. (2006) compared the correlation coefficient between the amount of Si accumulated by sorghum and sugarcane in 5 acid soils and the amount of Si extracted by six different extractants (0.025 M H_2SO_4, 0.01 M H_2SO_4, 0.5 M acetic acid, 0.01 M $CaCl_2$, water and 0.5 M NH_4OAC) and found that the correlations between the total Si taken up by sorghum and sugarcane and Si extracted from soils by the extraction methods used were all statistically significant, with the 0.025 M H_2SO_4 extractant showing the best correlation with total Si uptake by plants. They also proposed that a positive response to the application of Si to be likely when the soil test level using 0.025 M H_2SO_4 is below 45 mg Si kg^{-1} for sandy soils, below 65 mg Si kg^{-1} for loamy sands to sandy clay loams and 100 mg Si kg^{-1} for clayey soils.

2.4.6 Acetic Acid Extraction Method

Barbosa et al. (2001) developed a soil testing method using acetic acid as an extractant for determining plant-available Si in paddy and sugarcane soils in South Florida, and this method has been well accepted (Table 2.9). Critical values for soil Si test ranges of low (<7 mg Si L^{-1}), medium (7–24 mg Si L^{-1}) and high (>24 mg Si L^{-1}) were established (Snyder 2001).

2.4.7 Phosphate Extraction Method

Khalid et al. (1978) proposed extracting water-soluble Si by shaking 3 g of soil with 30 mL distilled water for 4 h to measure the 'intensity factor' and using a phosphate extractant to gauge plant-available Si as the 'capacity factor'. Briefly, 3 g of soil are

Table 2.9 The procedure of acid extraction method

Extractant	Procedure
0.5 M acetic acid	(1) Scoop 10 cm^3 of air-dried and sieved (<2 mm) soil into a 75-mL plastic extraction bottle
	(2) Add 25 mL of 0.5 M acetic acid to the bottle and let the mixture stand overnight (approximately 20 h)
	(3) Shake on a reciprocating shaker (120 rpm) for 50 min
	(4) Filter and collect the extract into plastic containers
	(5) Measure Si in the supernatant by ICP-OES
	(6) Calculate Si on a soil volume basis (mg Si L^{-1}) by multiplying mg Si L^{-1} in soil extract with 2.5

According to Barbosa et al. (2001)

shaken for 4 h with 30 mL 0.1 M acetic acid containing 50 mg P L^{-1} as $Ca(H_2PO_4)_2$ at pH 3.5 (adjusted with NH_4OH). The results obtained from 5-year field trials showed that the amount of Si taken up by rice seedlings was higher than extracted by the acetic acid plus phosphate (Khalid et al. 1978). Kato and Sumida (2000) proposed a phosphate buffer method for measuring plant-available Si, in which 5 g soil is shaken for 24 h with 50 mL of 0.04 M phosphate buffer solution at pH 6.2 made by titrating 0.04 M 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 and Sumida (2000) reported a better correlation between the amount of Si taken up by rice with soil Si extracted by the phosphate buffer than by the acetate buffer method. They concluded that the phosphate buffer method was better for assessing the Si-supplying power in paddy soils than the traditional acetate buffer method because the proposed method did not overestimate Si availability in soils previously treated with calcium silicate fertilizers.

2.4.8 Alkaline Extraction Method

Alkaline wet chemical dissolution extracts such as NaOH, a strong base, and Na_2CO_3, a weak base, are frequently used to extract Si in soils. The NaOH- or Na_2CO_3-extractable Si is considered to represent the fraction of amorphous Si in soils (Foster 1953; Follett et al. 1965) and amorphous biogenically derived Si in sediments (DeMaster 1981; Mortlock and Froelich 1989; Koning et al. 2002). The principle of these alkaline-extractable methods is based on the fact that the solubility of amorphous Si increases with increasing pH values (Iler 1979). While NaOH is more often used in soils than Na_2CO_3, the latter is the most commonly used method to extract amorphous biogenically derived Si in aquatic sediments (Conley 1998). Foster (1953) used 0.5 M NaOH to extract amorphous soil Si at soil–solution ratio of 1 g : 50 mL in a boiling water bath for 4 h. Since then, this NaOH-based extraction has become a standard method to assay amorphous Si in soils. As NaOH also partly dissolves the silicate minerals, Hashimoto and Jackson (1960) proposed using 0.5 M NaOH to extract amorphous Si within 2.5 min to reduce the dissolution of silicate minerals.

Some extractants can dissolve or extract different components from certain siliceous soils. For example, dithionite–citrate–bicarbonate (DCB) (Weaver et al. 1968) and ammonium oxalate extracts (Wang and Schuppli 1986) which are originally prepared for determining crystalline and amorphous Fe also are often used for analysis of crystalline and amorphous Si.

Although numerous extractants have been proposed to assay the soil Si-supplying power all over the world, the most widely used extract is 1.0 M acetate buffer at pH 4.0 proposed by Imaizumi and Yoshidai (1958) as there are threshold or critical values below which plant response to Si fertilizers can be expected. The critical value of acetate buffer-extracted Si, below which positive response of rice to slag-based Si fertilizers can be expected, is 105 mg SiO_2 kg^{-1} in Japan, 100 mg SiO_2 kg^{-1} in Korea, 40 mg SiO_2 kg^{-1} in Chinese Taiwan (Lian 1976) and 95 mg SiO_2 kg^{-1} in China (Zang et al. 1982).

In fact, no extraction has been found to work equally well on all soils (Snyder 2001). The Si content extracted by all of the discussed extractants can only be considered as a reference index to estimate the Si-supplying power in soils, but it does not measure the exact amount of plant-available Si and should be used to make diagnosis for Si deficiency in plants together with plant Si content, the truely important variable. Research is also warranted on testing whether the Si extracted by any of the established extractants is well correlated with Si uptake by plants.

2.5 Analysis of Plant-Available Silicon in Fertilizers

Procedures for determination of total Si in soils such as alkaline fusion method can apply to analysis of Si in fertilizers. However, total Si content in Si fertilizers, which is not related to Si availability, can provide little information on plant-available Si, which is most important to assessing the quality and Si-supplying power of the fertilizers. Therefore, a powerful method for assaying plant-available Si content is needed to assess the Si-supplying capacity of the fertilizer of interest. Unfortunately, it is difficult to select a universally suitable method or extractant for assessing the Si-supplying capacity of all types of materials, all soils and soil conditions (Gascho 2001; Berthelsen and Korndörfer 2005). While a number of chemical extractants have been developed to estimate soluble or extractable Si in silicate materials, often the correlations between the Si contents in a fertilizer and a response of the Si concentrations in plants on fertilized fields are rather low (Berthelsen and Korndörfer 2005). Actually, a lot of physical and chemical properties of the materials such as pH, molar ratio of $CaO–SiO_2$ and mineral particle size can greatly influence Si solubility and plant availability (Ma and Takahashi 2002).

Up to recently, many researchers have used different extractants to assay the plant-available Si in solid fertilizers. These extractants include HCl+HF, Na_2CO_3

Table 2.10 Quantities of total and extractable Si in the waste materials tested[a]

Material	Total Si (%)	NH_4 acetate-extractable Si (g kg^{-1})	HCl-extractable Si (g kg^{-1})	Water/cation exchange resin Si (g kg^{-1})	Na_2CO_3–NH_4NO_3-extractable Si (g kg^{-1})	Na_2CO_3–NH_4NO_3 + 5 d equilibration-extractable Si (g kg^{-1})
Ca silicate	24.2	1.8 (0.78)	1.9 (0.78)	28.3 (11.7)	58.8 (24)	64.5 (27)
BF slag 1	17.3	29.9 (17.2)	49.9 (28.8)	7.2 (4.2)	3.1 (1.8)	17.2 (9.9)
BF slag 2	14.8	27.1 (18.3)	66.2 (44.7)	1.9 (1.3)	1.7 (1.1)	7.2 (4.9)
BF slag 3	16.1	31.5 (19.6)	58.1 (36.1)	1.8 (1.1)	0.17 (0.11)	0.67 (0.41)
Steel slag	5.4	25.7 (47.6)	38.3 (70.1)	11.3 (20.9)	3.63 (6.7)	4.6 (8.5)
Processing mud	6.8	33.3 (49.0)	47.9 (70.4)	3.2 (4.7)	0.14 (0.21)	0.37 (0.54)
Fly ash	29.1	0.01	0.02	0.02	0.07 (0.02)	0.30 (0.10)

From Haynes et al. (2013)

[a] Percentage of total Si present in extractable form is shown in parentheses

(10 g L^{-1}) + NH_4NO_3 (16 10 g L^{-1}), citric acid (50 g L^{-1}), HCl (0.5 mM) and ammonium citrate (Buck et al. 2011; Korndörfer and Pereira 2011; Sebastian et al. 2013). Based on the correlation coefficients, the best extractant for available Si in solid fertilizers was Na_2CO_3 + NH_4NO_3, while for liquid fertilizers, HCl + HF was found to be superior for total Si assessment (Buck et al. 2011; Korndörfer and Pereira 2011). It is shown that the 5-day Na_2CO_3–NH_4NO_3 soluble Si extraction method can be applied to quantify the plant-available Si in solid fertilizer products at levels ranging from 0.2 to 8.4 % Si, and the single-laboratory validation of the 5-day Na_2CO_3–NH_4NO_3 soluble Si extraction method has been approved by the Association of American Plant Food Control Officials for testing nonliquid Si fertilizer products (Sebastian et al. 2013) and the Association of American Plant Food Control Officials (AAPFCO) (Korndörfer and Pereira 2011).

Given in Table 2.10 are quantities of total and extractable Si in the waste materials tested (Haynes et al. 2013). The data listed in Table 2.10 clearly indicate that the total Si was over 20 % in fly ash and Ca silicate and between 14 % and 18 % in the BF slags, while it ranged from 5.4 % in the steel slag to 6.8 % in the processing mud. The water/exchange resin method extracted 11.7 % of total Si from Ca silicate, but ammonia acetate and HCl extracted < 1 %. The two Na_2CO_3–NH_4NO_3 methods extracted the greatest proportions of total Si from the Ca silicate (i.e. 24 % and 27 %). In the BF slags, approximately 17 %–20 %, 28 %–44 %, 1 %–5 %, 0.17 %–3.1 % and 0.67 %–17 % of total Si were extracted by ammonium acetate, HCl, water/exchange resin, Na_2CO_3–NH_4NO_3 and Na_2CO_3–NH_4NO_3 plus a 5-day equilibration, respectively. Although the total Si was lower in steel slag and processing mud than in the BF-slag samples, the proportions of ammonia acetate- and HCl-extractable Si were much greater in steel slag and processing mud than in the BF-slag samples. This was also true for the water/exchange resin extraction for steel slag. For the Na_2CO_3–NH_4NO_3 method, adding 5 days of equilibration prior to Si analysis could extract greater amount of Si from all the materials tested. Haynes et al. (2013) draw a conclusion that the BF slags tested are the most effective as sources of Si fertilizer and that, in slag-amended soils, $CaCl_2$ and NH_4OAC are the most reliable soil test extractants.

2.5.1 Acid Extraction Methods

The earliest widespread commercial Si fertilizer used for rice crop in Japan is slag-based calcium silicate (Ma and Takahashi 2002). Si extraction with 0.5 M HCl at 30 °C for 1 h is proposed as an 'official' method of gauging Si availability in slags in Japan (NIAES 1987; Ma and Takahashi 2002). In China, this procedure is also a commonly used method to gauge the plant-available Si in Si materials (Wang et al. 1995; Li et al. 2004). Wang et al. (1995) reported that both 0.5 M HCl and 2 % citric acid could be satisfactorily used to assess plant-available Si content in fertilizers. The amount of Si extracted by 0.5 M HCl was higher than that by 2 % citric acid. The amounts of plant-available Si extracted from different slag-based calcium silicates by 0.5 M HCl and 2 % citric acid at 30 °C were strongly correlated with the increment of the plant-available Si in both alluvial deposit- and red soil-derived paddy soils fertilized by slag-based calcium silicates. Considering that plant roots release organic acids to the rhizosphere, Wang et al. (1995) believe that citric acid is recommended as a more suitable extractant to estimate plant-available Si in fertilizers. It was reported that, however, Si extraction with 0.5 M HCl at 30 °C for 1 h was not an appropriate procedure to predict Si uptake by rice as the amount of Si extracted from the Si fertilizer was not related to the Si uptake by plants (Takahashi 1981; Kato and Owa 1997; Snyder 2001).

2.5.2 Acetate Buffer Method

The 1.0 M acetate buffer at pH 4 method proposed by Imaizumi and Yoshidai (1958) has also been recommended for assessing Si availability in slags (NIAES 1987). However, this method has been found unsuitable for gauging plant-available Si in soils fertilized by slag-based calcium silicate (Takahashi 1981; Takahashi and Nonaka 1986; Nonaka and Takahashi 1990).

2.5.3 Acidic Cation Exchange Method

Kato and Owa (1997) also demonstrated that the acid extraction method commonly used in Japan was unsuitable for gauging available Si content in slag-based calcium silicate fertilizers. They developed a procedure using a weakly acidic cation exchange H^+-resin (Table 2.11).

This method is reported to provide the best indicator of plant-available Si in the fertilizer, and the Si extracted is correlated well with both the indirect chemical

Table 2.11 The procedure of acidic cation exchange H-resin method

Extractant	Procedure
Acidic cation exchange H-resin	(1) Put 0.2 g air-dried and sieved (<2 mm) slag into a 500-mL plastic extraction bottle
	(2) Add 0.5 g of weekly acidic cation exchange H-resin (e.g. Amberlite IRC-50) into the bottle
	(3) Add 400 mL distilled water
	(4) Immediately shake the bottle for a while by hand
	(5) Shake on a reciprocating shaker at 100 rpm at 25°C for 96 h
	(6) Filter and collect the extract into plastic containers
	(7) Measure Si in the supernatant colorimetrically at 650 nm

According to Kato and Owa (1997), also see Snyder (2001)

Table 2.12 The procedure of column method

Extractant	Procedure
Acidic cation exchange H-resin	(1) Put 3 g of silicon source and 5.0 g medium-density polyethylene into a 20-mL plastic syringe slag and mix
	(2) Use glass wool above and below the mix to ensure that the mixture is retained in the centre of the syringe
	(3) Insert a stopper fitted with a glass tuber in place of the syringe plunger
	(4) Use a peristaltic pump to pass 0.1 M TRIS buffer (pH 7) upwards through the syringe (the 'column') at a rate of 1 mL min^{-1}
	(5) Collect the water solutions passing through the column in each of 2 successive 24-h periods for analysis of Si
	(6) Use a similar analysis of finely ground wollastonite with each analysis of candidate Si sources to serve as a reference

According to Snyder (2001)

extraction results and also soil and plant Si and yield in the pot experiments (Kato and Owa 1997). Pereira et al. (2003) also tested this 'resin' method and found it to give the highest correlation between Si extracted from 12 different sources of Si materials and Si uptake by rice.

2.5.4 'Column' Method

Snyder (2001) and his colleagues also developed a 'column' method to compare mineral Si sources on the basis of plant availability of Si, maintenance of neutral solution pH, low Ca concentration near the Si source and sufficiently low dissolved Si concentration to minimize polymerization (Table 2.12). However, Si laboratory analysis to identify promising mineral Si sources is required to correlate with both the crop responses and crop Si uptake through greenhouse and field trials to ultimately assess the Si-supplying capacity of the sources.

2.5.5 *Sodium Carbonate–Ammonium Nitrate Method*

More recently, Sebastian et al. (2013) have developed a 5-day method for determining the soluble Si concentrations in nonliquid fertilizer products using a $Na_2CO_3 + NH_4NO_3$ extractant followed by visible spectroscopy with heteropoly blue analysis at 660 nm. This 5-day Na_2CO_3–NH_4NO_3 soluble Si extraction method has recently been approved by the Association of American Plant Food Control Officials (AAPFCO) for testing nonliquid Si fertilizer products (Sebastian et al. 2013) (Table 2.13).

Table 2.13 The procedure of 5-day Na_2CO_3–NH_4NO_3 soluble Si extraction method

Extractant	Procedure
0.047 M sodium carbonate and ammonium nitrate solutions	(1) Grind test sample: grind fertilizer material to pass a 300-μm sieve
	(2) Weigh out a 0.2 g test portion (±0.005 g at most), transfer to a 250-mL tarred plastic flask, weigh again after transfer, and record test portion weight
	(3) Add 100 ml each of sodium carbonate and ammonium nitrate solutions (0.047 M Na_2CO_3 + 0.10 M NH_4NO_3) using a plastic graduated cylinder
	(4) Cap flask tightly and shake solution at 140 rmp (table unit) at ambient temperature for 1 h
	(5) Remove from shaker and let stand undisturbed for 5 days
	(6) Prepare a spiked talc sample by extracting talc using steps (1–5) above. Before step 4, add 3 mL 500 mg L^{-1} Si spike solution to the talc test sample. This talc-spiked test sample is processed and used for the matrix spike recovery test to verify that soluble (spike) rather than insoluble Si (talc) is extracted and reported using this method
	(7) Make a duplicate of at least one of the unknown test samples
	(8) At the end of 5 days, transfer 2 mL (4 mL for materials expected to be $<3\%$ Si) of resting extraction sample (step 5 above) to a 200-mL polypropylene volumetric flask and dilute to 200 mL with distillate water. Stopper flask and mix by inverting 10 times and pipette 20 mL of diluted test solution into a plastic test tube
	(9) Prepare Si calibration standards, blank (0 mg Si L^{-1}) and standards 1–4 (0.25, 0.50, 1.0 and 2.0 mg Si L^{-1})
	(10) Add 2 mL 0.42 M ammonium molybdate solution containing 1.84 M H_2SO_4 and mix well for 10 s using a touch agitator; wait 10 min and then add 2 ml 1.33 M tartaric acid solution. Stopper test tube and mix well for 10 s using a touch agitator. Wait 5 min and then add 2-mL 0.017 M ascorbic acid solution. Stopper test tube and mix well for 10 s using a touch agitator
	(11) Allow test sample, blank and standards to stand for 1 h for colour development. Colour gradation from blue to purple should be seen with increasing Si concentration
	(12) Measure the absorbance at 660 nm

According to Sebastian et al. (2013)

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