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Microwave Digestion for Colorimetric Determination of Total Si in Plant and Mineral Samples

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ABSTRACT

A new method for determining the soluble silicon (Si) concentrations in nonliquid plant and mineral samples was developed using sodium hydroxide (NaOH)–hydrogen peroxide (H₂O₂) matrix for microwave digestion (MWD–Na) followed by colorimetric Si testing. MWD–Na was compared with autoclave-induced digestion and alkali fusion. The data have shown no significant difference between these three methods. HNO₃–H₂O₂ or HNO₃–H₂O₂–HF microwave technique results in Si loss. The reduction of the total Si can be realized via low solubility of Si in the acid solutions or silicon tetrafluoride formation. The Mullen and Riley method for colorimetric testing of Si in a solution that uses ascorbic acid to reduce the silicomolybdate complex formed under acid conditions to an intensely blue complex was modified using iron sulfate. The combination of MWD–Na and modified colorimetric blue method provides cheap and valid data on determining the total Si in both plant and mineral samples.

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KEYWORDS

Alkali fusion; autoclave digestion; microwave digestion; plant sample digestion; silicon

Introduction

Silicon (Si) is the second most abundant element in the Earth's crust. The total content of Si in plant can range from 1 to 100 g Si kg⁻¹ of dry weight, depending on plant species (Epstein 1999). Silicon concentrations in plant tissues sometimes even exceed the concentrations of nitrogen and potassium (Epstein 1994, 2009). Beginning in 1840, numerous laboratory, greenhouse, and field experiments have shown benefits of silicon fertilization for rice (15–100%), corn (15–35%), wheat (10–30%), barley (10–40%), sugarcane (10–55%), and other crops and benefits for maintaining a sustainable agriculture (Snyder, Matichenkov, and Datnoff 2006). Si fertilization has a double effect on the soil-plant system. Firstly, improved plant Si nutrition reinforces plant protective properties against diseases, insect attacks, and unfavorable climatic conditions. Secondly, the soil treatment with Si soil amendment optimizes soil fertility through improved water, physical, and chemical soil properties and maintains nutrients in a plant-available form (Bocharnikova and Matichenkov 2014). During the last decade, the interest in Si fertilizer and Si-rich soil amendment has remarkably increased (Bocharnikova and Matichenkov 2014; Epstein 2009; Kraska and Breitenbeck 2010). Increasing of the studies in this area is accompanied by increasing volume of Si analyses. So, the demand on fast, simple, cheap, and highly informative methods for Si determination in plant tissue and Si-rich materials is actual.

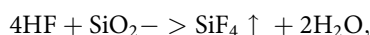
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Many procedures for determining Si content in plant tissue and Si-rich minerals have been developed. At the beginning, the gravimetric methods were used. Because plant tissue mainly consists of organic compounds, two stages in the gravimetric procedure of Si analysis were suggested. The first stage includes the removal of organic matter through sample oxidation at 550 °C. After solubilizing non-Si elements in 6 M HCl, the plant samples are filtered through an ashless paper that retains the Si precipitate. The paper is ignited and weighed. Then hydrofluoric acid (HF) is used to evolve the Si so that the weight loss is assumed to be Si (Snyder 2001).

Yoshida et al. (1976) suggested testing Si by gravimetric method after chemical oxidation of the organic matter and acid dissolution of all remaining components of the plant tissue except Si, the remaining residue was assumed to be SiO₂ (termed “crude silica”), which is removed by filtration. The dried precipitate is transferred to a weighing vessel, and the increase in weight was assumed to be SiO₂.

The development of modern spectrometry has led to the general replacement of the gravimetric methods by much more sensitive spectrometric analysis. However, this method requires the total dissolving of a test material. Such methods involving fusion are both time and labor intensive, require potentially hazardous manipulation of the molten flux, and are subject to losses by spattering during the melting process (Elliot and Snyder 1991). The hydrofluoric acid solubilization requires the use of the hazardous reagent and is also subject to Si losses as a result of the reaction:



where SiF₄ is a colorless gas, which can be dissolved in water or organic solutions (Shimizu 2001). By this means, the use of HF for dissolving Si-rich materials may lead to the loss of Si via evaporation. Elliot and Snyder (1991) suggested using NaOH–H₂O₂ digestion technique in autoclave – autoclave-induced digestion (AID). The NaOH–H₂O₂ media provides the destruction of the organic matter by hydrogen peroxide and complete dissolving of Si anions. The modified autoclave digestion method was suggested by Karska and Breitenbeck (2010), where several drops of octyl-alcohol are added prior to adding H₂O₂ and NaOH to eliminate excessive foaming.

At present, the AID is altered by microwave digestion technique (MWD) (Maher et al. 2002). The microwave instruments are cheaper and more often present in the laboratories than autoclave. MWD of the plant or mineral samples now is a routine technique in many laboratories. Many authors use MWD for total Si testing with different media: HNO₃–HF–H₂O₂ (Lajunen, Piispanen, and Saari 1992; Krushevskaya, Barnes, and Amarasiriwaradena 1993; Formento, Spadacini, and Ceserani 1994; Krushevskaya and Barnes 1994), HF (Wilson et al. 1997), HNO₃–HCl–HF (Le Blond et al. 2011), HNO₃–H₂O₂–HF–HClO₄ (Pouget, Schnautz, and Walker. 1992), HNO₃–H₂O₂ (Haysom and Ostatek-Boczkowski 2006; Karska and Breitenbeck 2010; Liu, Jorgensen, and Laerke 2013), and HCl–HF (Taber, Shogren, and Lu. 2002). However, as was described above, this method requires very accurate use of the bomb technique of MWD, because solid forms of Si can be transformed into SiF₄ gas and a part of tested Si may be lost. Secondly, because of the presence of HF, expensive equipment such as inductively coupled plasma–optical emission spectrometry (ICP-OES) or inductively coupled plasma atomic emission spectrometry (ICP-AES) is required for testing Si in the solution or additional operation in colorimetric testing is necessary (Haysom and Ostatek-Boczkowski 2006; Kraska and Breitenbeck 2010; van der Vorm 1987).

The NaOH–H₂O₂ media is potentially preferred for wet oxidation procedure in microwave digestion because it allows using colorimetric method for Si determination in solution based on ammonium molybdate.

Several modifications have been suggested to test Si in a solution colorimetrically. These methods are based on the reaction between the silicic acid (Si(OH)₄) and molybdic acid (or ammonium molybdate) at pH 1.5–2 to form the yellow isomer beta silicomolybdate (SiMo₁₂O₄₀)^{4–}. Subsequently, molybdate can be transformed to silicomolybdenum blue for increasing spectrophotometric sensitivity (Iler 1979). This allows determination of monosilicic acid concentration at a detection limit of >60 nM with a precision of ±50 nM in the 0.1–0.3–140 μM (Rimmel-Maury, Moutin, and Queguiner 2007).

The reaction with ammonium molybdate serves as a basis for several modifications of Si testing in a solution, as suggested by Bunting (1944), Mullin and Riley (1955), Eaton with coauthor (1995), Hallmark with coauthor (1982), and others. The modifications are usually aimed at eliminating the interference between soluble phosphorus and other components in the solution. In our previous investigations, we used the modified Mullen and Riley method, in which metol (4-(methyamino) phenol sulfate) as a reducing agent was changed on $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Matichenkov 2007). It is important that this method can be used for testing monosilicic acid in any natural solution, including soil solution, natural waters, and plant sap (Biel, Matichenkov, and Fomina 2008).

The aim of this investigation was to compare AID, MWD ($\text{HNO}_3\text{--H}_2\text{O}_2$ $\text{HNO}_3\text{--H}_2\text{O}_2\text{--HF}$, and $\text{NaOH--H}_2\text{O}_2$ media), and alkali fusion (AF) methods for determining total Si in plant and mineral samples.

Materials and methods

Dried rice plants for Si analysis were obtained from the Institute of Soil and Fertilizer, Hunan Agricultural Academy of Sciences (Changsha, China). Total Si was analyzed in the following plant and mineral subjects.

Rice leaf (RL) (middle part of a leaf)

Rice stem (RS) (middle part of stem without nodules)

Rice grain without husk (RG)

Amorphous silicon dioxide (chemically pure SiO_2 , Sigma-Aldrich, CAS-No. 1408–60,-7, size – 0.5–10 μm).

Zeolite (brand DSP, ZeoTradeResource Ltd., Orlov region, Russia) in powder form (10–20 μm) which contained SiO_2 – 69.0%, TiO – 0.8%, Al_2O_3 – 14.0%, Fe_2O_3 – 1.8%, MnO – 0.05%, CaO – 1.73%, MgO – 1.7%, K_2O – 5%, Na_2O – 0.9%, P_2O_5 – 0.4, pH 6.5 (the data were presented by ZeoTradeResource Ltd.).

Monosilicic acid (100 mg L^{-1} of Si) was prepared from metasilicic acid (Fisher Scientific, CAS-No 7699–41-4) by dilution with deionized water (DW).

Wet oxidation methods

Autoclave-induced digestion by Elliot and Snyder (1991)

Samples weighing 100 mg were wetted with 2 mL of 50% H_2O_2 in 100-mL polyethylene tubes previously rinsed with 0.1 M NaOH and DW. Four and a half (4.5) g of 50% NaOH at ambient temperature was added to each tube, then the tubes were gently vortexed. The tubes were individually covered with loose fitting plastic caps. The rack of tubes was placed in an autoclave at 138 kPa for 1 h. After atmospheric pressure was reached, the tubes were removed and the volume was brought to 50 mL with DW. The solution was then transferred to a 500-mL volumetric flask, made to volume, mixed well, and analyzed for Si by the modified molybdenum ammonia method.

Alkali fusion

Nickel crucibles 40 cm tall containing 500 mg of dry, ground samples were placed in a muffle furnace at room temperature, and the temperature was stepped to 600 °C over 90 min and then held for 4 h. After cooling, 2.5 g of solid NaOH was added to each crucible, and the crucibles were carefully swirled to mix the contents. The crucibles were then returned to the muffle furnace, and the temperature was stepped to 500 °C over 1 h and then held for another 30 min. After cooling, the fused contents were dissolved in 10 mL of warm DW. The contents of the crucibles were then transferred to a 300-mL plastic beaker and the excess NaOH was neutralized with 2 M nitric acid (using phenolphthalein indicator). The solution was then transferred to a 500-mL volumetric flask, made to volume, mixed well, and analyzed for Si by the modified molybdenum ammonia method.

Microwave digestion

Acid base 1 (MWD-H). One hundred (100) milligrams of dried prepared sample was weighed into each Teflon microwave digestion tube and 4 mL of concentrated HNO_3 was added. Then 2 mL of 30% H_2O_2 was added, and the tubes were immediately capped, placed in the ceramic tubs, and kept overnight. When each of the reaction vessels was assembled, the microwave rotor was placed in the cavity of the microwave (CEM MARS 6 MS5181) and the acid digestion step was conducted during 60 min. The contents of the crucibles were then transferred to a 300-mL plastic beaker and the excess acid was neutralized with 2 M NaOH (using phenolphthalein indicator). Then the solution was transferred to a 500-mL volumetric flask, made to volume, mixed well, and analyzed for Si by modified molybdenum ammonia method.

Acid base 2 (MWD-HF). One hundred (100) milligrams of dried prepared sample was weighed into each Teflon microwave digestion tube and 3 mL of concentrated HNO_3 and 2 mL of concentrated HF (40%) were added. Then 3 mL of 30% H_2O_2 was added, and the tubes were immediately capped, placed in the ceramic tubs, and kept overnight. When each of the reaction vessels was assembled, the microwave rotor was placed in the cavity of the microwave (CEM MARS 6 MS5181) and the acid digestion step was conducted during 60 min. The contents of the crucibles were then transferred to a 300-mL plastic beaker and the excess acid was neutralized with 2 M NaOH (using phenolphthalein indicator). Then the solution was transferred to a 500-mL volumetric flask, made to volume, mixed well, and analyzed for Si by modified molybdenum ammonia method.

Alkaline base (MWD-NA). One hundred (100) milligrams of dried prepared sample was weighed into each Teflon microwave digestion tube and 2.5 g of solid NaOH was added. Then 2.5 mL of DW was added and tubes were kept for 12 h. After that, 3 mL of 30% H_2O_2 was added, and the tubes were immediately capped and placed in the ceramic tubs for 1 h. When each of the reaction vessels was assembled, the microwave rotor was placed in the cavity of the microwave (CEM MARS 6 MS5181) and the alkaline digestion step was conducted during 60 min. The contents of the crucibles were then transferred to a 300-mL plastic beaker and the excess NaOH was neutralized with 2 M nitric acid (using phenolphthalein indicator). Then the solution was transferred to a 500-mL volumetric flask, made to volume, mixed well, and analyzed for Si by the modified molybdenum ammonia method.

Modified molybdenum ammonia method

Two solutions were prepared before the analysis.

Solution 1. Ammonium molybdate: 10 g of $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ was dissolved in 470 mL of DW and 30 mL concentrated HCl (30%) was added. The solution was stored in a plastic bottle.

Solution 2. Reduction solution: 20 g of oxalic acid was dissolved in 500 mL of DW and 6 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added. In parallel, 250 mL of concentrated H_2SO_4 (18 M) was carefully diluted by 250 mL DW. After air cooling of the diluted sulfuric acid, both solutions were mixed. The solution was stored in a plastic bottle.

Procedure

An aliquot of sample or Si standard solution that contains 2–40 μg Si was placed in a 50-mL volumetric flask. If pH of the aliquot was more than 4, several drops of concentrated HCl were added. Then 10 mL of Solution 1 was added. After 10 min, 10 mL of Solution 2 was added and the volume was brought to 50 mL with DW and mixed well. The absorbance of the solution was measured at 660 nm (or 880 nm) after 3 h and before 24 h. A blank that contained all reagents except the Si solution was prepared.

A suitable standard curve was established by adding 1 mL of solutions containing 0, 1, 2, 5, 10, 20, 50, 75, and 100 mg L^{-1} Si prepared from standard Si solution by dilution with DW. This standard

curve was used to determine the coefficient of correlation between absorbance reading and concentration of Si in 1 mL of aliquot (Ck). Silicon concentration was calculated as follows:

$$\text{g Si per kg dry sample} = (\text{Ad} - \text{Ablk}) \times \text{Ck} \times \text{Vd} \times 1000 / (\text{Va} \times \text{Ws}),$$

where Ad is the absorbance reading of the sample, Ablk is the absorbance of reagent blank, assuming no intercept, Vd is the final volume of solution after digestion, Va is the volume of aliquot used for colorimetric analysis, and Ws is the weight of the oven-dry sample in grams.

We used FeSO_4 as a reduction agent in the molybdenum blue technique. Considering the possible impacts this agent may have on the speed of the reaction between the monosilicic acid and ammonium molybdate or the product of this reaction may have on the activity of FeSO_4 , special test on determining optimum time interval between the application of Solution 1 (ammonium molybdate) and Solution 2 (FeSO_4) was conducted. The Si concentrations used were 10, 50, and 100 mg L^{-1} and the intervals between addition of Solution 1 and Solution 2 were 0.5, 1, 3, 5, 7, 10, 20, 30, 60, and 120 min.

Each test had five replications. Each value represents the mean \pm standard deviation (SD). An analysis of variance by the least significant difference test (95% LSD test) was performed with the Excel 2010 software to determine whether there was a significant difference ($p \leq 0.05$) between the means of treatments. The correlation coefficients were determined by Excel 2010.

Results and discussion

Modification of the molybdenum blue technique

The molybdenum blue technique for Si testing is based on two main reactions – the reaction between Si and ammonium molybdate and reduction reaction. Ammonium molybdate reacts with monosilicic acid forming a yellow color complex (Iler 1979). This complex has low sensitivity and the same color complex is formed with phosphate anion if it is present in the test solution (Iler 1979; Mullin and Riley 1955). The reduction agent (sulfate) with a high concentration of sulfuric acid transforms the yellow complex into blue complex, thus increasing sensitivity and allowing the decomposition of less-stable phosphate–molybdenum complex. Colorimetric testing is possible after 3–24 h waiting for the reduction reaction to be complete. The reduction agent also provides stopping of the reaction between the monosilicic acid and ammonium molybdate. Therefore, at the time period between adding Solution 1 and Solution 2, all monosilicic acid in the test solution is supposed to react with ammonium molybdate. As evident from our results (Figure 1), the time period of 7 min between adding Solution 1 and Solution 2 was enough for the formation and coloring of the silicon–molybdate complex. The prolongation of the time period until 2 h had no influence on the result obtained.

Wet oxidation methods

The results of total Si determination in plant and mineral samples by five different techniques of digestion are presented in Table 1. The average values of Si for each sample tested by different AID, AF, and MWD-Na techniques had no significant difference. However, the average Si content in same samples, but tested by MWD-H and MWD-HF techniques was significantly lower. The maximum difference was observed for both Si-rich minerals. Among the digestion techniques used, AID provided slightly higher Si concentrations and AF provided the lowest Si concentrations. The lowest SD was detected with both MWD methods and the highest SD was detected with AF.

The reduction of the measured total Si content in both types of samples (plant and mineral) with using MWD-H can be explained by the low solubility of Si in the acidic condition (Iler 1979). The use of HF during microwave digestion can initiate the following reaction with formation of silicon tetrafluoride as gas (Shimizu 2001). In the result, the minimum total Si content was observed in samples treated by the MWD-HF technique. Part of Si can be lost via Si evaporation.

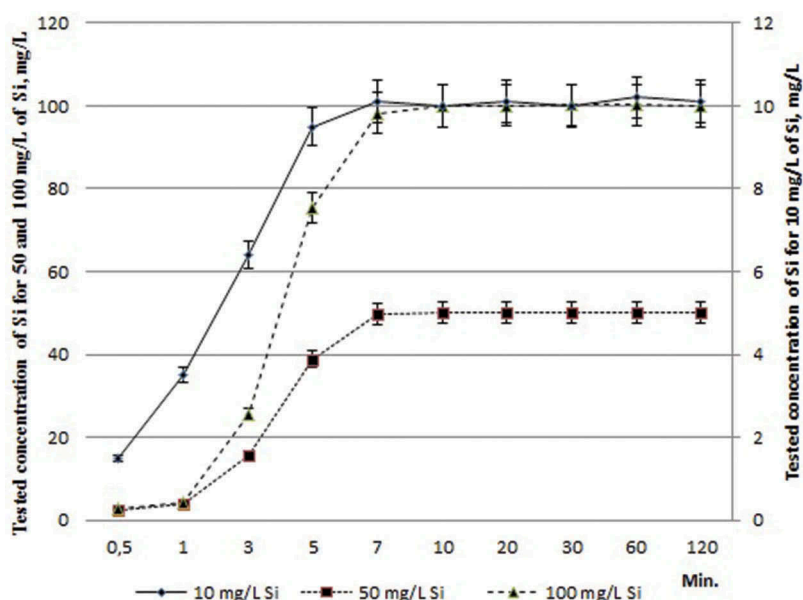


Figure 1. Results of Si determination based on the time period between adding olution 1 and olution 2 in colorimetric analysis.

Table 1. Si determined in the reference materials from various methods of digestion.

Sample	AID (n = 5)		AF (n = 5)		MWD-H (n = 5)		MWD-H-F (n = 5)		MWD-Na (n = 5)	
	Mean Si %	SD	Mean Si %	SD	Mean Si %	SD	Mean Si %	SD	Mean Si %	SD
RL	4.66	0.08	4.58	0.12	4.20	0.10	4.11	0.11	4.62	0.07
RS	3.58	0.05	3.56	0.06	3.11	0.05	3.04	0.05	3.57	0.03
RG	0.06	0.01	0.05	0.03	0.05	0.03	0.05	0.02	0.06	0.01
SiO ₂	46.72	0.19	45.91	0.21	44.02	0.20	42.30	0.20	46.64	0.17
Zeolite	32.38	0.27	32.11	0.32	30.41	0.25	29.45	0.20	32.43	0.21

The correlation coefficients between Si values determined by different methods were estimated. The coefficient of correlation between Si by AID and AF was 1.0152, by AID and MWD-Na – 1.0005, and by AF and MWD-Na – 0.9854. The coefficient of correlation between Si by AID and MWD-H and by AF and MWD-H and between Si measured by AID and MWD-HF and by AF and MWD-HF ranged between 0.9834 and 0.9921. By this means, MWD-H and MWD-HF techniques have a systematic error.

The combination of MWD-Na and modified colorimetric method can provide a simple and sensitive technique for testing total Si in both organic and inorganic samples. Only low budget equipment is necessary for this analysis, so many laboratories are able to conduct research in this area. The use of the NaOH–H₂O₂ matrix has some advantages and disadvantages. The advantages include low cost of chemicals, high sensitivity, and accuracy due to the formation of steady reaction between the monosilicic acid and molybdenum ammonia, the possibility to use such budget equipment as photometer, whereas the acid-based matrix can be used safely only with final testing by such complicated and expensive equipment as ICP-OES or ICP-AES. The NaOH–H₂O₂ matrix protects against the Si loss possible if the HF matrix is used for digestion via a potential risk of volatilization of SiF₄. One of the disadvantages of the method is that it is impossible to analyze any other metals in the obtained solution because they can precipitate in alkaline media.

Conclusions

MWD method with NaOH–H₂O₂ matrix used for testing total Si in plant and mineral samples provides more precise data than AID or AF. Iron sulfate suggested as a reduction agent for the formation of blue color silicon–molybdenum complex is more chemically stable and not expensive. The use of HF in the microwave digestion can initiate Si loss during the procedure of sample treatment.

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