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POSTER PAPER

Rapid, Wet Oxidation Procedure for the Estimation of Silicon in Plant Tissue

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Abstract: The quantification of silicon (Si) in plant samples is being requested more frequently, especially in agricultural laboratories associated with the determination of nutritional requirements of sugarcane (*Saccharum officinarum* L.) and rice (*Oryza sativa* L.). The analysis of plant material for Si can be protracted, especially if laboratories do not have access to X-ray flourescence (XRF) instrumentation and large numbers of samples are involved. A simplified procedure using equipment considered standard in most agricultural laboratories is reported. Dry, ground plant material is subjected to nitric acid/peroxide oxidation in a low-pressure laboratory microwave digestion system. The hydrated silica liberated from the organic matrix is dissolved in a small volume of sodium hydroxide solution also using the microwave digestion system. Silicon is measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). This method gives results that are linearly correlated with the much slower conventional techniques and avoids using hazardous chemicals (hydrofluoric acid) sometimes employed in other microwave methods.

Keywords: ICP-AES, microwave-assisted digestion, plant analysis, silicon

INTRODUCTION

Silicon (Si) is the second most abundant element in the earth's crust: 27% by weight. Silicon does not exist in free form but occurs as silicates or as the oxide, SiO_2. Although most plants can absorb Si during the growing phase, it has never been clearly established that Si is an essential element for optimum productivity for all plant species. However, for crops such as rice and sugarcane, the yield responses to added Si products are such that Si is

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now considered as agronomically essential for sustained production (Savant et al. 1999; Cheng 1982). The determination of Si concentration in leaf samples from sugarcane (Berthelsen, Noble, and Garside 1999) or straw samples from rice (Snyder, Jones, and Gascho 1986) provides a useful tool in developing management practices for Si applications in the field. The ability to determine Si in plant material accurately is therefore a basic requirement when evaluating yield responses to applied Si products in the field.

The traditional gravimetric method for Si analysis is slow, tedious, and not well-suited for the operations of commercial laboratories. The dry ashing and alkali fusion method (Fox et al. 1969) also has productivity problems, but the final measuring step can be automated for colorimetry, atomic absorbtion spectroscopy (AAS), or ICP-AES instrumentation. Both the gravimetric method and the dry ashing and alkali fusion method are established analytical procedures that are still reliable for the determination of total Si in biological samples.

The majority of chemical methods employed for Si analysis of plant material have been developed for use in the rice industry (Elliott and Snyder 1991) and have been utilized by the sugarcane industry as a matter of convenience. In a recent study of soil and plant Si levels in sugarcane in Australia (Berthelsen, Noble, and Garside 1999), the autoclave-induced digestion (AID) method was used to determine the Si content of leaf and stalk samples from 12 varieties of sugarcane. This method involves digesting prepared plant material with hydrogen peroxide and sodium hydroxide in an autoclave, and then analysing the digestate for Si by colorimetry (Elliott and Snyder 1991). Although the method gives reliable results for Si analysis in rice straw samples, the results obtained for sugarcane samples may be influenced by the chemistry involved, especially as the final digests are usually turbid and contain suspended solids. In a separate comparative study by BSES Limited based on 35 sugarcane leaf samples collected from different locations in North Queensland, the AID method underestimated the Si content by an average of 26.7% compared to the BSES microwave method and 26.8% compared to the dry ashing/alkali fusion method. Other investigators (Taberet, Shogren, and Lu 2002) also reported low recoveries of Si from corn stalks (12.1%), peach leaves (41.2%), and bluegrass (12.1%) by the AID method and claimed that the AID method gave consistently lower Si values when compared to alternate extraction techniques.

The method used by BSES Limited is based on a microwave-assisted nitric acid and sodium hydroxide digestion system that has been calibrated against the lithium borate fusion XRF method and the dry ashing/NaOH fusion method. Accurate and reproducible results are obtained for up to 2% Si on a dry matter basis in sugarcane tissue (Ostatek-Boczynski and Haysom 1993). The method makes use of the rapid destruction of plant material in acid mixtures contained in closed vessel systems and allows for the solubilisation of hydrated Si in the Teflon® (TFM) reaction vessels without transfer losses. The daily productivity of this method is four times

higher than the dry ashing/alkali fusion method, which, when coupled with an ICP finish, makes it a method of choice when large numbers of plant samples are submitted for analyses. The method combines existing plant digest procedures and does not rely on the use of highly hazardous hydrofluoric acid (HF) to solubilise the plant Si (Taber, Shogren, and Lu 2002; Novozamsky, van Eck, and Houba 1984). Consequently, the method does not require the use of HF-resistant nebuliser, spray chamber, and torch assembly for the ICP-AES system.

The object of this investigation was to evaluate the reliability of the BSES microwave method for the determination of Si in sugarcane, rice, and other plants belonging to the *gramineae* species, all of which are known to have a minimum Si requirement for maximum productivity. As a proposed standard method, it should be as reliable as the high-temperature lithium borate fusion XRF method or the dry ashing/sodium hydroxide fusion technique and be readily implemented by commercial soil and plant testing laboratories using modern instrumentation.

MATERIALS AND METHODS

Eight plant samples were selected for Si analysis by each of the two methods described. Two samples of rice straw were obtained from the Yanco Agricultural Institute in New South Wales. These were dried at 60°C and then ground to pass a 1-mm screen using a microhammer mill. Four samples of sugarcane material (tops, leaf, stalk, and trash), which represent the aboveground part of the plant, were also dried and ground. The two remaining samples were received dried and ground, one sample being a mixed pasture provided by the Australasian Soil and Plant Analysis Council (ASPAC) and the remaining sample being a certified reference material (CRM) from China, NCS DC 73350 poplar leaf. Each of the samples were analysed 6 times by the dry ashing/NaOH fusion method and 10 times by the microwave-assisted digestion method.

Dry Ashing/Fusion Method

Nickel crucibles 40 cm tall containing 500 mg of dry, ground plant tissue 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 (BDH pearl form) were 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 deionized water. The contents of the crucible were then transferred to a 300-ml plastic beaker and the excess

NaOH neutralised 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 ICP-AES using the 251.611-nm line. Operating conditions for the ICP are shown in Table 1.

BSES Microwave-Assisted Digestion Method

Two hundred mg of dried prepared sample were weighed into each of the 12 Teflon® microwave digestion tubes, and 3 ml of 70% nitric acid (AR grade) was added. The tubes were capped and allowed to stand for 5 min to thoroughly wet the sample. Two ml of 30% H_2O_2 (AR grade) were then added, and the tubes were immediately capped and placed in the ceramic tube holders of the Anton Paar programmable microwave system. When each of the reaction vessels was assembled, the rotor was placed in the cavity of the microwave unit and the acid digestion step conducted. (The operating conditions for the microwave system are shown in Table 1.) On completion of the cycle, the tubes were allowed to cool, and then 20 mL of 10% NaOH solution was added to the digestate. The tubes were recapped and returned to the microwave system for the second heating step, which results in the solubilisation of amorphous Si. After the final cooling step, the contents of the tubes were neutralized with 2 M nitric acid in a plastic beaker (phenolphthalein indicator) and then diluted to volume in a 500-mL

Table 1. Operating parameters for Anton Paar Multiwave microwave system and Varian Vista ICP-AES

Parameter	Value
Anton Paar Multiwave Microwave	
Rotor	12 LF 100
Power settings—acid decomposition	500 W step to 1000 W over 5 min, maintain at 1000 W over 10 min, and cool for 15 min at fan setting 2
Power settings—alkali dissolution	500 W step to 1000 W over 5 min, maintain at 1000 W over 10 min, and cool for 15 min at fan setting 2
Varian Vista RL ICP-AES	
Wavelength	Si 251.611
Power	1.25 kW
Plasma flow	15 L/min
Detector	VistaChip CCD 167–785 nm
Spray chamber	Sturman–Masters double pass
Nebulizer	V grove
Nebulizer pressure	200 kP
Autosampler	SPS-5
Sample flow rate	0.6 mls/min
Replicate read time	3 s
Replicates	3

volumetric flask with deionized water. Silicon determinations were carried out by ICP-AES using the 251.611-nm line.

Calibrating standards for the ICP-AES instrument were prepared from a 1000-mg/l standard (Merck CetiPUR, traceable to NIST) for both methods of analysis. The dry ashing/NaOH fusion standards covered the range 0–50 mg/l of Si, whereas the standards for microwave-assisted digests covered the range 0–20 mg/l of Si. Blank determinations were performed on each batch of reagents used.

RESULTS AND DISCUSSION

Very little modification to the original microwave settings was necessary during this study. Consistent results for higher Si values in the plant material analyzed were obtained when the microwave power and time settings used for the alkali digestion step were kept the same as for the initial nitric acid digestion step (Table 1). There is a strong linear relationship between the Si measured by the BSES microwave method and the Si measured by the dry ashing/NaOH fusion method ($p < 0.001$). The regression equation shown in Figure 1 has a slope of 1.0063 and an intercept of 0.0131 with a coefficient of determination of 99.98%. Therefore, when analyzing sugarcane plant material, rice straw, or pasture samples by the microwave-assisted acid and alkali digestion method, values up to 4.5% Si dry matter should be as reliable as those determined by the traditional dry ashing/NaOH fusion method.

The reproducibility tests of the microwave-assisted digestion method for the replicated analysis of the eight sample types is shown in Table 2. The CRM

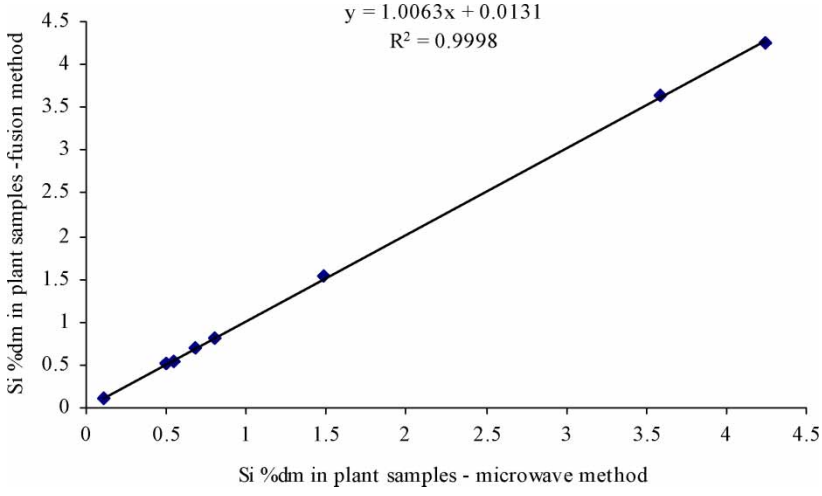

Figure 1. Relationship between Si determinations in plant samples by BSES microwave-assisted digestion and dry ashing/NaOH fusion method.

(poplar leaf) was stated as having a total Si content of 0.71% Si (SD 0.06). The dry ashing/fusion method and the microwave-assisted digestion method gave a mean value of 0.69% and 0.68% Si respectively, with a standard deviation for the microwave method of 0.027, about half that stated for the CRM. The coefficient of variation for the remaining seven samples ranged from 1.06% for the mature rice straw to 7.90% for the sugarcane stalk sample. Considering the magnitude of the mean values obtained, the microwave-assisted digestion method is capable of producing very consistent results.

The BSES microwave-assisted digestion method offers several advantages over the traditional Si analysis procedures for biological samples. The initial oxidation of plant material is rapid, and the ability to solubilise the hydrated Si in the same reaction vessel avoids transfer errors. The dangers associated with handling molten NaOH are completely avoided, and the need to have Si in a specific ionic form for colorimetric purposes is no longer necessary when ICP-AES is used for the measuring step. AAS can also be used in place of the ICP-AES to analyze the final solutions for Si, but if colorimetric methods are employed, low recoveries of Si may be obtained, especially using the microwave settings stipulated in this method. This situation was observed in the initial stages of method development when the reduced molybdenum blue colorimetric method (820 nm) was used for the measuring step. Experimenting with power settings from 600 W to 1000 W during the alkali dissolution step resulted in a measurable loss of Si recovered from the CRM. This is attributed to a secondary effect of microwave energy on the molybdate reactive form of silicon. Conducting the dissolution step on a hotplate in stainless steel beakers and sodium hydroxide can give acceptable results, but daily productivity is reduced. If atomic emission or atomic absorption methods are used at the measuring step, then any problems associated with the ionic forms of Si present in solution are overcome.

There is ample evidence in the literature that different plant species assimilate widely varying amounts of Si from the soil during the growing phase (Savant et al. 1999). Some of the organic compounds associated with the deposition of Si as opal phytoliths are difficult to degrade. The level of lignin in apple and peach leaves resulted in low recoveries of total Si even when hydrofluoric acid was included in the extracting step (Taber, Shogren, and Lu 2002). For this reason, the application of the microwave-assisted digestion method discussed here should only be applied to crops belonging to the *gramineous* species until further investigation can be carried out.

CONCLUSIONS

A previous study by BSES Limited has confirmed the reliability of the microwave-assisted digestion method for the estimation of Si in sugarcane

Table 2. Reproducibility tests for BSES microwave-assisted digestion method compared to standard dry ashing/NaOH fusion method

	Sample description							
					Sugarcane			
Method parameters	Poplar leaf, CRM[a]	Mixed pasture, ASPAC 84	Rice straw, 2 months old	Rice straw, mature	Leaf	Stalk	Tops	Trash
BSES microwave								
No. of assays	10	10	10	10	10	10	10	10
Average Si %dm	0.68	0.55	3.59	4.24	0.50	0.11	0.80	1.48
SD	0.02726	0.00957	0.10427	0.04477	0.01135	0.00876	0.02258	0.04320
CV	4.01%	1.77%	2.90%	1.06%	2.27%	7.90%	2.80%	2.95%
Dry ash/NaOH fusion								
No. of assays	6	6	6	6	6	6	6	6
Average Si%dm	0.69	0.55	3.65	4.25	0.51	0.12	0.82	1.54
SD	0.02338	0.01169	0.09138	0.05465	0.01211	0.01033	0.01414	0.05215
CV	3.39%	2.12%	2.50%	1.29%	2.37%	8.60%	1.72%	3.39%

[a]CRM, certified reference material NCS DC 73350 (poplar leaves), Si content 0.71%dm; SD 0.06.

tissue up to 2% Si dry matter. The results were confirmed by the high-temperature lithium borate fusion XRF procedure. This current study included additional plant samples (rice straw and pasture) and has confirmed that the microwave-assisted acid and alkali digestion procedure for the analysis of Si can be carried out with precision equal to that of the dry ashing/alkali fusion technique up to 4.5% Si in dry matter. The microwave-assisted acid and alkali digestion method can be implemented in plant testing laboratories servicing the rice or sugarcane industries as a standard method involving minimum chemical usage, reduced handling error, and high sample throughput.

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