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Inductively coupled plasma optical emission spectrometry as a reference method for silicon estimation by near infrared spectroscopy and potential application to global-scale studies of plant chemistry

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ABSTRACT

Inductively coupled plasma optical emission spectrometry (ICP OES) is used to produce reference calibration samples for Si determination in plants by near infrared spectroscopy (NIRS). A certified reference material (CRM) of hay was used to validate the ICP OES reference procedure, which is based on strong base digestion in an autoclave. No statistically significant difference was observed between certified and ICP OES-determined values at a 95% confidence level (*t*-test). The limit of detection (LOD) for this procedure was calculated as 10 μg/L (0.05% m/m). A calibration dataset with 346 plant samples (including grass, forbs, legumes, woody plants, and bryophytes) was analyzed by the reference procedure and the results were used to create a partial least squares (PLS) regression model to determine Si in dried, ground plant samples by NIRS. We explored options for optimizing NIRS predictive strength, and excluding bryophytes from the calibration set resulted in a PLS model with a validation R^2 of 0.83. The optimal NIRS model was then used to determine Si concentrations in more than 800 samples. Plant functional types exhibited significant variation in their Si concentration, with most legumes and woody plants presenting values below the method's LOD. Silicon concentrations in the 0.05–4.46, 0.07–1.00, and 0.11–4.67% range were found for forbs ($n = 179$), legumes ($n = 23$), and graminoids ($n = 398$), respectively. NIRS is non-destructive and requires virtually no sample preparation and almost no training prior to instrument operation. The rapid determination of Si by NIRS is a powerful strategy for global-scale analyses of plants. It is a simple, effective and relatively low-cost approach, with important implications on food crop, livestock forage and ecological theory research.

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1. Introduction

Silicon occurs ubiquitously in the Earth's lithosphere and biosphere. It is second only to oxygen in the Earth's crust and accounts for more than 25% of its mass, most commonly occurring in the form of silicate minerals [1]. In the biosphere, Si plays a vital role in many living organisms: it precipitates as solid silica (SiO_2), forming the skeletons of sponges and diatoms as well as specialized cells of plant tissue, referred to as phytoliths. Most plants accumulate relatively small amounts of Si-rich phytoliths, but some plants (*e.g.* rice, horsetail, and certain mosses) hyper-accumulate silicon, with dry weight concentrations higher than 10% m/m [2]. Although not considered an essential plant nutrient, Si is known to alleviate a broad range of abiotic stress, from drought and salinity to toxic-metal stress [3]. It may also prevent or reduce herbivory by insects and mammals [4,5], thus making it of great interest in a broad range of research.

The benefits associated with plant Si accumulation emphasize its biological significance, yet plant Si remains difficult to quantify for several reasons. Simple ashing and gravimetric determination involve many poorly controlled steps, with high potential for contamination and analyte loss [6]. On the detection end, traditional colorimetric methods, such as the one based on molybdenum blue, require the preparation of specifically-optimized reagents and are highly time-sensitive [7]. Silicon commonly occurs as solid silica deposits in a complex organic matrix within the plant tissues. A liquid solution containing the analyte is required for most instrumental analytical techniques, but releasing Si into solution from the sample matrix is no trivial task. Open-vessel digestion may be the most common approach to sample preparation for Si determination using spectrochemical methods [8,9]. However, considering the large amounts of reagents required and potential sources of contamination involved, other alternatives are usually considered. Closed-vessel microwave-assisted digestion is an efficient example of such sample preparation alternatives. It allows for a more controlled digestion environment, which minimizes contamination and analyte loss, while providing improved precision and accuracy

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[10,11]. Despite their efficiency, procedures based on closed-vessel microwave-assisted acid digestion may become cumbersome for the specific case of Si determination. Hydrofluoric acid is usually required to dissolve Si compounds. Excess fluoride in the digested sample solutions can then react with instrument components (*e.g.* quartz torches) releasing Si, which ultimately compromises accuracy and reduces the instrument lifetime. Therefore, an additional step is usually required to remove F^- from solution, *e.g.* H_3BO_3 is added after digestion to form HBF_4 and prevent reactions with glass and quartz surfaces [12,13].

Another approach to solubilizing Si compounds is based on digestion with alkaline solutions. Elliot and Snyder used a combination of NaOH and H_2O_2 to digest plant samples using an autoclave [9]. Kraska and Breitenbeck modified this procedure by adding dilute NH_4F to the digested samples to improve accuracy [14]. Barros et al. used a two-step closed-vessel microwave-assisted digestion procedure based on diluted HNO_3 and H_2O_2, and then diluted NaOH, to simultaneously determine Si and eleven other elements by inductively coupled plasma optical emission spectrometry (ICP OES). Recoveries for certified reference materials and for plant roots and leaves were in the 91–109% range [15].

Notably, all of the aforementioned methods are destructive in nature. In spite of the labor-intensive procedures and sometimes hazardous reagents required, Si solubilization and subsequent determination remain difficult, especially considering precision, accuracy and sample throughput [16,17]. Although there is a great deal of interest in plant Si research, many questions pertaining to the role of this element in natural ecosystems remain unanswered. The constraints associated with sample preparation and analysis and the consequent lack of certified reference materials for Si are largely to blame [18]. Such limitations hinder progress toward answering questions beyond the laboratory or local site scale. Addressing landscape, ecosystem, and even global-scale questions about plant Si accumulation necessitates the use of cost-effective and high-throughput methods. Recently, near infrared spectroscopy (NIRS) has been proposed as a time-efficient and accurate way to estimate plant Si [19,20]. Smis and colleagues, for example, were able to create a strong statistical calibration method based on NIRS spectra and extrapolate Si concentration for a large collection of samples with up to 95% validation (accuracy) depending upon the breadth of samples included in the calibration model [20]. NIRS is a non-destructive technique that requires minimal user training and no complex or time-consuming sample preparation, while allowing for the analysis of many samples in a reduced amount of time. It has been applied to a broad range of analytical challenges, especially for plant and soil research. For instance, functional biodiversity research has recently benefited from the use of NIRS to predict concentrations of important plant molecules including sugar, starch, and non-structural carbohydrates [21].

In the present work, we used ICP OES and a certified reference material (CRM) of hay to produce reference samples that can be used to construct NIRS calibration models for accurately predicting plant Si. The CRM was used to validate the reference method, which is based on digestion in an autoclave using NaOH, H_2O_2 and NH_4F [14], and Si determination by ICP OES. The ICP OES-based method was then used to analyze a subset of 346 samples and build a calibration dataset for NIRS. The NIRS method was used as a fast, accurate, and non-destructive strategy to determine Si in 600 plant samples from collection sites around the world.

2. Experimental

2.1. Instrumentation

A Cyclone belt drive sample mill (UDY Corp., Fort Collins, CO, USA) and a Precision drying oven (OV702F, Thermo Scientific, Dubuque, IA, USA) were used for grinding and then drying the plant samples. Sample digestion was carried out in an Amsco Renaissance 3011 autoclave (STERIS Corp., Mentor, OH, USA). A Prodigy ICP OES system (Teledyne Leeman Labs, Hudson, NH, USA) composed of an automatic sampler, a double-pass spray chamber, and a concentric nebulizer was used in all Si determinations. The ICP OES operating conditions are summarized in Table 1.

NIR spectra were measured by diffuse reflection in the 7692–3774 cm^{-1} region using a MPA FT-NIR analyzer (Bruker Optics Inc., Billerica, MA, USA). When possible, a macrosample rotator (*ca.* 15 mm) was utilized to control for within-sample heterogeneity, and a stationary microsample chamber (*ca.* 4 mm) was used when plant biomass was below the threshold required for the rotating chamber. Three individual subsamples of each dried, ground plant sample were scanned, and an average spectral signature was calculated in the R statistical programming environment [22].

2.2. Certified reference sample, standard reference solutions and reagents

A standard reference material (CRM) of hay (BCR 129, hay powder, Institute for Reference Materials and Measurements, Geel, Belgium) was used to validate the ICP OES reference method (*i.e.* alkaline digestion and Si determination by ICP OES). Concentrated HCl (Certified ACS Plus, Fisher, Pittsburgh, PA, USA) and distilled-deionized water (18.2 MΩ cm, Milli-Q, Millipore, Bedford, MA, USA) were used to prepare solutions used in the ICP OES determinations. Standard reference solutions used for calibration were prepared by dilution of a Si stock solution (1000 mg/L, High Purity Standards, Charleston, SC, USA) in 1% v/v HCl. Sodium hydroxide (NaOH, NF/FCC pellets, Fisher Scientific, Waltham, MA, USA), H_2O_2 50% v/v (Fisher), 1-octanol (Carolina Biological Supply, Burlington, NC, USA), and NH_4F (Acros Organics, Fair Lawn, NJ, USA) were used for sample digestion.

2.3. Sample collection and preparation

Plant samples were collected from a series of grassland plots around the world as part of an ongoing experimental network, the *Nutrient Network*. The standardized protocol of this collaborative project includes experimental plots which manipulate both grazing and nutrient availability in a fully factorial manner [23]. During collection, each sample was classified to plant functional type by local researchers as either graminoid, forb, legume, woody plant, or bryophyte. Plant samples were shipped to Wake Forest University where they were finely ground into a homogenous powder using a belt drive sample mill, and oven-dried at 60 °C for a minimum of 24 h prior to analysis.

After scanning all samples using NIRS, the top-ranked samples from a Kennard-Stone selection ($n = 346$) were subjected to autoclave-assisted base digestion [14]. A sample aliquot of approximately 100.0 mg was placed in a sterile 50.0 mL polypropylene tube and wetted with 1-octanol to reduce foaming and prevent incomplete digestion. Next, 2.00 mL of H_2O_2 50% v/v and 3.50 mL of a 50% m/v NaOH aqueous solution were added to each tube. Samples were briefly vortexed and immediately digested in an autoclave at 250 °C and 238 kPa for 1 h. Following digestion, samples were allowed to cool and 1.00 mL of a 5.0 mM NH_4F solution was added to each digestion tube, which were then filled to 50.0 mL with distilled-deionized water. Finally, 0.100 mL

Table 1
ICP OES operating conditions.

Instrumental parameter	Operating condition
Radio frequency (RF) applied power (kW)	1.30
Silicon analytical wavelength (nm)	251.611
Sample flow rate (mL/min)	0.60
Plasma gas flow rate (L/min)	18.0
Nebulizer pressure (psi)	30
Torch view	Axial
Integration time (s)	30
Replicates per sample	3

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