

## Lithium metaborate fusion for silicon, calcium, magnesium, and potassium analysis of wild rice

MICHAEL L. MEYER and PAUL R. BLOOM

Metropolitan Waste Control Commission, St. Paul, MN 55106, USA and Soil Science Department, University of Minnesota, St. Paul, MN 55108, USA

Received 19 January 1993. Accepted in revised form 4 June 1993

**Key words:** calcium, lithium metaborate fusion, magnesium, plant tissue, potassium, silicon, wild rice

### Abstract

A rapid batch method was developed for the analysis of Si, Ca, Mg, and K in a large number of plant tissue samples by fusion with lithium metaborate ( $\text{LiBO}_3$ ) in graphite crucibles with the use of a molybdenum blue spectrophotometric analysis of silicon and FAAS for Ca, Mg, and K. Our method was tested for whole plant analysis of mature wild rice (*Zizania palustris* L.). Analysis of Si in plant tissue with  $\text{LiBO}_3$  in graphite crucibles is reliable and fast. Thirty-six samples can be ashed overnight, fused in one hour the next day, and analyzed for Si within approximately two hours.

### Introduction

Analysis of silicon in plant tissue may be accomplished using dissolution techniques and solution analysis or gravimetrically after ashing and extraction of the soluble components of the ash. The former requires the complete dissolution of biogenic opal and possible  $\text{SiO}_2$ /organic complexes (Novozamsky, 1984). This can be accomplished by digestion with mixtures of  $\text{HNO}_3$ - $\text{HClO}_4$ -HF (Wikoff, 1986), extraction with  $\text{HCl}$ -HF without wet or dry ashing of organic material (Novozamsky, 1984), ashing with concentrated  $\text{H}_2\text{SO}_4$  in platinum crucibles and fusion with  $\text{Na}_2\text{CO}_3$  (Volk and Weintraub, 1958), and ashing overnight at  $550^\circ\text{C}$  in Ni crucibles followed by fusion with  $\text{NaOH}$  (Fox et al., 1969).

Most fusion techniques require heating individual samples over a flame to a dull redness in Pt crucibles for approximately 10 minutes to ensure complete reaction of the silica with the molten salt. The fused material is then dissolved in acid. Silicon can be determined by a silicomolybdenum blue spectrophotometric method,

flame atomic absorption spectrometry (FAAS), or, by inductively coupled plasma atomic emission spectrometry (ICP-AES). Fusion in crucibles, however, is time consuming, especially for a large number of samples, and Pt crucibles are expensive.

Digestion (wet ashing) requires destruction of plant organic matter with an oxidizing acid and dissolution of silica with HF followed by FAAS analysis or ICP-AES using an HF resistant nebulizer assembly. The commonly used silicomolybdenum blue method is not suitable for the determination of Si following digestion with HF because  $\text{F}^-$  strongly complexes silica. This procedure is flexible enough to accommodate processing of large numbers of samples in a relatively short period of time. However, a typical complaint about this method is the build-up of carbon on the FAAS burner head (Hallmark et al., 1982). This method also requires the use of HF and special procedures to prevent loss of volatile  $\text{SiF}_4$ .

A rapid gravimetric procedure for determination of Si in plant tissue requiring the oxidation of plant tissue was developed by Elliott et

al. (1988). With this procedure, finely ground dried plant tissue is placed in fritted-glass Gooche crucibles, washed with 2 M HCl, H<sub>2</sub>O, and acetone, and dried at 80 °C. The sample is ashed at 550 °C, cooled, washed as above, and dried. The remaining mass after all treatment is considered to be silica. The procedure is rapid, but requires a separate digestion for Ca, Mg, K, and other plant nutrients.

Determination of Ca, Mg, and K in plant tissue is often accomplished by digestion with mixtures of HNO<sub>3</sub>-HClO<sub>4</sub> or HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> (Wikoff, 1986), digestion with H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> (Lowther, 1980), or by ashing at 550 °C followed by addition of HCl or HNO<sub>3</sub> (Munter, 1984). Silicon cannot be directly determined by any of these methods.

Our objective was to develop a batch method for the rapid analysis of Si, Ca, Mg, and K in a large number of mature wild rice (*Zizania palustris* L.) samples by fusion with lithium metaborate (LiBO<sub>3</sub>) in graphite crucibles with the use of a molybdenum blue spectrophotometric analysis of silicon and FAAS for Ca, Mg, and K. Our method is an adaptation of techniques used for the analysis of silicate minerals (Feldman, 1983; Khalid et al., 1978; Suhr and Ingamells) and estuarine sediment (Cantillo et al., 1984). Their procedure for analysis of silicate minerals was as to carefully mix 100 mg of material with 500 mg of lithium metaborate in tared graphite crucibles (Suhr and Ingamells, 1966). The sample was heated to 950 °C for 10 to 15 minutes. The molten flux was transferred to 50 mL of 3% HNO<sub>3</sub> in a teflon container and stirred until solution was complete. Cantillo et al. (1984) followed essentially the same procedure with estuarine sediment. They found that incomplete fusion may result if sediment comes in direct contact with the graphite crucible.

### Materials and methods

Wild rice (*Zizania palustris* L.) whole plant tissue samples were obtained from a CaSiO<sub>4</sub> fertility experiment in a peat soil. Four treatments of CaSiO<sub>4</sub> were applied, 0.0 (controls), 2250, 6750, and 13500 kg ha<sup>-1</sup> with four replications. Three treatments of CaCO<sub>3</sub> (agricultural

limestone) were applied as Ca and pH controls at the same rates as CaSiO<sub>4</sub> with four replications.

At physiological maturity, plants from 1.0 m<sup>2</sup> area subplots, 3 per plot, were harvested and dried at 60 °C. Whole plant tissue samples were prepared for analysis by milling samples to pass a 1-mm sieve.

### Si analysis: Lithium metaborate fusion

Graphite crucibles (SPEX Industries), 10 mL capacity, were tared and 300 mg of LiBO<sub>3</sub> was added. One hundred milligrams of plant tissue was added, taking care that the sample was not in contact with the wall of the crucible. Eighteen to twenty crucibles were placed on flat stainless steel trays (14 gage) 14 cm by 28 cm. The edges of the trays were bent upward to provide a border one cm high to prevent the crucibles from sliding off the trays.

The trays were placed in a muffle furnace and heated slowly to 485 °C over a period of five hours to ash the plant tissue. Heating was continued for 24 hours at 485 °C. The trays were removed from the oven and the oven temperature was increased to 950 °C. During this time the plant ash was carefully mixed into the surface of the LiBO<sub>3</sub> with a small clean spatula. With large long-handled (40 to 50 cm) tongs and leather gloves one tray was placed in the furnace for approximately 15 minutes or until the temperature returned to 950 °C. The tray was removed and placed on a heat resistant slab to cool. The fused LiBO<sub>3</sub> and plant ash formed a small solid spherical bead which was dropped in 50 mL or 100 mL of 2 M HCl in a high density polyethylene plastic bottle prepared by washing with 0.1 M HCl. Occasionally, small pieces of fused LiBO<sub>3</sub> were not consolidated with the spherical bead. However, they were easily transferred to the 2 M HCl. Pouring molten LiBO<sub>3</sub>, as suggested by Cantillo et al. (1984) was difficult, dangerous, and not necessarily. Larger volumes of acid can be used if the sample is expected to contain larger amounts of silica.

The bottles were capped and placed on a shaker for two hours. Dissolution appeared to be complete in 30 to 40 minutes. Appropriate dilutions were made and the silicon content was determined by the molybdenum-blue method (Hallmark et al., 1982). Precision for the lithium

metaborate fusion method in graphite crucibles was tested in ten wild rice tissues samples analyzed in triplicate for Si over a six month period. Samples included husks, stems, leaves, and whole plant samples. Accuracy and precision of the fusion method was determined by fusion of three samples of amorphous silica ( $H_2O < 1\%$ ) which is chemically similar to opal phytoliths. Precision for the gravimetric method was determined by duplicate analysis of wild rice samples from the  $CaSiO_4$  experiment.

Subsamples of the plant tissue were sent for Si analysis to Dr. George Snyder at the University of Florida Agriculture and Research Center at Belle Glade for comparison with our results. Si was determined gravimetrically according to Elliot et al. (1988).

*Ca, Mg, and K analysis: Lithium metaborate fusion*

Wild rice was obtained from a nitrogen response study conducted in a greenhouse with pea soil. Growth and development was highly variable among treatments. Two plants were harvested at maturity from each pot, dried, and milled. Lithium metaborate fusion was conducted on all samples. Diluted solutions were analyzed for Ca, and Mg by FAAS and for K by flame emission spectrometry with standard prepared on the same solution matrix as the Si samples.

For comparison with the standard dry ash procedure used in our laboratory, dried plant samples (500 mg) from the nitrogen response study were placed in quartz crucibles and ashed at 550 °C. The ash was treated with 2 M HCl and analyzed for Ca, Mg, and K by inductively coupled plasma emission spectrometry (ICP-AES) (Munter, 1984).

Statistical analysis was conducted using STATISTIX, a microcomputer program (NH Analytical Software, Roseville, MN). Confidence intervals and significance at the 95% level.

**Results and discussion**

The accuracy and precision for the determination of Si in amorphous silica, with a Si content of 46.7%, was 45.5% with a coefficient of variation of 4.7% (n = 3). The triplicate analysis of 10 wild rice samples with Si contents of 1.3 to 4.7% resulted in coefficients of variation ranging from 1.1 to 8.2% for analysis repeated over a period of several months. Improvement in precision for Si could probably be achieved with a combination of finer milling of plant tissue and ashing of 200 mg rather than 100 mg of sample.

A comparison of the lithium metaborate results for Si in wild rice tissue with the gravimetric method is shown in Figure 1 ( $r^2 = 0.95$ , SE = 0.22). The slope and intercept, with confidence

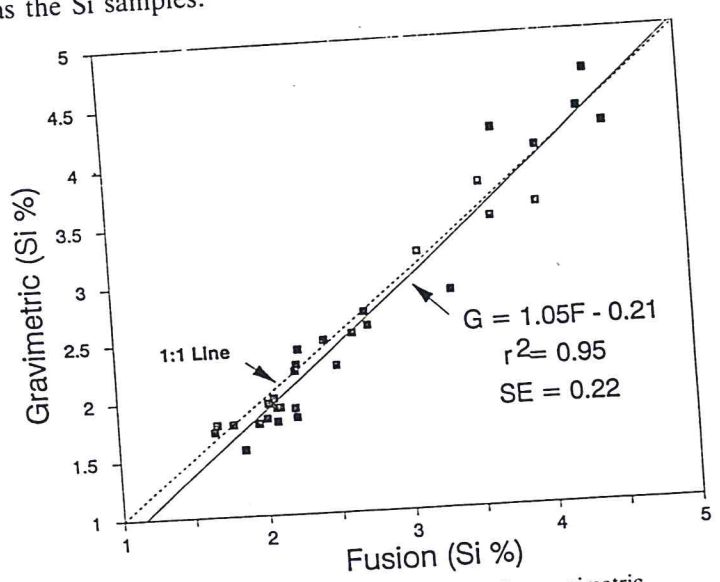


Fig. 1. Si in wild rice tissue. F = fusion, G = gravimetric.

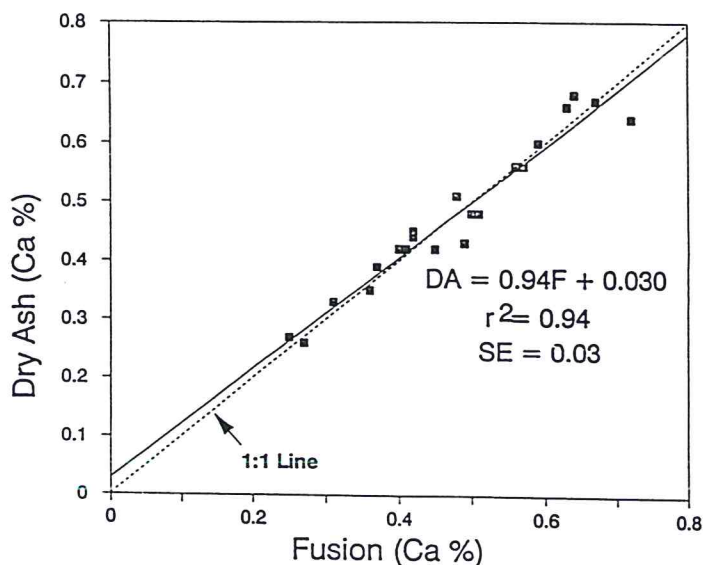


Fig. 2. Ca in wild rice tissue: dry ash vs. fusion.

intervals (Table 1), indicate no significant difference between the two analytical techniques.

The plot in Figure 1 and the intercept value in Table 1, however, suggest a tendency for Si concentrations to be lower with the gravimetric method at low plant Si content. Perhaps the small amount of Si dissolved in the washing is significant for the low ash samples.

Results of Ca, Mg, and K analysis by dry ashing and ICP analysis vs. lithium metaborate fusion and FAAS are presented in Figures 2, 3, and 4, respectively, with the coefficient of simple

determination ( $r^2$ ) and standard error of mean (SE). Linear regression analysis indicates that both methods provide similar results for the elemental content of wild rice tissue. Slopes and intercepts are equal to 1.0 and 0.0, respectively, for Ca and Mg. The slope for the K plot is 1.0, the intercept confidence interval of the K plot is 0.029 to 0.195, suggesting that for very low K contents the dry ash procedure may give slightly higher values.

Analysis of Si in plant tissue with  $\text{LiBO}_3$  in graphite crucibles is reliable and fast. Thirty-six

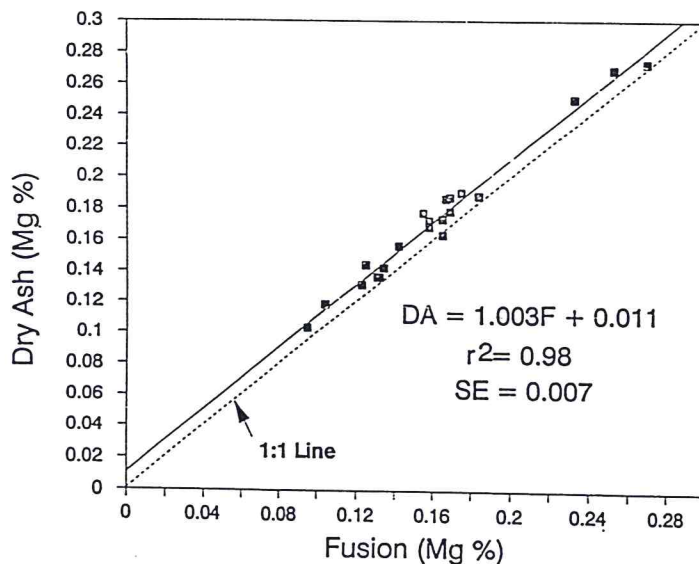


Fig. 3. Mg in wild rice tissue: dry ash vs. fusion.

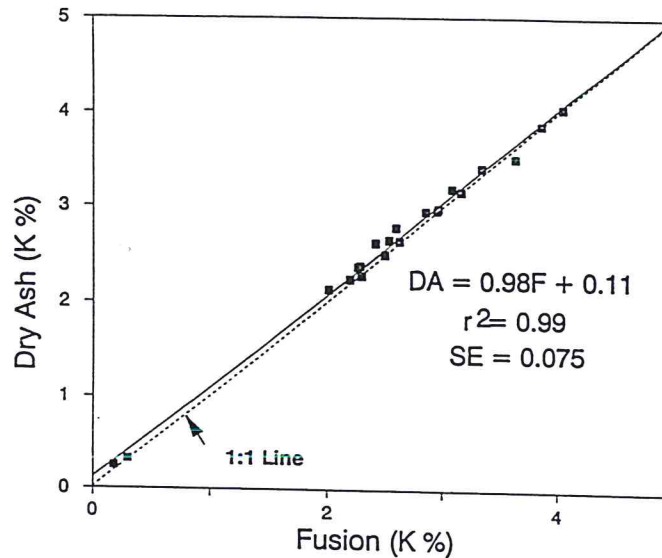


Fig. 4. K in wild rice tissue: dry ash vs. fusion.

Table 1. Linear regression results comparing dry ashing and ICP analysis vs. lithium metaborate fusion and FAAS analysis for Si, Mg, Ca, and K

Element	Regression analysis	Slope ( $\pm$ )	Intercept ( $\pm$ )
Si	$G = 1.05 F - 0.21$	0.093	0.27
Ca	$DA = 0.9 F + 0.03$	0.09	0.04
Mg	$DA = 1.003 F + 0.011$	0.057	0.042
K	$DA = 0.98 F + 0.11$	0.03	0.083

G = gravimetric analysis.

DA = dry ash.

F = samples prepared by  $\text{LiBO}_3$  fusion.

samples can be ashed overnight, fused in one hour the next day, and analyzed for Si within approximately two hours. The technique can also be used for analysis of Ca, Mg, and K in plant tissue.

### Acknowledgements

We would like to thank Dr George Snyder, Everglades Research and Education Center, University of Florida, Belle Glade, FL, for his help and cooperation in this project.

### References

Cantillo A Y, Sinex S A and Helz G R 1984 Elemental analysis of estuarine sediments by lithium metaborate

fusion and direct current plasma emission spectrometry. *Anal. Chem.* 56, 33-37.

Elliott C L, Snyder G H and Jones D B 1988 Rapid gravimetric determination of Si in rice straw. *Commun. Soil Sci. Plant Anal.* 19, 1543-1550.

Feldman C 1983 Behavior of trace refractory minerals in the lithium metaborate fusion-acid dissolution procedure. *Anal. Chem.* 55, 2451-2453.

Fox R L, Silva J A, Plucknett D L and Teranishi D Y 1969 Soluble and total silicon in sugar cane. *Plant and Soil* 30, 81-92.

Hallmark C T, Wilding L P and Smeck N E 1982 Silicon. *In* Methods of Soil Analysis. Part 2. Eds. A L Page, R H Miller and D R Keeney. 2nd ed. *Agronomy* 9, 263-273.

Khalid R A, Silva J A and Fox R L 1978 Residual effects of calcium silicate in tropical soils: I. Fate of applied silicon during five years cropping. *Soil Sci. Soc. Am. J.* 42, 89-94.

Lowther J R 1980 Use of a single  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$  digest for the analysis of *Pinus radiata* needles. *Commun. Soil Sci. Plant Anal.* 11, 175-188.

Munter R C, Halverson T L and Anderson R D 1984 Quality assurance for plant tissue analysis by ICP-AES. *Commun. Soil Sci. Plant Anal.* 15, 1285-1322.

Novozamsky R and Houba V J G 1984 A rapid determination of silicon in plant material. *Commun. Soil Sci. Plant Anal.* 15, 205-211.

Suhr N H and Ingamells C O 1966 Solution technique for analysis of silicates. *Anal. Chem.* 38, 730-734.

Volk R J and Weintraub R L 1958 Microdetermination of silicon in plants. *Anal. Chem.* 30, 1011-1014.

Wikoff L R and Moraghan J T 1986 Determination of plant iron, manganese and zinc by wet ashing procedures. *J. Sci. Food Agric.* 37, 839-844.

Section editor: H. Lambers

of mean  
cates that  
s for the  
slopes and  
spectively,  
plot is 1.0,  
the K plot is  
very low K  
ive slightly

$\text{LiBO}_3$  in  
Thirty-six