A Procedure for Rapid Determination of the Silicon Content in Plant Materials

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An efficient, reliable and low-cost procedure to determine the silicon content in plant material is presented which allows to monitor the agricultural aspects like growth and yield. The presented procedure consists of a hydrochloric acid pre-treatment and a subsequent thermal oxidation. The method is compared to other processes like dissolution in hydrofluoric acid combined with ICP OES, energy-dispersive X-ray fluorescence spectroscopy (EDXRF) or *aqua regia* treatment.

Key words: Silica Determination, Silicon Content, Plant Material

Introduction

It is well known that silicon is the second most abundant element in minerals and soils. In the lithosphere silicon is found as amorphous and crystalline silicon dioxide [1]. In a large variety of plants silicon is deposited as amorphous silica or as opal [2]. These silica polymers in the plant tissues are formed by the uptake of monomeric silicic acid (H_2SiO_4) from soil [3]. For the transport, the silicic acid is coordinated to polysaccharides like hemicelluloses, pectin [4] and polyphenols [5]. Some plant species contain up to 16 % silica in the dry residue [1, 6–8]. The highest silicon content is found in rice (*Oryza sativa*) [3] and horsetails (*Equisetum*) [1], and smaller amounts in dicots (*Dicotyledoneae*) [3]. The silicic acid is transported into the tissues and the plant vessels by transpiration, where silica is stored *e. g.* in cell walls, the cell lumen and the intercellular spaces [9–11]. Silica is mainly accumulated in the outer epidermis as amorphous silica or opal phytoliths as already mentioned above [1–3, 6]. The function of silicon deposits in the outer epidermis and in general in the cell walls is analogous to the stabilizing function of lignin [8]. Active and passive transport mechanisms of silica in plants have been discussed [12], but are still not fully understood [2]. The deposition of silica also depends on the transpiration rate. The higher the transpiration rate, the higher is the silica deposition [1, 9]. Therefore the silica content in perennial plants is higher than in annual or biennial plants [3, 13].

In general plants may be divided into silicon accumulators and silicon non-accumulators. Typical silicon accumulators are species like *Oryza sativa*, *Equisetaceae* and *Pinaceae*, which are also distinguished by their high transpiration rates. Silicon accumulators may contain more than 3 mg Si per gram of dry residue [3].

The interest in the function of silicon in agriculture has increased in recent years because of its effect on disease resistance [2]. Silicon has many positive effects on several plant species, in particular under specific growth conditions. Therefore, silicon is called a quasi-essential element [14] because no universality of nutritional requirements in higher plants was found [15]. On the other hand its absence does not prevent plants to complete their life cycle [3]. Silicon dioxide supports the resistance against biotic stress, like fungal diseases such as blast and sheath blight of rice [3, 15, 16], protects against abiotic stress, *e. g.* by forming silica cuticle double layers to reduce the transpiration rate [15, 16], and is responsible for the homogeneous distribution and decreasing uptake of manganese by promoting the oxidizing power (especially in barley and beans) [15, 17]. Furthermore, silica deposition alleviates the limited crop production and root

growth caused by aluminum toxicity, and in general promotes the growth of plants [15]. Silicon dioxide forms hydrogen bonds to the organic matrix (building a supporting connective tissue); therefore, silica next to lignin is responsible for the mechanical strength in silicon-accumulating plants [18]. In agriculture, calcium silicate slag (furnace slag) is used as a silicon fertilizer especially for rice and related species to enhance the crop yield by supporting several physiological processes in plants [19–21]. The availability of soluble silicon sources in soil thus increases the silicon content in plants and is generally beneficial [22].

However, in agriculture some negative effects on the economic efficiency must also be emphasized. The cell walls of plants can be hardened through silification, and therefore farm animals may not be able to ingest herbs and other plants effectively [23]. Sharp-edged and rough plants generate mucous membrane injuries [24] and decrease the digestibility and the nutritional value [25].

Plant silica is also important as a suitable and renewable source of silicon for material sciences. Silica can be used *e. g.* as a mesoporous material with a high surface area [4], as a template for zeolite macrostructures [26] or as a source of β-SiC ceramics through the direct carbothermal conversion of plant tissues [27,28].

Hence, a fast and cheap analysis of the silicon content in gramineous and nutritional plants is important. The conventional analytical methods to determine silicon or silicon dioxide in biological and geological systems are as follows: i) hydrofluoric acid treatment in combination with ICP OES, ii) energy-dispersive X-ray fluorescence spectroscopy (EDXRF) and iii) dissolution in *aqua regia*. Often samples vary in their chemical composition and a calibration or a reference is necessary to exclude matrix effects. These standard methods are associated with initial and current operation costs, especially for the EDXRF and ICP OES equipment, as well as health hazards from hydrofluoric acid. With the commonly used standard photometric methods it is also not easy to determine silicate ions next to phosphate ions.

We now present an efficient and low cost routine procedure to determine the silica content in a variety of biomaterials.

Experimental Section

In this study we used biomaterials in which the silicon content varies over a broad range. The used samples were from the species *Equisetum hyemale*, *Equisetum arvense*, *Equisetum pratense*, *Equisetum palustre*, *Equisetum telmateia*, *Phragmites communis*, *Miscanthus sinensis*, *Cortaderia selloana*, *Urtica dioica*, *Brassica napus*, *Cannabis sativa*, *Ricinus communis*, *Triticum aestivum*, *Avena fatua*, *Hordeum vulgare*, *Leymus arenarius*, *Spartina anglica*, *Oryza sativa*, and mixed samples of *Coniferopsida* and *Fagaceae* (Table 1 shows the numbering of the samples and the corresponding biomaterials). The plant material was dried at 105 °C and powdered to a particle size of less than 500 μm in diameter.

Table 1. Sample numbers and their corresponding biomaterial.

Samples	Biomaterial
001 – 039	*Equisetum hyemale*
040 – 045	*Equisetum arvense*
046 – 047	*Equisetum pratense*
048 – 049	*Equisetum palustre*
050 – 094	*Equisetum telmateia*
095 – 107	*Arundo phragmites*
108 – 117	*Miscanthus sinensis*
118	*Cortaderia selloana*
119	*Urtica dioica*
120	*Brassica napus*
121	*Cannabis sativa*
122	*Ricinus communis*
123 – 124	*Triticum aestivum*
125	*Avena fatua*
126	*Hordeum vulgare*
127 – 128	*Leymus arenarius*
129 – 130	*Spartina anglica*
131 – 138	*Oryza sativa*
139 – 142	mixed samples of *Coniferopsida*
143	mixed sample of *Fagaceae*

For comparison, samples were ashed at 750 °C in a muffle furnace at atmospheric pressure until mass constance. Test samples were taken in intervals of 30 min. The weight of the residue (see Table 2) specified the whole inorganic material after the decomposition of the organic components like celluloses, hemicelluloses and lignin.

(i) Energy dispersive X-ray fluorescence spectroscopy (EDXRF) was used to quantify the silicon content. A spectrometer x-LAB$_{2000}$ (Spectro Analytical Instruments, Kleve, Germany) which permits the determination of concentrations higher than 0.1 μg g^{-1} was used. All samples were dried and powdered (particle size smaller than 60 μm), weighed in using a binding agent (wax or lithium tetraborate), and compressed or fusion-melted to a pill before measurement.

(ii) The optical emission spectroscopy of atoms excited by inductively coupled plasma (ICP OES) is currently one of the most efficient methods for the quantitative determination of elements in materials. The method is characterized by low detection limits and a high selectivity combined with good reproducibility and accuracy. The solid samples were dissolved with the microwave sample preparation technique. 15 to 25 mg of the sample was weighed into a PTFE reactor

vessel, and 5 mL concentrated hydrofluoric acid and 3 mL of *aqua regia* were added. The closed vessel was heated in a microwave oven up to 250 °C and under a pressure of up to 8 bars. The cooled vessels were filled with distilled water to a volume of 100 mL. This analytical solution was directly injected into the hot argon ICP plasma (6000 – 8000 K). The spectral line at 251.611 nm which is characteristic for silicon was used for the determination of the element concentration. A commercial standard solution (1.000 g L^{-1} Si in nitric acid (1 mol L^{-1}) with 2 wt.-% HF, Bernd Kraft GmbH, Germany) was used for calibration. The ICP OES data were recorded by an OPTIMA 3000 XL (Perkin Elmer) spectrometer. A microwave oven MDS 2000 (CEM) was used for the sample preparation.

(iii) For the treatment of the samples with *aqua regia* 1 g of the biomaterial was weighed in a 100 mL one-necked flask, and 3 mL of *aqua regia* was added. The mixture was kept at room temperature (20 °C) for 2 h, and then refluxed for 5 h with stirring. The cooled mixture was filled up with distilled water to 100 mL and filtered with a glass filter (G4). The residue, which only consisted of silicon dioxide, was dried at 105 °C for 4 d. The mass of the residue was determined, and the silicon content was calculated.

(iv) The samples (5 g biomaterial) were diluted with 25 mL distilled water and 25 mL aceotropic (20.24 %) hydrochloric acid. The mixture was boiled for 2 h and then filtered through a glass filter (G4). The procedure resulted in a loss of all inorganic compounds other than silicon dioxide [29]. The residue was washed with water and dried at 105 °C for 12 h. The samples were incinerated at 750 °C under atmospheric conditions to decompose the entire organic matrix. The sample weight was monitored in intervals of 30 min until mass constance was reached.

Results and Discussion

Table 2 presents the results of different analytical techniques for the determination of silicon for a series of samples compared to the bulk residue after incineration. The EDXRF method (i) appears to be a very precise procedure to quantify elements in biomaterials. The determined silicon content of our samples of biomaterials varies in the range smaller 0.1 % (*Coniferopsida*, *Fagaceae*) to 12.0 % (*Equisetum telmateia*), for silicon non-accumulators as well as silicon accumulators [3]. The amount of the incineration residues is much higher than the EDXRF values (approximately by a factor of 10, see Table 2). The residue is characterized by the absence of the organic matrix like cellulose, hemicelluloses and lignin, but still includes some inorganic material without any differentiation. The common elements in plants next to silicon are Mg, Ca, Al, Fe, K, S, Mn, and P in the form of carbonates, phosphates, sulfates, oxides and other compounds [22, 29]. The oxidation of dried biomaterials at 750 °C in a muffle furnace without any further pre-treatment is thus not an acceptable technique to quantify silicon in plants. It is noticeable that the different wood samples (samples 139 – 143) in our series only contain small percentages of inorganic material other than silica.

Table 2. Ash residue and the results of different techniques for the determination of silicon for a series of samples.

Sample	Ash	EDXRF Method (i)	HF, ICP Method (ii)	*aqua regia* Method (iii)	HCl/750 °C Method (iv)
	ω_{ash} (%)	ω_{Si} (%)	ω_{Si} (%)	ω_{Si} (%)	ω_{Si} (%)
001	17.91	5.8	5.59	6.06	5.26
003	15.10	5.3	4.72	5.99	5.89
007	20.91	6.0	6.77	7.26	7.10
008	17.23	3.2	4.45	4.79	3.81
010	13.88	3.6	4.81	4.89	4.34
013	15.55	3.7	4.61	4.78	4.56
018	3.69	1.7	1.62	1.90	1.58
024	14.46	3.4	4.03	4.29	3.39
029	13.03	3.3	3.80	4.24	3.67
037	15.78	4.2	4.44	4.48	4.50
050	32.76	9.5	10.28	10.45	9.76
053	34.11	9.9	10.00	10.80	10.47
054	36.53	12.0	12.48	13.35	12.29
056	31.63	9.6	10.22	11.70	10.33
061	28.64	7.5	7.88	8.13	7.77
062	32.40	9.1	9.33	9.60	9.03
063	22.78	5.8	6.03	6.19	5.80
073	33.37	11.3	12.72	12.92	12.67
074	24.69	8.6	9.90	10.11	9.24
084	35.26	11.0	10.46	11.53	10.49
097	5.18	2.2	1.88	1.14	1.71
098	3.15	1.3	1.41	1.35	1.21
103	9.09	2.8	3.02	3.19	3.08
108	2.86	0.9	0.99	0.81	0.89
111	6.26	1.6	1.65	1.83	1.63
139	0.27	< 0.1	–	–	0.05
140	0.29	< 0.1	–	–	0.11
141	0.19	< 0.1	–	–	0.00
142	0.19	< 0.1	–	–	0.03
143	1.02	< 0.1	–	–	0.01

The quantification of silicon in plants by ICP OES was used as an alternative spectroscopic method (ii). The biomaterial was dissolved in a mixture of concentrated hydrofluoric acid and *aqua regia* by a microwave digestion (Table 2, column 3). Most of the silicon values determined by this method are somewhat higher than the EDXRF data, but of the same magnitude. In general, amorphous and crystalline silica found in plants [1–3,6] are readily soluble in the hydrofluoric acid/*aqua regia* mixture. Differences to the EDXRF data can be explained by interfering species like phosphate ions always present in biomaterials.

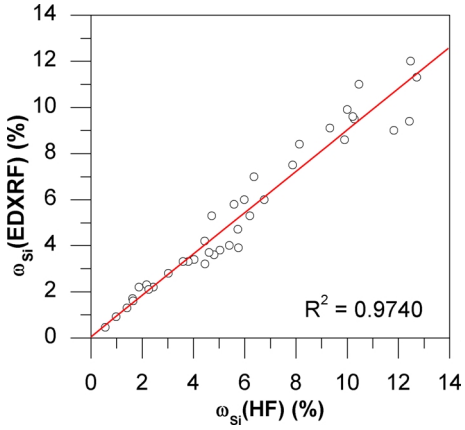

Fig. 1. Correlation diagram of the silicon content in different biomaterials obtained by ICP OES and the EDXRF analysis.

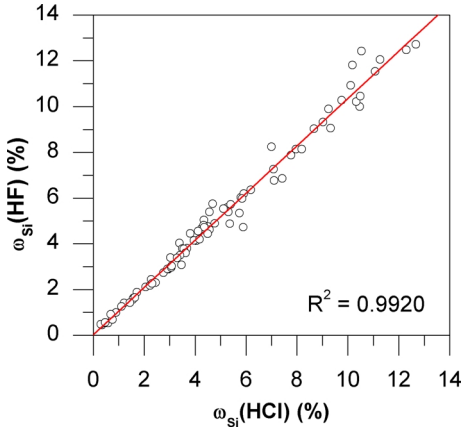

Fig. 2. Correlation of the silicon content in different biomaterials analyzed by the HCl/750 °C (HCl) method and the ICP OES (HF).

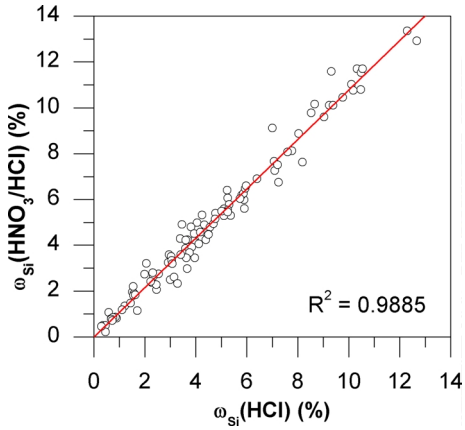

Fig. 3. Correlation diagram of the silicon content in different biomaterials obtained by the HCl/750 °C method (HCl) and treatment with *aqua regia* (HNO_3/HCl).

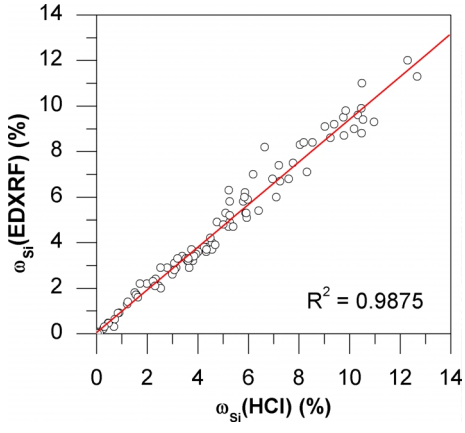

Fig. 4. Correlation of the silicon content in different biomaterials analyzed by the HCl/750 °C method (HCl) and the EDXRF analysis.

The exclusive treatment of the samples with *aqua regia* (method (iii)) gives the highest values for the silicon content. The large differences to both spectroscopic methods are significant. Both, EDXRF as well as the ICP OES, are very precise methods for element quantification. The larger amount of residue after the *aqua regia* treatment can be a consequence of the presence of undissolved inorganic material beside silica. Our silicon data determined with the new procedure including a wet HCl pre-treatment and a thermal oxidation at 750 °C under atmospheric conditions (method (iv)) are very close to the values of both established spectroscopic measurements (EDXRF and ICP OES). Recently we reported about the high purity of our produced silica [31]. Only small differences between the silicon contents were found. All three procedures are well suited to determine the silicon content in plants precisely. Fig. 1 shows the correlation between the ICP OES and EDXRF method ($R = 0.9740$). However, the disadvantages of these two procedures are considerable. Our new fast method (HCl/750 °C) consists of a chemical pre-treatment of the samples with 10 % hydrochloric acid, followed by combustion at 750 °C under atmospheric conditions until constant mass. Figs. 2–4 show the comparison of the results of our method with those of the other techniques (ICP OES, *aqua regia* treatment and EDXRF). All graphs show a good consistency and high regression values between 0.9875 and 0.9920. Therefore, the accuracy of the easy HCl/750 °C method is comparable to the

Table 3. Statistic analysis of samples 073 (*Equisetum telmateia*, leaves) and 074 after chemical pre-treatment (HCl) and thermolysis at 750 °C (*Equisetum telmateia*, stems) to represent the degree of reliability.

Sample	HCl/750 °C ω_{Si} (%)	Sample	HCl/750 °C ω_{Si} (%)
073	12.67	074	8.71
073.1	12.70	074.1	8.49
073.2	12.75	074.2	8.71
073.3	12.62	074.3	9.20
073.4	12.64	074.4	9.19
073.5	12.68	074.5	9.17
073.6	12.52	074.6	9.21
073.7	12.62	074.7	9.15
073.8	12.66	074.8	9.13
073.9	12.77	074.9	9.16
073.10	12.79	074.10	9.15
073.11	12.83	074.11	9.18
073.12	12.80	074.12	9.11
073.13	12.82	074.13	9.11
073.14	12.83	074.14	9.12
∅	12.73	∅	9.05
σ	0.10	σ	0.22

Table 4. Detection of quantification limits for the HCl/750 °C method.

Sample 073 a–n m (g)	750 °C ω_{Si} (%)
10.00	12.85
9.00	12.82
8.00	12.89
7.00	12.78
6.00	12.74
5.00	12.77
4.00	12.81
3.00	12.82
2.00	12.74
1.00	12.91
0.75	12.80
0.50	11.00[a]
0.25	10.32[a]
0.10	10.72[a]
∅	12.81
σ	0.05

[a] Not suitably reproducible.

more expensive and time-consuming ICP OES measurement (Fig. 2) with an R-value of 0.9920. This also holds for the comparison of the HCl/*aqua regia* (0.9885) and HCl/EDXRF (0.9875) methods. The statistic investigations present the degree of reliability. The samples 073 (*Equisetum telmateia*, leaves) and 074 (*Equisetum telmateia*, stems) were determined 15 times with similar results (Table 3). The determined average silicon contents in the samples 073 and 074 were 12.73 % and 9.05 % with low standard deviations of only 0.10 % and 0.22 %, respectively.

In a further study we investigated the quantification limit. Table 4 presents the residue of sample 073 after treatment with 50 mL 10 % hydrochloric acid and the following thermal oxidation at 750 °C for 1.5 h. The used dry mass of plant material was varied between 0.10 g and 10.00 g. In the range from 0.75 g to 10 g of dried biomaterial nearly the same silicon content was found. The average silicon content of 12.81 % is in the same range as the result of the reliability experiments (12.73 ± 0.10 %). The variation of the values can be explained by the natural inhomogeneity of biomaterials. Differences of the silicon content between top and bottom of the plant or between different plant sections (*e. g.* leaves, stems) are known [4, 30]. For samples with a dry mass less than 750 mg biomaterial to determine the silicon content in plant materials, significant deviations (12.80 % silicon for 0.75 g, 11.00 % for 0.50 g and 10.32 % for 0.25 g sample mass) were found and therefore, these are below the limit for an exact determination with the HCl/750 °C method.

Table 5. EDXRF analysis: Elements other than silicon in the pure biomaterial and in the HCl/750 °C-treated samples.

ω (%)	∅ 073 Original biomaterial	073 HCl/750 °C
Mg	0.18 ± 0.02	< 0.077
Al	0.011 ± 0.002	< 0.022
S	1.64 ± 0.25	0.04
Ca	2.60 ± 0.30	0.04
Fe	0.051 ± 0.019	0.02
Sr	0.012 ± 0.000	0.0004
K	0.64 ± 0.06	0.11
Mn	0.0082 ± 0.0003	< 0.0009
Ti	0.0039 ± 0.0022	0.012
P	0.11 ± 0.01	< 0.0057
Cl	0.32 ± 0.03	< 0.006

Table 5 shows the EDXRF data for HCl/750 °C treated biomaterial and the data of some dried samples of the series 073 (*Equisetum telmateia*, leaves). The EDXRF measurements for the dried and untreated samples of *Equisetum* were repeated four times, and the contents of the elements Mg, Al, S, Ca, Fe, Sr, K, Mn, Ti, P, and Cl were determined. The main inorganic elements in the dry biomaterial of *Equisetum telmateia* were silicon (11.3 %) (Table 2), magnesium (0.18 %), sulfur (1.64 %), calcium (2.60 %), potassium (0.64 %), phosphorus (0.11 %), and chlorine (0.32 %) (Table 5). As minor components in sample 073 are found aluminum (0.011 %), iron (0.051 %), strontium (0.012 %), manganese (0.0082 %), and titanium (0.0039 %). The results for iron should be considered critically, because the relatively high standard deviation is of the same magnitude as the absolute value. Table 5 also contains the results of the ele-

mental analysis after the HCl/750 °C process (1.5 h). All elements with the exception of silicon, aluminum and titanium were lower in their content. The elements strontium (0.0004 %), manganese (< 0.0009 %), phosphorus (< 0.0057 %), and chlorine (< 0.006 %) were removed nearly completely. The contents of manganese (< 0.077 %), sulfur (0.04 %), calcium (0.04 %), and iron (0.02 %) had decreased significantly. Potassium (0.11 %) was only partially removed, while aluminum and titanium were obviously not affected. The hydrochloric acid process apparently depletes the most inorganic materials other than silicon dioxide [29].

Conclusion

Three established techniques to quantify silicon in plant materials were investigated and compared with a new protocol which includes an HCl pre-treatment and a subsequent thermolysis at 750 °C. This new method was found to be a rapid, effective and cost-efficient alternative for a wide range of biological materials. Reliable reproducibility was achieved with sample amounts of up to 750 mg biomaterial. This method can be used for many biological systems with various contents of silicon and is hardly influenced by matrix effects.

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