Journal of Scientific Research & Reports
11(3): 1-11, 2016; Article no.JSRR.27239
ISSN: 2320-0227

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A Proposal for Measuring Solubility of the Silica in Rice Husk Ash

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Authors' contributions

This work was carried out in collaboration between all authors. Author MT designed the study, wrote the protocol, and wrote the first draft of the manuscript. Authors MY and AY managed the literature searches and analyses of the study data. Author RS managed the experimental process. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2016/27239
Editor(s):
(1) Cheng-Fu Yang, Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung, Taiwan.
Reviewers:
(1) Wenjie Yuan, Wuhan University of Science and Technology, China.
(2) Elza Bontempi, University of Brescia, Italy.
(3) Simon Sembiring, University of Lampung, Indonesia.
(4) Monica A. Villaquiran-caicedo, Universidad Del Valle, Colombia.
Complete Peer review History: http://sciencedomain.org/review-history/15191

Original Research Article

Received 25th May 2016
Accepted 23rd June 2016
Published 28th June 2016

ABSTRACT

Aims: At present, rice husk is being used in many applications as a biomass resource. The method of rice husk quality evaluation, especially solubility, is not codified and therefore values cannot be compared across regions and institutions. In this study, the solubility of silica in rice husk ash was analyzed, and a systematic measurement process was proposed so as to make global sharing of data easier.
Study Design: Producing black and white ash using a boiler in the field and an electric furnace in a laboratory, respectively, the solubility of silica in rice husk ash and those physical properties were analized.
Place and Duration of Study: Rice husk incineration: a local agricultural association located in Imizu, Toyama, Sample analysis: Toyama Prefectural University.
Methodology: The Japanese standard method 4.4.1.c was evaluated for measuring the solubility

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of silica in rice husk. The current study also assessed the physical state and solubility of silica in both white and black rice husk ash.
Results and Conclusion: From the analysis results, we determined that the Japanese standard method 4.4.1.c could be simplified to reduce the complexity of the measurement procedure. For a consistent and high accuracy measurement of the solubility of silica in rice husk ash, an acid treatment procedure is necessary. Since solubility increases as the surface area of ash decreases, powdering of samples is not necessary and ash can be used as-is for solubility measurements. Ash became bulky as the burning temperature increased, indicating that the silica did not fully transit to crystalline state in the conditions tested. Fixed carbon, volatile matter, and moisture content may also affect solubility up to 800℃. Additional factor s that we did not study may also affect the solubility of silica in rice husk.

Keywords: Rice husk; ash; silica; solubility; Amorphous state.

1. INTRODUCTION

Rice husk accumulates a large percentage of silica by weight. Since silica is used for a variety of purposes, rice husk has been previously considered as a possible silica source, although it has currently been abandoned. Rice husk could potentially be considered a bio-ore of silica, rather than a waste [1]. Much research has been conducted on silica for being used as a fertilizer [2,3], and many other industrial purposes have been considered [4]. An essential requirement for silica to be used as a resource is an amorphous physical state [3]. “Amorphous” is, however, very vague, and cannot be clearly defined. Iker [5] divided amorphous silica into three types; vitreous silica, silica M, and microamorphous silica. Vitreous silica was made by fusing quartz, silica M was formed when either amorphous or crystalline silicas are irradiated with high speed neutrons, and microamorphous silica consists of particles less than a micron in size or have a specific surface area greater than about 3 m^2/g. Alexander et al. [6] showed identical structures for amorphous silica among finely divided powder, wet silica gel, and colloidal particles in the form of a sol. The state of silica in rice husk ash is evaluated by its solubility, a useful tool since the formation of silica is amorphous when its solubility is high and crystalline when its solubility is low. Since the solubility of silica in water is extremely low [6], it is usually measured by using a NaOH solution. The fundamental objective for our study, then, was to find how the solubility of silica could be measured with NaOH. In Japan, there is no standard method for measuring the solubility of the silica in rice husk ash. Solubility measurement protocols vary from place to place, and the values cannot, therefore, be compared with each other. In light of this, the purpose of this study was to propose an appropriate measurement method for the solubility of silica in rice husk ash. Factors that affect the solubility of the silica were assessed and the current standard procedure was simplified based on the results. If the same measurement method is adopted worldwide, it will be easy to share the information about solubility and the physical state of silica produced in any part of the world, especially Asian countries.

2. MATERIALS AND METHODS

2.1 Rice Husk Source

Rice husk from Koshihikari (*Oryza sativa L.*) was used in this study. The city where Toyama Prefectural University is located generates approximately 600 tons of rice husk annually, half of which (300 tons) is used as flooring material for domestic animals and in water drainage systems for rice paddies. However, such usage of rice husk is not stable and sustainable, and the entire amount of 600 ton/year will soon have to be treated as waste. The density of rice husk is very low, at 0.1-0.2 ton/m^3, meaning that extremely large storage spaces would be necessary for disposal unless recycling methods are developed.

2.2 Ash Preparation

Two types of rice husk ash, black and white, were prepared for analysis. Black ash was produced from the boiler described in Tateda [3] without washing (retention time in the boiler: less than 3 days). White ash was produced with a laboratory scale electric furnace (Koyo, KBF794N1) after washing rice husks with acetic acid (5 %) (retention time in the furnace: 2 hours). Fig. 1 shows the appearance of black and white ash produced.

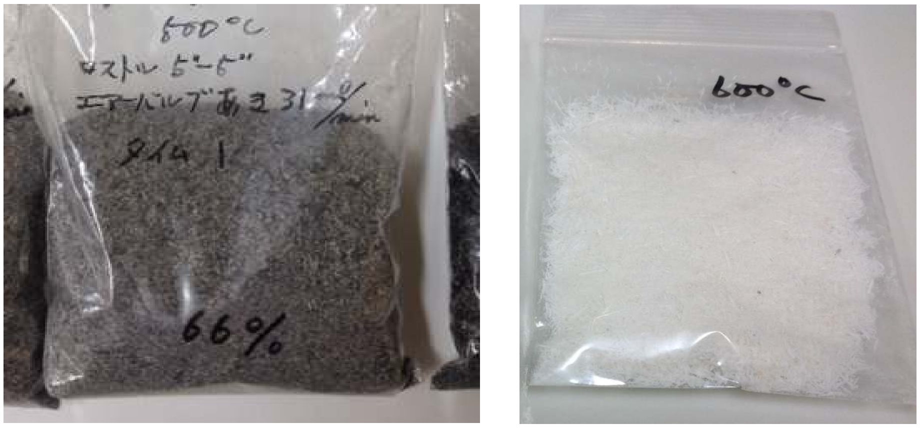

Fig. 1. Sample appearance: Black ash (Left), White ash (Right)

2.3 Qualitative Analysis of Crystallized or Amorphous State of the Silica in Rice Husk Ash

The physical state of the silica in the rice husk ash was determined by X-ray diffraction analysis (XRD: MultiFlex 40 kV, 30 mA, RIGAKU, CuKα, 2θ:5-80°). The samples burned at 500-1,000˚C were grinded into powder and measured by XRD.

2.4 Measurement of Fixed Carbon, Ash, Volatile Matter, and Moisture

Fixed carbon, ash, volatile matter, and moisture content in the rice husk ash samples were determined following the Japanese Industrial Standards (JIS) M 8812-8, -6.4.1, -7.2.4, and -5.2.4a, respectively [7].

2.5 Measurement of the Solubility of Silica in Rice Husk Ash

Japan has standard methods for measuring the solubility of silica in fertilizers (4.4.1.a-c) [8]. The testing method 4.4.1.a is for silica that can be dissolved in acid, the method applied to blast furnace slag, which is usually used for silica fertilizer. Method 4.4.1.b is for silica that can be dissolved in alkali, and silica solubility of gel fertilizer can be measured by this method. Method 4.4.1.c is for silica that can be dissolved in acid and alkali and was used for the foundation of measurement in this study. In our analysis, the 2011 version was used even though it is slightly different from the 2015 version. Flow charts of 4.4.1.c are presented in Fig. 2. The KCl solution was prepared by dissolving KCl (150 g) in ethanol (250 mL) and distilled water (750 mL), which is half of the typical amount because of the difficulty in dissolving KCl in solution.

Soluble silica (S-Silica) as a weight percentage (%) was then calculated as:

$$\text{S-Silica (\%)} = \mathrm{vs} \times \mathrm{C} \times \mathrm{f} \times \frac{V1}{V2} \times \frac{15.021}{W} \times \frac{100}{1000} \quad (1)$$

where,

- VS: Volume of NaOH solution (0.2 mol/L) consumed for titration (mL)
- C: 0.2 mol/L (Estimated concentration of NaOH solution)
- f: 1.000 (A factor of 0.2 mol/L NaOH solution (Wako) as provided on the bottle) (Unitless)
- V1: 250 ml (Volume of Solution A)
- V2: 5 ml (Volume of aliquot taken from each Solution, A or B)
- 15.021: 1 ml of 0.2 mol/L NaOH = 1.5021 mg of SiO_2 (mg·L)/(mL·mol)
- W: 1 g (Sample taken)
- 100: A factor to obtain percentage (%)
- 1000: 1000 mg/g (Conversion factor for mg to g)

According to Kato [9], the silica in slag dissolves as a result that the formation of Si with alkali metals was broken down due to alkali metals such as Na, Ca, and K being extracted by the acid. The resulting silica is often referred to as "free silica [10]." The silica of silica gel, conversely, dissolves by becoming ionized in an alkali environment. However, the testing method for the silica in rice husk ash has not been designated since the physical characteristics of the silica were not yet known. Solubility of the silica in rice husk ash was therefore investigated based on the method of 4.4.1.c, which uses both acid and alkali treatments (4.4.1.c-Whole, Fig. 2). For alkali-only treatment, the procedure for making Solution A was skipped and the process for making Solution B proceeded after taking one gram of Sample (4.4.1.c-Solution B w/o acid, Fig. 3). Method 4.4.1.c-Solution B with acid measured dissolution of silica in acid (Fig. 4).

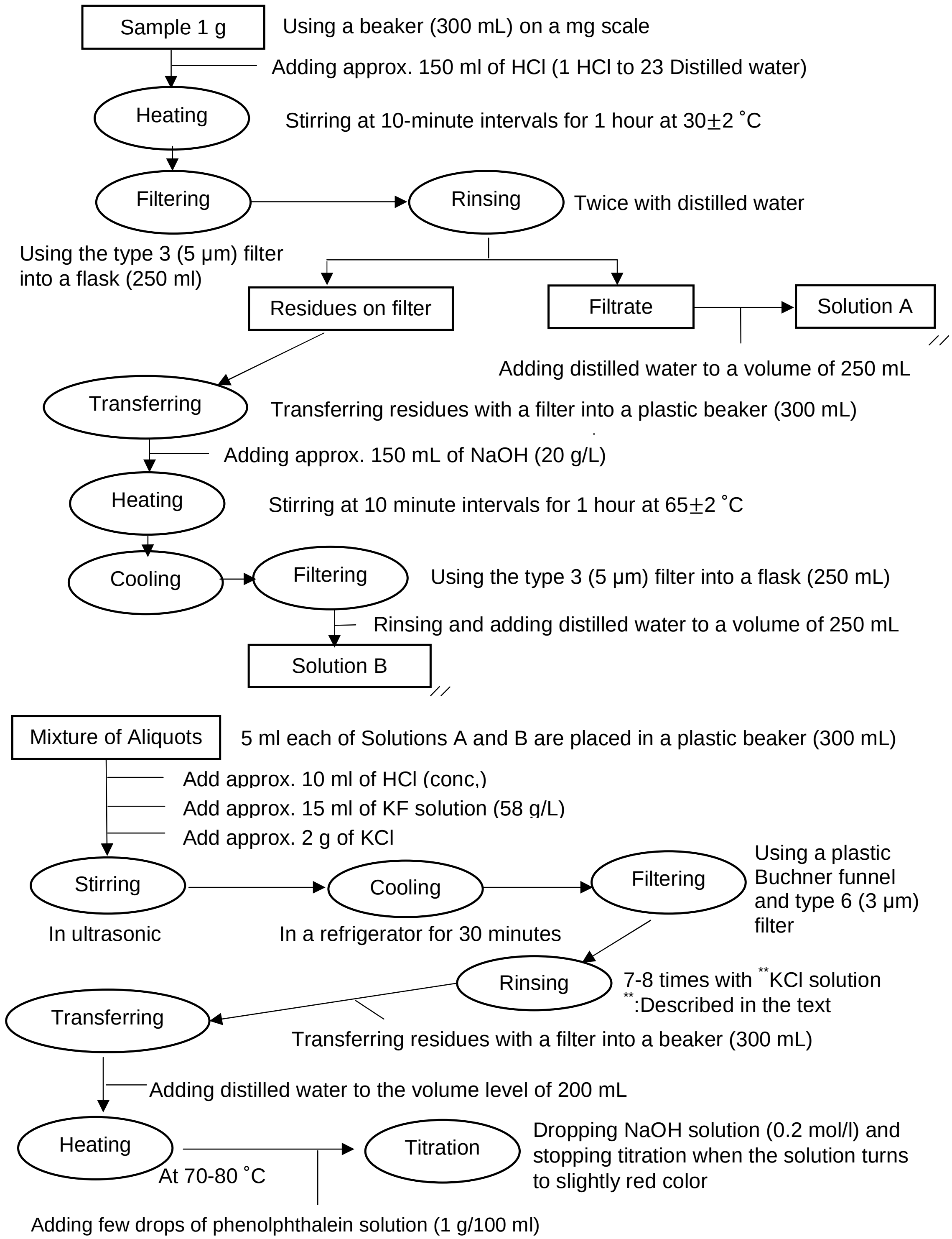

Fig. 2. Testing method 4.4.1.c for soluble silica in fertilizer

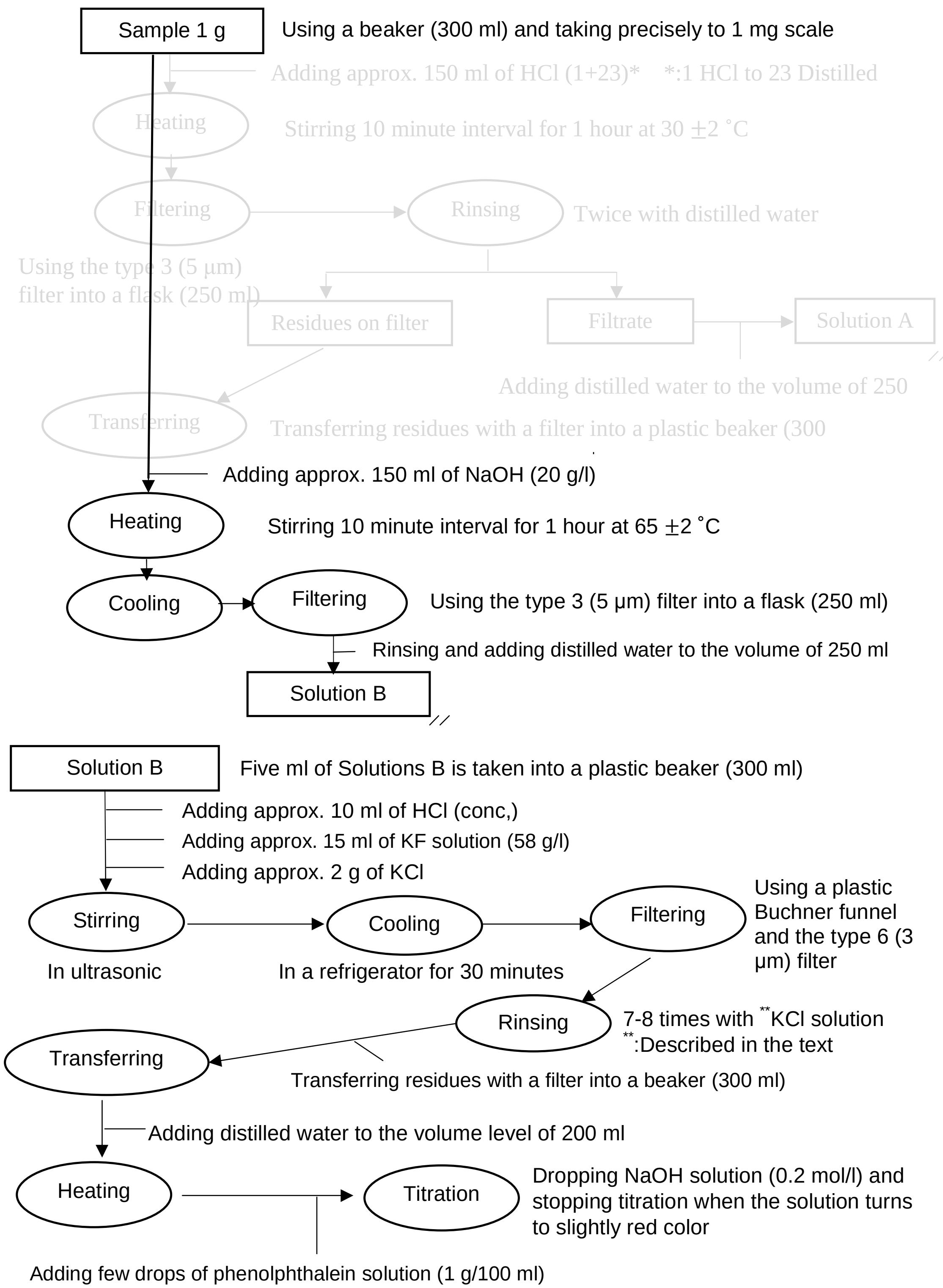

Fig. 3. Testing method 4.4.1.c-Solution B w/o acid

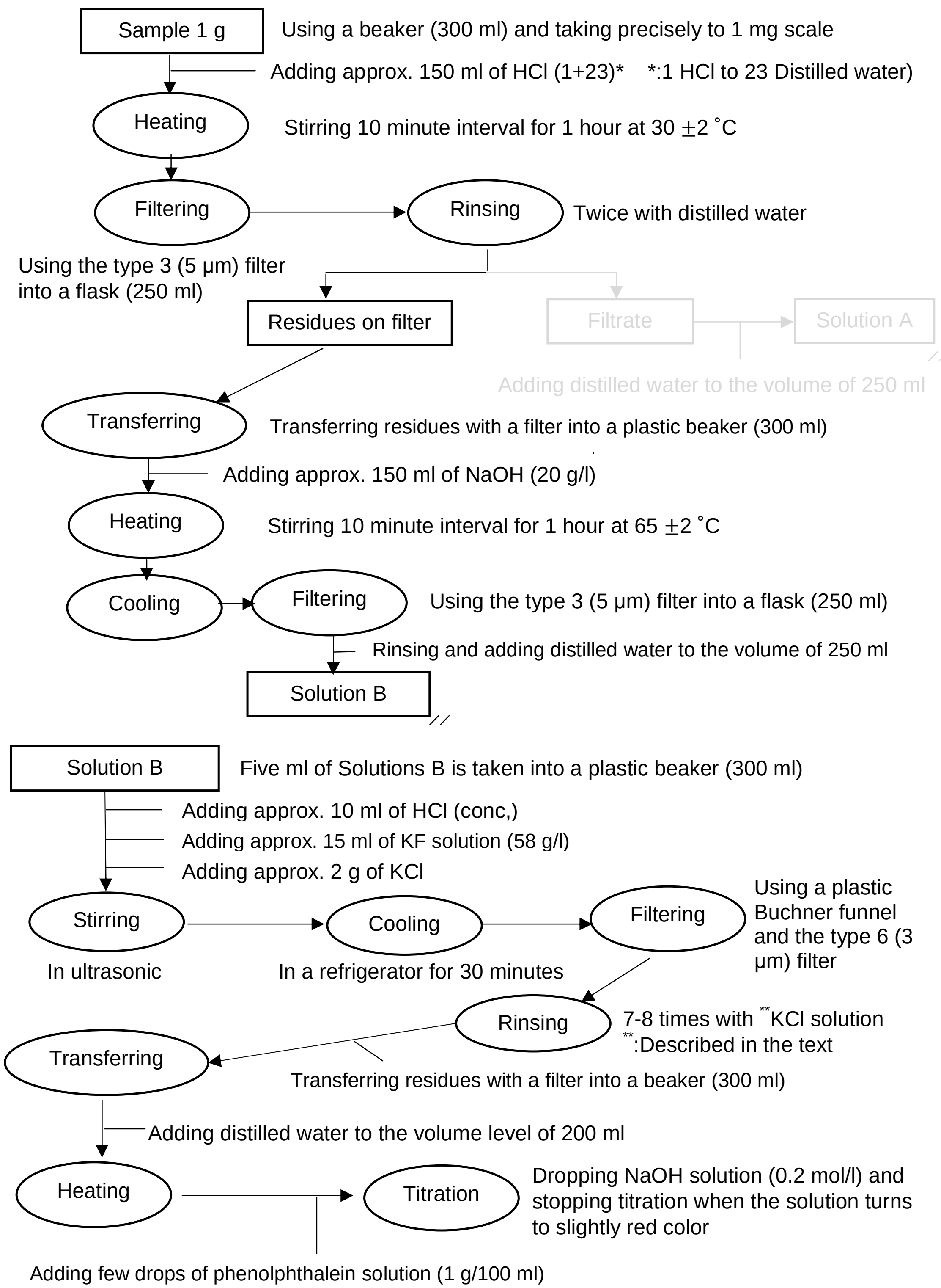

Fig. 4. Testing method 4.4.1.c-Soulution B with acid

Rice husk was burned as-is, whether by boiler or electric furnace, so that the ash maintained the shape of the rice husks. Since ash samples for solubility measurements were only one gram (Fig. 2), non-silica contents in the samples could have affected solubility of the silica. Samples were powdered by grinding 100 times manually in a grinding bowl and the solubility was compared to samples left as-is. Method 4.4.1.c-Whole was applied for the solubility measurements in this comparison. Solubilities of tridymite and quartz were also measured by the method 4.4.1.c-Whole.

3. RESULTS AND DISCUSSION

The values shown here are statistically significant ($p<0.01$) values obtained from multiple replications, unless otherwise stated.

3.1 Necessity of an Acid Treatment Procedure

As described in Section 2.5, the methods for dissolving the silica in slag and in gel are different. The silica in slag from a blast furnace dissolves in an acid solution, while the silica composed of silica gel fertilizer dissolves in an alkali solution. Table 1 shows the results measuring silica solubility in rice husk ash using 4.4.1.c-Whole, -Solution B w/o acid, and -Solution B with acid. Solubility shown here of the black ash (produced by the boiler, which uses a regular exothermic reaction) shows high, implying that silica in black ash produced by the boiler was completely amorphous. Solubilities of tridymite and quartz were 0.4% for comparison. Values of solubility by only alkali dissolution were lower than that by acid and alkali dissolution, meaning that the silica in rice husk ash could be dissolved in acid, and that there might be free silica.

Due to the small difference in solubility of silica in Solution B measured by the methods 4.4.1.c-Whole and 4.4.1.c-Solution with acid, it was assumed that the silica dissolved in Solution A would be negligible (0-$\pm$.0.5 point). The results, taken together, indicate that the silica in rice husk cannot be dissolved in acid, but that the solubility increases after acid treatment (+ 2.4-7.5 points). Therefore, the analysis procedure shown in Fig. 2 can be shortened as shown in Fig. 4. In the modified procedure, only Solution B is needed for measurement, which lessens the complex manners of the measurement procedure.

3.2 Factors Which Influence Silica Solubility

3.2.1 Powdering ash samples as pretreatment

The results are given in Table 2.

Table 1. Solubility of the silica from using methods 4.4.1.c-Whole, 4.4.1.c-Solution B w/o acid procedures, and 4.4.1.c-Solution B with acid procedures

Sample	4.4.1.c-Whole (%)	4.4.1.c-Solution B w/o Acid (%)	4.4.1.c-Solution B with Acid (%)
A (Black ash)	67.5	60.0	67.8
B (Black ash)	63.9	57.3	64.4
C (Black ash)	55.8	52.0	56.1
D (Black ash)	75.0	70.5	75.2
E (White ash)	87.6	85.2	87.6
F (Black ash)	66.2	60.6	66.4
G (Black ash)	72.8	66.6	72.6
H (Black ash)	60.1	55.8	60.1
I (Black ash)	60.1	53.0	60.1
J (Black ash)	65.9	58.4	65.9

Table 2. Comparison of solubility of Black ash samples: Powdered and As-Is

Solubility of the silica (4.4.1.c-whole)	Powdered	As-Is
Mean Value (%)	65.5	65.5
Standard Deviation (%), n = 10	0.63	0.57

Mean values of "powdered" and "as-is" were the same, but the standard deviation of "as-is" was smaller than that of "powdered." These results indicate that ash samples do not need to be powdered prior to solubility measurements.

Inoue [11] found that solubility increased as specific surface area (SSA) of rice husk ash increased, using rice husk ash with SSA 0.98-117 m^2/g. One of our previous experiments gave contradictory findings of decreasing solubility as SSA increased, using rice husk ash with SSA 40-196 m^2/g (data not shown). Results from our current study (Table 3) show the same trend as our previous study. We therefore conclude that SSA does not influence solubility of the silica, which contradicts the conclusion of Inoue [11].

3.2.2 Fixed carbon, volatile matter, and moisture

Because only 1 g of ash was sampled for solubility measurements, it was possible that an impurity such as fixed carbon might strongly affect silica solubility. We investigated whether the percentage of fixed carbon decreased the solubility of silica. Representative data are given in Table 3.

Solubility was lower when fixed carbon, volatile matter, and moisture content were also lower. Fixed carbon, especially, seemed to have a strong influence on solubility. Solubility was further measured by omitting the influence of fixed carbon (Table 4) by producing white ash (which does not contain fixed carbon). White ash was produced by burning rice husks at temperatures of 500-1,000℃ in a laboratory electric furnace.

Volatile matter and moisture decreased as the burning temperatures increased. Conversely, ash increased with increasing temperatures. Solubility, volatile matter, and moisture were plotted as a function of temperature (Fig. 5).

Volatile matter and moisture both decreased as burning temperatures increased. Solubility increased up to 800℃, and then decreased thereafter. From the results, existence of volatile matter and moisture only seemed to affect solubility up to 800℃, above which effects became negligible.

A Silica Activity Index (SAI) was introduced by Deshmukh et al. [10]. SAI is the percentage of available silica dissolved in an excess of boiling NaOH (0.5 M) during a 3-minute extraction period. They found that SAI is a function of burning temperature, and the solubility in Fig. 4 shows a similar trend. The SAI increased up to 500 ℃ and it decreased after the temperature to 900 ℃.

The observed decline in solubility above 800℃ was not influenced by volatile matter and moisture, since solubility increases as volatile matter and moisture decrease. Above 800℃, the silica in rice husk ash might be crystalized. At high temperatures, the solubility of crystalized silica becomes low. To investigate the physical state of the silica, the ash burned at 500 – 1,000℃ were analyzed with an XRD (Fig. 6). The charts for 1,000℃ were chosen since the charts for 500 to 1,000℃ displayed the same trends. It was apparent that silica at any temperature did not crystalize, rather staying in an amorphous state. The question then became: What was the cause of decreasing solubility?

Fig. 7 shows the physical appearance of the ash at each burning temperature, as taken by a handy zoom mobile recorder (Digital Micro Mobile Z, Biomedical Science) at 50-60x. The ash showed a broken and powdered-like state at low burning temperatures. The ash became bulky at high temperatures, however, and the shapes of rice husk remained as the temperature increased. These results indicate that the physical state of the silica shifted from amorphous to a more crystalized state. The silica was not fully crystalized, however, even at high temperatures, indicating that tiny parts of the amorphous silica might start to change to crystalline form (Frondel [12] and Kondo [13]).

Table 3. Physical properties of black ash samples and their solubility

	Dry base (%)			Wet base (%)	Solubility (%)
Ash sample	**Fixed carbon**	**Ash**	**Volatile matter**	**Moisture**	**4.4.1.c-whole**
A	0.4	97.6	2.0	2.3	71
B	0.3	97.0	2.7	2.3	66
C	6.5	88.4	5.1	3.1	49

Table 4. Physical properties of white ash samples and their solubility

	Dry base (%)			Wet base (%)	Solubility (%)
Ash sample	Fixed carbon	Ash	Volatile matter	Moisture	4.4.1.c-whole
500	0.0	97.7	2.3	5.7	86.7
600	0.0	98.6	1.4	5.5	89.5
700	0.0	98.8	1.2	3.8	90.6
800	0.0	99.3	0.7	2.7	91.7
900	0.0	99.8	0.2	1.8	90.6
1,000	0.0	99.9	0.1	0.8	83.1

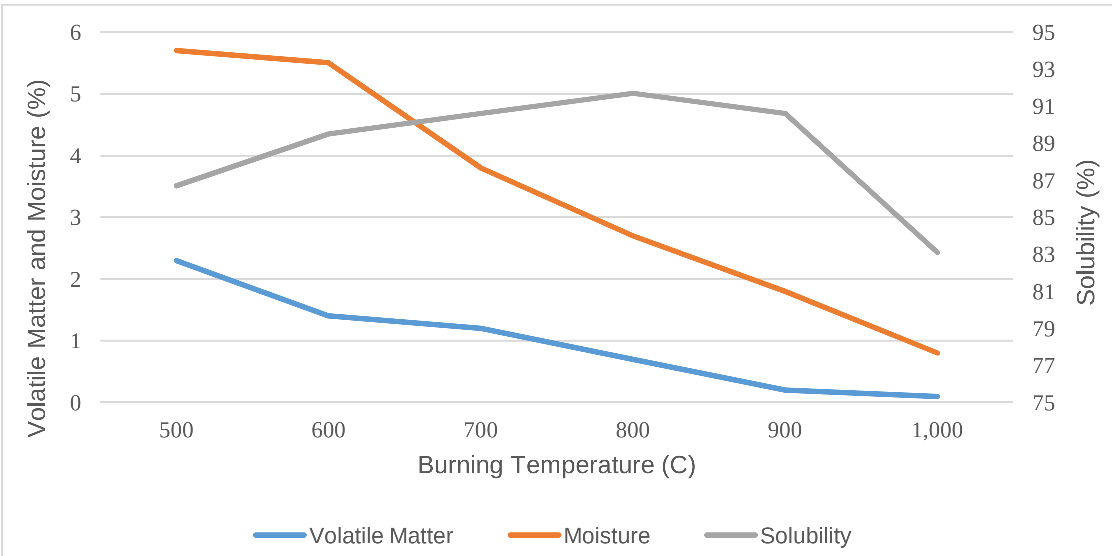

Fig. 5. Trends of volatile matter, moisture, and solubility as a function of burning temperature

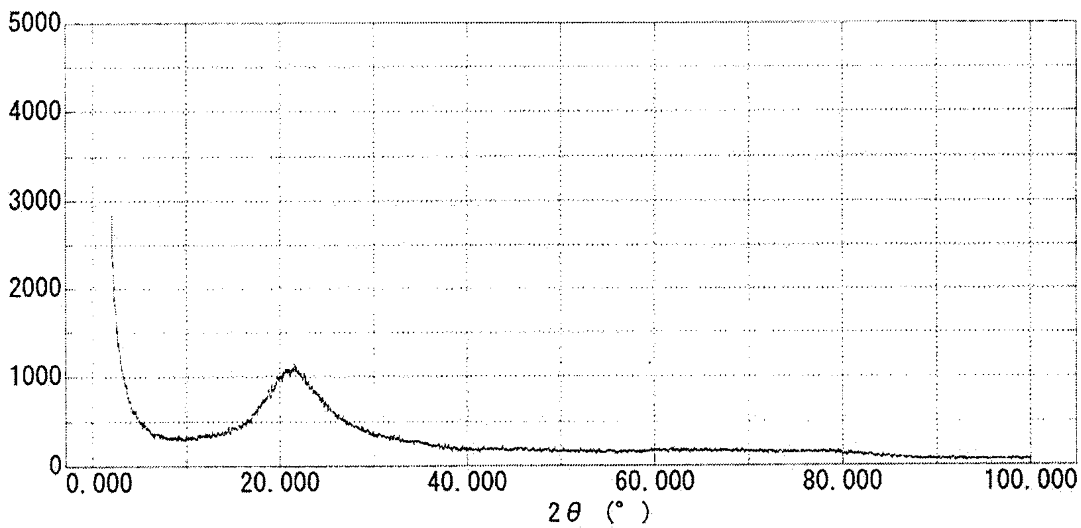

Fig. 6. XRD charts for 1,000℃ burning temperature

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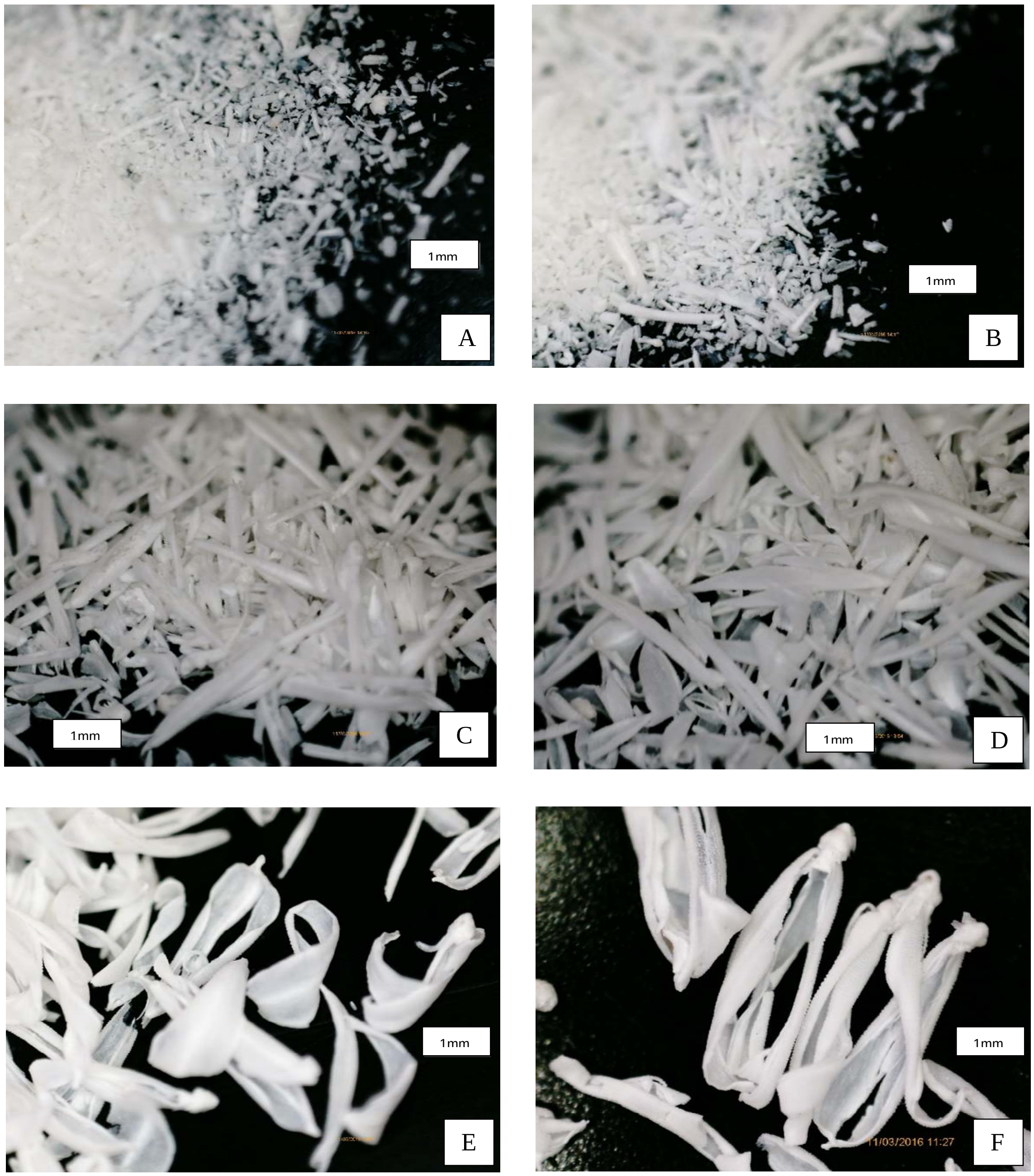

Fig. 7. Magnified appearance of rice husks burned at 500℃ (A), 600℃ (B), 700℃ (C), 800℃ (D), 900℃ (E), and 1,000℃ (F)

4. CONCLUSIONS

This study concluded the following:

- For solubility measurements of silica in rice husk ash, an acid treatment procedure is necessary to obtain accurate values.
- The Japanese standard method 4.4.1.c can be simplified to reduce the complexity of the measurement procedure.
- Solubility increased as surface area of ash decreased.
- Powdering of samples was not necessary for solubility measurement (ash can be used as-is).

- Ash became bulky as the burning temperature increased.
- Fixed carbon may affect solubility, as well as volatile matter and moisture contents up to an 800℃ burning temperature.
- Other, unstudied factors may exist that affect the solubility of silica in rice husks.

ACKNOWLEDGEMENT

This research was supported by grants from the Project of the NARO Bio-oriented Technology Research Advancement Institution (Integration research for agriculture and interdisciplinary fields).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Tateda M. A sustainable local energy system producing amorphous silica from rice husk and developing its use in geopolymer concrete April 3- 6, 2016, Philadelphia, PA, USA, Session 5A. 2016;584-591.
2. Ishibashi H. Suitonae ni Taisuru Yakimomigara no Keisan no Koka (Effects of Silica in Burned Rice Husk to Rice Plants), In Okuda Azuma editor. Keisanshitu Shizai no Donyu niyoru Nousanbutsu no Kyukyokuryou Koujo ni Kansuru Kenkyu, Ministry of Education Research Fund Report. 1958;48:233-239. Japanese.
3. Tateda M. Production and effectiveness of amorphous silica fertilizer from rice husk using a sustainable local energy system. Journal of Scientific Research and Reports. 2016;9(3):1-12.
4. Ramchandra P. Potential applications of rice husk ash waste from rice husk biomass power plant. Renewable and Sustainable Energy Reviews. 2016; 53:1468-1485.
5. Iker RK. The chemistry of silica. John Wiley & Sons; 1979.
6. Alexander GB, Heston WH, Iler RK. The solubility of amorphous silica in water. The Journal of Physical Chemistry, 1954;58(6): 453-455.
7. Japan Industrial Standard. Coal and coke−Methods for proximate analysis. Available:http://kikakurui.com/m/M8812-2006-01.html Accesses April 18, 2016 (in Japanese).
8. Food and Agricultural Materials Inspection Center (FAMIC). Standard Method for Fertilizer Analysis; 2015. Available:http://www.famic.go.jp/ffis/fert/obj/shikenho_2015_2.pdf#page=121 Accessed April 13, 2016 (in Japanese).
9. Kato N. Dissolution of slag fertilizer in paddy soil and evaluation of silicon availability in slags. Report of National Institute for Agro-Environmental Sciences. 1998;16:19–75. Available:http://agriknowledge.affrc.go.jp/RN/2010572845.pdf Accessed April 26, 2016.
10. Deshmukh P, Bhatt J, Peshwe D, Pathak S. Determination of silica activity index and XRD, SEM, and EDS studies of amorphous SiO2 extracted from rice husk ash. Transactions of Indian Institute of Metals. 2012;65(1):63-70.
11. Inoue K, Hara N. Thermal treatment and characteristics of rice husk ash. Kyushu Kogyo Gijutu Kenkyusho Report 60. 1998;3731-3737. Japanese.
12. Frondel C. The system of mineralogy of DANA. 7th ed. vol.3. Silica Minerals, Wiley, New York; 1962.
13. Kondo R. Plant Opal Illustrated book: Introduction of plant silica by scanning electron microscope. Hokkaido University Press. Japanese. 2010;186.

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The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/15191