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Analytical Method of Silicon Dioxide in Health Functional Food Products using ICP-OES

Mi-Hyun Ka, Kwang-Geun Lee[1], Heung-Youl Lim, Gunyoung Lee[2], Sang Soon Yun[2], Ho Soo Lim[2], and Yong-Suk Kim[3]*

Korea Health Supplements Association Sub. Korea Health Supplements Institute, Sungnam, Korea
[1]Department of Food Science and Biotechnology, Dongguk University Biomedi Campus, Goyang, Korea
[2]Food Additives and Packaging Division, National Institute of Food and Drug Safety Evaluation, Osong, Korea
[3]Department of Food Science & Technology, College of Agriculture and Life Sciences, Chonbuk National University, Jeonju, Korea

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ABSTRACT - The analytical method of silicon dioxide (SiO_2) in health functional food products was developed employing inductively coupled plasma optical emission spectrometry (ICP-OES) method assisted by acid (hydrofluoric acid and boric acid) digestion in open system without alkali fusion. The limit of detection (LOD) and limit of quantification (LOQ) of this method were found to be 0.07 and 0.20 mg/L, respectively. Linearity (r^2) and linear range were 0.99 and 0.20~20.0 mg/L, respectively. The accuracy and precision of SiO_2 (0.4, 1.0, and 2.0%, w/w) in spiked glucosamine exhibited to be the range of 90.22~94.14% and 0.72~1.67%, respectively. The contents of SiO_2 in 11 health functional food products were detected in range of 0.02~1.80% (w/w). Every sample showed below content of the permitted use level (2%, w/w) of SiO_2. Therefore ICP-OES method with acid can analyze the content of SiO_2 in health functional food products easily and rapidly. Consequently, the application of specification analysis of SiO_2 in health functional food products could be a significant work.

Key words: Silicon Dioxide, ICP-OES, Analytical Method, Health Functional Food Products, Acid Digestion

Silicon dioxide (SiO_2) has synonyms such as silica and defined silica aerogel, hydrated silica, silicic acid and dehydrated silica gel. Description of SiO_2 is silica aerogel (a microcellular silica occurring as a fluffy powder or granules) and hydrated silica (a precipitated, hydrated SiO_2 occurring as fine white, amorphous powder, or as beads or granules). SiO_2 is insoluble in water and ethanol and soluble in hydrofluoric acid and alkalis (80-100°C)[1,2]. Synthetic amorphous silica (SAS) is also known as untreated fumed silica. SiO_2 and synthetic amorphous silica are chemically identical. SiO_2 in its forms can be used as a direct ingredient in food and as a component of food-packaging materials, at levels in accordance with good manufacturing practices.

When directly added to food, SiO_2 has the following uses: anticaking agent, antifoaming agent, stabilizer, adsorbent, carrier, conditioning agent, chill proofing agent, filter aid, emulsifying agent, viscosity control agent, and anti-settling agent. In addition, SiO_2 is also used as an indirect additive in manufacture of adhesives, coatings, antifoaming agents, grease and lubricants, paper and paperboard and polymers that are then used as components of food-packaging materials. The level of SiO_2 in food is also regulated by a legislation. According to the regulation of MFDS, SiO_2 and any diluted additives containing it should not be used unless these are indispensable for food manufacturing or processing. SiO_2 should be removed before the final food process. For anticaking agents, however, the content of SiO_2 should not be more than 2% (w/w) for anticaking agent in the food[3-5]. Human daily intake of silicon ranges up to approximately 50 mg per person: males have a higher daily intake than women[6].

The SiO_2 content is determined by a titration method. SiO_2 in crystal is measured by potentiometric titration with fluoride-selective electrode. Crystal is decomposed with a mixture of sodium fluoride and nitric acid[7]. SiO_2 content of magnesite and dolomite is determined by titration method. Samples are decomposed with a mixture of nitric acid (1:1) and hydrochloric acid[8]. SiO_2 as a food additive content is determined by gravimetric method using hydrofluoric acid[1]. Gravimetric method by alkali fusion using sodium carbonate

*Correspondence to: Yong-Suk Kim, Department of Food Science & Technology, Chonbuk National University, 567 Baekje-daero, deokjin-gu, Jeonju-si, Jeollabuk-do 54896, Korea
Tel: 82-63-270-2567, Fax: 82-63-270-2572
E-mail: kimys08@jbnu.ac.kr

(900°C) is used to determine the silica in a silicate sample[9]. SiO_2 as a food additive content is determined by atomic absorption spectrometry (AAS) with alkali fusion using potassium peroxide (360°C)[2]. SiO_2 content in glasses is determined by alkali fusion using potassium peroxide and sodium hydroxide using AAS method[10,11]. Si content in plant samples is determined by inductively coupled plasma optical emission spectrometry (ICP-OES) with alkaline dissolution and alkali fusion method using alkali and carbonate[9-12]. Si content of silicates is determined by AAS method using designed vessel made from teflon containing hydrofluoric and boric acid[13].

Hydrofluoric acid cannot be used with instruments equipped with glass parts such as inductively coupled plasma (ICP) and ICP- mass spectrometry (ICP-MS). Hydrofluoric acid is known to dissolve glass by reacting with SiO_2 from silicon tetrafluoride gas and hexafluorosilicic acid[14]. But hydrofluoric and boric acid reaction are the formation of fluoroboric acid. Therefore, it can be used with instruments equipped with glass parts. A two-step exothermic reaction is shown in chemical reaction[9].

$$H_3BO_3 + 3HF \rightleftarrows HBF_3OH + 2H_2O \quad (1)$$

$$HBF_3OH + HF \rightleftarrows HBF_4 + H_2O \quad (2)$$

Alkali fusion using fusion reagent (KOH/H_3BO_3) was melted completely using a torch burner[2,14]. As the sample (0.5 g) and fusion reagent (5 g KOH/ 2 g H_3BO_3) have to be completely melted in alkali fusion method. This method takes long sample preparation time, needing torch burner in sample preparation and is extremely dangerous and difficult to handle. Due to these limitations, the development of new analytical method for SiO_2 was established.

The purpose of this study was to develop not only comprehensive but also simple analytical method for health functional food products where ICP-OES was applicable. Since there is no direct measurement of the contents of SiO_2 in the health functional food products, the content of Si that can be converted into soluble form is measured and converted into SiO_2 content.

Materials and Methods

Reagents and materials

Silicone standard was purchased from Fluka (St. Louis, MO, USA). Hydrofluoric acid (36%) and boric acid (99.5%) were purchased from J.T. Baker (Phillipsburg, NJ, USA) and Junsei (Tokyo, Japan). Water was purified using the Milli-Q ultrapure water purification system (Milipore Co, Billerica, MA, USA). All other chemicals were analytical grade. SiO_2 (98.9%) of Korea food grade from Tae Wang Mulsan (Seoul, Korea) and SiO_2 (99.5%) from Sigma-Aldrich (St. Louis, MO, USA) were used in this study. Three types of SiO_2 (0.4, 1.0, and 2.0%) were provided from SH company (Seongnam, Korea). Eleven health functional food products were evaluated for SiO_2 content analysis. These products were purchased from markets and pharmacies in Seongnam-si, South Korea. The health functional products were selected according to the products that contain SiO_2 contents and kid's products. These were including 3 vitamin C supplements, 2 kid vitamin C supplements, 2 calcium and vitamin D supplements, and 3 multiple vitamins and glucosamine products.

Sample preparation

Samples (0.02~0.05 g) were accurately weighed in propylene conical tube, then 2 mL distilled water and 1.5 mL hydrofluoric acid were added. The tube was closed by propylene cap, shaking until dissolution was completed, and cooled to ambient temperature. Then, 1.4 g of boric acid was added, its dissolution aided by sonication for 30 min. The solution was made up to 50 mL with distilled water. The test solution was prepared by dilution 1~50 times with sample preparation solvent (contained 1.5 mL of hydrofluoric acid and 1.4 g of boric acid).

ICP-OES analytical method

The content of SiO_2 in health functional food products was determined after measuring Si which is converted to a soluble form by acid digestion. The content of Si in test solution was determined by ICP-OES (Prism ICP, Teledyne, Camino Dos Rios, CA, USA). The analytical operation conditions are shown in Table 1. Calibration standard solution containing 0.2~20 mg/L was prepared from 1,000 mg/L solution by diluting sample preparation solvent. SiO_2 (%) on a dried or ignited basis was calculated from determined values of Si in the solutions. The SiO_2 content of sample was calculated using the following equation:

$$SiO_2\ (\%) = 2.139 \times \text{Concentration of Si (mg/L)} \times 50\ \text{mL} \times \text{Dilution factor} / \text{Weight of sample (g)}$$

*2.139 is conversion factor of SiO_2 (60.08) from Si (28.09) by calculated molar mass

Table 1. ICP-OES analytical operation parameters

Parameter	Value
RF Power	1200 Watt
Plasma gas flow	18 L/min
Nebulizer gas flow	32 psi
Auxillary gas flow	0.6 L/min
Pump	1.5 mL/min
Wavelength	251.611 nm

Method validation

Validation to determine recoveries, coefficient of variation (CV, %) values, limit of detection (LOD), limit of quantification (LOQ), and linearity (r^2) were conducted. Intra and inter-day recovery and CV were performed at samples (SiO_2 of 0.4, 1.0, and 2.0%). LOD and LOQ of SiO_2 were carried out by 3.3 × sigma (s)/slope of calibration curve and 10 × sigma (s)/slope of calibration curve. Sigma was obtained by determining the standard deviation. Linearity (r^2) were calculated using each standard curve for quantification. Accuracy and precision were evaluated for SiO_2 at the level 0.4, 1.0, and 2.0%.

Statistical analysis

All statistical analysis was conducted using the Statistical Analysis System software (SAS User Guide, ver. 6., SAS Institute, Inc., Cary, NC, USA). Mean values and standard deviations were calculated. All experiments were performed in triplicate. A probability (p) level of 0.05 was considered significant.

Results and Discussion

Validation of method

A calibration curve was obtained by spiking 0.2, 0.5, 1.0, 2.0, 5.0, and 20.0 mg/L of Si in sample preparation solvent. The recovery, coefficient of determination (R^2), limit of detection (LOD) and limit of quantification (LOQ) are presented in Table 2. The linearity was reliable with coefficient of regression, 0.999. The LOD and LOQ were calculated based on the standard deviation and the slope of calibration curve. The LOD and LOQ were 0.07 and 0.20 mg/L respectively. LOD and LOQ of sample were 0.007 and 0.02%.

Recoveries, LOD, LOQ, accuracy and precision for SiO_2 are shown in Table 3. The recovery was obtained from glucosamine products which were formulated 0.4, 1.0 and 2.0% of SiO_2. Recovery tests were conducted for sample with an intra- and inter-day test. Recoveries of intra and inter-day test were 90.60-94.14% and 90.22-93.83%, respectively. Standard (99.5%) and food additive (98.9%) in ICP method were applied to determine recovery of SiO_2. Recovery rates (%) of SiO_2 are shown in Table 3. Using ICP method, the recoveries of SiO_2 standard and food additive were 96.05% and 94.38%; the coefficient of variation was < 2%. According to Motoh Mutsuga et al[14], LOD and LOD of sample were 0.2 mg/L and 0.08%, respectively. The LOD and LOD of sample in ICP with alkali fusion was higher than this study. These results suggest that the ICP analysis method by acid digestion would be similar or better than the alkali fusion method. This validated method could be much safer and provide a shorter sample preparation step taken about 30 minutes than Motoh Mutsuga et al[14] and JECFA[2] in detecting SiO_2 content as Si from food additives and functional foods.

Table 2. Coefficient of determination (R^2), limit of detection (LOD) and limit of quantification (LOQ) for Si analysis by ICP-OES method

Slope	Intercept	R^2	LOD (mg/L)	LOQ (mg/L)
372295	172139	0.999	0.07	0.20

Silicon dioxide levels in health functional food products in Korea

For anti-caking agents, the content of SiO_2 or diluted additives containing it should not be more than 2% of the food. The levels of SiO_2 in 11 samples of health functional foods consumed in Korea market and pharmacy are presented in Table 4. SiO_2 was detected in range of 0.02 to 1.80%. The highest SiO_2 content was detected in glucosamine product. The mean contents of vitamin C supplements, kid vitamin C, calcium and vitamin D supplements were 0.33, 0.03, 0.73 and 0.48%, respectively. Every sample showed below content of permitted use level (2%) of SiO_2.

We have established analytical methods for SiO_2 using acid digestion with ICP-OES for food additive and health functional food products. This study provides better accuracy, reproducibility, and efficiency in detecting SiO_2 contained in health functional food products than the method regulated

Table 3. Accuracy and precision of silicon dioxide in standard (99.5%) and food additive (98.9%) and spiked in glucosamine product (0.4, 1.0, 2.0%) analyzed by ICP-OES method

	Recoveries (%)	Concentration (%)	Intra-day (n = 3)		Inter-day (n = 3)	
			Accuracy[2] (%)	CV[3] (%)	Accuracy (%)	CV (%)
Standard	96.05 ± 0.48[1]	0.4	94.14	0.68	93.83	0.57
Food additive	94.38 ± 1.76	1.0	91.77	1.67	91.20	1.08
		2.0	90.60	0.15	90.22	0.72

[1]Each value is the mean (%) ± standard deviation (SD) (n = 3)
[2]Accuracy: (mean/concentration) × 100
[3]Coefficient of variation (CV): (standard deviation/mean) × 100

Table 4. Silicon dioxide levels in health functional food products

Sample type	Content (%) of SiO_2	Mean contents (%) of SiO_2
Vitamin C supplement-1	0.50 ± 0.01[1)]	0.33
Vitamin C supplement-2	0.48 ± 0.01	
Vitamin C supplement-3	0.03 ± 0.01	
Kid vitamin C supplement-1	0.03 ± 0.01	0.03
Kid vitamin C supplement-2	0.04 ± 0.00	
Calcium and vitamin D supplement-1	0.02 ± 0.00	0.73
Calcium and vitamin D supplement-2	1.43 ± 0.02	
Multiple vitamin-1	0.49 ± 0.01	0.48
Multiple vitamin-2	0.45 ± 0.02	
Multiple vitamin-3	0.51 ± 0.00	
Glucosamine product	1.80 ± 0.01	-

[1)]Data are mean ± SD (n = 3).

by JECFA 2001[1)] and 2013[2)]. ICP method by alkali fusion[2,11)] takes long sample preparation time, needs torch burner in sample preparation and is both extremely dangerous and difficult to handle. But this method with acid digestion can analyze easily and rapidly. Speciation of analysis is an important part in chemical analysis. The application of specification analysis in health functional food products is of particular significance. The results of such analysis could be useful to set an allowable content level of SiO_2 in health functional food products. Consequently, this analysis method was effective in providing useful food specification policy.

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국문요약

건강기능식품에서 이산화규소 분석 방법을 확립하기 위하여 산(불산과 붕산)분해를 이용한 ICP-OES 방법을 수행하였다. 이 방법의 검출한계와 정량한계는 각각 0.07 mg/L, 0.20 mg/L 이었다. 검량선은 0.2~20.0 mg/L의 농도범위에서 우수한 직선성(r^2 0.99)을 보였다. 글루코사민 제품에 이산화규소 0.4, 1.0, 2.0% (w/w)를 첨가하여 시험한 결과 90.22~94.14%의 회수율과 0.72~1.67%의 정밀성을 나타내었다. 확립된 방법으로 시중에 유통되는 건강기능식품 11품목의 이산화규소 함량을 분석한 결과 0.02~1.80% (w/w)로 나타났다. 이 결과는 건강기능식품에 이산화규소의 사용기준 2% (w/w) 이하를 만족하는 결과로 시험한 제품들은 규격에 적합하였다. 따라서 본 연구에서 확립된 이 방법은 건강기능식품 중 이산화규소를 쉽고, 빠르게 분석할 수 있으며, 건강기능식품 중 이산화규소 함량 분석에 효율적으로 사용될 수 있다

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