Chemical and Biomolecular Engineering
2024; 9(1): 8-13
http://www.sciencepublishinggroup.com/j/cbe
doi: 10.11648/j.cbe.20240901.12
ISSN: 2578-8876 (Print); ISSN: 2578-8884 (Online)

Comparative Analysis of Dietary Silica in *Vigna subterranean* (Bambara Nut) and *Arachis hypogeal* (Ground Nut or Peanut)

Terhemba Simeon Iningev*, Elizabeth Ochanya Agbo, Otuwole Esther Abu

Department of Chemistry, Faculty of Science, Benue State University, Makurdi, Nigeria

Email address:
iningevt@gmail.com (Terhemba Simeon Iningev)
*Corresponding author

To cite this article:
Terhemba Simeon Iningev, Elizabeth Ochanya Agbo, Otuwole Esther Abu. (2024). Comparative Analysis of Dietary Silica in *Vigna subterranean* (Bambara Nut) and *Arachis hypogeal* (Ground Nut or Peanut). *Chemical and Biomolecular Engineering*, *9*(1), 8-13. https://doi.org/10.11648/j.cbe.20240901.12

Received: October 17, 2023; **Accepted**: November 7, 2023; **Published**: January 11, 2024

Abstract: Nutritional awareness has been longtime challenge in Nigeria even among literate populace. Many Nigerians preferred food that has characteristic taste to nutritional value. A comparative study to estimate the amount of silica in bambara nut (BN) and groundnut (GN) was carried out in order to create awareness on the preferred grain to be consumed, due to nutritional health benefits of silica. The pulverized sample of each cotyledon was carbonized at 350°C for 30 minutes using muffle furnace to obtain bambara nut ash (BNA) and ground nut ash (GNA), respectively. To produce silica, 10 g ash of each sample was digested separately with NaOH solution to form sodium trioxosiicate. The solution was treated with HCl solution to yield silica at pH adjusted to 7.0. The yield of 2.29% and 9.66%, for BN and GN, respectively, was obtained. Characterization using FT-IR technique has indicated the presence of silanol (Si-OH) and siloxane (Si-O-Si) functional groups in the spectra of the two samples. In addition, Scanning Electron Microscope (SEM) analysis respectively revealed the morphological structure of SiO_2 extracted from BNA and GNA to be amorphous. Thus, the form in which cells of the body can assimilate.

Keywords: Bambara Nut, Ground Nut, Silica, Characterization, FT-IR and SEM

1. Introduction

Elements like nitrogen, phosphorus and potassium are essential nutrients without which plants can not complete their life cycle. While element like silicon (Si) is non-essential, but is of beneficial to plants and provide certain health benefits to higher animals [1, 2]. Si is the second most abundant element present in the earth's crust after oxygen. Silicon dioxide or silica (SiO_2); the chemically combined form of the element is the most important Si-containing inorganic substance [3]. It occurs in crystalline, poorly crystalline and amorphous phases. Amorphous silicon dioxide or silica is an important natural source that release ortho-silicic acid as abioavailable form of silicon. Amorphous silica is acid anhydride of monomeric ortho-silicic acid (H_4SiO_4) that is water soluble and highly stable in diluted aqueous solution. Other hydrated forms of ortho-silicic acid include meta-silicic acid (H_2SiO_3 or lower oligomers such as di-silicic $H_2Si_2O_5$) and tri-silicic acids ($H_2Si_3O_7$), all these can exist in aqueous solutions [3, 4].

Silicic acid [$Si(OH)_4$], is an uncharged monomeric molecule at pH of solution below 9, and it is the form in which Si is taken up by the plant roots from the soil solution. The ability of plants to absorb and accumulate Si differs considerably, ranging from 0.1% to 10.0% (dry weight). However, this depends much on the plant species and Si concentration within the vicinity [5]. Researchers have reported the absorption of Si by monocotyledonous and dicotyledonous species. According to the report, monocot in their tissues, accumulate Si in the order of 5% or more on a dry weight basis and are described as Si accumulators. The dicots on the other hand contain about 0.1% Si on a dry weight basis, and are portrait as intermediate accumulators [6]. The difference in the Si uptake and accumulation of the two cotyledons is that; in the monocots, Si uptake is an active process whereas for dicotyledonous plants, Si is absorbed passively [7]. The absorption of Si by plants from soil in the form of silicic acid is accumulate as silica, where it gets deposited on epidermal cells or as phytoliths in lumen cells. Silicon in the food is ingested as silica when feed by man and other animals [2].

The ortho-silicic acid or amorphous silica is a major form of bioavailable source of silicon that plays numerous key roles in plants, animals and human's health. It has been reported that the presence of silica in plants help to alleviate many abiotic and biotic stresses, leading to protective effect such as physical barrier to penetration and reduction in enzymatic degradation by fungal and other pathogens [8]. It has also been reported that single mineral, typically calcium is not the only mineral involved in bone health formation. It worked synergistically with other minerals such as silica in bone maintenance. Silica is most important to elderly people because it help to prevent the decalcification of bones and improve bones tensile strength [9]. People having silica deficiency are prompt to be affected by diseases like Alzheimer which is caused by accumulation of aluminium in brain tissues [10].

Silica is an important optimal for collagen synthesis that activate the hydroxylation enzymes that improve skin strength and elasticity. It was suggested that hair strands with higher silica content have lower falling rate and higher brightness. Silica also improves quality of nails, and increase protection against nail infections. Deficiency of it can lead to soft and brittleness of nails because silicon is one of the predominant elements in nail composition [11]. All the above mentioned problems were in connection with people that are advanced in age. Other health benefits include protection of the heart by reducing atherosclerosis risk, or lowering the cholesterol level in order to harden the arteries. The University of Memphis (2018) reported that the mineral (silica) can support the immune response and also help to control body inflammation, thereby keeping the heart in good working conditions [12]. Also another studies carried out on some animals have proved that silicon ingested in form of silica helps to prevent the occurrence of streptozotocin-induced diabetes [13].

Though despite the extra-ordinary medicinal and nutritional values one can derive from Vigna subterranean and Arachis hypogea, there are some ill-health linked with consumption of the two cotyledons. BN and GN are both contaminated by *Aspergillus* species (*A.flavus*, *A. parasiticus*, and *A.nomius*) due to poor agricultural practices (preharvest and postharvest conditions). These fungi produced aflatoxins that are known to cause cancer in humans. This significant risk is associated to eating the seeds raw. Besides, GN is also known to contain anti nutrients factors such as phytic acid, tryps in inhibitor, tannin, saponin, which inhibit absorption of some nutrients in diet [13-15]. However, we have seen the nutritional, biological and therapeutic effects of silica; it's depletion level in our body system via kidney and skin flushing needs to be replenished by eating the right meal that contain relative amount of silica. Though many literatures had reported food sources that contain silica [3, 13, 16-18], but published literatures on comparing the amount of silica in edible food is rare. Hence the purpose of this paper has been aimed at comparative analysis of dietary silica in *Vigna subterranean* and *Arachis hypogea*, respectively.

2. Materials and Methods

2.1. Materials

Sodium hydroxide purchased from Merck, hydrochloric acid from QualiKems, and distilled water was used as received.

2.2. Methods

BN and GN samples were washed to remove impurities. These were dried for four days and pounded separately using mortar and pestle. The pulverized samples were carbonized at 350°C for 30 minutes using a muffle furnace to obtain BNA and GNA, respectively. 10 g, each of the carbonized samples was weighed into a 250 mL separate conical flask. 40 mL 0.1 M NaOH solution was added and heated at 60°C for 1h with constant stirring. The solution was allowed to cool to ambient temperature and filtered using Whatman filter paper No 42. The filtrate was treated with 0.1 M HCl with stirring until the pH of the solution was adjusted to 7.0. The silica formed was aged for 24h; filtered, washed and dried at 40°C for 4h. It was stored in an airtight plastic bag prior to analysis

The reaction involving conversion of silicon dioxide to sodium trioxiosilicate (IV) is shown in equation (1), whereas production of silica is shown in equation (2).

$$SiO_2\,(s) + 2NaOH\,(aq) \longrightarrow Na_2SiO_3\,(aq) + H_2O \quad (1)$$

Treatment of sodium trioxosilicate with HCl forms silica

$$Na_2SiO_3\,(aq) + HCl\,(aq) \longrightarrow SiO_2\,(s) + NaCl\,(aq) + H_2O \quad (2)$$

(a) (b) (c) (d)

(e) (f) (g) (h)

Figure 1. *Plates (a) BN seeds (b) GN seeds (c) Pounded BN seeds (d) Pounded GN seeds (e) Crystal formation from BNA (f) Crystal formation from GNA (g) Filtered crystal formation from BN sample (h)Filtered crystal formation from GN sample.*

2.3. Determination of Physicochemical Property of Silica

Determination of Percentage Yield

The percentage yield of the silica extracted was calculated using the formula

$$\%\ \text{Yield} = \frac{\text{Actual Yield (g)}}{\text{Sample (g)}} \times 100$$

2.4. Characterization

2.4.1. FT-IR Measurement

IR spectrum was recorded as Nujol mulls using KBr pellets on FT-IR spectrophotometer Shimadzu (FT-IR8400S). One milligram (1 mg) of each sample was weighed into a small agate mortar and a drop of nujol was added and ground. The mull obtained was suspended on the cell of the spectrophotometer and scanned between 4000-400 cm^{-1} at 32 runs per minute.

2.4.2. SEM Measurement

The morphology of the prepared silica powder was investigated by SEM (Quanta 400, FEI, USA). The sample was coated with a very thin film of gold (Au) using a sputter coater (SPI, 12150AX, USA) and prior to SEM analysis.

3. Results and Discussions

3.1. Percentage Yield of Silica Extracted

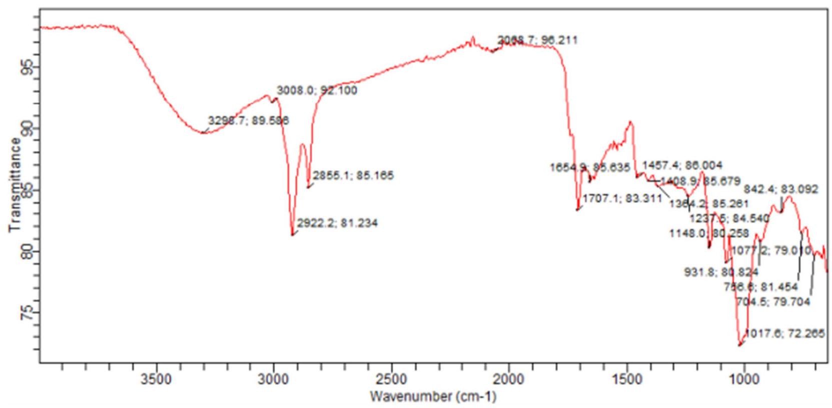
The percentage yields of silica extracted from BNA and GNA digested with 0.1 M NaOH solution were found to be 2.29% and 9.66%, respectively (Table 1). The results indicate that silica is present in both the mono-and dicotyledon grains. From the study it was observed that GN has higher yield compare to BN. Though the literature [6] established that monocot (Si accumulator) grains have higher silica content than dicot. However, the higher yield observed could be attributed to the oil present in GN [19]. In this study, the yield of the monocot is $< 5.0\%$; this could be probably due to incomplete conversion of Si to SiO_2 during carbonization. Besides, literatures [20, 21] have shown that concentration and volume of alkaline solvent as well as extraction temperature and time factors can affect the yield of silica. It means, the more the solvent, the higher the surface area for the distribution of solvent to ash. Hence, there would be increased in the formation of Na_2SiO_3 as well as the yield of silica.

Table 1. *Percentage yield of the extracted silica.*

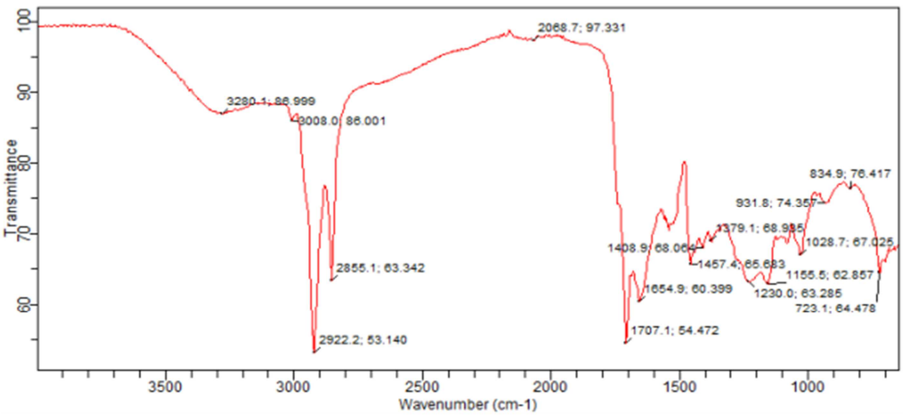
Sample	Percentage Yield
BN	2.29
GN	9.66

3.2. Infrared Spectral Analysis

The FT-IR spectra of silica extracted from BN and GN carbonized at 350°C were shown in Figure 2a and 2b, respectively. A peak at 1654.9 cm^{-1} and abroad band that appeared at 3298.7 cm^{-1}, (Figure 2a) was ascribed to bending and stretching vibrations of the O-H bond from the silanol groups (Si-OH), respectively. This implies that a water molecule is trapped on the silica surface [22]. Similar vibration bands (1654.9cm^{-1} and 3208.1 cm^{-1}) were observed on spectrum of GN, (Figure 2b).



(a)

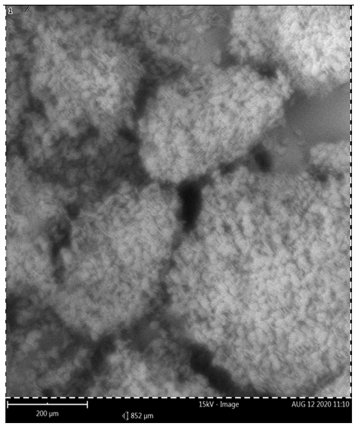


(b)

Figure 2. *a. FT-IR spectrum for silica (BN); b. FT-IR spectrum for silica (GN).*

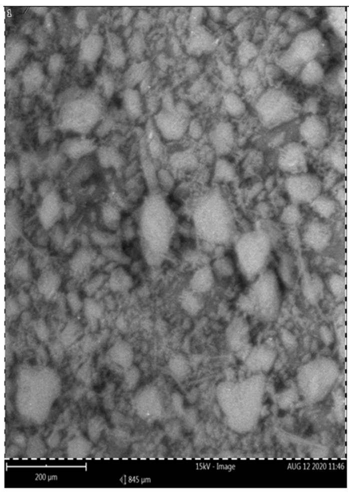
The peaks at 1017.6 cm^{-1} and 1028.7 cm^{-1} from Figure 2a and 2b, respectively, were ascribed to Si-O asymmetric stretching vibration [23]. Peaks at 1148.0 cm^{-1}, (Figure 2a) and 1230.0 cm^{-1}, (Figure 2b) were assigned to stretching mode of Si-O-Si (siloxane), which clearly showed silica formation. The absorption frequency bands observed at 2922.2 cm^{-1} and 2855.1 cm^{-1} from both figures were ascribed to bending mode of $-CH_2$ and $-CH_3$, respectively. Appearance of these bands in the spectra signifies the presence of an organic compound in the two samples [24, 25].

3.3. SEM Measurement



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	83.16	61.25
17	Cl	Chlorine	2.59	5.63
22	Ti	Titanium	1.68	4.94
13	Al	Aluminium	2.93	4.85
41	Nb	Niobium	0.77	4.38
39	Y	Yttrium	0.68	3.71
15	P	Phosphorus	1.53	2.90
16	S	Sulfur	1.43	2.81
14	Si	Silicon	1.24	2.13
19	K	Potassium	0.89	2.12
11	Na	Sodium	1.49	2.10
12	Mg	Magnesium	1.15	1.71
23	V	Vanadium	0.47	1.47
26	Fe	Iron	0.00	0.00
20	Ca	Calcium	0.00	0.00

(a)



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
17	Cl	Chlorine	35.34	49.65
6	C	Carbon	46.62	22.19
16	S	Sulfur	8.83	11.22
47	Ag	Silver	0.96	4.10
41	Nb	Niobium	0.71	2.62
39	Y	Yttrium	0.62	2.20
13	Al	Aluminium	1.55	1.66
11	Na	Sodium	1.45	1.32
20	Ca	Calcium	0.75	1.20
19	K	Potassium	0.72	1.12
14	Si	Silicon	0.98	1.09
12	Mg	Magnesium	0.89	0.85
15	P	Phosphorus	0.45	0.56
22	Ti	Titanium	0.12	0.23
23	V	Vanadium	0.00	0.00
26	Fe	Iron	0.00	0.00

(b)

Figure 3. *a. Micrograph of BN at 750 × magnification.b. Micrograph of GN at 750× magnification.*

Images of silica obtained from *Vigna subterranean* and *Arachis hypogea* as well as total analysis were depicted in Figure 3a and Figure 3b, respectively. The images have shown that the prepared silica derived from both samples carbonized at 350°C were of average size particle and irregular in shape, that is, amorphous [23]. SEM analysis also showed that silicon content in BN (2.13 weight concentration) is more than in GN (1.09 weight concentration); see Figure 3a and Figure 3b. This information is in supportive of the literature which established that, monocotyledon grains are Si accumulator whereas dicotyledons are Si intermediate.

4. Conclusion

The yield of silica (BN: 2.29%, GN: 9.66%) obtained from 10 g ash of each grain using 0.1 M NaOH analytical reagent revealed that BN and GN contain silica. The FT-IR data had shown that the prepared silica contain silanol and siloxane groups. In addition, SEM analysis depicted amorphous state of the extracted silica and has shown that, Si in BN is higher compared to GN. We therefore, recommended consumption of more BN to promote healthy bone formation, improve skin strength and elasticity, lower falling rate of hair, lowers cholesterol level thereby reducing the risk of heart disease such as atherosclerosis.

Acknowledgments

The authors acknowledged the National Research Institute of Chemical Technology, Zaria, Nigeria, for running the FTIR and SEM analyses. We thank technical staff headed by Dr.G.H. Atoo at the Department of Chemistry Benue State University, Makurdi-Nigeria, for their assistance during the study.

Conflicts of Interest

Regarding the publication of this paper, the authors declare no conflicts of interest.

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