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ORIGINAL PAPER

DETERMINATION OF THE SILICON CONTENT IN DIETARY SUPPLEMENTS AND IN WATER*

Paulina Putko[1], Mirosław Kwaśny[2]

[1] Biomedical Engineering Center, Institute of Optoelectronics
[2] Institute of Optoelectronics
Military University of Technology in Warsaw, Poland

ABSTRACT

Silicon (Si) is one of the most important elements on the Earth, and an essential element for all living organisms. In the last two decades, the benefits of silicon in plants, animals and humans have been proven. The content of this element in the human body is from 6 to 7 g, almost twice as much as iron, which confirms its biological significance. The level of Si in the body decreases significantly with age, and a need for its supplementation arises. The mean daily requirement for the element is 20-40 mg, and a diet does not fully provide this amount. Many plant-based supplements with a low content and low bioavailability of the element as well as preparations in the form of aqueous solutions with a high Si concentration, up to 2%, are supplied commercially. The target of the research was to determine the content of silicon in the bioavailable form of orthosilicic acid (H_2SiO_4) in dietary supplements, seawater, tap water, carbonated water and still water, tested with the colorimetric method. The silicon content in bottled waters was determined to be in the range of concentrations of 1 to 20 mg dm^{-3}, while in tap water, seawater and plant preparations it ranged from 0.2 to 1700 mg dm^{-3}. Commercially available preparations with a high concentration of Si (0.1-2%) are characterized by a varied level of bioavailability of H_2SiO_4, not exceeding 20%. The colorimetric method for the determination of orthosilicic acid is well-known, but requires strict conditions to the complex to be formed. The kinetics of the steps during the reaction of complex formation, and the influence of the ambient pH on possible complications were investigated.

Keywords: silicon, dietary supplement, bioavailability of orthosilicic acid.

Paulina Putko, MSc, Biomedical Engineering Center, Institute of Optoelectronics, Military University of Technology in Warsaw, Gen. Witolda Urbanowicza 2, 00-908 Warsaw, Poland, e-mail: paulina.putko@wat.edu.pl

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INTRODUCTION

Silicon is one of the 10 most important natural elements in our body, with its content in the human body equal about 7 g, which is twice as much as the iron content. In the human organism, the highest concentration of silicon is mainly in the connective, cartilage and bone tissue, and the amount of Si in individual internal organs depends mainly on the Si content of the connective tissue. It is found in the bone-joint system, tendons, skin, walls of blood vessels, heart valves and blood, where it reaches the levels of about 10 mg dm^{-3}.

The important role of Si in the body is associated with ensuring the elasticity of blood vessels, counteracting the crystallization of ingredients in the urinary system, delaying the ageing process, and removing toxic substances from cells. In addition, this element positively affects the proper development of the skeleton, removes irritation and inflammation of the skin, improves the condition and prevents hair loss or brittleness of nails, it also has a curative effect in cases of varicose veins, psoriasis and plaques acne (BOGUSZEWSKA et al. 2003, BAREL et al. 2005, JUGDAOHSINGH 2007). Silicon is the basic nutrient of plants and promotes toughness of roots, and is also important in the process of growth and plant resistance to disease. Particularly rich in silicon are herbs, for example, nettle, prostrate knotweed, wheatgrass, Icelandic moss, sedge or alchemilla (ZIELECKA 1996). Silicon is taken passively by plants in the form of orthosilicic acid together with water, and then it is incorporated into plant tissues, as evidenced by the presence of this element in the dry matter of plants. In addition, silicon combines with plant substances (sugars, proteins or phenolic compounds), which occur in all types of their tissues, and this prevents the fungal mushroom from penetrating into the plant. Results of the research carried out by JUGDAOHSIGH (2007) have shown that oligomers of silicic acid, unlike silicic acid, protect the human body against aluminum absorption. The inhibitory activity of silicon was also confirmed in the Belles's syndrome tests, in which 450 mg per day of an aluminum compound and various doses of silicon contained in drinking water (59 and 118 mg dm^{-3} Si per day) were administered to laboratory rats for 5 weeks. As a result of the analysis of aluminum concentrations in internal organs (spleen, brain and liver), less of the examined element was found in rats whose drinking water was enriched with silicon (BELLES et al.1998, RONDEAU et al.2009).

In everyday life, people are in contact with many silicon compounds, but they ingest them mainly in food. However, diatomaceous earth and silica are used as clarifying and filtering substances for example in the production of oils, margarines and beer. They can cause contamination of the final product, which is not desirable from the technological point of view, because silica has been classified as a slightly toxic substance, and its LD$_{50}$ is 3.16 g kg^{-1} (ŁUKASIAK, CZAROBAJ 2002).

The concentration of silicon in drinking water should not exceed 2 mg dm^{-3}. Many experiments by Persha et al., on the content of silicon in bottled still, low-carbon mineral and spring waters as well as in fruit juices showed that among the mineral waters selected for testing the lowest concentration of silicon was contained in the water Kinga Pienińska (3.33 mg dm^{-3}), while the highest one was was obtained for Kryniczanka (30.05 mg dm^{-3}). In the case of natural spring waters, the determined content of the microelement ranged from 3.34 mg dm^{-3} to 11.81 mg dm^{-3}. Analyzing the results of tests on the concentration of silicon in juices, it appears that its highest content occurred in apple juices, and the richest of this element product contained 1.93 mg Si per 100 g, while the poorest in silicon was orange juice, with just 0.21 mg Si 100 g^{-1}. Of all the studied groups of juices, the most popular were fruit juices in which the silicon content varies from 0.89 to 1.6 mg 100 g^{-1} (Presha et al. 2011).

Deficiencies of silicon can cause many ailments, hence supplementation in older people becomes so important. There is a large group of various commercially available silicon preparations on the market, although the element they contain differs significantly in bioavailability. Silicon in the form of insoluble (mineral) is poorly absorbed, as it is estimated that about 10% of non-specialized proteins can actively activate silicon. It is believed that the only form that is available to living organisms is orthosilicic acid.

Currently used dietary supplements containing silicon compounds can be divided into two groups. One comprising preparations with silicon of natural origin, containing extracts from plants rich in silicon or diatoms. The other group includes preparations containing orthosilicic acid, or silicates with various additives protecting against polymerisation (osmolytryglycerol, taurine, choline). The composition of alkali metal silicates with stabilizers can ensure high concentrations of the element, in the range of 0.02-1.6 mol dm^{-3}. Twenty-fold dilution with water makes it possible to obtain silicate solutions stable for two weeks at pH 7-8.

The chief purpose of this research was to compare the assimilable form of various commercially available preparations, using the colorimetric method for determinations. The influence of various reaction conditions on the formation of silicon complex with molybdate- pH, equilibrium time, and complex stability was investigated. Analysis of orthosilicic acid was also carried out in selected mineral waters. The determination of the total Si content was carried out using the ICP method. The colorimetric method of the H_3SiO_4 content in a very wide range of concentrations enabled the monomer-dimer reaction equilibrium to be studied.

General properties of silicon compounds

At room temperature, silicon is a chemically inactive element because the surface of its crystallites is always covered with a thin layer of silicon dioxide. The most common forms of silicon in nature are silicic acid (from orthosilicic acid to insoluble silica) and silicates. The crystalline silica is made of SiO_2 and its basic structural element is the silicon-oxygen tetrahedron $[SiO_4]^{4-}$. There are 13 polymorphic forms of crystalline silica, depending on the locations of silicon-oxygen tetrahedrons. The most common types of silica are quartz and cristobalite. Both forms are also characterized by high melting point and high resistance to weak alkalis and acids.

Amorphous silica is the result of the chaotic spatial location of the tetrahedrons $(SiO_4)^{4-}$. There are varieties of amorphous silica which are obtained in technological processes, such as glass fibers or quartz glass. Some of its forms come from living organisms and are commonly referred to as Biogenic Amorphous Silica. The source of BAS are both plants, diatoms, sponges as well as viruses and fungi (ŁUKASIAK, CZAROBAJ 2002).

The main source of different silicon compounds in soils is the wind erosion of primary and secondary silicates and aluminosilicates. In the soil solution, silicas occur in the form of both monosilicic acids and polysilicic acids. Orthosilic acid enacts an important role in soil because it facilitates access to certain elements necessary for plants. Scientific research (HALL, MORRISON 1906) showed a relationship between phosphorus ions and silicon ions. As a result of research into soil fertilization with fertilizers containing amorphous silica or silica gel (GLAKOVA 1982, MATICHENKOV, AMMOSOVA 1996, BROGOWSKI 2000), the increase in the availability of phosphorus for plants has been proven. However, a reverse dependence was found in the case of aluminum ions. Studies have shown that soil fertilization with appropriate silicon compounds contributes to the reduction of toxic effects of aluminum.

The majority of silicates are aluminosilicates present in soil and rock minerals. Silicon has a very high affinity for oxygen, with which it forms a bond with a stable tetrahedral structure, but in water it appears in the form of weak orthosilicic (monosilicic) $Si(OH)_4$ acid. The equilibrium dissociation constant pKa is 9.8, which means that at pH 9.8 mono-silicic acid is present in 50% in the undissociated form and 50% as silicate ions. The remaining pKa values for further dissociation levels are in the range of 11.8-13.5. Only the addition of a very strong base is able to dissociate all four acidic groups into silicate ions.

The most characteristic feature of silicon is its ability to react with highly diluted solutions of hydroxide alkali. Aqueous solutions of potassium metasilicate are called “water glass” and the hydrolysis of silicates present in the soil gives it an alkaline reaction, because silicic acid is a weak acid.

$$\mathrm{SiO} + 2\mathrm{NaOH} + \mathrm{H_2O} \rightarrow \mathrm{Na_2SiO_3} + 2\mathrm{H_2}$$

Silicon is the only element which in its acidic form reacts with nitric and hydrofluoric acids. This element in mineral form reacts with hydrofluoric acid to form hexafluorosilicic acid, whose degree of hydrolysis increases with the pH value. In a neutral environment, the salts of hexafluorosilicic acid are completely hydrolyzed according to the reaction below.

$$SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H_2O^+$$

$$SiF_6^{2-} + 2H_2O \rightarrow 6F^- + SiO_2 + 4H^+$$

Monosilicic acid at the pH of environment 8 is a neutral molecule, and above 0.03 mol it condenses to form polysilicic acids, which together with the increase in polymerization show an increasingly worse solubility in water. This prevents the production of stable high performance orthosilicic acid without the addition of stabilizing substances. In the first reaction step, the $(OH)_3$-Si-O-Si-$(OH)_3$ dimer is formed, which forms the basis for further polymerization. Depending on the concentration of Si, other ions, the polymerization takes place with the formation of trimer, tetramers and larger linear and cyclic oligomers. All these structures in the suspension are hydrolyzed over time during dilution and again smaller molecules are formed during the attachment of water. At higher concentrations, silicic acid is formed with larger linear molecules which further condense to form colloidal or amorphous silica structures. For organisms (plants, algae, lichens, animals, humans) only monosilicic acid and its dimer are available. These molecules are accessible in soil water, rivers and seas, but the concentration of their biologically available forms is limited to a value of 3-5 mmol (DUGDALE et al. 1995, RAGUENEAU et al. 2000, ROBBERECHT et al. 2009, EHRLICH et al. 2010, FRINGS et al. 2016). The solubility of silica in water is below 200 mg dm^{-3}. In process waters, silica is removed by osmosis or ion exchange techniques to inhibit precipitation or deposition on machine membranes, and purified drinking water contains very little silicon. Silica particles contain highly hydrolysed attractive and binding surfaces, through hydrogen bonds they bind macromolecules containing OH groups, such as polysaccharides, proteins, phenols. There are speculations and the first literature reports that, in addition to silicic acid, silicates also have biological availability. Small molecules of silicic acid are able to penetrate all kinds of cell membranes and specific entry channels (aquaporins) or orthosilicic acid transport proteins have been detected in plants and algae. Similarly, silicate ions can penetrate, but it is difficult to chemically show differences between them and acids. It is also possible to convert the silicates into orthosilicic acid during introduction into the membrane or other aquaporins for silicates. The silicates are industrially prepared from silica under strongly basic conditions by dissociation of the Si-O-Si bond. The solutions contain a mixture of silicate anions with varying degrees of polymerization depending on the concentration of alkali metal hydroxide added. The building block of all these anions is a tetrahedral anion with a silicon atom in the center and oxygen in the corner (SiO^{4+}) similar to orthosilicic acid. The mixture of silicate anions contains linear and cyclic structures of mono-, di-, tri- and more anions of the general formula $xSiO_2$:Me_2, where Me is an alkali metal atom. For values of $x<2$, higher concentrations of mono and di-silicates are obtained, for higher x-values complex polymers are formed. For pH>11, stable solutions of monomeric and polymeric silicate ions are obtained, without amorphous, insoluble silica. Below this pH, only a small portion is present as a monomeric silicate anion. Polymers or silica gels are formed, characterized by the loss of interstitial alkali metal ions from the three-dimensional network. Dilution of concentrated silicate solutions in water causes new distributions of silicate structures, because the pH of the solution drops. Figure 1 shows the reactions.

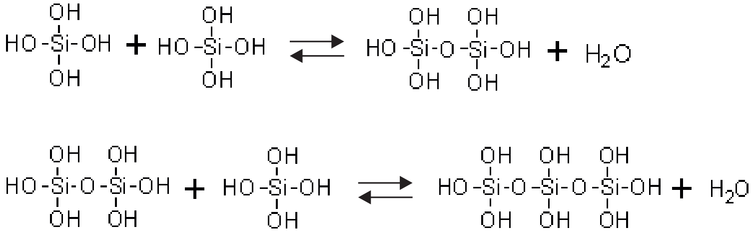

Fig.1. Silicic acid condensation reactions

On the basis of the studies of vegetable silica and occurring in primitive animal organisms, the following structures were obtained: Q_2 $(\mathrm{Si(OSi}\equiv)_2(\mathrm{OH})_8)$ and Q_3 $(\mathrm{Si(OSi}\equiv)_3(\mathrm{OH})_{10})$ – Figure 2.

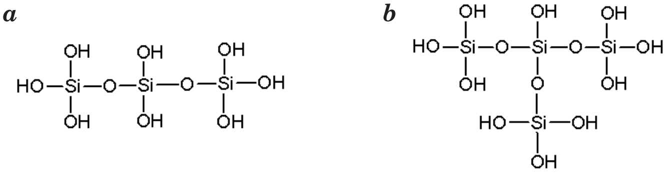

Fig. 2. Silica structures: *a* – Q_2, *b* – Q_3

MATERIALS AND METHODS

The UV-VIS calibration diagram was based on the method of determining silicon in a dissociated form. This method is based on reaction in the acidic environment of dissociated silicon with ammonium molybdate. The result is a yellow-colored, silicomolybdic acid which changes color to intense silicomolybdenum blue as a result of the introduction of the reducing solution. From literature data shows that the complexation reaction in the 1st stage should take place at the pH of the environment equal to 1. Measurements pH under the given conditions, however, show that the pH is about 1.5-1.7 depending on the acidity of the analyzed preparation. In the assays, the value of 1.5 was chosen as the optimal pH, which gives reproducible results, high durability of the resulting complex (Łukasiak, Czarobaj 2002, Mojsiewicz-Pieńkowska, Łukasiak 2003).

A silicon standard of $[NH_4]_2SiF_6$ at 1000 mg dm^{-3} (SINGLE-ELEMENT ICP-Standard-Solution by ROTI®STAR) was used to determine the calibration graph. First, the standard solution was diluted in a 50 cm^3 flask to obtain a 5 mg dm^3 solution. Then 15 different samples were prepared, for this purpose different amounts were taken from the prepared standard solution, so that its final concentration in a 25 cm^3 flask was in the range of 0.05-1.1 mg dm^3. The following reagents were then added to each sample in the following order: 0.25 cm^3 1.25 mol dm^{-3} sulfuric acid(VI) and 1.25 cm^3 of a 5 % aqueous solution of ammonium molybdate.

$$(NH_4)_6Mo_7O_{24} + 3H_2SO_4 \leftrightarrow H_6Mo_7O_{24} + 3(NH_3)_2SO_4$$

Molybdenum acid $H_6Mo_7O_{24}$ with silicic acid H_4SiO_4 form yellow silicomolybdic acid:

$$7H_4SiO_4 + 12Mo_7O_{24} \leftrightarrow 7H_4SiMo_{12}O_{40} + 36H_2O$$

After 20 min (Figure 3), the flask was added successively: 5 cm^3 of distilled water, 1.25 cm^3 of a 5% aqueous solution of oxalic acid and 0.75 cm^3 of a 0.25% aqueous solution of Mohr's salt. After introducing all the reagents, each 25 cm^3 flask was made up to the mark with distilled water.

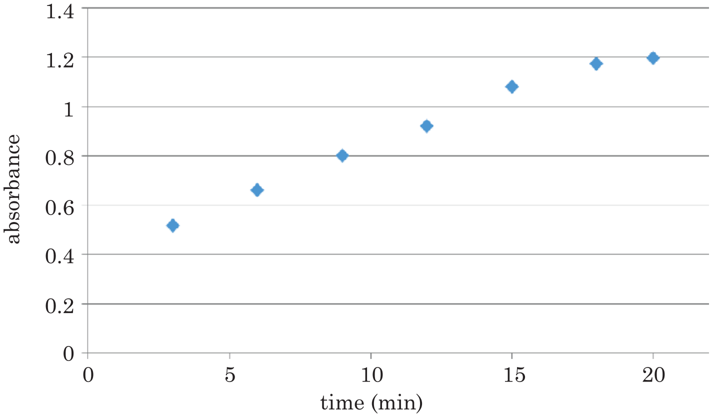

Fig. 3. Kinetics of the reaction of formation of silicomolybdic acid

The silicomolybdic acid formed in the first reaction step is reduced with an aqueous solution of Mohr's salt in the presence of a solution of oxalic acid, which ensures a suitable pH of the solution.

$$H_4SiMo_{12}O_{40} + (NH_4)_2Fe(SO_4)_2 \leftrightarrow H_6SiMo_{12}O_{40} + (NH_4)_2Fe(SO_4)_2$$

In $H_6SiMo_{12}O_{40}$ acid, adjacent molybdenum ions combined with the silicon ion are reduced to Mo^{5+}; moreover, the bond is responsible for the blue colouration of the solution.

Then, after 30 min (Figure 4), the absorbance at the analytical wave-

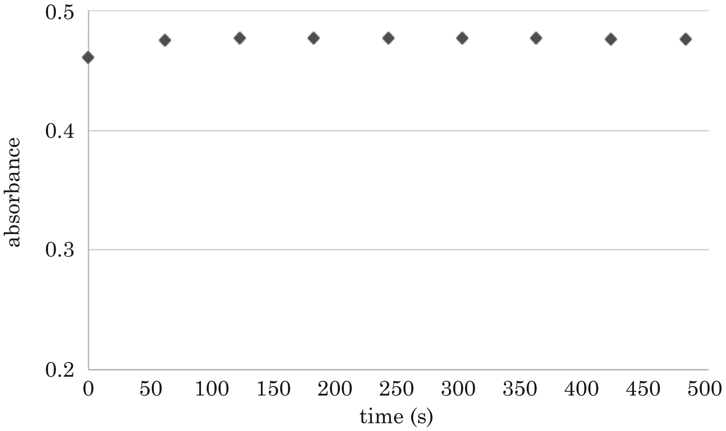

Fig. 4. Kinetics of the reaction of formation of silicomolybdenic acid in the 2^{nd} stage

length $\lambda = 814$ nm was measured, and the results and spectrum of the available silicon form in the standard are given below. Below is a calibration graph for the available silicon form (orthosilicic acid) and its spectrum (Figures 5, 6).

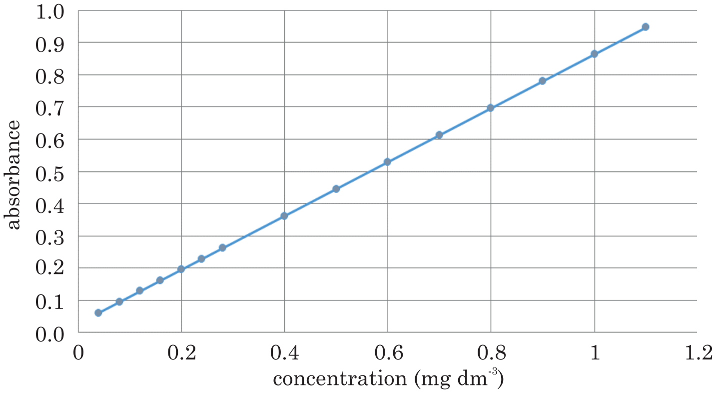

Fig. 5. Calibration diagram of silicon in the dissociated form

For the determination of silicon in the assimilated form, dietary supplements have been selected: human cantein silicon in form MMST (preparation 1, 3, 4) and choline-stabilized orthosilicic acid (preparation 2, 5, 6, 7) as well as animal (preparation 8). Prepartion 6 and 7 are the same supplement, which differ method of obtaining.

Each preparation was appropriately diluted and then introduced at 3 cm^3 into 25 cm^3 flasks. In the first stage, 0.25 cm^3 of 1.25 mol dm^3 sulfuric acid(VI) solution and 1.25 cm^3 of a 5% ammonium molybdate solution were added into the test samples. Then, after 20 min, 5 cm^3 of distilled water was added, after which 1.25 cm^3 of a 5% solution of oxalic acid and 0.25% Mohr's salt solution were introduced. Subsequently, each flask was filled

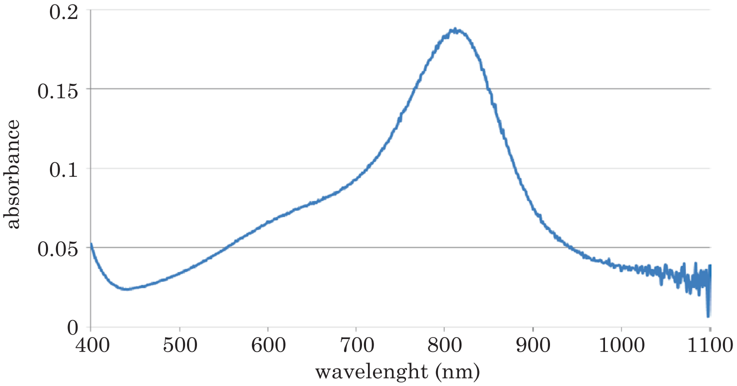

Fig. 6. The spectrum of the form of the silicon absorbed in the model

with distilled water to the grade, and after 20 min the absorbance was measured at the analytical wavelength λ = 814 nm. Spectra of the tested preparations are presented below (Figures 7, 8).

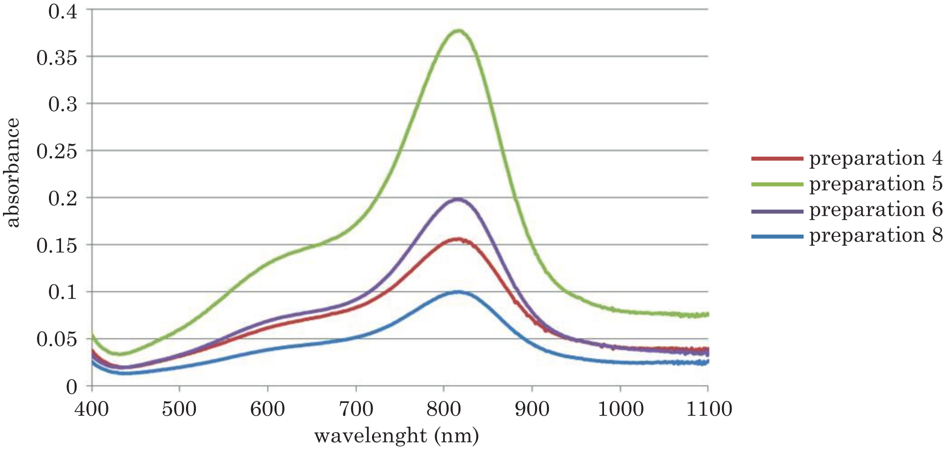

Fig. 7. Spectra of preparations containing a higher amount of silicon in the form of orthosilicic acid

RESULTS AND DISSCUSION

In the case of preparation 2, greenish colouration of the test solution and peak cleavage were observed, hence an individual calibration graph (Figure 9) was prepared and the absorbance at the analytical wavelength λ=1025 nm was measured. A different colour may result from the difference in pH of the reaction medium (pH=2), whereas the final pH value after the addition of all reagents in the other mixtures was 1.5. Another explanation

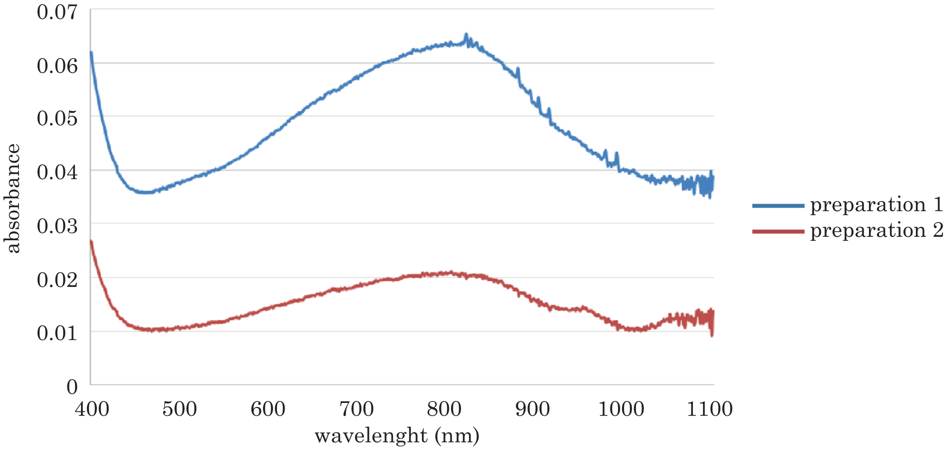

Fig. 8. Spectra of less absorbable preparations

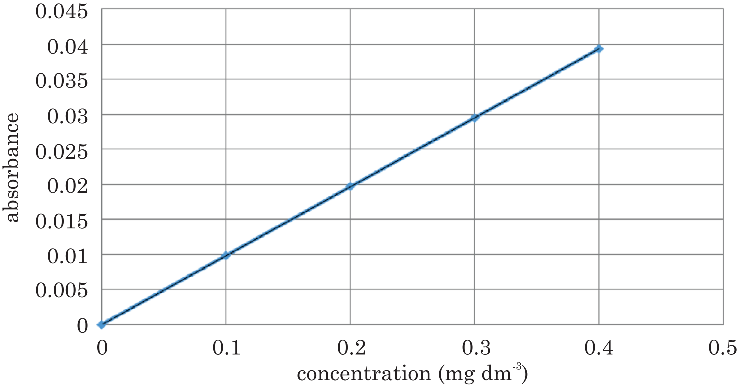

Fig. 9. Silicon calibration graph in an available form for preparation 2

may be the effect of silicon stabilizing additives that affected the peak cleavage. The results of the study are presented in the Table 1 together with the spectra (Figure10).

The results of UV-Vis tests indicate that the highest concentration of silicon in the available form is contained in preparations 6 and 7. In contrast, preparations 1, 3 and 4 contain less than 0.6 mg dm^{-3} of silicon.

In addition, the preparations were examined with the ICP-OES method to compare their content of silicon in the available form with total silicon, and the results are summarized in Table 2.

The results obtained with both techniques show that the lowest content of silicon in the bioavailable form was included in preparations 3 and 4. Furthermore, the highest ratio of bioavailable silicon to the total content of this microelement was obtained for preparation 1 (18.5 %) and preparation 8 (16.6%).

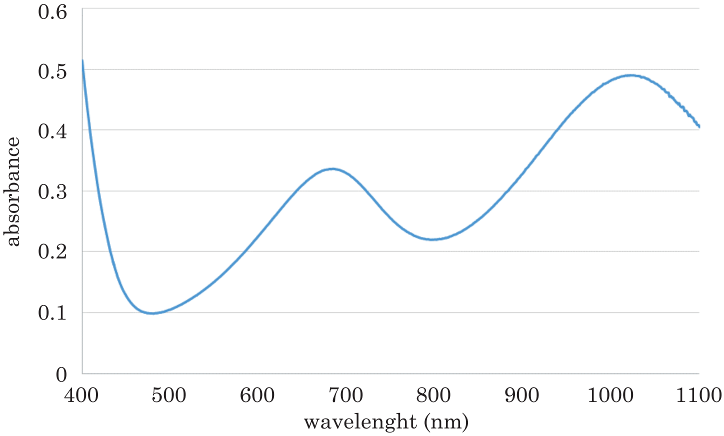

Fig. 10. The spectrum of preparation 2

Table 1

The results of the determination of silicon in the bioavailable form in selected preparations using the UV-Vis technique

Name preparation	Concentration of available form Si in sample (mg dm^{-3})	Dilution (multiplicity)	Concentration of available form Si (mg dm^{-3})
Peparation 1	0.040 ± 0.011	5	0.270± 0.066
Preparation 2	0.236±0.007	15	3.600±0.110
Preparation 3	0.033±0.004	15	0.539±0.064
Preparation 4	0.033±0.003	10	0.449±0.039
Preparation 5	0.220±0.021	255	56.299±5.355
Preparation 6	0.408±0.004	4000	1672±16
Preparation 7	0.224±0.001	4000	915.0±4.0
Preparation 8	0.209±0.005	5	0.869±0.025

Based on the daily requirement of the body for silicon, which is from 20 to 40 mg, the amount of individual preparations that should be consumed was estimated. The results are presented in the Table 3.

Tests were also carried out to determine silicon in the available form in several still mineral waters, sparkling mineral waters, tap water and in seawater collected in August 2017 from the Baltic Sea in the village Jastarnia together with tap water from that locality. Bottled water was purchased in hypermarkets in Warsaw, from July to August 2017. In addition, tap water was drawn for testing in Warsaw in August 2017, and the content of silicon in the same water was filtered through a filter with actived carbon.

Table 2

Comparison of the content of silicon determined with UV-Vis and ICP-OES

Name preparation	Concentration of available form Si (mg dm^{-3})	Bulk concentration of Si (mg dm^{-3})	Determination of available form Si in preparation (%)
Preparation 1	0.270± 0.066	1.462±0.132	18.5
Preparation 2	3.600±0.110	990±64	3.6
Preparation 3	0.539±0.064	3121±91	0.02
Preparation 4	0.449±0.039	2286±55	0.02
Preparation 5	56.299±5.355	4100±121	1.4
Preparation 6	1672±16	21073±980	8
Preparation 7	915.0±4.0	21073±980	4.3
Preparation 8	0.869±0.025	5.24±0.31	16.6

Table 3

Estimated amounts of the test preparations that correspond to the body’s daily demand for silicon

Name of preparation	Concentration of available form Si (mg dm^{-3})	The volume of preparation that corresponds to the body’s daily demand for silicon (dm^3)
Preparation 1	0.270	74-148
Preparation 2	3.600	5.6-11.1
Preparation 3	0.539	37-74
Preparation 4	0.449	45-89
Preparation 5	56.299	0.36-0.71
Preparation 6	1672	0.012-0.023
Preparation 7	915.0	0.022-0.044
Preparation 8	0.869	23-46

The spectra of individual waters (Figures 11, 12) shown below clearly demonstrate that carbonated waters have the highest content of silicon in the form of orthosilicic acid. An exception is still water 4, in which the available form of the analyzed element is slightly lower than in the carbonated water distributed by the same producer, but higher than that in carbonated water 2 and 3 or in other non-carbonated waters.

The results of this part of the research (Table 4) show that most silicon in the available form was found in carbonated water 1 (11.26 mg dm^{-3}), and

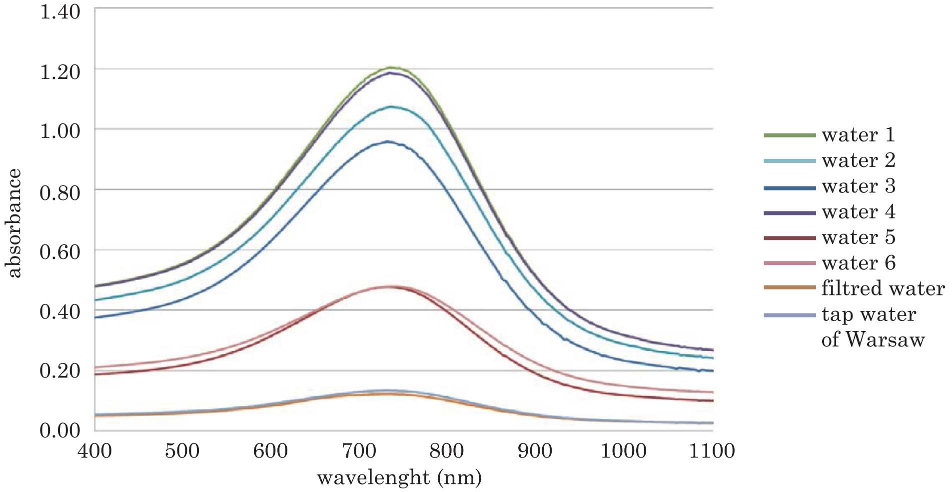

Fig. 11. Diagram of the silicon content in the dissociated form in individual waters

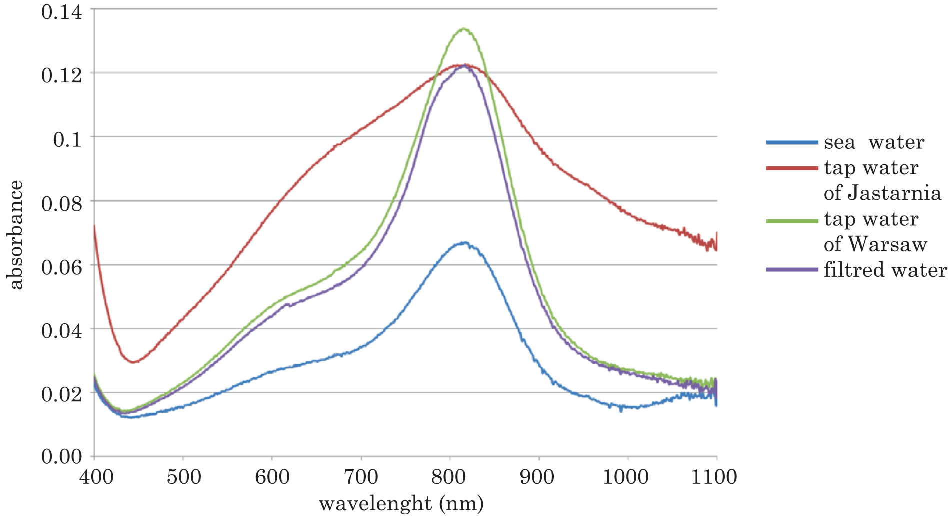

Fig. 12. Diagram of silicon content in the available form in tap water and seawater

the least was in still water 5 (3.84 mg dm^{-3}). In comparison with the results obtained by Prescha (2011), such as from 5 to 30 mg dm^{-3} in mineral waters and from 3 to 12 mg dm^{-3} in spring waters, our data are convergent despite having been obtained with different methods.

Comparing the content of the studied element in the bioavailable form, it can be concluded that in the sea water and tap water filtered there is a small amount of it, slightly higher content was obtained for tap water. However, commercially available waters contain at least 4 times more silicon in the form of orthosilicic acid compared to tap water.

Table 4

Results of the determination of silicon in the available form in the tested water samples by the colorimetric method

Type of water	Name of water	Concentration of available form Si in sample (mg dm^{-3})	Concentration of available form Si in water (mg dm^{-3})
Sparkling mineral water	water 1	1.41±0.01	11.26±0.11
	water 2	1.25±0.09	10.1±0.9
	water 3	1.11±0.07	8.90±0.62
Still mineral water	water 4	1.34±0.06	10.7±0.6
	water 5	0.48±0.02	3.84±0.07
	water 6	0.54±0.04	4.33±0.17
Water collected for testing	seawater	0.050±0.009	0.370±0.003
	tap water of Jastarnia	0.11±0.01	0.91±0.09
	tap water of Warsaw	0.13±0.01	1.01±0.01
	filtered water	0.11±0.01	0.91±0.09

CONCLUSIONS

The results of the tests show that the content of silicon in the available form (orthosilicic acid) in relation to total silicon in food supplements does not exceed 20%. Preparation 1 (18.5%) turned out to be the best specimen in this regard, and the lowest content of the analysed compound was in preparations 3 and 4 (0.02%). However, the highest content of both available silicon and total silicon was found for supplements 6 and 7 (so-called nano silicon).

Comparing the results obtained for water with both methods, it can be concluded that carbonated waters contain more silicon in the available form non-carbonated waters. The high overall silicon concentration determined by the ICP-OES method in waters results from the presence of the studied element in an indeterminable form (SiO_2).

On the basis of the determination of the content of orthosilicic acid by the colorimetric method, approximate assimilation of the tested preparations can be estimated. The actual amount of available silicon in the body is determined by comparing the amount of silicon introduced and excreted through the urine. In addition, it is assumed that the forms of acids in the stomach do not change, which may be an erroneous assumption because under the influence of the acidic environment in the stomach they may undergo monomerization and consequently their assimilation will increase significantly. An example is organic silicon (MMST) preparations, which are assimilable after hydrolysis to acid (Aguilar et al. 2016).

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