Silicon-containing compounds in horsetail (Equisetum Equisetaceae) composition

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Abstract: The article presents the results of a chemical and phase composition study of ash obtained from the aerial parts of three horsetail species growing in different regions of Primorsky Krai, namely forest (Equisetum sylvaticum L.), wintering (Equisetum hyemale L.) and field (Equisetum arvense L.) horsetail. It is shown that the conditions for processing raw materials affect the content of silicon dioxide (32–98%) in the ash residues. X-ray phase analysis has shown that the amorphous or amorphous-crystalline state of ash residues depends on the conditions of their production. The absorption bands typical for amorphous silicon dioxide are observed in the IR spectra of ash samples, which correspond to bending (467 cm⁻¹) and stretching vibrations (802 and 1092 cm⁻¹) of Si-O-Si siloxane bonds. The elemental analysis of silicon-containing products indicates an increase of silicon dioxide content in the samples with an increase in acid concentration during the processing of the aerial part of the horsetails, which also depends on the plant species: the field horsetail contains the lowest quantity of SiO₂ as compared to the forest and wintering horsetails, but is characterised by a high content of potassium and calcium compounds. The sorption characteristics of ash obtained from the aerial part of horsetails are assessed: iodine adsorption capacity (5–42%) and methylene blue (164–260 mg/g) and methyl orange (40–241 mg/g) organic dye adsorption capacities. The obtained information can be used in the development of sorbents from vegetable raw materials for the purification and after-purification treatment of natural and waste waters from pollutants of various types.

Keywords: horsetail (Equisetum), ash, amorphous silica, elemental composition, sorption properties

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SiO-Si. The elemental analysis of the silicon-containing compounds revealed that with an increase in the concentration of silicon in the process, the silicon content in the plant increases, which is due to the deposition of silicon dioxide in the plant. The size of the plants of this genus varies from a few centimetres to several metres [1]. 13 horsetail species are represented in the flora of the Russian Federation [2]. As studies have shown [3], the plants of the horsetail genus contain more than 35 macro- and microelements. A comparison of the elemental content indicates a similar chemical composition among the different horsetail types. In addition to silicon, there is a general tendency towards the accumulation of such elements as calcium, sodium, iron and zinc. However, amongst the various species there is a significant difference in the quantitative content of these elements. In the aerial part of horsetails, there is a large amount of silica (up to 25% of the dry weight), which structure is considered in a number of works [4-8]. Depending on species and other factors, the silicon content in horsetails can differ by a factor of up to three, which probably affects their pharmacological activity [1, 9]. Silica deposits are observed in all organs of the field horsetail, including the rhizome, stem, leaves and spores. Numerous plant structures, including cell walls and stomata, are silicified. Silicon is associated with hemicellulose and callose in horsetails in the same way as in other silicophilous plants [10]. It was established that the callose polysaccharide can serve as the basis for the silicon deposit [11]. The mechanical role of silica in strengthening and hardening of tissues is described in [5, 12, 13]. The existence of a unique connection between Si(OH)₄ and callose is indicated as providing protection against fungal infection [11, 14]. Horsetails have fodder and technical value [15, 16], as well as being of great interest for the production of pharmacological preparations [3, 17, 18]. Horsetail (E. arvense L.) is used in mainstream medicine. However, although raw materials containing a large amount of silicon are formed following the extraction of biologically-active substances, the composition and properties of this residue have been little studied.

The aim of the work is to study the silicon-containing products of aerial part of three types of horsetails (forest, field and wintering).

EXPERIMENTAL PART

The aerial parts of forest horsetail (E. sylvaticum L.; Primorsky Krai, Kiparisovo), wintering horsetail (E. hyemale L.; Primorsky Krai, Roschino, Partisans, Ussuriisk) and field horsetail (E. arvense L.; Primorsky Krai, Pshenitsyno) were used as a (raw) material for the study.

The ash was obtained by the oxidising firing of the raw material (Scheme 1) or raw materials after processing (Schemes 2a–3b) (Table 1). The hydrolysis of the raw material was carried out in a ratio S:L = 1:13 when heated up to 90 °C for 1 h and stirred. The residue after hydrolysis was filtered, dried and calcined in a muffle furnace at 650 °C to constant weight.

The numbers of horsetail ash samples (No. 1–15) are given in Table 2. The ash samples of rice fruit shells (No. 16, 17) obtained according to Schemes 1 and 3a (see Table 1) were used for comparison.

Elemental analysis was performed by energy dispersive X-ray fluorescence spectroscopy using an EDX 800 HS spectrometer (Shimadzu, Japan) with a Rh anode tube and an exposure time of 100 s. The concentration of elements was calculated using a calibration curve.
Table 1

Schemes for obtaining the ash from the aerial parts of horsetails

| Scheme number | Conditions                                                                 |
|---------------|-----------------------------------------------------------------------------|
| 1             | Calcination at 650 °C                                                      |
| 2a            | The hydrolysis of raw materials with water, then according to Scheme 1     |
| 2b            | Processing raw materials with ethyl alcohol, then according to Scheme 1    |
| 2c            | Processing raw materials with ethyl alcohol, then the hydrolysis of the residue of raw materials with 0.1 M HCl solution, then according to Scheme 1 |
| 3a            | The hydrolysis of raw materials with 0.1 M HCl solution, then according to Scheme 1 |
| 3b            | The hydrolysis of raw materials with 1.0 M HCl solution, then according to Scheme 1 |

Table 2

Characteristics of ash obtained from the horsetail aerial parts

| Raw materials, collection place | Ash production scheme | Sample number | Ash yield, %, Colour | Bulk density, g/m³ | Ash characteristics   | XRF data                   | Amorphous phase interplanar distance, Å |
|---------------------------------|-----------------------|---------------|----------------------|-------------------|------------------------|---------------------------|---------------------------------------|
| Field horsetail, commercial drug | 1                     | 1             | 16.8 grey 9.5 light grey 6.5, light beige 5.5 white | 99                | amorph.-cryst.         | sylvite (KCl), anhydrite (CaSO₄) sylvite (KCl), larnite (β-Ca₂SiO₄) | 4.08                                  |
|                                 | 2a                    | 2             | 18.8 light grey 12.6 white | 74                | amorph.-cryst.         | sylvite (KCl), wollastonite (CaSiO₃), sylvite (KCl) | 4.17                                  |
|                                 | 3a                    | 3             | 14.4 light grey 10.3 white | 56                | amorph.                | cristobalite (SiO₂), quartz (SiO₂) | 3.85, 2.85                           |
|                                 | 3b                    | 4             | 15.0 grey 10.2 white | 62                | amorph.                | cristobalite (SiO₂), brucite (Mg (OH)₂) | 4.05                                  |
| Forest horsetail, Kiparisovo settlement | 1                     | 5             | 14.4 light grey 10.3 white | 66                | amorph.-cryst.         | cristobalite (SiO₂), quartz (SiO₂) | 3.85                                  |
|                                 | 3a                    | 6             | 15.0 grey 10.2 white | 48                | amorph.-cryst.         | cristobalite (SiO₂), brucite (Mg (OH)₂) | 4.05                                  |
| Wintering horsetail, Roshchino settlement | 1                     | 7             | 16.8 grey 9.5 light grey 6.5, light beige 5.5 white | 99                | amorph.-cryst.         | calcium carbonate (CaCO₃), calcium silicate (CaSiO₃), calcium carbonate (CaCO₃), calcium oxide (CaO) quartz (SiO₂) | –                                     |
|                                 | 3a                    | 8             | 14.4 light grey 10.3 white | 66                | amorph.-cryst.         | calcium carbonate (CaCO₃), calcium silicate (CaSiO₃), calcium carbonate (CaCO₃), calcium oxide (CaO) quartz (SiO₂) | –                                     |
| Wintering horsetail, Ussuriisk town | 2b                    | 9             | 14.4 light grey 10.3 white | 66                | amorph.-cryst.         | calcium carbonate (CaCO₃), calcium silicate (CaSiO₃), calcium carbonate (CaCO₃), calcium oxide (CaO) quartz (SiO₂) | –                                     |
|                                 | 2c                    | 10            | 15.0 grey 10.2 white | 48                | amorph.-cryst.         | calcium carbonate (CaCO₃), calcium silicate (CaSiO₃), calcium carbonate (CaCO₃), calcium oxide (CaO) quartz (SiO₂) | –                                     |
| Rice husks | 1                     | 16            | 15.0 light grey 12.0 white | 37                | amorph.                | –                          | 4.07                                  |
|                                 | 3a                    | 17            | 15.0 light grey 12.0 white | 25                | amorph.                | –                          | 4.07                                  |
The content of silicon dioxide in the obtained samples was also determined by the gravimetric method. About 2.0 g of the preparation was placed in a platinum crucible, calcined to constant weight at 800–900 °C and weighed. The calcined residue was moistened with 2 cm³ of water, followed by the addition of 0.25 cm³ of sulphuric acid and 10 cm³ of hydrofluoric acid and heating on a hotplate until the volatilisation of the liquid and the sulphuric acid vapours was complete. The preparations were further calcined for another 5 min at 600–700 °C and weighed. At the same time, a non-volatile residue in the reagents used was determined under the same conditions.

The mass fraction of silicon oxide (IV) \( X \) in percent was calculated by the formula:

\[
X = \frac{m - m_1 - (m_2 - m_3)}{m} \cdot 100,
\]

where \( m \) is the mass of the preparation, g; \( m_1 \) is the mass loss on ignition, g; \( m_2 \) is the mass of residue after the treatment of the calcined preparation with hydrofluoric acid, g; \( m_3 \) is the mass of the residue of the used reagents after the treatment with hydrofluoric acid.

X-ray diffraction patterns were recorded using a D8 Advance diffractometer (Bruker, Germany) with Cu Kα-radiation. Phase identification was performed using the EVA software and PDF-2 database on powder diffraction.

IR absorption spectra of samples suspended in petroleum jelly were recorded in the range of 400–4000 cm⁻¹ using a FTIR Prestige-21 Fourier transform spectrophotometer (Shimadzu, Japan).

The pH determination of the aqueous extract of ash samples was carried out as follows. 5 g of the ash sample was placed in a flask, 50 cm³ of distilled water was added and boiled for 3 minutes in a flask with reflux condenser. Further the flask content was filtered, the filtrate was cooled and the pH was determined using a FiveEasyPlus 20 pH metre (Mettler Toledo, Switzerland).

To determine the mass fraction of watersoluble substances \( X_1 \) in the ashes, 5 g of the sample was placed in a conical flask, 250 cm³ of water was added and boiled in a reflux condenser for 2 h, then the flask content was filtered. The filtrate was evaporated, and the resulting residue was dried at 110 °C to constant weight. The mass fraction of water-soluble substances \( X_1 \) was calculated by the formula:

\[
X_1 = \frac{m_1 \cdot 100}{m},
\]

where \( m_1 \) is the mass of dry residue, g; \( m \) is the sample weight, g.

Ash bulk density \( \rho_a \) was determined by the following method. The test sample was poured into a pre-weighted cylinder 10 cm high until a cone was formed, which was removed with a ruler up to the brim (without compaction), after which the cylinder with the sample was weighed.

The bulk density of the sample was calculated by the formula:

\[
P_b = \frac{(m_1 - m)}{V},
\]

where \( \rho_b \) is the bulk density of the sample, kg/m³; \( m_1 \) is the mass of the measuring cylinder with the sample, kg; \( m \) is the mass of the measuring cylinder, kg; \( V \) is the volume of the measuring cylinder, m³.

To determine the methylene blue (MB) and methyl orange (MO) adsorption capacity, 0.1 g of the ash sample was placed in a conical flask, 25 cm³ of dye solution (1500 mg/dm³) was added and shaken with a stirrer during 20 min. After shaking, the suspension was centrifuged. The dilution factor for the determination of the methylene blue (MB) adsorption capacity is 10, and methyl orange (MO) adsorption capacity is 100. The optical density of the solutions was measured using an UNICO-1201 spectrophotometer (United Products & Instruments Inc., USA) with a light filter with \( \lambda = 400 \) nm wavelength. Sorbent’s indicator adsorption capacity \( X \) in milligrams per 1 g of the product was calculated by the formula:

\[
X = \frac{(C_1 - C_2) \cdot K \cdot 0.025}{m},
\]

where \( C_1 \) is the mass concentration of the initial solution, mg/dm³; \( C_2 \) is the mass concentration of the solution after contacting with the sample, mg/dm³; \( K \) is the dilution factor of the solution; 0.025 is the volume of the model solution, dm³; \( m \) is the sample mass, g.

To determine the iodine adsorption capacity of ashes, 1.0 g of ash sample was placed in a conical flask with the volume of 250 cm³, 100 cm³ of iodine solution in potassium iodide with a molar iodine concentration of 0.1 mol/dm³ was added, closed with a stopper and stirred for 15 min at an intensity of at least 100–125 vibrations per minute. Further a 10 cm³ of solution was taken by a pipette, placed in a conical flask with the volume of 50 cm³ and titrated with a solution of sodium thiosulphate (0.1 mol/l). At the end of the titration, 1 cm³ of starch solution was added and titrated until the blue colour had disappeared. At the same time, the initial iodine content in the solution was determined. For this, 10 cm³ of iodine solution in potassium iodide was taken and titrated with sodium thiosulphate solution, with a starch solution added at the end of the titration. The iodine adsorption activity of sorbents \( X \) in percent was calculated by the formula:

\[
X = \frac{(V_1 - V_2) \cdot 0.0127 \cdot 100 \cdot 100}{10 \cdot m},
\]

where \( V_1 \) is the volume of sodium thiosulphate solution...
lution used for the titration of 10 cm³ of iodine solution in potassium iodide, ml; \( V_2 \) is the volume of sodium thiosulphate solution used for the titration of 10 cm³ of iodine solution in potassium iodide, after treatment, ml; 0.0127 is the mass of iodine, corresponding to 1 cm³ of sodium thiosulphate solution with a concentration of exactly 0.1 mol/l, g; 100 is the volume of iodine solution in potassium iodide taken for clarification, ml; \( m \) is the weight of the sample, g.

RESULTS AND DISCUSSION

Below are the results of the study of ash samples obtained from the aerial parts of horsetails.

Ash yield, product colour, bulk density. Ash content in horsetails depended on the type of plant and the scheme for processing of raw materials (see Table 2). Thus, the ash yield obtained according to Scheme 1 ranged from 14.4 (Sample 7) to 18.8% (Sample 5), and according to scheme 3a – from 6.0 (Sample 14) to 12.6% (Sample 5). The amount of ash did not depend on the plant collection place, as shown by the example of wintering horsetail. The ash colour changed from grey to white, depending on the conditions of production. The bulk density of the ash obtained according to Scheme 1 also depended on the type of horsetail and varied within 99.0 (Sample 1) – 48.0 kg/m³ (Sample 11).

Phase composition. X-ray phase analysis of ash showed that, unlike the reference sample (No. 16), all samples obtained according to Scheme 1 (No.1,5,7,11, 13) were in an amorphous-crystalline state (Table 2; Fig. 1, X-ray diffraction Patterns 1, 5 and 7). The presence of an amorphous phase in the samples is indicated by a diffuse peak on the X-ray diffraction patterns in the region 2θ = ~15–35°. In the amorphous phases, the interplanar distances have different values (Table 2), indicating their varying structure. The composition of the crystalline phase varies depending on the plant type and its collection place (Samples 7 and 11). All ash samples obtained according to Schemes 2b, 3a and 3b (No. 3, 4, 6, 8, 10, 12, 17) are in an amorphous state, with the exception of Samples 14 and 15 (see Table 2). A typical X-Ray diffraction pattern for Sample 3 is shown (Fig. 1, Pattern 3), on which a blurred – but narrower as compared with Patterns 1, 5 and 7 – peak is observed; this is characteristic of the amorphous structure of the substance [19]. The interplanar distance of this reflex for these samples is 4.03–4.08 Å, indicating their similar structure.

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\[ \text{Fig. 1. X-Ray diffraction patterns of silicon-containing samples obtained from the horsetail aerial parts according to different Schemes (the pattern number corresponds to the sample number in Table 2)} \]

Рис. 1. Рентгенограммы кремнийсодержащих образцов, полученных из надземной части хвощей по разным схемам (номер линии соответствует номеру образца по табл. 2)
IR absorption spectra. Fig. 2 shows the IR absorption spectra of ash samples obtained according to Scheme 1 (Samples 1, 5, 7) and Scheme 3a (Sample 3). IR spectrum of Sample 3 is typical for the amorphous silicon dioxide [19]: there are absorption bands corresponding to bending (467 cm⁻¹) and stretching (802 and 1092 cm⁻¹) vibrations of Si-O-Si siloxane bonds. Weak absorption bands at 3181–3684 (stretching) and 1639 (bending) cm⁻¹ indicate the presence of a small number of O – H bonds. According to the IR spectra, siloxane bonds are also present in Samples 1, 5, 7. The band in the region of 615 cm⁻¹ indicates the presence of a crystalline silica phase, which is consistent with the ash phase composition (see Table 2). A more complex spectrum of Sample 1 and the appearance of additional band at 1047 cm⁻¹ do not exclude the presence of Si – OM bonds (M – Mg, Al) due to the possible presence of silicate compounds in the sample [20]. The primary substance comprising horsetail ash is silicon dioxide, as is the case with ash from rice tissues (husks and straw) [19].

Chemical composition. Table 4 shows the elemental composition of horsetail ash. The content of the main elements is given in oxides, and trace elements in the form of elements. The analysis of samples obtained according to Scheme 1 shows that field horsetail (Samples 1 and 13) contains the smallest SiO₂ amount in comparison with the forest (Sample 5) and wintering (Samples 7 and 11) horsetails, whose silica concentration is two times greater. It should be noted that rice straw and husks accumulate more of this compound in comparison with horsetails (Sample 16 [19]). At the same time, the horsetail is characterised by the significantly higher content of calcium, potassium and magnesium compounds, and the absence of titanium and barium. Processing the horsetails with a 0.1 M acid solution before firing led to the production of ash (Table 2) containing amorphous silica (81.1–91.2%), and did not depend on the type of horsetail (Samples 3, 6, 8, 12, 14). Increasing the acid concentration for treating the raw materials can increase the content of silica in the ash (Sample 4). However, it should be noted that ash with a higher SiO₂ content is formed from raw rice materials under the same conditions (Sample 17) [19].
Table 3

Elemental composition of silicon-containing samples obtained from the aerial part of horsetails according to different Schemes, wt.%

| № | SiO₂   | CaO     | K₂O    | MgO    | Al₂O₃  | Fe₂O₃  |
|---|--------|---------|--------|--------|--------|--------|
| 1 | 32.92  | 26.58   | 20.27  | 7.56   | 1.78   | 0.120  |
| 2 | 50.03  | 27.33   | 10.89  | 4.86   | 0.68   | 0.230  |
| 3 | 87.84  | 8.06    | 0.82   | 0.41   | 0.88   | 0.460  |
| 4 | 98.33  | 0.23    | 0.11   | n/d    | 0.94   | 0.120  |
| 5 | 68.43  | 9.05    | 14.41  | 3.82   | 1.43   | 0.330  |
| 6 | 91.24  | 1.11    | 1.67   | 0.58   | 0.57   | 0.280  |
| 7 | 67.78  | 14.06   | 9.57   | 4.29   | 2.76   | 0.790  |
| 8 | 87.57  | 3.80    | 1.69   | 0.95   | 0.57   | 0.260  |
| 9 | 57.40  | 17.85   | 13.01  | 4.03   | 2.12   | 0.600  |
| 10| 88.10  | 3.90    | 1.70   | 0.96   | 0.58   | 0.450  |
| 11| 67.27  | 13.44   | 12.08  | 5.55   | 1.14   | 0.360  |
| 12| 89.62  | 2.28    | 1.95   | 0.38   | 0.38   | 0.170  |
| 13| 32.45  | 8.27    | 24.42  | 2.63   | 0.26   | 0.040  |
| 14| 81.10  | 5.49    | 1.82   | 0.41   | 0.42   | 0.100  |
| 15| 89.22  | 0.09    | 0.66   | –      | 0.79   | 0.090  |
| 16| 91.70  | 0.86    | 0.19   | 0.45   | 0.06   | 0.060  |
| 17| 99.50  | 0.15    | 0.16   | 0.07   | 0.02   | 0.021  |

Table 3

Элементный состав кремнийсодержащих образцов, полученных из надземной части хвощей по разным схемам, % масс.

| № | P | S | Cl | Sr | Rb | Br |
|---|---|---|----|----|----|----|
| 1 | 0.64 | 3.98 | 4.93 | 0.079 | 0.058 | 0.028 |
| 2 | 0.95 | 2.05 | 2.57 | 0.084 | 0.030 | 0.012 |
| 3 | 0.78 | 0.40 | n/d | 0.012 | 0.003 | n/d |
| 4 | 0.19 | 0.01 | n/d | n/d   | n/d   | n/d |
| 5 | 0.51 | 0.46 | 2.01 | 0.098 | 0.023 | 0.018 |
| 6 | –   | 0.21 | –   | 0.013 | –     | –     |
| 7 | 1.15 | 0.32 | n/d | 0.102 | 0.018 | n/d   |
| 8 | –   | 0.02 | –   | 0.011 | 0.002 | –     |
| 9 | 1.69 | 3.16 | n/d | 0.095 | 0.014 | 0.002 |
| 10| 0.88 | 0.24 | –   | 0.080 | 0.010 | n/d   |
| 11| 1.25 | 0.40 | n/d | 0.077 | 0.008 | 0.003 |
| 12| –   | 0.02 | –   | 0.014 | 0.002 | –     |
| 13| 0.47 | –    | 0.160 | 0.040 | 0.040 | 0.003 |
| 14| 0.30 | –    | –   | 0.020 | –     | –     |
| 15| 0.10 | –    | –   | –     | –     | –     |
| 16| –   | 0.87 | –   | 0.001 | 0.003 | –     |
| 17| –   | n/d | –   | <0.001 | <0.001 | –     |

| № | Mn | Zn | Cu | Ti | Cr | Mo | Zr | Ni | Ba |
|---|----|----|----|----|----|----|----|----|----|
| 1 | 0.025 | 0.02 | 0.17 | n/d | n/d | n/d | n/d | n/d | n/d |
| 2 | 0.035 | 0.036 | 0.021 | 0.029 | 0.019 | n/d | n/d | n/d | n/d |
| 3 | 0.099 | 0.015 | 0.018 | 0.021 | 0.010 | n/d | n/d | n/d | n/d |
| 4 | n/d | n/d | 0.012 | 0.014 | 0.024 | n/d | n/d | n/d | n/d |
| 5 | 0.166 | 0.022 | 0.012 | 0.083 | n/d | n/d | n/d | n/d | n/d |
| 6 | 0.041 | 0.017 | 0.018 | 0.078 | – | n/d | n/d | 0.001 | 0.002 |
| 7 | 0.125 | 0.042 | 0.014 | 0.065 | n/d | n/d | n/d | n/d | 0.250 |
| 8 | 0.024 | 0.020 | 0.003 | 0.050 | n/d | n/d | n/d | n/d | 0.005 |
| 9 | 0.096 | 0.032 | 0.017 | n/d | n/d | n/d | n/d | n/d | 0.330 |
| 10| 0.028 | 0.029 | 0.011 | 0.050 | n/d | n/d | n/d | n/d | 0.111 |
| 11| 0.052 | 0.050 | 0.013 | 0.026 | n/d | n/d | n/d | n/d | 0.260 |
| 12| 0.009 | 0.020 | 0.004 | 0.054 | n/d | n/d | n/d | 0.0001 | 0.003 |
| 13| 0.005 | 0.010 | 0.004 | – | – | – | – | – | – |
| 14| 0.004 | 0.010 | 0.006 | – | – | – | – | – | – |
| 15| –   | –    | 0.004 | – | – | – | – | – | – |
| 16| 0.029 | 0.002 | 0.001 | 0.880 | 0.003 | – | – | 0.001 | – |
| 17| 0.018 | 0.004 | <0.001 | 0.009 | n/d | <0.001 | n/d | n/d | n/d |

n/d – not detected
Due to the wide range of applications of silicon-containing products, depending on the structure of the substance and the purity of the product, as well as its physicochemical characteristics [21], we have investigated some properties of the obtained ash samples.

**Mass fraction of water-soluble ash.** The content of water-soluble ash components (Table 4) varies from 3.2% (Sample 4) to 26% (Sample 1), which correlates with the results of chemical analysis (see Table 3). The greatest quantity of water-soluble components is found in the field horsetail; the smallest – in the forest horsetail.

The pH of the ash aqueous extract is presented in Table 4. The aqueous extracts of samples obtained according to the Scheme 1, have a pH of 11.2 (Sample 1 (Table 3), containing a large amount of calcium and magnesium) to 7.1 (Sample 5). Sample 4 is characterised by the lowest pH value, which main substance is amorphous silica (Table 3).

### Table 4

**Characteristics of ash obtained from the horsetail aerial parts (Samples 1–9) and rice husks (No. 16)**

| Indicator                                | The sample number according to the Table 2 |
|------------------------------------------|--------------------------------------------|
| pH of the aqueous extract                | 1  | 2  | 3  | 4  | 5  | 7  | 9  | 11 | 13 | 14 | 15 | 16 |
| The mass fraction of water-soluble ash, %| 11.2 | 10.7 | 8.9 | 6.7 | 7.1 | 9.2 | 8.5 | 9.7 | –  | –  | –  | 10.3 |
| MO adsorption capacity, mg/g             | 240.9 | 238.1 | 186.3 | 43.3 | 39.7 | 105.8 | 223.1 | 123.4 | 157.0 | 216.0 | –  | 87.9 |
| MB adsorption capacity, mg/g             | 176.8 | 173.5 | 243.5 | 259.7 | 190.7 | 181.5 | 164.3 | 172.2 | 139.0 | 164.0 | 179.0 | 150.3 |
| Iodine adsorption capacity, %            | 41.9 | 35.6 | 13.3 | 9.5 | 5.1 | 7.6 | 7.6 | 14.0 | 40.1 | 17.8 | 10.2 | 17.6 |

**MB, MO and iodine adsorption capacity.** The adsorption capacity of the studied ash samples was determined using the conventional substances with different molecular weights and ionogenicity, such as iodine and organic dyes (MB, MO), which have a different chemical nature. The obtained values of the adsorption capacity of ash samples are given in Table 4.

The adsorption capacity of all the studied horsetail ash samples ranged from 164 (Samples 9 and 14) to 260 mg/g (Sample 4), exceeding the activity of Sample 13, obtained from rice husks (150 mg/g). The magnitude of the MO adsorption capacity of ash has a wide scatter from 40 to 240 mg/g. The dependence of this indicator on the plant species is observed when comparing the samples obtained according to Scheme 1. The field horsetail (Sample 1) has the greatest, and the forest horsetail (Sample 5) has the lowest adsorption capacity. The wintering horsetail ash (Samples 7 and 11) absorbs the MO two times worse than the field horsetail ash. Such a difference in MB and MO adsorption capacity can be explained by a higher basicity of MB, in the molecule of which there are three nitrogen atoms and a conjugation due to nitrogen and sulphur atoms between two benzene rings. Evidently, each of the molecules of these substances (MB and MO) has its own active centres, which participate in the interaction with the surface of the sorbent (horsetail ash), obtained from different plant species.

The iodine adsorption capacity of the studied samples ranged from 5 to 42%. Sample 1 is characterised by the highest and Sample 5 by the lowest (Table 4) adsorption capacity, which indicates the dependence of iodine adsorption on the plant species.

### CONCLUSION

Silicon-containing horsetail ash samples, characterised by chemical, X-ray diffraction and IR spectroscopic analysis, are promising raw materials for use in various industries, including as pure forms of amorphous silica. The product yield (6.5–18.8%), the content of the SiO₂ primary substance (32–98%) and the pH of the aqueous suspension depend on the taxonomic affiliation and plant processing conditions. The sorption characteristics of ash obtained from the aerial part of horsetails are assessed for the first time: iodine (5–42%), methylene blue (164–260 mg/g) and methyl orange (40–241 mg/g) organic dye adsorption capacities of the samples are determined.

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Contribution

Lyudmila A. Zemnukhova, Olga D. Arefieva, Anna V. Kovekhova, Natalya V. Polyakova, Aleksandr E. Panasenko, Antonina Yu. Kamaeva carried out the experimental work, on the basis of the results summarized the material and wrote the manuscript. Lyudmila A. Zemnukhova, Olga D. Arefieva, Anna V. Kovekhova, Natalya V. Polyakova, Aleksandr E. Panasenko, Antonina Yu. Kamaeva have equal author’s rights and bear equal responsibility for plagiarism.

Conflict of interests

The authors declare no conflict of interests regarding the publication of this article.

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Критерии авторства

Земнухова Л.А., Арефьева О.Д., Ковехова А.В., Полякова Н.В., Панасенко А.Е., Камаева А.Ю. выполнили экспериментальную работу, на основании полученных результатов провели обобщение и написали рукопись. Земнухова Л.А., Арефьева О.Д., Ковехова А.В., Полякова Н.В., Панасенко А.Е., Камаева А.Ю. имеют на статью равные авторские права и несут равную ответственность за плагиат.
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