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Determination of the Microelement Composition of Dog Rose (*Rosa canina*) from Various Growing Locations by the SRXRF Method

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Abstract

Concentrations of K, Ca, Mn, Fe, Zn, Sr, Cu, Br, Rb, Pb in fruits of dog rose (*Rosa canina*) collected in areas with various technogenic load: Novosibirsk, Istaravshan City (Tajikistan), Gorny Altai have been determined by the method of X-ray fluorescence analysis using the synchrotron radiation (SRXRF). The highest concentrations of essential elements (K, Ca, Mn, Fe, Cu, Zn) have been discovered for samples from Istaravshan City. It has been found that in pulp of plant fruits growing near the highway (Novosibirsk) concentrations of essential elements of K, Mn, Fe are several times lower, in comparison with data for the territory not experiencing the technogenic load (the forest area of Novosibirsk) and the concentration of Pb in them does not exceed the maximum permissible concentration (MPC).

Key words: X-ray fluorescence analysis, synchrotron radiation, microelements, dog rose

INTRODUCTION

The study of the chemical composition of plants is necessary for discovering their potential in the treatment and prevention of various diseases. Plants have therapeutic and restorative effects on the organism due to the presence in them of biologically active substances (vitamins, antioxidants, glycosides, alkaloids, ethereal oils *etc*.) and a rich set of mineral complexes. In addition to their own nutritional value that macro- and microelements have their role in the formation and interaction with organic components of medicinal plants, useful for humans. For instance, manganese in the organism of plants participates in the formation of riboflavin, ascorbic acid and carotene [1], and many flavonoids form chelate complexes with copper and iron ions [2]. Microelements are involved in complex multistep physiological processes on all stages of plant development, provide photosynthesis, breath protection, full growth and, consequently, affect directly or indirectly the accumulation and formation of biologically active compounds, useful or toxic for humans. Therefore, data on the quantitative content of microelements in medicinal plants are necessary for the investigation of their effectiveness in the treatment of various diseases and understanding of their pharmacological action.

The content of microelements in vegetative and generative parts of the plant is known to depend on ecological factors [3]. In connection with the problem of pollution, the ability of plants to accumulate heavy elements, for example, lead from the environment is actively studied; moreover, the degree of lead accumulation varies greatly for various types of plants [4].

A number of works are devoted to the element analysis of food and medicinal plants and this topic does not lose its relevance. For the analysis of the element structure of plant samples the following the methods are used: atomic absorption flame spectrometry [5, 6] atomic absorption electrometric spectrometry [7], atomic emission spectrometry with the inductively coupled plasma [8, 9], mass spectrometry with the inductively coupled plasma [10, 11], energy dispersive X-ray fluorescence analysis [12, 13] and neutron activation analysis [14]. Among these methods, XRF has some advantages: it is multi-element, non-destructive; it does not require the translation of the analyzed elements into the solution. The absence of time consuming procedures for sample dissolution reduces the risk of contamination and losses of analyzable elements and it is especially valuable in those cases when the amount of the investigated material is small. In addition to a relatively fast and simple preparation of samples of the plant material for XRF the simplicity of spectra registered and a short analysis time (several minutes) should be noted. The use of the highly intense high-intensity synchrotron radiation in the method of XRF (SRXRF) allows to reduce the detection limits and analyze samples that have the weight of just a few milligrams.

The goal of this work is the study of the elemental composition of the fruit of the dog rose (*Rosa canina*) depending on the place where it grows.

MATERIALS AND METHODS

Sampling and sample preparation

Mature fruits of the dog rose (*Rosa canina*) grown in Istaravshan City (Tajikistan), in Gorny Altai and Novosibirsk were studied. The Novosibirsk collection is presented by samples from zones with a different with a various technogenic load: the fruits of three plants have been collected in the forest area of the Central Siberian Botanical Garden (CSBG) of the SB RAS; fruits of other three plants have been collected at the distance of 3 m from the intersection of two roads (Ul. Pirogova and Universitetskiy Pr.) in the Soviet District of Novosibirsk. It is known [15, 16] that the flow of vehicles has both the physical and chemical action on the biocenosis of the roadside areas leading to the decrease of the soil fertility, toxic substances, *viz.*, the products of the combustion of hydrocarbon fuels in engines are accumulated in it. In Novosibirsk, from the plants studied, in addition to fruits, leaves (middle tier of bushes) were collected and soil samples were also taken from the root area from layer of the depth of 15–20 cm. Fruits and leaves were carefully washed with deionised water. Each fruit was separated into the pulp and seeds. Samples of the pulp, seeds, leaves and soil were dried at the temperature of 45 °C to the constant mass, then grinded in a mortar of jasper. The powder obtained was dried at the temperature 45 °C to the constant mass [17]. Tablets with the mass 15–20 mg from the samples of leaves, the pulp and seeds, and from the samples of the soil with the mass of 30 mg were pressed. All the tablets had the diameter of 8 mm and they were pressed under the pressure of 150 kg/cm^2. The quantitative definition of microelements was carried out using the external standard that was served by international standard samples: NIST 1575 Pine Needles; B 215 Cabbage Leaf; NIST 1571 Orchard Leaves; NIES No. 2 Pond Sediment; BIL-1 No. 381-9 – Baikal Il; IAEA (Soil-7). Tablets from standard sample were produced following the same method, as tablets of samples under investigation. All tablets were placed between two Mylar films and fixed in fluoroplastic rings.

Measurements of SRXFA spectra

The analysis was conducted at the experimental station of X-ray fluorescence element analysis in the Siberian Synchrotron and Terahertz Radiation Center (SSTRC) at the Budker Institute of Nuclear Physics, SB RAS (Novosibirsk). The station of SRXFA has the following characteristics: monochromator that is monocrystal Si (111); the thickness of the beryllium film of 1 mm; the camera for the analysis is made from alconite; the size of the photon beam is from 1 to 30 mm^2, exposition time is from 20 to 1000 s, the excitation energy varies from 12 to 47 keV, elements from K to U

TABLE 1

Correctness of analysis results

Elements	C_{st}±SD, μg/g	C±SD, μg/g
K	$(2.7±1.5) \cdot 10^4$	$(2.7±0.1) \cdot 10^4$
Ca	$(4.7±2.6) \cdot 10^4$	$(4.8±0.2) \cdot 10^4$
Mn	21±3	20±1
Fe	(23±3) · 10	(24±5) · 10
Cu	2.8±1.0	2.3±0.8
Zn	17.5±1.75	21.4±2.8
Br	53.1*	69
Sr	169*	210
Pb	0.909±0.319	0.884±0.206
Rb	12.0*	11.4

Notes. 1. For all elements (except for Rb) B 215 Cabbage Leaf was used as a standard; for Rb NIST 1571 Orchard Leaves. 2. C_{st} is the passport concentration of the element in the standard sample; C is the calculated concentration of the element; SD is the standard deviation.

* Reference values of concentrations.

are identified. The registration of the fluorescent radiation is carried out using an OXFORD Si(Li) detector (Oxford Instruments Inc, the USA) with the energy resolution of approximately 140 eV on the line of 5.9 keV. The primary synchrotron radiation beam hits the sample under the angle of 45°, relatively to its surface, generating the characteristic fluorescent radiation that is registered by a semiconductor detector. The latter is situated is located at an angle 90°, relative to the direction of the primary exciting radiation.

The samples of brier and soil under investigation were analyzed at the energy of excitation of 23 keV, the time of one measurement is 400 s. Measurements were conducted according to the following scheme: three samples analyzed, then three standard samples, again three analyzed ones *etc*. This excluded errors related to the cyclical nature of the work of the storage ring. Concentrations of the following elements were defined: K, Ca, Mn, Fe, Zn, Sr, Cu, Br, Rb, Pb.

TABLE 2

Convergence of analysis results

Elements	C_{av} (n = 8), μg/g	SD, μg/g	S_r, %
K	$1.6 \cdot 10^4$	$0.07 \cdot 10^4$	4
Ca	$6.5 \cdot 10^3$	$0.3 \cdot 10^3$	5
Mn	12.0	0.2	2
Fe	20	3	15
Cu	3.0	0.1	3
Zn	9.7	0.2	2
Br	2.7	0.2	7
Rb	4.9	0.1	2
Sr	20.0	0.2	1

Note. C_{av} is the average concentration of a chemical element in the sample; SD is the standard deviation; S_r is the relative standard deviation.

RESULTS AND DISCUSSION

To verify the correctness of SRXFA method concentrations of chemical elements studied in standard samples B 215 Cabbage Leaf (cabbage leafs), NIST 1575 Pine Needles (pine needles) and NIST 1571 Orchard Leaves (leaves of fruit trees), relatively to each other (Table 1). It has been established that calculated concentrations of the elements studied fall in the confidence interval of the certified values.

The convergence of the results of the analysis was evaluated according to eight measure-

TABLE 3

Limits of detection at the energy of excitation of 23.0 keV (C_{min}) for the International standard samples: NIST 1575 (Pine Needles), B 215 (Cabbage Leaf), μg/g

Elements	Cabbage Leaf		Pine Needles	
	C_{st}	C_{min}	C_{st}	C_{min}
K	$2.7 \cdot 10^4$	60	$3.7 \cdot 10^3$	15
Ca	$4.7 \cdot 10^4$	25	$1.1 \cdot 10^3$	10
Cr	1.2	0.8	2.6	2
Mn	21	1.4	680	1
Fe	230	2	200	1
Ni	0.37	0.1	3.5	0.5
Cu	2.8	0.85	3	0.47
Zn	18	0.7	n/c	–
As	0.58	0.3	n/c	–
Se	0.04	0.01	n/c	–
Br	53	4	9.0	1.3
Rb	n/c	–	11.7	0.2
Sr	170	0.23	4.8	0.15
Mo	2.4	0.7	n/c	–
Cd	0.22	0.06	n/c	–
Sb	n/c	–	0.2	0.08
Pb	0.91	0.9	10.8	2

Notes. 1. C_{ST} is the passport value of the concentration of the element in the standard sample. 2. n/c is not certified.

ments of the sample of the pulp of dog rose hip (Table 2). The relative standard deviation varies from 1 to 7 % for all elements defined. The relative standard deviation for iron is 15 %, what is probably explained by its uneven distribution in the sample. The detection limits with the confidence probability of 90 % were calculated according to standard samples B 215 Cabbage Leaf and NIST 1575 Pine Needles. Values are varied depending on the element and standard used sample (Table 3).

Concentrations of elements in the pulp and seeds of rose hips are shown in Figs. 1, 2. It can be seen that a richer complex of microelements is formed in the pulp of fruits of dog rose hips, grown in Istaravshan (Tadzhikistan). For these samples, medium concentrations of K, Ca, Mn, Fe, Cu and Zn in fruits exceed their concentrations in plants fruits from other territories. Probably, this is due to a high content in the soil of bioavailable forms of these elements. In the pulp of fruits of plants that grew near the auto road (Novosibirsk), the concentration of essential elements (Mn, Fe) is several times lower, in comparison with data for the other studied areas. In fruits of rose hips grown near the auto road lower concentrations of Rb and Sr (see Fig. 1, *b*) have been found. Very little is known about the biological role of Rb, Sr and Br, though these elements are present in all living organisms. Data on their concentration will help to define biochemical functions of these elements and use correctly medicinal plants in medical practice.

It is interesting to note the ratio of contents Cu/Zn in the pulp and seeds of dog rose hips from all territories investigated are constant and equal to 1 : 2 (see Figs. 1, *c* and 2, *b*, *c*)

In the content of chemical elements seeds (see Fig. 2) are very different from the pulp and this is due to functional features of parts of plants. Seeds are the source of nutrients for growing plant. The maximal content of Mn and Fe has been established for seeds plants growing in the forest area of Novosibirsk. Manganese and iron are very important in the life of plants and they participate actively in the process of photosynthesis [1, 18], therefore, their certain concentrations in seeds are necessary for a normal development of the embryo.

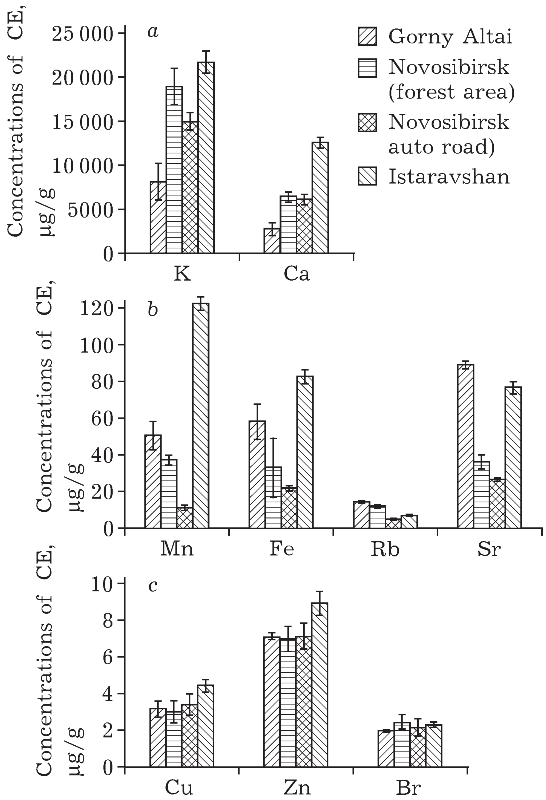

Fig. 1. Concentrations of K, Ca (*a*), Mn, Fe, Rb, Sr (*b*), Cu, Zn, Br (*c*) in the pulp of dog rose hips.

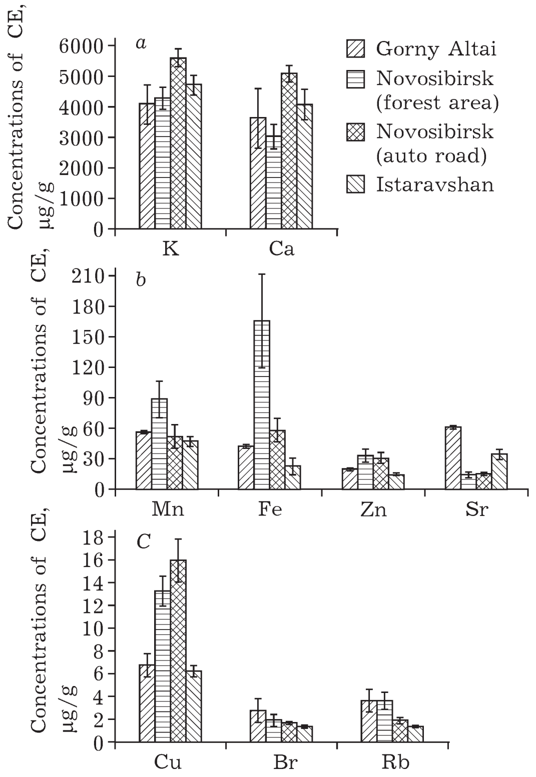

Fig. 2. Concentrations of K, Ca (*a*), Mn, Fe, Zn, Sr (*b*), Cu, Br, Rb (*c*) in the seeds of dog rose hips.

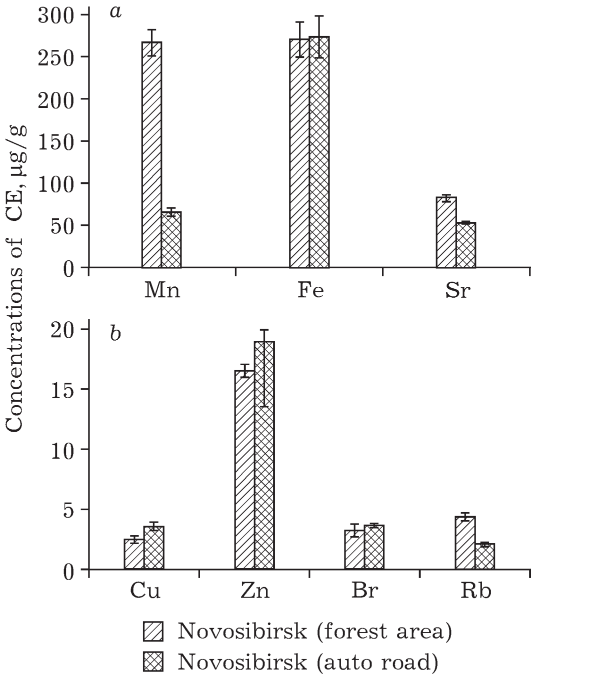

Fig. 3. Concentrations of Mn, Fe, Sr (*a*), Cu, Zn, Br, Rb (*b*) in leaves of dog rose hips.

Data on concentrations of chemical elements in leaves of plants growing on the territory of Novosibirsk in zones with a various technogenic load (the forest zone and zone near auto road) are presented in Fig. 3. It can be seen that in leaves of rose hips growing in the forest area the concentration of Mn is 4 times higher, in comparison with this in leaves of rose hips growing by the auto road. The content of other elements either does not have significant differences or differs slightly.

The elemental structure of the soil from the forest zone and zone near the auto road (Novosibirsk), where the plants under investigation grow is presented in Fig. 4. It can be seen that the content of chemical elements in the soil from the forest zone and zone near by the auto road has no significant differences on all elements, except for lead. The concentration of this element in the soil near the auto road exceeded in six times of magnitude the one in the soil of the forest zone. At the same time, the amount of lead in the leaves, fruits and seeds of hip grown on the soil with an increased concentration of lead proved to be below the detection limit (0.9 μg/g) and did not exceed permissible concentration.

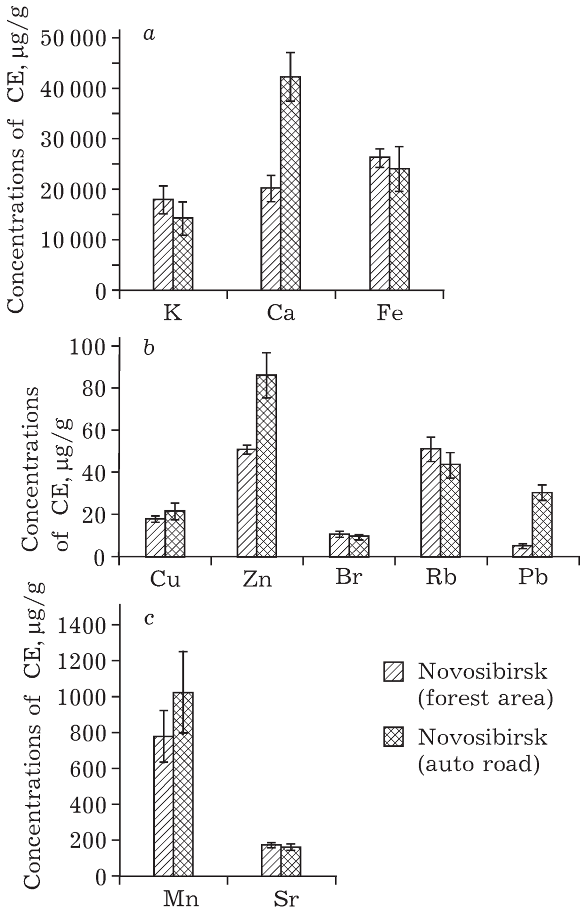

Fig. 4. Concentrations of K, Ca, Fe (*a*), Cu, Zn, Br, Rb, Pb (*b*) in soil.

Therefore, the element structure of rose hips fruits under investigation varies for different elements depending on the place of the sample selection. Concentrations of Mn, Fe and Sr for different territories differ in magnitudes and data for K, Ca, Cu, Zn, Rb and Br do not have such pronounced differences (see Figs. 1, 2).

Lower concentrations of essential elements (Mn, Fe) in fruits and leaves of plants grown near by the auto road (Novosibirsk) agree well with data [15, 16] where the decrease of concentrations of organic forms of iron in roadside soils and deterioration of their natural qualities have been established.

CONCLUSION

The elemental analysis of fruits of rose hips has revealed increased concentrations of essential elements (K, Ca, Mn, Fe, Cu, Zn) in fruits of rose hip from Istaravshan City (Tajikistan).

The maximal content of Mn and Fe that are elements, necessary for the subsequent photosynthesis of the developing plant is typical for seeds of plants from the forest zone (Novosibirsk). It has been discovered that the content of Pb in leaves and fruits of hip grown near by the auto road does not exceed the permissible concentration and it is lower the detection limit (0.9 μg/g), despite its increased concentration in the soil. Concentrations of essential elements Mn, Fe in the fruit pulp and leaves of plants grown near the auto road are several times below, in comparison with plants from other studied territories

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