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Bioindication of the Ecological Status of Ichthyofauna using the SR-XRF Method

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Abstract—At the SR-XRF stations (X-ray fluorescence analysis using synchrotron radiation) of the VEPP-3 and VEPP-4M storage rings of the Budker Institute of Nuclear Physics (BINP), Siberian Branch, Russian Academy of Sciences, a test quantitative analysis of chemical elements in the soft tissues of fish is carried out and one-coordinate scanning of fish scales is performed. In the studied samples, the concentrations of 20 chemical elements are determined and differences are identified depending on the type of tissue analyzed, the growth conditions (natural/aquaculture), gender, and taxonomic affiliation of the analyzed individuals. The analysis of biological tissue with minimal sample preparation and the ability to study large samples is an undeniable advantage of the SR-XRF method and can be an effective tool for the environmental monitoring and control of growing process of aquaculture fish products.

Keywords: SR-XRF, environmental monitoring, Baikal region

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INTRODUCTION

Determination of the elemental composition of fish tissues and organs is carried out for the purpose of the environmental monitoring of polluted water bodies [1, 2] of unique protected natural zones [3], as well as to control the content of toxic elements in the tissues of commercial fish [4, 5]. There are not many publications on the topic of the elemental analysis of fish tissues, and most of them are limited to the analysis of several elements from the toxic (Cd, Pb, Hg, As) and essential (K, Ca, Fe, Cu, Zn, Br, Se) groups. Inductively coupled plasma mass spectrometry (ICP-MS) [1], inductively coupled plasma optical emission spectrometry (ICP-OES) [3, 5], and less commonly atomic absorption spectroscopy (AAS) [3, 6] are mainly used; only a few works use synchrotron-radiation-induced X-ray fluorescence (SR-XRF) methods in the case of total internal reflection (TIR) [7] and microSR-XRF. The preparation of samples under study can be performed in two ways: destructive, using chemical reagents and heat treatment, and nondestructive. Minimal losses and contamination of the sample are possible only when using a nondestructive sample-preparation method. Systematic studies and routine methods in the field of determining the microelement composition of fish tissues are not presented in published materials.

The presented works determined the concentrations of elements in various organs of fish: muscles, liver, kidneys, gonads, gills, and fins, while only a few tissue types are most often examined, such as comparing the concentrations of elements in the fins and muscles of fish to search for a possible correlation [6] or determination of metal concentrations in the liver and gonads, which could affect the health status of fish and their reproductive systems [3].

Studies show that the concentrations of chemical elements in different organs of fish are species specific and also depend on the position of the fish in the trophic chain [6]. In addition, there is a seasonal dependence, which is caused by physical–chemical changes in the water resource [7].

Works on determining the bioavailability of trace elements in a medium are interesting. In one study, the chemical forms of selenium were determined in the aquatic system, in habitats of a river downstream from uranium mines, where inorganic forms of selenium (selenate and selenite) are a byproduct of processing. Results on the chemical forms of selenium were obtained using X-ray absorption spectroscopy (XAS) with SR; in fish tissues it is most often found in the form of selenium methionine, which is a bioavailability marker [2]. Phibbs et al., concluded that the main source of selenium in fish tissues is the invertebrates that fish feed on [8]. Selenium is an essential element and is needed in trace amounts in the body, but becomes toxic when the dose increases.

There are a number of works on studying chemical transformations and the bioavailability of nanoparticles. Studying the distribution, forms, and bioavailability of nanoparticles in the environment becomes more important the faster the number of industrial enterprises using nanoparticles in production (catalysts, paints, textiles, etc.) increases. Works examine the chain of distribution in space (water column, bottom sediments, benthos, plants, fish), and chemical transformations that occur with nanoparticles (sulfitation, chlorination, reduction, and complexation with organic matter) [9–12].

When analyzing low-mass biological tissue samples (<10 mg), a nondestructive sample preparation method may be the only one available [13].

We perform a quantitative analysis of the chemical elements determined by XSR-XRF. For the analysis, tissues of fish of different ages, habitats, and taxonomic affiliations are used.

MATERIALS AND METHODS

Samples

Baikal lake-river whitefish (*Coregonus pidschian* natio *fluviatilis* Issatschenko, 1925) of the Angara-Yenisei basin, grown from artificially fertilized fish eggs of the Verkhne-Angarsk population in a closed-water-supply installation on Angara tap settled water, age 10 months, only 5 individuals, samples of muscles were taken for each: liver, kidneys, heart, brain, gills and scales.

Whitefish (*Coregonus pidschian* natio *fluviatilis* Issatschenko, 1925) of the Angara-Yenisei basin, mature fish caught in the Irkut River (September 2020) during spawning migration, male (5 years old) and female (6 years old), scale samples.

Baikal omul (*S. migratorius* Georgi, 1775) of the coastal morphoecological group, Lake Baikal, 16 km from the town of Slyudyanka, September 2021, 2 females over 2 years old, a male over 4 years old, samples of red and white muscles.

Sample Preparation

The SR-XRF method uses external standards to quantify the content of chemical elements in the studied samples. Sample preparation does not require either heat or chemical treatment. The SR-XRF method requires stability of the density and uniformity of the samples and standards.

Biological-tissue analysis with minimal sample preparation is an undeniable advantage of the SR-XRF method, which is necessary in the field of biochemical studies of tissues and organs [14]. When using reagents to destroy the sample, contamination is possible, when heating, such elements as: As, Hg, Sb, Se, Sn, Te, can be lost.

At the same time, detection limits can be up to 0.01 μg/g, and it is also possible to determine the content of chemical elements in a wide range of concentrations (from 0.01 μg/g to tens of percent of mass fractions).

A film was prepared from a low-mass sample (<10 mg) by drying under a load, with the sample material placed between two fluoroplastic films. From samples whose weight exceeded 10 mg, powder tablets were prepared. The international standard samples were in the form of tablets. Work [14] shows that it is permitted to use powdered international standard samples to determine concentrations in samples prepared in the form of films.

EXPERIMENTAL

Experiment at VEPP-3

A fish-tissue analysis experiment was conducted at the SR-XRF station of the VEPP-3 accelerator complex. The characteristics of the SR-XRF station at the VEPP-3 source and its experimental equipment are described in detail in [15].

Synchrotron radiation was generated by a shifter installed in the rectilinear gap of the VEPP-3 accelerator ring. The operating energy of the electron bunch in the accelerator was 2 GeV with an average electron current of about 100 mA. The magnetic field in the shifter was 2.0 T. These parameters made it possible to provide a high flux of X-ray photons with energies up to 25 keV.

The experiment was carried out using the method of external standards; the following international standard samples of biological tissues were selected for each type of tissue (Table 1). The selection of standard samples for comparison was carried out primarily based on the similarity of the nature of the spectrum of standard and test samples so that the basic ratios between elements, such as Ca/K, Cu/Zn, were maintained. The second important criterion for selecting a standard sample was the correspondence of matrices of the standard and test samples; thus, to study the ele-

Table 1. International standard samples for SR-XRF analysis of fish tissues

Tissue type	Standard sample
White muscles	NIST 1556 Oyster tissue, NIES #6 Mussel
Red muscles	NIST 1556 Oyster tissue, NIES #6 Mussel
Heart	NIST 1556 Oyster tissue, NIES #6 Mussel
Liver	NIST 1577 Bovine Liver
Kidneys	NIST 1577 Bovine Liver
Brain	NIST 1556 Oyster tissue, NIES #6 Mussel
Scales	BCR-32(Apatite)
Gills	NCS ZC 81002b Human hair, NCS DC 73347 Human hair

mental composition of muscle tissue, the standard sample of mollusk muscles NIST 1556 Oyster tissue and NIES #6 Mussel was used [16]; for the liver and kidneys, the standard liver sample NIST 1577 Bovine Liver [17]. To study the scales, a standard sample of apatite, BCR-32, was chosen; this natural mineral is most similar in structure and content to apatite, which is the main inorganic substance of teeth, bones, and similar structures. Particularly difficult was the selection of standard samples for the study of brain and gill tissues; for these tissues, the standard samples were selected based on their similarity to the spectra of standard samples; muscle sample NIST 1556 Oyster tissue and hair samples NCS ZC 81002b Human hair, NCS DC 73347 Human hair, respectively [18].

To determine the quantitative content of the chemical elements in the tissues and organs of fish, the samples were irradiated with a monochromatic beam with an excitation energy of 23 keV and exposure time of 250 s.

Experiment at VEPP-4M

At the VEPP-4M storage ring of the SR-XRF station, one-coordinate scanning of the fish scales was carried out. The VEPP-4M storage ring of the SR-XRF station characteristics and its experimental equipment are described in detail in [19].

Synchrotron radiation was generated by a nine-pole wiggler installed in the rectilinear gap of the VEPP-4M storage ring. The operating energy of the electron bunch in the storage ring was 4.5 GeV with an average electron current of about 20 mA. The magnetic field in the wiggler was 1.9 Tesla. These parameters made it possible to ensure a high flux of X-ray photons with an energy of more than 50 keV.

The fish scales were irradiated with a monochromatic beam with an excitation energy of 45.4 keV. The scanning step was 250 μm vertically and 500 μm horizontally. The spectrum accumulation time at each scanning point was 300 s. The diameter of scales is 10–12 mm and the thickness is 180–220 μm. Images of the scales and scanning direction are shown in Fig. 1.

RESULTS AND DISCUSSION

Results of Elemental Analysis

Tables 2–4 present the results of elemental analysis of the fish organs and tissues being studied. In total, 41 samples of fish tissues were analyzed and the concentrations of 20 chemical elements were determined.

Table 5 presents the SR-XRF metrological data for the international standard sample NIST 1556 Oyster tissue. These data show the closeness of values obtained by us using the SR-XRF method and the international standard-sample passport values. Sc, Ti, V, Y, Zr, Nb, and Mo were below the detection limits, that is, their concentrations were not determined. These elements are characteristic of inorganic substrates, and their absence in biological tissues is natural.

The standard-deviation values for different elements vary in the range of 0.4–19.7 wt %, which corresponds to the spread given in the passport values for the standard samples we used (NIST 1556 Oyster tissue, NIES #6 Mussel).

The data obtained show that the studied samples of various fish tissues are characterized by different sets of chemical elements, this is shown by the results of cluster analysis (Fig. 2). The greatest differences were found in K, Cl, Ca, S, and P, which are macroelements in the samples being studied.

It was found that the taxonomic groups studied (Baikal omul, *C. migratorius* Georgi, 1775 and lake-river whitefish *Coregonus pidschian* natio *fluviatilis* Issatschenko, 1925) can be characterized by different

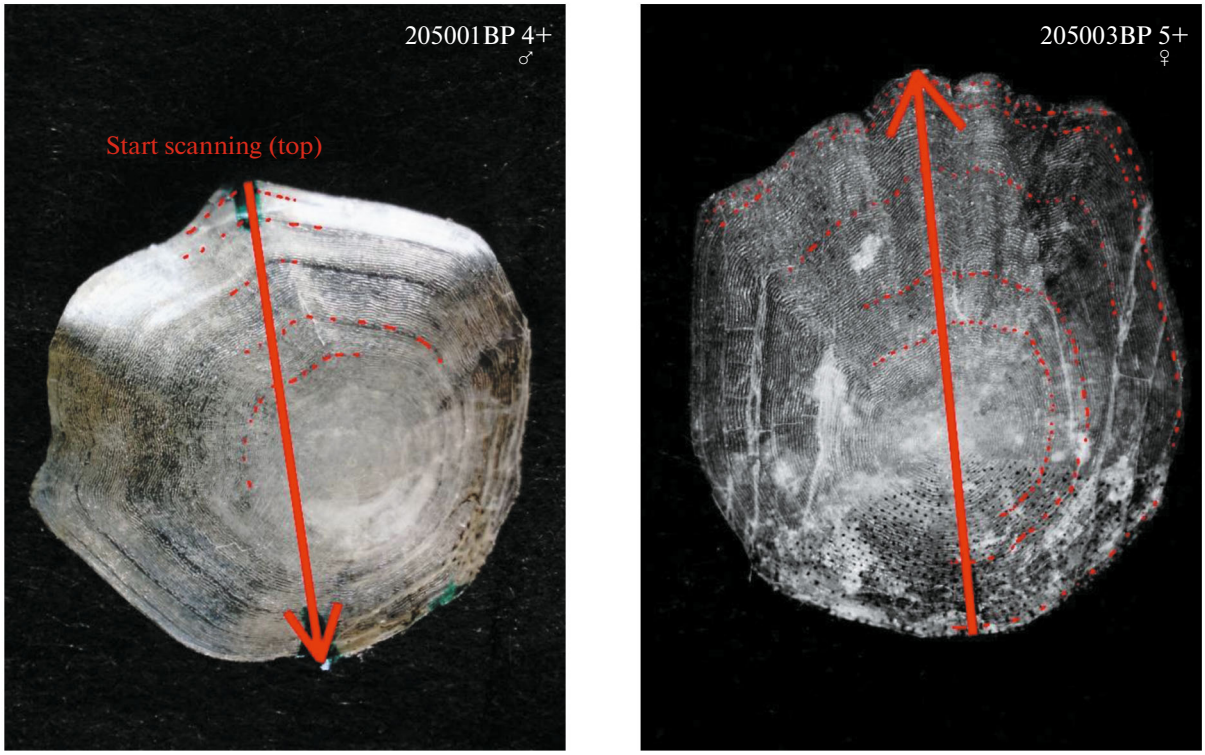

Fig. 1. Images of scales and scanning directions taken with an optical microscope.

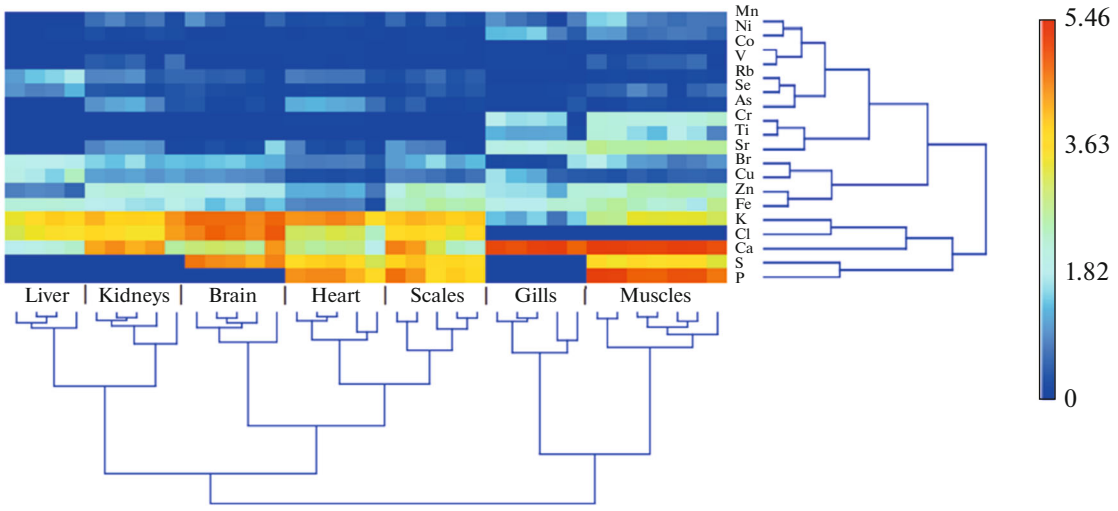

Fig. 2. Distribution of the chemical elements in whitefish based on the results of cluster analysis.

ratios of chemical elements. The content of elements such as S, Fe, Zn, Br, and Rb is significantly higher in the white muscles of Baikal omul (Table 2, Fig. 3), which is most likely due to the physiological characteristics of the species. However, since the analyzed individuals have significant differences in age and development conditions (natural and aquaculture), additional research into the reasons for the identified differences is necessary.

Data on the distribution of chemical elements in the analyzed muscle samples of omul and lake-river whitefish were compared with those for omul from the

Table 2. Results of elemental analysis of fish muscles, μg/g

	Muscles															
	whitefish				Baikal omul						whitefish					
					red			white			heart					
	1	2	3	4	1-K	2-K	3-K	1-B	2-B	3-B	1	2	3	4	5	
S	5970	7780	9070	6140	5730	5150	7020	11400	13600	6830	10670	9370	6537	9809	28396	S
Cl	1130	1010	1730	1260	705	790	1330	1470	1990	970	6685	4057	3220	3236	18786	Cl
K	22700	24300	32300	22800	10300	11800	14500	23300	28700	18600	13419	7414	7370	7850	23750	K
Ca	730	400	600	660	725	416	600	627	520	200	16275	26849	20370	13897	408	Ca
Mn	1.28	1.61	1.88	1.53	1.1	0.573	1.06	0.634	1.81	1.18	4.6	7.78	5.75	3.89	1.37	Mn
Fe	8.37	7.07	7.12	7.69	70	77	100	19.5	10.1	7.9	70	62	40.6	46.5	88	Fe
Co	0.15	0.15	0.18	0.24	0.157	0.191	0.278	0.251	0.217	<0.1	0.121	0.233	0.68	0.333	0.478	Co
Ni	<0.3	<0.3	<0.3	<0.3	<0.3	0.38	0.51	0.33	0.37	0.83	1.72	0.769	1.78	0.81	1.32	Ni
Cu	1.52	1.74	1.35	1.76	8.54	7.73	8.9	1.64	1.4	2.12	13.7	12.2	10.5	14.5	14.2	Cu
Zn	17.8	18.2	15.8	19.5	84	110	120	38.7	25.4	27.4	113	153	88	150	111	Zn
As	17.2	20.1	16.3	14.5	2.17	2.04	2.3	1.5	0.56	0.6	10.2	14.7	7.63	18.2	2.08	As
Se	1.03	1.25	1.11	0.94	1.4	1.04	1.24	1.4	1.37	1.3	2.38	2.1	1.14	2.05	2.08	Se
Br	6.71	6.18	6.69	6.94	21.5	23.7	25.7	33.1	39	36.2	33.7	25.7	18.6	43.1	25.1	Br
Rb	6.55	5.6	5.31	5.39	7.8	8.8	11.1	12.8	18.9	21.1	7.6	7.9	2.58	9.85	3.82	Rb
Sr	7.41	1.6	1.17	2.29	1.4	0.84	1.2	1.65	0.55	0.41	7.67	12	10	12.2	0.356	Sr

V and Cr are below the detection limit.

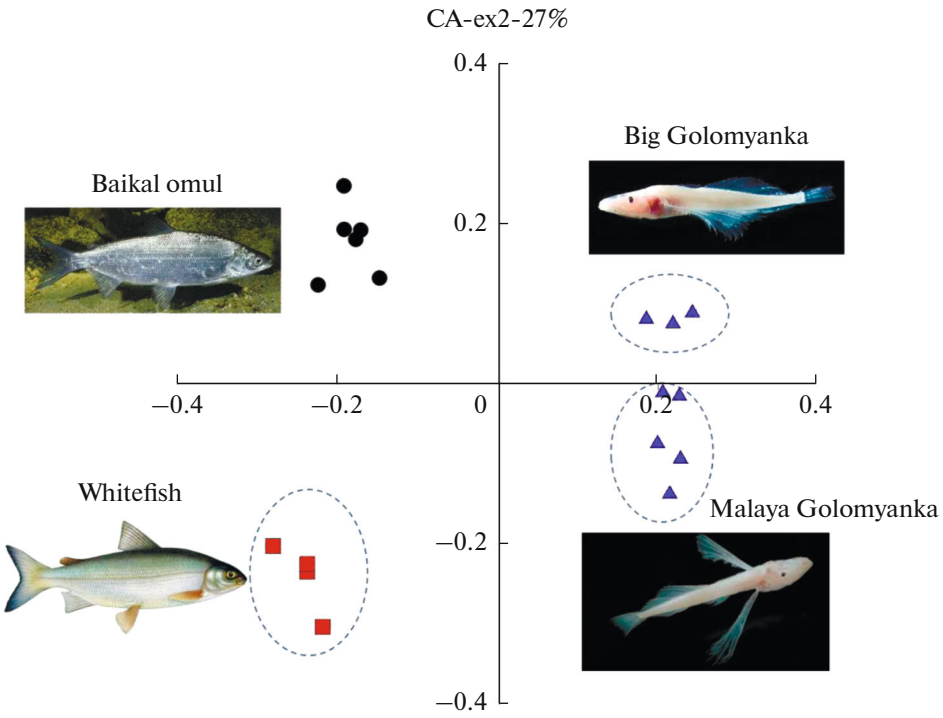

Fig. 3. Typification of taxonomic groups according to the distribution of chemical elements in white muscles based on correspondence analysis.

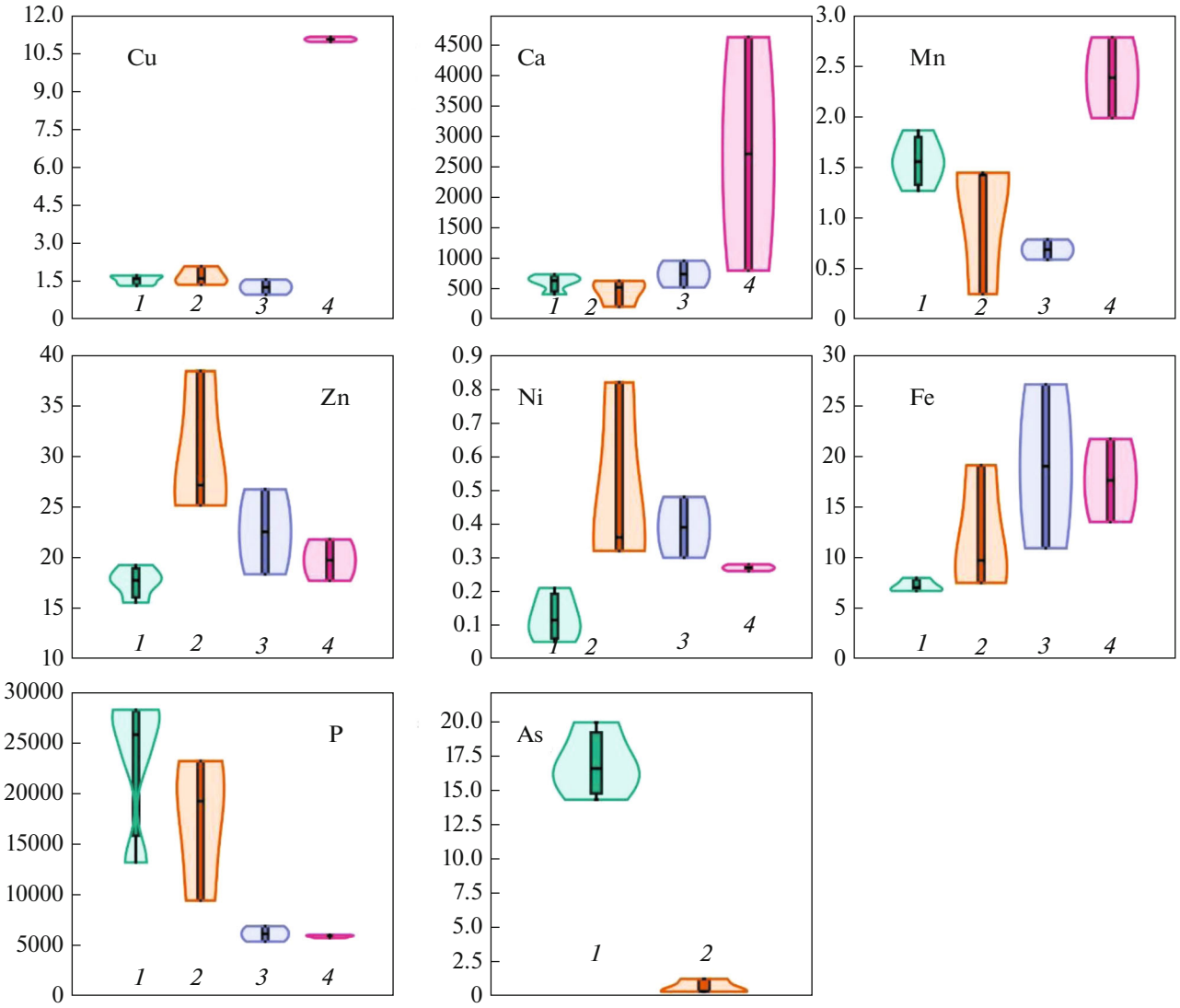

Fig. 4. Ratio of chemical elements (μg/g) in muscles: *1* is whitefish; *2* is omul from Southern Baikal, 2021; *3* is omul from the Lena River delta, 1997 (Rudneva, 2001); *4* is omul from the Selenga River, 1999 (Rudneva, 2001).

Selenga River, caught downstream from the city of Ulan-Ude in 1999, and Arctic Sea omul from the Lena River delta in the Tiksi settlement area in 1997 (Rudneva, 2001) [20]. Figure 4 shows that omul muscles from the Selenga River were enriched in Cu, Ca, and Mn. This fact can be explained by the influence of wastewater discharge from the city of Ulan-Ude, and as a consequence, the low quality of the Selenga River waters. Thus, the studied omul from Southern Baikal was immature, and, therefore, did not come to spawn in the Selenga River and did not experience this influence.

The prohibitively high concentrations of As, up to 14–20 μg/kg in farmed whitefish, are of concern. The most likely reason for the high concentration of arsenic may be their living conditions (feed, water, other factors), which requires further research.

Scale Scanning Results

Fish scales are an ideal object for SR-XRF studies. Due to their small thickness (180–250 μm), scattered background radiation from the sample is reduced, which in turn allows a reduction in the exposure time and scanning.

When scanning, it is necessary to take into account the principle of scale growth, when a lower, larger diameter (young) layer is formed under the upper (old) layer of scales and the layers creep on top of each other, thereby forming annual layers.

Then, when scanning the scales, in the center we receive information about the elemental composition from all annual layers. Further, when moving towards the periphery of scales, the number of annual layers decreases.

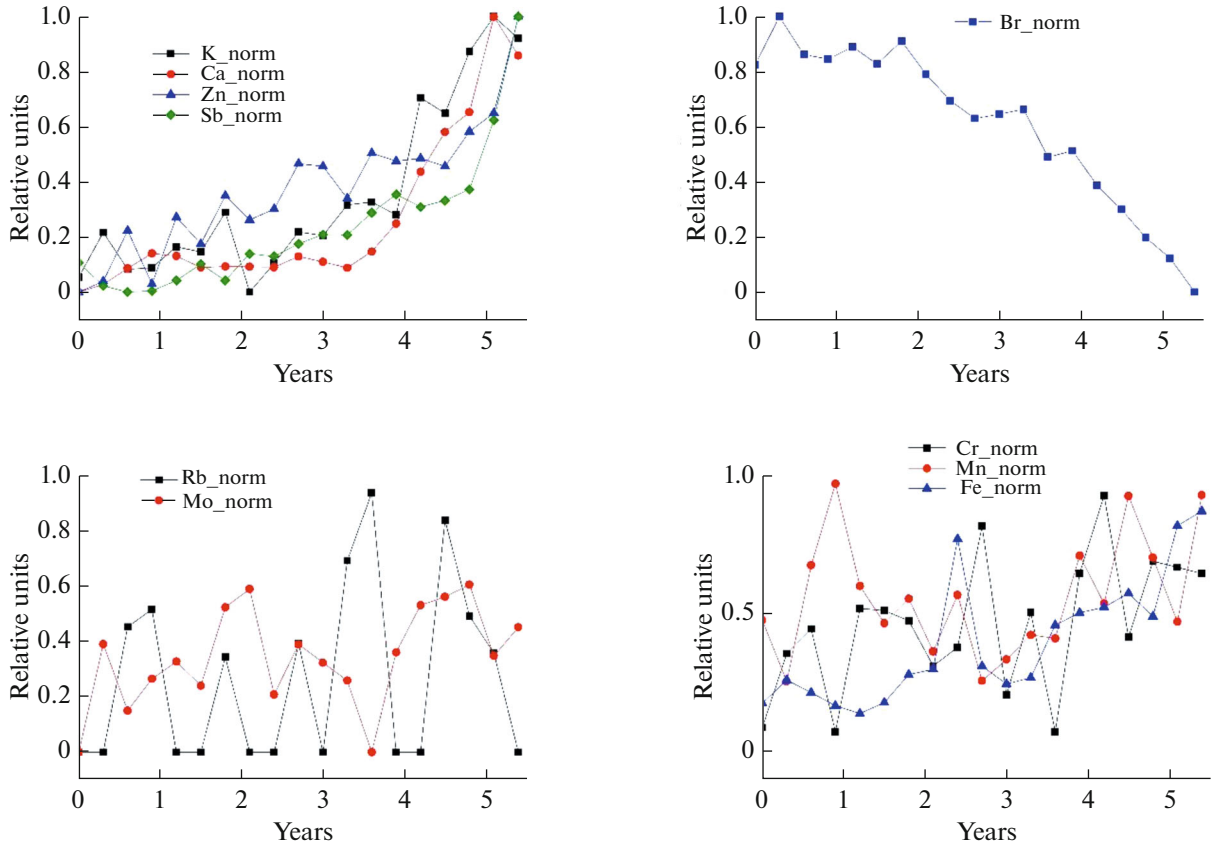

Fig. 5. The dependences of the concentrations of chemical elements, divided into four groups, is shown. Years are plotted along the horizontal axis, concentrations in arbitrary units are plotted along the vertical axis.

Table 3. Results of elemental analysis of internal organs of fish, μg/g

	Internal organs														
	liver				kidneys					brain					
	whitefish				whitefish					whitefish					
	1	2	3	4	1	2	3	4	5	1	2	3	4	5	
S	3880	7128	9378	10710	7290	6870	6380	11100	5600	27536	39390	31726	13986	23271	S
Cl	1490	2670	3430	3780	4060	2340	5260	6810	4330	59826	31719	72638	27923	41461	Cl
K	2360	5520	6990	8610	9510	7930	10500	13800	9460	49740	52243	53368	29517	49113	K
Ca	63	93	207	136	33100	229	1510	19800	177	1061	769	21698	424	838	Ca
Mn	5.36	5.39	7.22	5.49	4	1.72	4.1	1.2	1.1	4.04	10.1	3.72	0.825	0.864	Mn
Fe	147	144	125	153	191	270	389	228	328	24.7	56	27.3	14.7	38.3	Fe
Co	0.062	0.044	0.076	0.124	0.106	0.196	0.13	0.171	0.078	0.256	0.272	0.305	0.243	0.238	Co
Ni	0.09	0.07	0.18	0.16	0.106	0.196	0.13	0.27	0.09	0.387	<0.3	<0.3	0.541	<0.3	Ni
Cu	97	56	232	32.6	7.5	3.2	5	6.8	5.1	11.6	10.1	5.6	8.44	9.38	Cu
Zn	7.1	8.4	3.7	7.8	95	109	199	272	146	64	102	54.2	54.7	69	Zn
As	0.51	0.363	2.6	0.369	1.55	0.39	0.75	3.3	1.07	0.767	2.26	0.35	1.75	0.643	As
Se	10.6	7	20.3	7.8	0.52	1.8	2.9	1.5	2.4	1.42	2.61	0.692	0.99	1.19	Se
Br	81	71	60	66	12.4	14	39	18.1	22.9	27.1	23.2	18.2	20.7	29.9	Br
Rb	12.6	26.6	56	34	1.33	1.95	4.6	2.8	2.8	2.8	3.81	0.752	1.84	3.14	Rb
Sr	0.789	0.49	<0.1	0.574	12.3	0.5	6.3	7.2	<0.1	1.76	0.642	36.6	1.34	1.05	Sr

V and Cr are below the detection limit.

Table 4. Results of elemental analysis of fish gills and scales, μg/g

	Gills					Scales							
	whitefish					whitefish							
	1	2	3	4	5	5 years old, male	6 years old, female	1	2	3	4	5	
S	13980	10581	7235	13874	22342	4210	2930	4410	3780	5590	5160	2000	S
Cl	16492	6843	2799	18370	12503	10849	8352	29296	21299	24548	3219	11301	Cl
K	8649	6195	3237	12205	5246	570	510	2330	2070	2240	2200	1260	K
Ca	33589	25417	15013	24641	76472	286300	237000	151000	137000	202000	193000	95800	Ca
Ti	2.45	5.63	1.25	6.88	4.9	146	132	38.6	23.5	73	44.9	7.46	Ti
Cr	1	0.915	0.587	0.381	1.58	141	127	113	112	91	122	178	Cr
Mn	4.84	3.31	3.94	2.76	8.19	31.8	38.6	8.3	6.1	4.5	5.9	5.7	Mn
Fe	76	181	58	92	210	275	445	239	150	176	53	547	Fe
Co	0.315	0.241	0.196	0.542	0.323	0.169	0.195	0.327	0.297	0.603	0.396	0.216	Co
Ni	1.77	0.873	0.631	0.572	2.21	12.8	11.6	4.4	5	6.2	5.9	3.5	Ni
Cu	2.91	2.65	3.12	2.43	4.21	2.4	1.94	3.2	2.2	3.4	3.6	3.1	Cu
Zn	107	125	89	121	151	136	120	300	268	325	308	221	Zn
As	0.22	0.157	0.251	0.177	0.174	1	0.51	1.73	1.55	0.82	1.17	1.27	As
Se	1.12	1.32	1.39	1.11	1.13	2.8	3.2	8.2	4.7	0.15	3.4	5.5	Se
Br	7.54	7.52	6.08	7.17	23.2	72	35.1	12.6	11.2	5.8	7	10.8	Br
Rb			*			0.69	1.02	0.55	0.95	0.75	1.26	0.88	Rb
Sr	199	156	136	100	150	537	355	361	443	394	442	418	Sr
U			*			3.38	2.32	1.91	2.31	1.12	2.56	2.76	U

V is below the detection limit, * not in the standard sample.

Table 5. SR-XRF metrological data for the international standard sample NIST 1556 Oyster Tissue

Element	S	Cl	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Rb	Sr
Detection limit, μg/g	1100	300	42	18	0.61	0.51	0.47	0.1	0.34	0.46	0.39	0.14	0.15	0.11	0.09	0.09
Sr wt % NIST 1566 Oyster Tissue ($N = 7$)	6.9%	5.3%	4.1%	4.0%	19.7%	3.5%	1.5%	2.9%	6.9%	1.1%	1.4%	0.5%	1.4%	0.4%	1.2%	1.1%

The experimental results of scanning the scales of a male whitefish, 5 years old, and a female, 6 years old, are shown in Fig. 5.

From Fig. 5 the following conclusions can be drawn. The concentration of elements such as K, Ca, Zn, and Sb increases towards the periphery of the scales. Perhaps these elements are redistributed to the periphery as the fish grows. The Br concentration can be considered uniform as the fish grow from annual layer to layer. Using elements such as Rb and Mo, one can observe an annual rhythm.

Despite the fact that the studied whitefish individuals from the Irkut River were of a similar age group and had the same ecological habitat, the content of elements in the scales of the female and male was different (Fig. 6). Thus, increased contents of elements are characteristic of male scales.

CONCLUSIONS

The SR-XRF method used in this work made it possible to study samples of ultra-low masses (0.5–10 mg) and determine the elemental composition in various

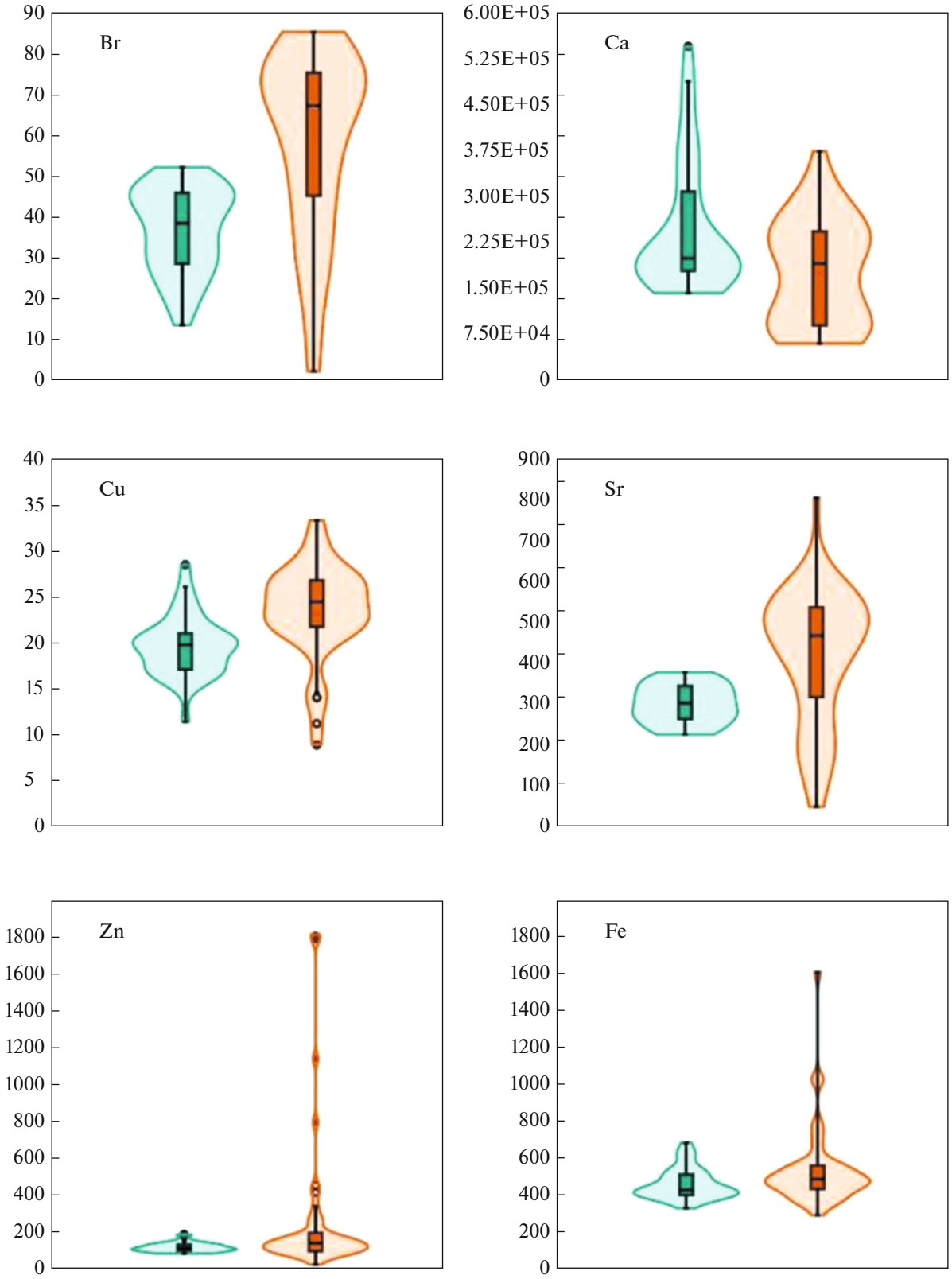

Fig. 6. Content of elements in the scales of a male (green fill) and female (orange fill) whitefish from the Irkut River, caught in 2020.

organs/tissues of fish. From the results presented in the article (Tables 2–5) it is clear that 18 elements can be determined in these samples (above detection limits, Table 5), such as (S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, and U). Depending on the research problem, by using the SR-XRF method it is possible to reduce the detection limits for specific elements of interest to us. This is achieved by changing the energy of excitation quanta on the VEPP-3 and VEPP-4M installations.

The results of our work show that studying the elemental composition of fish tissues using the SR-XRF method, which has such advantages as minimal sample preparation, the ability to analyze large samples, and the ability to reduce detection limits for specific elements, can be an effective tool for environmental monitoring and control of the process of growing aquaculture fish products.

Also, interesting results can be obtained by comparing the intensity of the accumulation of elements in different populations of Baikal omul, and comparing the obtained data not only with each other, but also with the existing abstract collections of scales collected from the middle of the last century.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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