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### Application of Nondestructive X-Ray Fluorescence Method (XRF) in Soils, Friable and Marine Sediments and Ecological Materials

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#### 1. Introduction

X-ray fluorescence (XRF) analysis is accepted as the most suitable physical method for the exploration of the elemental composition of rocks and minerals. This is due to fusing the sample with appropriate flux. The desired result is achieved because rocks and minerals are oxidic systems relative to major components. Soils, friable and marine sediments, silt and ecological materials differ from the above in the presence of an organic constituent (Corg), the weight fraction of which may vary considerably. The bioorganic diversity of Corg is the main source of errors, arising from sampling and analyzing procedure (Bock, 1972). Therefore, the possibility to analyze samples without having them destructed (nondestructive), preserving the study material after the results have been obtained, remains the unique advantage of XRF. This chapter reports information on nondestructive XRF procedures to determine the contents of rock-forming and some minor elements in powder of the materials listed. A satisfactory quality of XRF results, their validity and prospective viability for multi-purpose interpretations and environment monitoring have been discussed.

## 2. Nondestructive X-ray fluorescence (XRF) analysis of soils, friable and marine sediments

Their organic constituents consist of a mixture of plant and animal products, decomposed to different extents, and compounds which are chemically and biologically synthesized in soil. The resultant products of these processes are humic matter, low and high molecular weight organic acids, carbohydrates, proteins, peptides, amino acids, lipids, waxes, polycyclic aromatic hydrocarbons and lignin fragments. In addition, the secretions of root systems, consisting of a wide range of simple organic acids, are also present in the soils. The humic matter has the structure of a twisted polymer chain and consists of a relatively large number of functional groups (CO<sub>2</sub>, OH, C=C, COOH, SH, CO<sub>2</sub>H). Owing to a specific combination of various groups (particularly OH and SH), the humic matter is capable of producing complex compounds with some cations (Kabata-Pendias & Pendias 1986; Bolt & Bruggenwert 1976; Greenland & Hayes 1978; Lindsay 1979). The composition and properties of the organic constituents of soil depend on climatic conditions, the type of soil and agrotechnical techniques. Their interactions with soil metals may be described with the help of such

phenomena as ion-exchange reaction, surface sorption, chelate formation, coagulation and peptization. Biochemical complexity of the organic constituent of the materials considered radically alters melting with the flux. The formation of metal carbides, conversion of organic carbon into its modifications, the combustion point of which is very high (is not below 1600°C) and other phenomena arising in this situation inhibit homogenization. Therefore, the formal utilization of XRF analysis of rocks for soils and sediments seems to be possible only when their Corg. content does not exceed 1.5-2% (Kabata-Pendias & Pendias 1986). In all other instances fusing leads to the isolation of carbon at the glass disc surface. Concerning the materials ashed, because of the large number of non-investigated effects taking place under the recommended ashing at temperature  $525 \pm 25^{\circ}$  C conversion from the ashed to the initial system is so uncertain that its analysis becomes meaningless.

This part of paper reports information on the nondestructive XRF determination of Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, S, Ba, Sr and Zr in secondary natural matters. Except for drying at 105° C and pressing, it does not require any preliminary treatment of the sample. The necessity for additional drying is connected with the fact that the certified estimates of composition for standard materials used for calibration are given for those dried and sterilized at 105°C.

#### 2.1 Radiator preparation

Tablets from the powder samples were pressed on a boric acid backing under constant pressure. The amount of material required to produce a specimen for XRF analysis is different because of the varying organic content. Thus, if for soil and loam 6 g are sufficient, then for deposits the amount should not be less than 8 g. For humus and forest litter, its total trace element content does not exceed 5-6%, so that an 'infinitely thick' layer is ensured by about 12-14 g.

#### 2.2 XRF equipment

The intensities of analytical lines were measured with a CPM-25 x -ray spectrometer with 16 fixed channels. The rhodium target x-ray tube was operated at 40 kV. The scattered Rh K $\alpha$  - line intensity measured with the 16th channel was used as an internal standard for some elements. It should be kept in mind that the wavelength of this line is the shortest among those measured.

#### 2.3 Standard set for calibration

For calibration and assessment of the accuracy of analysis we used sets of Russia national certified standards of soils, marine sediments and friable deposits (Arnautov 1987). With the help of Chinese reference standards of soils and river sediments the possibility of the joint use of the Russia and Chinese national collections was also estimated.

In Table 1 for standard materials of various types of soil, sediment and friable deposits, the results obtained by the proposed XRF procedure (XRF) are compared with the certified values. For Al and Si, the XRF values were calculated using the set of calibration standards restricted to standards of the same type. The agreement between the XRF and certified values is satisfactory (Ostroumov 1979). With the exception of Si and partly for Al, for all elements the

differences among them are not significant and do not exceed the permissible standard deviations for all types of the above materials. The discrepancies observed for Al and Si are not surprising. In our opinion, the reason is that these elements are major and present in distinct mineral phases. However, our aim was to show the accuracy of the analytical results which the proposed method will provide for samples prepared in the required way. If the analytical data user is to obtain such results, real-world samples must be treated in the same manner, otherwise the quality of the final results will be significantly worse than the above.

ompo- nt	SP-1 black	c earth soil	SP-2 poc	izol soil	SKR red	earth soil	SSK gre carboné	y earth ate soil	
	Certified	XRF	Certified	XRF	Certified	XRF	Certified	XRF	
0	$0.80 \pm 0.03$	$0.81 \pm 0.02$	$1.15\pm0.05$	$1.09\pm0.02$	$0.15\pm0.03$	<0.2	$1.64 \pm 0.05$	$1.76\pm0.03$	
C	$1.02\pm0.03$	$1.10\pm0.02$	$0.77\pm0.01$	$0.64\pm0.02$	$0.92\pm0.05$	$0.79\pm0.03$	2.99±0.09	$3.17\pm0.06$	
$\mathcal{D}_3$	$10.37\pm0.08$	$10.56\pm0.09$	9.57±0.06	9.43±0.07	$17.01\pm0.26$	$17.02\pm0.14$	$11.48\pm0.14$	$11.51\pm0.10$	
2	69.53±0.21	$70.40\pm0.26$	78.33±0.12	78.68±0.27	$59.18\pm0.30$	58.93±0.24	52.65±0.17	53.28±0.21	
5 D	$0.170\pm0.010$	$0.180\pm0.010$	$0.075\pm0.006$	$0.067\pm0.008$	$0.100\pm0.010$	$0.110\pm0.020$	$0.170\pm0.010$	$0.170\pm0.010$	
	2.29±0.06	2.28±0.02	2.47±0.05	2.50±0.03	$0.98\pm0.03$	$1.08 \pm 0.02$	2.09±0.04	2.07±0.02	
	$1.63\pm0.05$	$1.73\pm0.03$	$0.81 \pm 0.04$	$0.74\pm0.03$	$0.17\pm0.04$	$0.17\pm0.01$	$11.47\pm0.10$	$11.48\pm0.06$	
2	$0.75\pm0.02$	0.75±0.01	$0.84\pm0.03$	$0.83\pm0.01$	$1.56\pm0.04$	$1.61 \pm 0.04$	$0.64 \pm 0.02$	$0.63\pm0.01$	
0	$0.077\pm0.002$	$0.079\pm0.002$	0.070±0.002	0.069±0.002	$0.051\pm0.002$	$0.052 \pm 0.001$	$0.089 \pm 0.003$	$0.085\pm0.002$	
<b>D</b> 3	$3.81 \pm 0.05$	3.87±0.04	2.98±0.05	$3.01\pm0.03$	7.86±0.08	7.97±0.05	$4.60\pm0.05$	$4.73\pm0.05$	
	$0.069\pm0.015$	0.63±0.005			$0.040\pm0.010$	$0.040\pm0.005$	$0.040\pm0.010$	$0.040\pm0.005$	
-odu	SDPS podzoi	l sandy loam	SDO-2 marii	ne sediment	SGH-1 c backgro	arbonate vund silt	SGHM-3 aluminosilic	3 friable ate deposit	
	Certified	XRF	Certified	XRF	Certified	XRF	Certified	XRF	
0	$0.51\pm0.03$	$0.53\pm0.01$	$4.03\pm0.04$	$4.03\pm0.03$	$0.53\pm0.02$	$0.56\pm0.02$	$0.61 \pm 0.04$	$0.65\pm0.04$	
0	$0.13\pm0.05$	$0.11 \pm 0.01$	$4.67\pm0.08$	$4.34\pm0.09$	$6.06 \pm 0.11$	$6.01 \pm 0.16$	$11.70\pm0.14$	$11.80\pm 0.20$	
<b>D</b> 3	$3.36\pm0.11$	$3.23\pm0.14$	$14.33\pm0.17$	$14.29\pm0.12$	$9.48\pm0.14$	9.32±0.07	$5.03\pm0.10$	$5.06\pm0.04$	
5	$91.24\pm0.23$	90.86±0.65	43.61±0.12	$44.43\pm0.27$	$47.00 \pm 0.20$	46.68±0.29	25.07±0.29	25.24±0.21	
5	0.036±0.006	$0.037\pm0.002$	$0.280\pm0.020$	$0.290\pm0.010$	$0.13.\pm0.01$	$0.150 \pm 0.005$	$1.820\pm0.050$	$1.830\pm0.020$	
_	$1.23\pm0.03$	$1.31\pm0.02$	$1.36\pm0.02$	$1.37\pm0.03$	$2.26 \pm 0.07$	2.26±0.02	$1.13\pm0.04$	$1.11\pm0.02$	
(	$0.27\pm0.03$	$0.25\pm0.02$	7.81±0.12	7.93±0.08	$7.76 \pm 0.10$	7.77±0.08	$17.76\pm0.22$	$17.99\pm0.31$	
2	$0.29\pm0.01$	$0.25\pm0.01$	2.32±0.06	2.30±0.03	$0.50 \pm 0.02$	$0.55\pm0.01$	$0.27\pm0.01$	$0.27\pm0.01$	
C	$0.011\pm0.001$	$0.011\pm0.001$	$0.270\pm0.010$	$0.270\pm0.005$	$0.30 \pm 0.01$	$0.300\pm0.005$	$0.500\pm0.030$	$0.500\pm0.010$	
$D_3$	$0.99\pm0.05$	$0.95\pm0.04$	$11.91\pm0.09$	$11.99\pm0.20$	$5.92 \pm 0.04$	$5.94 \pm 0.04$	$10.59 \pm 0.20$	$10.92 \pm 0.20$	
			(0.04; 0.16)		(0.037)		$0.050\pm0.010$	$0.050\pm0.005$	_

							E	, , , , , , , , , , , , , , , , , , , ,
Compo-	SGH-3 terr backgro	rigeneous und silt	SGH-5 anom	alous silt	SGHM-1 triat silicate	ole carbonate- deposit	SChT typi	cal black soil
111911	Certified	XRF	Certified	XRF	Certified	XRF	Certified	XRF
$Na_2O$	$1.61 \pm 0.05$	$1.48\pm0.03$	2.33±0.06	$2.36\pm0.02$	0.87±0.05	$0.91 \pm 0.02$	$0.81 \pm 0.02$	$0.76\pm0.02$
MgO	$1.60\pm0.05$	$1.59\pm0.03$	$2.54\pm0.06$	$2.34\pm0.05$	$5.82\pm0.10$	$5.70\pm0.10$	$0.95\pm0.03$	$1.01 \pm 0.03$
Al <sub>2</sub> O <sub>3</sub>	$16.46\pm0.19$	$15.73\pm0.20$	$14.40\pm 0.11$	$13.69\pm0.12$	$11.60\pm0.13$	$10.77\pm0.10$	9.81±0.14	$10.07\pm0.07$
SiO2	$60.54\pm0.20$	59.42±0.22	60.85±0.14	60.95±0.23	45.59±0.29	46.90±0.60	71.49±0.27	72.35±0.25
$P_2O_5$	$0.190\pm0.010$	$0.180 \pm 0.010$	$0.180 \pm 0.10$	$0.110\pm0.010$	$0.150\pm0.010$	$0.130\pm0.005$	$0.180\pm0.020$	$0.180\pm0.010$
K <sub>2</sub> O	2.43±0.08	2.45±0.03	$3.56\pm0.09$	$3.39\pm0.03$	2.96±0.07	2.90±0.03	2.42±0.04	$2.49\pm0.02$
CaO	$0.41\pm0.03$	$0.48\pm0.03$	2.95±0.05	2.87±0.04	$7.05\pm0.20$	$6.81\pm0.07$	$1.60\pm0.05$	$1.79\pm0.20$
TiO <sub>2</sub>	$0.98\pm0.03$	$0.96\pm0.01$	$0.62\pm0.01$	$0.58\pm0.01$	$0.63\pm0.04$	$0.68\pm0.01$	$0.74\pm0.03$	$0.73\pm0.01$
MnO	$0,130\pm0.010$	$0.140\pm0.005$	$0.087\pm0.003$	$0.086\pm0.002$	$0.073\pm0.004$	$0.082 \pm 0.002$	$0.079\pm0.002$	$0.081 \pm 0.002$
Fe <sub>2</sub> O <sub>3</sub>	8.76±0.08	8.77±0.06	$5.45\pm0.10$	$5.28\pm0.04$	$4.62 \pm 0.06$	$4.75\pm0.05$	$3.48\pm0.06$	3.45±0.04
s	(0.027)		(0.10)		$0.050\pm0.010$	$0.050\pm0.005$	$0.050\pm0.010$	$0.068\pm0.005$
Compo-	GSS-4, lim	y-red soil	GSS-2,chest	nut soil	GSS-5, yell	ow-red soil	GSD-10, strea	um sediment
nent	Certified	XRF	Certified	XRF	Certified	XRF	Certified	XRF
Na <sub>2</sub> O	$0.11 \pm 0.01$	0.12	$1.62 \pm 0.02$	1.65	$0.122\pm0.009$	<0.1	(0.04)	<0.1
MgO	$0.49\pm0.02$	09.0	$1.04\pm0.02$	1.05	$0.61\pm0.02$	0.67	$0.12\pm0.02$	0.20
$Al_2O_3$	$23.45\pm0.11$	25.92	$10.31 \pm 0.05$	10.17	21.68±0.09	24.46	$2.84 \pm 0.04$	3.35
SiO2	50.95±0.08	57.31	73.35±0.11	74.56	52.57±0.25	50.85	88.89±0.12	89.42
$P_2O_5$	$0.159\pm0.003$	0.218	$0.102\pm0.002$	0.085	$0.089 \pm 0.004$	0.102	0.062±0.002	0.054
$K_2O$	$1.03\pm0.03$	1.17	$2.54\pm0.02$	2.39	$1.50\pm0.02$	1.57	$0.125\pm0.007$	0.27
CaO	$0.26\pm0.02$	0.36	2.36±0.02	2.37	(0.095)	0.01	0.70±0.02	0.71
TiO <sub>2</sub>	$1.801 \pm 0.027$	1.969	$0.452\pm0.005$	0.415	$1.049\pm0.015$	1.121	$0.212\pm0.005$	0.18
MnO	$0.183\pm0.004$	0.202	$0.066\pm0.001$	0.061	$0.176\pm0.004$	0.175	$0.130\pm0.002$	0.12
Fe <sub>2</sub> O <sub>3</sub>	$10.30\pm0.05$	11.16	$3.52\pm0.03$	3.33	$12.62 \pm 0.08$	13.34	$3.86 \pm 0.04$	3.38
S	$0.018\pm0.003$	<0.02	$0.021 \pm 0.003$	<0.02	$0.041\pm0.004$	0.038	00.09±0.00	<0.02

Table 1. Comparison of XRF results and certified and recommend values for Russia national certified and Chinese reference standards (%), respectively

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## 3. A case study of the XRF determination of Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Zr in dry powder of fish muscle tissue

The study of fundamental relations between natural constituents of aquatic ecosystems, as well as multi-purpose ecological investigations, focused on assessment of environment state and its protection from man-made impact, necessitates development of targeted analytical methods. Notice that when investigating aquatic ecosystems in the context of indicative ecology attention was so given to Hg, and to a lesser extent to Cd and Pb behavior (Nemova, 2005). The list of other elements to be examined was very constrained (Moiseenko, 2009) because multielement instrumental techniques became available only in the late the 20th century (Vetrov & Kuznetsova, 1997). At the moment diverse instrumental techniques, e.g. AAA, XRF, AES, NAA, AES ICP and MS ICP, are widely applied in the investigations of living matter of aquatic ecosystems (Moiseenko, 2009; Tolgyessy & Klehr, 1987), each method having specific limitations in terms of detection limit, selectivity and expressness (Vetrov & Kuznetsova, 1997; Kuznetsova et al., 2002).

The living matter of aquatic ecosystems is the medium uncommon for XRF, because of specific bioorganic composition; high and low contents of water and total mineral components, correspondingly, and in addition, lack of proper multicomponent certified standard materials (CRM) of both of national and international production. Utilization of artificial mixtures for calibrating and evaluating the accuracy by the «introduced-defined» method is restrained by the lack of inert material of required purity, as well uncertainty of modeling mixtures compositions. This part of paper reports information on nondestructive XRF procedure to determine the contents of elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Zr in dry powder of fish muscle tissue.

#### 3.1 Samples and their preparation

A series of 60 emitters were produced from certified reference material of composition of Baikal perch muscle tissues BOk-2 (CRM No.9055-2008 (BOk-2)) (CATALOGUE, 2009) to be employed in the experiment. Three emitters were made of the materials of twenty sealed and labeled polyethylene jars. Besides, our objective was muscle tissue powders of omul, golyan and river perch (group I), the same as perch and plotva (group II). Fishes of group I were collected in the Chivyrkuy Bay of Baikal Lake, while those of group II were caught in various parts of the Baikal and Bratsk man-made water reservoir. The sampling sites differed in the rate of technogenic pollution.

The muscle tissues of group II fishes were lyophilized to a steady weight using a Labconco lyophilizer (method 1). The muscle tissue of omul, river perch and golyan (fishes of group I) were slowly dried to a steady weight on the water bath at  $T=60\pm3^{\circ}C$  (method 2). The emitters weighing 4 g were pressed under 4 tons pressure in the mold heated to  $T=38\pm0.1^{\circ}C$  (Gunicheva et al., 2005). The temperature was regulated by TRM-101 thermostat manufactured by TERMIK Co. in Moscow. The emitting layer for the analytical lines of elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Ni, Cu and Zn is thick, whereas for the lines of elements Rb, Sr, Zr and Rh it is intermediate. The uncertainty of the thickness of emitting layer is assigned to weighing mass 4 g on weights BP 61S Sartorius, Max 61, d=0.1 mg.

#### 3.2 XRF equipment

The intensities of analytical lines and background were measured in vacuum by the X-ray spectrometer with wave dispersion S4 Pioneer (Bruker Firm, Germany). Temperature in a vacuum cell is equal to 38° C. The conditions for excitation and registration of x-ray fluorescence and background are listed in Table 2.

X-ray tube with Rh–target, Be-window, 0.0075 cm thickness, and incidence angle of the primary and exit one of the secondary radiations are equal to 63 ° and 45 °, accordingly.

1.00	20, °			Detec			Voltago	Curront	Collimator
lyte	Κα1-	Back- ground	Crystal	tor	Time	, s	kV	mA	o
NT.	24.00	23.87		DC	100	50	20	10	0.46
Na	24.90	25.89	-000-55	PC	100	50	-30	40	0.46
Mg	20.58	21.96	OVO-55	РС	30	30	30	40	0.46
Al	144.61	145.82	PET	РС	60	60	30	40	0.23
Si	108.99	109.78	PET	PC	30	30	30	40	0.23
Р	89.43	91.40	PET	PC	10	10	30	40	0.46
S	75.75	74.77	PET	PC	10	10	30	40	0.46
C1	65.41	66.87	PET	PC	10	10	30	40	0.46
Κ	136.67	139.54	LiF(200)	PC	10	10	30	40	0.46
Ca	113.11	115.17	LiF(200)	РС	10	10	30	40	0.46
Ma	(2.07	62.26	L :E(200)	DC	20	15	EO	10	0.22
IVIII	02.97	63.72	LIF(200)	rC	30	15	50	40	0.23
Fe	57.52	58.28	LiF(200)	PC	30	30	50	40	0.23
NI:	19 66	48.17	I :E(200)	CC	20	15	50	40	0.22
111	40.00	49.08	LIF(200)	CC	30	15	50	40	0.23
Cu	45.04	44.40	I = (200)	CC	20	15	50	40	0.22
Cu	45.04	45.71	LII <sup>(200)</sup>		30	15	50	40	0.23
Zn	11 75	40.98	I;E(200)	CC	20	15	50	10	0.22
ZII	41.75	42.53	LII <sup>(200)</sup>	CC	30	15	50	40	0.23
Dh	26.61	26.08	I (E(200)	CC	20	15	50	10	0.22
KU	20.01	27.23	LIF(200)		30	15	50	40	0.23
C۳	25.14	24.61	I = (200)	CC	20	15	50	40	0.22
51	23.14	25.62	LII <sup>(200)</sup>	CC	30	15	50	40	0.23
7.	22 51	21.74	I :E(200)	CC	20	15	50	40	0.22
Σľ	22.31	23.21	בור(200)		50	15	-50	40	0.23
Rh	18.47	-	LiF(200)	CC	10	10	50	40	0.23

Table 2. Conditions of excitation and registration of XRF by S4 Pioneer spectrometer.

The emitter was being measured for no more than 19 minutes. After measuring 9 emitters (in ~6 hours) "the reference emitter" made from certified reference material of Tr-1 (see

Table 3) was measured in order to control the equipment drift. It permitted to use both absolute and relative intensities. For estimating the long-time stability of emitter from dry powder of fish muscle tissue all measurements were carried out during a year. The measurements for every emitter were executed 6 < n < 12 times, in total 480.

Sample No	Reference Material	Producers
1	Tea (GSV-4)	Institute of Geophysics. & Geochem. Exploration (IGGE), Heibei, China
2	Leaf of birch (Lb-1)	Siberian Branch of Russian Academy of Sciences, Institute of Geochemistry, Irkutsk, Russia.
3	Mixture of meadow herbs (Tr-1)	Siberian Branch of Russian Academy of Sciences, Institute of Geochemistry, Irkutsk, Russia.
4	Canadian pondweed (Ek-1)	Siberian Branch of Russian Academy of Sciences, Institute of Geochemistry, Irkutsk, Russia.
5	Baikal perch tissue (BOk-2)	Siberian Branch of Russian Academy of Sciences, Institute of Geochemistry, Irkutsk, Russia.
6	Potatoes tuber (SBMK-02)	Central Institute of Agrochemical Service of Agriculture and Sverdlovsk Branch VNIIM
7	Wheat grain (SBMP-02)	Central Institute of Agrochemical Service of Agriculture and Sverdlovsk Branch VNIIM
8	Cereal herb mix (SBMT-02)	Central Institute of Agrochemical Service of Agriculture and Sverdlovsk Branch VNIIM
9	Milk Powder IAEA - 153	Report: IAEA/AL/010 Australia
10	Milk Powder IAEA A11	Report: IAEA/AL/010 Australia
11	Microcrystal cellulose	Sigmacell Cellulose, Type 50, S5504-1KG
12	Aminoethanole acid	analyzed by ICP-OES using certified technique
13	L-asparagine	analyzed by ICP-OES using certified technique
14-16	Milk-based infant formulas	International Nutrition Co, Denmark

Table 3. Specifications of certified reference materials and samples

#### 3.3 Content computation

The key points of procedure: generation of calibrating samples set, taking into account their physical and chemical properties; optimization of approximation capacity of calibration functions due to a proper selection of regression equation and regression approach to determine the parameters of calibration function. The certified reference materials and samples are tabulated in Table 3. Characteristics of calibration collection are given in Table 4. The influence of inadequacy of composition of organic matrix of the certified reference materials set and bioorganic matrix of fish muscle tissue on the XRF results of fish tissues was not studied yet. Only the principal XRF fitness was estimated. Admitting a rough similarity of bioorganic compositions of dry residue of cow milk and fish muscle tissue, it is believed that the systematic error due to this effect will not be over 8 %

(Gunicheva, 2010). The calibration functions have been selected out of the calibrations implemented by the software of X-ray spectrometer S4 («SPECTRAPLUS», 2002). The approach of alpha coefficients was applied for correcting the matrix effects when measuring elements Na, Mg, Al, Si, P, S, Cl, K and Ca:

$$C_i = m_i I_i^* (1 + \sum \alpha_{ij} I_j), \tag{1}$$

where: (a)  $C_i$  is the concentration of analyte *i*; (b)  $I_i$  is intensity of its analytical line corrected for the background; (c)  $m_i$  is slope of calibration plot; (d)  $I_j$  is intensity of matrix element analytical lines corrected for the background; (e)  $\alpha_{ij}$  is the value of the corresponding alpha coefficient calculated by the linear regression equation. The contents of Mn, Fe, Ni, Cu, Zn, Rb, Sr and Zr were analyzed by the background standard method. A characteristic line of the x-ray tube anode (see Table 2), incoherently scattered from sample, was the standard. The concentration of analyte *i* was calculated by the equation:

$$C_i = m_i^* (I_i + K_i) / I_j,$$
 (2)

where: (a)  $I_j$  is pure intensity of comparison line; (b)  $K_i$  is expression of intensity correction, (c)  $m_i$  is slope of calibration plot. Intensity  $I_j$  is proportional to 1/ (1+M), where M is the coefficient for correcting matrix effects. The parameters of calibration functions (1-2) were optimized by regression approach («SPECTRAPLUS», 2002).

	Analyte	Interval, ng/g	RM quantity	
	Na	40 - 6900	9	
	Mg	40- 4400	10	
	Al	20 - 3000	8	
	Si	2- 5450	9	
	Р	80 - 3600	11	
	S	1000 - 3600	11	
	C1	200 - 8400	8	
	K	20 - 23900	11	
114	Ca	10 - 16200	11	
	Mn	0.2 - 1240	10	7
	Fe	2.5 - 990	8	
	Ni	0.7 – 5.8	8	
	Cu	0.4 - 17.3	10	
	Zn	2 - 94	9	
	Rb	3.5 - 74	10	
	Sr	2.2 - 72	10	
	Zr	0.2 – 5.5	8	

Table 4. Characteristics of calibration collection

#### 3.4 The temporal trends of X-ray fluorescence intensities

The regression equations of temporal trends for x-ray fluorescence intensities, both absolute and relative ones, for the elements to be determined are provided in Table 5.

Parameters of equations are presented as the range of their magnitudes, obtained for the entire series of emitters. Both absolute and relative intensities of all elements are expressed as  $R^{2}_{exp} < r_{xy}$ . It is proposed to accept: (a) absence of paired correlation and (b) contribution of temporal change is small in comparison with the discrepancy in values of  $a_0$  and  $a_1$  for the emitters pressed from various polyethylene jar materials. This fact is no surprise, since material of CRM BOk-2, as any biological medium, is *a priori* natural non-equilibrium system (Vernadsky 1978; Marchenko, 2003). The data in Table 5 disclose stress of processes proceeding within substance when converted in powder state, x-ray irradiation and effects of increased temperature and vacuum, set by instrument parameters of S4 Pioneer («SPECTRAPLUS», 2002). The influences of the specified processes on the accuracy of XRF data on fish tissue are still to be properly considered. The further study would require a thorough planning and implementing with fish tissue material of a set mass and fresh sample preparation.

	Absolute intensities	R <sup>2</sup> exp	Relative intensities	R <sup>2</sup> exp
Na	y=-0.001x+(28÷45)	0.3÷0.5	y=-(0.001÷0.002)x+(25÷63)	0.0÷0.2
Mg	y=-(0.001÷0.003)x+(43÷82)	0.3÷0.6	$y=-(0.001\div0.002)x+(40\div72)$	0.1÷0.6
Al	y=-(0.000÷0.001)x+(12÷45)	0.3÷0.5	$y=-(0.000\div0.001)x+(14\div36)$	0.0÷0.1
Si	y=0.001x+(28÷45)	0.3÷0.5	$y = -(0.000 \div 0.001)x + (12 \div 46)$	0.0÷0.2
Р	y=-(0.01÷0.03)x+(463÷980)	0.2÷0.5	$y=-(0.000\div0.001)x+(15\div40)$	0.0÷0.1
S	y=-(0.03÷0.07)x+(1087 ÷2155)	0.2÷0.6	$y=-(0.000\div0.001)x+(14\div33)$	0.1÷0.3
C1	y=-(0.004÷0.010)x+(183÷348)	0.1÷0.5	$y=-(0.000\div0.001)x+(17\div28)$	0.1÷0.3
K	$y=-(0.05\div0.11)x+(0.11\div0.43)$	0.1÷0.4	$y=-(0.000\div0.001)x+(18\div32)$	0.1÷0.2
Ca	y=-(0.004÷0.007)x+(169÷288)	0.3÷0.5	y=-(0.00÷0.01)x+(13÷25)	0.1
Mn	y=-(3E-06÷7E-05)x+(1.1÷1.9)	0.2÷0.5	$y=(0.6\div0.7)x+(0.24\div0.38)$	0.5÷0.6
Fe	y=-0.001x+(47÷551)	0.5	y=-0.001x+(21÷58)	0.5
Ni	y=-9E-05x+(3.6÷4.8)	0.2÷0.3	y=-(0.000÷0.001)x+(16÷37)	0.0÷0.1
Cu	y=-0.001x+(30÷53)	0.3÷0.2	y=1.0x+(0.01÷0.03)	0.4
Zr	y=-1E-05x+(0.1÷2.8)	0.0÷0.3	$y=-(0.000\div0.001)x+(15\div40)$	0.2÷0.5
Sr	y=-1E-05x+(2÷10)	0.02	$y = -(0.000 \div 0.001)x + (14 \div 24)$	0.2÷0.5
Rh	$y=-(0.000\div0.001)x+(2.6\div2.8)$	0.0÷0.4	$y=-(0.000\div0.001)x+(5\div9)$	0.3÷0.5

Table 5. Regression equations of temporal trends; \*  $r_{xy} = 0.537$  for p < 0.01

#### 3.5 Selection of intensities for concentration computation

The series of absolute and relative intensities for the emitters were compared by two-factor analysis of variance with different dispersions. The results are given in Table 6.

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Analyte	Trend	Average	Dispersion	n	t <sub>exp</sub>	Resume	
N -	abs.	0.4413	0.0325	20	1 75	By absolute	
INa	rel.	0.3229	0.0577	20	1.75	intensities	
Ма	abs.	0.4905	0.0171	20	2.00	By absolute	
Mg	rel.	0.3760	0.0424	20	2.08	intensities	
A 1	abs.	0.2177	0.022	20	1 70	By absolute	
AI	rel.	0.1400	0.0187	20	1.70	intensities	
Ci	abs.	0.3236	0.0212	20	1.02	Both schemes are	
51	rel.	0.2679	0.0354	20	1.05	comparable	
	abs.	0.3874	-0.0180	- 19	1.45	Both schemes are	
Г	rel.	0.3064	0.0423	20	1.45	comparable	
C	abs.	0.4072	0.0177	19	1 56	Both schemes are	
5	rel.	0.3214	0.0404	20	1.50	comparable	
Cl	abs.	0.3003	0.0161	20	0.12	By absolute	
CI	rel.	0.1941	0.0328	20	2.15	intensities	
V	abs.	0.2822	0.0104	19	2 10	By absolute	
K	rel.	0.1871	0.0259	20	2.19	intensities	
Ca	abs.	0.2270	0.0159	20	0.74	Both schemes are	
Ca	rel.	0.1921	0.0267	20	0.74	comparable	
Mn	abs.	0.2776	0.0622	20	0.19	Both schemes are	
10111	rel.	0.2922	0.0701	20	-0.10	comparable	
Fo	abs.	0.5318	0.0427	20	0.24	Both schemes are	
re	rel.	0.5456	0.0282	20	-0.24	comparable	
Ni	abs.	0.2250	0.0152	20	1 45	Both schemes are	
111	rel.	0.1635	0.0207	20	1.45	comparable	
Cu	abs.	0.3976	0.0726	20	0.34	Both schemes are	
Cu	rel.	0.3574	0.0849	20	0.34	comparable	
Zn	abs.	0.2205	0.0198	20	0.36	comparable Both schemes are	
Ζ.11	rel.	0.2400	0.0452	20	-0.30	comparable	
Ph	abs.	0.0215	0.0014	18	3 71	By relative	
KU	rel.	0.1001	0.0104	20	-5.21	intensities	
7.	abs.	0.1272	0.0368	20	1 72	By relative	
ZI	rel.	0.2324	0.0374	20	-1.75	intensities	
C.	abs.	0.0653	0.0058	20	1.92	By relative	
51	rel.	0.1534	0.0407	20	-1.02	intensities	
Dh	abs.	0.1577	0.06786	20	0.02	Both schemes are	
	rel.	0.1554	0.0377	20	0.05	comparable	
t crit	tical one-	way <i>p</i> =0.01		1.69	abs. –al	osolute intensities	
t <sub>crit</sub>	tical two-	way <i>p</i> =0.01		2.03	rel. –re	elative intensities	

Table 6. Comparison of absolute and relative intensities.

The empirical values of t - Student coefficients  $t_{exp}$  are more tabular  $t_{tab}$  for elements Na, Mg, Al, Cl, K (set 1) and less for Rb, Zr and Sr (set 2). Therefore to compute concentration for elements

of set 1 the absolute intensities were used and for set 2 elements these were relative ones. For elements Si, P, S, Ca, Mn, Fe, Cu II Zn selection of the intensities for concentration computation is non-critical and XRF analysis results are comparable when using both intensity sires.

#### 3.6 The metrological characteristics of the XRF procedure

Constituents of random error were assessed by three-factor analysis of variance. The values characterizing convergence error of intensity measurement  $S_{r,c}$ , the error of emitter preparation and its setting up in the holder  $S_{rp}$  and total intralaboratory XRF accuracy error  $S_{r,tot}$  are summarized in Table 7. It also provides the ranges  $N_{min} - N_{max}$  and the maximum values of count statistics error  $1/\sqrt{N}$  (N denotes the number of counts) to ease understanding.  $N_{max}/N_{min}$  ratios are changed from 2.5 for Zr to ~1.1 for elements Mg, Al, Si, P, K, Cu, Zn and Rb. In column of S  $_{r,tot}$  values the brackets enclose the estimations computed for relative intensities. It is evident that for only Ca and S statistics errors are the dominant contributions into evaluation of total intralaboratory XRF random error. For the rest of analytes the effects are not so simple. For elements Si, Cl, Mn, Ni, Cu, Zn, Rb, Sr and Zr values of S  $_{r,tot}$  are mainly caused by error of intensity measurement. For analytes Na, Mg, Al. P, K, Fe and Rh the errors of emitter preparation and its setting up in the holder are maximal signified, i.e. behavior of each analyte is unique and requires careful consideration.

Ana- lyte	$N_{min}$ - $N_{max}$ , counts	$1/\sqrt{N}$	S <sub>r.c</sub>	S <sub>rp</sub>	S <sub>r,tot</sub>	t <sub>2,1 exp</sub>	t <sub>3,2 exp</sub>	C <sub>min</sub> , ppm
Na	83.6÷184.8	0.11	2.26	10.14	9.23 (13.61)	47.90	2.00	*
Mg	0.76÷0.82	1.15	0.45	1.36	1.19 (1.21)	19.25	2.32	*
Al	0.854÷0.885	1.08	0.34	0.81	0.74 (0.93)	12.32	1.99	*
Si	0.233÷0.242	2.07	8.92	n.s.	8.45 (7.60)	1.17	0.08	*
Р	1.482÷1.567	0.82	0.31	0.93	0.81 (0.97)	19.19	1.45	*
S	0.13÷0.15	2.77	0.48	1.97	1.67 (2.36)	34.03	2.77	*
C1	0.0291÷0.0448	5.86	12.60	n.s	10.34 (9.04)	0.50	1.22	3.2
Κ	1.119÷1.142	0.95	1.06	2.24	2.08 (2.77)	10.00	2.37	5.0
Ca	0.0134÷0.0216	8.64	4.61	9.06	8.55 (10.47)	8.71	1.64	4.3
Mn	0.0315÷0.0448	5.63	12.60	n.s.	10.34 (8.42)	0.50	1.22	0.9 (2.8)
Fe	0.922÷1.170	1.04	4.50	4.81	5.71 (6.13)	3.29	0.94	1.3 (2.6)
Ni	0.173÷0.218	2.40	7.67	n.s.	7.01 (6.98)	0.98	0.05	0.4 (0.8)
Cu	1.144÷1.257	0.94	2.03	n.s.	1.67 (1.76)	0.53	1.92	1.4 (1.4)
Zn	2.566÷2.775	0.62	1.32	n.s.	1.16 (1.20)	0.8	1.25	0.4 (1.1)
Rb	4.79÷5.11	0.46	1.24	n.s.	1.15 (1.32)	1.06	2.50	0.5 (1.6)
Sr	0.435÷0.590	1.52	8.71	n.s.	7.15 (7.25)	0.51	1.65	0.3 (1.8)
Zr	0.095÷0.238	3.24	21.74	n.s.	20.79 (19.93)	1.22	0.64	0.3
Rh	1.667÷1.988	0.77	1.97	2.68	2.85 (3.12)	4.72	1.09	
$t_{2,1}(0,$	01,40,60) <sub>tab</sub> .=3.99	n.s ins	ignificar	nt; * star	ds for the elem	ents wit	h limits	of contents
$t_{3,2}(0,$	01,19,40) <sub>tab</sub> .=2.03	]	-	being	essentially bey	vond 10c	5.	

Table 7. Estimates, % of random error components

Column of  $C_{min}$  presents detection limits, calculated with  $3\sigma$ -criterion using the results of 20 measurements of emitters produced from powder of L- asparagine, aminoethanole acid, cellulose and reference samples OM-1 and OK-1 (muscle tissues of the Baikal omul and perch). They vary from (3÷9) x10<sup>-6</sup> for elements of Mn, Ni, Zr, Rb, Sr and Zn to (2÷5) x10<sup>-5</sup> for Cl, K, Ca, Fe and Cu, which is to say that XRF data are acceptable to investigate the living matter of aquatic ecosystems.

The detection limits were not given for elements of Na, Mg, Al, Si, P and S, because their contents in fish tissues exceed substantially the limits of quantitative determination  $(10\sigma)$ . The brackets enclose detection limits from reference (Gunicheva et al., 2005). The larger magnitudes for the latter are due to the difference in bioorganic and organic compositions of dry powder of fish muscle tissues and plant materials.

#### 3.7 The accuracy of XRF data

The classical assessment of accuracy of XRF data on the fish tissues would be impossible because of unavailability of proper certified reference materials and reference samples (ISO, 1994). Therefore, the XRF results for muscule tissues of various fishes have been compared with similar literature data. These data (Vetrov & Kuznetsova, 1997; Leonova, 2004; Moore & Ramamurti, 1987; Grosheva et al., 2000) are given for the fishes, collected in the southern and middle Baikal, Selenga River estuary, Angara River in the environments of Bratsk and Ust'- Ilimsk man-made water reservoirs (i.e. for the sites of CRM BOk-2 sampling), and were acquired by the authors through span 1987-2005 by different instrumental techniques.

Table 8 presents their types and sample preparation described in the references. It indicates that digestion is prevailing in sample preparation, when investigating the living matter of aquatic ecosystems.

Reference	Type of benefic	Sampling site	Instrumental	Sample
Leonova, 2004	Golyan, perch, plotva, omul	Chivyrkuy Bay of Baikal Lake	Atomic emission spectrometry (AES)	Digestion
Leonova & Bychinskiy, 1998	Perch	Bratsk man-made water reservoir, Lake Baikal	AES with evaporating sample powders in canal of arc graphite electrode	Digestion
Grosheva et al., 2000	Perch, plotva	Lake Baikal	Substoichiometric isotope dilution	Lyophlization
Moore & Ramamurti., 1987	Perch	The upper stream of river Ob' in site of town Barnaul water intake	Atomic absorption spectrometry (AAS)	Solubilizing
Vetrov & Kuznetsova, 1997	Omul, plotva, perch	Lake Baikal	AES	Digestion

Table 8. Details of instrumental techniques and sample preparation used in references

Comparison is presented in Tables 9-10. At Table 9 the column of analytes shows the elements certified for reference material BOk-2 by bold print; italics type designate for recommended

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	Ciesielski et al., 2005		672				2.0			80								
cal	Leonova, 2004; Ciesielski et al, 2000	3.8±0.9	57.2±3.9		3.2±0.6	2.24±0.18			194±31.1	113.4±17.1	4911±119	1484±103	5444±495	9977±12.37		6.3±0.1		
e parts of the Bail	Vetrov & Kuznetsova, 1997	17±8	41±21		$0.64 \pm 0.06$	$0.26\pm0.13$				24±6					)(	1 U J		7
ithern and Middle	Grosheva et al., 2000		$61.87 \pm 7.17$		$2.24\pm0.22$					$9.29 \pm 1.25$								
Sou	XRF <sup>+</sup>	31±3	33.4±2.4	15653±88	$1.09 \pm 0.18$	$0.54{\pm}0.16$	21.9±0.4	10412±54	$2.7\pm03$	27.5±4.7	1452±34	1261±29	2778±42	9289±63	2494± 24	106±8	55±0.2	
	XRF*	8.6±1.6	$10.97 \pm 3.83$	15476±307	$1.11 \pm 0.35$	$1.07 {\pm} 0.06$	33.9±1.2	$8723 \pm 226$	$2.4\pm0.3$	27.3±1.4	859±114	1325±54	3438±258	9329±211	$2074\pm157$	$33.7 \pm 15.3$	99±6	
made water reservoir	Leonova &, Bychinskiy, 1998; Moore & Ramamurti, 1987		10.0		10.0	0.2			(	$18.2 \div 37.2$								
Bratsk man-	XRF*	10.3±2.6	25.9±7.2	14002±589	0.60±0.35	$1.09 \pm 0.05$	19.3±2.4	9304 ±259	$3.5\pm0.8$	32.4±2.6	1125±174	1066±66	4836±648	7946±293	2499±404	35.9±6.7	23.3 ±5.7	
	CRM BOk-2	28±18	53±11	15900±700	$1.66 \pm 0.24$	$0.42 \pm 0.27$	$21.9 \pm 4.3$	$11000\pm2000$	$2.8\pm0.3$	$23.0 \pm 1.2$	1720±250	$1040{\pm}110$	2770±90	9500±500	$2800\pm200$		$49 \pm 5$	
	Ana- lyte	Al	Fe	Κ	Mn	Ni	Rb	S	$\mathbf{Sr}$	Zn	Са	Mg	Na	Ρ	CI	Si	Br	

Application of Nondestructive X-Ray Fluorescence Method (XRF) in Soils, Friable and Marine Sediments and Ecological Materials

Table 9. Contents of analytes in perch muscle tissues (dry weight, ng/g

A.m.a	Gol	yan	On	nul	Per	rch	Plot	tva
Ana- lyte	XRF*	Leonova, 2004	XRF*	Leonova, 2004	XRF*	Leonova, 2004	XRF+	Leonova, 2004
Na	6184 <b>±</b> 182		4840 <b>±</b> 118	3166±171	4229 <b>±</b> 163	2600±204	3000 <b>±</b> 500	5750±531
Mg	820 <b>±</b> 21	32,70	1108 <b>±</b> 23	2700±307	1454 <b>±</b> 50	1933±1160	1250 <b>±</b> 80	2750
Al	43 <b>±</b> 3	2,43	41 <b>±</b> 3	105±51	26 <b>±</b> 4	0,9±0,3	11 <b>±</b> 4	46
Si	145 <b>±</b> 4		159 <b>±</b> 4	968±354	82 <b>±</b> 10	7,5±1,8	33 <b>±</b> 9	550±437
Р	11328±317		8732 <b>±</b> 168	6333±341	8618 <b>±</b> 278	3500±341	8710±390	2500±625
S	6762 <b>±</b> 110		6182 <b>±</b> 73		9176 <b>±</b> 270		8310 <b>±</b> 340	
Cl	3032 <b>±</b> 94	5	3492 <b>±</b> 125	7	2289±96		1660 <b>±</b> 370	
K	8730 <b>±</b> 150		14052 <b>±</b> 210		13620 <b>±</b> 336		14800 <b>±</b> 400	
Ca	13100 <b>±</b> 210		740 <b>±</b> 10	6333±341	1268 <b>±</b> 30	$1000 \pm 546$	830 <b>±</b> 80	2500
Mn	3,65 <b>±</b> 0,67	0,22	1,34 <b>±</b> 0,42	3,3±1,8	0,66 <b>±</b> 0,22	2,4±1,0	1,03 <b>±</b> 0,08	
Fe	68 <b>±</b> 1	3,14	35 <b>±</b> 8	146±20,5	62 <b>±</b> 1	55,0±13,6	26 <b>±</b> 6	34,5
Ni	0,80±0,02		1,05 <b>±</b> 0,07	0,39±0,08	0,92±0,04	0,3±0,1	1,08 <b>±</b> 0,11	1,7
Zn	22,30±0,71	0,72	24,4 <b>±</b> 0,8	12,6±0,7	13,16 <b>±</b> 0,05	27,3±9,5	39,7 <b>±</b> 6,6	47,5
Rb	1,6 <b>±</b> 0,1		26,1 <b>±</b> 1,4		2,4 <b>±</b> 0,2		9,1 <b>±</b> 1,1	
Sr	11,7 <b>±</b> 0,1		3,2 <b>±</b> 0,2	52±2,7	0,5 <b>±</b> 0,1		3,1 <b>±</b> 1,1	
Br	11,4 <b>±</b> 0,2		55,1 <b>±</b> 1,5		8,9±0,2		29,3 <b>±</b> 12,1	

Table 10. Contents of analytes in muscle tissues of different fish kinds, (dry weight, ng/g) The sampling site is the Chivyrkuy Bay of Baikal Lake

value; \* denotes for the median of sampling and empty cell shows data absence. The data of the XRF columns have been gained by statistic treatment of no less than ten samples (free emitters for each). It is safe to say that the XRF information bulk for fish tissues is more excessive in comparison with the referenced information. It should be noted that information on content of Br, Cl, S, K, Cs, Sr and Sc in fishes of Baikal region is entirely absent in the references. Contents for the other elements belong in concentration intervals given by the other authors.

Microelement contents in perch tissues from Novosibirsk man-made reservoir (river Ob') (Leonova, 2004) are also comparable with the data for BOk-2. Notice that among the references, the only the data of (Leonova, 2004) is close to XRF results being conformable. Considering features of used analytical techniques some discrepancy being visible to the human eye is existent. Nevertheless the observed ranges of element contents are beyond methodical errors. They are indicative of fish tissue composition dependence on situation of aquatic ecosystems. We emphasize that irrespective of the difference in analytical techniques, the levels of concentrations and a series of decreasing element contents P> Na> Ca > Mg > Zn > Mn are fairly similar in all data.

As to Table 10 for all fish kinds in general consistency of data is enough apparent regardless of the fact that instrumental techniques and sample preparations are not identical.

Table 11 gives some relationships between the XRF concentrations of some elements for muscle tissues of plotva and perch fish, collected in the southern and middle Baikal and Bratsk man-made water reservoir, as well as omul. Statistically significant interrelationships are given by bold print. These correlations are conformable to those, represented in the liver

of Baikal seal (Ciesielski et al., 2006). They reflect not only techniques used when preparing samples and conditions of ecosystem in the sampling sites, but also fish trivial heredity. They can give usable information to interpret environment impact and element interactions with numerous factors, both biotic and abiotic. These correlations also demonstrate that the XRF data may be utilized as the efficient and sensitive indicator of changing element constituents of geochemical background.

Analyte pair	Bratsk n water r	nan-made eservoir	Various the l	s parts of Baikal	the Chivyrkuy Bay
	perch	plotva	perch	plotva	omul
Mn-Br	0.05	-0.28	-0.46	-0.91	-0.13
Fe-Br	-0.43	-0.54	-0.80	-0.93	0.13
Zn-Br	-0.76	-0.65	-0.94	-0.99	-0.58
Rb-Br	0.97	0.99	0.92	1.00	0.16
Sr-Br	-0.47	0.92	-0.38	-0.62	-0.15
Zn - Rb	-0.62	-0.57	-0.65	-0.97	0.47
Zn - Sr	0.84	-0.40	-0.09	0.36	-0.34
Rb - Sr	-0.31	0.77	0.41	-0.49	-0.24
Fe - Zn	0.12	0.84	0.73	0.66	0.39
Zn - Al	0.36	0.28	0.91	-0.31	-0.11
Mn - Fe	-0.32	0.25	0.09	0.26	-0.41
Fe - Ni	-0.56	-0.18	-0.09	0.46	0.20
Na - Cl	0.97	0.98	0.95	0.62	0.95
Na - K	-0.91	0.48	0.53	-0.06	0.96
Mg - Ca	0.35	0.91	0.93	-0.57	0.90
S - P	-0.06	0.93	0.90	0.22	-0.05
S - Cl	0.60	0.74	0.82	0.33	-0.19
Cl - P	-0.67	0.86	0.00	0.89	0.99
Ca - P	0.34	0.77	-0.49	0.74	0.93
Al - Ca	-0.53	0.06	0.04	-0.61	0.48
Al - Na	-0.90	-0.12	-0.10	-0.82	0.53
Al - Si	0.77	0.49	-0.17	-0.54	0.41
Al - Sr	-0.20	0.10	-0.17	-0.48	-0.27
Ca – Na	0.48	0.87	0.02	0.89	0.81
Ca – Si	-0.58	0.56	-0.09	0.96	0.80
Ca – Sr	0.94	0.95	-0.09	0.90	0.02
Fe - K	0.70	-0.73	0.18	-0.30	0.32
Fe - Mg	-0.62	0.05	-0.12	-0.87	0.24
Fe - P	0.08	-0.51	-0.28	-0.73	0.30

Table 11. Some element correlations

#### 4. Conclusion

Environmental problems and the modelling cycle of major and minor elements in soil-plant systems under natural conditions and in response to man's activities require the extensive analyses. Most of the analytical problems that occur are simple to solve by XRF spectrometry. This technique provides accurate analyses of rocks and materials which may be homogenized by fusion with an appropriate flux. Such an approach as a rule is impossible for XRF analysis of materials which are abundantly supplied with organic constituents. Its biochemical complexity inhibits homogenization and, as a result, does not allow the extension of this procedure.

We have demonstrated that the use of nondestructive XRF method ideally suits the quantitative determination of Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Rb, Sr and Zr contents in dry powders of muscle fish tissues. The regression equations of temporal trends for x-ray fluorescence intensities, both absolute and relative ones, for the elements were determined and shown that contribution of temporal change is small in comparison with the discrepancy in values of  $a_0$  and  $a_1$  for the emitters pressed from various polyethylene jar materials. This fact is not subitaneous because of material of CRM BOk-2, as any biological medium, is *a priori* natural non-equilibrium system. This imposes the strict initial conditions of the similarity: means of sampling and treatment.

Constituents of random error were assessed by three-factor analysis of variance. It is evident that behavior of each analyte is unique and requires careful consideration and tracing.

The quantitative analyses indicate that in various environmental situations the samples of all kinds of fish contain enumerated elements in different amounts and, therefore, they confirm validity of using fishes as indicating metal contamination. The metrological parameters of the technique allowed the sources of the errors to be identified, and the issues of further investigations to be projected.

The tendencies identified with the XRF results on the dry powders of fish muscle tissues do not contradict the features recognized in toxicology of aquatic ecosystems and environmental biogeochemistry. They disclose the potential of their utilization for multipurpose interpretations in environmental monitoring of freshwater ecosystems.

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#### Geochemistry - Earth's System Processes

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This book brings together the knowledge from a variety of topics within the field of geochemistry. The audience for this book consists of a multitude of scientists such as physicists, geologists, technologists, petroleum engineers, volcanologists, geochemists and government agencies. The topics represented facilitate as establishing a starting point for new ideas and further contributions. An effective management of geological and environmental issues requires the understanding of recent research in minerals, soil, ores, rocks, water, sediments. The use of geostatistical and geochemical methods relies heavily on the extraction of this book. The research presented was carried out by experts and is therefore highly recommended to scientists, underand post-graduate students who want to gain knowledge about the recent developments in geochemistry and benefit from an enhanced understanding of the dynamics of the earth's system processes.

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