MULTIELEMENT COMPOSITION OF ATMOSPHERIC AEROSOLS IN THE NOVOSIBIRSK REGION IN SUMMER SEASON

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This paper compares the data on the multielement composition of atmospheric aerosols sampled in the town of Karasuk and in the settlement Klyuchi of the Novosibirsk region in summer season of 1997. The measurements of multielement composition of atmospheric aerosols were performed by the X-ray fluorescent method using the synchronous radiation. The results of the factor analysis of atmospheric aerosols are presented and the obtained results are interpreted.

INTRODUCTION

This paper is devoted to the investigation of multielement composition of atmospheric aerosols (AA) of the Novosibirsk region. The investigation results given below are related to realization of the problems of analytical block of the complex project "Aerosols of Siberia" (Ref. 1). We measured the multielement composition of the samples from the settlement Klyuchi in the vicinity of Novosibirsk for the period from 14 of June to 13 of July, 1997, (30 samples) and in the town of Karasuk of the Novosibirsk region for the period from 20 of June to 18 of July, 1997, (29 samples). The samples were collected with the filters of AFA–KhA–20 type during one day with blowing of about 300 m^3 of air through the filters for a day. The measurements of multielement composition were performed by the *X*-ray fluorescent method using synchronous radiation (XRFMSR) at the station of *X*-ray fluorescent element analysis on synchronous radiation beams (accumulator of VEPP–3 type) at the Institute of Nuclear Physics SB RAS.[2]

MEASUREMENT TECHNIQUE

The AA characteristic features determining the choice of the method for multielement composition measurement are the multicomponent structure of atmospheric aerosols, a wide variation range of content of separate components, and low mass concentration of samples. The XRFMSR method used in our investigations is one of modern nuclear-physical highly sensitive analytical methods. The peculiarities of XRFMSR method application to measuring the AA multielement composition are considered in Ref. 3.

The low mass concentration of AA samples enables us to consider the AA samples as "thin" ones, i.e., when measuring quantitatively the multielement composition it is possible to neglect the secondary effects in a sample (absorption and subexcitation of fluorescent radiation, as well as multiple scattering inside a sample). On the other hand, "thinness" of a sample restricts a possibility to determine the trace concentrations due to small weight content of some elements in a sample. However, a significant store of energy when using synchronous radiation enables the sample thickness to be decreased significantly without loss of sensitivity.

The XRFMSR method makes possible the determination of only relative content of elements in a sample proportional to the area of characteristic radiation belonging to a given element.

To obtain the quantitative results, the reference samples were used containing the set of elements Ca, Cr, Fe, Cu, Sr with the same surface density varying from 1.75 to 11.5 μg/cm^2 for each of 5 elements depending on the weight density of a sample for obtaining the optimal detector loading.

Characteristic spectrum of samples was recorded twice at excitation energies of 27.8 and 22 keV. This double processing enabled us to extend, to a some degree, the range of measured elements, as well as to increase the reliability of measurements. Spread in values for the two series of measurements did not exceed 10–15% for the elements with characteristic energy up to 6 keV and 5% for characteristic energies more than 6 keV.

Numerical processing of the above spectrum for obtaining the relative ratio of element concentrations in a sample was made using standard procedure.[4]

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Essentially, the procedure is as follows: the spectrum (line contours and background curve) is approximated by the polynomial where the background curve is represented as a certain function with the unknown parameters. These parameters are determined by minimizing the root-mean-square deviation of the measured contour from the calculated one. The measured spectrum and the calculation model are the initial data. The model is the set of the background curve shape and the list of chemical elements considered in calculation and other parameters determining the process of spectrum recording and processing. An exponential function of the third-order polynomial, which introduces the least error in the AA spectra processing, was selected as the background curve.[3] In calculation, the elements from K to Nb (22 keV) and from K to Mo (27.8 keV) were considered. When determining the concentration of these elements, the lines of *K*-series were used. The elements from Ru to Sn (or from Mo to Sn for the energy of 22 keV) were not considered, because the greater excitation energy is needed to record their characteristic spectra.[3] For the elements from Sb to μ , the characteristic lines of *L*-series were used. The model contains the elements with concentration higher than the detection limit if only in one sample. When processing the sample data from the settlement Klyuchi, the model incorporates the following elements: K, Ar, Ca, Ni, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Ni, I, La, Ce, Sm, Gd, Tb, Ta, Pb, Ra, μ . For the samples from Karasuk the model includes Ar, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Nb, I, La, Ce, Sm, Gd, Tb, Ta, Pb, Ra, μ . As indicated in Ref. 3, the model should necessarily incorporate all the elements, which availability in a sample is possible. The availability of Ar in the model is caused by the presence of the characteristic Ar line being of air origin. The neglect of Ar in the model leads to the distortion of the results for adjacent (in the characteristic energy) elements.

To assess the reliability and reproducibility of measurements, the same sample (Klyuchi, 15 of July) was measured repeatedly (10 times) under the same conditions of processing: the exposition time of 200 s, the detector load depending on the intensity of exciting radiation of the order of 500 Hz.

Table I gives the results of measurements of the surface concentration of chemical elements using the sample (μg/cm^2) for stably observed elements, which lines are present in all the measurements. Table I shows that the spread in the measurement results decreases with increasing element concentration and energy of characteristic radiation. For a given sample, the surface density of 1 μg/cm^2 corresponds to the element content in the atmosphere of 60 ng/m^3. The similar picture is also observed for the sample from Karasuk (14 of July, 1997).

TABLE I.

Element	Characteristic radiation energy	Mean surface concentration, μg/cm^2	Mean statistical deviation, μg/cm^2	Mean deviation, %
Ca	3.69	193	5.4	3
Ti	4.51	11.4	0.47	4
Cr	5.41	0.504	0.16	32
Mn	5.9	2.385	0.174	7
Fe	6.4	57.2	1.01	1.8
Ni	7.5	0.567	0.0064	11
Cu	8.04	0.1018	0.0127	12
Zn	8.63	0.718	0.009	1.3
Br	11.9	0.108	0.0053	5
Rb	13.375	0.142	0.0105	7
Sr	14.14	0.313	0.0085	2.7
Y	14.93	0.0372	0.0068	18
Zr	15.75	0.2234	0.0079	3.5
Nb	16.6	0.0164	0.0026	16
La	4.65	1.195	0.15	12
Ce	4.83	0.661	0.167	25
Sm	5.63	0.585	0.059	10
Gd	6.05	0.55	0.061	11
Tb	6.27	0.588	0.103	17
Pb	10.54	0.177	0.021	12

MEASUREMENT RESULTS

The measurement results on mass concentrations of chemical elements in the atmosphere ($<x_i>$) are given in Table II for the samples from Karasuk and Klyuchi. Table II gives also the mean geometric deviations of mass concentrations (σ_{gi}) and the number of nonzero measurements (n_i). For all the elements, except for Ra and μ , the number of nonzero results exceeds 10 in the experiments made in Klyuchi. It is seen from the above results that within the variations of absolute values the mean values of mass concentrations coincide at both points of observations. The values of the geometric mean deviations vary from 1.5 to 2.9. In most cases this value is close to 2. This means that in some cases (70%) the mass concentration varies from 2 to 8 times and in 96% cases the similar variations are between 5 and 70 times.

Table II presents also the data on the relative content ($<x_{\text{Fe}}>_i$) of different elements at two points. The relative content of different elements was scaled to the iron (Fe) content in the samples. The above data show that the relative element concentrations at two points spaced 450 km apart practically coincide. Besides it is clear that the rms deviations of relative mass concentrations are in most cases less than that of their absolute values. This points to the constancy of the AA multielement composition in this region.

TABLE II. Characteristics of AA multielemental composition of Novosibirsk region in 1997.

Element	Karasuk, 20 June – 18 July, 1997 mass (ng/m^3) and relative concentrations					Klyuchi, 14 June – 13 July, 1997 mass (ng/m^3) and relative concentrations				
	$\langle x_i \rangle$	σ_{gi}	$\langle x_{Fe} \rangle_i$	σ_{gi}	n_i	$\langle x_i \rangle$	σ_{gi}	$\langle x_{Fe} \rangle_i$	σ_{gi}	n_i
q a	2100	1.72	1.3	1.46	29	5700	2.29	3.3	1.3	30
Sc	35	1.55	0.016	1.89	11	–	–	–	–	–
Ti	370	2.3	0.23	1.12	29	430	2.02	0.25	1.08	30
Cr	22	1.99	0.013	1.41	27	16	2.24	0.0092	1.48	28
Mn	70	2.23	0.042	1.17	29	76	2.03	0.044	1.08	30
Fe	1650	2.16	1	–	29	1700	2.06	1	–	30
Co	3.7	2.03	0.0024	1.73	14	–	–	–	–	–
Ni	1.8	1.66	0.0011	2.36	26	1.2	1.88	0.0006	1.93	21
Cu	2.3	2.78	0.0013	3.32	27	2.3	1.87	0.0014	2.3	28
Zn	31	1.98	0.019	1.65	29	24	1.56	0.014	1.82	30
Br	5.9	1.52	0.0036	2.06	29	3.8	1.5	0.0022	1.91	30
Rb	4.1	2.47	0.0025	1.23	29	5.0	2.16	0.0029	1.15	30
Sr	12.2	2.12	0.0074	1.17	29	12.6	1.88	0.0074	1.36	30
Y	1.2	2.16	0.0007	1.36	27	1.2	1.98	0.00064	1.59	28
Zr	7.5	2.42	0.0045	1.31	29	5.3	2.13	0.0042	1.23	30
Nb	0.36	2.92	0.0002	2.0	26	0.61	1.87	0.00033	1.55	26
I	56	2.0	0.024	1.55	18	–	–	–	–	–
La	36	2.38	0.017	1.54	23	30	2.23	0.016	1.45	27
Ce	32	2.76	0.014	1.25	21	31	1.75	0.016	1.40	27
Sm	14	2.04	0.0055	1.33	19	11	2.09	0.0051	1.48	24
Gd	14	2.67	0.0077	1.53	26	15.8	2.14	0.0085	1.26	29
Tb	20	2.3	0.0082	1.64	20	15.4	2.22	0.0090	1.53	30
Ta	0.79	2.2	0.0005	1.93	11	–	–	–	–	–
Pb	5.8	1.84	0.0035	1.62	29	7.6	1.73	0.0044	1.9	29
Ra	0.31	1.55	0.0003	2.04	7	0.21	2.06	0.00016	2.68	11
μ	0.33	1.76	0.0002	2.0	8	0.29	2.11	0.00019	1.89	12
V	–	–	–	–	–	20	1.66	0.0093	1.62	15
Se	–	–	–	–	–	0.47	1.50	0.00039	2.12	16

Table III gives the calculated values of the enrichment factors (EF) characterizing the degree of proximity of different element content in AA as compared with their content in basic rocks of the crust. The proximity of the EF values to unity suggests that the relative content of the element is close to its concentration in the airing crust. Table III shows that the most elements in their content are close to the material forming the Earth's crust.

The results of the factor analysis are given in Table IV indicating that the first factor incorporates 16 to 19 elements in Karasuk and 14 to 19 elements in Klyuchi. Eleven elements in this factor are common to the both observation points. In Table IV the coincident elements are given in boldface font. All the elements falling within the first factor, except for a group of lanthanides, have the enrichment factor close to unity. This points that this factor is evidently connected with the soil-erosion mechanism of formation. The high EF for the lanthanides is due to either their enrichment at the cost of local geochemical anomaly or the part caused by the plant fragments on the ground surface. To check this explanation, the multielement composition of different plants should be studied.

TABLE III. The enrichment factors (EF) of different AA elements in the Novosibirsk region (summer 1997).

Element	Karasuk, 20 June – 18 July 1997			Klyuchi, 14 June – 13July 1997		
	$<\text{EF}>_i$	σ_{gi}	n_i	$<\text{EF}>_i$	σ_{gi}	n_i
Ca	1.66	1.46	29	4.3	1.28	30
Ti	2.1	1.12	29	2.3	1.08	30
Cr	6.3	1.41	27	4.6	1.48	28
Mn	2	1.17	29	2.3	1.08	30
Ni	0.81	2.36	26	0.42	1.93	21
Cu	1.3	3.3	27	1.4	2.33	28
Zn	13	1.65	29	9.4	1.82	30
Br	58	2.06	29	36	1.91	30
Rb	1.0	1.23	29	1.17	1.15	30
Sr	1.1	1.17	29	1.12	1.36	30
Y	0.97	1.36	27	0.92	1.59	28
Zr	1.26	1.31	29	1.35	1.23	30
Nb	0.45	2.0	26	0.75	1.55	26
La	19	1.54	23	18	1.45	27
Ct	9.8	2.2	21	12	1.40	27
Sm	37	1.38	19	34	1.48	24
Gd	54	1.53	26	–	–	–
Tb	370	1.64	20	410	1.53	30
Pb	12	1.62	29	15	1.94	29
Ra	–	–	–	–	–	–
μ	4.2	2.6	8	34	1.89	12
Sc	45	1.89	11	–	–	–
Co	5.2	1.73	14	–	–	–
I	2500	1.55	18	–	–	–
Ta	9.0	1.93	11	–	–	–
Fe	1	–	29	–	–	30
V	–	–	–	34	1.62	15
Se	–	–	–	300	2.12	16

TABLE IV.

Observation point	Factor 1	Factor 2	Factor 3
Karasuk	**Ca**, **Ti**, Cr, **Mn**, **Fe**, Co, Br, **Rb**, **Sr**, **Y**, **Zr**, **Nd**, I, **La**, **Gd**, Pb	Ni, **Cu**, Zn	
Klyuchi	**Ca**, **Ti**, **Mn**, **Fe**, **Rb**, **Sr**, **Y**, **Zr**, **Nb**, **La**, Ce, Sm, **Gd**, Tb	**Cu**	Zn, Br

As to the other factors, they are formed by the elements of nonferrous metals and bromine. It can be assumed that these factors are caused by some anthropogenic effect. However, it is evident from the previous data that for Ni and Cu the enrichment factor is close to unity. For Zn EF ≅ 10, and for Br EF = 36 ... 58. The type of aerosol source corresponding to the second and third factors is so far difficult to be interpreted.

REFERENCES

1. K.P. Koutsenogii, Atmos. Oceanic Optics **7**, No. 8, 542–545 (1994).

2. V.B. Barychev, Yu.P. Kolmogorov, G.N. Kulipanov, and A.N. Skrinskii, Zh. Analit. Khimii **31**, 389–401 (1986).

3. K.P. Koutsenogii, G.A. Koval'skaya, A.I. Smirnova, N.S. Bufetov, and V.B. Baryshev, Atmos. Oceanic Optics **10**, No. 7, 512–517 (1997).

4. P. Van Espen, H. Nullens, and F. Adams, Nucl. Instr. Meth. **142**, 243 (1977).