DETERMINATION OF THE COMPOSITION OF ATMOSPHERIC AEROSOL IN SIBERIA BY NEUTRON ACTIVATION METHOD

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The results are presented of determination of multielement composition of atmospheric aerosol (AA) at three sites of the Novosibirsk region by neutron activation analysis (NAA). The data are obtained on the multielement composition of aerosol sampled on filters (total content) and two–stage virtual impactors capable of determining the multielement composition of two size fractions of AA (submicron – $d_{50} < 1$ μm and coarse $d_{50} > 1$ μm ones). The conclusion about the principal aerosol sources in Siberian region is drawn based on the enrichment coefficients and the results of statistical processing.

The neutron activation method is widely used in the last decades when investigating the environment.[1] This is explained by its high sensitivity and possibility of simultaneous determination of up to 30 and more different elements in a sample analyzed. This method is often used for the analysis of element composition of atmospheric aerosol of different size in order to identify the type of the source and to study the features of transformation of aerosol particles when it is transported by air.[2–5] Information about using NAA for the analysis of the atmospheric aerosol composition in different regions of the former USSR appeared for the first time in the middle of 70ths.[6,7]

As a rule, the major part of proceedings of topical conferences on the use of NAA for the analysis of the content of different elements in the environmental objects are the papers devoted to the determination of the atmospheric aerosol composition.[1,8–10]

The specific peculiarity of using NAA to determine multielement composition of atmospheric aerosol is described in detail in Ref. 11. The results of using NAA for the analysis of the aerosol composition in Siberian region are also presented there. Although the majority of the data presented in Ref. 11 relate to measurements of the composition of the samples collected in big industrial cities of Siberia, the authors arrived at a conclusion about identity of the relative elemental composition of aerosols on the global scale on the basis of the comparison of the data obtained with that known from literature.

However, as the authors[11] note, so serious conclusions need to be confirmed by a more representative experimental material. So in this paper we present the results of the analysis of the experimental data on multielement composition of atmospheric aerosols in Novosibirsk region, obtained in the frameworks of the project "Siberian aerosols".

SAMPLING SITES

The samples were collected at three sites:

1. At the south of Novosibirsk region – the stationary site of the Institute of Systematics and Ecology of Animals SB RAS (Lake Chany).

2. Geophysical station of the Institute of Geology SB RAS, approximately 12 km far from Akademgorodok (village Klyuchi).

3. The top of the building of the Institute of Chemical Kinetics and Combustion SB RAS (Akademgorodok).

The samples were collected on the AFA–HA–20 filters or on the two–stage virtual impactor with separation to the coarse ($d > 1.3$ μm) and submicron ($d < 1.3$ μm) fractions. The duration of sampling was approximately 24 hours. The total volume of pumped through aerosol reached 300 m^3 for the AFA filters and 20 m^3 for impactor sampling. The data on the site, data of the sample collection and the type of the sampling device are presented in Table I.

TABLE I. Sites and dates of aerosol sampling.

Sampling site	Sampling dates	Kind of sampler
Klyuchi	June 10–30, 1994	virtual impactor
Klyuchi	Jan. 24–Feb	virtual impactor
Chany	June 10–27, 1994	virtual impactor
Klyuchi	June 10–27, 1995	AFA filter
Akademgorodok	June 10–26, 1995	AFA filter

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TABLE II. Mean geometrical values of element concentrations in aerosol particles, assessed from the samples on the AFA–HA–20 filters, ng/m^3*, June 1995.*

Element	Br	Cd	La	Sm	Au	Na	Lu	Yb	U	Mo	Hf	Ce	Ca	Th	Cr	Se	Ag	Cs	Sc	Fe	Co	Eu
Klyuchi																						
$< x_i >$, ng/m^3	1.4	5.0	0.2	0.06	0.01	200	0.01	0.1	0.6	2.4	0.08	0.46	2080	0.11	1.9	0.3	0.8	0.2	0.2	480	0.26	0.03
σ_g	1.6	1.4	2.6	2.0	–	1.9	1.5	1.2	1.3	2.4	1.7	2.7	1.4	1.5	3.2	1.5	1.4	1.9	1.5	1.6	1.6	1.8
Akademgorodok																						
$< x_i >$, ng/m^3	8.2	20	1.2	0.2	0.03	670	–	0.4	1.0	130	0.3	2.2	9900	–	7.4	1.3	1.8	0.7	1.0	2000	1.5	0.15
σ_g	1.4	1.3	2.1	2.3	1.6	1.8	–	1.5	2.0	3.0	1.2	3.8	1.2	–	3.8	1.6	3.3	1.8	2.2	1.8	1.8	2.5

TABLE III. Mean geometrical values of element concentrations in aerosol particles, assessed from the samples on the virtual impactor, ng/m^3.

Element	Chany, June 1994				Klyuchi, June 1994				Klyuchi, Junuary 1995			
	1st stage, ($d > 1.3$ μm)		2nd stage, ($d < 1.3$ μm)		1st stage, ($d > 1.3$ μm)		2nd stage, ($d < 1.3$ μm)		1st stage, ($d > 1.3$ μm)		2nd stage, ($d < 1.3$ μm)	
	$< x_i >_1$, ng/m^3	σ_{g1}	$< x_i >_2$, ng/m^3	σ_{g2}	$< x_i >_1$, ng/m^3	σ_{g1}	$< x_i >_2$, ng/m^3	σ_{g2}	$< x_i >_1$, ng/m^3	σ_{g1}	$< x_i >_2$, ng/m^3	σ_{g2}
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
Na	620	1.4	620	1.5	430	1.4	430	1.5	530	1.3	430	1.2
Mg	170	1.4	230	2.4	240	1.5	130	–	360	1.6	98	1.1
Al	320	1.7	160	1.8	590	1.6	170	2.6	1070	2.1	190	1.6
Cl	420	1.5	410	1.4	2300	1.3	3800	1.3	140	2.1	210	1.7
Ti	210	6.8	–	–	680	2.7	–	–	39	1.4	8.7	–
V	0.9	1.7	0.56	1.7	1.9	1.3	0.75	3.0	2.5	1.7	1.1	1.9
Mn	23	2.5	7.7	1.7	25	1.6	5.4	1.7	23	1.6	12	1.6
Cu	93	2.2	63	1.9	25	1.4	37	2.1	38	1.7	30	1.9
In	0.25	2.1	0.33	1.6	0.15	3.3	0.12	4.2	0.2	2.4	0.09	3.8
I	0.58	2.0	1.1	1.5	0.4	1.8	0.59	1.5	0.75	1.4	0.56	2.8
K	990	1.4	3100	–	750	5.3	–	–	1600	1.9	730	1.1
Sc	0.09	1.5	0.12	2.9	0.11	1.6	0.11	2.5	0.08	2.2	0.04	2.4
Cr	4.9	1.9	24	–	6.4	1.4	19	1.3	2.3	3.9	3.0	1.4
Fe	106	1.7	360	2.7	140	2.2	980	3.2	330	2.2	180	2.2
Ni	5.3	1.9	4.4	2.3	2.3	2.1	2.4	5.4	2.2	2.3	4.5	2.0
Co	0.65	2.1	0.42	2.2	0.38	1.9	0.5	1.7	0.42	3.1	0.6	2.2
Zn	86	2.5	102	3.1	22	2.3	64	1.8	40	1.8	77	2.9
As	0.3	2.1	0.47	1.6	0.38	2.4	0.58	1.6	1.1	3.3	2.4	2.2
Br	1.6	1.7	2.0	1.9		1.9	7.8	1.8	1.5	1.8	2.5	1.2
Rb	0.7	3.2	2.2	1.4	1.1	1.8	1.7	4.1	1.1	2.4	0.46	2.5

Table continued

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
Mo	1.2	3.1	0.92	1.8	0.3	2.5	0.72	2.4	0.45	1.8	0.79	2.0
Ag	0.24	4.4	0.20	2.6	0.08	1.7	1.19	8.4	0.21	1.7	0.19	2.2
Cd	0.5	1.2	0.74	2.8	–	–	0.5	1.1	0.32	1.8	0.48	2.6
Sb	0.04	2.4	0.04	5.6	0.04	2.4	0.07	2.8	0.16	2.0	0.40	1.7
Cs	0.02	2.3	0.03	1.9	0.04	1.7	0.03	2.5	0.09	2.1	0.07	2.2
Ba	8.1	3.7	20	2.2	11	3.1	11	4.0	11	1.9	2.6	2.4
La	0.08	4.4	0.18	13	0.3	2.7	0.46	2.9	0.27	3.0	0.15	2.8
Ce	3.1	–	13	–	–	–	5.7	3.0	0.19	4.6	0.07	–
Eu	0.09	1.8	0.1	–	0.07	1.6	0.06	1.5	0.08	2.6	0.06	1.2
Sm	0.02	1.8	0.01	2.0	0.05	1.8	0.01	2.7	0.06	2.2	0.02	2.1
Tb	0.04	1.6	0.05	2.7	0.02	2.3	0.02	2.8	0.006	2.6	0.006	2.2
Ta	0.009	–	0.03	2.4	0.002	2.0	0.02	9.0	0.009	2.0	0.03	1.3
W	0.6	2.8	0.45	6.0	0.43	4.5	0.42	3.4	0.66	3.6	1.1	2.3
Au	0.009	2.1	0.01	1.8	0.003	2.2	0.002	3.2	0.005	3.2	0.005	1.6
Th	0.05	1.8	0.09	1.8	0.11	1.6	0.06	3.6	0.08	2.3	0.002	3.8
U	0.036	1.3	–	–	0.04	1.65	0.007	–	0.05	2.8	0.04	1.5

TABLE IV. Classification of elements by the value of the enrichment factor (EF).

Sampling site and kind of sampler	Date	Group of elements			
		1st group $EF < 10$	2nd group $10 \le EF < 100$	3rd group $100 \le EF < 1000$	4th group $EF \ge 1000$
Klyuchi, AFA–HA	June 1995	La, Sm, Na, Lu, Yb, Mo, Hf, Ce, Ca, Th, Cr, Cs, Sc, Co, Eu	Br, U	Se, Au	Cd, Ag
Akademgorodok, AFA–HA	June 1995	La, Sm, Na, Yb, U, Hf, Ce, Ca, Th, Cr, Cs, Sc, Co, Eu	Br	Au, Se, Ag	Cd
Chany, 1st stage of impactor	June 1994	Na, Mg, Al, V, Mn, Sc, Rb, Cs, Ba, La, Sm, Ta, Th, U	Ti, K, Cr, Mn, Ni, As, Sb, Se, Eu, Tb, Co	Cl, Cu, In, I, Zn, Br, Mo, W	Ag, Cd, Au
Chany, 2nd stage of impactor	June 1994	Na, Mg, Al, V, K, Sc, Mn, Co, Rb, La, Sm, Tb, Ta	Ni, As, Mo, Sb, Eu, W	Cl, Cu, Br, In, I, Zn, Ag, Cd, Au	
Klyuchi, 1st stage of impactor	June 1994	Na, Mg, Al, V, Mn, Sc, Co, Rb, Cs, Ba, La, Sm, Tb, Ta, Th, U	Ti, K, Cr, Ni, As, Mo, Sb, Eu, W	Cu, In, I, Zn, Br, Au, Ag	Cl
Klyuchi, 2nd stage of impactor	June 1994	Na, Al, V, Mn, Sc, Co, Rb, Sb, Ba, La, Eu, Tb, Ta, W, Th	Cu, In, I, Cr,Zn, As, Mo, Ce, Au	Cl, Br, Ag	Cd
Klyuchi, 1st stage of impactor	January 1995	Na, Mg, Al, V, Mn, K, Ti, Sc, Cr, Ni, Co, Sr, Rb, Cs, Ba, La, Ce, Sm, Tb, Ta, Th, U	Ce, Zn, As, Br, Mo, Sb, Eu, W	Cu, In, I, Ag, Cd, Au	
Klyuchi, 2nd stage of impactor	January 1995	Na, Mg, Al, V, Mn, Ti, Ca, Sc, Cr, Co, Rb, Cs, Ba, La, Ce, Sm, Th, Ta, Tb, U	K, Ni, Eu	Cl, Cu, In, I, Zn, As, Br, Mo, Cd, Sb, W, Au	Ag

TABLE V. Classification of elements by their mass portion.

Sampling site and kind of sampler	Date of sampling	Elements with $x_i > 0.01$	Mass fraction of elements $x_i > 0.01$
Klyuchi, AFA–HA	June 1995	Na, Ca, Fe	99.5
Akademgorodok, AFA–HA	June 1995	Na, Ca, Fe	99.6
Chany, 1st stage of impactor	June 1994	Na, Mg, Al, Cl, Ti, K, Fe, Zn	95.0
Chany, 2nd stage of impactor	June 1994	Na, Mg, Al, Cl, K, Fe, Zn	98.0
Klyuchi, 1st stage of impactor	June 1994	Na, Mg, Al, Cl, Ti, K, Fe	98.0
Klyuchi, 2nd stage of impactor	June 1994	Na, Mg, Al, Cl, Fe, Zn	97.0
Klyuchi, 1st stage of impactor	January 1995	Na, Mg, Al, Cl, K, Fe	95.8
Klyuchi, 2nd stage of impactor	January 1995	Na, Mg, Al, Cl, K, Ca, Fe, Zn	98.3

TABLE VI. Results of the factor analysis of aerosol samples.

Sampling site and kind of sampler	Factor									
	1st factor		2nd factor		3rd factor		4th factor		5th factor	
	Elements	Stat. weight	Elements	Stat. weight	Elements	Stat. weight	Elements	Stat. weight	Elements	Stat. weight
Klyuchi, AFA–HA June 1995	La, Ce, Th, Sc, Fe, Co	0.25	Eu, anti Cr, anti Yb	0.17	Ca, Br	0.12	Sm, Au, Se	0.11	Na	0.10
Akademgorodok, AFA–HA, June 1995	Mo, Cr, Se, Ag, Sc, Eu, Br, Cd	0.37	La, Na, Ce, Cs, Fe	0.26	Yb, anti U	0.10	Ca	0.10	Au	0.07
Chany, 1st stage of impactor June 1994	Na, Cr, I, Zn	0.27	Mo, Ag, Th	0.23	Ni, Co, anti V, anti Mn	0.22	Br, Cs, W	0.16	Cu	0.08
Chany, 2nd stage of impactor June 1994	Na, I, Zn, As, Sb	0.28	In, anti Au	0.18	Al, V, Mn, anti Sm	0.22	Mo	0.10	Cu, Cl	0.14
Klyuchi, 1st stage of impactor June 1994	Na, Cl, Mn, Fe, Br, Sm, Th	0.40	Al, Co, Sb, La, W	0.25	In, anti Ti, anti Rb	0.15	Au	0.08	Zn	0.08
Klyuchi, 2nd stage of impactor June 1994	Al, Zn	0.20	Mn, Co, Au	0.30	Cl, I, Sb	0.28	Cs	0.11		
Klyuchi, 1st stage of impactor January 1995	In, I, Sc, Fe, Co, Br, Rb, Cs, Ba, La, Sm, Au, U	0.63	Mn, anti Cl	0.12	Na	0.13				
Klyuchi, 2nd stage of impactor January 1995	As, Mo, Sb, anti Al	0.24	Co, Sm, Au	0.19	Mn, I, Br	0.19	Cl, W	0.14	Zn, anti In	0.15

The samples collected with a virtual impactor were analyzed at the Laboratory of neutron physics of the Joint Institute of Nuclear Research (Dubna). The AFA–HA–20 filters were analyzed at the Institute of Nuclear Physics at Tomsk Polytechnical University. The technique for neutron activation analysis is described in detail in Refs. 12 and 13.

RESULTS OF DETERMINATION OF THE MULTIELEMENT COMPOSITION

Table II presents the mean–geometric values of concentrations of different elements ($<x_i>$) and the rms errors of the means–geometric values (σ_g) determined for the samples collected on the AFA–HA–20 filters.

Table III presents analogous data for the samples collected by means of the virtual impactor. According to the results of determining the mass concentration of the elements contained in the aerosol particles, the values of the enrichment factors (EF) were calculated by the following relationship:

$$EF = (C_i/C_{Fe})_{aer} / (C_i/C_{Fe})_{crust},$$

where C_i is the mass concentration of the ith element in the sample analyzed and C_{Fe} is the iron concentration in the sample analyzed. The indices "aer" and "crust" show that in the first case the relative content is calculated of the ith element related to iron in the aerosol sample, and analogous ratio in the second case means the Clark content of the ith element in the Earth's crust. The latter value is taken from Ref. 14. The data on the distribution of elements are presented in Table IV as a function of the EF value. All the determined elements were divided into several groups. The elements with the values $EF < 10$ make up the first group. The elements with $10 \le EF < 100$ are placed in the second group. The elements with EF 10 times higher were grouped in the third, forth, etc., groups.

The elements, concentration of which is more than 1% of the total mass concentration, as well as of their total fraction in the multielement composition determined by means of NAA, are listed in Table V.

The results on measurements of the multielement composition and its temporal variations were statistically processed (the factor and correlation analysis). The results of such a processing made it possible to isolate the most significant factors that are presented in Table VI.

ANALYSIS OF THE DATA OBTAINED

As is seen from Tables II and III, NAA makes it possible to determine simultaneously up to 36 elements in the multielement composition of both submicron and coarse fractions of atmospheric aerosol of West Siberia. Classification of particles by the enrichment factor (see Table IV) shows that the majority of elements (more than 50%) are related to the first group ($EF < 10$). Usually the elements of such a type are related to the particles produced due to wind erosion of soil and weathering of rocks. However, such a mechanism normally generates the coarse particles. In addition, in winter soil in Siberia is frozen and covered with thick snow cover. It should lead to a significant decrease in the soil erosion. At the same time, the data from Table IV do not show any significant difference in the complex of the elements of the first group, so one can consider the problem of relating the particles to one or another type of source only by the value of the enrichment factor with care. One should consider the elements with big enrichment factor ($EF > 100$) no less carefully. One usually think that such particles are produced by anthropogenic source (thermal power plants, enterprises of ferrous and nonferrous metallurgy, motor and air transport, different electrical plants, etc.). The main portion of aerosols of anthropogenic origin are the particles of submicron size, so, as a rule, one note that the value EF increases as the particle size decreases. The relative portion of particles from anthropogenic sources should increase in winter. However, as is seen from the data presented in Table IV, no great difference in aerosol composition is observed at big EF. It may happen that qualitative differences in composition of aerosol at simultaneous determination of more than 30 elements in different size fractions partially depend on the local peculiarities of the landscape. In any case, additional investigations are needed for making a more reliable statement.

Let us note that the multielement composition is very constant for the elements, the mass fraction of which is more than 1%. As is seen from Table V, they are the element of soil–erosion origin. It is necessary to note that the main portion of these elements is the same both in coarse and submicron particles. Then, one can conclude that the particles produced by the soil erosion play a significant role in atmospheric aerosols of the background area of West Siberia. Second, the role of this mechanism in formation of atmospheric aerosols in this region is important not only for the coarse, but also for the submicron fraction.

The important role of the soil erosion mechanism of formation of atmospheric aerosols is well revealed from the factor analysis (Table VI). It is easy to see that the first factor is related to the particles of the first group ($EF < 10$). The greatest portion of such elements is related to the first factor for the coarse particles. The particles related to the 2nd, 3rd, 4th and 5th factors are more different in their composition. If one has taken into account the differences in the composition of the factors related to the particles of different size, one can say that the use of multistage impactors in combination with the multielement analysis of particles, allows one to identify up to 10 and more different sources, that is comparable with the technique of multielement composition of individual aerosol particles.

CONCLUSION

1. The results obtained show that it is possible to determine up to 36 elements in atmospheric aerosols of different size by means of NAA when pumping approximately 20 m^3 of air.

2. The data on the multielement composition of atmospheric aerosol have been obtained at three sites

of West Siberia, which are approximately 400 km far from each other, at the simultaneous collection of samples. The closeness of the element composition of aerosols is indicative of the regional (possibly, global) scale of formation of the structure of aerosol formations.

3. Different methods for identification of the source types show that the particles produced due to the soil erosion and weathering of the rocks compose the main portion of atmospheric aerosols in Siberian region.

4. When identifying the source type, it is necessary to apply a complex of different techniques. Use of the classification by the enrichment factor has a limited range of applicability.

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