

# Analysis of the Surface Layers of Atmospheric Aerosol Particles of East Siberia by Means of Secondary Ion Mass Spectrometry

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## Abstract

The elemental and phase composition of the surface layers of atmospheric aerosol (AA) particles sampled in winter 1998 in Irkutsk, Listvyanka and Ulan-Ude, is investigated by means of secondary ion mass spectrometry. It is stated that the source of AA is erosion of aluminosilicate soil. The surface of AA particles is covered by adsorbed hydrocarbons, nitrogen-containing compounds and partially by organic particles with a size of about 30 nm.

## INTRODUCTION

Recently, an assumption has been made that many photocatalytic reactions can occur on the surface of solid aerosol particles in the troposphere under the action of light, thus affecting the global atmospheric chemistry [1–5]. At present, only the experimental data on the volume composition of atmospheric aerosol are available, though it is necessary to know the composition of the surface of atmospheric aerosol particles in order to estimate the role of aerosol in atmospheric photocatalytic processes, because the main role in photochemical processes is played by the elemental and phase composition of surface layers. Taking this circumstance into account, we developed a procedure to investigate the composition of surface layers of atmospheric aerosol (AA) particles with the detection of the distribution of elements over depth, by means of the secondary ion mass spectrometry (SIMS) [6]. This analysis allows us

to solve two tasks, *i. e.* to determine chemical composition of the surface layers of AA particles, and, on this basis, to predict possible photocatalytic reactions, simultaneously carrying out monitoring of the chemical composition of AA, because the composition of deep-lying layers detected in course of ion etching corresponds to the volume composition. For the monitoring of AA, the SIMS technique has some advantages over other physical methods. Really, it allows one to record all the elements of the Periodic Table; only a small amount of the substance without any pretreatment is necessary for the analysis. It should be noted that the number of works dealing with the investigation of the composition of the surface of atmospheric aerosol particles is very small [7].

In the present work, we investigate the elemental and phase composition of the surface layers of atmospheric aerosol of East Siberia sampled in January and February 1998 in Irkutsk, Listvyanka, and Ulan-Ude.

## EXPERIMENTAL

The AA samples were collected in different sites by pumping the air through Whatman filters for several hours.

The elemental composition of the surface layers was examined with MS-7201 instrument equipped with the monopole mass analyzer with automatic control system collecting and processing the information on the basis of DVK-3 computer with CAMAC interface. The set-up and investigation procedure were described in detail in [6]. It should be noted that the diameter of the primary ion beam falling at an angle of  $45^\circ$  to the holders surface is 2 mm, while the area of the surface under bombardment is  $5 \text{ mm}^2$ . The pressure of residual gases does not exceed  $3 \cdot 10^{-6} \text{ Pa}$ . The surface is bombarded by argon ions with an energy of 4 keV and current density of  $j = 20 \mu\text{A}/\text{cm}^2$ .

The preparation of samples for analysis involved rubbing a part of aerosol deposit, scraped with a scalpel off the filter, into the substrate made of high-purity indium (99.99999 %). No fibres of the filter remained on indium after this operation. The analysis of the substrate and filter samples without aerosol shows that this method of the investigation of dielectric samples allows one to eliminate their

charging under the ion beam but does not bring any impurities.

## RESULTS AND DISCUSSION

The surface layers of AA particles were investigated by means of cyclic recording of spectra within the range  $m/z = 10-120$ . In each experiment, six spectra were recorded sequentially within this mass range; each spectrum was recorded for 170 s. A characteristic mass spectrum of the secondary ion emission (SIE) is shown in Fig. 1. The first spectrum is marked with a dashed line. The spectrum marked with a continuous line is the sixth spectrum observed after the ion currents reach their steady state. The latter spectrum corresponds to the etching depth of  $\sim 40 \text{ nm}$ . Since ion currents of elements reach their steady state at such a depth, one can assume that they correspond to the volume concentrations of elements.

The identification of peaks observed in mass spectra is explained in Table 1. For each  $m/z$  value, possible ions and the sources of their formation are indicated. Below the designations for formation sources are explained.

\* – designates ions that are due to the spraying of major and minor elements of the AA,

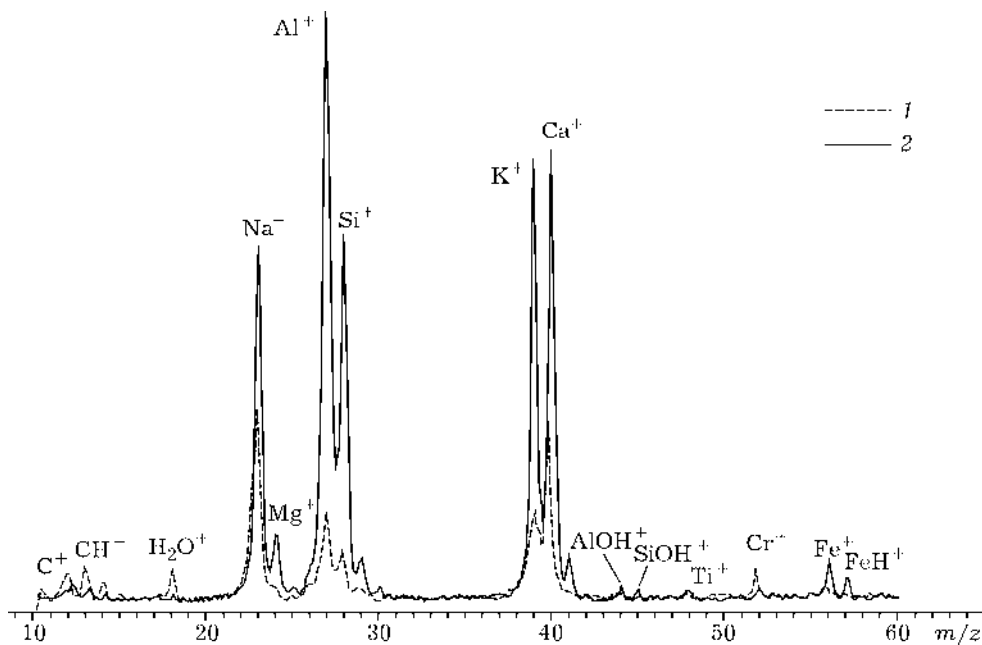


Fig. 1. Secondary ion emission mass spectrum for a typical AA sample collected in Irkutsk: 1 – surface, 2 – volume.

TABLE 1

Peaks observed in the secondary ion emission mass spectra of AA, and their identification (for explanation, see text)

$m/z$	Ion type	Source of formation	$m/z$	Ion type	Source of formation
12	C <sup>+</sup>	1	39	K <sup>+</sup> , C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	*, 1
13	CH <sup>+</sup>	1	40	Ca <sup>+</sup> , Ar <sup>+</sup> , C <sub>3</sub> H <sub>4</sub>	*, 1
14	CH <sub>2</sub> <sup>+</sup> , N <sup>+</sup>	1, 2	41	K <sup>+</sup> , C <sub>3</sub> H <sub>5</sub> <sup>+</sup>	*, 1
15	CH <sub>3</sub> <sup>+</sup> , NH <sup>+</sup>	1, 2	42	Ca <sup>+</sup>	*
16	O <sup>+</sup> , NH <sub>2</sub> , CH <sub>4</sub> <sup>+</sup>	*, 1, 2	43	AlO <sup>+</sup>	**
17	OH <sup>+</sup> , NH <sub>3</sub> <sup>+</sup>	2	44	SiO <sup>+</sup> , AlOH <sup>+</sup>	**
18	H <sub>2</sub> O <sup>+</sup>		45	SiOH <sup>+</sup>	**
23	Na <sup>+</sup>	*	48	Ti <sup>+</sup>	*
24	Mg <sup>+</sup> , C <sub>2</sub> <sup>+</sup>	*	52	Cr <sup>+</sup>	*
25	Mg <sup>+</sup> , C <sub>2</sub> H <sup>+</sup>	*, 1	56	Fe <sup>+</sup> , CaO <sup>+</sup> , Si <sub>2</sub> <sup>+</sup>	*, **
26	C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	1	57	FeH <sup>+</sup>	**
27	Al <sup>+</sup> , C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	*	59	Co <sup>+</sup>	*
28	Si <sup>+</sup> , CO <sup>+</sup> , C <sub>2</sub> H <sub>4</sub> <sup>+</sup> , N <sub>2</sub> <sup>+</sup>	*, 1, 3	64	TiO <sub>2</sub> <sup>+</sup>	**
29	Si <sup>+</sup> , COH <sup>+</sup> , C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	*, 1, 3	72	FeO <sup>+</sup>	**
30	Si <sup>+</sup> , COH <sub>2</sub> <sup>+</sup> , NO <sup>+</sup>	*, 3			

because they are observed at any time of bombardment.

1 – means ions formed when adsorbed hydrocarbons or organic particles are sprayed by Ar<sup>+</sup> beam. A characteristic feature of the behaviour of these ions is rapid decay of the intensity of ion currents because of rapid decrease in concentration in the adsorbed layer. In addition, the spraying coefficient for adsorbed hydrocarbon compounds is much larger than that for solids [8]. It should also be noted that the intensity of ion currents of C<sub>*n*</sub>H<sub>*m*</sub><sup>+</sup> decreases with increasing *n*. Actually, one can see in Fig. 1 that the intensity of C<sub>2</sub>H<sub>2</sub><sup>+</sup> ion is much lower than that of the CH<sup>+</sup> ion. Because of this, the contribution from C<sub>2</sub>H<sub>3</sub><sup>+</sup> ions into the peak of ions with  $m/z = 27$  can be neglected. A similar consideration is true for the peaks with  $m/z = 28, 39, 40$ , etc. Under bombardment by argon ion beam, there is the possibility to observe Ar<sup>+</sup> ion in the spectra. However, its presence can be manifested by argon isotope with  $m/z = 36$ . It is not recorded within the sensitivity limit. It should be noted that the relative concentration of Fe (see below) was determined using the intensity of the peak with  $m/z = 56$  taking into account the contribution from Si<sub>2</sub><sup>+</sup> and CaO<sup>+</sup> ions into this peak:

$$I(\text{Fe}^+) = I(m/z = 56) - 0.007I(28) - 0.002I(40)$$

Numerical coefficients in this equation were determined by investigating SiO<sub>2</sub> and CaO.

2 – means ions formed during bombardment of nitrogen-containing compounds. It is necessary to note that the resolution of the instrument is insufficient to separate ions formed by spraying hydrocarbons and nitrogen-containing compounds, for example CH<sub>3</sub><sup>+</sup>, NH<sup>+</sup>, etc.; however, the presence of N<sup>+</sup>, N<sub>*n*</sub>H<sub>*m*</sub><sup>+</sup>, NO<sup>+</sup> ions in the spectra cannot be excluded because trace amounts of NO, N<sub>2</sub>O, NH<sub>3</sub> are present in the atmosphere [2].

3 – designates the emission of CO<sup>+</sup>, COH<sup>+</sup>, COH<sub>2</sub><sup>+</sup>, NO<sup>+</sup> ions, which is also due to the adsorbed compounds. This conclusion is drawn from rapid decay of ion current during bombardment (within the time of recording one spectrum).

\*\* – are molecular ions which appearance is due to the emission of lattice fragments.

The results obtained demonstrate that in addition to the ions of major and minor elements Si<sup>+</sup> ( $m/z = 28, 29, 30$ ), Ca<sup>+</sup> (40, 42), Al<sup>+</sup>(27), Na<sup>+</sup>(23), Mg<sup>+</sup>(24, 25), K<sup>+</sup>(39, 41), Fe<sup>+</sup>(56), Ti<sup>+</sup>(48), Cr<sup>+</sup>(52) and Co<sup>+</sup> (59), molecular ions are observed in the SIE spectra, which is explained by the presence of hydrocarbons (C<sup>+</sup>(12), CH<sup>+</sup>(13), CH<sub>2</sub><sup>+</sup>(14), CH<sub>3</sub><sup>+</sup>(15), C<sub>2</sub>H<sup>+</sup>(25), C<sub>2</sub>H<sub>2</sub><sup>+</sup>(26), C<sub>2</sub>H<sub>3</sub><sup>+</sup>(27), C<sub>2</sub>H<sub>4</sub><sup>+</sup>(28), C<sub>2</sub>H<sub>5</sub><sup>+</sup>(29), C<sub>2</sub>H<sub>6</sub><sup>+</sup>(30)), nitrogen-containing compounds

( $N^+$ (14),  $NH^+$ (15),  $NH_2^+$ (16),  $NH_3^+$ (17)), as well as adsorbed water ( $H_2O^+$ (18),  $OH^+$ (17)) and carbon oxide ( $CO^+$ (28) on surface. The intensity of these molecular peaks decreases rapidly during bombardment. The intensity of such molecular ions as  $AlO^+$  (43),  $AlOH^+$  +  $SiO^+$ (44),  $SiOH^+$ (45),  $FeH^+$ (57), that appear as a result of the emission of lattice fragments, increases while etching is in progress. The very fact of the emission of oxide fragments allows us to assume that the aerosol is composed of oxide compounds.

The most typical dependencies of ion peaks of elements on etching depth are shown in Figs. 2–4. Etching depth is connected with bombardment time by the equation  $Z = vt$ , in which the spraying rate was estimated using the equation  $v = 0.006jSA/\rho$ , where  $S$  is spraying coefficient. It was assumed in calculations that aerosol particles were spherical. It is natural that in this case argon beam always falls on them along a normal to the surface. When the

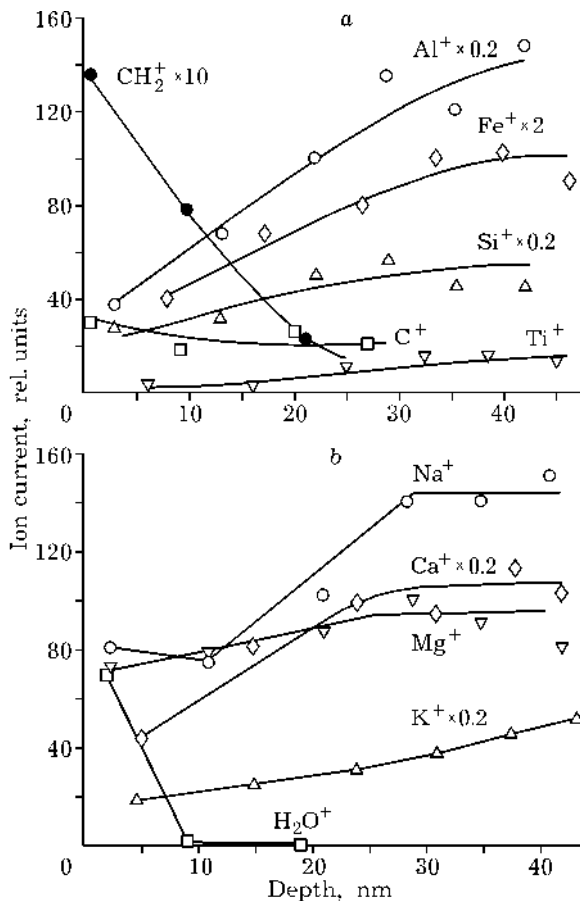


Fig. 2. Dependence of secondary ion current on etching depth for the AA sampled in Irkutsk.

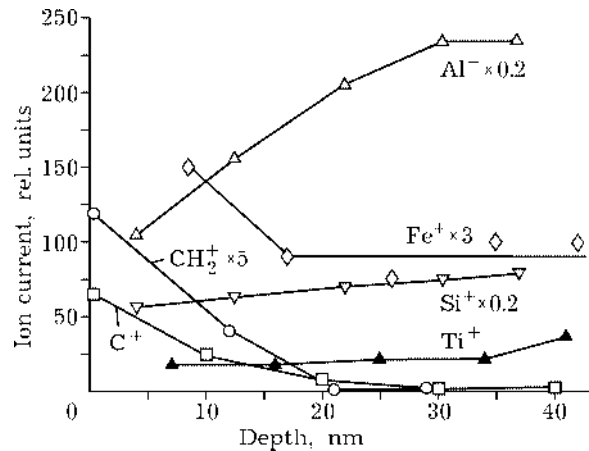


Fig. 3. Dependence of secondary ion current on etching depth for the AA sampled in Listvyanka.

primary  $Ar^+$  beam with  $E = 4$  keV falls along a normal to surface,  $S_0$  may be accepted to be equal to 2 for most oxides [9]. The analysis of the spraying of a spherical particle shows that the integral spraying coefficient is equal to  $1.5S_0$  [8]. Because of this, the spraying coefficient was taken to be 3.

$A/\rho$  is the ratio of mean molar mass of a compound ( $A$ ) to its density  $\rho$ ,  $g/cm^3$ . Really, for  $SiO_2$  and  $Al_2O_3$ , this ratio is close to 7; because of this, to estimate the etching rate, we accepted  $A/\rho = 7$ ;  $j$  is current density of the primary ion beam,  $\mu A/cm^2$ .

The rate of ion etching, determined as described above, was 2.5 nm/min.

The profiles of the intensity of elements for one of the AA samples collected in Irkutsk are shown in Fig. 2. It should be stressed that these dependencies are most typical, *i. e.*, such

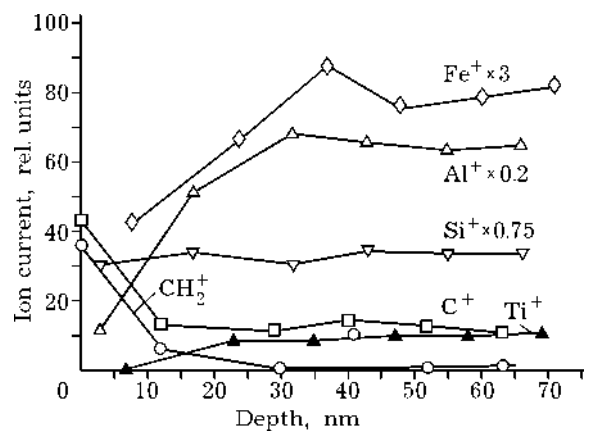


Fig. 4. Dependence of secondary ion current on etching depth for the AA sampled in Ulan-Ude.

a profile of distribution over the depth is characteristic of more than 50 % of all the AA samples investigated in the present work. One can see that the current of  $\text{H}_2\text{O}^+$  ions decreases sharply nearly to zero in the very first cycle of bombardment. The ion currents of  $\text{C}^+$  and  $\text{CH}_2^+$  decrease somewhat slower, while the ion currents of other elements increase; at the depth of 30–40 nm, the currents of all the elements reach their steady level. It follows from this fact that the surface layer of AA particles is covered by the adsorbed water and organic particles which screen the emission of the ions of the major elements. An important result is that the ion currents of elements reach their steady levels simultaneously. This allows us to assume that the elements under measurement are present in one and the same phase. As we demonstrate below on the basis of the quantitative data, aerosol particles are aluminosilicates with admixed alkaline metals, alkaline earths, iron and titanium.

Another type of the change of ion currents depending on the depth of etching is shown in Fig. 3 for the sample collected in Listvyanka. One can see that the  $\text{Fe}^+$  ion current changes not in phase with the currents of  $\text{Si}^+$  and  $\text{Al}^+$  ions. We believe that this sample

may contain the  $\text{Fe}_2\text{O}_3$  phase, perhaps because a separate iron particle has got into it. However, we have already mentioned that these examples are not numerous. It is very difficult to perform quantitative measurements, for example to measure the fraction of such samples, because this requires long time for the statistical analysis, including the analysis of the same AA samples from different parts of a filter.

The profiles of ion currents for the elements of one of the AA samples collected in Ulan-Ude are shown in Fig. 4. One of the major differences in this case is a more abrupt decrease in the current of  $\text{C}^+$  than that shown in Figs. 2 and 3. In agreement with this fact, a more rapid increase in the currents of  $\text{Al}^+$ ,  $\text{Fe}^+$ ,  $\text{Ti}^+$ , etc. is observed. Such an abrupt decrease in the currents of  $\text{C}^+$  and  $\text{CH}_2^+$  ions is explained by the spraying of adsorbed hydrocarbons but not coarse organic particles as it was in the case for the AA from Irkutsk and Listvyanka.

One can see in the curves shown in Figs. 3 and 4 that the currents of the ions  $\text{Si}^+$  and  $\text{Ti}^+$  change from the surface to the volume in a manner different from the current of  $\text{Al}^+$  ions. A reason may be the fact that along with alu-

TABLE 2

Elemental composition of AA after etching ~40 nm off by means of ion bombardment, % at.

Sampling site	Na	Mg	Al	Si	K	Ca	Ti	Fe
Listvyanka	10.0	1.7	12.2	54.2	1.2	13.1	1.8	5.2
	3.1	2.4	12.4	46.0	<b>1.8</b>	21.0	<b>7.2</b>	5.5
	<b>33.7</b>	1.8	<b>8.0</b>	28.9	<b>10.0</b>	14.5	1.0	2.2
	<b>1.9</b>	2.9	14.5	63.2	1.1	11.4	1.6	3.3
	7.9	2.9	13.1	39.1	2.8	26.4	2.8	4.2
	10.1	2.7	<b>40.3</b>	31.5	2.0	6.1	0	6.3
	5.7	2.1	19.3	54.8	1.8	13.4	<b>0.6</b>	2.0
Irkutsk	14.9	2.5	12.5	28.9	6.5	24.7	2.7	7.1
	3.5	2.3	9.4	61.0	2.0	15.5	1.5	4.6
	6.6	3.8	9.6	54.5	1.3	23.2	1.1	1.9
	18.8	3.7	31.1	35.2	2.6	6.9	0.4	1.1
	11.1	1.9	10.8	59.4	2.2	11.0	0.8	2.7
	6.4	3.8	21.2	62.0	0.1	2.5	0.6	3.6
	10.1	2.8	14.6	49.3	4.1	14.1	0.5	4.4
Ulan-Ude	3.6	1.5	16.9	55.2	1.7	16.6	0.4	4.1
	3.8	2.8	16.1	53.3	3.5	11.8	3.0	5.6
	3.0	2.5	25.5	57.1	2.0	5.6	1.1	3.2

TABLE 3

Relative sensitivity coefficients of elements, determined by the analysis of reference samples of soil

Sample title	Sample characteristic	Na	Mg	Al	K	Ca	Ti	Fe
ST-1a	Effusive	6.9	4.3	4.1	28.7	4.7	1.5	1.9
SSK-2	Soil with anthropogenic contamination	4.6	7.0	9.7	46.4	6.3	2.3	3.7
SKP-3	The same	6.1	5.5	11.3	20.3	7.8	1.4	2.0
SGKhM-1	Carbonate-silicate sediments	3.2	2.5	8.1	20.9	3.0	1.4	2.4
SGKhM-2	Aluminosilicate sediments	3.6	5.8	8.7	42.6	10.0	1.5	2.6
SGKhM-3	The same as SGKhM-1	4.1	1.8	8.1	25.7	2.9	2.5	1.4
SGKhM-4	The same as SGKhM-2	3.9	8.5	10.8	38.4	12.8	1.7	2.6
<i>Mean</i>		4.6	5.0	8.7	31.8	6.8	1.76	2.4
<i>Standard deviation</i>		1.3	2.1	2.1	10.2	3.7	0.45	0.06

minosilicates, AA particles contain SiO<sub>2</sub> with Ti admixture.

Let us consider the results of the quantitative elemental analysis that may be related to the monitoring of the chemical composition of atmospheric aerosol. The fractions of elements in AA corresponding to the depth of 40 nm are listed in Table 2. One can see in Figs. 2–4 that these data relate to the steady ion currents; we assume that they provide a satisfactory characterization of the volume composition.

It is reasonable to give a brief description of the procedure of quantitative analysis. It is based on the proportionality of the current of secondary ions of an *i*-th element ( $I_i$ ) to its concentration ( $C_i$ ) multiplied by the coefficient of its relative sensitivity ( $\gamma_i$ ):

$$I_i = k\gamma_i C_i \quad (1)$$

The coefficients of relative sensitivity were determined using the same equation and the results of the analysis of reference materials with known concentration. Relative concentration of an element with *i*-th mass was determined in per cent from the ratio

$$C_i = \frac{C_i^* \cdot 100}{1 + \sum C_i^*} \quad (2)$$

where  $C_i^* = \frac{I_i / I_{Si}}{\gamma_i}$ , while  $I_i$  and  $I_{Si}$  are ion currents of an element with *i*-th mass and

with silicon mass ( $m/z = 28$ ), respectively, because the coefficient of relative sensitivity for silicon was accepted to be unity in these calculations.

Ideally, reference materials should be of the same nature as the materials under investigation, because the coefficients of relative sensitivity depend on the chemical composition of samples. Since the composition of AA is due to the erosion of soil, the State Standard Samples of soils were used as references: SGKhM-1, SGKhM-2, SGKhM-3, SGKhM-4, SSK-2, SKP-3, ST-1A [10]. Relative sensitivity coefficients for these soil standards are listed in Table 3, along with brief characteristics of the soils used. For example, the standards SGKhM-1 and SGKhM-3 are carbonate-silicate mellow sediments, while SGKhM-2 and SGKhM-4 are aluminosilicate mellow sediments. It is natural that it is impossible to choose a reference material ideally corresponding to the aerosol matter to be analyzed for chemical composition. Because of this, as a first approximation for the quantitative analysis, we used relative sensitivity coefficients averaged over all the reference samples listed in Table 3. This approximation allows us to demonstrate that concentrations of separate elements in AA samples collected during different days can vary several times up to 10 (see Table 2); it also allows us to compare the elemental composi-

TABLE 4

Elemental composition of AA, obtained by averaging the data presented in Table 2, % at.

Sampling site	Na	Mg	Al	Si	K	Ca	Ti	Fe
Listvyanka	10.3	2.6	17.1	45.4	3.0	15.1	2.1	4.1
Irkutsk	9.4	2.8	15.7	50.7	2.6	14.0	1.0	3.7
Ulan-Ude	3.4	2.7	20.8	55.2	2.8	8.7	2.0	4.4
Listvyanka [12]*	3.7	3.7	17.0	—	—	5.7	—	3.2
Clarke	6.4	6.0	17.0	56.6	3.7	5.1	0.5	4.6

\*The data obtained by means of neutron activation analysis.

tion of AA with the Clarke content of elements (Table 4). In spite of the fact that the used set of relative sensitivity coefficients corresponds to the averaged soil, one can see in Table 4 that the composition of AA and the Clarke content of elements are consistent with each other, excluding the concentrations of calcium and titanium.

Another more precise approximation to the determination of chemical composition of AA can be the data of elemental analysis of AA obtained by different methods, these data being used to compare and calculate relative sensitivity coefficients. However, it seems impossible to perform such a comparison. The main difficulty is the fact that other physical methods do not allow one to determine the concentrations of the elements measured by SIMS [11]. Table 4 lists the data of neutron activation analysis of AA collected in winter 1990–1993 in Listvyanka. The comparison indicates that the application of averaged relative sensitivity coefficients leads to overestimated Ca concentration but to underestimated Na concentration, as determined by means of SIMS.

A satisfactory agreement between the indicated data can be obtained if we use a set of relative sensitivity coefficients corresponding, for example, to soils of SGKhM-2 type, *i. e.* to aluminosilicate sediments. Sensitivity coefficients for Na and K should correspond to the soils with anthropogenic contamination, which is characteristic for AA sampled in cities. It is impossible to perform a comparison for Ti concentration because of the absence of data. However, it follows from the SIMS data that its concentration in the investigated AA samples is really overestimated in comparison with the Clarke content, because the relative sen-

sitivity coefficient for titanium is only weakly dependent on the chemical state of the soil (see Table 3).

Aluminosilicates can act as the photocatalysts of acid-base type. In addition, the ions of transition elements (titanium and iron) are present on the surface. They can catalyze a broad set of reactions. This leads to the appearance of a new channel of reaction. In particular, in the recent years, a method being widely used in catalysis is the oxidation of organic compounds by nitrogen oxides, first of all  $N_2O$ , which is present in the atmosphere mainly as a result of anthropogenic processes. Active centres in the catalysts of oxidation with  $N_2O$  are iron ions in the aluminosilicate matrix. Under comparatively mild conditions, dinitrogen oxide is decomposed with the formation of highly active atomic oxygen. This reaction is also likely to be initiated photochemically, because nitrogen oxides have intensive absorption bands in the ultraviolet region. Since both iron ions and organic compounds are present on the surface of aerosol samples investigated, one can assume that the above-considered reaction leading to highly reactive oxygen can also take place on atmospheric aerosol particles.

## CONCLUSIONS

1. The surface layer (1–2 monolayers) of all the aerosol particles is covered by the adsorbed hydrocarbons, nitrogen-containing and other more complicated compounds, and water. A small part of the surface is coated with organic particles several tens nanometers in size.

2. Elemental analysis of the investigated aerosol samples shows that the main source of the aerosol formation is erosion of aluminosili-

cate soils with admixed iron, titanium, alkaline metals and alkaline earths.

3. Aluminosilicates with the surface admixture of transition metal ions can act as photocatalysts.

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