Chemical Composition of Superficial Layers of Particles of Atmospheric Aerosols (Novosibirsk and Irkutsk Regions)

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Abstract

An elemental analysis of superficial layers of the particles of atmospheric aerosols (AA) in Novosibirsk Region and the Baikal region has been performed with the technique of Secondary Ion Mass Spectrometry. It has been found that superficial layers (one-two) of monolayer of all aerosols are covered by adsorbed hydrocarbons, nitrogen-bearing compounds, by other more complex compounds, and water. It has been demonstrated that an erosion of aluminosilicate soils with admixtures of iron, titanium, alkaline and alkali-earth metals provides the basic source for AA formation. Action of water results in Na and Ca "washing out" from superficial layers and formation of hydroaluminosilicates. By means of X-Ray Absorption Near Edge Structure technique, the phase and charge state of iron in AA samples taken in Irkutsk have been determined. With the aim of analysing the composition of gases adsorbed on the surface, an attempt has been made to apply a technique of temperature-programmed desorption.

INTRODUCTION

Great attention, which is paid now to studying chemical composition of atmospheric aerosols (AA), stems from their involvement in a number of the major processes that occur in the atmosphere. By an atmospheric aerosol is meant a set of suspended particles with the sizes exceeding molecular, *i. e.* with radius more than 10^{-9} m [1]. Atmospheric aerosols make a significant contribution to dispersion and absorption of both direct solar energy and ascending thermal radiation together with many other components of the atmosphere as a result of adsorption and condensation of water vapour, various gases, and metal compounds, *etc.* [1, 2].

AA surface can serve as a catalyst of various photostimulated reactions. Recently, on a basis of semiquantitative estimations it has been suggested in works [3–5] that many of the photocatalytic reactions may run on the surface of aerosol particles of an oxidic nature under the effect of light in troposphere, exerting thereby a material effect upon the global chemistry of atmosphere.

For photocatalytic processes, the spectral characteristics and intensity of solar energy at different heights are of great importance. It is common knowledge that the solar energy with $1 < 300$ nm is virtually completely absorbed even before its entering the troposphere. Therefore, in troposphere, the reactions can proceed over those photocatalysts, which absorb light with

TABLE 1

Forbidden gap and long-wave limits of optical absorption for some oxides

Oxide	E_g, eV	l, nm
NiO	0.93	1340
Cr_2O_3	1.4	890
CuO	1.7	735
CdO	2.1	595
Fe_2O_3	2.2	570
TiO_2	3.0	420
ZnO	3.2	390

the wavelength l > 300 nm. Table 1 presents the oxides, which are capable of absorbing such light quanta and consequently can act as photocatalysts in all layers of Earth's atmosphere [3]. Many of these oxides can be represented in soils. Since erosion of soil provides one of the sources of solid aerosols (up to 35 %) [1, 2], it is this type of aerosols that most likely has a dominant role in the atmospheric photocatalytic processes. In addition, photocatalytic reactions may run not over the oxidic phases, but on the isolated ions of transition elements or their associates.

An estimation for the values of speed of possible photocatalytic reactions has been made in [3]. This contribution has demonstrated that among the oxides given in Table 1 TiO_2, Fe_2O_3, and ZnO deserve special attention, as they are the catalysts of the following reactions that involve the basic components of the atmosphere:

Formation of ammonia and hydrazine:

$N_2 + 3H_2O \circledR 2NH_3 + 3/2O_2$

$N_2 + 3H_2O \circledR N_2H_4 + O_2$
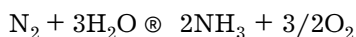
and formation of organic compounds:

$CO_2 + H_2O \circledR HCOOH, CH_2O, CH_3OH$

It will be remarked that TiO_2 is active also in the reactions of photodecomposition of water, in oxidation of water into hydrogen peroxide, and during formation of organic compounds from CO_2 and H_2O.

It is reasonable that the chemical composition of aerosol surface in these processes plays a leading part, and it is especially important to know the composition of superficial layers of aerosol particles.

Taking into account the aforesaid, we have devised a technique for studying the composition of superficial layers of atmospheric aerosols by method of Secondary Ion Mass Spectrometry (SIMS) with distribution over the depth [6, 7]. Performing such analysis enables elemental and phase compositions of AA superficial layers with distribution throughout the depth of particles to be determined, and also the possibility of particular photocatalytic reactions to be predicted. In addition, such an analysis allows the monitoring of chemical composition of AA to be conducted, since the composition of deep layers, as the process of ionic pickling of particles goes on, is in agreement with composition by volume. For the problems of AA monitoring, SIMS technique shows a number of advantages over the alternative physical procedures, because it enables conducting the quantitative analysis of all basic elements of the atmospheric aerosols formed as a result of soil erosion: Si, Al, Ca, Fe, Ti, Mg, Na, K, *etc*. The important factor is also the circumstance that the analysis requires a minor amount of analyzed material without its prior treatment.

SIMS technique also enables conducting the phase analysis based on the emission of molecular ions, but its potentials in this case are strongly restricted. For example, emission of FeO^+ ions is possible both from iron oxides, and from aluminosilicates, which contain iron in the form of admixtures. At the same time, the determination of the phase composition of aerosols and of the charge state for atoms of transition elements in aerosols is extremely important to solve the problem of the photocatalysis in the atmosphere. That is the reason why the technique of near-edge X-ray absorption fine structure spectroscopy (X-ray Absorption Near Edge Structure, XANES) with synchrotron radiation (SR) has been applied for determination of phase composition and charge state of some heavy elements.

The processes of interaction of water, gases, and various particles (for example, smog, pesticides) with inorganic AA also exert an influence on chemistry of the troposphere. This was exactly the cause of applying a method of Temperature-Programmed Desorption Mass Spectrometry (TPDMS) for study of the volatile constituents of AA.
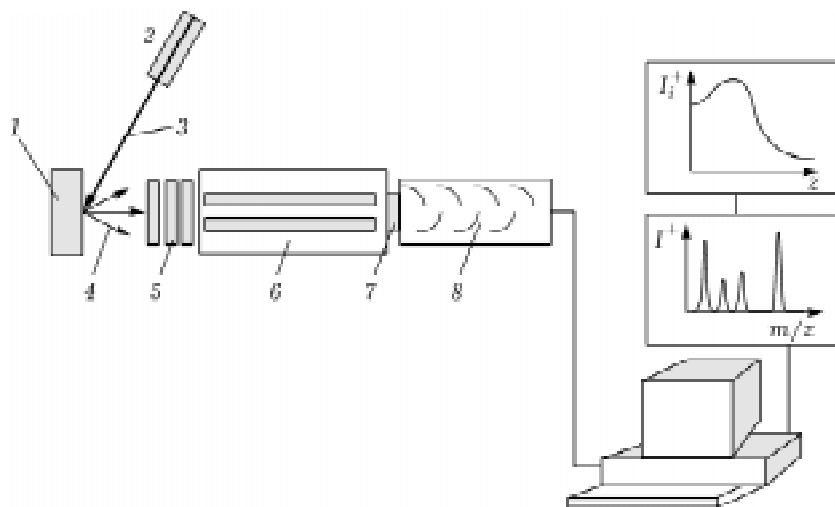
Fig. 1. SIMS schematic diagram: *1* − sample, *2* − ionic gun, *3, 4* − primary and secondary ionic currents, respectively, *5* − focusing lens, *6* − separation by weights, *7* − ionic-electronic transducer, *8* − secondary electron multiplier (SEM).

Methical difficulties, which restrain application of various methods (including XANES and TPDMS) for the specified purpose, are a scarce amount of aerosols, and what is worse, they are collected on the substrate. The measurements of such samples with the use of standard procedures are very difficult because of their low accuracy. To carry out a thermal desorption research with scarce amount of ultrafine materials, a vacuum setup has been created and the special holder [8] has been designed. The use of SR allows an accuracy of measurements to be raised owing to greater intensity of X-ray. A detailed description of AA investigation technique by means of XANES spectroscopy is given in [9].

This work presents the review of the results of investigations into the superficial composition of atmospheric aerosols in Novosibirsk Region (the samples were taken in the neighbourhood of Karasuk and in a settlement of Klyuchi (Akademgorodok, near Novosibirsk) in summer, 1992 and in spring, 1993) and also in the area of the Baikal Lake (the samples were taken in 1998−2000 in Irkutsk, a settlement of Listvyanka, Ulan Ude, at the station Baikal and at the high-mountain station Mondy). The samples were taken on the paper filters of the "Whatman paper" type by means of air circulation through them for 1 day when sampling in Novosibirsk Region, Irkutsk, and Listvyanka, and for 3−5 days at the station Mondy [10].

A superficial composition of AA particles, which were caught during a snowfall [11], has been investigated too. AA samples of clog snow (AACS) were collected in plastic basins. Snow thawing had been conducted in the covered enamel pans, typically from evening till morning. Then the thawed snow was pumped through the filters, and the solid matter settled on the filter.

CHARACTERIZATION OF THE TECHNIQUES

The technique of secondary ion mass spectrometry

The technique of Secondary Ionic Mass Spectrometry (SIMS) is based on mass spectrometer registration of ions, which are knocked out of the superficial layers of a solid at its bombardment by an ion beam. A schematic diagram of the SIMS procedure is shown in Fig. 1.

A sample-target is bombarded by a beam of the primary ions typically having an energy of several keV, which results in the sputtering of atoms of the target either in neutral, or in a charged state. The knocked out (secondary) ions are pulled out of the target area and then they enter the mass-analyser where they are separated according to their weight/charge *(m/z)* ratio and are detected in the subsequent process.

Despite the simplicity of SIMS procedure, it is very complicated for a theoretical descrip-

tion of the processes of sputtering and emission of the charged particles, which creates definite difficulties in the quantitative analysis of, especially, multiphase and multicomponent materials.

The current intensity of the secondary ions registered by the mass spectrometer is described by the following equation:

$$I_i^m = \text{const}\, I_p\, C_i^m Y P^{\pm} \tag{1}$$

where I_i^m is the current intensity of the secondary ions of an element with i-th mass m; I_p is the current intensity of primary ions; C_i^m is the concentration of i-th element with mass m, this concentration being equal to $\alpha_i^m C_i$; C_i is the concentration of i-th element; α_i^m is the content of isotope with the mass m; Y is a sputtering ratio, which is equal to the quantity of knocked out particles (atoms + ions + molecules) that are due to one primary ion; $P^{\pm}$ is the probability of a positive or negative ion formation.

It is evident from the eq. (1) that the secondary ionic emission is described by two phenomena − sputtering and ionization. The first phenomenon is represented in formulas by the sputtering ratio; the second is represented by the probability of ionization.

The value of sputtering ratio depends on many factors: mass, energy and angle of incidence of primary ions, the weight of target atoms and their bonding energy, *etc.* [12]. For the majority of single-component materials its value linearly increases up to 1 keV with an increase in energy of the primary beam, flattens out further at 3−5 keV with a maximum value (for the majority of materials it is equal to 1−5), and then drops a little. For organic materials its value may be 100 and more times higher than for metals and inorganic solids [13, 14]. This fact is rather important for the correct exploration of the concentration profiles throughout the depth of catalysts, since usually their surface is covered by the adsorbed hydrocarbons and water. It is reasonable that the substantially greater sputtering ratio of organic compounds results in their fast sputtering. Consequently, these adsorbed layers available on AA particles have practically no effect on the results of investigations of the superficial layers.

The basic feature of the sputtering process for multicomponent and multiphase materials, which can have a pronounced effect on the elemental and phase analysis of catalysts, is a different sputtering rate for components and phases. Nevertheless, the ratio between the quantities of the sputtered atoms in the sputtering regime should be equal to the ratio between volume concentrations:

$$n_A/n_B = C_A/C_B \tag{2}$$

The ratio (2) is also valid for sputtering of multiphase materials if individual phases do not interact when acted upon by ionic bombardment. However, an interaction occurs at the energies and current densities of the ion beam greater than those used in this work.

Much evidence is published on the sputtering ratios for single-component materials, especially, sputtering by means of ions of inert gases, while little is known about the total sputtering ratios of multicomponent materials. Measurements of the sputtering ratios for oxides suggested that in most cases they were the same as those for metals; Al_2O_3 and MgO represent an exception, for which it is somewhat lower than for Al and Mg, respectively [15].

At low bombardment dozes, the sputtering of such systems can be thought of as a superposition of the processes, which proceed on the single-phase crystallites. At high dozes, an equilibrium is established due to selective sputtering. In this case, the total sputtering ratio remains close to the value of a hardly dispersed phase and it increases up to the values typical for the alternative phase only at the very high concentration of this phase [15].

To estimate the pickling depth of AA surface, the sputtering ratio was assumed to be equal to 3, since its value is »2 for the majority of materials when an energy of primary ions is 3−4 keV and at the normal incidence of the primary beam. For spherical particles its value is about 1.5 times more [16]. We believe that the thickness of a sputtered layer (the depth of the analysis) calculated in this way was determined by us with an accuracy of factor 2.

The properties found experimentally for the secondary ionic emission are as follows.

1. The ionic yield of a certain element ($Y^{\pm} = YP^{\pm}$) from materials of the identical nature (metals, oxides, halogens, *etc.*) is

TABLE 2

Atomic relative sensitivity coefficients (with the coefficient of sensitivity of silicon taken as 1)

Standard sample	Composition	CRS						
		Na	Mg	Al	K	Ca	Ti	Fe
ST-1a	The effusive rock	6.9	4.3	4.1	28.7	4.7	1.5	1.9
SSK-2	The ground contaminated with technogenic elements	4.6	7.0	9.7	46.4	6.3	2.3	3.7
SKR-3	The same	6.1	5.5	11.3	20.3	7.8	1.4	2.0
SGKHM-1	Carbonate-silicate loose depositions	3.2	2.5	8.1	20.9	3.0	1.4	2.4
SGKHM-2	The same, aluminosilicate	3.6	5.8	8.7	42.6	10.0	1.5	2.6
SGKHM-3	The same, carbonate-silicate	4.1	1.8	8.1	25.7	2.9	2.5	1.4
SGKHM-4	The same, aluminosilicate	3.9	8.5	10.8	38.4	12.8	1.7	2.6
Average		4.6	5.0	8.7	31.8	6.8	1.76	2.4
Standard deviation		1.3	2.1	2.1	10.2	3.7	0.45	0.06

characterized by the reciprocal exponential dependence on the ionization potential for the positive ions and by the same dependence on electron affinity for the negative ions.

2. The yield of the positive ions of an extrinsic element essentially depends on the nature of matrix material being investigated, and for the negative ions, this matrix effect is much less.

3. The yield of the positive ions drastically increases in the presence of oxygen or other electronegative elements and decreases in the presence of electropositive elements.

4. Emission of MO^+ ions from the majority of oxidic materials has fragmentary character.

From a theoretical point of view, the question regarding the mechanism of ion formation in SIMS is complicated and it is described currently by a number of models, which are difficult to use in practice [17−20].

In this relation the quantitative elemental analysis of superficial layers of multicomponent materials is based, as a rule, on the use of the coefficients of relative sensitivity q_i, since it follows from eq. (1) that under otherwise equal conditions the current intensity is proportional to the concentration C_i:

$$I_i = k q_i C_i \qquad (3)$$

In this work the coefficients of relative sensitivity (CRS) were determined using the same formula, but from the results of analysis for the reference materials of known concentration. The relative concentration of an element with i-th mass was determined from the relationship

$$C_i = \frac{C_i^*}{1 + \sum C_i^*} 100\% \qquad (4)$$

where $C_i^* = (I_i/I_{Si})/q_i$; I_i, I_{Si} are the respective intensities of ionic current of the element with i-th mass and with mass of silicon ($m/z = 28$), since in the calculation of relative concentrations, the coefficient of relative sensitivity silicon is taken as a unity.

The state standards of soils were used as reference substances: SGKHM-1, SGKHM-2, SGKHM-3, SGKHM-4, SSK-2, SKR-3, ST-1A [21]. The values of coefficient of relative sensitivity for the specified standards of soils are listed in Table 2. This table also presents the concise description of the soils in use. So, the standards SGKHM-1 and SGKHM-3 represent carbonate-silicate loose depositions, and the standards SGKHM-2 and SGKHM-4 represent loose aluminosilicate depositions. It is reasonable that during the analysis of the AA composition one cannot pick up the reference material, which would ideally match the aerosols under investigation. Therefore, we used the values of coefficient of the relative sensitivity, which were averaged over all standard samples (see Table 2), as the first approximation for the quantitative analysis. Such approach facilitates a qualitative comparison of chemical composition for the superficial layers of AA samples.

The studies were performed in the MS 7201 mass spectrometer, which was equipped with the automated control and data acquisition sys-

tem that was developed in the Institute of Catalysis, SB RAS. The programmed control complex afforded the survey analysis of the entire spectrum of mass in the range 1−250 and the measurement of ionic current of eight preset mass during the process of bombardment with synchronous visualization of the peak shapes and temporal diagrams of the peak heights. The samples in their initial form were used in all measurements, *i. e.* no additional treatment of them has been made. Preparation of samples for the analysis consisted in that some part of a deposit of aerosols taken off by a scalpel from the filter in the form of scrapes was rubbed into a substrate from high-purity indium (99.999 %). There was virtually no residue of fibres from the filter on the indium surface. As was implied by the results of the analysis of the substrate and the samples of filter without aerosols, such research technique for dielectric samples makes it possible to eliminate their charging under an ion beam, but does not bring any impurities. Note that the diameter of the primary ion beam impinging at an angle of 45° to the normal of a holder surface was equal to 2 mm, and the area of the bombarded surface, 5 mm^2. The pressure of residual gases in the mass spectrometer chamber did not exceed $2 \cdot 10^6$ Pa, which provided performing the analyses under dynamically pure conditions, *i.e.* the particle flux from the gas phase was less than the flux of primary ions.

Thermodesorption mass spectrometry

Thermal desorption is one of the most widespread methods now in use in research of gas interaction with the surface of solids [16, 22]. This owes both to the relative simplicity of the experiments and a small cost of instrumentation, and to the possibility for obtaining a great deal of the important experimental data. The typical schematic diagram for carrying out the experiments on TPDMS is as follows. The sample under investigation is placed into a high-vacuum setup, and then is heated. As the temperature increases, the adsorbed molecules desorb from it, or so do their parts, if it was a dissociative adsorption and no recombination

occurs during the desorption. Desorption products are registered by the mass spectrometer. A plot of signal strength of the mass spectrometer, which has been adjusted to the definite m/z value (or pressure), as a function of temperature (or of time) represents the thermal desorption spectrum.

To perform the thermal desorption studies, a vacuum setup equipped by exclusive MX-7304 mass spectrometer has been made. The setup has been designed and assembled explicitly for the analysis of ultrafine samples in the wide pressure range [8]. To perform the thermal desorption experiments with powdered materials, a special holder has been made, which represented a tantalic foil 0.5 mm thick with the area 8 ´ 8 mm^2. The temperature of the foil was measured with the help of tungsten-rhenium thermocouple (5 and 20 % Re) point-welded to the foil. A heating rate was maintained constant, and it measured @1.5 K/s. The advantage of the designed setup is in the fact that it enables the measurements with high speed of heating (several degrees per second) to be conducted with ultrafine materials, which affords the spectral resolution close to optimum at the evacuation rate of 5−10 l/s.

Near-edge X-ray absorption fine structure technique

The method of determination of a charge state of chemical element from the form and position of an edge of its X-ray absorption spectrum (XANES) has been recently in general use in mineral science [23]. The structure of XANES is very sensitive to both the electronic state of absorbing atom and its local environment. Therefore, the increasing number of researchers starts application of XANES technique to obtain data on the electronic and crystalline structure of matter.

Determination of a charge state with XANES technique is performed from the position of the absorption edge in *K*- or *L*-spectra of absorption (photoionization of $1s$ and $2p$ levels respectively), which shifts towards greater energies with an increase of effective charge on the atom. For some elements, determination of charge state is possible from the pre-edge struc-
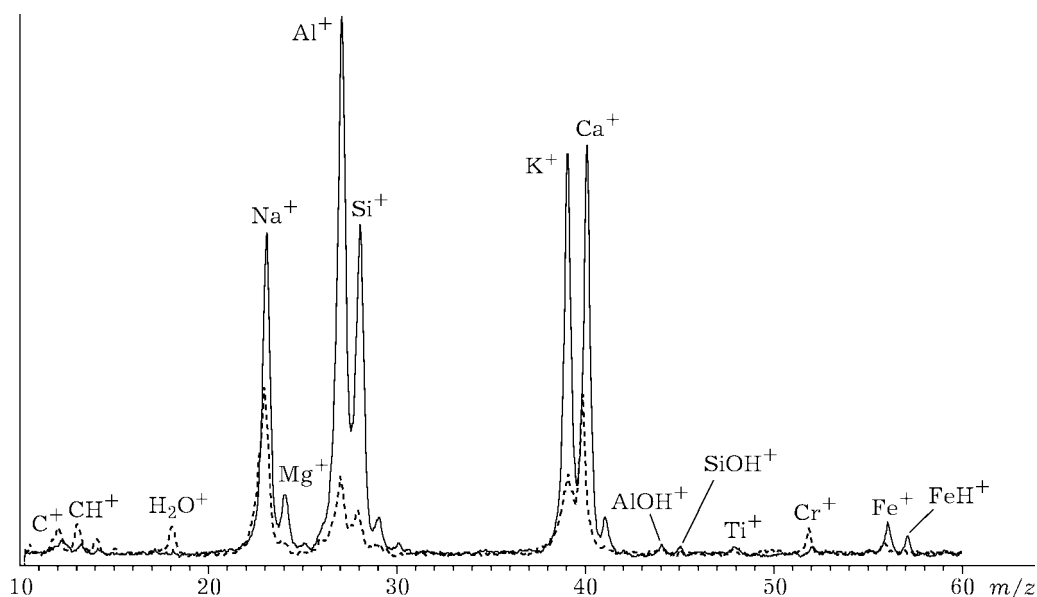
Fig. 2. Typical mass spectrum of the secondary ionic emission. The dashed curve corresponds to the first cycle, the surface; the continuous curve corresponds to the sixth cycle, the bulk of the sample.

ture arising because of the transfers forbidden by selection rules, for example $1s - 3d$. These elements include, for example, iron, titanium, and vanadium.

XANES spectra for K-edge of absorption for iron were taken at the EXAFS spectroscopy station in the Siberian Centre of SI with 2 GeV energy of electrons in the VEPP-3 Storage Ring and at an average current of 80 mA. The monochromatization of SI was performed by means of a Si (111) reducing single-crystal monochromator. The spectra were registered in the fluorescent mode. A photomultiplier with a scintillator operating in the current mode was used as a detector. The samples were arranged with respect to SI beam in order that the maximum area was covered. Filters of the $(Z - 1)$ type were not employed [9]. To record XANES spectra, 1–2 mg of chemical element under investigation must be available on the irradiated area of a sample. Therefore, both the total amount of aerosols collected on the filter, and the percentage of chemical element in question are essential. Such determination of valence, as a rule, can be conducted for chemical elements starting with titanium. A possibility to determine the charge state for atmospheric aerosols with a scarce amount of heavy elements requires verification.

RESULTS AND DISCUSSION

Composition and surface structure of aerosol particles

A typical mass spectrum of the secondary ionic emission obtained during the analysis of one of the samples of aerosols taken in Irkutsk is shown as an example in Fig. 2. Typically, the mass spectra were registered by continuous cycles in a range of mass 10–60 in each cycle.

Mass spectra of the secondary ionic emission of all AA samples contain signals of the following ions, (m/z): Na (23), Mg (24–26), Al (27), Si (28–30), K (39, 41), Ca (40, 42, 44), Ti (46–50), V (51), Cr (50, 52), Fe (54, 56), Co (59), Ni (58, 60, 62), and Cu (63, 65) (see Fig. 2). The signals of molecular ions are also present in the spectra, m/z: AlO^+ (43), SiO^+ (44), and $SiOH^+$ (45), and the values of current ratios for the mass 43/27 and 44/28 are close to the corresponding values for the hydrated aluminosilicates.

The ions being formed during the Ar^+-beam sputtering of the adsorbed hydrocarbons $\{C^+(12), CH^+(13), CH_2^+(14), CH_3^+(15), C_2H^+(25), C_2H_2^+(26)\}$, carbon- and nitrogen-bearing compounds $\{CO^+(28), COH^+(29), COH_2^+(30), NO^+(30)\}$, and the adsorbed water H_2O^+ (18) are also observed in the mass spectra
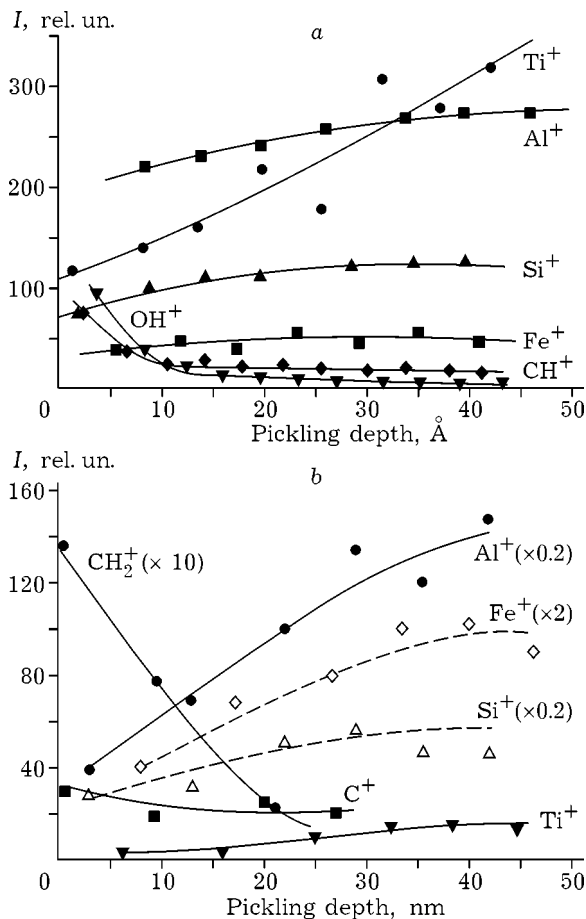
Fig. 3. Dependences on the pickling depth for the currents of the secondary ions: *a* − for aerosols of Akademgorodok (a settlement of Klyuchi), *b* − for Irkutsk aerosols.

of AA samples. A prominent feature in the behaviour of such ions is a quick drop in the intensity (the ionic currents) because of the quick decrease in the concentration inside the adsorbed layer, which can be seen from the character of dependences of the ionic current intensities of CH^+ and OH^+ on the pickling depth (Fig. 3, *a*). Such character of relationship between the ionic currents and the pickling depth is most typical, *i.e.* the similar distribution profile over the depth is characteristic of samples from Novosibirsk Region and the samples from clean regions of the Baikal area (Baikal and Mondy stations). Figure 3, *b* depicts the profiles of elemental intensities for one of the AA samples taken in Irkutsk. The similar depth distribution profile is characteristic for more than 50 % samples taken in Irkutsk and in the settlement of Listvyanka. It is evident that the intensity of C^+ and CH_2^+ ionic currents

decreases somewhat slower than in the case of C^+ (see Fig. 3, *a*). This derives from the fact that the surface of aerosols contains some organic particles (smog), the size of which is about 10 nm. The ionic currents of the rest of basic elements, as a rule, symbately increase and flatten out at a stationary level. The important result is the circumstance that the ionic currents of elements flatten out at a stationary level simultaneously. This allows an assumption that the elements in the samples under investigation, the concentration of which was measured, are the constituents of one phase. It follows from the analysis of the quantitative data that aerosol particles represent aluminosilicates with the impurities of alkaline and alkali-earth metals, iron, and titanium. Exception to this rule is the behaviour of Ti^+ current in the samples from Novosibirsk aerosols (see Fig. 3, *a*), which can bear witness to the existence of TiO_2 in these samples in the form of a separate phase.

It is rather inconvenient to conduct the quantitative measurements and, for example, to determine the percentage of similar samples, since the statistical analysis is a time-consuming procedure, which involves the analysis of the same AA samples from the various spots of the filter.

Thermal studies of aerosols have been executed with the samples collected by means of air circulation through the filters "Whatman paper 41" for 24 h on February 4−5, 1998, in Irkutsk. In addition, the thermal desorption spectrum of the paper filter has been studied too. A batch of samples was about 0.5 mg, the heating rate for the samples was maintained constant and equal to 0.2 K/s. In the course of heating, about 20 successive mass spectra in the range $m/z = 1-100$ were recorded. Thermal desorption spectra (TD spectra) of particular weights were constructed from the obtained mass spectra.

In connection with the circumstance that the particles of aerosols cannot be completely separated from the filter fibres, thermal desorption spectra of aerosols represent the superposition of spectra for particles of aerosols and those for fibres of whatman paper. The contribution of the filter was taken into account by the deduction of a spectrum of the pure filter (fibres without aerosols) from the spectrum of aerosols plus the filter. The survey difference
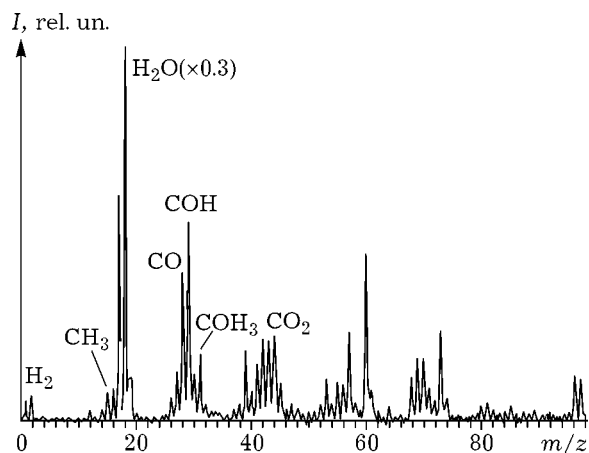
Fig. 4. The survey thermal desorption mass spectrum observed during the linear heating of aerosols taken in Irkutsk on February 24–25, 1998.

spectrum obtained in this way at a temperature of 600 K is shown as an example in Fig. 4.

On the basis of the survey spectrum, some qualitative conclusions can be drawn concerning the possible compounds inherent in aerosols. The availability of peaks with weight 17 and 18 is an unambiguous indication of water desorption.

Thermal desorption spectrum of mass 18 (Fig. 5, a) is represented by two peaks, which are strongly different in intensity. The first peak is observed in the range 380–450 K, the second wide peak is observed in the range 500–700 K. The low-temperature peak shows the symmetrical form characteristic of the second order desorption, $i.\ e.$ it may be considered to be caused by desorption of chemisorbed water.

The high-temperature peak of weight 18 shows a complex structure, but a sharp drop in intensity at the high temperature is characteristic of zero desorption order, which may be due to the release of water into the gas phase as a result of decomposition of organic particles available on the surface of aerosols (see Fig. 3).

The similar form of peaks is evidenced also for the mass 15 and 29, 31, 43, 44, and for some others (see Fig. 5, b). Rather intensive spectra of the mass 40, 41, 54, and 68, most likely, are due to the decomposition and/or to the desorption of nitrogen-bearing compounds: $40 - CH_2CN$, $41 - C_2H_2NH$, $54 - CH_2CH_2CN$, $68 - (CH_2)_3CN$.

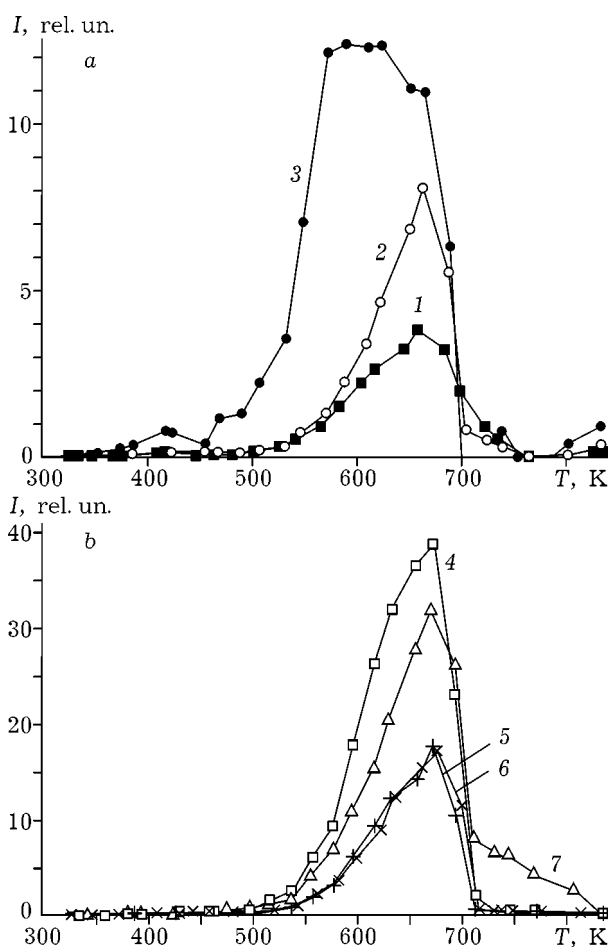The measurements of spectra of K-edge of absorption for iron are conducted by XANES

Fig. 5. Thermal desorption spectra for the mass 2, 15, 18 (a) and 29, 31, 43, 44 (b): $1 - 2$ (H_2), $2 - 15$ (CH_3^+), $3 - 18$ (H_2O), $4 - 29$, $5 - 31$, $6 - 43$, $7 - 44$ (CO_2).

method only for the AA samples collected in Irkutsk [9]. It should be noted that the sensitivity has appeared to be insufficient for registering the XANES spectra for the majority of samples. XANES spectra exhibited the small signal/noise ratio, which made it impossible for them to conduct the analysis of the shape of the absorption edge. In this connection, just the results of studying the samples, which contain a maximum quantity of iron, are given. a-Fe_2O_3 oxides, γ-Fe_2O_3, and a sample of the ground (sand) taken from the depth of 3 m was used as a standard for comparison.

Two parameters were taken into account in the course of determination of the charge state of iron ions from the K-spectrum of absorption. These parameters include the position of inflection point at the edge of absorption (the ionization potential) and the position of the pre-edge maximum. The last-mentioned arises due
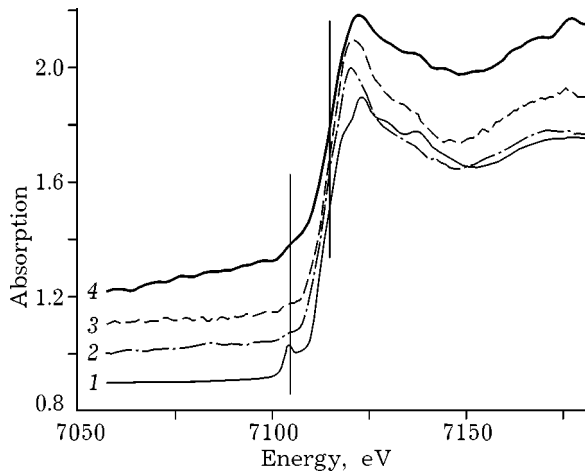
Fig. 6. XANES spectra of *K*-edge of iron absorption for a-Fe_2O_3 (*1*), sand (*2*), and for the Irkutsk aerosols (*3*, *4*).

to the removal of a ban on the electronic transfers from 1*s* to the vacant 3*d* level when an asymmetry of oxygen ions exists in the environment around the iron ion. Figure 6 presents the XANES spectra of AA samples, sand, and a-Fe_2O_3. The works devoted to the study of iron state in minerals [24, 25] have demonstrated that the intensity of the pre-edge maximum in such materials drastically decreases. This is related to the fact the iron ions in silicate compounds for the most part are isolated and thus the quantity of Fe−O−Fe bonds is small. This causes a degree of distortion of the iron environment for the sand sample to reduce (see Fig. 6, curve *2*) as compared to iron oxide (curve *1*), which manifests itself in the spectrum by a diminished pre-edge maximum. It should be pointed out that a pre-edge maximum is missing from the spectra of Irkutsk aerosols too (curves *3*, *4*). This allows a suggestion that iron ions in them are present also in the isolated form. Coincidence of the inflection points at the edges of absorption in the spectra of all samples (see Fig. 4) also suggests that in these samples iron has the oxidation state +3.

Aerosols of Novosibirsk Region. The studies of AA composition are performed with the aerosols with particle sizes in the following ranges: 1−3, 3−6, 6−9, 9−19, and over 19 μm. Table 3 lists the quantitative analysis data for AA samples with the particles 1−3 and 6−9 μm in size, taken in the settlement of Klyuchi in spring, 1993. Investigation of the elemental composition of the aerosol surface has demonstrated that the variability of data is rather significant even for the subsamples of the same specimen taken from different parts of the filter. It is our belief that this is related to the nature of the object, as an accuracy of the procedure comprises approximately 25 % for elements with high relative concentration (Si, Al, Ca) and approximately 50 % for the elements, the concentration of which is less than 1 %. Hence, it is possible to speak about the difference in concentrations of any element between samples, if their values differ at least twice.

It should be noted that because of a moderate quantity of samples of analyzed material it was impossible to make up the appropriate set of samples. Taking into account the aforesaid, it is possible nevertheless to assert that the composition of aerosols with the particle size less than 3 μm differs from the average terrestrial abundance and from the composition of soil samples in the settlement of Klyuchi (see Table 3) by a greater content of sodium, calcium, potassium, and titanium. For AA with the particle size of 6−9 μm, the same effect holds true for calcium, and titanium. This suggests that the aerosols are brought from the other regions.

For aerosols with the particle sizes of more than 9 μm, the sharp (up to 5-fold) concentration spikes of Fe, Mg, and Al are evidenced some days, which are due supposedly to the entry of specific particles of an anthropogenic origin. Aerosols with such particle size are of no interest because of their low concentration.

If extrapolation is made to the initial point in bombardment time of the distribution curves for ionic currents of basic elements of aerosols (Si, Ti, Fe, Ca, *etc.*) (see Fig. 3, *a*), it is evident that their values will be non-zero. Consequently, the particles are free from a continuous film of chemisorbed water. However, it is impossible to rule out the existence of the continuous film of physically adsorbed water on the fine particles, since the analysis was conducted in vacuum at the pressure »10^{-6} Pa.

The obtained data suggest that aluminosilicates, perovskite-type titanium compounds $CaTiO_3$, TiO_2, and the isolated ions of titanium can be the active components for the reactions with aerosols in the atmosphere.

TABLE 3

Elemental composition of the surface of aerosol particles and soil samples taken in the settlement of Klyuchi in 1993

Element	Content, rel. at. %			
	Particle size, µm		Clarke*	Soil, the settlement of Klyuchi
	1–3	6–9		
Na	23	2.6	6.4	3.4
Mg	4.1	3.2	6.0	1.9
Al	8.7	11.6	17.0	7.5
Si	39.7	51.8	56.6	78.9
K	4.6	3.7	3.7	1.4
Ca	14.2	19.9	5.1	2.1
Ti	0.9	1.4	0.5	0.7
Fe	3.3	4.2	4.6	3.4
V	0.02	0.03	0.016	–
Cr	0.05	0.07	0.022	–
Co	0.16	0.18	0.038	–
Cu	0.30	0.48	0.063	–

*The values of the abundance ratio of elements are given also in the relative atomic percentage.

Aerosols of the Baikal region. In the Baikal region, AA samples were taken on different days. Results of the analysis of these samples bear witness to the wide scatter in values of Na, K, and Ca concentration, but the spikes of Al and Ti concentrations are sometimes observed too. Quantitative analysis of AACS samples shows that the relative concentration of the specified elements in AACS samples is substantially lower than in AA. Table 4 presents the composition of AA and AACS samples averaged over a period of several days and also the average terrestrial composition of soil. It is evident that AAs show an elevated (as compared to the average terrestrial abundance) content of Na, Ca, and Ti. At the same time the reduced content of Na, K and Ca, on the contrary, is evidenced for AACS. Undoubtedly, this is related to the fact that water "washes out" the compounds with these elements from the initial aerosol during the process of obtaining the AACS samples.

It should be noted that the elevated concentration of Ti and the reduced concentration of Mg is observed for all samples. We cannot also neglect the fact that the elevated concentration of titanium (in comparison with its average terrestrial abundance) may be caused by TiO_2 presence.

It should be ascertained that chemical composition of the surface of AA and AACS samples for all sampling areas (Irkutsk, the settlements Listvyanka and Mondy) within the limits of error is indistinguishable, even though the city of Irkutsk is an industrial area, while Mondy is the clean mountain area at an elevation over 2000 m above sea level. Apparently, it makes sense, as the sampling of the majority of AA was made in winter when there was a snow cover and the source of aerosols was

TABLE 4

The averaged composition for AA and AACS

Place of sampling	Content, rel. at. %							
	Na	Mg	Al	Si	K	Ca	Ti	Fe
Listvyanka								
AA	10.3	2.6	17.1	45.4	3.0	15.1	2.1	4.1
AACS	1.3	2.02	18.6	70	1.1	2.90	1.1	2.4
Irkutsk								
AA	9.4	2.8	15.7	50.7	2.6	14.0	1.0	3.7
AACS	1.9	2.9	14.7	71.4	1.3	2.7	0.7	4.4
Mondy								
AA	7.4	3.1	13.5	41.8	4.0	20.3	2.1	7.4
AACS	1.4	4.8	14.6	65.7	2.9	4.0	1.5	4.5
Karasuk, Novosibirsk Region								
AA	7.7	1.3	8.7	39.8	3.5	22.8	12.2	4.8
Clarke	6.4	6.0	17.0	56.6	3.7	5.1	0.5	4.6

localized nowhere close to the specified areas. Moreover, the scatter of Na, K, and Ca concentrations in AACS samples is substantially less than in AA samples.

Table 4 presents also the average composition for AAs, which have been collected in Karasuk, Novosibirsk Region, in winter, 1993. Comparison of composition of these aerosols with AA composition from the settlement of Klyuchi (see Table 2) and with AA composition from the Baikal region suggests that AA collected in Karasuk are characterized by significantly greater concentration of titanium. We failed to detect any other difference between AA taken in Novosibirsk Region and the Baikal region.

The intensity of the molecular ions, which has been caused by emission of the fragments of the crystal lattice such as AlO, SiO, SiOH, CaOH, increases as the pickling proceeds and the mere fact of emission of oxidic fragments permits one to suppose that aerosols constitute silicate and aluminosilicate compounds. For AACS samples a peak of mass 45 (SiOH) shows greater intensity than a peak of mass 44 (SiO). For AA samples, except for some particular samples, the peak 44, on the contrary, is more than the peak 45. It is our belief that the action of water on aluminosilicates may give rise to hydroaluminosilicates.

Aluminosilicates can act as the photocatalysts of the acid-base type. In addition, there are ions of transition elements, titanium, and iron on the surface, which can catalyze a wide number of reactions. This gives rise to a new channel of the reaction. In particular, a procedure of oxidation of organic compounds by nitrogen oxides is coming recently into wide use in catalysis and first of all, N_2O is employed, whose presence in the atmosphere is caused by the technogenic processes. The iron ions in the aluminosilicate matrix act as active centres in the catalysts of N_2O oxidation. The decomposition of nitrogen oxide to form highly active atomic oxygen proceeds under rather soft conditions. Seemingly, this reaction can also be initiated photochemically as nitrogen oxides exhibit strong absorption bands in the ultra-violet region. Since both the iron ions and the organic compounds are present on the surface of particles of the investigated aerosols, it can be inferred that the above reaction of obtaining the highly active oxygen can occur on the atmospheric aerosols too.

CONCLUSIONS

1. The superficial layer (one or two monolayers) of particles of all aerosols is covered by the adsorbed hydrocarbons, nitrogen-bearing compounds, and by other, more complex compounds and water. The small part of surface of AA taken in Irkutsk and in the settlement of Listvyanka is covered by the organic particles (smog) of several tens nanometers in size.

2. An elemental analysis of the investigated aerosols suggests that the basic source of their formation is an erosion of aluminosilicate soils with admixtures of iron, titanium, alkaline, and alkali-earth metals. The presence of TiO_2 in the form of an individual phase is possible for AA from Novosibirsk Region.

3. The composition of superficial layers of winter atmospheric aerosols from Novosibirsk Region and the Baikal region (Irkutsk, the settlement of Listvyanka, Ulan Ude, Baikal, Mondy) averaged over a period of several days is independent from the sampling area within the limits of error. This composition differs from the average terrestrial abundance by the elevated content of Na, K, Ca and Ti.

4. Action of water leads not only to "washing out" of Na, Ca, and Ti from the superficial layers, but also to formation of hydroaluminosilicates. Such a factor of water action allows believing that the wide scatter of the concentrations of elements over the samples is caused by the action of atmospheric moisture during their stay in the atmosphere.

5. Determination of the phase and charge state of iron by XANES method in AA samples taken in Irkutsk has suggested that iron in these samples is present in the state of oxidation +3 and supposedly in the form of isolated ions in an environment close to octahedral.

6. Aluminosilicates and silicates with superficial admixtures of ions of transition elements can act as photocatalysts. For Novosibirsk Region, TiO_2 can supposedly act as a photocatalyst too.

Acknowledgements

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