Effect of forest fires on the chemical composition of aerosols

**B.S. Smolyakov, K.P. Koutsenogii, V.I. Makarov, G.A. Koval'skaya,
A.I. Smirnova, L.A. Pavlyuk, and S.N. Filimonova**

*Institute of Inorganic Chemistry,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk
Institute of Chemical Kinetics and Combustion,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk*

Received March 3, 1999

The data on the dynamics of mass concentration of 32 heavy elements, organic and inorganic carbon, and ionic composition of the surface aerosol obtained at two observation stations of the Novosibirsk Region are presented for the period of burning forest fires. It is demonstrated that the forest fires engender the greatest changes in the ratios of concentrations $[K^+]/[Na^+]$ and $[NO_3^-]/[SO_4^{2-}]$.

Aerosols generated by forest fires and combustion of other species of biomass are classified as a separate type of natural aerosols, taking into account the specific composition of the initial material and the high temperature of their formation.[1,2] According to average estimates, their annual inflow in the atmosphere is compared to the contribution of volcanic eruptions (130 million tons and 150 million tons, respectively[2]). The effect of natural fires on the surface aerosol characteristics, obviously, is inhomogeneous in time and depends on the type of the underlying surface. It can be assumed that the large areas of forests and marshes in landscapes of Siberia predetermine an enhanced contribution of natural aerosols of this type.

The possibility of field observations of the effect of forest fires on the chemical composition of the surface aerosol appeared in October 1997, when in the vast territory of Southwestern Siberia (in Novosibirsk and Tomsk regions, Altai Krai, and Krasnoyarsk Krai) forest areas, peat bogs, and dry grass burned. In this period the aerosols were collected every day at two stations located in the village Klyuchi 40 km to the south of Novosibirsk (station 1) and near Karasuk 400 km to the west of Novosibirsk (station 2). In aerosol samples the following components were determined: the content of 32 heavy elements (from Ca to U), the content of organic and inorganic carbon, and the ionic composition of water-soluble fraction. Thus, the integrated observations of chemical composition of the surface aerosol characterized the regional scale of manifestation of forest fires in Southwestern Siberia.

Experimental technique

Aerosols were collected simultaneously on AFA-KA filters ($13\ m^3 \cdot h^{-1}$) for their multielemental analysis and determination of ionic composition of the water-soluble fraction and on Dassel 50-mm porous glass filters ($1.4\ m^3 \cdot h^{-1}$ at station 1 and $1.8\ m^3 \cdot h^{-1}$ at station 2) for an analysis of organic and inorganic carbon. The AFA-KA filters were weighed before and after their daily exposure to estimate the total mass concentration M of aerosol particles. After the exposure, the AFA-KA filters were cut into two parts, one of which was used to determine the mass concentration of Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Sb, Ba, La, Nd, Sm, Gd, Hf, Ta, W, Ir, Pb, and U by the method of X-ray fluorescence analysis using the synchrotron radiation (XRFASR) at the Institute of Nuclear Physics of the SB RAS. The XRFASR method and its capabilities for measuring the multielemental composition of the atmospheric aerosols were described in Refs. 3 and 4.

Another part of the exposed AFA-KA filter was put for a day in a container with 10 mL of deionized water to produce a water extract, in which the pH factor was measured. The concentration of ions F^-, Cl^-, NO_3^-, SO_4^{2-} (sorbent KIKS, carbonate-bicarbonate eluent), Na^+, NH_4^+, and K^+ (sorbent Katieks, eluent HNO_3) was determined by the method of ionic chromatography with conductometric detection, and the concentrations of HCO_3^- and of the sum $(Ca^{2+} + Mg^{2+})$ were evaluated by titration. The above-enumerated ions reflect completely the ionic composition of water-soluble fraction of aerosols, which allows one to identify the contribution of various sources and mechanisms to the formation of aerosol particles from their proportion.[5,6]

Concentrations of organic and inorganic carbon after catalytic conversion into methane were measured by the gas chromatographic method with flame-ionization detection of CH_4 by the technique described in Refs. 7 and 8.

The results of all analyses were normalized to the content of the compound in aerosol particles comprised in 1 m^3 of air.

0235-6880/99/06 504-05 $02.00

Effect of forest fires on the mass concentration of compounds of aerosol particles

The variations of the mass concentration M of aerosol particles and their compounds including the total concentration E of heavy elements, the sum of organic and inorganic carbon C, and the water-soluble fraction (the sum of ions) I, measured for the surface aerosols at the stations 1 and 2 in October, 1997 are illustrated by Fig. 1. During the first ten days, the increase of the concentration of all compounds is seen at both observation stations in comparison with the second ten days of the month. Just in this period high smoke content was seen by the eye in the Novosibirsk environs. Obviously, a significant increase in the mass concentration of aerosol compounds was directly connected to the forest fires burned in the large territory of Southwestern Siberia. In the third ten days, analogous tendencies were more pronounced for Karasuk (station 2); probably, the local centers of the dry grass combustion were here.

Proceeding from the data shown in Fig. 1, for each observation station two periods were identified – with the reduced and enhanced daily mass concentrations of E, C, and I, reflecting the absence and presence of forest fires. The results of determination of the multielemental composition, organic and inorganic carbon, and ionic composition of the aerosol for these periods are compared below.

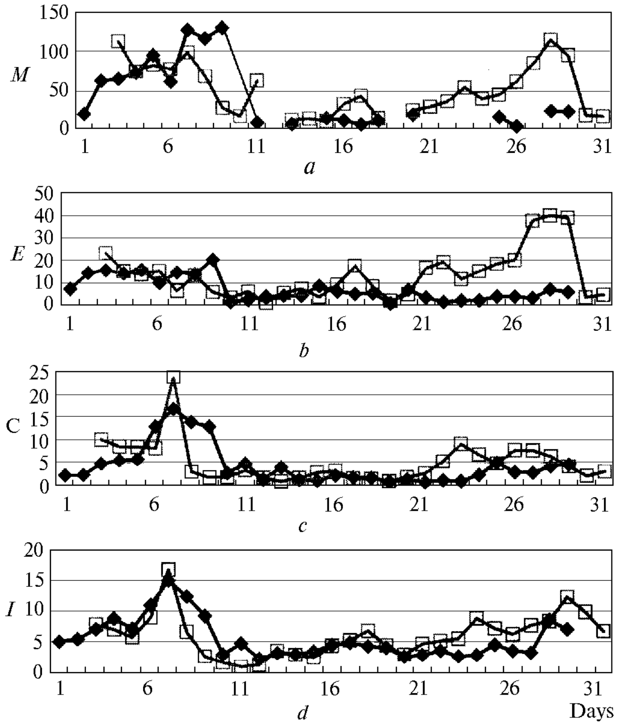

Fig. 1. Dynamics of the mass concentration (in μg·m^{-3}) of aerosol particles (a), total concentration of heavy elements (b), carbon (c), and the sum of ions of the water-soluble fraction (d) for the surface aerosol at observation stations 1 (◆) and 2 (□).

Table 1. Elemental composition of the surface aerosol in October, 1997 measured at stations 1 and 2.

Element	With fires					Without fires					Ratio	
	$\langle x_i\rangle_f$	σ_{gi}	$\langle x_{i\mathrm{Fe}}\rangle$	σ_{gi}	n_i	$\langle x_i\rangle_{nf}$	σ_{gi}	$\langle x_{i\mathrm{Fe}}\rangle_{nf}$	σ_{gi}	n_i	$\langle x_i\rangle_f/\langle x_i\rangle_{nf}$	$\langle x_{i\mathrm{Fe}}\rangle_f/\langle x_{i\mathrm{Fe}}\rangle_{nf}$
	Station 1											
Ca	5527	1.5	1.36	1.21	9	1690	2.00	1.38	1.49	21	3.27	0.98
Sc	184	2	0.045	1.41	8	54	2.69	0.044	1.81	11	3.44	1.04
Ti	715	1.5	0.175	1.12	9	204	2.19	0.167	1.30	21	3.50	1.05
V	67	1.0	0.016	1.00	1	17.0	3.02	0.014	3.64	5	3.92	1.18
Cr	66	1.7	0.016	1.26	9	15.3	3.08	0.013	2.17	20	4.32	1.30
Mn	225	1.6	0.055	1.14	9	62	2.01	0.050	1.26	21	3.64	1.10
Fe	4073	1.5	1	1.00	9	1226	1.88	1	1.00	21	3.32	1.00
Ni	2.24	2.35	0.0006	2.72	5	1.67	2.20	0.0014	2.54	17	1.34	0.40
Cu	8.4	1.7	0.002	2.08	9	6.2	1.63	0.0051	2.37	21	1.34	0.40
Zn	67	1.3	0.016	1.68	9	30	2.46	0.024	2.47	21	2.26	0.68
Ga	2.89	1.63	0.0007	1.76	9	0.77	1.97	0.0006	2.01	10	3.78	1.14
Ge	0.91	1.54	0.0002	1.53	4	0.45	1.37	0.0004	2.35	3	2.01	0.60
As	3.79	2.22	0.0009	2.20	2	0.82	2.72	0.0007	1.94	4	4.65	1.40
Se	0.20	11.2	0.000049	8.92	3	0.33	1.84	0.0003	2.47	9	0.60	0.18
Br	14.8	1.5	0.0036	1.76	9	5.4	1.71	0.0044	1.99	21	2.74	0.83
Rb	15.2	1.4	0.0037	1.12	9	3.7	1.82	0.003	1.31	21	4.09	1.23
Sr	40	1.3	0.0098	1.35	9	15.6	1.76	0.013	1.63	21	2.55	0.77
Y	3.05	1.8	0.0008	1.23	9	0.83	2.25	0.0007	1.63	20	3.68	1.11
Zr	23.9	1.5	0.006	1.22	9	8.7	2.02	0.007	1.53	21	2.74	0.83
Nb	1.35	1.7	0.0003	1.30	9	0.56	1.54	0.0005	1.50	16	2.43	0.73
Sb	543	1.7	0.133	1.52	9	189	1.79	0.155	1.37	14	2.86	0.86
Ba	227	2	0.056	1.39	9	99	2.08	0.08	1.75	16	2.30	0.69
La	98	1.8	0.024	1.34	8	27	2.21	0.022	1.53	14	3.61	1.09

Table 1. (continued).

Element	With fires					Without fires					Ratio	
	$<x_i>_f$	σ_{gi}	$<x_{i\mathrm{Fe}}>$	σ_{gi}	n_i	$<x_i>_{nf}$	σ_{gi}	$<x_{i\mathrm{Fe}}>_{nf}$	σ_{gi}	n_i	$<x_i>_f/<x_i>_{nf}$	$<x_{i\mathrm{Fe}}>_f/<x_{i\mathrm{Fe}}>_{nf}$
Nd	38	1.5	0.009	1.52	7	11.8	2.48	0.010	1.69	9	3.28	0.99
Sm	34	2.4	0.008	1.70	9	7.8	3.59	0.006	2.65	12	4.43	1.33
Gd	30	2	0.007	1.62	9	10.3	2.17	0.008	1.72	16	2.90	0.87
Hf						0.89	1.78	0.0007	1.06	2		
Ta						1.30	2.54	0.0011	1.50	3		
Ir	1.13	1.53	0.0003	1.02	2	0.74	1.93	0.0006	2.00	5	1.52	0.46
Pb	23	1.5	0.006	2.13	9	12.3	2.61	0.010	2.80	21	1.90	0.57
Station 2												
Ca	7951	2.1	1.52	1.83	15	1714	2.72	1.046	2.48	15	4.64	1.45
Sc	203	2.7	0.039	2.12	12	81	2.13	0.049	1.61	6	2.51	0.79
Ti	1009	1.5	0.193	1.19	15	333	2.03	0.203	1.3	15	3.03	0.95
V	49	1.6	0.009	1.68	4	14.4	3.28	0.009	2.25	2	3.37	1.06
Cr	128	2.5	0.025	1.85	2	68	4.79	0.042	3.57	14	1.88	0.59
Mn	293	2.2	0.056	1.53	15	157	2.97	0.096	2.28	15	1.87	0.59
Fe	5226	1.6	1	1	15	1638	1.99	1	1	15	3.19	1
Co	15.1	1.5	0.003	1.34	5	6.1	2.1	0.0037	2.51	5	2.49	0.78
Ni	5.3	2.3	0.001	2.18	12	3.54	2.33	0.0022	1.97	9	1.50	0.47
Cu	6.2	3.0	0.0012	2.75	15	3.46	2.85	0.0021	1.78	14	1.79	0.56
Zn	112	2	0.0214	1.85	15	68.6	1.89	0.0418	1.71	15	1.63	0.51
Ga	3.5	1.9	0.0007	1.76	11	2.6	2.03	0.0016	1.75	5	1.36	0.42
Ge	0.88	1.4	0.0002	1.95	4	1.17	1.21	0.0007	1.55	2	0.75	0.24
As	4.90	1.71	0.0009	2.05	6	3.37	1.52	0.0021	2.02	3	1.45	0.46
Se	1.76	1.47	0.0003	2.01	4	1.18	1.23	0.0007	2.27	6	1.49	0.47
Br	32	2	0.0061	2.68	15	11.9	1.92	0.0073	2.2	15	2.70	0.85
Rb	16.3	1.6	0.0031	1.19	15	4.03	2.51	0.0025	1.49	15	4.04	1.27
Sr	60	1,6	0,012	1,28	15	17	2,15	0,011	1,44	15	3,51	1,1
Y	4.11	1.64	0.0008	1.31	15	1.61	1.93	0.001	1.43	14	2.56	0.8
Zr	28	1.7	0.005	1.18	15	9.6	2.13	0.0059	1.39	15	2.86	0.9
Nb	1.75	1.52	0.0003	1.3	15	0.61	1.62	0.0004	1.35	10	2.88	0.9
Mo	0.7	2.71	0.0001	2.75	11	0.21	3.77	0.0001	4.2	5	3.28	1.03
Sb	512	2	0.98	1.68	10	194	2.36	0.118	1.68	8	2.64	0.83
Ba	340	3	0.065	2	9	129	2.35	0.079	1.32	9	2.63	0.82
La	141	2	0.027	1.23	13	55.7	1.56	0.034	1.39	10	2.53	0.79
Ce	93	2	0.018	1.67	6	36.8	2.02	0.23	2.48	5	2.53	0.79
Nd	46	1.5	0.0087	1.45	7	25.8	1.46	0.016	1.75	5	1.77	0.56
Sm	64	1.7	0.012	1.21	15	24.6	1.79	0.015	1.43	13	2.60	0.81
Gd	40	2.2	0.0077	1.52	15	14.2	2.69	0.009	1.48	12	2.85	0.89
Yb						2.44	1.88	0.0015	1.47	2		
Ta	1.28	1	0.0002	1	1	2.42	1.7	0.0015	2.09	7	0.53	0.17
W	3.92	1.45	0.0008	1.9	3	1.68	1.69	0.001	2.44	5	2.34	0.73
Pb	34	2	0.0065	1.66	15	29,7	1.65	0.018	1.85	15	1.15	0.36
U	1.07	2.03	0.0002	1.88	3	0.44	1	0.0003	1	1	2.44	0.76

Effect of forest fires on the elemental aerosol composition

The data on the mass concentration of heavy elements for two observation stations with (indicated by the subscript *f*) and without fires (indicated by the subscript *nf*) are summarized in Table 1 as absolute concentrations (geometric mean values $<x_i>$, in ng·m^{-3}) and normalized to the content of the reference element, for which Fe, $<x_{i\mathrm{Fe}}>$, was chosen. Here, the ratio of these parameters is also given for the periods with fires and without them.

The concentrations of the majority of the examined heavy elements during fires increased by a factor of 1.5–4; moreover, the concentration of the reference lithophile element Fe in Klyuchi increased by a factor of 3.3, whereas in Karasuk – by a factor of 3.2. As can be seen from Table 1, the concentrations normalized to $<x_{i\mathrm{Fe}}>$, as a rule, are in the interval 0.7–1.4 for the elements recorded in the majority of aerosol samples ($n_i > 5$). Among these elements are those whose high volatility determines a high coefficient K_{enr} of aerosol enrichment (Sb and Br), and lithophile elements with low K_{enr} (Sc, Ti, Ca, Mn, and Sm) (see Ref. 2). We note that the contents of these elements in vegetation differ by several orders of magnitude. From this we can conclude that an increase in the concentration of many elements in aerosols during fires is determined not so much by the combustion source – biomass – as by an increased contribution of erosion processes.

At both observation stations the concentrations of Ni, Cu, Zn, and Pb changed below the above-indicated limits, which calls for more detailed analysis.

As a whole, among the heavy elements there were no elements characteristic of forest fires at the regional level.

Organic and inorganic carbon

The data on the content of C_{org} and C_{inorg} without and with fires for both observation stations are compared in Table 2, where the geometric mean mass concentrations $<C>$, in $\mu\text{m}\cdot\text{m}^{-3}$, their standard deviations σ_g, and the number of daily aerosol samples n are given. At both observation stations not only the mass concentrations of organic and inorganic carbon, but also their ratio noticeably increased (in Klyuchi it increased by a factor of 1.76, in Karasuk – by a factor of 1.36 in comparison with the period without fires). In the present work, we did not identify organic compounds in aerosol particles, and their nature requires a special study. Probably, some of them can be characteristic indicators of not only local, but also remote natural fires.

Influence of fires on the ionic aerosol composition

The ionic composition of water-soluble fraction of aerosols with and without fires for two observation stations is given in Table 3 in the form analogous to Table 2. The effect of fires on an increase in the mass concentration of different ions is manifested differently. From ions whose precursors are gas-phase reactions in the atmosphere, the minimum increase of the concentration (by a factor of 1.1–1.5) is characteristic of sulfate and ammonium, whereas the concentration of nitrate increases by a factor of 4.3–6.8. It is obvious that this significant increase of the nitrate concentration is caused by the nitrogen oxidation in air at high temperatures in seats of the fire. Among cations preceded by the erosion processes, the sodium concentration increases less than that of the sum of calcium and magnesium, though K_{enr} of the last is lower.[2] The potassium concentration, whose clark in vegetation exceeds the sodium clark by an order of magnitude and even more and K_{enr} is lower, increases more noticeably during fires. Hence it follows that the enrichment of aerosol particles with potassium during forest fires is engendered by the combustible material – biomass.

Table 2. Mass concentrations of organic and inorganic carbon, in $\mu\text{g}\cdot\text{m}^{-3}$, at stations 1 and 2.

Station	With fires					Without fires				
	$<C_{\text{org}}>$	σ_g	$<C_{\text{inorg}}>$	σ_g	n	$<C_{\text{org}}>$	σ_g	$<C_{\text{inorg}}>$	σ_g	n
1	5.179	0.002	1.721	0.002	10	1.121	0.002	0.656	0.002	19
2	5.096	0.002	1.389	0.002	15	1.358	0.002	0.503	0.002	15

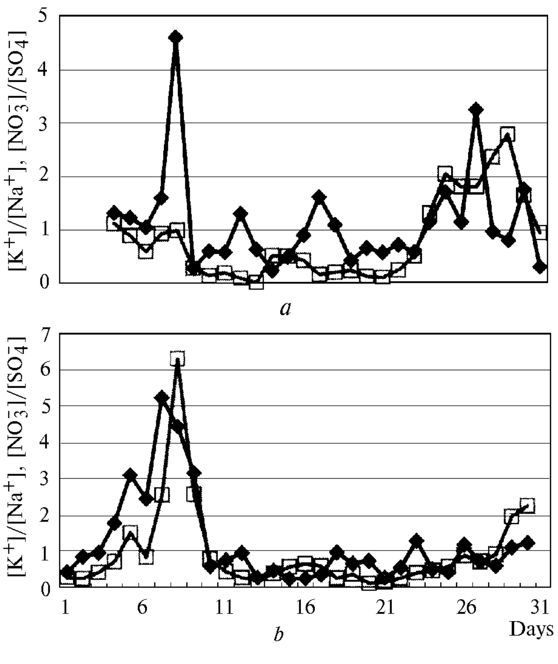

Fig. 2. Dynamics of ratios of molar concentrations $[\text{K}^+]/[\text{Na}^+]$ (◆) and $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ (□) for the surface aerosol in Karasuk (*a*) and Klyuchi (*b*) in October, 1997.

Figure 2 illustrates the dynamics of ratios of molar concentrations $[\text{K}^+]/[\text{Na}^+]$ and $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ in October, 1997. Periods of fires are more clearly manifested in comparison with the data shown in Fig. 1. Hence it follows that in Western Siberia the ratios of molar concentrations $[[\text{K}^+]/[\text{Na}^+]$ and $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ for the surface aerosol can serve as indicators of forest fires.

Conclusions

Occasional forest fires in Siberia may cause an increase in the mass concentration of heavy elements, carbon, and water-soluble fraction of surface aerosols recorded at considerable distances. An increase in the concentration of 32 heavy elements (from Ca to U) that differ by their aerosol enrichment coefficient and contents in biomass is about the same. This testifies that the reason for their enhanced inflow into the atmosphere during fires is the intensification of the erosion processes. Because the analogous effect can be caused by different circumstances (for example, wind erosion and plowing the land in fields), an increase in the mass concentration of these elements in the aerosol cannot be an unambiguous criterion of forest fires. They manifest more noticeably through an increase in the mass concentration of carbon (especially C_{org}) and water-soluble fraction of aerosol particles, for which the ratios of molar concentrations $[K^+]/[Na^+]$ and $[NO_3^-]/[SO_4^{2-}]$ sharply change. Obviously, just these parameters of the chemical composition of surface aerosols can be fairly reliable criteria of forest fires.

Table 3. Mass concentration of ions, in μg/m^3, at stations 1 and 2.

Parameter	NH_4^+	Ca, Mg	Na^+	K^+	H^+	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}
					Station 1					
					With fires					
$<I>_f$	0.40	1.23	0.13	0.44	0.001	2.04	0.15	0.11	2.48	1.30
σ_g	0.002	0.001	0.002	0.002	0.006	0.005	0.002	0.004	0.002	0.001
n	10	10	10	10	2	10	10	10	10	10
					Without fires					
$<I>_{nf}$	0.28	0.35	0.10	0.09	0.002	0.15	0.028	0.060	0.576	1.228
σ_g	0.001	0.002	0.002	0.002	0.005	0.009	0.002	0.002	0.002	0.002
n	20	20	20	20	18	20	20	20	20	20
$<I>_f/<I>_{nf}$	1.4	3.5	1.3	4.8	0.6	13.3	5.5	1.8	4.3	1.1
					Station 2					
					With fires					
$<I>_f$	0.43	0.89	0.33	0.63	0.001	0.27	0.089	0.277	2.627	1.963
σ_g	0.001	0.002	0.002	0.002	0.009	0.003	0.004	0.002	0.002	0.001
n	15	15	15	15	15	15	15	15	15	15
					Without fires					
$<I>_{nf}$	0.29	0.31	0.15	0.18	0.007	0.13	0.036	0.078	0.389	1.637
σ_g	0.002	0.002	0.002	0.002	0.003	0.001	0.003	0.002	0.004	0.002
n	15	15	15	15	15	15	15	15	15	15
$<I>_f/<I>_{nf}$	1.5	2.9	2.3	3.5	0.2	2.1	2.5	3.5	6.8	1.2

Acknowledgments

The work was supported in part by the INTAS (Grant 93–0182 ext) and the Russian Foundation for Basic Research (Grant 98–03–32467a).

References

1. K.Ya. Kondrat'ev, Usp. Khim. **59**, No. 11, 1587–1600 (1990).
2. S.G. Malakhov and E.P. Makhon'ko, Usp. Khim. **59**, No. 10, 1777–1798 (1990).
3. K.P. Koutsenogii, N.I. Bufetov, V.I. Makarov, G.A. Koval'skaya, and V.B. Baryshev, Nuclear Instruments and Methods in Physics Research **A405**, 572–573 (1998).
4. K.P. Koutsenogii, G.A. Koval'skaya, A.I. Smirnova, N.S. Bufetov, and V.B. Baryshev, Atmos. Oceanic Opt. **10**, No. 7, 512–517 (1997).
5. B.S. Smolyakov, L.A. Pavlyuk, K.P. Koutsenogii, V.I. Makarov, and I.Yu. Konchenko, Khimiya v Interesakh Ustoichivogo Razvitiya **5**, No. 2, 193–200 (1997).
6. B.S. Smolyakov, L.A. Pavlyuk, K.P. Koutsenogii, I.Yu. Konchenko, and A.I. Smirnova, Atmos. Oceanic Opt. **10**, No. 6, 407–412 (1997).
7. S.Yu. Armalis and A.K. Nika, Physics of the Atmosphere. Aerosol and Gas Admixtures in the Environment, No. 11, 155–159 (1986).
8. V.I. Makarov, Yu.N. Samsonov, V.V. Korolev, and K.P. Koutsenogii, in: *Nucleation and Atmospheric Aerosols* (Pergamon Press, 1996), pp. 714–717.