

STUDY OF SULFATE COMPONENTS OF ATMOSPHERIC AEROSOL NEAR NOVOSIBIRSK CITY

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We present some results of H₂SO₄ and ammonium sulfate concentration measurements with an ECN thermodenuder system. Data on aerosol composition obtained with standard filter-sampling based analysis are presented. It is shown, that SO₄²⁻ is present in the particulate matter not only in the form of secondary aerosol of ammonium sulfate, but also in the form of associates with the lithophyll cations of calcium and magnesium.

INTRODUCTION

The problem of climate change on the planet that becomes more and more urgent nowadays assumes considering the feedback effects. Most probably it is because of these effects that no predicted increase in temperature of the Earth's atmosphere due to an increase in carbon dioxide in the air was observed so far. The aerosol atmospheric component, being involved in the radiation transfer in the atmosphere, is among the factors that can affect the radiation balance.¹ Chemical composition of the particulate matter determines its optical properties thus being an important feature of aerosol.

Among the basic components of atmospheric aerosol there are sulfates whose content is normally determined in the form of an anion in water extract. In that case analysis does not enable one to identify a particular chemical form of a sulfate in the initial particles (before it is dissolved). The lack of such information makes it difficult to solve the problem on the source and lifetime of SO₄²⁻ in the atmosphere. Recently, new methods, to determine the concentration of concrete chemical forms of sulfate in aerosol, have been developed. In this paper we present the results, obtained with this new technique and standard analysis, performed in different laboratories.

SAMPLING AND TECHNIQUES OF STUDYING THE AEROSOL SAMPLES

Atmospheric aerosol was sampled on AFA-KhA-20 filters (manufactured at "Izotop" firm, Ekaterinburg) with a centrifugal pump in Novosibirsk Akademgorodok locality. Approximately 100 m³ of air was pumped through every filter at an average rate of 100 liters per minute. The pump was located at the height of 2.5 m above the ground. Before and after the exposure filters

were stored in an exsiccator above the annealed silica gel and were weighted several times. Such a procedure enabled us to reduce the error of determining the mass concentration of aerosol down to 15%.

Ion composition of the particulate matter was identified in the following way. Each filter with the aerosol deposits was divided into two equal parts and subjected to analysis at two different laboratories – one at the Institute of Inorganic Chemistry (INC) and second at the Institute of Chemical Kinetics and Combustion (ICK & C) SB RAS (Table I). In both cases the halves of the filter were placed in plastic containers with 10 ml of demineralized water (Milli-Q purification system with $R = 10 \text{ M}\Omega$). Ion concentrations in water extract were determined by the method of liquid chromatography with a conductometric detector (see Table I).

TABLE I. Basic parameters of chromatographic analysis.

Parameters	INC	ICK&C
device	HPI	ILC-1 (Waters Asc.)
sorbent	HIKS (anion exchange) KATIEKS (cation exchange)	IC PAK-A
eluter	carbonate- carbonate HNO ₃	potassium phtalic acid
detected ions	SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ , F ⁻ , NH ₄ ⁺ , K ⁺ , Na ⁺	SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻

Total ion concentration (Ca²⁺ + Mg²⁺) was determined by the method of conductometric titration of diluted (1:5) aliquot of water extract with EDTA. Before the titration the value pH was measured in this solution, from which the concentration of H-ions

was calculated. The accuracy of determining the ion concentration is no less than 25%. The correctness of analysis was checked by comparing data on summed equivalents of cations and anions. Analysis of dummy testing was also performed. In water extract of pure filter small concentration of SO_4^{2-} was detected. It was taken into consideration when calculating concentrations of the given components in samples.

Concentration of sulfuric acid and ammonium sulfate in air was determined with the help of thermodenuder system, developed at the Energy Center of Netherlands ECN.² The basic principle of system operation is in accumulation of examined components on the internal surface of the tube due to the selective thermal decomposition of the substances examined. During the analysis stage the substance accumulated at the sampling stage is decomposed and the SO_2 product is detected with a highly-sensitive fluorescence analyzer. The accuracy of such a determination of the ammonia sulfate is $\pm 0.3 \mu\text{g}/\text{m}^3$ and that of sulfuric acid $\pm 0.1 \mu\text{g}/\text{m}^3$. The presence of sulfur-containing organic compounds ($(\text{CH}_3)_2\text{S}$, HSCH_3 , H_2S , OCS) in air produces a strong disturbing effect. The system is operated in an automatic mode and makes one measurement every 1.5 hour.

RESULTS AND DISCUSSION

The samples of atmospheric aerosol were collected in April 1996. Simultaneously the measurements with thermodenuder system were carried out, the air samples for which were pumped at 2-meter distance from the filter inlet. To make a comparison of the techniques used, let us consider the efficiency of sampling particles of different size. In so doing, it is important to consider aerosol losses in the inlet channels of the thermodenuder due to diffusion and sedimentation. Calculated percentage of particles passed through the sampling channel (ratio of the number of passed to the total number of incoming particles) is above 50% for particles with $0.08 < d < 5 \mu\text{m}$. As to the filters the efficiency of particle capture by fibers depends on particle size. Using the expressions from Ref. 3, we have calculated the percentage of aerosol particles passed through AFA-KhA-20 filter at the velocity of filtration of 100 l/min. The maximum value corresponds to 0.1- μm -diameter particles and is about 50%. However, the particles of larger and smaller size are captured more efficiently, and thus the filter catches no less than 90% of the atmospheric aerosol by mass. Thus, both techniques have comparable efficiencies of particle sampling.

The results of measurements obtained are presented in Fig. 1 (*a* – according to data of filter analysis, *b* – according to data from the

thermodenuder system). Mass aerosol concentration, calculated as the ratio of the difference between the final and initial weights of the filter to the pumped air volume changed within the range 20–60 $\mu\text{g}/\text{m}^3$ at average magnitude of 33 $\mu\text{g}/\text{m}^3$. This variability range is typical for the atmosphere of urban territories. Approximately a third part of aerosol mass was soluted in the water that considered as high enough magnitude. A mean value of pH water extracts is equal to 6.5. The correlation between the content of sulfate- and nitrate-anions in the samples of atmospheric aerosol, selected at the filters, is observed. At that time the concentration of nitrate-anion is 8 times less. Apparently, these observations can be explained by existence of sources of global-scale (outbreaks of sulfur dioxide and nitrogen oxide) and by a relatively long lifetime of the aforementioned substances in an atmosphere.

The concentrations of ammonium sulfate and sulfuric acid in air weakly changed during the period of measurements and were 1.7 and 0.6 $\mu\text{g}/\text{m}^3$. Average concentration ratio was 3.5 that compares with the value, measured in Europe on the North sea coast.² Apparently, this similarity is occurs due to common mechanism of the ammonium sulfate and sulfuric acid formation at transformations of the sulfur dioxide in an atmosphere.

Shown in Fig. 2 are the results of interlaboratory analysis of the atmospheric aerosol samples by the method of liquid-ion chromatography. The discrepancy observed for the content of anion-sulfate is not so great. It may most likely be explained by differences in sample preparation at the stage of dissolving the aerosol deposits. The spread of data on the content of ammonium nitrate is caused by relatively small values of its concentration and, as the consequence, by large error of its determination.

Data on ion concentration in the aerosol samples (average over the whole period of measurements) are presented in Table II. In the anion composition the sulfate anion dominates, while in the composition of cations dominate Ca^{2+} and Mg^{2+} . The mean value of concentration ratio of equivalents $\text{NH}_4^+/\text{SO}_4^{2-}$ is about 0.3, while for the pure ammonium sulfate it is equal to 1. That means that the content of NH_4^+ anion is stoichiometrically insufficient for neutralization of the anion sulfate. Hence, part of the SO_4^{2-} in aerosol was related to lithophyllic cations of calcium (and magnesium). This conclusion also applies to the data from thermodenuder system.

TABLE II.

NH_4^+	K^+	Na^+	$\text{Ca}^{2+} + \text{Mg}^{2+}$	F^-	Cl^-	NO_3^-	SO_4^{2-}
20	5.5	14.5	60	1.5	4.5	10	84

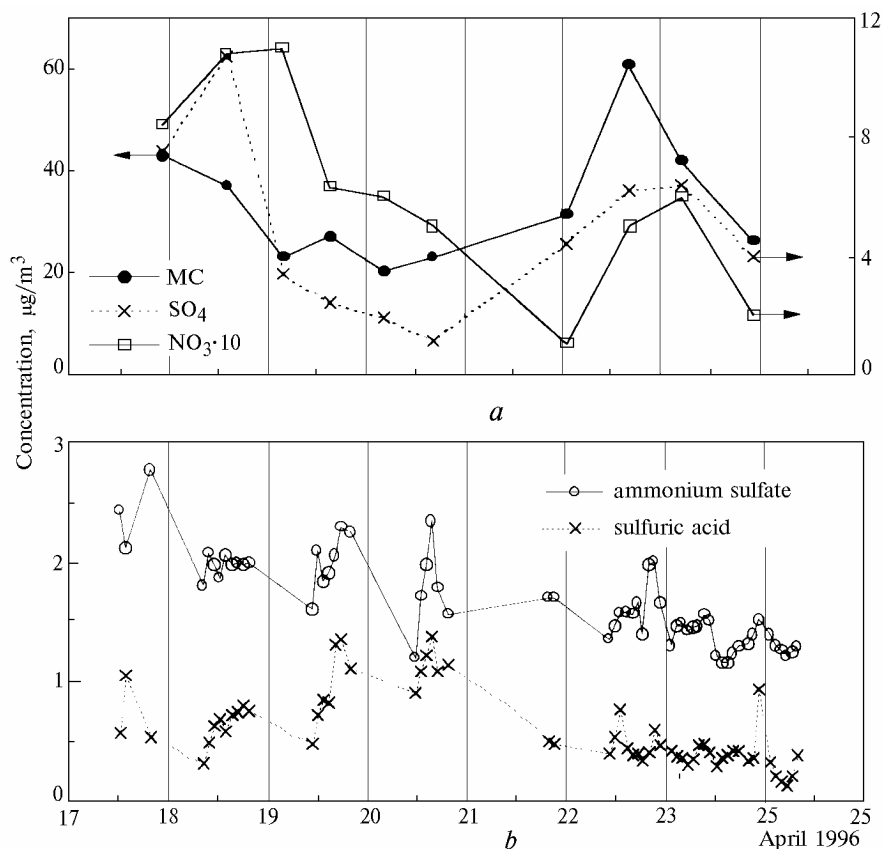


FIG. 1. The dynamics of changes in mass concentration (MC) and concentration of some components of atmospheric aerosol.

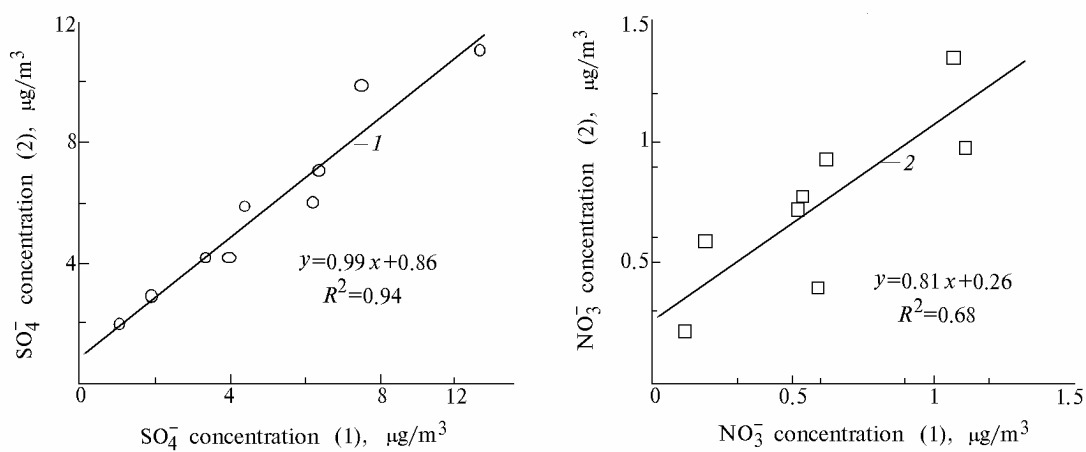


FIG. 2 Comparison of chromatographic data on sulfate and nitrate anions in water extracts of aerosol samples: data from a laboratory at the ICK&C (1); from a laboratory at the INC (2).

Shown in Fig. 3 is the content of sulfate calculated from the concentration of ammonium sulfate and sulfuric acid and averaged over the period of sampling on the filter. These components are formed in the atmosphere at transformation of sulfur dioxide and are referred to as secondary aerosols. It is seen that those make up approximately 30% fraction of the total content of sulfates in the aerosol. This means, that besides the gas-phase sources

contributing to the formation of aerosol chemical composition in the region of observations the sources of earth origin play an important role either. In our case, sulfate can come to aerosol in the form of CaSO_4 (primary particles) directly, and at neutralization of lithophilic cations Ca^{2+} Mg^{2+} (that primarily exists in the form of carbonates and hydrocarbonates) by sulfuric acid of atmospheric origin.

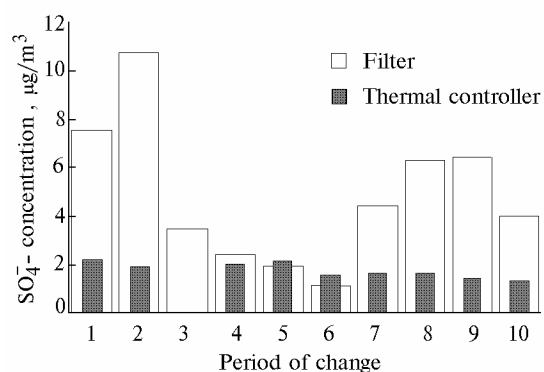


FIG. 3 The composition of sulfate-anion in atmospheric aerosol (data are obtained with the help of different techniques: sampling of aerosol on filters and by analysis with an ECN thermodenuder system).

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