Calibration of a thermal denuder system with the help of an ammonium-sulfate model aerosol

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An ammonium-sulfate aerosol was produced with the help of a nozzle. A study of the stability of particle generation and the dependence of the dispersed composition on the concentration of the sputtered solution was performed. A comparison was made of results of measurements of the mass concentration of a model aerosol obtained using three independent methods. It has been shown that the results agree to within 10% for aerosol concentrations less than 40 $\mu g/m^3$.

Introduction

To understand the processes of formation and depletion of atmospheric aerosol requires a knowledge of its chemical composition. Usually this information is obtained by analyzing particles deposited on a filter. For this purpose it is necessary to use highly sensitive analytical methods since the mass of the sample does not exceed a few milligrams. The most widespread analytical methods give information either about the elemental or the ionic composition. Here the question remains, in which chemical form the ions and elements in the original particles are found. This latter point is important because it allows one to separate out the contributions of different sources on the formation of an atmospheric aerosol.

A method has appeared relatively recently for recording the individual components of an atmospheric aerosol with the help of a thermal denuder system.[1] The principle of selective thermal decomposition combined with high-sensitivity recording allows one to measure the concentration of sulfuric acid and ammonium sulfate in atmospheric air. These components are of interest since they are products of the photochemical transformation of sulfur dioxide and are sources of secondary aerosol formation.[2]

The goal of the present paper is to compare the results obtained with the help of a thermal denuder system with the results of other methods of determining the particle mass concentration.

Technique

In the present work we used three different methods of determining the aerosol mass concentration − using a thermal denuder system, collecting the aerosol onto a filter with subsequent analysis of the deposited aerosol, and using an automated diffusion battery.

Let us dwell in more detail on the principle of operation of the thermal denuder system. The use of denuder systems to measure the concentration of atmospheric components is already in its second decade. The basic principle of the method is selective absorption of the gaseous components of air by a coating on the walls of a tube as air is pumped through it, where this selective absorption is afforded by their high diffusion mobility. In a thermal denuder setup this principle is combined with heating the sample to a high temperature, which leads to selective decomposition of the components of the dispersed phase. Figure 1 shows a diagram of the setup operating in different regimes. First, air is sampled by pumping it through the tract. Different segments of the denuder tube are held at different temperatures. In the first segment the sulfuric-acid component of the aerosol evaporates and then diffuses to the inner walls and reacts with the Cu/CuO coating. In the second segment (heated to a higher temperature) ammonium sulfate decomposes into sulfuric acid, which is also captured by the coating. Accumulation of the substances for analysis takes place during a sampling time on the order of a half-hour. Then, in the analysis regime, the denuder is heated to 850°C in a nitrogen cross-flow. Under these conditions, successive decomposition of the accumulated material occurs in different segments of the tube with liberation of SO_2. The gas concentration is recorded by a fluorescence analyzer (Thermo Electron Instruments). The time-integrated signal is proportional to the concentration of the analyzed components in the air sample. The system is computer driven, automated, and makes one measurement every 1.5 hours.

Sampling of aerosol on a filter is the mostly widely used method of determining the mass concentration of the dispersed phase. In our case, sampling was performed with the help of AFA-KhA-20 ("Izotop") filters with a flow-through rate of 65 l/min and exposure time on the order of three hours. Next, each filter was placed in a plastic container with 10 ml demineralized water ("Millipore" Milli-Q water purification setup). After two minutes of processing with an ultrasound disperser, the solution was analyzed for sulfate content. We used the liquid ion chromatography method (Waters ILC-1) for this

purpose. From the measured SO_4^- concentration in the solution and the volume of air pumped through the filter, we calculated the aerosol mass concentration.
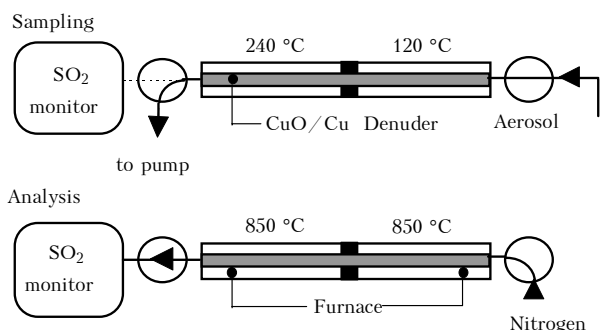
Fig. 1. Diagram of operation of the thermal denuder system under various regimes.

The concentration and dispersed state of the particles were monitored with the help of an automatic diffusion battery.[3,4] The last two parameters for known density of the particles and making some assumptions about their shape allow one to calculate the aerosol mass concentration.

The model aerosol is produced with the help of the experimental setup shown in Fig. 2. The particles are generated by a Collison nozzle, which works by sputtering a solution of ammonium sulfate. The drops are directed into a chamber, where they are mixed with filtered air to dry. Sputtering solutions with different concentrations produced particles of different size.
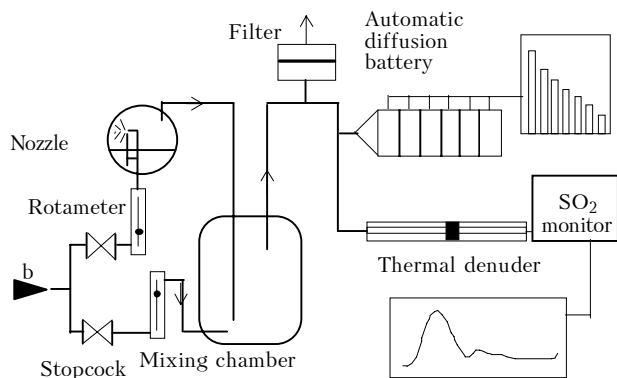

Fig. 2. Diagram of experimental setup. B is filtered air with relative humidity less than 20%.

Results and discussion

First of all, we need to characterize the nozzle-generated aerosol. Figure 3 displays distribution spectra of particles produced by sputtering solutions of ammonium sulfate in demineralized water. The displayed spectra present the mean values for the two-hour series of measurements. The points on the graph are joined by a smooth curve generated by spline interpolation.

Using the procedure of minimizing the mean-square deviation, the obtained experimental points were fitted using a logarithmic distribution. The calculated parameters of the distributions D_g and σ_g are listed in Table 1. The aerosol polydispersion index σ_g (geometrical standard deviation) is significantly less than two. This is explained by the presence of a getter in the implemented nozzle. The absence of a getter in the nozzle leads to the formation of aerosols with σ_g greater than two.
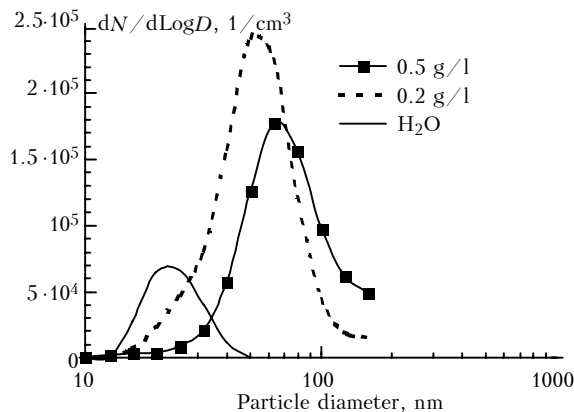
Fig. 3. Dispersed composition of particles produced by sputtering a solution of ammonium sulfate in demineralized water.

Table 1. Spectral parameters of particle distribution obtained from solutions of ammonium sulfate.

Parameter, nm	Concentration, g/l	
	0.2	0.5
D_g	53	70
σ_g	1.5	1.6
D_V (meas.)	76 ± 8	96 ± 7
D_V (calc.)	77	104

Note. D_g is mean geometric diameter; σ_g is standard geometric deviation; D_V (meas.) is measured mean-volume diameter; D_V (calc.) is calculated mean-volume diameter.

The measured mean values of the mean-volume diameter of the aerosol D_V (meas.) are comparable with the calculated values D_V (calc.). These values were calculated using formula (1) for known diameter (for a given nozzle) of the initial (before drying) droplets $D_0 = 1.6$ μm, density of the droplets $\rho = 1$ g/cm^3, and density of the dry particles $\rho_0 = 1.8$ g/cm^3

$$D_V(\text{calc.}) = D_0 \sqrt[3]{\rho_0\, c/\rho} , \qquad (1)$$

where D_0 and ρ_0 are the diameter and density of the droplets, c is the concentration of the droplet solution, and D_V(calc.) and ρ are the diameter and density of the particle after complete evaporation of water.

It can be seen from Table 1 that the deviation of the calculated size from the measured size of the particles is greater in the case of a larger-particle-size aerosol. This is explained by a decrease in the size of the particles during recording by the diffusion battery. The measured particle spectrum is close to the upper recording limit of the device (200 nm), leading to an undercount of larger-size particles, i.e., a lower inferred mass concentration. Therefore, to reduce the error in our experiments we decided to generate aerosol from an ammonium-sulfate solution with a concentration less than 0.5 g/l. We calculated the mass concentration from the particle concentration, measured with the help of the diffusion battery, and the mean-mass diameter

$$C = \pi \, D_V^3 \rho \, N / 6 \; . \qquad (2)$$

Here C is the aerosol mass concentration, N is the particle number density, D_V is the mean-volume diameter of the aerosol, and ρ is the density of the particles (1.8 g/cm^3).

The nozzle device allowed us to generate particles for 3.5 hours. This used up around 70 ml of solution. During this process, the solution became steadily more concentrated due to preferential evaporation of water during sputtering. This is the reason for the positive drift of the mean-volume diameter of the aerosol particles. After three hours of continuous operation of the nozzle D_V(meas.) increased on average by 30%, which leads to roughly a twofold increase in the mass concentration of the ammonium-sulfate aerosol. At the same time, the concentration of the generated particles depends weakly on time. During sputtering of the ammonium-sulfate solutions a concentration of $(1–2) \times 10^5$ cm^{-3} obtains (after dilution with pure air in the ratio 1:2). During sputtering of demineralized water, particles are obtained having a diameter around 20–25 nm. At the same time, in the distribution spectrum obtained with the diffusion battery, a mode is observed at a diameter less than 3 nm. Apparently, some of the particles have a diameter less than the recording threshold of the device and are not detected. These particles make up about half of the total since the concentration of particles produced by sputtering water is two times less than the concentration of particles obtained when sputtering the ammonium-sulfate solution.

During the exposure time of one filter the thermal-denuder system makes three measurements. Here an increase in the system signal is observed which, as in the case of the increase of the mean-volume diameter of the particles, is connected with the concentrating of the sputtered solution. The reproducibility of the data generated by this system for two successive measurements is not worse than 10%.

A summary graph comparing the aerosol mass concentration obtained by various methods is shown in Fig. 4. As can be seen, good agreement is obtained for concentrations of the ammonium-sulfate particles less than 40 μg/m^3. This is important since the concentration of ammonium-sulfate particles in the atmosphere usually does not exceed 40 μg/m^3. The overestimate of the concentration based on the diffusion-battery data is probably due to the fact that the real density of the generated particles is less than the assumed value [for $(NH_4)_2SO_4$]. The aerosol was mixed with dry air; however, complete drying and crystallization could not occur due to formation of a supersaturated solution in the drops.[5] The underestimate of the mass concentration based on the thermal-denuder data referenced to the filter-sampling data is probably explained by incomplete decomposition of the ammonium sulfate in the sampling regime.
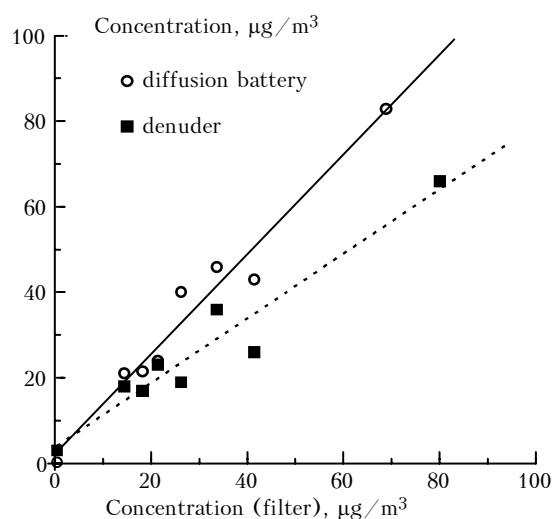

Fig. 4. Comparison of ammonium-sulfate mass concentrations obtained by different methods.

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