Determining concentration of the aerosol forming substances in the atmosphere

A.N. Ankilov, A.M. Baklanov, A.L. Vlasenko, A.S. Kozlov, and S.B. Malyshkin

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

The fast and high-sensitivity technique has been developed for determining the concentration of aerosol forming substances in the atmosphere. The technique makes it possible to determine the concentration of non-volatile admixtures starting from 1 ng/m^3. It takes about 4 minutes to make single measurement. In combination with the measurement of microphysical properties of atmospheric aerosol the technique allows one to estimate the resultant rate of the processes of formation of the aerosol forming substances in the atmosphere and to determine their basic physicochemical properties, in particular, the coefficient of molecular diffusion. The new experimental setup was examined under laboratory and field conditions.

Introduction

The problem of transformation of the atmospheric gas admixtures into aerosol due to chemical reactions is one of the most important and unsolved problems of physics and chemistry of the atmosphere. Apart from the variety of processes and substances participating in them, the difficulty in determining the concentrations of the products hampers solving this problem. In this case one deals with molecules and molecular clusters of non-volatile substances formed in the atmosphere but not settled on the present aerosol particles and not coagulating with each other up to a detectable size. The difficulty is caused both by the low value of absolute concentration of the products of such reactions in the atmosphere as well as by its small magnitude as compared with the mass of the existing aerosol. Thus, the question is still to be addressed on the measurement of mean values of concentration to say nothing about measurements of its instantaneous values on real-time scale.

As an attempt of solving this problem, the technique has been developed and the experimental setup created for determination of the total concentration of aerosol forming admixtures in the atmosphere starting from 1 ng/m^3 concentration. In combination with measurement of microphysical properties of atmospheric aerosol, the technique allows one to estimate the resultant rate of the processes of formation of the aerosol forming substances in the atmosphere and to determine their basic physicochemical properties, in particular, the coefficient of molecular diffusion.

Description of the technique

The principle of operation is based on entrapping molecules and their clusters by water fog produced at fast cooling of atmospheric air by liquid nitrogen vapor. Once the droplets of admixtures have been vaporized, particles of nanometer size are formed, the size and number density of which are determined with a diffusion aerosol spectrometer. The spectrometer has been designed at the Institute of Chemical Kinetics and Combustion SB RAS.[1] Taking into consideration that the diffusion coefficient does not depend on the density of particle substance and assuming the particles to be spherical, one can calculate their total volume in a unit volume of air. This value is the volume of the condensed phase, which can be formed from these molecules due to coagulation with each other or with the atmospheric aerosol particles. If one supposes that the density of condensed matter equals unity, then one can interpret it as the mass concentration. For the presentation convenience, let us use these terms.

Block-diagram of the setup is shown in Fig. 1. Water droplets with their concentration significantly greater than the concentration of natural aerosol are formed when mixing air with liquid nitrogen vapor inside a fog former *6*. To provide for maximum decrease of the diffusion losses, the setup has no special channels for the air inflow, and air enters directly to the mixer of the fog former. The mean size of droplets depends on humidity of the surrounding air, ratio of the flow rates of air and nitrogen, and on the number density of the fog particles n. One can estimate the time of absorption of the molecules of admixture τ by the following relationships:

$$\frac{dC_m}{dt} = -\frac{C_m}{l},$$

$$l = (4\pi D n \bar{r})^{-1}, \qquad (1)$$

$$\bar{r} = \sqrt[3]{3\, C_{W_s}(T)\, \eta\, Q_{Air} / [4\,\pi\, n\, (Q_{Air} + Q_{N_2})]}\,.$$

Here C_m is the number density, D is the diffusion coefficient of the molecules of non-volatile admixture, $C_{W_s}(t)$ and η are the concentration of the saturated

water vapor and relative humidity of air, respectively, Q_{Air} and Q_{N_2} are the volume flow rates of air and nitrogen, respectively. The number density n, along with other parameters, depends on the regime of mixing. Choosing the proper parameters of the setup is mainly reduced to the search of conditions for complete capture of admixtures by the droplets, that means that the parameters must provide for obtaining small l value as compared with the time of fog residence in the fog former and small value of the diffusion losses on the walls.
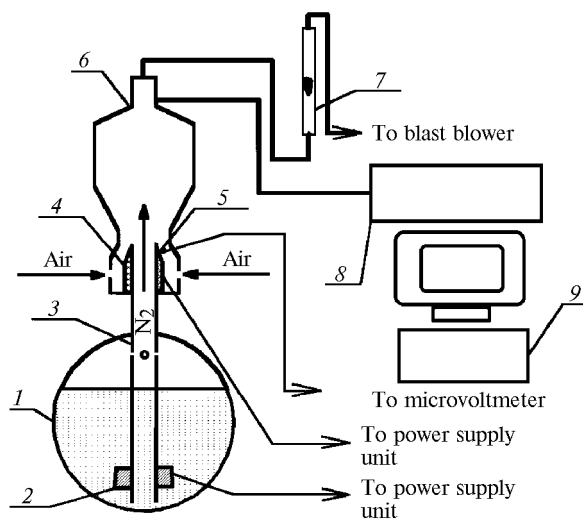
Fig. 1. Block-diagram of the setup: container with liquid nitrogen (*1*); heater of nitrogen evaporator (*2*); connecting pipe (*3*); heater of the nozzle (*4*); thermocouple (*5*); fog former (*6*); flow rate meter (*7*); diffuse aerosol spectrometer (*8*); computer (*9*).

In the final result, the parameters chosen were as follows. The total flow rate of nitrogen and air through the chamber was approximately 1200 l/hour and was approximately the same in all experiments. This flow rate provided for small losses (less than 1%) on the walls of the chamber at the time of the fog existence of 2.5 s and complete entrapping of the admixtures characterized by the diffusion coefficient above 0.01 cm²/s. The flow rate of air changed from 150 to 600 l/hour. The change of the flow rate of air at the constant total flow rate was used for optimizing the measurement process. The time of a single measurement was about 4 minutes. The temperature of evaporation ($\approx 20°C$) made it possible to determine the concentration of the substances with the saturated vapor pressure less than $10^{-8} - 10^{-9}$ mm Hg.

Laboratory tests

One can demonstrate the operation of the technique in experiments with the particles and vapor of non-volatile substances produced by the generator of tungsten oxide particles (WO_x generator). The vapor was produced by means of heating a bead of tungsten oxides using a heating coil from Nichrome. In addition to the tungsten oxides, they contain a noticeable fraction of non-volatile carbon-containing products. The vapor was transferred by the airflow to the cool zone where the particles were condensed thus forming ultrafine aerosol particles with the size of a few nanometers. The completeness of the vapor-to-particle conversion depends on the time of condensation.

The experiments have been conducted in four variants, as is shown in Fig. 2.
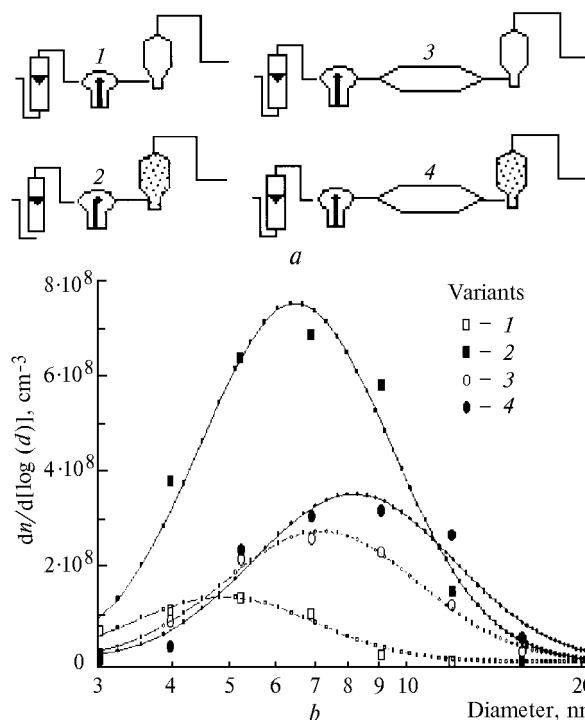
Fig. 2. Regimes of the WO_x generator and measured particle size distributions. N_2 is switched off, delay is 0 sec (*1*); N_2 is switched on, the delay is 0 sec (*2*); N_2 is switched off, the delay is 4.3 sec (*3*); N_2 is switched on, the delay is 4.3 sec (*4*).

In the first variant the outlet of the WO_x generator was connected directly with the inlet of the fog former chamber. The heater of the nitrogen evaporator was switched off. The measured were the disperse composition, number and mass densities of particles (see Fig. 2*b* and Table 1). This figure shows the results of one series of the experiments.

Table 1. Measurement data on the mass density of WO_x

Measurement No.	Variant	Mass density, ng/m³	Scatter, ± ng/m³
1	3	466	70
2	4	821	41
3	2	823	63
4	1	63.3	2.3
5	2	619	31
6	4	656	79
7	3	290	7
8	4	573	8
9	2	743	124
10	1	33.7	2
11	2	537	44
12	4	411	43
13	3	176	11

The same was done in the second variant, but the evaporator was switched on. Water droplets captured small particles and vapor. It is seen that all the aerosol parameters measured at the outlet of the fog former changed. The mass concentration of aerosol increased by more than one order of magnitude.

In contrast to the first variant, in the third one the additional chamber, which provided for the delay of 4.3 sec, was installed at the output of the WO_x generator. In this case, significant part of the molecules and clusters that could not be detected in the first variant had enough time to coagulate. The mass concentration in this case significantly exceeds that measured in the first variant and is 30–50% of that measured in the second variant.

The difference between the fourth and the third variants was that the evaporator was switched on. In this case, deformations of the distribution function and changes in the number density are less significant. However, the mass concentration becomes twice as much and becomes close to that detected in the second variant.

The sequence of the variants of the experiment was that the fourth followed the second. It was necessary for decreasing the influence of the drift of the characteristics of the WO_x generator on measurements of the mass concentration. That means, that the sequence of experiments was 1–2–4–3 or back. The results are presented in Table 1. It is seen that the concentration measured in the second regime is always higher than in the fourth one. This is explained by the diffusion losses on the walls of the delay chamber. For the same reason, it is impossible to achieve the coincidence between the results obtained in the second and third variants by increasing the time of coagulation. At the same time, the regimes can be easily created when the results of measurements in 3 and 4 regimes coincide within the limits of the data scatter.

Measurements of the characteristics of atmospheric admixtures and discussion of the results

Measurements of the concentration of aerosol forming substances were carried out nearby the institutes of Novosibirsk Akademgorodok and in the rural area to the east of it near Klyuchi village. The sampling site in Akademgorodok was at about 1-m height above the concrete surface of the institute yard. The results show strong diurnal variability of the mass concentration of aerosol forming substances. This may be related to the anthropogenic effect of the smoking liquid production (200 m to the south), intense traffic (300 m to the west) and the activity of the institutes. Examples of diurnal behavior of the mass concentration are shown in Fig. 3. It is seen that the level of the content of aerosol forming substances varied in the daytime from 100 to 300 ng/m^3. Powerful peak up to 10000 ng/m^3 is caused by the work of the smoking liquid production

facility. The most intense emissions and their accumulation in the near-ground layer of the atmosphere are observed in the period from 7 p.m. until 3–5 a.m. Short-time clearing of the atmosphere to 6–9 ng/m^3 occurs in the end of work of this production or when the wind changed its direction and it is observed in the nighttime or in the morning. In the beginning of the workday, the level returns to the previous value of 100–300 ng/m^3.
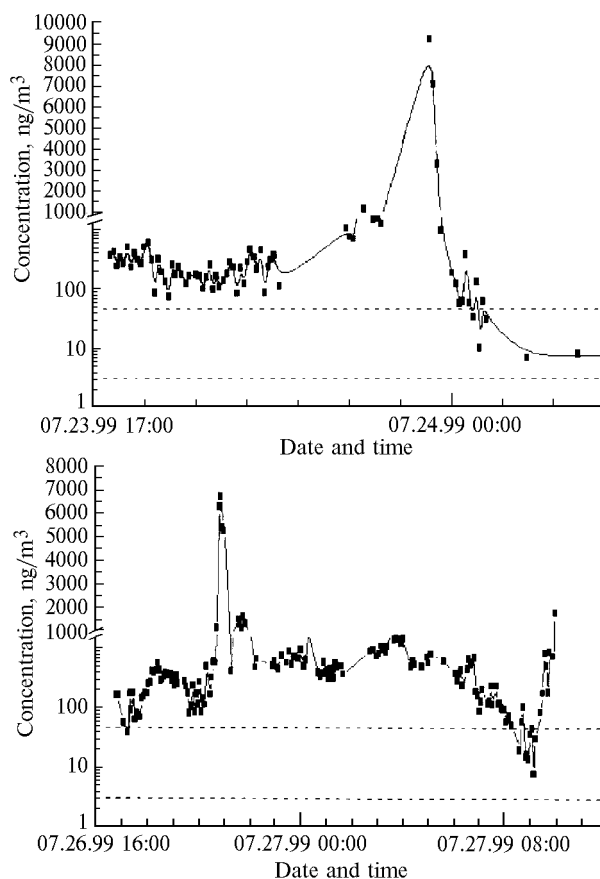

Fig. 3. Time behavior of the concentration of aerosol forming substances.

Dashed lines in the figure show the range of variation of this value during the observations in Klyuchi village. The mean value of the mass concentration is at the level of 7–10 ng/m^3. Measurements were carried out near the pumping station of the gardening society outside the settlement of summer cottages. There were no permanent residence, nor cultivated areas near the measurement site. No obvious signs of the effect of nearby sources of emissions were observed during the whole period of experimenting.

Measurements were also carried out in Klyuchi village of the characteristics of the products that are being formed in atmospheric air under the effect of radiation of a medium-pressure mercury lamp. The flow photochemical reactor was used for this purpose. The block-diagram is shown in Fig. 4. A PRK–2 mercury lamp was used in standard mode as a light source. The

sampled atmospheric air passed through the smoothing mesh *1* and the long part of the tube to be transformed into the laminar flow. Then air was irradiated by the mercury lamp *2* and was thrown out by the ventilator *4* through the smoothing mesh *3*. The sampler *5* was installed in front of the lamp in order to exclude the effect of convective flows from it. The flow velocity in the tube was about 0.25 m/s, the path length from the outlet mesh to the samples was 50 cm, the lamp was situated 5 cm behind the sampler, the effective dose of radiation corresponded to irradiation by the PRK–2 lamp during 0.2 s from the distance of 5 cm. The total length of the reactor was 2 m. The arrangement of the devices excluded repeated inflow of the irradiated air into the reactor. Formation of the aerosol particles with the detectable size was not observed under these conditions at the outlet of the sampler. The mass concentration of the non-volatile products was at the level of 30–50 ng/m^3.
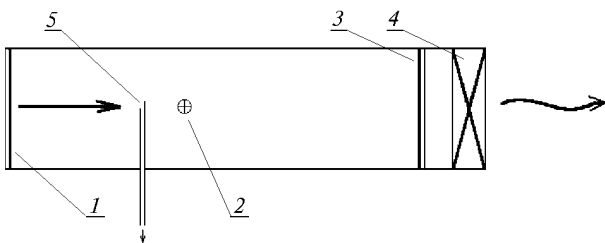

Fig. 4. Diagram of the flow photochemical reactor: front and rear smoothing grids (*1* and *3*); mercury lamp (*2*); ventilator (*4*); sampler tube (*5*).

Measurements of the mean values of the diffusion coefficients of aerosol forming substances have been carried out in all cases. The work was performed during daytime. Air was directed to the inlet of the fog former through the pipes of different length. The ratio of the mass of aerosol forming substances to their total mass makes it possible to estimate the diffusion coefficient. Copper and polyethylene pipes with the inner diameter of 8 mm were used in the experiments. The length l of the pipes used was 10, 20, 40, and 80 cm. In order to decrease the effect of natural fluctuations of the concentration, long series of experiments were carried in the sequence 0–10–0–20–0–40–0–80–0–10–0–20–0 and so on. When processing the data in the subsequence 0–l–0, the value of the total concentration $\overline{C}(0)$ averaged over two values was used for determining the slip coefficient $K(l)$:

$$K(l) = C_m(l)/C(0). \tag{2}$$

No significant differences were observed between the results obtained with the use of copper and polyethylene tubes.

The data obtained in the coordinates of the parameter $P = \pi l/Q_{Air}$ are shown in Fig. 5*a*. The use of this parameter makes it possible to show the data measured at different rates of the airflow on the same plot. Black circles in this figure correspond to the data obtained in Akademgorodok, open circles show the data obtained in Klyuchi village.
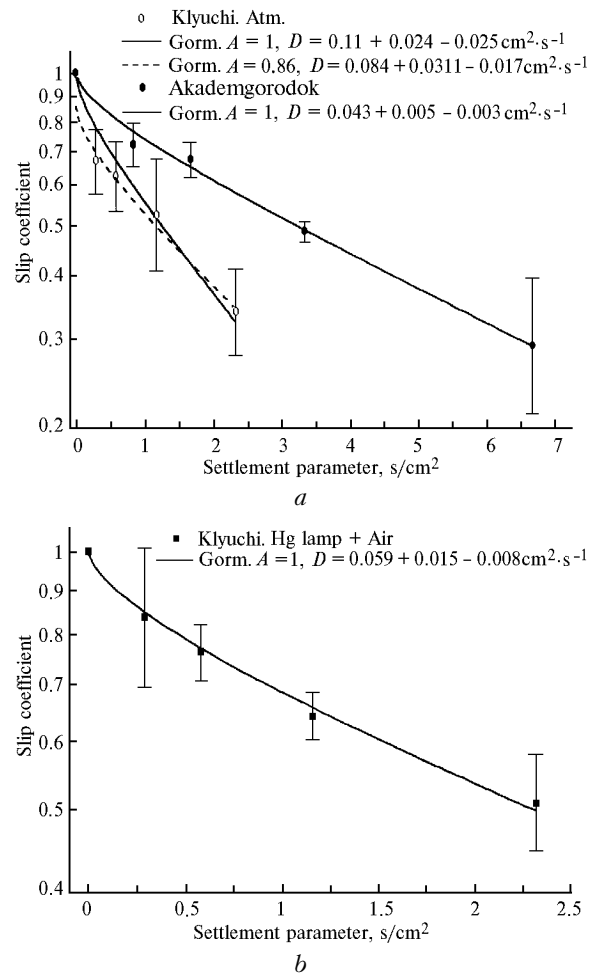

a

b

Fig. 5. Slip coefficient as a function of the settlement parameter $\pi l/Q_{Air}$. D is the mean diffusion coefficient calculated by the Gormley-Kennedy ratio.

The results were processed using the Gormley-Kennedy approximation.[2] The coefficient of particle slip through the round pipe in the laminar flow $G(\mu)$ depends in this approximation on the single parameter $\mu = DP$, where D is the diffusion coefficient.

$$G(\mu) = 1 - 2.56(\mu)^{2/3} + 1.2\mu + 0.177(\mu)^{4/3}$$

$$\text{at } \mu < 0.03, \tag{3}$$

$$G(\mu) = 0.891 \exp(-3.657\mu) +$$

$$+ 0.097 \exp(-22.3\mu) + 0.032 \exp(-57\mu)$$

$$\text{at } \mu \geq 0.03.$$

In the general case one can write

$$K(l) = AG(\mu), \tag{4}$$

where A is the parameter.

Since in our case the approximation curve should pass through 1 at $l = 0$, then $A = 1$ and only the diffusion coefficient is to be sought by the method of least squares. The results of search are shown in Fig. 5*a* by solid lines. The range is also shown, in which the

data obtained can be unambiguously described using mean diffusion coefficient. It is seen from the data obtained that the diffusion coefficients in these two cases are strongly different. The diffusion coefficient of 0.043 cm^2/s is an evidence of the fact that, obviously, heavy organic compounds and carbon clusters were prevalent in the near-ground air in the zone nearby institutes of Akademgorodok.[3]

Significantly higher diffusion coefficient of 0.11 cm^2/s allows us to suppose that less complex substances, possibly, sulfates and nitrates, oxides of metals, etc. compose the main fraction mass of aerosol forming substances in Klyuchi village. It is interesting that substances formed under the effect of mercury lamp of medium pressure have medium diffusion coefficient at the level of 0.059 cm^2/s and, probably, heavy organic is also prevalent in their composition (Fig. 5b).

The fact attracts our attention, that the data obtained in Klyuchi village show a pronounced tendency to systematic deviation from the Gormley-Kennedy curve. In this case, both the diffusion coefficient and the parameter A were sought by fitting using the method of least squares. The corresponding curve is shown in Fig. 5a by dotted line. The value of the diffusion coefficient in this case is 0.084 cm^2/s. The numerical value $A = 0.86$ is an evidence of the fact that, probably, the portion of substances ($\sim 10\%$) forming the non-volatile admixtures in the atmosphere has the diffusion coefficient higher than 0.14 cm^2/s. Hypothetically, they can be ozone and active particles such as OH, H_2O_2, HO_2, etc. These particles can form non-volatile substances due to the liquid-phase reactions in the fog former, and, in nature, in droplets of fogs and clouds. Wide scatter of the data and isolated character of measurement do not make it possible to transform the aforementioned suppositions to the affirmative form. Besides, the estimate of the lifetime of aerosol forming substances determined by the diffusion sink on the atmospheric aerosol particles, gives the value ~ 100 s assuming typical conditions. Obviously, this explains large fluctuations of the concentration. Therefore, the question on representativity of these results in space and time is still open. It is necessary to continue the work aimed at both development of the technique and performing the laboratory and field experiments.

Conclusion

For summary, one can say that the technique is sufficiently sensitive to provide for the determination of concentration of aerosol forming substances in the atmosphere. The data obtained are, on the other hand, an evidence of the role of local processes in the formation of these substances, due to short lifetime of such substances. In combination with the short time of analysis, it can make it possible to study the processes of aerosol formation characteristic of the considered geographical site. Spatial scale of the effect of 1 km sharply decreases the number of such processes in comparison with that on the scale of region or continent and significantly simplifies the problem.

Let us note, finally, that the technique is applicable not only to the problems in atmospheric studies. Its modifications can be useful in many cases when one needs to determine the content of low concentration of substances with low partial pressure of vapor in gas. The working substance of the fog former can be any substance, which allows one to create the fog satisfying the conditions of the type (1). These conditions can be removed, and the sensitivity can be enhanced if the particle size has been controlled.

Water is the preferred substance for atmospheric research only because no new reagents are added to the system in this case, and due to its non-toxicity. Replacement of water with substances of other classes can give additional information about the gas-to-particle transformation processes in the atmosphere.

Acknowledgments

References

1. G.P. Reischl, A. Majencowicz, A. Ankilov, et al. J. Aeros. Sci. **22**, 325–331 (1991).
2. N.A. Fuks, *Mechanics of Aerosols* (Academy of Sciences Publishing House, Moscow, 1955).
3. *Handbook of chemist*, Vol. 3 (Khimia, Leningrad, 1964).