

The generator of vapors of PreAerosol compounds. Application to calibration and as a thermal-condensation source of aerosol

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A new, simple and fast method for calibration of water-absorbing method for measuring mass concentration of PreAerosol Compounds (PreAC) in atmospheric air is developed. The method is realized in a generator of a given concentration of low-volatile vapors of a wide class of substances. The principle of generation is based on insertion of a known amount of the substance saturated vapor into the studied airflow. As is shown by means of the generator, the uncertainty of the vapor content measured by the water-absorbing method is less than 10% in the mass concentrations range from 10 up to 3000 ng/m³. Applicability of the generator as a thermal-condensation source of aerosol nanoparticles is shown.

Introduction

Formation of vapors of PreAerosol compounds (PreAC)¹ is limiting and the least studied step of the gas-to-particle transformation process. By their physical properties, PreAC take an intermediate position between gaseous aerosol precursors and aerosol particles. PreAC can be formed either as a result of direct emission or in the course of atmospheric chemical reactions. The case in point concerns molecules and molecular clusters of low-volatile substances at the step before they have settled on aerosol particles and coagulated with each other up to a detectable size. PreAC are the precursors of atmospheric condensation nuclei. Being absorbed by surfaces of existing aerosol particles, they influence their optical, hygroscopic, and other properties. Hence, the knowledge of physical and chemical properties of PreAC is important for understanding of aerosol particle properties throughout the size range.

The main difficulty in experimental determination of PreAC concentration is caused by their insignificant absolute content and smallness of this amount in comparison with the mass of already formed aerosol.

As an attempt to solve this problem, a technique was developed and an experimental setup was designed at the ICKC for determining the summary concentration and diffusion coefficient of atmospheric PreAC at a concentration of up to 1 ng/m³. The technique is based on PreAC absorption by atmospheric water drops formed at a sharp air cooling by liquid nitrogen vapors. In this case, gaseous substances with a vapor pressure of less than 10⁻⁸ mm Hg are concentrated to traceable aerosol particles, and natural condensation process accelerates by a factor of about 10 000. The experimental setup, operating on this principle, has been called *drop concentrator*. This technique is described in Ref. 2 in more detail.

To study the gas-to-particle transformation in the atmosphere on the present-date level, a fast, reliable, and simple calibration method is required, which can be usable, in particular, in expedition conditions. To this end, the authors have designed a stabilized generator of a certain concentration of low-volatile PreAC vapors; for operation, it needs only in power supply and small amount of substance with the known temperature dependence of the vapor expansibility.

However, the possibility to use the generator as a thermal-condensation source of aerosol particles⁵ is of the greatest practical importance. Therefore, the gas-to-particle transformation process was reproduced in laboratory conditions. As generator's working substance, the colophony was used (often used in aerosol optical researches). The main purpose was to obtain a stable concentration of particles of controllable size.

The generator of low-volatile vapors

The principle of the generator operation is based on introducing a known amount of saturated vapor into the airflow under study. The block-diagram of the generator is shown in Fig. 1.

The generator consists of a 2-kg heat-insulated copper cylinder providing a stable thermal mode. A quartz cell of 220 cm³ in volume is mounted inside the cylinder, where vapor source and a cone, providing for vaporizing into the calibrating air, are located. The cone and cell are equipped with Nichrome heaters. Cell temperature of (20–300 ± 2)°C is controlled by a contact thermometer, commutating the heater circuit. To exclude substance condensation inside the generator, the cone temperature is kept equal to the cell temperature by means of a differential thermocouple and electron control unit.

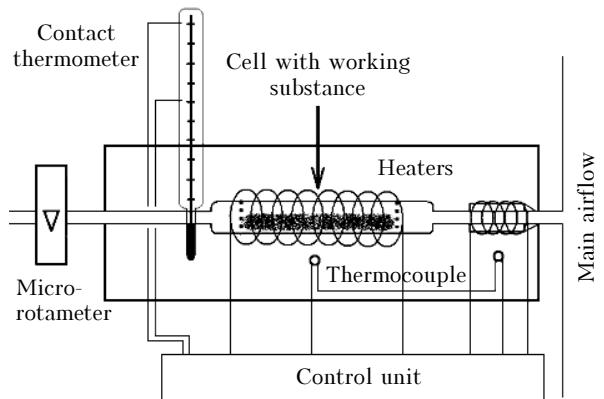


Fig. 1. Block-diagram of the PreAC vapors generator.

During the work, filter-purified air comes through a micro-rotameter into the heated cell, containing working substance, with the $10-200 \text{ cm}^3/\text{min}$ rate. Here the air is expanding, the pressure of working substance vapors attains the saturation state (for the cell temperature), and the mixture comes to the main calibration airflow though the cone.

Selection of the generator working substance

The working substance for calibration is chosen by its physical properties. Under standard conditions, the pressure of its vapors should not exceed 10^{-8} mm Hg , which is the threshold pressure for the water-absorption method; its content in air at the generator inlet should not be lower than $1 \text{ ng}/\text{m}^3$, which is also determined by the technique sensitivity. The substance should not experience phase and chemical transformations in the generator temperature range. In addition, reliable and consistent reference data on the temperature dependence of substance vapor pressure should be available.

Among substances, available to the moment of calibration, selenium (Reakhim, reagent grade, pellets) answered the above criteria. Variation between literature data on vapor density^{3,4} does not exceed 2% within the 300–500 K temperature range. Under standard conditions (293 K), the reference vapor pressure is $0.2 \cdot 10^{-12} \text{ mm Hg}$ and vapor density is $0.0029 \text{ ng}/\text{m}^3$. Such parameters corresponded to unregistered selenium content at the generator inlet at the room temperature in the cell and provided aerosol purity of the experiment.

Besides, selenium exhibits hydrophobic properties. Its use in water-absorption calibration method as a working substance allows the solution of a disputable question about the influence of macrophysical properties of substance relative to water on measurement results.

Determination of water-absorption method accuracy

The calibration scheme is presented in Fig. 2. Air, purged of aerosol particles, selenium-vapor

saturating in the generator, are diluted down to total rate of $10 \text{ l}/\text{min}$ and come into the drop concentrator. The concentration and dispersion composition of generated aerosol particles are measured with a diffusion aerosol spectrometer (DAS). In case of high countable concentrations of the generated aerosol, an additional 20-fold diluter of capillary type is mounted at the DAS entry.

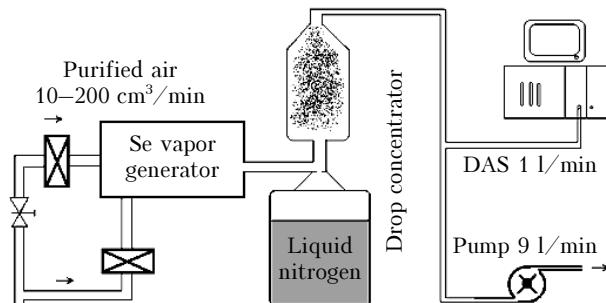


Fig. 2. Scheme of calibration of the water-absorption method with the PreAC generator.

At such experiment procedure, the mass concentration of Se vapors can be calculated, on one hand, by consistent reference data and on the other hand, by measured aerosol volume, generated of Se in the drop concentrator – this is the point of calibration process.

The Se vapor density M_{lit} in the generator cell was calculated from tabulated reference data by the equation

$$M_{\text{lit}} = e^{(A-B/T)}. \quad (1)$$

Here A and B are the reference constants of temperature dependence of Se vapor pressure; T is the absolute temperature.

The Se vapor density M_{fact} in the generator cell was calculated from the concentration and mean countable size of Se aerosol, DAC-measured at the drop concentrator inlet, with accounting for temperature expansion and dilution, by the equation

$$M_{\text{fact}} = \frac{\pi d^3}{6} N \frac{Q}{q} \rho \varepsilon \frac{T_0}{T}, \quad (2)$$

where d is the mean countable size of aerosol particles; N is the particle number density; Q and q are the total air rate and the rate through the generator, respectively; ρ is the Se density; ε is the dilution factor at the DAC inlet; T_0 is the room temperature; T is the generator cell temperature.

The comparison of reference and measured temperature dependences of Se vapor density is shown in Fig. 3.

In the experiments, the generator cell temperature varied from 140 to 204°C and the mass concentration of Se vapors varied from 10 ng to 3 µg per 1 m³ of air. Totally, forty measurements at different temperatures were carried out. The difference between average experimental values and reference data did not exceed 8%.

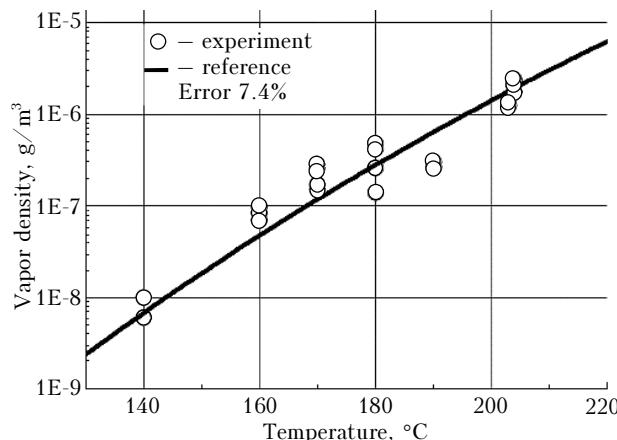


Fig. 3. Comparison of reference and measured temperature dependences of Se vapor density [calculated by Eqs. (1) and (2)].

It should be noted that aerosol purity of the setup was checked before each experiment. Particle generation was not recorded at the de-energized cell heater. Mean-square fluctuations of the Se vapor mass concentration during for a half-hour measurement run at a fixed cell temperature did not exceed 5% mean value. The measurements were carried out at the linear portion of the dependence of the vapor mass concentration on the generator rate, which gave a certainty that the vapor density in the cell corresponded to the saturated one.

Use of the generator as a source of aerosol particles

The field of applications of the designed generator of low-volatile vapors is not limited to water absorption method calibration. The use of the generator as a stabilized thermal-condensation source of aerosol particles of different sizes is of greatest practical importance. To test this possibility, cylindrical flasks of different volume were mounted at the generator inlet (so-called controllable delay line), in which the natural condensation of the working substance took place. The diffusion aerosol spectrometer was used as a detector of size and concentration of particles, vapor-generated during the delay time. Thus, two controllable parameters, i.e., generator cell temperature (vapor source power) and vapor-condensation time (delay time), were available to use. The source power increase results in the condensation rate increase, while the delay time prolongation — to more complete vapors-to-particles transformation.

As a working substance, colophony was chosen, which is often used in aerosol optics as a test object. Unfortunately, natural dispersion of physical parameter at such a choice does not allow *a priori* judge about exact substance amount. Nevertheless, the

generator construction provides for stable parameters of the obtained aerosol particles. Normalized size distributions of colophony particles, generated at different vapor source powers and condensation delay times are shown in Fig. 4.

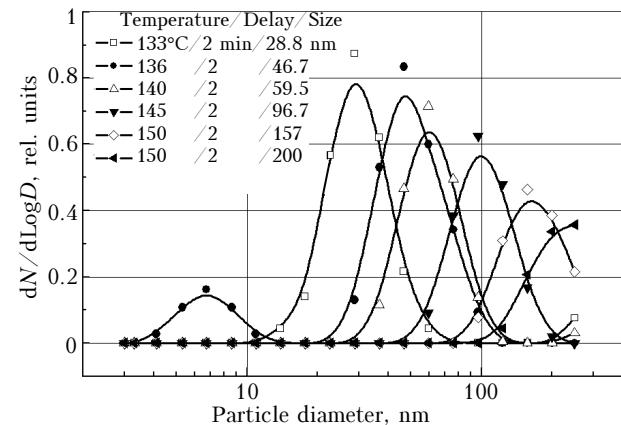


Fig. 4. Normalized size distribution of colophony particles, generated at different vapor source powers and condensation delay times.

Thus, stable generation of colophony particles of 30–200 nm in size with mass concentration of about 1 $\mu\text{g}/\text{m}^3$ was reached. The standard deviation of particle number density within a half-hour measurement run did not exceed 8.4%.

Conclusion

The generator of low-volatile vapors of wide class of substances has been designed. Its principle of operation is based on the injection of a certain amount of saturated vapor into the used airflow. An error of vapor content measurements by the water-absorption method has been determined; it is less than 10% in the range of mass concentrations from 10 to 3000 ng/m^3 . The use of the generator as a stabilized thermal-condensation source of aerosol particles has allowed the generation of colophony particles with an average size of 30–200 nm and mass concentration of about 1 $\mu\text{g}/\text{m}^3$.

References

1. G.V. Rosenberg, Izv. Akad. Nauk SSSR. Fiz. Atmos. Okeana **19**, No. 3, 56–59 (1983).
2. A.N. Ankilov, A.M. Baklanov, A.L. Vlasenko, A.S. Kozlov, and S.B. Malyshkin, Atmos. Oceanic Opt. **13**, Nos. 6–7, 597–601 (2000).
3. *Element Properties*. P. 1 (Metallurgiya, Moscow, 1976), 600 pp.
4. *Guide for a Chemist*. Vol. I. (Khimiya, Leningrad, 1966), 1072 pp.
5. N.A. Fuks, *Aerosol Mechanics* (USSR Academy of Sciences Press, Moscow, 1955), 351 pp.