

Measurements of aerosol absorption of the 694.300 nm radiation in the atmospheric surface layer

V.S. Kozlov, M.V. Panchenko, A.B. Tikhomirov,* and B.A. Tikhomirov

Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk
**Tomsk State University*

Received May 15, 2002

The absorption efficiency (the mass absorption coefficient) of radiation of wavelength 694.300 nm by the soot aerosol in air ($\alpha = (3.36 \pm 1.67) \text{ m}^2/\text{g}$) is determined based on the results of synchronous measurements of the aerosol absorption coefficient, using an optoacoustic spectrometer with a pulse ruby laser, and the mass concentration of soot in air, using an aethalometer. A concentrator of acoustic pulse energy, consisting of two parabolic mirrors, was used as a part of the optoacoustic detector in order to gain the threshold sensitivity to the absorption coefficient $k_\lambda^{\text{min}} = 6.8 \cdot 10^{-10} \text{ cm}^{-1}$ at the laser pulse energy 30 mJ and the air pressure 760 Torr in the cell.

In recent years, great interest has been expressed to experimental studies of absorbing characteristics of the atmospheric aerosol in visible and near infrared spectral ranges.¹⁻⁸ The importance of such studies is primarily connected with strong influence of soot, as a basic absorbing component of aerosol particles, on radiation transfer in the atmosphere and a change of climate.^{1-3,6}

On the Jacobson data,⁷ the soot aerosol (containing the crystal carbon) makes a greater contribution into the global warming than methane and ranks next to carbon dioxide.

According to the paper by Hansen and coauthors,⁸ the control over soot particles in the atmosphere for purposes of studying their effect on the climate is possibly even more necessary at present time than the control over CO₂ content. Therefore, high-precision experimental data on the aerosol absorption coefficient, obtained under conditions of the real atmosphere for visible and near infrared spectral ranges, are of significance in improvement of radiation and climatological models.

Note, that the short-wave radiation absorption by the soot aerosol is characterized by the absorption efficiency $\alpha \leq 20 \text{ m}^2/\text{g}$.⁵ For correct and informative investigations of aerosol absorption under natural conditions, the instrumentation is required providing measurements of spectral values of the aerosol absorption coefficient at the threshold sensitivity $k_\lambda^{\text{min}} \leq 10^{-8} \text{ cm}^{-1}$. Therefore, the experimental results obtained in this field and available in the literature are few in number and insufficient for the reliable radiation-climatic estimates.⁵

In Ref. 9 we presented the results of experimental investigations of weak nonresonance absorption of the ruby laser radiation by the atmospheric air and by the mixture of H₂O with nitrogen. It was determined that for the H₂O – nitrogen mixture the measured value of the molecular absorption coefficient at $\lambda = 694.300 \text{ nm}$, corresponding to the selective H₂O absorption minimum of the frequency-tuned ruby laser radiation, coincided

with the calculation results within the measurement error. At the same time, the results of similar studies of the atmospheric air indicated that the measured value of the absorption coefficient exceeded greatly the calculated value of the molecular absorption coefficient.

Simultaneous measurements of the soot mass concentration in air and the radiation absorption coefficient at $\lambda = 694.300 \text{ nm}$ have shown¹⁰ that the observed excess of the measured absorption coefficient over the value of the molecular absorption coefficient is due to the presence of absorbing aerosol in air. The experiment was conducted with the use of two instruments. With the aethalometer located at the aerosol station of IAO SB RAS (<http://aerosol.iao.ru>), we measured the soot mass concentration in the atmosphere. The ruby laser radiation absorption coefficient was measured using the pulse optoacoustic (OA) spectrometer with time resolution of the signal.

The drawbacks of these measurements¹⁰ are the following. The spectrometer and aethalometer were located in different rooms of the building at a distance of 100 m apart. The procedures of the air intake in the instrument cells were not completely synchronized. This resulted in some decrease of cross-correlation of the parameters under study. The correlation coefficient R did not exceed 0.8. Threshold sensitivity of the OA spectrometer by the absorption coefficient was $k_\lambda^{\text{min}} \sim 10^{-8} \text{ cm}^{-1}$, that was only 5–7 times lower than the values of the aerosol absorption coefficient. Such sensitivity was due to compilation of 25 OA signals in the computer memory that increased the time of measurements.

The goal of our work was to find the efficiency of aerosol absorption of radiation at $\lambda = 694.300 \text{ nm}$ by the air soot aerosol. Simultaneous measurements of the aerosol absorption coefficient with the ruby laser OA spectrometer and the soot mass concentration using the aethalometer were carried out during the fall-winter period of 2001.

The problems to be solved were:

- to bring the threshold sensitivity of the OA spectrometer to $k_{\lambda}^{\min} \sim 10^{-10} \text{ cm}^{-1}$;

- to optimize the air sampling through the aethalometer filter and the OA detector cell so that to provide the synchronization conditions of measurements with the two instruments:

- to conduct the measurements with the air sampling at one point.

The real time measurements of the soot mass concentration M_S [$\mu\text{g}/\text{m}^3$] in air were carried out using the optical meter,¹¹ analogous by the principle of operation to the aethalometer-type instrument developed by Hansen and coauthors.¹² Its operation consists in continuous measurements of diffuse light extinction by an aerosol particle layer directly during the process of the particle deposition on the filter from the delivered air. In this case the magnitude of the recorded diffuse light extinction by the particle layer is directly proportional to the surface soot concentration on the filter and, hence, the soot mass concentration in air.¹³ The applicability of the technique to measuring the absorbing aerosol concentration is justified by the results of theoretical and experimental investigations^{12,13} and is based on the fact that the radiation extinction by the particle layer, deposited on the diffusely scattering filter, is determined by the particle absorptance and is independent of the particle scattering characteristics.

The results of numerous studies of absorbing characteristics of the atmospheric aerosol submicron fraction over a period of two last decades (see, e.g., Refs. 1–4) testify that the main absorbing component in the composition of fine aerosol in the short-wave spectral range is the soot component revealing the typical nonselective absorption spectrum in the wide wavelength range up to the near and middle infrared ones. Other basic components of the atmospheric submicron aerosol (ammonium sulfate, organic matter, water) are unlikely to absorb in the visible range, i.e., in the submicron aerosol the soot is a dominating radiation absorber. Some contribution to the aerosol absorption in the visible range can be made by a coarse aerosol fraction of dust particles of more than $1 \mu\text{m}$ size. However, the mass absorption coefficient of such particles is almost by three orders of magnitude lower than the soot absorption coefficient, and, as is shown in the literature,⁴ the dust contribution to the absorption can reach 10–25% only under conditions of high-power dust storms in arid zones.

Thus if the intake of the coarse particles to the recording meter is limited, then the magnitude of the aerosol absorption depends only on the soot content in aerosol and, hence, the measurements present the information only on the soot absorbing characteristics. Note that in the considered aethalometer the coarse aerosol of more than $1 \mu\text{m}$ size is mainly deposited in an input hose of an air pipe line of the instrument. The block diagram of the meter is given in Fig. 1.

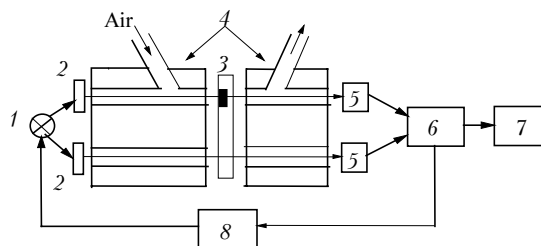


Fig. 1. The aethalometer block diagram: a halogen lamp 1; diffuse scatterers 2; aerosol filter 3; optical cell 4; photodiodes 5; signal converter 6; computer 7; the lamp power unit 8.

A halogen quartz lamp of 100 W power was used as a radiation source. The light from the halogen lamp came through a light pipe to the diffuse scatterers and uniformly illuminated two segments on the aerosol filter of AFA-Kha-20 type mounted in the optical cell of the meter. The light fluxes passed through the measuring and reference optical channels were recorded by photodiodes. Air was pumped through the filter section in the measuring channel and the soot was deposited on it. The filter section in the reference channel during measurements was not “exposed” and remained clean. The signal converter operates by the differential scheme and, in the course of the filter blackening at particle deposition, continuously measures the signal difference between the measuring and reference channels. Then the difference signal is converted from the voltage to the frequency with the subsequent digital coding using a 16-bit pulse counter. Then the digital information comes to the computer for processing and documentation. The air soot concentration is calculated by the program, which also controls the automated operation of the meter through setting the duration of a single air intake and the time between air intakes.

In contrast to its analogues, the aethalometer¹¹ measures in the pulse mode with a periodic switching-on and switching-off of the source lamp with 1 Hz frequency. A crystal oscillator of a stable frequency being a part of the signal converter controls the pulse mode of the radiation source and provides its synchronous operation with the electronic-recording circuit of the meter. The developed system of the signal processing and recording accumulates the difference pulses in the “light” and “dark” intervals and their subsequent subtraction. Realization of the pulse mode of the measurements together with procedures of accumulation and subtraction of pulses enabled us to increase the meter sensitivity, stability, and reproducibility of results, as well as to exclude to a great extent the influence of temperature background effects. The meter’s design allows regular pulse matching of levels of the measuring and reference signals (balancing) through smooth inserting of attenuator in a reference light channel, as well as separate measuring of the initial optical signal in a measuring channel (calibration of a zero signal). Procedures of the on-line calibrating of the zero signal and the meter balancing create optimal conditions for time stability of the aethalometer sensitivity.

The absolute calibration of the aethalometer for measurements of the soot mass concentration is based on a comparison of data of synchronous optical and gravimetric measurements.¹⁴ In the calibration we used 50–200 nm soot particles formed during pyrolysis of butanol vapor in the nitrogen atmosphere at 1150°C. Figure 2 shows the calibration dependence of a signal of the diffuse light extinction on the soot mass concentration (for 18 different in intensity generation regimes). On its basis the aethalometer calibration constant $K = (16.1 \pm 3.2) \text{ cm}^2/\mu\text{g}$ was determined (for more detail, see Ref. 14).

The quantitative estimates (methodically close to those described in Ref. 14) indicate that the electronic recording circuit of the aethalometer with regard to the value of the calibration constant makes it possible to record the minimal surface soot concentration on the filter of about $1.5 \text{ ng}/\text{cm}^2$. This means that when pumping through the filter section about 35 liters of air, the minimal recorded concentration (the meter sensitivity) is about $0.02 \mu\text{g}/\text{m}^3$. To increase the meter sensitivity, we have to increase the air volume pumped through the filter. In its turn, the upper boundary of the measurement of great soot concentrations is limited by reaching the values of the surface soot concentration on the filter about $8 \mu\text{g}/\text{cm}^2$ (Ref. 14) In this case, at the intake of 35 liters of air, the values of the soot concentration up to $110 \mu\text{g}/\text{m}^3$ are permissible. The upper limit of measurements can be increased at the cost of a decrease of the air intake volume.

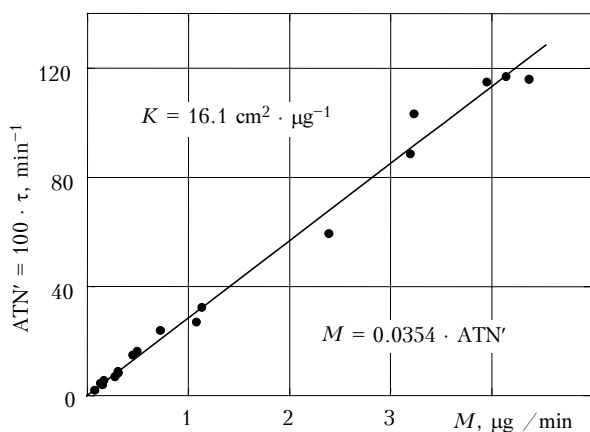


Fig. 2. Comparison of data of gravimetric measurements (intensity of soot formation M , $\mu\text{g}/\text{min}$) and synchronous optical measurements (intensity of the aethalometer signal increase ATN').

This paper describes the measurements of the air soot concentration carried out with the periodicity 15 min and the air intake duration 7 min. The rate of pumping equal to 3 liters per minute was determined before the start of the air intake. Such a duration and the rate of pumping were found to be optimal for the meter operation as a result of long-term use of the aethalometer at the aerosol station of the Institute of Atmospheric Optics SB RAS.¹⁵ The aethalometer was

located in a working room of the Institute of Atmospheric Optics (the east outskirts of Tomsk). The outside air entered the filter section through the hose from the intake pipe located at the 3 m height above the ground.

The measurements of coefficient of aerosol absorption of radiation at $\lambda = 694.300 \text{ nm}$ in air were performed using a pulse OA spectrometer with the time resolution of signals. The detailed description of the spectrometer is given in Ref. 9. In this paper, for the purpose of increasing the OA spectrometer sensitivity,^{9,10} the cell of 30 cm length and 20 cm diameter was equipped with the concentrator of the acoustic pulse energy. In the design of the cell (Fig. 3), the concentrator consists of two parabolic mirrors. The axis of the laser radiation beam coincides with the focus axis of cylindrical paraboloid with a focus of 10 mm and length of 150 mm. The acoustic pulse, generated in the cell as the result of absorption of a part of radiation by air and reflected from the surface of the cylindrical paraboloid, was directed to a spherical paraboloid with focal length of 100 mm and reflecting area of $150 \text{ mm} \times 114 \text{ mm}$. At the focus of the spherical paraboloid, a half-inch condenser microphone MK-201 ("Robotron") was located, which recorded pressure pulses enhanced as a result of reflection from the mirrors.

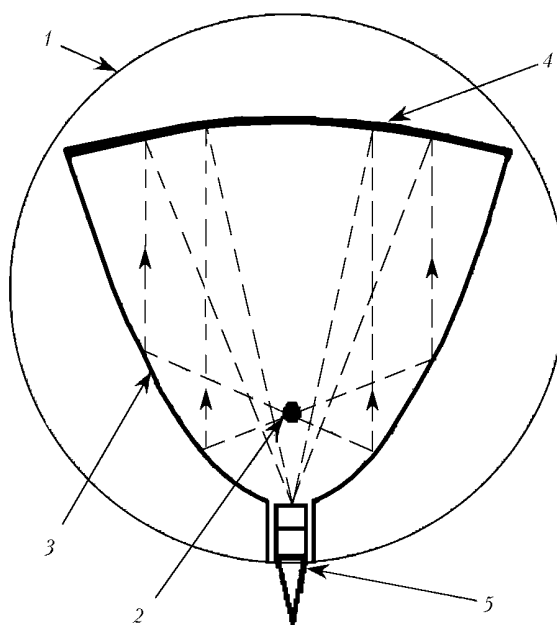


Fig. 3. Design of the OA-spectrometer cell with the concentrator of acoustic pulse power: the OA cell block 1; laser beam 2; cylindrical paraboloid 3; spherical paraboloid 4; microphone 5.

The sensitivity α_1 of the OA spectrometer in the preceding measurements^{9,10} was $(2.8 \pm 0.6) \cdot 10^6 \text{ V} \cdot \text{cm} \cdot \text{J}^{-1}$. The spectrometer was calibrated by the absorption in the H_2O absorption line maximum at $\lambda = 694.380 \text{ nm}$. For this purpose, the experimental data on the H_2O absorption line parameter at $\lambda = 694.380 \text{ nm}$ were used taken from Ref. 16. The value of the effective absorption coefficient (see Ref. 9) was calculated in the absorption

line maximum with the use of the program package.¹⁷ Relative error of determining the constant calibration α_1 was 23%. Using this technique, in the present work we obtained the value of the spectrometer's sensitivity $\alpha_2 = (3.7 \pm 0.9) \cdot 10^7 \text{ V} \cdot \text{cm} \cdot \text{J}^{-1}$ at the atmospheric pressure.

The increase of the spectrometer's sensitivity is attributed to the following factors. Figure 4 shows the oscillogram of an electric signal of OA detector. We see that the amplitude of an enhanced acoustic pressure pulse (in Fig. 4 it is denoted by 2) exceeds the amplitude of the original pulse by a factor of 5 (1). In the experiments^{9,10} the laser beam was at $\sim 2 \text{ cm}$ distance from the microphone that enabled us to separate the spurious pulse stipulated by the incidence of the scattered radiation to the microphone from the useful pulse. When using the filter section with the concentrator and operating with an amplified pulse, the effect of a spurious pulse does not appear. A laser beam is at the focus of the cylindrical paraboloid at a distance of 1 cm from the microphone that enabled us to increase the sensitivity of OA spectrometer further by about a factor of 2.8. The obtained estimate of the sensitivity increase by a factor of 14 is in a good agreement with results of calibration of spectrometers with different cells: $a_2/a_1 = 13.2$.

The increase of the spectrometer's sensitivity made it possible to obtain the minimally measurable absorption coefficient $k_\lambda^{\text{min}} = 6.8 \cdot 10^{-10} \text{ cm}^{-1}$ with storing 10 OA signals at the laser pulse power $E = 30 \text{ mJ}$. This value of the threshold sensitivity by the absorption coefficient was determined based on a comparison of the OA signal amplitude, corresponding to the coefficient of molecular absorption of the ruby laser radiation by water vapor at the center of H_2O absorption line (694.380 nm), with the detector noise level $U_m = \pm 2.5 \text{ mV}$.

The air sampling in the OA spectrometer cell and in the aethalometer cell was performed from one point. The air flow rate in the pumping was 10 l/min. The air delivering to the OA cell started 3 minutes before the start of the air delivering to the aethalometer and continued 10 min. In this case the correlation between the readings of the instruments was the best.

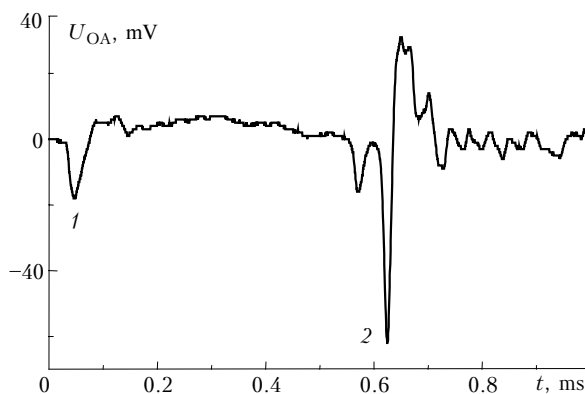


Fig. 4. Time development of OA detector signal generated in the cell with parabolic reflectors of an acoustic pulse.

Figure 5 shows the dependence of the radiation absorption coefficient at $\lambda = 694.300 \text{ nm}$ on the soot mass concentration obtained with the use of the above-mentioned instrumentation system. The experimental results are approximated by the linear dependence with the correlation coefficient $R = 0.97$. The efficiency of the radiation ($\lambda = 694.300 \text{ nm}$) absorption by the air soot aerosol, determined from this dependence, was $(3.36 \pm 1.67) \text{ m}^2/\text{g}$. The error of the determination includes the errors of calibration of the spectrometer (23%) and aethalometer (20%), as well as the approximation errors ($0.23 \text{ m}^3/\text{g}$). The residual absorption in the absence of soot in air, seen in Fig. 5, is caused by water vapor. The measured coefficient of molecular absorption of radiation by water vapor is $k_{\text{H}_2\text{O}} = 5.02 \cdot 10^{-8} \text{ cm}^{-1}$. This value agrees well with the calculated value of the molecular absorption coefficient $k_{\text{H}_2\text{O}(\text{calc})} = 4.85 \cdot 10^{-8} \text{ cm}^{-1}$ at the absolute humidity of the air under study $\rho_{\text{H}_2\text{O}} = 6.26 \text{ g}/\text{m}^3$.

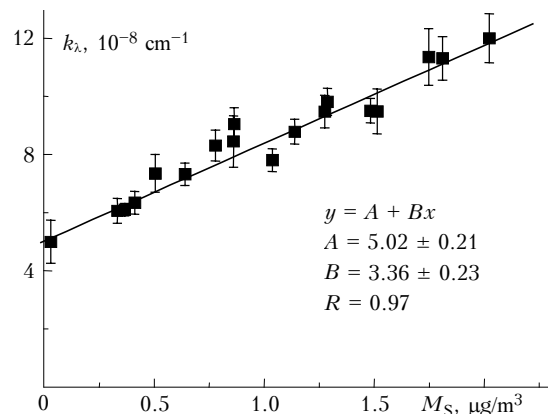


Fig. 5. The dependence of the radiation absorption coefficient at $\lambda = 694.300 \text{ nm}$ on the soot concentration in the atmospheric air. Straight line is the result of linear approximation (with the correlation coefficient R).

Figure 6 shows the change of the air soot content and the aerosol absorption coefficient in time. When constructing the time dependence of the aerosol absorption coefficient, the contribution of the radiation absorption by water vapor was excluded. The latest in time points on the plots (Fig. 6) correspond to the readings of instruments when the air intake in the cells was performed through the aerosol filters. As is seen, time behaviors of the aerosol absorption coefficient and the soot concentration agree well.

The vertical lines in Fig. 5 and Fig. 6 show maximal deviation of the values of the absorption coefficient measured by OA technique under the action of one laser pulse from the values of the absorption coefficient obtained as the result of the data averaging over 10 laser pulses.

In Ref. 5 authors used the aethalometer to measure the soot concentration and the resonance OA spectrometer with an AlGaInP-diode laser to measure the radiation absorption coefficient ($\lambda = 685 \text{ nm}$) by the soot aerosol – crystal carbon (black carbon⁵) in air.

Depending on the time (series) of measurement, the value of α at $\lambda = 685$ nm varied from 4.14 to 10.51 m^2/g . Based on the analysis of the data totality, the authors have found $\alpha(685 \text{ nm}) = 5 \text{ m}^2/\text{g}$ to be the most certain. The obtained value of the efficiency of the ruby laser radiation absorption by the soot aerosol in air is less than that obtained in Ref. 5 at $\lambda = 685$ nm.

One of possible reasons of the discrepancy between the values of α for close wavelengths $\lambda = 685$ nm and $\lambda = 694$ nm can be due to the fact that the use of a high-sensitive resonance OA detector for recording the weak aerosol absorption does not allow one to completely eliminate the contribution to OA signal from the absorption of radiation scattered in the air volume by the cell walls. From the analysis of the results of their own measurements and data of other investigations of aerosol absorption by the method of resonance OA spectroscopy the authors of Ref. 5 have found that the aerosol absorption efficiency in the region from 400 nm to 1000 nm depends on the radiation wavelengths as $\alpha \sim \lambda^{-2.7}$. Such spectral behavior of the aerosol absorption efficiency differs greatly from the data of Ref. 6, the authors of which have obtained the dependence $\alpha \sim \lambda^{-1}$ based on the filter measurements.

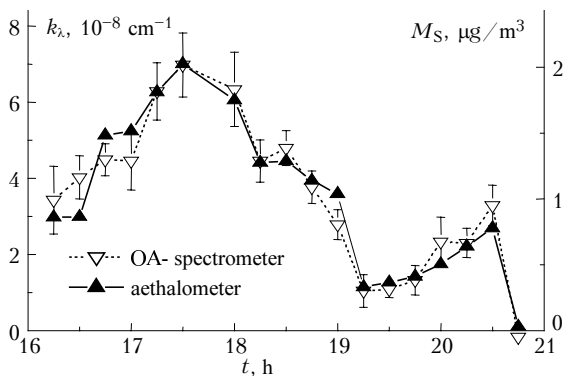


Fig. 6. The data on synchronous measurements of the fine soot aerosol concentration (M_S) and the aerosol absorption coefficient of radiation at $\lambda = 694.300$ nm (k_λ) in the air by the methods of diffuse extinction (aethalometer) and OA laser spectroscopy (OA spectrometer), respectively.

One of the merits of the pulse OA spectrometers with time resolution of signals is the possibility to record the useful signal from the radiation absorption by a gas under study against a zero background. In this connection, of great interest is to measure the efficiency of aerosol absorption of pulse radiation at other wavelengths with the use of the OA method with time resolution of signals and to determine the spectral dependence $\alpha(\lambda)$ under atmospheric conditions. We plan to conduct such measurements in the near future using YAG-laser for radiation of wavelengths 1064 and 532 nm.

Acknowledgments

The authors thank K.M. Firsov for computer programs presented for the calculation of the effective molecular absorption coefficient.

This work was supported by the Russian Foundation for Basic Research (Grants No. 00-05-65204 and No. 02-05-06121).

References

1. G.V. Rosenberg, *Izv. Akad. Nauk SSSR, Ser. Fiz. Atmos. Okeana* **15**, No. 12, 1280–1292 (1979).
2. G.V. Rosenberg, *Izv. Akad. Nauk SSSR, Ser. Fiz. Atmos. Okeana* **18**, No. 11, 1192–1198 (1982).
3. Yu.S. Lyubovtseva, U.I. Yudin, and L.G. Yaskovich, in: *Atmospheric Optics and Aerosol* (Nauka, Moscow, 1986), pp. 65–81.
4. A.D.A. Hansen, V.N. Kapustin, V.M. Kopeikin, D.A. Zhilet, and V.A. Bodein, in: *Soviet-American Experiment on Research of Arid Aerosol* (St. Petersburg, 1992), pp. 84–90.
5. H. Moosmuller, W.P. Arnott, C.T. Rodgers, J.C. Chow, C.A. Frazier, L.E. Sherman, and D.L. Dietrich, *J. Geophys. Res.* **103**, No. 21, 28149–28157 (1998).
6. R.W. Bergstrom, P.B. Russel, and P.J. Hignett, *J. Atmos. Sci.* **59**, 567–577 (2002).
7. M.Z. Jacobson, *Nature* **409**, 695–697 (2001).
8. J. Hansen, M. Sato, R. Ruedy, A. Lavis, and V. Oinos, *Proc. Nat. Acad. Sci. USA* **97**, 9875–9880 (2000).
9. B.A. Tikhomirov, A.B. Tikhomirov, and K.M. Firsov, *Atmos. Oceanic Opt.* **14**, No. 9, 674–680 (2001).
10. V.S. Kozlov, M.V. Panchenko, A.B. Tikhomirov, and B.A. Tikhomirov, in: *Abstracts of Reports at VIII Joint International Symposium on Atmospheric and Ocean Optics. Atmospheric Physics*, Irkutsk (2001), pp. 181–182.
11. M.V. Panchenko, V.S. Kozlov, S.A. Terpigova, V.P. Shmargunov, and V.V. Burkov, in: *Proc. of the Tenth ARM Science Team Meeting*, San-Antonio, Texas, 13–19 March 2000, <http://www.arm.gov/does/documents/technical/conf-0003/panchenko-mv.pdf>.
12. A.D.A. Hansen, H. Rosen, and T. Novakov, *Sci. Total Environ.* **36**, No. 1, 191–196 (1984).
13. H. Rosen and T. Novakov, *Appl. Opt.* **22**, No. 1, 1265–1267 (1983).
14. A.M. Baklanov, V.S. Kozlov, M.V. Panchenko, A.N. Ankilov, and A.L. Vlasenko, *J. Aerosol Sci.* **29**, Supp. 1, 919–920 (1998).
15. V.S. Kozlov, M.V. Panchenko, A.G. Tumakov, V.P. Shmargunov, and E.P. Yausheva, *J. Aerosol Sci.* **28**, Supp. 1, 231–232 (1997).
16. I.S. Tyryshkin, "Investigation of broadening of atmospheric water vapor lines in the visible range by the method of high resolution laser spectroscopy," Author's Abstract of Cand. of Phys.-Math. Sci. Dissert. Tomsk, IAO SB RAS (1988), pp. 19.
17. A.A. Mitsel, I.V. Ptashnik, K.M. Firsov, and B.A. Fomin, *Atmos. Oceanic Opt.* **8**, No. 10, 877–850 (1995).