Retrieval of size distribution for urban aerosols using multispectral optical data

M Kocifaj and H Horvath
Institute for Experimental Physics, University of Vienna, Boltzmangasse 5, 1090 Wien, Austria
E-mail: kocifaj@ap.univie.ac.at

Abstract. We are dealing with retrieval of aerosol size distribution using multispectral extinction data collected in highly industrialized urban region. Especially, a role of the particle morphology is in the focus of this work. As well known, at present, still many retrieval algorithms are based on simple Lorenz-Mie’s theory applicable for perfectly spherical and homogeneous particles, because that approach is fast and can handle the whole size distribution of particles. However, the solid-phase aerosols never render simple geometries, and rather than being spherical or spheroidal they are quite irregular. It is shown, that identification of the modal radius $a_M$ of both, the size distribution $f(a)$ and the distribution of geometrical cross section $s(a)$ of aerosol particles is not significantly influenced by the particle’s morphology in case the aspect ratio is smaller than 2 and the particles are randomly oriented in the atmospheric environment. On the other hand, the amount of medium-sized particles (radius of which is larger than the modal radius) can be underestimated if distribution of non-spherical grains is substituted by system of volume equivalent spheres. Retrieved volume content of fine aerosols (as characterized by PM$_{2.5}$ and PM$_{1.0}$) can be potentially affected by inappropriate assumption on the particle shape.

1. Introduction
Knowledge of the size and chemical composition of aerosols is important to assess their role in several processes occurring in the atmosphere. The aerosol environment represents a mixture of anthropogenic, industrial or bio-aerosols, which may differ in optical, physical and chemical properties. Specifically, often the main constituents of atmospheric aerosols are inorganic ions, carbonaceous material, crustal elements and water (Moya et al., 2004). A substantial fraction of aerosols can be composed of solid materials (Arimoto et al., 1997). This implies non-spherical particle shapes and corresponding size distribution, shape distribution, and an orientation distribution as well. Airborne particles are therefore of complex morphology and do not have smooth spherical surfaces (Shi et al., 2001).

The scattering and absorption of solar radiation by such aerosol particles significantly attenuates the direct component of ground reaching solar irradiance. The attenuation is characterized by aerosol optical thickness $\tau_a$, widely used in atmospheric optics and radiation measurements (Latha et al., 2003). The quantity $\tau_a$ is an appropriate indicator of air pollution’s density and spatial distribution over extended areas (Schäfer et al., 2002). In the last years,
there is an urgent need to determine variation of aerosol concentration, extinction and optical thickness, especially in the urbanized areas (Okada and Heintzenberg, 2003). But, in many cases several sources simultaneously produce different emissions including different kinds of particles, each having a specific impact on solar radiation penetrating the atmosphere. Besides, the spectral behaviour of the solar radiation attenuation depends also on the actual meteorological conditions (e.g. wind direction, or relative humidity).

Determining the aerosol size distribution from spectral extinction measurements requires the inversion of a Fredholm integral equation of the first kind. This equation gives the extinction as an integral over the size distribution with a kernel determined by scattering theory. The general description of light scattering by spherical particles is given by conventional Mie theory (Born and Wolf, 1987). Many retrieval algorithms are still based on such simple approximation, among others because Lorenz-Mie theory is fast and can handle the whole size distribution of particles. Nevertheless it is a well-established fact that scattering by non-spherical particles is generally different to that of spherical particles, so an assumption of spherical, homogeneous particles may result in errors.

2. Inverse problem for particle size distribution

Optical thickness $\tau_a$ is a complex function of aerosol’s characteristics, such as columnar size distribution $f(a)$, shape, and chemical composition

$$\tau(\lambda) = \pi \int_0^\infty Q_{ext}(a, \lambda, m) a^2 f(a) \ da,$$

where $Q_{ext}(a, \lambda, m)$ refers to the efficiency factor for extinction and $m$ is a mean particle refractive index. The extraction of information on the particle size distribution from multispectral extinction measurements is, in general, an ill-posed problem, which is notoriously difficult to solve. Such problems fail to fulfill at least the existence of a solution, the uniqueness of the solution, and the continuity of the solution on the data function. Several methods were developed to solve such inverse tasks, although no general rules can be formulated. The singular-function theory or eigenfunction theory (Box et al., 1992) are well-applicable. But one must be aware that the extinction is usually measured in a restricted spectral region $\lambda \in (\lambda_1, \lambda_2)$. An inversion of the measured data will therefore produce a distribution function $f(a)$ restricted in particle size: $a_1 \rightarrow a_2$. Here Eq. (1) represents a mapping in a Hilbert space from $L^2[\lambda_1, \lambda_2]$ to $L^2[a_1, a_2]$ constructed over the set of quadratically integrable and continuous functions $f(a)$. If measured extinction data cover the visible spectrum range, the size distribution $f(a)$ can be successfully retrieved in the submicron region.

Fast calculation of the efficiency factor $Q_{ext}(a, \lambda, m)$ is based on rigorous Mie’s theory (Bohren and Huffman, 1983). The kernel of the integral equation (1) can be transformed into a product-type kernel when the anomalous diffraction approximation is accommodated (Franssens, 2001). Then the efficiency factor for the extinction depends exclusively on the ratio of $a/\lambda$ (Schmeidler, 1955). For such kernels, the Mellin transform can be employed to simplify the solution of the integral equation (1) (Kocifaj et al., 2001). However, it is important to obtain the data concerning $\tau_a(\lambda)$ in the domain of its maximum. Shiffrin and Perel’man (1964) have shown that the procedure can be applicable if: i) the relative error of the measured data is about 1-5%, ii) the particle polydispersive system has not too narrow distribution, and iii) the measured extinction data cover the region containing a main mode of $\tau_a(\lambda)$.

Irregularities of the solid-phase atmospheric aerosols causes major difficulties when inverting multispectral extinction data. The kernel of the integral equation (1) then employs a quite complex form and must be obtained by extensive numerical calculations (including orientational averaging). The Fredholm integral equation can be split into a system of linear equations

$$\tau_a(\lambda_i) = A_{ij} f_j + \epsilon,$$

where $\epsilon$ is the error in the data.
where \( A \) is a matrix of type \( A_j(\lambda_i) \) and \( \epsilon \) is an error which arises due to the difference between the measured \( \tau^M_\lambda \) and theoretical \( \tau_\lambda(=\sum A_j f_i) \). We applied an adapted Tikhonov’s regularization (Kocifaj, 2004) to solve the integral equation (1). This method has been proven to be useful for spherical particles and the only difference is a different kernel for the particles of a non-spherical shape.

3. Optical measurements and data processing

3.1. The locality

The city of Bratislava (south-west Slovakia) was selected as investigation area because it is located in a high industrialised region with an air pollution and solar radiation monitoring station. Bratislava, capital of Slovakia, has a variable weather caused by the general circulation of the atmosphere in Central Europe and by orographical deformation of the surrounding terrain. Bratislava is situated in the boundaries of warm and mild warm climatic zone on the both banks of the river Danube in the contact territory among Podunajská lowland, Small Carpathian Mountains and Zhorská lowland.

The characteristics of aerosol were systematically collected, since 1991, in order to characterize the optical properties of an urban atmosphere. The measurements were performed during the whole year (under clear sky conditions) except December. The number of the data available in December was less than one half of the number of the data available for any other month during year. Most often, air mass in Bratislava corresponded to continental polar (cP, the probability of its occurrence is approximately 54%), or to maritime polar (mP, with 34% occurrence). The probability of continental tropic air mass is very small (about 5%). Such air mass can be observed during winter (its origin is mostly in north-eastern Africa or Arabian peninsula), or during summer (coming from Balkan region or middle Asia). Other situations (corresponding to other types of air mass) were highly infrequent.

3.2. Instrumentation

The measurements of the spectral direct solar radiation ware made with the multiwavelength solar spectral photometer model SPM 1040. The instrument operates at six narrow band filters. The effective wavelengths of the individual filters are: 377, 406, 520, 599, 749 and 857 nm. A few measurements were made under suitable atmospheric conditions to monitor aerosol environment during transformation of air mass and during the change of the air masses. The Smithsonian long method (Liou, 1980) was applied to get the instrumental solar constant. To calibrate the instrument we selected days with the aerosol characteristics almost stable during some hours (Lučák and Kocifaj, 1995). All measurements were made in the spectral bands with no water vapour influence. The total ozone absorption was computed using the UV radiation data collected at station Poprad-Gánovce.

Periodic calibrations of the instrument limited the uncertainty of the solar constant to 2-3%. The actual meteorological data (such as air pressure, or temperature) were measured to minimize an error of the Rayleigh component of atmospheric optical thickness. In average, the error margin of the aerosol optical thickness was approximately 4%.

3.3. Aerosol properties

Air quality in respect to aerosol contamination is often characterized in terms of \( PM_{2.5} \) (fine fraction) and \( PM_{10-2.5} \) (coarse fraction) (Farinha et al., 2004, Harrison et al., 2003). From the health point of view, particulate matter in the fine mode is of great concern (Gokhale and Patil, 2004) and these particles also typically dominante in the industrial region of Bratislava city.

Optical constants, chemical composition, shape and size distribution of aerosol species depend significantly on the source of pollution (primary particles). Secondary particles can also be emitted indirectly as a result of chemical reactions of polluting gases in the air (Pomeroy et al.,
2000). In Bratislava city, the largest contribution of primary particles arise from the combustion
products of road traffic and industry. Acid rain also forms the urban smog.

The station, at which experimental data were collected, is located approximately 3.5 km
north-west from Bratislava center. Within the 5 km radius of the station, 30% of land is
parkland and wasteland with grass and plants, 35% is urban and suburban housing with roads
and 35% is woodland mainly deciduous. The approach to the motorway (via Prague) is only
200 m from the measurement site.

**Figure 1.** Columnar distribution of geometrical cross section $s(a) \sim a^2 f(a)$ as calculated
from measured aerosol optical thickness data (collected in Bratislava city during June 16,
1993). The standard mean square-root error of $\tau_a$ is approx. 8%. The dashed curves cor-
respond to distribution of non-spherical particles (aspect ratio 1.4), while solid curves were
obtained for volume equivalent spheres.

**Figure 2.** Volume aerosol distribution function $v(a) \sim a^3 f(a)$ recalculated for the
whole atmosphere (in accordance with Fig. 1). The aerosol optical thickness data were
collected in Bratislava city on June 16, 1993. The dashed curves correspond to distribution
of non-spherical particles (aspect ratio 1.4), while solid curves were obtained for volume
equivalent spheres.

Solid phase aerosols, which we are interested in, can be usually collected during summer-time.
The measurement realized on June 16, 1993 corresponds to one of the very frequent situations,
when the aerosol optical thickness correlates to the dust loading into the atmosphere. Solving
the inverse problem for the distribution of the geometrical cross section $s(a) \sim a^2 f(a)$ we
obtained a set of results for this day (Figs. 1, 2). One can see that the aerosol characteristics
were almost stable during some hours, so we do not associate individual curves to an exact time.
Results for both, spherical particles as well as irregular particles (with most typical aspect ratio
1.4, Okada et al. 1987) are depicted in the same figure. We found no serious differences between
modal radii corresponding to both particle systems. However, the distribution functions differ
in their shape and slope. The surface size distribution $s(a)$ shows a second mode at $a \approx 1.5 \mu m$
in case the aerosol environment is assumed to be composed of spherical particles. It appears
to be a typical effect of interference structure with Mie scattering functions. In contrary, size
distribution $s(a)$ found for non-spherical particles is more or less monomodal with only a slight
indication of a second mode. An occurrence of enhanced concentration of large particles (as found
for Mie spheres) evidently withdraws the amount of medium-sized particles (i.e. for $a \approx 0.4−1.0$
µm) and leads to sudden fall of $s(a)$ in this size range.

As usual, each method of regularization may give negative regions. But, if the method of regularization is suitable for the specified ill-posed problem, the errors of inversion, including the negative regions, are actually negligible (Figs. 1 and 2).

The existence of the secondary mode within size distribution function has important consequences when focusing to volume/mass distribution of aerosol particles. As shown in Fig. 2, the results obtained for irregularly shaped particles and volume equivalent spheres differ significantly in the region $r \in (1 \, \mu m, 2 \, \mu m)$. In other words, the interpretation of results for spherical particles is different from non-spherical grains when we are interested in $PM_{2.5}$ and $PM_{1.0}$. Extinction data measured in visible spectrum reflect inefficiently the changes within the aerosol system consisting of large micron-sized particles, so the resulting curves are obtained with low accuracy for $r > 1 \, \mu m$ (Fig. 2). Although the sensitivity of the presented method goes rapidly down with growing of particle size, there is no doubt about a potential impact of particle shape on retrieval of microphysical characteristics of fine aerosols (corresponding to $PM_{1.0−2.5}$). As shown in Fig 2, a dominant contribution of $PM_{1.0}$ to $PM_{2.5}$ has been proven for irregularly shaped particles. In contrary, submicron-sized particles of the spherical shape occur to be of less importance, and significant influence in evaluation of fine fraction of aerosols is referred to $PM_{1.0−2.5}$.

4. Summary
Morphology of the solid-phase aerosols can definitely affect the retrieval of particle size distribution function when inverting multispectral optical thickness data. Particle’s irregularity eliminates the interference structure and ripple typical for Mie particles. Such matter may result in disappearance of subsidiary mode in particle size distribution, which usually occurs with spherical particles (Fig. 1). The results obtained for dust particles shown that the distribution functions for irregular grains and volume equivalent spheres differ in the shape and slope. Usually, the amount of large particles can be underestimated when non-spherical particles are substituted with Mie spheres.

Acknowledgments
This paper was supported by Project M772-N02 by the Fonds FWF.

References
Arimoto R, Ray B J, Lewis N F, and Tomaz U J 1997 *J. Geophys. Res.* **102** 15867
Bohren K, Hufmann D 1983 *Absorption and Scattering of Light by Small Particles* (New York:John Wiley & Sons)
Born M, Wolf E 1987 *Principles of Optics* (Oxford: Pergamon Press)
Box G P, Sealey K M, and Box M A 1992 *J. Atmosph. Sci.* **49** 2074
Farinha M M, Freitas M C, and Almeida S M 2004 *J. Radioanal. Nucl. Chem.* **259** 203
Franssens G R 2001 *Atmos. Environ.* **35** 5099
Gokhale S B, and Patil R S 2004 *Environ. Monit. Assess.* **95** 311
Harrison R M, Jones A M, and Lawrence R G 2003 *Atmos. Environ.* **37** 4927
Kocifaj M, Kohút I, and Zaujec P 2001 *Atmos. Environ.* **35** 5105
Kocifaj M 2004 *Contrib. Astron. Obs. Skalnaté Pleso* **34** 141
Latha K M, Badarinath K V S, Rao T V R, Reddy R R, Ahmed Y N, Gopal K R, and Azeem P A 2003 *J. Quant. Spectrosc. Rad. Transfer* **78** 257
Liou K N 1980 *An Introduction to Atmospheric Radiation* (New York, London, Toronto, Sydney, San Francisco:Academic Press)
Lukáč J, Kocifaj M P 1995 *Contr. Geoph. Inst. SAS, Ser. Meteorol.* **13** 23
Mishchenko M I, Travis L D, Kahn R A, and West R A 1997 *J. Geophys. Res.* **102** 16831
Moya M, Grutter M, and Báez A 2004 *Atmos. Environ.* **38** 5651
Okada K, and Heintzenberg J 2003 *J. Aerosol Sci.* **34** 1539
Okada K, Kobayashi A, Iwasaka Y, Naruse H, Tanaka T, and Nemoto O 1987 *J. Meteorol. Soc. Japan* **65** 515

Pomeroy N, Webber D, and Murphy C 2000 *Environ. Monit. Assess.* **65** 175

Schäfer K, Fömmel G, Hoffmann H, Briz S, Junkermann W, Emeis S, Jahn C, Leipold S, Sedlmaier A, Dinev S, Reishofer G, Windholz L, Soulakellis N, Sifakis N, and Sarigiannis D 2002 *Water Air Soil Poll.* **2** 91

Schmeidler W 1955 *Integralgleichungen mit Anwendungen in Physik und Technik* (Leipzig: AV Geest & Portig K.-G.)

Shi J P, Harrison R M, and Evans D 2001 *Atmos. Environ.* **35** 6193

Shifrin K S, and Perel’man A Ya 1964 *Optika i Spektroskopya* **16** 117