

Physical parameters of atmospheric aerosols

Regina Hitzenberger

with contributions by A. Berner, H. Horvath and W. Szymanski

1. Introduction

Atmospheric aerosols originate from a variety of anthropogenic and natural sources and are highly complex physical and chemical systems. Coarse particles (with sizes above a few micrometers) mainly come from the disintegration of bulk material (soil, plant debris, sea spray), while small particles (with sizes of a few nanometers to some tens of nanometers) either are emitted directly from combustion or some industrial processes or formed in the atmosphere by gas-to-particle conversion by chemical reactions of precursor gases. Coarse particles have short residence times in the atmosphere of the order of hours to maybe a few days and are usually only of local importance. Heavy desert dust storms or volcanic eruptions may be of more than regional importance, but they are only sporadic events. Small particles grow fairly quickly into the size range between 0.1 and 2 μm . Particles in this size range have atmospheric residence times of the order of weeks and can therefore be subject to long-range transport and attain more than regional importance. These particles scatter light most efficiently, which leads to visibility degradation in the planetary boundary layer, and because of their scattering properties, they interact with incoming solar radiation and exert a negative forcing on the global radiative balance counteracting the greenhouse effect by infrared-absorbing gases. Light absorbing particles such as black carbon (BC, see this compendium, pp. 32 ff), however, exert a positive forcing and enhance the greenhouse effect. These interactions between (anthropogenic) aerosol particles and the global radiative balance are usually termed the direct aerosol effect (IPCC 2007), while radiative forcing caused by changes in the radiative properties of clouds due to changes in cloud condensation nuclei (CCN, see below) are termed the indirect aerosol effect. Apart from their optical properties, atmospheric aerosols also have effects on human health, which depend on their chemical composition and also on particle size.

Research in the field of atmospheric aerosols has been conducted at the University of Vienna since the early 1970ies, when Othmar Preining established the Aerosol Group, which became an internationally highly respected research group both for basic aerosol science conducted in laboratory experiments and for research on atmospheric aerosols. The group is part of several international research networks and has research cooperations with scientists in Europe, the USA and in Asia (Japan, Thailand, Taiwan). Members of the group chair working groups of international bodies and participate in international

research administration efforts. Over the years, the group also was very active in instrument development. Some of the most important recent method and instrument developments are given in this chapter as well as in this compendium, pp. 32 ff.

2. Cloud condensation nuclei counter CCNC

Cloud condensation nuclei (CCN), which originate from both natural and anthropogenic sources, are a subset of the atmospheric aerosol. They provide the nuclei for cloud droplet formation under the low super-saturations of water vapour typical for cloud formation in the atmosphere (ca. 0.1–2%). An automatic Cloud Condensation Nuclei Counter (CCNC) based on the principle of a static thermal diffusion chamber (originally implemented by Twomey 1977) was developed at the University of Vienna led by Regina Hitzemberger (Giebl et al. 2002, Dusek et al. 2006). It consists of a cylindrical chamber of 1 cm height and 10 cm diameter, which is formed by two parallel plates and a glass ring. The upper plate is kept at a higher temperature than the lower plate, and both are completely wetted with a water film, so humidity is 100% at the temperatures of the plates. After flushing the chamber with the aerosol containing the CCN, the chamber is sealed and linear temperature and water vapour gradients are established, which lead to a supersaturated region at half-height of the chamber where CCN grow to droplets. The droplets are illuminated by a laser beam passing along the centre line of the chamber and a CCD camera takes pictures of the droplets at user-selected time intervals. After a measurement cycle, the chamber is flushed with fresh aerosol, then sealed again and the next measurement cycle begins. Intensive field measurement campaigns were conducted with this instrument on Sonnblick (Hitzemberger et al. 1999) and Rax (Hitzemberger et al. 2000), in the urban aerosol of Vienna (Burkart et al. 2011), and also in the exhaust of aircraft engines under different operating conditions (Hitzemberger et al. 2003).

3. Inertial Impactors

Berner low pressure impactors (BLPI)

Axel Berner started to develop of cascade impactors at the University of Vienna already in the 1970ies (Berner 1978) and is still active in this area of research and instrument development. Cascade impactors segregate the aerosol particles into several size classes according to their mass and deposit them on impaction plates covered with suitable substrates for chemical or gravimetric analysis. In an impactor stage, an aerosol flow with constant volumetric flow rate is split into one or more jets with defined velocity which are deflected by an impaction plate. Particles with masses above a certain limit can not follow

the stream lines of the flow and are deposited on the plate. Smaller particles stay airborne and are carried along with the flow. In a cascade impactor, the velocity of the jets increases from stage to stage (the number of nozzles increases, while their diameter decreases), so particles with successively smaller masses are deposited. In conventional impactors operating at atmospheric pressure, particles smaller than about $0.3\text{ }\mu\text{m}$ diameter cannot be deposited. If the pressure inside the impactor is reduced from stage to stage, however, smaller particles can be collected. Current low pressure "Berner-impactors" separate the aerosol into five to 11 size classes according to specifications. The most widely used low pressure cascade impactors cover the size range between 0.06 and $16\text{ }\mu\text{m}$ with 9 stages and operate with flow rates of 25 or 30 Lpm. Pressure drops at the stages with the lowest cut sizes can reach 0.1 atm . Impactors with higher sampling flow rates (70 Lpm; used e.g. by Hitzemberger et al. 2006) or impactors with rotating stages that create uniform deposits were also constructed (Berner et al. 1996). Measurements of mass size distributions and size distributions of chemical species are performed world wide with Berner impactors (e.g. Berner et al. 2000, Berner et al. 2004). Latest developments include high temperature low pressure cascade impactors for stack sampling (Tursic et al. 2008).

Virtual impactors

Virtual impactors are a relatively new instrument development area led by W. Szymanski at the University of Vienna. In these impactors, particles are not deposited on impaction plates, but impact on "virtual" surfaces formed by openings through which part of the aerosol flow (the minor flow) is diverted from the total flow and collected on a filter. The latest development is the cascade virtual impaction surface impactor CAVIS, which is equipped with an omni-directional sampling head and allows parallel sampling and measurement of ambient particulate matter in size classes with separation boundaries at $10\text{ }\mu\text{m}$, $2.5\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$ aerodynamic diameter for PM₁₀, PM_{2.5} and PM₁ measurements. The major flow after the last stage contains PM₁ particles which are collected on the final filter. Multiple nozzles are used in order to maintain a pressure drop as low as possible across the whole device. As only small fractions (10%) of the total flow are drawn through each filter, the filter deposits are exposed only to the small fraction of the overall flow entering the CAVI, which minimizes the possibility of chemical modification of the deposits. As the filters can be easily removed, the separated fractions can be extracted from the CAVI in the airborne state and be measured by an alternative method. The upper limit of the size measuring range is determined by the adjustment of the inlet slot on the omni-directional sampling head and can be varied from 50 to $100\text{ }\mu\text{m}$. Total flow rate through the instrument is 12.5 Lpm. In a recent study,

the CAVI was used to investigate e.g. the optical properties of PM1 aerosol in Vienna (Sabbagh-Kupelwieser et al. 2010).

4. Electrical mobility spectrometers

Vienna-type DMA

"Vienna-type DMAs" (differential mobility analyzers) have been developed at the University of Vienna by Georg Reischl since the 1980ies (Reischl 1991, Winklmayr et al. 1991) and are used all over the world. These instruments classify charged aerosol particles according to their mobility in an electric field. The instruments are based on cylindrical condensers with adjustable voltages. The aerosol is first passed through a charger to establish charge equilibrium for the particles and then introduced into the condenser in a flow parallel to the central electrode. Depending on their size and charging state, the particles migrate to the electrode and are deposited there at distances from the inlet given by their electrical mobility. At the end of the electrode a small fraction of the flow is diverted through a slit. Depending on the (adjustable) voltage, particles with a specific mobility pass through this slit and are counted either with a condensation particle counter or measured with a Faraday-cup electrometer. Scanning mobility particle spectrometers (SMPS) consist of a DMA with automatically adjusted voltage to measure the aerosol number size distribution within ca. 10–20 minutes depending on the size range. SMPS for atmospheric applications typically have an upper cut size of 1 μm and lower cut sizes around 10 nm. Other instruments measure in the size range between 10 and 100 nm (Heim et al. 2004) or in other size ranges (e.g. 5–350 nm for emission monitoring). The most recent development are DMAs for the nano-size range. The UDMA ("ultra-fine-DMA", Steiner et al. 2010) gives high resolution measurements in the ultrafine size range (1–5 nm).

Parallel differential mobility analyzer PDMA

The PDMA is an extension of a DMA which allows for a more complete characterization of airborne particles (Patent AT502207A1, WO2007016711A1: Method for classifying and separating of particles and device for carrying out said method). The PDMA consists of two DMAs. One (DMA1) acts as a scanning mobility spectrometer and records the entire size distribution of an aerosol. The other (DMA2) allows the selection of a very specific size fraction for further analytical purposes. The scanned spectra can be measured by a Faraday Cup (FC) based aerosol electrometer, or by a condensational particle counter (CPC). Moreover, a quantitative characterization and interpretation of size spectra of non-spherical particles, where the shape might influence the measurement, can be done in a straightforward way. Parallel with the scan-

ning DMA 1 which scans and delivers the complete size spectrum of the investigated particles, an identical separation unit DMA 2 is in operation and can be set to one given voltage value (separation) and used for sampling or enrichment (collection) of the one selected size class of particles, hence the acronym PDMA. The extracted particles from DMA2 can also be injected into further characterization instruments without disrupting of the operation of the scanning DMA1. The instrument was already used e.g. to analyze nanopartcles (Allmaier et al. 2008).

5. Optical methods

Dual wavelength optical particle spectrometer DWOPS

Light scattered from a particle into a given angular range is determined by three parameters – the particle size, and the real and the imaginary part of the complex refractive index. Common optical configurations of optical particle counters (OPC) consist of a single light source and a detection system measuring the light flux scattered by the particle into a defined angular range. With these OPCs, no additional information about the particle can be obtained besides its size, but even this information is limited by the need to calibrate an OPC for specific refractive indices. The Dual Wavelength Optical Particle Spectrometer (DWOPS, development led by Wladyslaw Szymanski) is a pre-prototype which measures and evaluates light from two different lasers scattered by an individual particle into four different angular ranges (10° – 30° and 150° – 170°) in the forward and backward directions with respect to the direction of propagation of each laser. This scattered light is then separated by the dichroic beam splitters according to the wavelength, measured by an appropriate detector and converted into a voltage pulse with a magnitude proportional to the amount of scattered light. This procedure yields a quadruple set of independent voltage pulses for each single particle, in contrast to conventional OPCs which measure a single pulse from every detected particle. This set of four data is then compared in real-time with a pre-computed matrix which consists of four columns. Each row in this matrix was calculated for a particle of a certain size, and a real and an imaginary part of the refractive index. A fit procedure finds a quadruple of theoretical values from the matrix which best matches the quadruple of measured values.

For spherical particles the DWOPS (Nagy et al. 2007) allows accurate particle sizing (currently from about 300–3000 nm) together with an assessment of a real (n) and an imaginary (k) part of a complex refractive index (m) with an accuracy of about 15% in the range $n = (1.2, 2.0)$ and $k = (0.0, 1.0)$. For spherical particles the DWOPS technique does not require any re-calibration when the refractive index of measured particles changes, because size and complex refractive index are measured for each detected particle.

Telephotometer

It is a well known fact that an increased load of atmospheric aerosol particles gives rise to a decrease in visibility: The particles in between the observer and a visible object attenuate the light from the object and scatter daylight, thus altering the appearance of the object and making it more similar to the background and thus less visible. The maximum distance of an object recognized is inversely proportional to the extinction coefficient of the aerosol.

The telephotometer developed at the University of Vienna by Helmuth Horvath measures in analogy of a human visibility observation. It consists of a telescope with a spectrometer attached to it and determines the radiance of a small spot of the object, the background and a reference object (Horvath 1981). From this the spectral extinction coefficient of the atmospheric aerosol can be derived. After subtraction of the Rayleigh scattering of the gas molecules the spectral extinction of the aerosol is obtained. Using an inversion procedure the size distribution of the aerosol can be inferred. An example is the growth of the particles due to increase of humidity (Horvath 1996). Combining the horizontal extinction measurement with the determination of the vertical optical depth permits the determination of the scale height of the aerosol (mixing height, Horvath et al. 2002). The majority of the optically active particles in the atmosphere is below 1 μm , thus the extinction coefficient is a good characterization of the particles in the PM₁ fraction (Sabbagh et al. 2010a, b).

6. References

- Allmaier, G., Laschober, C., and W.W. Szymanski. 2008. "Nano ES GEMMA and PDMA, new tools for the analysis of nanobioparticles – Protein complexes, lipoparticles, and viruses." *Journal of the American Society for Mass Spectrometry* 19: 1062–1068.
- Berner, A. 1978. "5-stage cascade impingement device for measuring mass-size distribution of aerosols." *Chemie Ingenieur Technik* 50: 399–399.
- Berner, A., Arends, B., and D. Schell. 2000. "The main submicron mass mode of atmospheric aerosols: Evolution and relation to clouds. A case study." *Meteorologische Zeitschrift* 9: 203–219.
- Berner, A., Galambos, Z., Ctyroky, P., Frühauf, P., Hitzenberger, R., Gomišček, B., Hauck, H., Preining, O., and H. Puxbaum. 2004. "On the correlation of atmospheric aerosol components of mass size distributions in the larger region of a central European city." *Atmospheric Environment* 38: 3959–3970.
- Berner, A., Sidla, S., Galambos, Z., Kruisz, C., Hitzenberger, R., ten Brink, H.M., and G.P.A. Kos. 1996. "Size distributions of soot and other constituents of the atmospheric aerosol." *Journal of Geophysical Research* 101: 19559–19565.

R. Hitzenberger

- Burkart, J., Steiner, G., Reischl, G., and R. Hitzenberger. 2011. "Long-Term Study of Cloud Condensation Nuclei (CCN) Activation of the Atmospheric Aerosol in Vienna." *Atmospheric Environment* 45: 5751–5759.
- Dusek, U., Reischl, G.P., and R. Hitzenberger. 2006. "CCN activation of pure and coated carbon black particles." *Environmental Science & Technology* 40: 1223–1230.
- Giebl, H., Berner, A., Reischl, G., Puxbaum, H., Kasper-Giebl, A., and R. Hitzenberger. 2002. "CCN activation of oxalic and malonic acid test aerosols with the University of Vienna cloud condensation nuclei counter." *Journal of Aerosol Science* 33: 1623–1634.
- Heim, M., Kasper, G., Reischl, G.P., and C. Gerhart. 2004. "Performance of a new commercial electrical mobility spectrometer." *Aerosol Science and Technology* 38: 3–14.
- Hitzenberger, R., Berner, A., Giebl, H., Kromp, R., Larson, S.M., Rouc, A., Koch, A., Marischka, S., and H. Puxbaum. 1999. "Contribution of carbonaceous material to cloud condensation nuclei concentrations in European background (Mt. Sonnblick) and urban (Vienna) aerosols." *Atmospheric Environment* 33: 2647–2659.
- Hitzenberger, R., Giebl, H., Berner, A., Kromp, R., Reischl, G., Kasper-Giebl, A., and H. Puxbaum. 2000. "Measurements of CCN-concentrations in the European alpine aerosol using a newly developed static thermal diffusion counter." In *Nucleation and atmospheric Aerosols 2000*, edited by B.N. Hale, and M. Kulmala. American Institute of Physics, AIP Conference Proceedings 534: 861–864.
- Hitzenberger, R., Giebl, H., Petzold, A., Gysel, M., Nyeki, S., Weingartner, E., Baltensperger, U., and W.C. Wilson. 2003. "Properties of jet engine combustor particles during the PartEmiss experiment. Hygroscopic properties at supersaturated conditions." *Geophysical Research Letters* 30: 1779.
- Hitzenberger, R., Tursic, J., Grgic, I., Berner, A., Ctyroky, P., and B. Podkrajsek. 2006. "Particle size distribution of carbon in aerosols collected in Vienna and Ljubljana." *Chemosphere* 65: 2106–2113.
- Horvath, H. 1981. "The University of Vienna Telephotometer." *Atmospheric Environment* 15: 2537–2546.
- Horvath, H. 1996. "Spectral extinction coefficients of rural aerosol in southern Italy – a case study of cause and effect of variability of atmospheric aerosol." *Journal of Aerosol Science* 27: 437–453.
- Horvath, H., Alados Arboledas, L., Olmo, F.J., Jovanovic, O., Gangl, M., Kaller, W., Sanchez, C., Sauerzopf, H., and S. Seidl. 2002. "Optical characteristics of the aerosol in Spain and Austria and its effect on radiative forcing." *Journal of Geophysical Research* 107: 4386, pp. 9-1–9-18. doi:10.1029/2001JD001472.
- Nagy, A., Szymanski, W.W., Gal, P., Golczewski, A., and A. Czitrovszky. 2007. "Numerical and experimental study of the performance of the dual wavelength optical particle spectrometer (DWOPS)." *Journal of Aerosol Science* 38: 467–478.

- Reischl, G.P. 1991. "Measurement of ambient aerosols by the differential mobility analyzer method: Concepts and realization criteria for the size range between 2 and 500 nm." *Aerosol Science and Technology* 14: 5–14.
- Sabbagh-Kupelwieser, N., Horvath, H., and W.W. Szymanski. 2010a. "Urban Aerosol Studies of PM1 Size Fraction with Reference to Ambient Conditions and Visibility." *Aerosol and Air Quality Research* 10: 425–432.
- Sabbagh-Kupelwieser, N., Horvath, H., and W.W. Szymanski. 2010b. "Correlation between the PM1 fraction of the Vienna urban aerosol, its optical parameters, size distribution and atmospheric conditions." Paper presented at the International Aerosol Conference 2010, Helsinki, September 3.
- Steiner, G., Attoui, M., Wimmer, D. and G.P. Reischl. 2010. "A medium flow, high-resolution Vienna DMA running in recirculating mode." *Aerosol Science and Technology* 44: 308–315.
- Tursic, J., Grgic, I., Berner, A., Skantar, J., and A. Cuhalev. 2008. "Measurements of size-segregated emission particles by a sampling system based on the cascade impactor." *Environmental Science & Technology* 2008, 42: 878–883.
- Twomey, S. 1977. *Atmospheric Aerosols*. New York: Elsevier Sci. Publ. Co.
- Winklmayr, W., Reischl, G.P., Lindner, A.O., and A. Berner A. 1991. "A new electromobility spectrometer for the measurement of aerosol size distribution in the size range from 1 to 1000 nm." *Journal of Aerosol Science* 22: 289–296.

Address of the Author:

Univ.-Prof. Dr. Regina Hitzemberger
 Faculty of Physics, Aerosol Physics and Environmental Physics, University of Vienna
 Boltzmanngasse 5, A-1090 Vienna