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Abstract

The atmospheric aerosol has recently attracted considerable attention due to their effects on climate, atmospheric chemistry, and health. The newly triggered activities include the development of new analytical methods for a better characterization of atmospheric aerosol particles, some of which are presented here. Emphasis is laid on the description of methods for on-line and *in situ* analysis, since the analysis of many processes requires a good time resolution, and since *in situ* analysis methods are less prone to sampling artefacts.

Introduction

An aerosol is an assembly of liquid or solid particles which are suspended in a gaseous medium long enough to enable observation and measurement. The atmospheric aerosol thus describes the system of particles suspended in our atmosphere. Generally, the diameter D of aerosol particles is in the range 0.001 - 100 μm . The ensemble of aerosol particles is also called particulate matter (PM). According to the cutoff used during sampling, a suffix is often used, thus, PM_{10} denotes all aerosol particles with an aerodynamic particle diameter $D \leq 10 \mu\text{m}$.

In analytical chemistry, many techniques involve aerosols. Examples are the nebulization of a solution or laser ablation of solid samples prior to analysis. Here, aerosol characteristics determine, to a large extent, transport efficiency and analytical behavior in atomic spectrometry [1].

Environmental impact of aerosol particles

For a long time, the atmospheric aerosol has been neglected when considering the environmental impact of anthropogenic air pollution. Recently, this situation has changed quite drastically, mainly due to three different aspects. First, the atmospheric aerosol is considered to be responsible for a negative forcing, or cooling of the earth-atmosphere system, with the potential to compensate for part of the warming from greenhouse gases [2]. However, the involved effects are still poorly quantified.

Second, aerosol particles have a strong impact on atmospheric chemistry both in the stratosphere and troposphere. Here, heterogeneous reactions on the particle surfaces provide additional sources and sinks of gaseous molecules, with strong consequences for the atmospheric composition [3].

Third, recent epidemiological studies linked higher levels of aerosol concentrations to increased health problems including increased mortality [4]. For this reason, it is currently discussed to establish a new standard for PM_{10} in Switzerland [5] as well as in other countries.

These findings have initiated a number of national and international programs. These activities include the development of new methods for aerosol analysis, since a better understanding of atmospheric particles will lead to a better understanding of their effects on our health and climate, as Johnston and Wexler state [6]. The present overview tries to address some recent developments, however, it is by far not complete.

Aerosol analysis by physical methods

Unlike in the case of a specific gas (e. g., ozone), a single number such as the concentration is not sufficient to describe the aerosol. Depending on the size distribution or the chemical composition, the aerosol may have a quite variable impact on the environment. Thus there is a need for a much more complete analysis of aerosol particles, both physically and chemically. Many physical parameters can be determined by commercial instruments on a continuous basis. Most of these instruments are described in [7], e.g. instruments for the determination of the number concentration (condensation nuclei counter, CNC), surface area concentration (epiphaniometer), an instrument developed in our laboratory [8], or mass concentration (tapered element oscillating microbalance, TEOM). Other instruments determine the size distribution based on the mobility diameter (differential mobility analyzer, DMA), the optical diameter (optical particle counter, OPC), or the aerodynamic diameter (aerodynamic particle sizer, APS). In addition, instruments determine various optical properties, such as the scattering and backscattering coefficient (nephelometer) and absorption coefficient (aethalometer).

These physical parameters play a major role in the climate forcing. A selection of these instruments has therefore been operated by our group at the Jungfraujoch (3454 m), within the framework of Global Atmosphere Watch (GAW), a program of the World Meteorological Organization. As an example, Figure 1 shows the seasonal variation of the scattering coefficient σ_{SP} , the backscattering coefficient σ_{BSP} , the absorption coefficient σ_{AP} , the number concentration, and the surface area concentration of the aerosol particles at the Jungfraujoch [9]. The data indicate a maximum in summer and a minimum in winter. The seasonal variation is about an order of magnitude except for the CN concentration, where the variation is much smaller. The same variation is found in long-term aerosol measurements at the same site [10] and is due to the seasonal variation of thermal convection induced by solar radiation [11].

Aerosol analysis by chemical methods

In contrast, very few instruments are available for the continuous determination of chemical parameters. Most chemical measurements are therefore performed off-line, after sampling the aerosol on appropriate filters or, for size segregated samples, on cascade impactor substrates [7].

Heavy metals

There are many off-line methods for the determination of atmospheric heavy metal concentrations, either directly on the sampling substrate or after suitable digestion / extraction of the sample. Regarding on-line analysis, inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS) have the potential for on-line analysis of airborne particles with detection limits in the low nanogram per m^3 range [12], however, these instruments are clearly laboratory devices and are not suited for direct field applications. Only recently, new approaches have been published demonstrating the potential for the construction of robust mobile sensors with suitable detection limits [13].

Water soluble components

Water soluble components like sulfate, ammonium, nitrate, or calcium are usually sampled on teflon filters and analyzed by ion chromatography or ICP-OES after ultrasonic extraction [14]. However, some components, such as nitrate, exhibit partitioning between gas phase (as nitric

acid) and particulate phase (mostly ammonium nitrate). In order to distinguish between gas and particle phase, either filter pack or denuder methods are applied [15]. In the filter pack method, the teflon filter is followed by one or several other filters which absorb the gaseous compounds of interest. In this method, volatilization of particulate ammonium nitrate during sampling leads to a negative artefact for nitrate, while reaction of nitric acid with previously deposited aerosol particles or with the filter material leads to a positive artefact, with opposite effects for the gas phase values of the back-up filter. In the denuder method, the filter is preceded by a tube coated with an absorbent for the gas to be measured. For laminar flow conditions, aerosol particles pass the tube with close to 100% efficiency, while the gas molecules meet the wall due to their high diffusion coefficient, and stick to the absorbent. Still, volatilization from the filter may occur, which is compensated by a back-up filter as in the case of the filter pack method. These techniques are tedious and do not allow a high time resolution. Therefore, methods for automated on-line analysis of these components have been developed [16]. Here, the denuder is designed as a parallel plate diffusion denuder with a wetted surface, while aerosol particle collection is performed in a mist chamber, where a high supersaturation causes aerosol particles to grow into droplets, which then can be collected by an impactor. Both denuder and aerosol collector solution are then preconcentrated on ion exchange columns and analyzed by ion chromatography. This system has been shown not to suffer from the above mentioned artefacts [17]. It can be run unattended for about a week with an overall time resolution of 16 min (for two consecutive 8-min runs for the gas and particle phase). As an example, Figure 2 shows the time evolution of the concentrations of the gases HONO and HNO₃, and of the particulate species NO₃⁻ and SO₄²⁻ measured at the Jungfraujoch [18]. Varying ratios of nitric acid to particulate nitrate concentrations indicate a variation in acidity, which is mostly governed by the input of ammonia.

Carbonaceous material

Similar problems of gas - particle partitioning are encountered for organic carbon, which often comprises the largest fraction of PM_{2.5} [19]. Sampling of carbonaceous aerosol is usually performed on quartz fiber filters, with subsequent analysis of organic and elemental carbon [20], the latter being suspected to be carcinogenic [21]. In addition, polyaromatic hydrocarbons (PAHs) are determined by gas chromatography or high-performance liquid chromatography, however, information on the speciation of organic carbon is still very scarce. The involved procedures are again very time consuming. On-line techniques are available for the determination of black carbon [22] or for PAHs adsorbed to aerosol particles [23], however, there is no constant relationship to the concentration of elemental carbon. In addition, Zenobi and coworkers applied two-step laser mass spectrometry (L2MS) directly to the aerosol loaded quartz filters for the determination of PAHs [24]. They found excellent sensitivity with very little sample pretreatment, however, due to a variety of non-linear processes quantification was difficult. Thus, more work is needed in order to perform fast and reliable measurements of these components.

Thermal analysis

In order to gain some chemical information on the aerosol, thermal treatment of the aerosol can be combined with size distribution measurements. Most often, an optical particle counter was applied to determine the response of the particle size distribution to the thermal treatment, with a lower cutoff at $D = 100$ nm [25]. In our application, a differential mobility analyzer (DMA) [7] was applied in order to access the smaller particles (down to $D \approx 15$ nm). An example of these measurements, also performed at the Jungfraujoch, is shown in Fig. 3 [26].

The indicated temperatures were chosen because sulfuric acid is volatilized below 125°C, while ammonium sulfate is volatilized between 125 and 175°C [27], and organic carbon in both temperature ranges. Clearly, this aerosol did not contain appreciable amounts of sulfuric acid, since there was no significant difference between 30 and 125°C. These patterns varied substantially from day to day, indicating a variability in acidity of the Jungfrauoch aerosol, as mentioned above. The aerosol remaining above 275°C consists mainly of elemental carbon. Therefore, a good correlation between the volume of the aerosol remaining at 275°C and the black carbon concentration as determined by the aethalometer is found, as also shown by Smith and O'Dowd [25].

Single particle analysis

Most probably, the aerosol particles remaining at 275°C are internally mixed, i.e. they contain a core of elemental carbon with more volatile components adsorbed to it. This fact calls for single particle analysis. While there is a huge variety of methods for single particle analysis (see, e.g. the review by Van Grieken and coworkers [28]), laser microprobe mass spectrometry seems to be best suited for the identification of the chemical composition of individual particles. This method is applied both off-line and on-line. The off-line approach allows to take samples at virtually all places of the world, which are then analyzed in the laboratory [29]. However, this technique may suffer from artefacts similar to the ones described above. On-line analysis does not suffer from these artefacts [30], since particles are detected and analyzed *in situ*, however, the instrumentation is not yet mobile. Efforts are currently being undertaken to construct mobile devices, which promise to deliver highly interesting results on the chemical composition of individual aerosol particles at representative sites.

Surface analysis

The chemical composition of the aerosol particle surface governs the heterogeneous chemical reactions occurring at this surface. These reactions do not only modify the gas phase chemistry as mentioned above but also the particle surface itself. This is illustrated by an increase in the hydrophilic behavior of combustion aerosol particles from diesel or spark ignition engines as measured with a so-called tandem DMA system [31]: A narrow size cut from a first DMA is exposed to a high relative humidity, and the resulting new size distribution is measured with a second DMA. The growth behavior has been shown to increase with aging of the particles, due to surface chemical reactions. The actual compounds remain to be identified, and it is anticipated that surface characterization methods such as secondary neutral mass spectrometry and secondary ion mass spectrometry (SNMS and SIMS) as well as X-ray excited photoelectron spectroscopy (XPS) [32] might be a valuable tool, even though the required pressure regime will certainly result in desorption of volatile components.

Conclusions

Despite recent progress, much remains to be done. Where possible, emphasis should be laid on the development of methods for on-line and *in situ* analysis, as already stated by Niessner [33], since then artefacts can be minimized, and since many process studies require a good time resolution. Most probably, innovative solutions will result from a fruitful collaboration between analytical chemists and aerosol scientists.

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Figure Captions

Figure 1. Seasonal variation in daily median values of various aerosol parameters at the Jungfrauoch (3454 m) for the period from July 1995 to June 1996. a) aerosol total scattering coefficient σ_{SP} ; b) backscattering coefficient σ_{BSP} (both at 550 nm); c) aerosol absorption coefficient σ_{AP} ; d) number concentration of particles with $D \geq 10$ nm); e) epiphaniometer signal (where on the second axis the surface area concentration S is included). The heavy solid lines indicate 30-day running means. After [9]. Reproduced with permission of AGU.

Figure 2. Measurements of the gases HONO and HNO₃ (top), and of the particulate components NO₃⁻ and SO₄²⁻ (bottom) at the Jungfrauoch [18]. Gas phase data are given as mixing ratios (volumetric parts per trillion, pptv), while aerosol data are given as concentrations (ng/m³). Under Jungfrauoch conditions, 1 ppt HNO₃ corresponds to 1.8 ng/m³.

Figure 3. Size spectra of aerosol particles at the Jungfrauoch after thermodesorption. Date: 15 April, 1997. Data are averaged for the time 12:00 - 24:00 [26].

Fig. 1

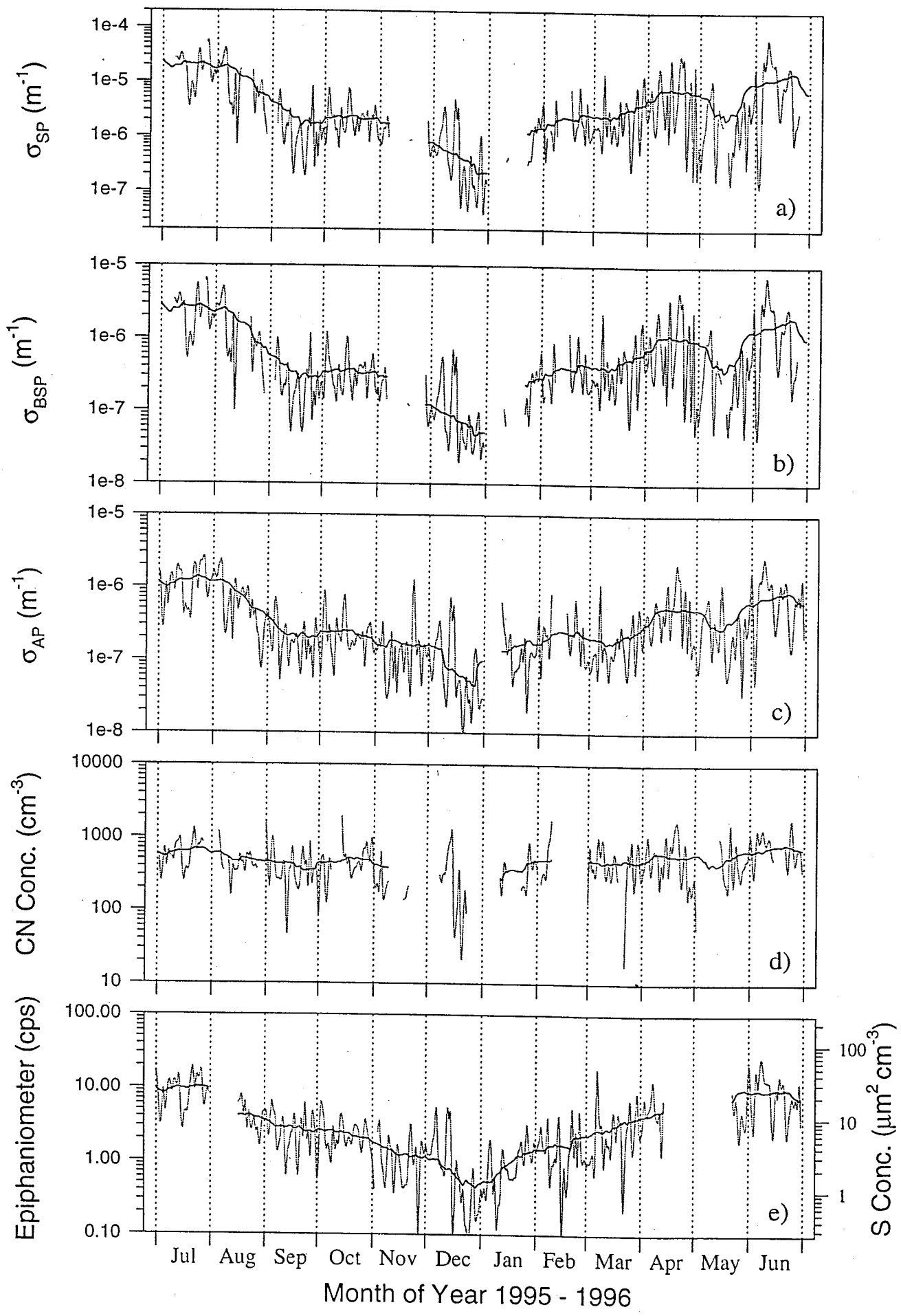


Fig. 2

