Chapter 5
Innovative Instrumentation for the Study of Atmospheric Aerosol Optical Properties

Vera Bernardoni, Alice C. Forello, Federico Mariani, Bruno Paroli, Marco A. C. Potenza, Alberto Pullia, Francesco Riccobono, Tiziano Sanvito, Sara Valentini, Gianluigi Valli and Roberta Vecchi

Abstract Aerosol optical properties (i.e. scattering and absorption) are of great importance to assess aerosol effects e.g. on visibility and Earth radiation balance. In this paper, we present innovative optical instrumentation developed at the Department of Physics "Aldo Pontremoli" of the University of Milan: a multi-wavelength polar photometer (PP_UniMI) and a Single Particle Extinction and Scattering (SPES). PP_UniMI is a filter-based device providing the aerosol absorption coefficient of aerosol at 4 wavelengths (λ). Such measurements are of interest to have insights into the λ-dependent behavior of aerosol absorption properties, which is still poorly

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V. Bernardoni (✉) · A. C. Forello · F. Mariani · B. Paroli · M. A. C. Potenza · A. Pullia · T. Sanvito
S. Valentini · G. Valli · R. Vecchi
Department of Physics "Aldo Pontremoli", Università degli Studi di Milano, Via Celoria 16, 20133 Milan, Italy
e-mail: vera.bernardoni@unimi.it

A. C. Forello
e-mail: alicecorina.forello@studenti.unimi.it

F. Mariani
e-mail: federico.mariani@eosinstruments.com

B. Paroli
e-mail: bruno.paroli@unimi.it

M. A. C. Potenza
e-mail: marco.potenza@unimi.it

A. Pullia
e-mail: alberto.pullia@unimi.it

T. Sanvito
e-mail: tiziano.sanvito@eosinstruments.com

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understood especially for what concerns weakly absorbing aerosol components. SPES allows to determine the size and refractive index of single particles. In case of absorbing particles, also information on the imaginary part of the refractive index—very important especially in the field of global models—can be provided with little assumptions. We describe the main features of the two instruments and their advantages and limitations. Examples of application are also presented.

5.1 Introduction

Light scattering and absorption properties by atmospheric aerosol are responsible for the aerosol effects e.g. on visibility impairment at local scale or the Earth radiation balance at global scale. The main physical parameters allowing the description of light scattering and absorption by a particle are its size, complex refractive index, mixing state, and shape [1].

Great uncertainty is still associated to the estimate of the aerosol-radiation effect on the Earth radiation balance [2] and refining the parameters used as input in climate models is mandatory for a reduction of such uncertainties. Aerosol absorption properties are of peculiar interest as they can provide positive contribution to the Earth radiation balance, but many aspects are not fully understood yet. Indeed, different species can absorb visible light. The main light absorbing component in atmospheric aerosol is recognized to be the black carbon (BC). Besides BC, in the last fifteen years, it was evidenced that there exist organic compounds weakly absorbing at long visible wavelengths (λ), but with enhanced absorption behavior at low visible and near-UV wavelengths (called brown carbon—BrC) [3]. BrC chemical properties, sources, and light absorption characteristics are still poorly investigated [4, and therein cited literature]. Consequently, it is currently barely accounted for in global models. Thus, developing instrumentation to gain insight into the parameters

S. Valentini
e-mail: sara.valentini@unimi.it

G. Valli
e-mail: gianluigi.valli@unimi.it

R. Vecchi
e-mail: roberta.vecchi@unimi.it

V. Bernardoni · A. C. Forello · B. Paroli · M. A. C. Potenza · A. Pullia · S. Valentini · G. Valli
R. Vecchi
INFN-Milan, Via Celoria 16, 20133 Milan, Italy

F. Riccobono
Joint Research Centre, European Commission, Via Fermi 2749, 21027 Ispra, Italy
e-mail: frariccco@gmail.com

T. Sanvito
EOS s.r.l., Viale Ortles 22/4, 20139 Milan, Italy

influencing the aerosol absorption properties and/or into the λ-dependent absorption coefficient in atmosphere is mandatory to better understand the role of atmospheric aerosol on the Earth radiation balance. As an example, it was evidenced that small variation on the imaginary part of the refractive index can have important impact on the modeled radiative forcing [5].

As the particle mixing state plays a key role in the aerosol-radiation interaction processes, it is important to perform measurement of light scattering and absorption properties of atmospheric particles with no sample pre-treatment. To this aim, two instruments were developed for the study of aerosol optical properties at the Department of Physics “Aldo Pontremoli” of the University of Milan: the multi-λ polar photometer PP_UniMI [6, 7] and the Single Particle Extinction and Scattering instrument [8].

PP_UniMI was originally developed to measure off-line the aerosol absorption coefficient at 635 nm on aerosol collected on 47-mm filters (i.e. filters commonly used during sampling campaigns) with no need of additional instrumentation. In this configuration, the agreement with an external reference instrument—the Multi-Angle Absorption Photometer (MAAP)—was within 2% [6]. Recently, implementations were realized to perform measurements at 4 λs and to extend the application of the methodology to samples collected with 1-h resolution [7]. In both cases, no sample pre-treatment is required. Multi-λ measurements of aerosol absorption properties can be exploited to gain insight into BrC properties applying optical source and component apportionment models (e.g. Multi-Wavelength Absorption Analyzer model—MWAA [9, 10]).

The SPES concept was recently introduced and validated for liquid suspensions [11] and in the following extended to particles suspended in air [8]. SPES is a single-particle device providing information on the real and imaginary parts of the adimensional scattering amplitude [12] according to the optical theorem [1, 13]. As a consequence, particle characteristics (i.e. particle size and refractive index) can be provided with few or no assumptions [14, 15].

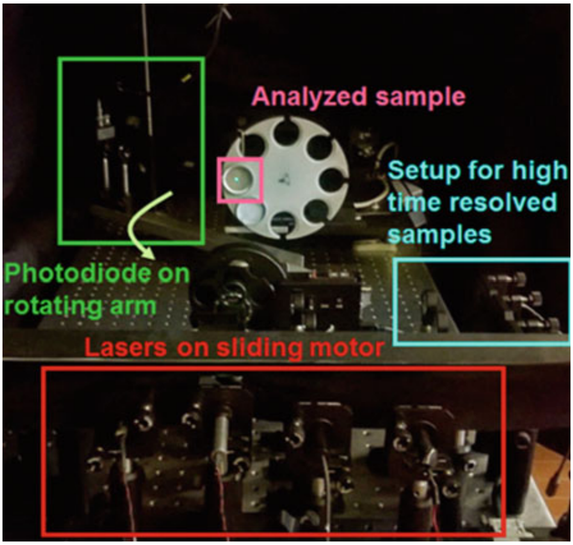
The features of PP_UniMI and SPES were presented at the Congress of the Physics of the University of Milan in June 2017 together with some applications. In this paper, the main contents of the presentation will be reported.

5.2 Description of the Instruments

5.2.1 The Polar Photometer PP_UniMI

PP_UniMI provides information on the aerosol absorption coefficient at four wavelengths (405, 532, 635, 780 nm) starting from measurements of the intensity of the light transmitted and scattered in the front and back hemispheres by a blank and aerosol-loaded filter. The chosen laser beam impinges on the sample, and the scan of the scattering plane (0–173° with about 0.4° resolution) is performed thanks to a

Fig. 5.1 PP_UniMI set-up



photodiode mounted on a rotating arm (see Fig. 5.1). Solid angle integration allows to determine the total amount of light diffused in the two hemispheres, and these data are the input to the radiative transfer model developed by Hänel [16, 17] for membrane filters and adapted by Petzold and Schönlinner [18] for the application to aerosol collected on fiber filters. The outputs of the model are the single scattering albedo (ω) and the optical depth (τ) of the layer containing the particles. Considering the sampled volume (V) and the deposit area (A), the aerosol absorption coefficient (b_{abs}, expressed in M m^{-1}) in atmosphere during the sampling is determined as:

$$b_{abs} = (1 - \omega)\tau \frac{A}{V}$$

PP_UniMI was recently upgraded to analyze samples collected with high temporal resolution using a streaker sampler [19], characterized by low loadings and collected on very thin substrates. Multiple scattering between the sample and an additional scattering matrix leaned against the sample were exploited to increase the instrument sensitivity. Good agreement with an external reference instrument—the Multi-Angle Absorption Photometer MAAP [18]—was evidenced (slope = 1.10, R^2 = 0.93). Further details can be found in Bernardoni et al. [7].

5.2.2 *Single Particle Extinction and Scattering (SPES)*

SPES allows gaining information on the real and imaginary parts of the forward complex scattering amplitude thanks to a self-interferometric scheme by exploiting the optical theorem (OT) [1, 13]. Currently, single wavelength measurements are performed at 640 nm.

Briefly, a particle crosses a beam waist perpendicularly. When the particle is exactly in the center of the beam, an attenuation figure is monitored onto a segmented quadrant photodiode (QPD) placed in the far field. The OT is used to relate the extinction cross section to the real part of the forward scattering amplitude. When the particle is slightly displaced from the optical axis of the system, transmitted and scattered radiation combine forming an interference figure: a small, asymmetric signal fluctuation is generated on the QPD [11], and it is related to the imaginary part of the forward scattering amplitude. Thus, combining the two measurements gives access to the whole complex forward scattering amplitude.

Acquisition of the QPD signals is performed by a custom, front-end electronics properly developed. It separates the signal into two components: the slow signal is isolated using a low-pass filter, allowing monitoring the laser intensity continuously; then a fast, zero-average signal corresponding to the rapid fluctuations related to the particle crossing the beam waist is digitized at 12-bit, thus allowing detailed signal analysis [20].

Among the advantages of the technique, it is noteworthy that:

- No calibration is required: the Mie theory is exploited to relate the complex forward scattering amplitude to the particle characteristics;
- Spurious signals are automatically rejected thanks to pulse-shape analysis;
- Information on the imaginary part of the refractive index can be obtained under few assumptions or performing size-segregation upstream SPES;
- Information on non-spherical particles can be obtained.

Further details on the SPES set-up for aerosol suspended in air can be found in Mariani et al. [8].

5.3 Results and Discussion

5.3.1 Example of Results by PP_UniMI

As an example of PP_UniMI application, 4-λ analysis of the absorption coefficient of aerosol collected using a streaker sampler is shown in Fig. 5.2. Aerosol was collected using a streaker sampler at an urban background site in Milan [see e.g. 7] in December 2016.

It is noteworthy that multi-λ analysis can be exploited to perform studies of optical source apportionment, using literature approaches—e.g. the Multi-Wavelength Absorption Analyzer model, which provides both source and component apportionment of the aerosol absorption coefficient at different λs [9].

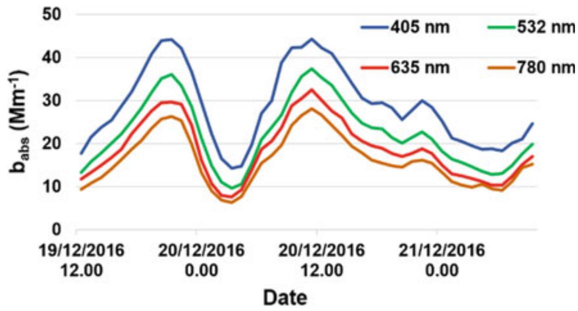


Fig. 5.2 Example of 4-λ measurements of the aerosol absorption coefficient

5.3.2 Examples of Results by SPES

SPES was tested on laboratory aerosol: water droplets, NaCl particles, and graphite nanoparticles. In Fig. 5.3 SPES measurements for each aerosol type are represented as two dimensional histograms showing the number of events recorded in each two dimensional bin in the $S(0)$ complex plane. Populations are characterized by size polydispersity, giving the main elongation of the data sets. Data exhibit different spreads along the imaginary axis, the smaller indicating higher homogeneity and sphericity. Changes in the complex amplitudes of the fields scattered by different aerosol types are evident.

SPES showed very good performances on test aerosol: for pure water droplets generated using an aerosol generator—ATM 220 by Topas—the retrieved real refractive index was 1.32 ± 0.01, in close agreement with the expected value (1.33). The maximum detected particle diameter was $d \sim 1$ μm, consistently with the atomizer cut-off diameter. The small spread of the measurements in the scattering plane (Fig. 5.3a) is indication of particle homogeneity and sphericity.

The same experimental set-up was used to generate and characterize NaCl particles. Spread of the data in the complex scattering plane (Fig. 5.3b) and consequent broader distribution of the retrieved real refractive index gave indication of non-spherical particles. The retrieved NaCl size distribution had a sudden drop at $d < 600$ nm. It is noteworthy that SPES provides geometric diameters (i.e. diameters of a spherical particle with the same surface area as the measured one), whereas the aerosol generator cut-off refers to aerodynamic diameter (i.e. diameter of a spherical particle with density $\rho = 1$ g/cm^3 having the same inertial properties of the measured particle). Considering the NaCl density (2.16 g/cm^3), the expected geometric cut-off diameter of the aerosol generator assuming spherical particles is 680 nm, which is consistent with the sudden drop observed in NaCl particle size distribution.

Graphite nanoparticles (proxy for black carbon) were also analyzed by SPES: they were produced by a graphite spark aerosol generator by Palas GmbH (Mod. DNP digital 3000). Graphite nanoparticles are expected to have high imaginary part of the refractive index. Furthermore, they are expected as agglomerates (i.e. far from

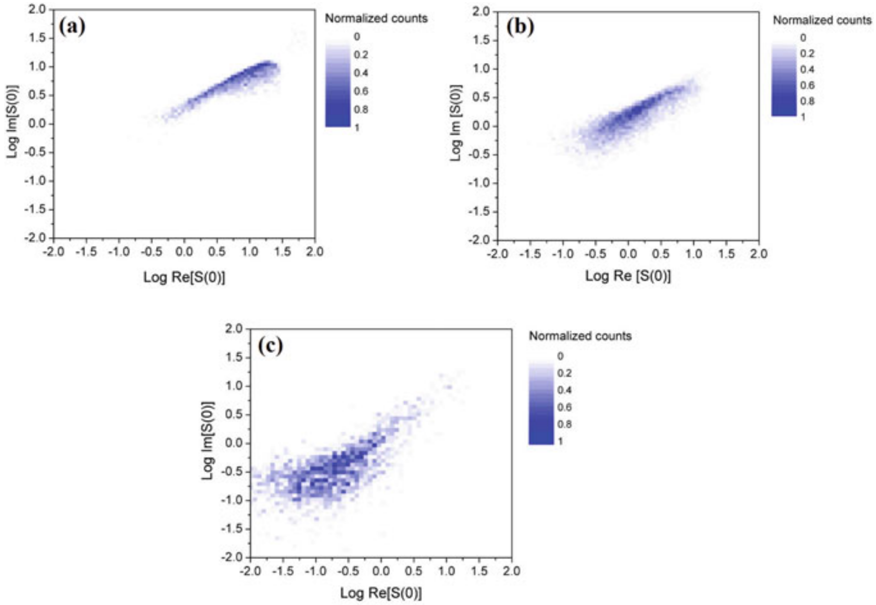


Fig. 5.3 SPES results represented as two dimensional histograms showing the number of events recorded in each two dimensional bin in the $S(0)$ complex plane. **a** Water droplets; **b** NaCl particles; **c** graphite nanoparticles

spherical shape). SPES measurement distribution is spread throughout the complex plane, as expected for non-spherical, inhomogeneous particles. Furthermore, measurements are generally placed in an area with lower imaginary part of the forward scattering function, which is an indication of absorptive particles (Fig. 5.3c). Calculation by the Mie theory was performed—even if inaccuracies in the results are expected due to the poor consistency of the graphite particles characteristics with the hypotheses of the theory i.e. particle sphericity and homogeneity—and the effective imaginary part of the refractive index resulted to be $k = 0.2$.

5.3.3 PP_UniMI and SPES Joint Application for the Characterization of Unknown Material

PP_UniMI and SPES can be separately used for aerosol characterization. Nevertheless, they can be used jointly for a more detailed characterization of unknown materials. This was performed by driving aerosol through SPES and sampling the aerosol at the instrument outlet on PTFE filters. The aerosol collected on filter was then analyzed by PP_UniMI. This procedure was performed to characterize a test material of unknown physical-chemical and optical features (pyrethrum smoke).

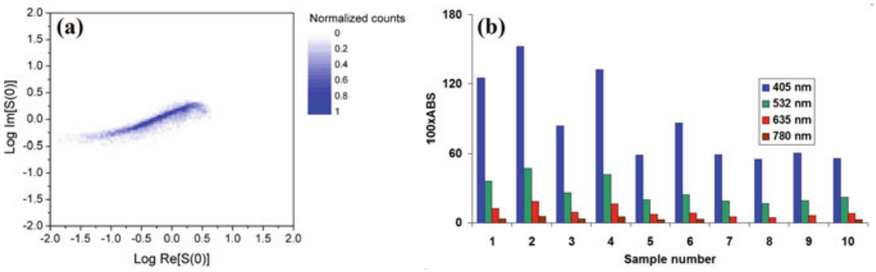


Fig. 5.4 **a** SPES results represented as in Fig. 5.3. **b** 4-λ sample absorbance measured by PP_UniMI

SPES results showed a very small spread of the data along the imaginary axis in the complex plane (Fig. 5.4a), thus providing indication for homogeneous, spherical particles. The evident change of the population shape occurring in the left-hand side of the plot indicates a modification of the overall structure of the particles. Pyrethrum smoke particles resulted to be weakly absorbing at 640 nm (imaginary part of the refractive index $k = 0.12$) and their size was in the range 200–700 nm diameter.

Furthermore, PP_UniMI measurements provided information on the λ-dependence of pyrethrum smoke sample absorbance (Fig. 5.4b). In general, it is expected a $\lambda^{-\alpha}$ dependence for the aerosol absorption coefficient, where α is called Ångström absorption exponent. α is expected to be 1 for pure BC particles in the Rayleigh regime, whereas it is expected to be much higher for BrC [e.g. 4, 21, 22, and therein cited literature]. Pyrethrum smoke showed $\alpha = 5$: as carbonaceous particles are expected in Pyrethrum smoke, our measurements suggest that they consist mainly of BrC (further details in Mariani et al. [8]).

5.4 Conclusions and Perspectives

Optical instruments for the characterization of atmospheric aerosol (PP_UniMI, SPES) were developed at the Department of Physics "Aldo Pontremoli" of the University of Milan. These instruments provide information useful to fill the gap of knowledge currently present in the aerosol absorption and scattering properties and in the evaluation of their effect, especially at global scale. Both instruments were developed to analyze samples with no need of pre-treatment, which is important to avoid modification of the optical properties related to particle mixing state.

The polar photometer PP_UniMI provides multi-λ measurements of the absorption coefficient of aerosol collected on filters. This information can be exploited in source and component apportionment studies [9] to gain information on BrC properties. Reliability of the methodology was successfully tested against independent measurements performed by a Multi-Angle Absorption Photometer (MAAP) at 635 nm.

The Single Particle Extinction and Scattering instrument (SPES) provides information on the size and real refractive index of non-absorbing particles. Furthermore, information on the imaginary part of the particle refractive index can be obtained with few assumptions. Single particle measurements are of great importance as they can both allow to study particle ensemble characteristics and to focus on possible subsets of interest.

Testing the joint application of the two instruments to measure particles of unknown material showed potentiality of providing very important information for the characterization of the size, shape, and λ-dependent light absorption behavior of the tested particles. This opens in perspective the possibility of better characterizing other test materials, and possibly ambient aerosol samples.

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