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Retrieval of complex refractive indices of mineral aerosols from the UV to the thermal infrared

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Abstract

High spectral resolution extinction measurements of calibrated particlesfrom the UV to the thermal infrared region of the electromagnetic spectrum have been obtained to derive accurate values of the corresponding complex refractive indices. The latter are generally performed through absorbance or transmittance measurements from bulk material or diluted particles in solid pellets leading to possible experimental limitation, such as lack of knowledge of the particle size distribution.

Calibrated amorphous silicasphere particles (99.9%, AngströmSphere) of diameters D = 0.5 and 1 µm were dispersed by a mechanical way in a flow of nitrogen (5 L/min) within a glass container. The continuous flow of aerosol particles was introduced into a 10 m multi-pass cell within an FTIR (Fourier Transform InfraRed) spectrometer (Antaris IGS Analyser, Thermo Scientific) and a 1 m single-pass cell within a UV-visible-NIR spectrometer (MAYA 2000 PRO, Ocean Optics). Aerosol size distributions have been measured at the exit of the spectrometers either with an Aerodynamic Particle Sizer spectrometer (TSI APS 3321), or with a Scanning Mobility Particle Sizer (TSI SMPS 3936L75).

The complex refractive indices are determined by combining Kramers-Krönig relations, the Mie theory and an iterative process. This allows minimizing errors in the retrieval procedure.

Keywords: Optical properties; Complex refractive indices; Mineral aerosol; Extinction spectra; Size distribution; Optimal Estimation Method (OEM)

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1. Introduction

Due to their ability to absorb and scatter radiations, aerosols play an important role in the energy budget of the earth-atmosphere system (Forster et al., 2007).

However, quantitative estimations of their effects are quite uncertain due to their large spatial and temporal variability in terms of concentration and physicochemical properties (Stocker et al., 2013).

Measurements from space-borne instruments are the only way to observe aerosol distributions from local to global scales. For instance, thermal InfraRed (IR) radiometers such as MODIS or SEVIRI are routinely used for aerosol detection. Nevertheless, these broadband sensors are not suitable to distinguish the aerosol chemical or mineralogical composition. Recent high spectral resolution infraredsounders such as IASI or TANSO-fts are able to overcome these limitations. However, to fully exploit the hyperspectral instrument capabilities, precise optical properties, in particular complex refractive indices, of various particles are needed.

Complex Refractive Indices (RI) commonly used, especially for dust are available in open database such as OPAC (Hess et al., 1998). These data are usually derived from reflectance and transmittance measurements (Di Biagio et al., 2014a, 2014b; Orofino et al., 1998; Zolotarev, 2009; Egan & Hilgeman, 1979; Longtin et al., 1988; Roush et al., 1991; Steyer et al., 1974; Volz, 1983; Querry, 1987). Most of these lab-experiment are performed with bulk materials (Lane, 1999; Zolotarev, 2009; Querry, 1987) or with particles compressed in KBr pellets (Di Biagio et al., 2014a; Egan & Hilgeman, 1979; Longtin et al., 1988; Roush et al., 1991; Steyer et al., 1974; Volz, 1983; Orofino et al., 1998). Nevertheless, some works (McPheat et al., 2002) have shown that these measurements are not suitable for the study of dispersed constituents (e.g. cloud, aerosol, or fog).

Optical properties determination from extinction spectra of aerosol particles is significantly more difficult.Indeed, these measurements have the disadvantage that the traditional inversions methods used to retrieve both the real and imaginary part of the RI in thatcase do not ensure the uniqueness of the solution and lead to questionable results (Ruan et al., 2007, 2011).

From these limitations, we propose a new methodology for determining optical properties of airborne particles.Firstly, high spectral resolution IR and UV-visible extinction spectra and size distribution have been recorded simultaneously for a suspension of calibrated spheres of amorphous silica particles.Then, from these experimental measurements, aerosol particles RIare determined using a new numerical procedure. The latter which combines the Kramers-Krönig relationships, Mie theory and optimal estimation method (Rodgers, 2000), offers the advantage to be useable for any type of extinction measurements whatever the nature or provenance of aerosols (calibrated particles of pure materials, aerosols produced chemically in a laboratory or in-situ sampling of atmospheric aerosols).

2. Experimental methods

The experimental setupis divided in 3 parts: aerosol generation, spectrometers, and size distribution, and presented in Fig. 1. All the experiments were carried out under fixed conditions: at room temperature (T ≈293 K), atmospheric pressure (P ≈ 1013 hPa) and low relative humidity (RH ≈ 4%).Details of this experimental setup are described in detail by (Hubert et al., 2016, submitted to JQSRT).

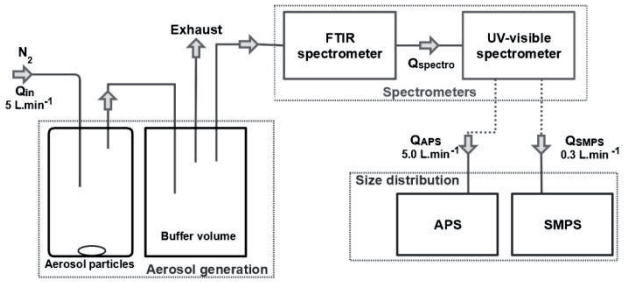

Fig. 1. Experimental setup used to record extinction spectra and size distribution of aerosols

Particles were aerosolized within a glass container. A continuous agitation of the powder (approx. 100 mg as minimum) is maintained using a magnetic stirrer. A total flow of pure nitrogen gas of about 5 L.min^{-1}, monitored by a mass flow controller, is used to carry aerosol through the whole experimental set-up. A buffer volume was introduced at the exit of the glass container in order to reach a constant well-mixed aerosol flow. The aerosols are flowing successively through a 10 meter multi-pass cell FTIR spectrometer (Antaris IGS Analyser, Thermo Scientific) and a1 meter single-pass cell UV-Visible-NIR (UV-Vis) spectrometer (MAYA 2000 PRO, Ocean Optics), in order to record the extinction in the range, from 650 to 4000 cm^{-1}and from 8900 to 33000 cm^{-1} (from 300 nm to 1000 nm) respectively. The spectral resolution is 1 cm^{-1} for the IR region and 1 nm for the UV-visible region.

For particle diameter less than 1 µm, aerosol size distributions were recorded by a Scanning Mobility Particle Sizer (SMPS) (TSI model 3936L75) spectrometer. For aerodynamical particle diameter between 0.523 and 20 µm, aerosol size distributions were recorded by an Aerodynamic Particle Sizer (APS) (TSI model 3321) spectrometer.

3. Experimental results

The smoothed experimental extinction spectra of 0.5 µm and 1.0 µm amorphous silica sphere particles (Fiber Optic Center, 99.9%, density 1.8) measured over the IR and UV-visible spectral ranges are presented in Fig. 2, and associated particle number size distributions (dN/dlogDp) are presented in Fig. 3. Calibrated silica sphere particles have been selected for methodology validation.

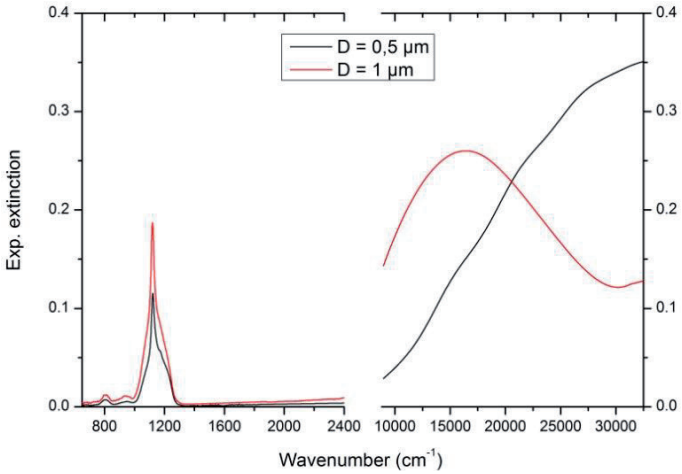

Fig. 2. Experimental extinction spectra of 0.5 and 1 µm amorphous silica sphere particles

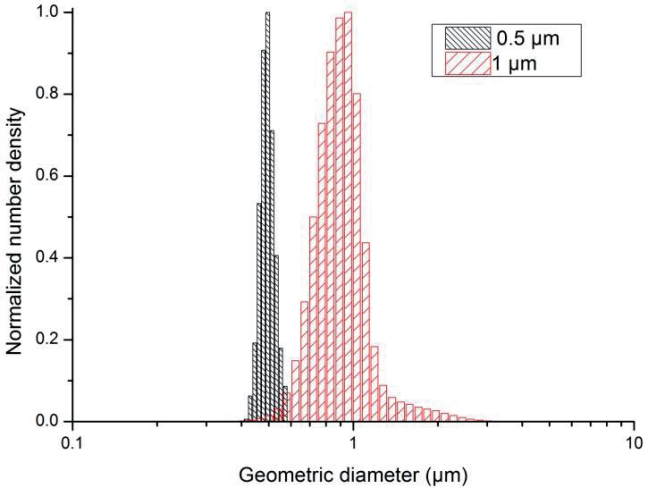

Fig. 3. Associated particle size distributions recorded by the SMPS and the APS, for 0.5 and 1 µm amorphous silica sphere particles, respectively

The Fig. 2 shows characteristic vibrational bands of silica particles, in the IR region. In the UV-visible region, where the scattering process is dominant, size distributions affect the experimental extinction spectra. Furthermore, in the IR region, the main difference concerns the characteristic vibration band of SiO_2 centered at 1100 cm^{-1}. Not only the shape of the band ischanged with the size of the particles but also the frequency which is red-shiftedfor larger particles.In the light of this observation, accurate size distribution and extinction spectra have to be simultaneously recorded.

4. Numerical procedure

The inversion process, to retrieve the RI from experimental extinction spectra and size distribution measurements, is presented in detail by (Herbin et al., 2016, submitted to JQSRT). The inversion process is briefly summarized here.

Firstly, from experimental extinction spectra and size distribution measurements, RI are estimated using Rayleigh theory and Kramers-Krönig relationships, respectively.Secondly, these *a priori*indices become input data for an iterative process, composed of an Optimal Estimation Method (OEM) and Mie theory, taking into account of experimental uncertainties.Lastly, this iterative process provides, in particular, the retrieved real and imaginary parts of the RI with associated uncertainties.

This inversion process has been also tested on non-spherical particles (randomly oriented quartz particles). Mie theory is still valid under this assumption (Pujol et al., 2012). However, depending of the shape or the orientation of the particles, other theorymay be used (e.g. T-Matrix).

5. Retrieved complex refractive indices for silica

The real (n) part and imaginary (κ) part of RI of amorphous silica and associated uncertainties have been retrieved from 650 to 32,500 cm^{-1} spectral range from the experimental data and are presented in the Fig. 4.Uncertainties take into account both experimental uncertainties and those from the numerical procedure. Their magnitude depends on the spectral region, namely less than 2% and 1%, in the IR and UV-visible region, respectively. These real and imaginary parts of the RI have been used to simulate the extinction spectra of silica sphere particles (D = 0.5, 1 and 2 μm) using Mie theory. Discrepancies between the simulated and the experimental extinction spectra are less than 2% in the whole spectral range for the two particle sizes, except around 1100 cm^{-1} corresponding to the intense absorption region.

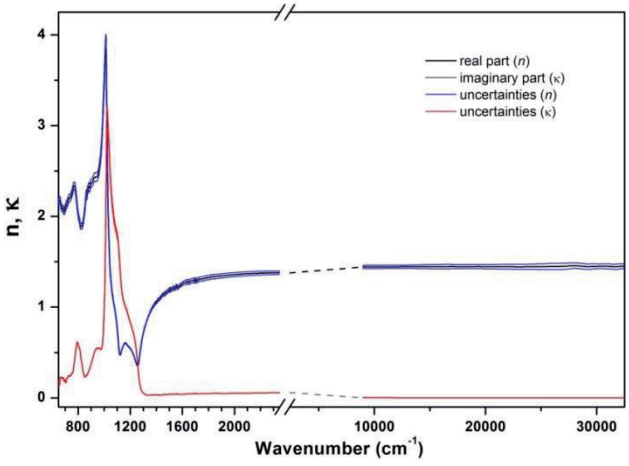

Fig. 4. Real part and imaginary parts, and uncertainties, of the complex refractive indices of amorphous silica particles

6. Conclusion

A new approach, by combining an experimental setup and a numerical procedure,has been presented to retrieve the RI of aerosol particles from measured extinction spectra and size distributions. Extinction spectra are recorded with a high spectral resolution and within a wide spectral range. These results have a great interest for remote sensing observations for which the knowledge of robust RI is crucial.

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