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Credit author statement

1. Vikas Goel – Writing original draft, simulations, sample collection.
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5. T. D. Senguttuvan – FIB analysis support
6. C Sharma – Discussion, review.
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**Three-Dimensional Physico-chemical Characterization of Coarse
Atmospheric Particles from Urban and Arid Environment of India:
An Insight into Particle Optics**

**Vikas Goel^{a,b}, Sumit K. Mishra^{a,b*}, Ajit Ahlawat^{a,b,c}, Prashant Kumar^d, T. D.
Senguttuvan^{a,b}, Chhemendra Shrama^{a,b}, Jeffrey S. Reid^e**

^aEnvironmental Sciences and Biomedical Metrology Division, CSIR-National Physical
Laboratory, New Delhi, India -110012

^bAcademy of Scientific and Innovative Research, Kamla Nehru Nagar, Ghaziabad, Uttar
Pradesh, India – 201002

^cLeibniz Institute for Tropospheric Research, Permoserstraße,15 Leipzig, Germany

^dGlobal Centre for Clean Air Research (GCARE), Department of Civil and Environmental
Engineering, University of Surrey, Guildford GU2 7XH, Surrey, United Kingdom

^eUnited States Naval Research Laboratory, Washington DC, United States.

Abstract

Aerosol particles scatter and absorb solar radiation and affects earth's radiation budget. The aerosol particles are usually non-spherical in shape and inhomogeneous in chemical composition. For simplicity, these particles are approximated as homogeneous spheres/spheroids in radiative models and in retrieval algorithms of the ground and spaceborne observations. The lack of information on particle morphology (especially shape), chemical composition (that govern their spectral refractive indices) and most importantly internal structure (three Dimensional, 3D spatial distribution of chemical species) lead to uncertainty in the numerical estimation of their optical and radiative properties. Here, we present a comprehensive assessment of the particles' volumetric composition. The particles were collected from typical arid and urban environments of India and subjected to Focused Ion-Beam (FIB) coupled with Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Particles from the arid environment were observed to be composed of Fe, Ca, C, Al, and Mg rich shell with Si and O rich core opposed to those from urban environment consisting Hg, Ag, C, S and N rich shell with Cu and S rich core. Based on the homogeneous sphere/spheroid assumption, conventional SEM-EDS and FIB-SEM-EDS results, different particle model shapes [single species homogeneous sphere (S1) and spheroid (SPH1); multiple species homogeneously mixed sphere (S2) and spheroid (SPH2); and core-shell (CS)] were considered for simulating their respective optical properties; SSA (Single Scattering Albedo) and g (Asymmetric parameter). The effect of internal structure on SSA was found to be prominent in particles having low value of the imaginary part of refractive index (k). While the same was observed to be low (nearly negligible) for the particle with the high value of " k ". The particles rich in copper are found to be highly absorbing in nature which causes positive radiative forcing.

Keywords: Aerosols particles; FIB-SEM-EDS; 3D characterisation; Core-Shell; Single Scattering Albedo

1. Introduction

Aerosol particles affect the Earth's climate and alter Earth's radiation budget. Particles rich in black carbon (Boucher et al., 2016; Goel et al., 2018a), and metals such as iron (Mishra and Tripathi, 2008) and chromium (Goel et al., 2018b) absorb the incoming solar radiation and cause positive radiative forcing (warming) while those rich in sulfate (Buseck and Posfai, 1999), nitrate, and quartz predominately scatter the solar radiation and cause negative radiative forcing (cooling). The net effect of aerosol particles on Earth's radiation budget can be better understood by calculating their optical properties like single-scattering albedo (SSA) and asymmetry parameter (g). SSA is the ratio of radiation scattered to the total radiation extinction and g is the average cosign of scattering angle (θ). SSA and g depend to a large extent on shape (Mishra et al., 2015; Mishra et al., 2010), size (Mishra and Tripathi, 2008), chemical composition (Goel et al., 2018b; Mishra et al., 2010, 2008; Mishra and Tripathi, 2008) and internal structure (Conny, 2013) of an individual particle. Efforts have been made to quantify the effect of particle's shape (Mishra et al., 2015; Mishra et al., 2010), size (Mishra and Tripathi, 2008) and chemical composition (Mishra et al., 2010, 2008; Mishra and Tripathi, 2008) on their optical properties. However, their internal structure is still the most challenging parameter, and its effect on optical properties is yet to be fully explored. There are very limited studies which have investigated the internal structure of aerosol particles, but none have explored the internal structure of the particles collected from typical urban and arid environment of India (Nousianien et al., 2011; Adler et al., 2013; Chen et al., 2013; Conny, 2013; Jeong and Nousiainen, 2014; Kemppinen et al., 2015). The internal structure can be defined by the different mixing configurations, in which

different species are mixed and distributed within the particle. Generally, in the atmospheric community, aerosols were assumed to be homogeneous isotropic spherical particles (Ganguly et al., 2005; Mishra et al., 2012) in retrieval algorithms of the ground and space-borne observations, which leads to significant uncertainties in results. Currently, spheroidal model particles are often used for retrieval purposes (Dubovik et al., 2006).

Mineral dust is an essential component of total atmospheric aerosols and plays a vital role in Earth's radiation budget (Formenti et al., 2011; Mishra and Tripathi, 2008; Sokolik and Toon, 1996; Tegen and Lacis, 1996). Mineral dust contributes about 50% of the global emission of tropospheric aerosols (Andreae et al., 1986). The net radiative forcing due to mineral dust ranges from -0.56 to $+0.1 \text{ Wm}^{-2}$ (Forster et al., 2007). The uncertainty associated with the net radiative effect of mineral dust is high (Boucher et al., 2016; Forster et al., 2007), and this can be minimised using more advanced characterisation techniques. It is worth noting that mineral dust is highly non-spherical amongst all species. Particles emitted from various sources get chemically processed when it comes in contact with urban pollution (Dey et al., 2008; Satheesh et al., 2007; Song and Carmichael, 1999). Chemical processing of dust particles in an urban environment results in various mixing configurations and modifies their optical and radiative properties.

Conventional techniques for single particle analysis like; Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and Transmission Electron Microscopy (TEM) give surfacial characteristics, and sometimes skewed elemental distributions due to x-ray self-absorption or matrix effects (Wentzel et al., 2003; Li et al., 2010; Arndt et al., 2016; Patterson et al., 2016; Fraund et al., 2017; Bahadar Zeb et al., 2018; Genga et al., 2018; Broström et al., 2019; Ching et al., 2019). They are not capable of revealing the actual three-dimensional (3D) structure

of the aerosol particle. Whether an absorber is on the shell or in the core of particles, these will impact the optical properties of an analysed particle. Such downsides highlight a significant need for multi-dimensional analysis of aerosol particles which could be capable of imaging 3D distribution of species and pores hidden from the conventional SEM/TEM-EDS analysis.

SEM and TEM coupled with EDS have been extensively used for the study of physical and chemical properties of individual aerosol particles (Goel et al., 2018b; Arndt et al., 2016; Cong, 2009; Li et al., 2011; Mishra et al., 2015). Focused Ion Beam (FIB) coupled with SEM and EDS, have been used to investigate the 3D distribution of species (internal structure) within an individual particle. FIB has been used to study the 3D composition of Asian dust and fly ash particles collected from different locations (Chen et al., 2013; Conny, 2013; Jeong and Nousiainen, 2014; Kemppinen et al., 2015). Conny et al., (2013) has shown the effect of atmospheric dust particle's internal 3D structure on their optical properties. They observed a remarkable difference in the results obtained from the conventional SEM-EDS with that of FIB-SEM-EDS (Conny, 2013; Kemppinen et al., 2015).

In this work, we analysed five coarse mode particles using FIB-SEM-EDS, two from the arid environment (The Thar Desert, Rajasthan, India) and three from the urban environment (New Delhi, India). In the Indian context, The Great Indian Thar Desert is a major source of mineral dust in South Asia (Deepshikha, 2005; Moorthy et al., 2007) and Delhi represents a typical urban environment (Goel et al., 2018a; Goel et al., 2018b). FIB-SEM-EDS was used to explore the internal structure of particles collected from the aforesaid sites. Model shapes of particles were designed based on the results obtained from FIB-SEM-EDS analysis. The purpose of this study is to provide the detailed 3D internal structure of the particle and its effect on particle optics. The

effect of particles' internal structure on particle optics was estimated by simulating optical properties (SSA and g).

2. Experimental details

2.1. Sampling site and particle collection: Aerosol particles were collected from arid [The Thar Desert, Jaisalmer (26.9157°N, 70.9083°E and 240m AMSL)] and urban environment [New Delhi (28.61°N, 77.20°E and 216m AMSL)] of India. In an arid environment, the particle collection was done using PM₅ (particulate matter with an aerodynamic diameter less than 5µm) sampler (Envirotech® APM801) during December 2013. Whereas, in an urban environment, the particle collection was done using fine particulate sampler with PM₁₀ (particulate matter with an aerodynamic diameter less than 10µm) inlet (Envirotech® APM550). The flow rate for the APM801 and APM550 samplers was maintained at 2.9 lpm and 16.7 lpm, respectively. The aerosol particles were collected on conducting tin sheets (dimension: 5*5mm), suitable for the FIB-SEM-EDS analysis. After collection, the samples were kept in small micro-biological tubes and stored in a desiccator to prevent them from contamination.

2.2. Particle analysis: FIB-SEM-EDS analysis requires a conducting sample. Therefore, particles were collected over the 99.99% pure tin substrate. The conducting sample prevents charge accumulation on the sample surface and enhances the secondary electron signal required for SEM imaging. The aerosol particles were initially analysed using SEM-EDS (Zeiss Auriga) which gives information of particle shape, size and elemental composition (of the upper surface). The aerosol particles were milled using a focused beam of gallium ions to investigate their internal structure. The focused gallium ion beam removes the unwanted material from the specimen surface, with nanometer precision, and

exposes the internal structure. After milling the particle, the elemental composition of the milled section was recorded using EDS. The morphological analysis (size and shape; aspect ratio) of the particles was done with the help of ImageJ software (Mishra et al., 2015; Goel et al., 2019b).

2.3. Modelling details: Optical properties (SSA and g) of the individual aerosol particles were numerically estimated using T-matrix and core-shell (Wu and Wang, 1991) models. The simulations were done for several model shapes like; single species homogeneous sphere (SP1), single species homogeneous spheroid (SPH1), multiple species mixed homogeneously in the sphere (SP2), multiple species mixed homogeneously in spheroid (SPH2) and core-shells structured particle (CS). Here, SP1 and SPH1 represent the homogeneous sphere/spheroid approximation which is generally considered in retrieval algorithms of satellite observations. SP2 and SPH2 model shapes have been generated on the basis of results obtained from conventional SEM-EDS. CS model shape is an advanced and more realistic 3-Dimensional model shape designed based on FIB-SEM-EDS results. In CS, variation in elemental composition with the depth of the particle was accounted. The simulation of optical properties for S1, SPH1, S2 and SPH2 were done with the T-matrix model, and for CS core-shell model was used. The generated schematic model shapes are shown in the Supplementary Information (SI, Fig. S1).

3. Results and Discussions

FIB-SEM-EDS is an ideal characterisation technique to investigate the internal structure of coarse atmospheric particles. The exposed internal structure can be studied in detail using SEM and EDS. Results obtained from the analysis were used to design model

shapes for simulating their optical properties (SSA & g). The specifics regarding the analysis and simulation are discussed in the following sections:

3.1. Particle characterization using FIB-SEM-EDS

3.1.1. Dust particles from the arid environment: The physico-chemical properties of particles collected from Jaisalmer, Rajasthan, are shown in Fig. 1 and Fig S2 (supplementary information). Fig. 1a shows the elemental composition of the particle using conventional SEM-EDS, i.e. without milling. Fig. 1a depicts that the particle is of spheroidal shape with rough surface. As the particle was collected from arid region, it was found to be rich in silicon (Si) and oxygen (O) with a good amount of iron (Fe), aluminum (Al), carbon (C) and trace amount of magnesium (Mg), calcium (Ca), copper (Cu), sulfur (S) and potassium (K). Fig. 1b shows FIB-SEM-EDS data of the internal structure of the same particle, i.e. after milling. Milling removes the upper layer of the particle and exposes its center. The EDS analysis was done after each milling to check the change in the elemental composition of the particle with depth. Results show that the core of the particle is rich in Si and O, which is identified as a quartz. The atomic percentage of Si and O (1:2) confirms the presence of SiO_2 (quartz) core. Fig. 1c confirms that the species like Fe, Cu, Ca, C, Mg, and Al are heterogeneously distributed at the surface of the particle. The findings suggest that the particle has core-shell mixing state, where the quartz-rich core is coated with a shell formed by the randomly distributed patches of Fe, Cu, Ca, C, Mg, and Al. The core-shell type mixing configuration of the quartz-rich particle may be attributed to the electrostatic charge at the quartz surface (J. D. Lee., 2008). The negatively

charged quartz surface can attract the positively charged metals, which result in a core-shell mixing configuration.

3.1.2. Particles from the urban environment: In an urban environment, chemical reactions between gases and other chemical species with pre-existing aerosol particles make particle chemistry more complex (Li et al., 2012, 2011; Srivastava et al., 2018). These reactions change the physical and chemical characteristics of the particles and alter their optical and radiative properties (Jacobson, 2001; Wang et al., 2010). Therefore, urban particles were also analysed using FIB-SEM-EDS. SEM-EDS data of the urban particles is shown in Fig. 2, S3 and S4. The spherical particles were found with rough surface. EDS shows the particle to be rich in Cu, Hg, C, N, O, and S with traces of Ag. Fig. 2a and b show SEM-EDS data observed before and after FIB milling, respectively. After milling, the mass percentages of C and N were found to decrease from 6% to 1% and 7% to 3%, respectively. Whereas, the mass percentage of Cu, Ag and S increased from 49% to 60%, 2% to 6% and 11% to 13%, respectively and Hg did not show any percentage variation, i.e. stayed at 17%. Results reveal that the mass percentage of C and N is decreasing with depth while the same for Cu, Ag, and S is increasing. After 3rd milling, a micron size pore was found inside the particle as shown in Fig. 2e. It is worth noting that the elemental composition of the particle is highly heterogeneous. Overall, the particle was found in core-shell mixing configuration, where Cu and S rich core is coated with a shell made of Hg, C, N, and Ag. FIB-SEM-EDS analysis of other two particles from the urban environment is shown in Figs. S3 and S4 of supplementary information.

The aforementioned particles may be emitted from brake wear as it is a major source of copper in the urban environment (Hulskotte et al., 2007; Mishra et al., 2017). There are nearly 88,32,192 vehicles registered in Delhi (delhi.gov.in). According to a survey, vehicles in Delhi crawl at the speed of 5km/h in peak hours which leads to excessive use of breaks and this may release copper in the atmosphere. There are many copper polishing industries, wastewater treatment plants, solid waste disposal plants in Delhi, making a potential contribution to copper in the atmosphere. Mercury (Hg) is a potent neurotoxin, particularly damages the development of fetus, infants and children. The United States Environmental Protection Agency report (2015) notes that the coal-based thermal power plants are the primary anthropogenic source of Hg in the atmosphere; almost 50% of total Hg content in American atmosphere comes from these sources (2005 National Emission Inventory, EPA). There are two coal-based thermal power plants near to the sampling site; one in Rajghat another is in Badarpur, both of them were fully functional during the sampling period and could be the significant source of Hg in the atmosphere.

3.1.3. Hidden pores: After FIB milling, pores were found inside the particles collected from the urban environment (Fig. 3). The particles were milled with FIB gun to explore the internal structure. The white arrows in fig. 3 indicate the pores found in the analysis these pores always remain hidden from the conventional SEM. The pores may be formed due to dehydration of the particle during different weather conditions (Adler et al., 2013; Jeong and Nousiainen, 2014). The optical properties of the particle with pores inside will be different than the solid spherical/spheroidal particle (Nousiainen et al., 2011).

3.2. Modelling framework: The optical properties of the individual aerosol particles were simulated using the T-matrix and core-shell model. T-matrix model was used for simulating optical properties of S1, SPH1, S2 and SPH2. And for CS, the core-shell model was used. In the aforementioned optical models, refractive index, size, shape and mixing configuration works as input. Shape and size of the individual aerosol particles were determined using the ImageJ software, and the refractive index was obtained from EDS analysis. The mixing configuration was identified with the help of FIB analysis. In the atmosphere, most of the elements are generally observed in their oxides. Therefore, the amount of oxygen found in EDS analysis was distributed among all elements, depending on their mole fraction in oxide form. The elemental to oxide conversion was done using the approach discussed in Agnihotri et al., 2015 and Goel et al., 2018b. Elements were converted into their respective oxides after the intensive literature survey. Thus, the elements were converted into their most probable oxide form (e.g. Mg considered as MgO; Fe considered as Fe₂O₃; etc.). Further details regarding elemental to oxide conversion can be found in the supplementary information. Refractive index (RI) is a function of chemical composition.

$$\text{Refractive Index} = n \pm ik$$

n = real part of refractive index

k = imaginary part of refractive index

Real part (n) is responsible for the scattering, and imaginary part (k) is responsible for the absorption of electromagnetic radiation. Higher the 'k' value higher will be the absorbing potential of the particle.

In aerosol particles, carbon is present in three different forms, i.e., black carbon (BC), brown carbon (BrC) and organic carbon (OC). All the types of carbon have a different refractive index (Feng et al., 2013; Gustafsson and Ramanathan, 2016). Therefore, the optical properties simulations were done for three different cases. In the first case, in all the model shapes, total carbon was assumed as BC, in second and third cases total carbon was considered as BrC and OC, respectively. The absorbing character among the abovementioned carbon species varies in the following order: BC > BrC > OC.

3.3. Spectral refractive index: The mass concentration of individual particles was converted into oxide fraction and finally into volume fraction (f_i) using the density data (Agnihotri et al., 2015; Liu and Daum, 2008) (Eqs. 1 and 2). Then, using the volume fraction (calculated above) and spectral refractive index of each oxide, we have computed the complex refractive index of an individual particle with the help of volume mixing rule (eq. 1 and 2).

$$n_{eff} = \sum_{i=1}^n n_i f_i \quad (1)$$

$$k_{eff} = \sum_{i=1}^k k_i f_i \quad (2)$$

Here, n_i and k_i are the real and imaginary part of the refractive index of i^{th} oxide at a given wavelength. f_i is the volume fraction of the i^{th} oxide in an individual particle. n_{eff} and k_{eff} are the effective real and imaginary part of the complex refractive index of an individual particle.

The spectral refractive index of oxides was taken from different sources (Ackerman and Toon, 1981; Agnihotri et al., 2015; Kim et al., 2015; Krueger, 2003; Martinson et al.,

2013; Mishra et al., 2008; Peterson and Weinman, 1969; Toon et al., 1976). Here, we studied optical properties such as SSA and g for mono-disperse dust particles of given chemical composition and size. Refractive index of the particles strongly depends on the interacting wavelength (Sokolik and Toon, 1999). Therefore, it becomes a point of significant concern to calculate the optical properties for a spectral range (440–860nm). This wavelength range covers the entire shortwave region, which is essential for understanding shortwave radiation impacts.

3.3.1. Modelling spectral optical properties of dust particle: Fig. 4 shows the spectral variation of SSA and asymmetric parameter of the dust particle shown in Fig. 1. The volume equivalent radius of the particle is $3.61\mu\text{m}$. In conventional SEM-EDS, the particle was found to be rich in silicon (Si) and oxygen (O) with a good amount of iron (Fe), aluminum (Al), carbon (C) and trace amount of magnesium (Mg), calcium (Ca), copper (Cu), sulfur (S) and potassium (K) (fig. 1a). After FIB milling, the particle was observed in core-shell mixing configuration, where the core is of quartz and shell is made of Fe, Cu, Ca, C, Mg, and Al (Fig 1b and c). Therefore, five different model shapes were designed using the aforementioned results. The model shapes are; 1) SP1 (quartz sphere), SPH1 (quartz spheroid), SP2 [sphere made of MgO , Al_2O_3 , CaCO_3 , Cu_2S , KCl , Fe_2O_3 and C (BC, Brc and OC)], SPH2 [spheroid made of MgO , Al_2O_3 , CaCO_3 , Cu_2S , KCl , Fe_2O_3 and C (BC, Brc and OC)] and CS is a core-shell structured particle. In core-shell particle, the core is of quartz (SiO_2), and the shell is of SiO_2 , Fe_2O_3 , MgO , Cu_2S , CaCO_3 , and C. The radius of core of the particle is $2.51\mu\text{m}$ and the shell thickness is $1\mu\text{m}$. Figs. 4a-f show the spectral variation of SSA and asymmetric parameter (g). In fig 4a and d, total C was

approximated as BC; in fig. 4b and e, total C was approximated as BrC and in fig. 4c and f, entire C was approximated as OC. In all the three cases, SSA for SP1 and SPH1 was observed to be ~ 1 at all wavelengths (Fig. 4a-c), showing strong scattering nature of the particle. The high value of SSA for SP1 and SPH1 was attributed to the very low value of 'k' for quartz. In figs. 4a and b, SSA of SP2 and SPH2 were observed to be significantly low, i.e., ~ 0.55 (Fig. 4a, b) which is attributed to the high value of imaginary part of refractive index (k) of hematite, BC and BrC at all wavelengths. SSA of S2 and SPH2 in fig. 4c was observed to vary from 0.55 (440nm) to 0.94 (860nm) which is attributed to the very high spectral variation of k of OC. SSA of SP2 and SPH2 was observed to be spectrally independent in Fig 4a, b and spectrally dependent in fig. 4c. In the case of OC, k decreases with wavelength. In CS, which is the most realistic model shape among the all considered shapes, the strong spectral variation of SSA was observed. In figs. 4a, b and c, SSA of CS was observed to vary from 0.55 to 0.67, 0.55 to 0.75 and 0.55 to 0.98, respectively. In all the three cases, SSA of CS was observed to be lower than SP1 and SPH1 and, higher than that of SP2 and SPH2. The results showed that in SP1 and SPH1 model shapes SSA is overestimated while in SP2 and SPH2, SSA is underestimated compared to that of CS model shape. The spectral difference in SSA between CS and SP2, SPH2 shapes increases with increasing wavelength (Fig 4a, b) and the maximum difference was observed at 860 nm. In all the three cases, the negligible difference between SP1 and SPH1 along with SP2 and SPH2, was observed. Therefore, in the case of sphere and spheroid, the effect of particle shape is nearly negligible in the present condition.

The bottom panel of Fig. 4 shows the spectral variation of the asymmetric parameter. For SP1 and SPH1, the value of g was observed to be minimum as compared to other model shapes (figs 4d-f). However, we found the maximum difference between SP1 and SPH1 on 670nm and minimum on 860nm. In the case of SP2 and SPH2, g was found to be relatively high. The strong spectral dependence of g was observed in Fig. In the present study, SSA and g are found to be sensitive to the particle's internal structure, and the sensitivity was observed to be high for the particles with a low value of imaginary part of the refractive index (k) and vice versa. Spectral variation of SSA and g depicts that the difference between CS and other model shaped increases with increasing wavelength and found to be maximum on 860nm and minimum on 440nm.

3.3.2. Modelling spectral optical properties of urban particle: In the case of the urban particle, three particles were analysed using FIB-SEM-EDS. Fig. 5 shows the spectral variation of SSA and g of the particle shown in fig. 2. Volume equivalent radius of the particle was observed to be 1.84 μ m. In conventional SEM-EDS, the particle was found to be a homogeneous mixture of various species as discussed in section 3.1.2. In FIB milling, the particle was found in core-shell mixing configuration. Therefore, five different model shapes were designed to check the sensitivity of internal structure, shape and chemical composition on particle optics. The developed model shapes are; SP1 (Cu₂S sphere), SPH1 (Cu₂S spheroid), SP2 (homogeneous sphere made of HgO, AgO, Cu₂S and C), SPH2 (homogeneous spheroid made of HgO, AgO, Cu₂S and C) and CS is a core-shell structured particle where core is of C, Cu₂S and shell made of in AgO, HgO, Cu₂S, and C. The radius of the core was 1.24 μ m And

the shell thickness was 0.6 μm . As discussed earlier also three different cases were considered where the total carbon was approximated as BC, BrC and OC. Spectral variation of SSA (upper panel) and g (bottom panel) for the three cases are shown in Fig. 5. In all the three cases, SSA for all model shapes was observed to be ~ 0.65 from 440-680nm wavelength, which indicates a highly absorbing character (Figs. 5a-c). Increase in SSA for SP1 and SPH1 on 860nm was observed due to a decrease in k (imaginary part of the refractive index) of Cu_2S . For SP2, SPH2 and CS, SSA was found to be ~ 0.60 , which is attributed to the high value of k for BC and BrC (Fig. 5a, b). In fig 5c, SSA for SP2, SPH2 and CS were observed to be ~ 0.60 from 440 to 670nm, but on 860nm SSA increases due to the decrease in k of OC. The internal structure of the particle was not found to have a pronounced effect on SSA (Fig. 5a-c) in the present case.

The bottom panel of Fig. 5 shows the spectral variation of the asymmetric parameter. The effect of particle shape and internal structure on the asymmetric parameter was found to be highest on longer (860nm) wavelength. SP1 and SPH1 were observed to vary from 0.73 to 0.57 and 0.73 to 0.62, respectively (Fig. 5d-f). In the case of SP2 and SPH2, an increasing pattern is observed from 0.77 to 0.79 and 0.77 to 0.79, respectively. Fig. 5f shows that the asymmetric parameter for SP2 was found to increase from 0.80 to 0.82, but for SPH2 it first increases from 0.80 to 0.82 (between 440 and 670nm) then decreases to 0.70 at 860nm. In the case of CS, the model could not converge on 440nm due to high shape parameter. In all the three cases, the asymmetric parameter was simulated from 550nm to 860nm where it was observed that g increases at 550 and 670nm whereas decreases at 860nm.

4. Conclusion:

FIB-SEM-EDS method described in the present study brings new insights into the field of aerosol characterization, which other conventional characterisation techniques could not. Although a limited number of particles from the arid and urban environment were analysed in the present study, given that FIB is time-consuming. This work successfully presents the methodology and demonstrates its usefulness in the context of particles from both arid and urban environments. Both the studied mineral dust particles had a core-shell configuration. Whereas, in the urban environment particles, one particle was found in core-shell mixing configuration and the other two were homogeneously mixed. SSA and g were observed to be dependent on particles' internal structure. SSA and g are observed to be more sensitive to the internal structure of the particle with a low value of the imaginary part of the refractive index (k) and vice versa. Optical properties of particles having higher k value were observed to be independent of the internal structure of particle on short wavelength and dependent on longer wavelength. The future studies would focus on accounting for the effect of pores on particle optics. The copper rich particles were observed to have high ' k ' value, which shows highly absorbing nature of the particles. The study will be useful in minimizing the uncertainties in numerical estimations of optical and radiative properties of aerosol particles.

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Figures

Figure 1. SEM-EDS analysis of dust particle, rich in Si and O: (a) without milling (b) with milling, and (c) with and without milling.

Figure 2. FIB-SEM-EDS analysis of urban particle collected from Delhi that are rich in Cu, Hg and S based on (a) without milling, (b) after 2nd milling, (c) after 3rd milling, (d) after 4th milling, (e) analysis of cavity observed after 3rd milling, and (f) analysis of the same cavity after 4th milling.

Figure 3. Pores observed inside the particles during milling: (a) urban particle shown in SI Fig. S3, and (b) urban particle shown in Fig. 2.

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25 **Figure 4.** Spectral variation of SSA (top panel, a-c) and g (bottom panel, d-f) for dust particle
 26 shown in Fig. 1.

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Figure 5. Spectral variation of SSA (top panel) and g (bottom panel) of urban particle shown in fig2.

Highlights:

1. Aerosols were collected from urban (New Delhi) and arid (Jaisalmer) environment.
2. Three-Dimensional characterization was done using FIB-SEM-EDS.
3. Particles were observed in core-shell mixing configuration with embedded pores.
4. Particle model shapes were generated using FIB-SEM-EDS Results.
5. Optical Properties (SSA, and g) were simulated using T-matrix and core-shell code.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: