Journal of Aerosol Science 126 (2018) 122–132

Contents lists available at ScienceDirect

Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

A semi-automatic analysis tool for the determination of primary particle size, overlap coefficient and specific surface area of nanoparticles aggregates

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ARTICLE INFO

Keywords:
Electronic microscopy
Image processing
Nanoparticles aggregates / agglomerates
Specific surface area

ABSTRACT

The high reactivity of nanostructured materials makes their use very attractive for various industrial applications. However, these materials may also have an important impact on health / environment / climate and on the performances of protective devices (i.e. high efficiency particulate air filters, electrostatic precipitators). Those properties are mainly due to their high specific surface area, which is directly related to the size of the non-porous primary nanoparticles and to the nature of the bridging between them (from point contact for agglomerates to partial fusion for aggregates).

In this paper, a straightforward image processing has been developed to measure, assuming a log-normal size distribution, the primary particle diameter (D_{pp}), the geometric standard deviation GSD (or σ_g), the projected overlap coefficient ($C_{ov,\ p}$) and the specific surface area (SS) directly from TEM images according to the approach introduced by Bau, Witschger, Gensdarmes, Rastoix, and Thomas (2010). Measurements have been performed from TEM images obtained for 22 different kinds of nanoparticles, from simple spheres to soot particles and virtual aggregates. The results show a good agreement (within ± 20%) between automatic and manual analysis of D_{pp}, σ_g and SS while the overlap coefficient has been compared to the manual analysis showing a reasonable agreement (within ± 40%).

1. Introduction

The study of environmental pollution caused by soot particles is an active research field. Recently, it has been shown that the morphological structure and the overlap coefficient between primary particles composing soot are directly correlated to their optical/radiative properties (Liu, Yon, & Bescond, 2015; Yon et al., 2014).

Beyond their climate impact, toxicity of those particles is now commonly assumed to have serious public health implications. Several authors have reported that exposure to diesel particulates increases the risk of mortality from lung cancer (Attfield et al., 2012) and that their toxicity is mainly correlated to their specific surface area (Schmid & Stoeger, 2016; Steiner, Bisig, Petri-Fink, &

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https://doi.org/10.1016/j.jaerosci.2018.09.001
Received 9 February 2018; Received in revised form 27 August 2018; Accepted 3 September 2018
Available online 05 September 2018
0021-8502/

Rothen-Rutishauser, 2016). The reference method for measuring this specific surface area is based on inert gas adsorption analysis (BET method, Sing, 1985), but as a minimal quantity of powder (at least 100 mg for nanostructured powders from Karg, Ferron, Schumann, & Schmid, 2008, which represents 10 m^2 for $S_{BET} = 100\ m^2/g$) is needed for such techniques, in certain cases it becomes necessary to derived the specific surface area from TEM images. Usually, determination of the morphological parameters (diameter of the primary particles and overlapping coefficient) from TEM pictures is made manually, which introduces a bias induced by the operator subjectivity and involves a limited number of analyzed images, about 100 depending on the dispersion of the measured parameter. Numerical image processing is a good compromise to improve the quality of those measurements and avoid the uncertainty related to subjectivity of the operator. If recent developments have mainly focused on the determination of the size of primary particles and the fractal dimension of the agglomerates/aggregates (Bescond et al., 2014; Dastanpour, Boone, & Rogak, 2016; Mirzaei & Rafsanjani, 2017), limited work has been performed regarding the overlap coefficient between primary particles (De Temmerman, Verleysen, Lammertyn, & Mast, 2014). To our best knowledge, there is no recent study dealing specifically with the issue of the automated determination of the specific surface area based on TEM image analysis.

Because of the potential health effects of such particles, it is necessary to develop suitable reduction devices such as High Efficiency Particulate Air Filters (HEPA), electrostatic precipitators or scrubbers. All these devices require the efficiency to be as high as possible in order to avoid any release of NOAA (NanoObjects, their Agglomerates and Aggregates) nanostructured particles in the atmosphere or human exposure. Nevertheless, for such situations, the pressure drop induced by the formation of a soot cake at the filtration medium surface represents a significant economic cost. Furthermore, for safety application and especially in the nuclear industry, containment of hazardous particulate materials must be maintained despite the situation. Prediction of airflow behavior of containment elements such as HEPA filters in case of fire directly depends on the properties of the particulate pollutants (Ishibashi, Tsuchino, Matsumoto, & Kasahara, 2014; Ouf et al., 2014). In the currently used phenomenological models of filter clogging (Bourrous et al., 2016; Kim, Wang, Shin, Scheckman, & Pui, 2009; Thomas, Ouf, Gensdarmes, Bourrous, & Bouilloux, 2014), the pressure drop of a filter clogged by soot particles can only be estimated from the primary particles size and the overlap fraction of particles between them. Nevertheless, most of the commercially available online measurements (Scanning Mobility Particle Sizer (SMPS), Aerodynamic Particle Sizer (APS), Electrical Low Pressure Impactor (ELPI)) only provide/report an equivalent diameter relative to the physical behavior of aggregates (settling velocity, electrical mobility…). None of them is able to determine in a direct way the primary particle size distribution and their overlap coefficient.

In most cases, Transmission Electron Microscopy is the reference method (Brasil, Farias, & Carvalho, 1999; Köylü, Faeth, Farias, & Carvalho, 1995) for measuring the morphological properties of fractal aggregates formed during combustion processes. Since the application of Mandelbrot's fractal theory by Jullien and Botet (1987) for describing the shape of nanoparticles aggregates/agglomerates formed by diffusion limited cluster aggregation (DLCA), many authors have proposed automatic tools for measuring the diameter of primary particles. Such developments were motivated by the need to reduce the time of analysis, to increase the statistics and finally to avoid as much as possible any human operator subjectivity. The latter effect has been investigated in the present work from TEM images of soot particles produced by an ethylene diffusion burner and sampled on TEM grids (Ouf, Yon, Ausset, Coppalle, & Maillé, 2010). Manual analysis by two separate human operators was carried out for the same samples and the corresponding mean primary particle diameters are compared in Fig. 1a. The agreement between each operator appears to be reasonable within a confidence interval of ± 20%. Other authors (Anderson, Guo, & Sunderland, 2017; Kondo, Aizawa, Kook, & Pickett, 2013) reported similar fluctuations for flame spray soot (respectively ± 14% and ± 17% from these sources). Then, ± 20% will be considered as the maximum acceptable discrepancy between the proposed automatic analysis and a manual one of primary particle diameter. Similar comparison has been conducted for the overlap coefficient and the results are presented in Fig. 1b. For this parameter, the discrepancy between the results obtained by two operators can reach nearly 35%. This bias can be problematic for predictive computations based on this value and for any application that (would) require(s) a fine knowledge of the particles properties/reactivity or

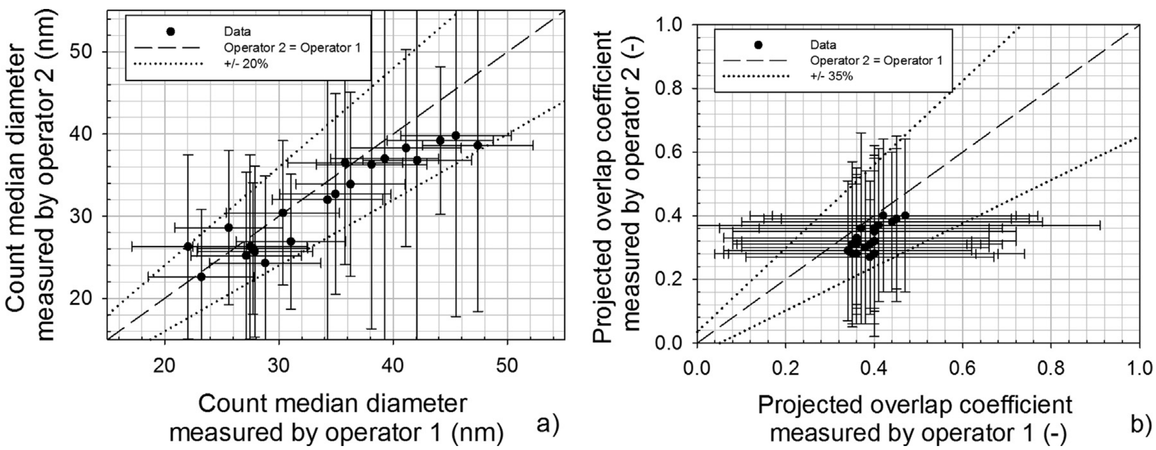

Fig. 1. Comparison between count median primary spheres diameters (a) and projected overlap coefficients (b) measured by two human operators for soot particles produced by an ethylene diffusion flame, (adapted from Ouf et al., 2010).