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# Phase-resolved particle size distribution: New insight into material characterization

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ABSTRACT

Particle size distribution (PSD) is a relevant property of powdered solid matter since it directly influences the functionality of solid products such as pharmaceutics, cosmetics, abrasives, ceramics, metals, pigments, catalysts, and chemical reactants. Several methods and techniques, based on various physical laws, are available to determine the PSD. In all the existing approaches particulate matter homogeneity is assumed, e.g. unique chemical composition, crystalline phases, refractive index, density, and shape for the entire population of particles. A real sample might be a mixture of a number of materials, each of them with well-defined physical properties and particle size distributions. The simultaneous measurement of particle size and particle nature is still not achievable with the existing technologies. Here we present the concept and the results of a new experimental setup able to simultaneously combine PSD and X-ray powder diffraction. The obtained analytical information is the *phase-resolved particle size distribution* (PR-PSD) of the solid matter in suspension.



Several chemicals are sold in form of powders or contain powders. Every industry dealing with chemicals in solid form carries out quality tests on the incoming raw materials and on the intermediate and final products. At least a few parameters representing the PSD of the solid matters are included in quality control protocols. Thus, one or more instruments for PSD measurement are comprised in the analytical instrument portfolio of modern laboratories. In research, the details of the PSD is more and more exploited to understand the mechanism of particles formation as well as how material properties are affected by few percent of solid matter which delimits the tails – towards both the bigger or the smaller limit – of the particle size distribution curve, which can influence the product quality. For instance, in electronic industry sub-micrometric metal oxide particles are used in the production of a number of thin layered ceramic components produced by tape casting. If the metal oxide slurry used in processing contains particles with a size comparable to the produced ceramic layer, the consequent defects will cause the entire device failure. It means that a very small (numerical) fraction of large particles have a direct influence on the device reliability. On the other hand, a minor (mass) fraction of very small particles could act as beneficial sintering aid.

Often the powdered matter is a mixture of solids of different nature. In these cases, the pragmatic approach consists in the identification of the composition via a suitable technique – which depends on the material nature under investigation – and afterwards the PSD is measured, assuming composition-averaged properties for the material mixture. It turns out that key material properties, as a consequence of the composition homogeneity assumption, may not be correctly assessed or even wrong conclusions might be made.

In order resolve the PSD component-by-component, a component-selective physicochemical property has to be measured and combined with the PSD data. In principle, it could be possible to sort the particles in size classes (e.g., by sieving) and then carry out a compositional analysis for each class. This method is clearly time-consuming, only a poor size resolution can be obtained, and it is not applicable in case of micrometric- or submicrometric-size particles. A more efficient method, fast, and suitable even for nanoparticles has to be found. Ideally, particle size and compositional analysis should be carried out simultaneously and without the need of dividing the sample in sub-samples. The concept of simultaneity implies that the compositional and particle size analysis methods have to fulfill some constraints, as discussed later.

Among instruments for particle size measurement, those based on sedimentation or centrifugal methods should be convenient for the present study. This method has been largely studied since the 1950's and nowadays several commercial analytical instruments

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are based on this concept [1]; it allows measuring particles in a relatively large size range (from few nanometers to micrometers) and the PSD can be resolved in an adjustable time frame (from few minutes to hours). The solid matter is suspended in a liquid (the moderating agent) that may be confined in the cavity of a spinnable disc. The sedimentation time can be controlled by the density and the viscosity of the moderating agent and by the centrifugal force, which is defined through the geometry and the rotational speed of the disc. The suspension is initially macroscopically homogenous while, upon rotation up to some thousands of revolution per minute, the particles sediment driven by the centrifugal force. This measuring method is known as the homogenous incremental centrifugal sedimentation method [1]. The physical law which defines the sedimentation speed is the well-known Navier-Stokes equation, also known as Stokes' law for the frictional force [2]. The signal related to the particle size is the attenuation of a laser or X-ray light, passing through the disc at a known distance (the measuring point, $r_m$) from the air-liquid meniscus ($r_0$), which takes place upon rotation (Fig. 1, inset). The volume under analysis around $r_m$ (beam spot size) has to be as small as possible since it defines the PSD resolution (*resolution constraint*). If X-rays are used, the beam attenuation is proportional to the mass concentration of the particle in suspension. The centrifugal force (i.e., the spinning speed) as well as the measuring position may be tuned during the measurement. The particle size distribution is then determined by the Kamack's equation [3], which correlates the particles size with their terminal velocity, time, and the disc geometry. The determined particles size is the "Stokes size" which corresponds to the diameter of spherical particles which sediment at the same speed of the particles under analysis.

The analytical method (i.e., the component-selective physico-chemical property method) used to identify the particle nature should be particle size insensitive. The analytical information has to be collected at $r_m$ in order to match the two data sets: particles size and particles nature. The analytical information must be collected in a rather short time compared to the sedimentation speed (*speed constraint*). An additional constraint rises from the quality of the analytical data collected, i.e. the signal-to-noise ratio, which depend on the instrumental setup used (*S/N constraint*). *Speed*, *S/N*, and *resolution constraints* are interlinked and the best trade-off has to be found for each combination of particle sorting and analytical methods applied.

The concept of the PR-PSD is here demonstrated combining a centrifugal sedimentation apparatus, as particle size sorting method, with a fast high resolution diffractometer, as analytical method, which is able to fulfill the *speed*, *S/N*, and *resolution* constraints. Specifically, an *ad-hoc* modified disc centrifuge is combined with the synchrotron X-ray diffractometer of the MS-X04SA beamline at the Paul Scherrer Institute [4].

Fig. 1 represents the experimental setup. The X-ray synchrotron beam (yellow dashed line) is focused at $r_m$. At defined time steps, for instance every one minute, a new Bragg diffraction pattern is accumulated with a Mythen detector [4]. Simultaneously, the overall X-ray attenuation signal is measured with a photodiode. Due to the particle sedimentation, the overall transmitted light intensity increases (decrease of the attenuation signal) while the intensities of the diffraction peaks decrease against time. The intensities of the Bragg diffraction peaks are phase-selective and are used to measure the PR-PSD. The attenuation signal is compared with the one collected by a commercial instrument (Brookhaven X-ray Photocentrifuge, BI-XDC), which can operate in the same conditions (suspension, speed, and disc). The method can be easily validated by measuring single phase samples: the normalized signal collected from the BI-XDC, from the photodiode at the beamline, and derived from the integral intensities of the diffraction peaks are related to the same physical process and the same PSD have to be deduced (Fig. S2–S4, Supporting Information).

Fig. S1 (Supporting Information) summarizes some of the common analytical questions that the PR-PSD instrument can elucidate in case of non-homogeneous samples. Two examples are here discussed in detail: (a) a mixture between $TiO_2$ anatase and $TiO_2$ rutile sub-micrometric particles, which correspond to the case *A* in Fig. S1 and (b) a mixture between $ZrO_2$ (monoclinic,

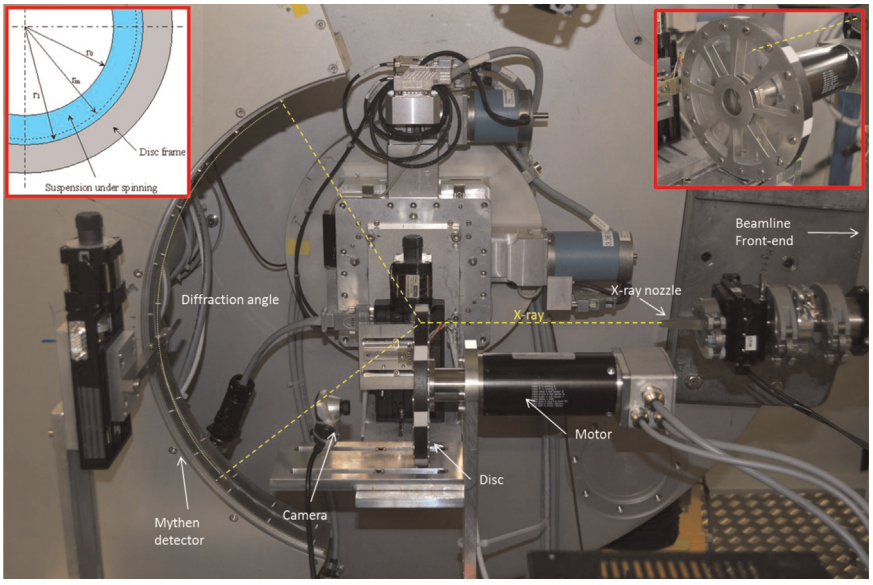


**Fig. 1.** Overall view of the experimental setup. An electric motor is connected to the central axis of a disc that contains the particles in suspension under analysis. The disc (upper-right inset) is composed by a metal frame and polymethacrylate X-ray transparent sectors. The X-ray patterns are collected through the transparent sectors by synchronization the disc rotation and the detector acquisition. The white and black strips on the disc surface are detected by an optical system for the synchronization. This special disc design allows very low background signal as well as appropriate mechanical strength to withstand the centrifugal force. The upper-left inset represents the liquid-air meniscus ($r_0$), the disc cavity radius ($r_1$), and the measuring distance ($r_m$) during rotation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)