Restructuring of Soot Fractals in Flames: Small-Angle X-ray and Light Scattering Experiments

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Keywords: SAXS, Laser Scattering, Soot Nanoparticle Aggregates, Restructuring

The recent issue of nanoantennas demonstrate that the electromagnetic wave interaction with nanostructures and the energy transfer does depend on the morphology in a wide spectrum of frequency from UV to IR to Microwaves. In particular the radiative transfer in atmosphere and the consequent dynamics of primary and secondary aerosol formation relies strongly on appropriate knowledge of the morphology and microstructure of the aerosol nanoparticle clusters. Examples of this crucial dependence, which can be as large as factor 10 with respect to single primary nanoparticle albedo and the condensation of water vapors on carbon cluster surface, may yield to possible breaking of primary-primary bonds and rearrangement of the original aggregates in closely packed globules.

This lecture proposes the comparative analysis of Polarized Laser Light Scattering (PLLS) and small angle X-ray scattering (SAXS) experimental studies performed on diffusion flame systems. The wavelengths of the two kinds of electromagnetic radiation differ of about 4 order of magnitudes (λ=514.5 nm for PLLS and λ=0.077 nm for SAXS at 16 keV energy in this work). The complimentary character of the two techniques is evident if one observes that the phase shift on the minimum observable particle lighted by the incident electromagnetic radiation must be detectable. A standard rule-of-thumb fixes at about λ/10 the minimum size of particles for which scattering techniques can be applied. This rough experimental criterion justifies the fact that a particle smaller than 20 nm very hardly will be detected by laser light. Vice versa, SAXS has an ideal down-size limit of a few Ångströms, and allows for detecting of very small particles and molecular clusters (di Stasio, 2001a; di Stasio et al, 2006). The fascinating thing is that in the case of PLLS the scattering techniques are relatively insensitive to the large variations of the soot optical constants (n, k) at visible wavelengths. On the contrary, for SAXS that probes the contrast, i.e., the square of background-particle differences in terms of electron density and not in optical constants, is very sensitive to the degree of microstructure order, that are the parcels of graphite-like matter composing the nanoparticles (di Stasio and Braun, 2006). This is really amazing for two techniques that are both treated on the basis of the same mathematics, that is the Hilbert transform of the real r-space to the Fourier transformed q-space. The complimentary character of SAXS with respect to PLLS is demonstrated when both techniques reveal the phenomenon of nanoparticle chain restructuring in a flame (di Stasio, 2001b; Mitchell et al, 2006). Useless to say, this mechanism is so delicate to occur that non only physical probing (TEM) but even the aspirating of partial flux for SMPS analysis would destroy completely the nature of the process.

I will show the experimental paradigm SAXS plus PLLA for a full characterization of the restructuring events by flame soot nanoparticle aggregates. Firstly, SAXS experiments on the flame will be used to gain information on soot size and concentration but also on the skeleton density and the pore fraction of the soot primary and sub-primary particles. These quantities are closely related to the restructuring event, in that soot particles are known to be oxidized in a flame from their interior. Thus, the scavenging of soot primary particles and the progressive consumption of the inner mass, which occur in several places concurrently and may generate pores (typically 20 to 40 Å) is expected to cause cluster structural instability with the collapse of the aggregates into lumps. Secondly, PLLS measurements on the flame will be used to measure the morphological quantities (radius of gyration and fractal dimension) that characterize the fractal-like nature of flame soot aggregates. Finally, a computational and very simple scheme will be introduced (Verdier and Stockmayer, 1961) borrowed from polymers modeling to show that, even at room temperature, restructuring events can occur. Also this last theoretical prediction was confirmed by our previous experimental work (Onischuk et al, 2004).

References


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In-situ X-ray scattering measurements for particle and chemical analysis in flames and reactors

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Keywords: Soot, Nanoparticles, Chemistry, Flames, X-ray scattering.

Small nanoparticles produced in gas-phase reactive systems such as combustion are of major concern for health and environment on both local and global scales. They can easily diffuse out of the combustion/reaction region, pass through biological barriers and also be transported far up into the atmosphere and be dispersed by jet streams. Nanoparticles are also of great interest for modern industry. Consequently, diagnostic tools that can provide enough detailed description of the particles will be strongly required. The physical and chemical properties of small particles are dependent on the atomic level structure, which can be revealed in-situ by the use of X-ray scattering techniques. Wide-angle X-ray scattering (WAXS) diagnostics has been used by our group to characterize the structure of carbon particles smaller than 2 nm [1]. Another technique, which has been applied more extensively by different groups is small-angle X-ray scattering (SAXS) that delivers data on the size distribution, morphology and concentrations in a wide size range 1-200 nm, up to the fractal structures of mature soot [2-6]. During approximately the last 10 years our group has been developing scattering diagnostics for flames and reactive systems, starting with WAXS and then combining it with SAXS in order to get a more complete picture of the formation dynamics of incipient carbon nanoparticles and phase transfers in connection to condensation in to materials [7,8].

In order to obtain sufficient resolution the wavelength of X-ray radiation should be in a wavelength range of 1-2 Å. The photon flux required for gas-phase experiments has to be very high and that can be obtained at 3rd generation synchrotron facilities typically such as the European Synchrotron Radiation Facility (ESRF), Grenoble, France, and the Advanced Photon Source (APS), Argonne (IL). Most of our techniques have been developed and experiments performed at MAX-lab, Lund, Sweden, that delivers less flux, but still have delivered important results.

On the technical side we have developed a combined multichannel detector system for simultaneous SAXS and WAXS in order to capture the formation dynamics of the size and structure of particles in flames and reactive systems [9,10]. The detector can continuously pipeline SAXS and WAXS data with 24-bit resolution and 120 dB analog bandwidth, at a rate of 204.8 k Samples s⁻¹. This means that single events can be measured if the scattering is sufficiently strong. The high dynamics range enables us to study condensation and phase transfers with the same settings on the detectors and the high resolution to evidence small signatures in the scattering.

In the last years we have continued the developments of diagnostics applying vertically polarized radiation, yielding a higher sensitivity at scattering angles around 90°, where most of the atomic level structure is contained and can provide chemical information on nanoparticles, precursors and the major gas species, e.g. from monoatomic to triatomic molecules, including CO2 [11]. Consequently, the diagnostics opens up for synergy between modellers and experimentalists on studies of flame/combustion and particle chemistry.

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Angular light scattering measurements of combustion aerosols with a custom developed portable instrument

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Keywords: soot, angular scattering, fractal dimension, RDG-FA theory.

Introduction

Soot particles have a fractal-like shape, are produced during incomplete combustion processes and are a major constituent in the atmosphere. These fractal-like particles have a self-similar structure, are composed of spherical primary particles (monomers) of black carbon. Due to the fractal-like shape the number of primary particles ($N$, proportional to the aggregate's mass) scales as a power law with the characteristic size of the aggregate ($R_g$, radius of gyration):

$$N = k_0 \left( \frac{R_g}{a} \right)^{D_f}$$

Where $k_0$ is a constant in the order of unity, $a$ is the radius of the primary particle and $D_f$ is the fractal dimension.

The angular light scattering of fractal aggregates depends on the wavelength of the incident light, the complex refractive index, the shape of the particle and the scattering angle. The Rayleigh-Debye-Gans theory for fractal aggregates (RDG-FA) is an approximate method to describe the scattering of aggregates, able to deliver differential cross sections averaged over all random orientations, but still captures the fractal-like behaviour and has a reasonable agreement with the more precise methods (Ma, 2011).

According to the RDG-FA theory the angular scattering is proportional to the particle’s structure factor which is a function of the magnitude of the scattering vector ($q$, proportional to the sinus of the half of the scattering angle), the particle’s fractal dimension and the radius of gyration (Dobbins & Megaridis, 1991).

Results

At the University of Applied Sciences Northwestern Switzerland a portable instrument was developed in order to measure the angular scattering of fractal-like aerosols. It is able to measure the scattering signal simultaneously at seven different angles. The aerosol enters a closed chamber where a laser diode illuminates the particles in the sampling volume. Avalanche photodiodes detect the scattered light at different angles simultaneously. The chamber is calibrated by ammonium sulphate particles, which form spherical crystals, of known number concentration and size.

Structure factors of different combustion type aerosols were measured by performing the exact same measurement two times and measuring the angular scattering as function of time using two different lasers at the wavelengths of 660 nm and 850 nm (see Figure 1 for one example). With the help of the RDG-FA theory the fractal dimension and the radius of gyration of the particles can be derived.

Figure 1. Angular scattering of aerosol particles produced by smouldering wood fire. The green markers are the measured values whereas the red line is the RDG-FA fit to the data.

The chamber is directly upgraded to a version where the two light sources can simultaneously be used. This will allow us to probe the structure factor at 14 different values at once with the two light sources at the wavelengths of 405 nm and 850 nm. The angles of the light sources and detectors are chosen in a way that the resulting $q$ values are almost evenly distributed within the possible $q$ range. This setup makes it possible to probe the structure factor with high time resolution and therefore to observe fast structural changes of the aerosol particles that are expected to happen in fires. This will allow us to identify how particles’ structure depends on the different burning conditions, fuels and burning phases.

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Time-resolved Investigations on Superparamagnetic Core-shell Nanoparticles by Means of a Laboratory-scale SAXS Device

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Keywords: SAXS, time-resolved, core-shell, nanoparticles, shell thickness.

In recent years, magnetite nanoparticles attracted the attention of many researchers. Once properly designed and functionalized, magnetite has great potential in many applications, e.g., magnetic bioseparation. However, due to strong magnetic dipolar interactions, the particles readily tend to agglomerate. As a consequence they show low dispersibility in aqueous media. Furthermore, the naked magnetite particles are vulnerable to oxidation, resulting in reduced magnetization. To overcome such undesirable effects, the magnetite can be coated by silica using various methods, e.g., the sol-gel method according to the classic Stöber process (Stöber et al., 1968). Many papers published in the past decade, show how a specific shell thickness can be achieved by adjusting appropriate coating conditions (Caruana et al., 2012). Mostly, TEM was used to determine the shell thickness off-line. However, due to fluctuation of process parameters, e.g., the catalyst concentration, an on-line control of the particle properties is often desired.

In this work we report how a small-angle X-ray scattering (SAXS) laboratory-scale device can be used to characterize the distribution of silica shell thickness. Figure 1a shows exemplarily the measured intensity profiles $I(q)$ versus the reaction time $t_r$ for an initial precursor concentration $c_{T_EOS} = 0.026 \text{ mol/L}$. The structure evolution of the intensity with increasing time indicates the production of a silica shell on the surface of the magnetite, which can be confirmed by TEM micrographs (Figure 1b). A core-shell sphere model was used for the determination of the mean shell thickness $T_s$ from the SAXS data. The $T_s$ values revealed by SAXS (Figure 1c, ◦) were compared with the results from an off-line micrograph analysis (Figure 1c, +), whereas the tendency of a slight underestimation by SAXS was observed (< 10%). According to calculated theoretical SAXS profiles of non-spherical core-shell particles, the discrepancy between SAXS and TEM could be explained by the non-spherical appearance of the synthesized particles.

The study of the influence by the initial precursor amount $c_{T_EOS}$ reveals that the mean shell thickness $T_s$ can be varied by adjusting the appropriate $c_{T_EOS}$ (Figure 1c, ◦). Furthermore, the time-dependent $I(q)$ curves, as exemplar shown in Figure 1a, revealed faster growth kinetics with increasing $c_{T_EOS}$ (Figure 1c, □). As another coating parameter, the reaction temperature $T_r$ and the catalyst concentration $c_{NH_3}$ were varied. As expected, $T_r$ and $c_{NH_3}$ significantly affect the growth kinetics. However, SAXS measurements revealed that $T_r$ and $c_{NH_3}$ must not exceed or fall below a critical level, respectively. Otherwise, the particles become significantly inhomogeneous because of the formation of pure silica in parallel to the coating process. Therefore, this study demonstrates how the SAXS data can be used for controlling the coating process due to the ability of on-line and in situ measurements.

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Small-angle X-ray Scattering Study of Surface Morphology of Oxide Support Particles Synthesized by CVS and Sintering

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Keywords: oxide support nanoparticles, surface morphology, chemical vapour synthesis (CVS), sintering, SAXS

Supported metal catalysts, composed of small metal dots like Pd and Pt nanodots on oxide support particles, are widely used in chemical and automotive industries for selective hydrogenation, control of automobile exhaust and many other processes due to their selectivity and activity. Support particles usually separate and stabilize the metal nanodots. However, the agglomeration of small nanodots into larger ones on the surface of the support particles especially at high temperatures will decrease the active surface area. Proper modification of the surface structure of the support particles helps to stabilize supported metal catalysts against sintering.

In this work, by means of small-angle X-ray scattering (SAXS) we study the surface morphology of some oxide support particles (SiO$_2$, TiO$_2$, Al$_2$O$_3$ and their binary mixed oxides) synthesized in the gas phase by an integrated chemical vapour synthesis (CVS) and sintering process (Heel & Kasper, 2005; Binder et al., 2010), as shown in Fig.1. In the first CVS reactor at 1000°C, alumina, silica, titania particles and mixed oxides are generated by thermal decomposition of the saturated metal alkoxide vapours delivered from the bubbling systems: aluminium-tri-sec-butoxide (ATSB), tetraethyl-orthosilicate (TEOS), and titaniumtetra-isopropoxide (TTIP), respectively. Resulting fractal agglomerates pass through a sintering furnace at 1500°C for defined restructuring and sintering of the particles.

Fig.1 Experimental setup of CVS and sintering.

The synthesized oxide support particles were analysed by using a SAXS laboratory camera. Details about this SAXS setup can be found elsewhere (Guo et al., 2013). By analyzing the scattering intensity $I(q)$ at small scattering angle 20 or scattering vector $q=(4\pi/\lambda)\sin(\theta/2)$, the radius of gyration of the particle $R_g$ can be determined with Guinier’s law (Guinier & Fournet, 1955), yielding the primary particle size $d_p=2\cdot(5/3)^{1/2}\cdot R_g$. For large $q$, the scattering intensity decays with a power law $I(q)\propto q^{-\alpha}$ (Schmidt 1991). The mass-fractal dimension $d_m$ equals the power-law exponent $\alpha$ in the case of mass fractals ($1<\alpha<3$), whereas the surface-fractal dimension $d_s$ equals $6-\alpha$ in the case of surface fractals ($3<\alpha<4$). For the particles, having ideal sharp boundaries and smooth surfaces, the exponent $\alpha$ equals 4. The rough surface will make $\alpha$ smaller than 4. Table 1 shows the surface-fractal dimensions determined with SAXS for respective pure oxide support particles and their mixed oxides with different mass fractions of Al$_2$O$_3$. It is seen that the surface of pure alumina particles is rougher than those of both pure silica and titania particles. By mixing a small amount of alumina, the surface morphology of silica particles changes, becoming much rougher. This modification of the surface morphology will help to prevent the metal nanodots from migrating, colliding and sintering on the support particle surface and hence reduce the deactivation of supported metal catalysts. SAXS measurements also indicate that a much larger fraction of alumina in the SiO$_2$-$\text{Al}_2\text{O}_3$ mixed oxide doesn’t increase the surface roughness significantly. Similar surface morphological property was observed in the TiO$_2$-$\text{Al}_2\text{O}_3$ mixed oxide. Metal nanodots on support particles were also analysed by SAXS.

Table 1. Particle surface-fractal dimension by SAXS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fraction of Al$_2$O$_3$ [-]</th>
<th>$\alpha$-Value [-]</th>
<th>$d_s=6-\alpha$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SiO$_2$</td>
<td>0.00</td>
<td>3.96</td>
<td>2.04</td>
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<tr>
<td>SiO$_2$-$\text{Al}_2\text{O}_3$</td>
<td>0.06</td>
<td>3.79</td>
<td>2.21</td>
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<td>SiO$_2$-$\text{Al}_2\text{O}_3$</td>
<td>0.10</td>
<td>3.87</td>
<td>2.13</td>
</tr>
<tr>
<td>SiO$_2$-$\text{Al}_2\text{O}_3$</td>
<td>0.45</td>
<td>3.88</td>
<td>2.12</td>
</tr>
<tr>
<td>Pure Al$_2$O$_3$</td>
<td>1.00</td>
<td>3.85</td>
<td>2.15</td>
</tr>
<tr>
<td>TiO$_2$-$\text{Al}_2\text{O}_3$</td>
<td>0.40</td>
<td>3.94</td>
<td>2.06</td>
</tr>
<tr>
<td>TiO$_2$-$\text{Al}_2\text{O}_3$</td>
<td>0.55</td>
<td>3.92</td>
<td>2.08</td>
</tr>
<tr>
<td>TiO$_2$-$\text{Al}_2\text{O}_3$</td>
<td>0.58</td>
<td>3.90</td>
<td>2.10</td>
</tr>
<tr>
<td>Pure TiO$_2$</td>
<td>0.00</td>
<td>3.99</td>
<td>2.01</td>
</tr>
</tbody>
</table>

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Determination of optical properties for miniCAST soot generator by coupling extinction and light scattering methods

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Keywords: soot aggregates, optical properties, extinction, Static light scattering.

Soot optical properties are not well known quantities. This is due to their dependence on the nature of the fuel, and on the burning conditions that affect their chemical composition and nanostructure. Furthermore, optical properties are hard to determine, in particular because the fractal-like morphology has to be taken into account (Dobbins, et al., 1994). Yet, the knowledge of the optical properties is important for many applications. In particular, the calibration of optical diagnostics (LII, extinction measurements) needs soot that is optically perfectly known.

The miniCAST5201 soot generator is a very stable and reproducible soot generator which becomes a standard for measurements calibration (Giechaskiel, et al., 2010). This device contains a laminar propane co-flow diffusion flame able to generate soot with different physico-chemical properties through active input flow control¹. This device is currently characterized in the framework of the French “Mermose” project and the present work is devoted to the determination of the optical properties of soot generated by this generator in the visible spectrum, for four operating conditions (Table 1).

Table 1. Working points of the miniCAST5201

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAST 1</td>
<td>50</td>
<td>200</td>
<td>1.2</td>
<td>20</td>
</tr>
<tr>
<td>CAST 2</td>
<td>60</td>
<td>0</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>CAST 3</td>
<td>60</td>
<td>0</td>
<td>1.15</td>
<td>20</td>
</tr>
<tr>
<td>CAST 4</td>
<td>60</td>
<td>0</td>
<td>1.5</td>
<td>20</td>
</tr>
</tbody>
</table>

The optical properties (absorption and scattering functions) are determined by interpreting the extinction spectra $K_{ext}(\lambda)$ with the Rayleigh-Debye-Gans theory for Fractal Aggregates (RDG-FA). Indeed, this theory is able to evaluate absorption and scattering cross sections by the knowledge of soot size probability density function expressed in gyration radius $P(D_g)$, particles concentration $N_{agg}$, primary particle size diameter $D_p$ and fractal dimension $D_f$. Thus, by coupling this theory with the Lorentz-Drude model, the inversion of the extinction spectra can be operated and $N_{agg}$ and $P(D_g)$ functions can be derived (Yon, et al., 2011) leading to the refractive index dispersion measurement.

In the present study, the soot size $P(D_g)$ is determined by static light scattering (SLS) measurements with the methodology developed by (Caumont-Prim, et al., 2013). The main advantage of this technique beside SMPS measurements is that the soot distribution is optically determined and directly expressed in terms of gyration radius unlike SMPS that delivers the mobility diameter. Transmission Electron Microscopy images are used to determine the fractal dimension $D_f$ (Köylü, et al., 1995; Brasil, et al., 1999) and the primary particle diameter $D_p$. The particles concentration $N_{agg}$ is determined by mass concentration measurements.

By this method, the optical properties of the different chosen operating conditions of the miniCAST5201 (Table 1) are presented.

Additionally, the influence on the determination of the optical refractive index of modified RDG-FA theory proposed by (Yon, et al., 2014) is evaluated. Indeed, this recent study highlights the strong influence of aggregates internal multiple scattering on absorption and scattering cross sections. The MERMOSE project is supported by DGAC (French Directorate-General for Civil Aviation) – see http://sites.onera.fr/MERMOSE

Chemical speciation and molecular structure analyses of carbonaceous particulate matter with C1s NEXAFS spectroscopy

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Keywords: soot, NEXAFS spectroscopy, molecular structure, source apportionment.

Carbon has a rich chemistry, which manifests also in its aerosols. The chemical speciation of such carbonaceous aerosol is tricky. Aerosols can be solid particulates with adsorbed volatiles, and those can react with the ambient environment and change its molecular structure and even its morphology during weathering and ageing. In the recent 10-15 years, soft X-ray spectroscopy has seen much development for the molecular speciation of carbonaceous particulate matter (PM). The development and application is still going on. The most basic observation one can make in the carbon C1s x-ray absorption spectra is that soot can have a strong aromatic signature from C=C bonds which can be interpreted as graphite-like structures. Depending on the fuel and engine operation conditions, the soot structure may change and this can be clearly seen in the x-ray spectra. The strong effect of fuel additives shows remarkable spectroscopic signatures.

The next step is then to see which kind of soot has which spectral signatures, such as carbon black from acetylene flames, or carbon nanotubes, mineral graphite, diamond like carbon, and soot from wood fires and biomass combustion, and not well defined aerosols collected from the ambient environment. The next study was to understand the soot from wood smoke and learn how its molecular structure systematically differs from diesel soot, for example. A simple “principal component analysis” on PM sampled in the ambient environment with residential wood burning, heavy truck traffic diesel soot and smoke from meat cooking was possible by identifying spectral signatures in NEXAFS spectra from well-defined reference samples. Finally we were able to transfer our know-how to toxicology studies where the interaction of lung cells with diesel smoke and wood smoke could be investigated.

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GIXRF as a method for the quantification of equally sized nanoparticle fractions

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Keywords: XRF, Aerosol characterization, Instrumentation, Elemental composition, Particle size distribution.

For chemical aerosol characterization the deposition of the aerosol using cascaded impactors is a common method. The subsequent chemical analysis of the aerosol samples from individual cascade stages can then be provided by different techniques, e.g. EDX, GC-MS, Raman, XRF, etc., but none of them measures particle size and size distributions. Particle size resolved quantitative chemical analysis either requires the additional use of particle classifiers (e.g. SMPS) or the quantitative analysis of the deposits on the cascade stages. The latter implies sample strengths above the lower threshold of the respective analytical method. Many environmental indoor or outdoor aerosols are polydisperse and consist of several chemical substances in different quantities. The quantification of one given chemical substance or a given element, superimposed by the background of all the other contributions, and its assignment to a particle size class is therefore not easy to achieve with the methods available.

A novel approach is Grazing Incidence X-Ray Fluorescence Analysis (GIXRF) which can be based on fundamental parameters. With this method we were able to determine size, quantity and chemistry of small nanoparticulate aerosol fractions within a poly-disperse aerosol.

The sampling was done with an electrostatic aerosol sampler (TSI 3089), using one square inch clean Si-wafers. We prepared monodisperse ZnTiO$_3$, TiO$_2$ nanoaerosol by use of an atomizer (Topas ATM 220) both with and without size selection by the Classifier and also a technically produced example of a polydisperse indoor aerosol.

For the experiments we used different excitation energy regimes at the beamlines of the PTB and BAM at the electron storage ring BESSY II. High spectral resolution enables studies of the chemical state of the elements (Reinhardt et al., 2009) while the low divergence of the excitation beam allows dedicated geometries, such as a grazing incidence setup. Based on total-reflection X-ray fluorescence analysis (TXRF), which offers very low quantitative detection limits in the pg to fg range (Beckhoff et al., 2007), in GIXRF the incident angle of the excitation radiation is tuned between 0° and about threefold the critical angle of total-reflection. Thereby the intensity distribution of the X-ray standing wave field (XSW) above the surface is tuned. Particles with a given diameter deposited on a flat substrate will be exposed to excitation radiation of varying intensity depending on the angle of incidence and the particle size.

Hence the measured X-ray fluorescence signal contains information on the atomic composition of the particles and information on the deposited size fraction.

Based on fundamental parameters we could use GIXRF measurements to determine the total amount of deposited nanoparticles of one size fraction on a flat surface. Besides the absolute determination of the deposited nanoparticles, the measurement is independent of small contaminations of the substrate with other materials or polydisperse nanoparticles. This makes the GIXRF method a unique and very promising method for nanoparticle characterization, especially regarding polydisperse and inhomogenic environmental aerosols.

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