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Development of absolute intensity multi-angle light scattering for the determination of polydisperse soot aggregate properties

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Abstract

This work investigates the capability of multi-angle light scattering to determine polydisperse aggregate parameters including the size distribution and the fractal dimension. The investigation considers one laser wavelength in the visible at 527 nm and a fixed angle range from 10° to 160°. The corresponding range of the scattering wave vector limits the measured section of the overall structure factor significantly and makes an unambiguous determination of the size distribution parameters using relative multi-angle scatter intensities difficult. An interplay of the distribution width parameter and the fractal dimension is significant and impairs the possibilities for determining both properties simultaneously. The ambiguity of solutions can be overcome by including the absolute scattering intensity which is obtained via comparison with a known Rayleigh scatterer. However, additional parameters like the primary particle diameter, the soot volume fraction, the fractal prefactor, and the scattering function of the refractive index $F(m)$ must be known with sufficient accuracy. We show how the analysis can be applied to a variety of soot sources ranging from very small aggregates in premixed flames, over intermediate aggregates in a laminar diffusion flame to large cooled soot emitted from a diffusion flame in inverted geometry.
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Keywords: Soot morphology; Polydisperse fractal aggregates; Elastic light scattering; Rayleigh–Debye–Gans

1. Introduction

The characterization of soot particulate emissions in the nanometer range is of great importance with respect to health and environmental impact. Its role in the environment is diverse;

including direct heating of the atmosphere, triggering cloud formation, and inducing glacial melting [1,2]. Important information for health related simulations, as for example deposition modelling in the human body, include morphological and size parameters [3]. As a comprehensive diagnostic, the challenge is to determine simultaneously the overall soot concentration, the effective soot surface, primary particle diameter, as well as aggregate morphology, size, and corresponding distributions in real-time.

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Scattering from fractal soot aggregates has been investigated in numerous experiments [4–8] and simulations [9–11]. However, only a limited number were dedicated to the influence of polydisperse size distributions, and even less to the inverse analysis in order to derive distribution characteristics from the experimental scattering signal explicitly [5,12]. Sorensen provided in 2001 a comprehensive overview on light scattering by fractal aggregates [13], including a recipe of how aggregate morphological and size distribution information can be derived from relative multi-angle scattering intensities. This full analysis, however, is not typically carried out, possibly owing to the fact that measurement of scattering from the Guinier regime through to the power-law regime is experimentally cumbersome or impossible in some cases.

Recent publications typically assumed values for the fractal dimension of 1.7–1.8 [4,5]. However, soot in early stages of the formation process or even in successive stages of aggregation can show significantly differing fractal dimensions [14,15]. Though the assumption of a fractal dimension can be justified in specific instances, a diagnostic method that does not rely on this precondition would be preferable.

There is no doubt about the pronounced polydispersity of the soot aggregates, but the question about the appropriate distribution shape is contentious. The majority of publications refer to it as a lognormal distribution [4,5,16], although Sorensen pointed out that a self-preserving distribution has to be applied in order to fit simulated N -distributions based on the Smoluchowski aggregation equation [6]. We focus in this contribution on the lognormal approach as we did not find improvements of our data analysis using a self-preserving distribution, and wished to develop conclusions easily related to the majority of published investigations in this field.

The scope of this work is to look in detail into the modifications of the monodisperse structure factor by the polydisperse size distribution and to overcome the increased ambiguity that arises for the fractal dimension and the distribution parameters. The discussion is constrained to a typical multi-angle scattering setup with one laser wavelength and a given range of angles, corresponding to a limited range of the scattering wave vector q . Finally, suggestions for an approach to simultaneously determine the fractal dimension and the polydisperse aggregate distribution, based on an absolute multi-angle scattering measurement are made.

2. Polydisperse fractal aggregates

Combustion generated soot aggregates are commonly approximated as fractals that obey the scaling law

$$N = k_f \left(\frac{R_g}{d_p/2} \right)^{D_f} \quad (1)$$

where N , R_g , d_p , D_f , and k_f , represent the number of primary particles per aggregate, the radius of gyration of the aggregate, the primary particle diameter, the fractal dimension, and the fractal prefactor.

The fractal dimension expresses the inner density of the fractal particle where a value of 1 expresses a very open structure made up of linear strings while a value of 3 corresponds to a dense sphere. Soot aggregates in a laminar diffusion flame as well as the overfire soot of a turbulent diffusion flame show very similar fractal dimensions of 1.7–1.8 which corresponds to open and branching structures as has frequently been documented by transmission electron microscopy (TEM) [17].

The aggregates show a polydisperse size distribution, which is commonly approximated by a lognormal distribution with geometric mean N_g and width parameter σ_g

$$p(N) = \frac{\exp(-1/2[(\ln N - \ln N_g)/\ln \sigma_g]^2)}{\sqrt{2\pi N \ln \sigma_g}} \quad (2)$$

where the i th moment of the distribution is given by $M_i = \int N^i p(N) dN$.

Multi-angle light scattering is primarily a function of the radius of gyration of the aggregate which is related to N via Eq. (1). The mean radius of gyration is defined as the expectation value of R_g over the size distribution $p(N)$

$$\begin{aligned} R_{g,\text{mean}} &= \int R_g(N) p(N) dN \\ &= \left(d_p / 2 k_f^{1/D_f} \right) M_{1/D_f}. \end{aligned} \quad (3)$$

However, the mean radius is not measured directly in the scattering experiment, but rather an effective radius $R_{g,\text{eff}}$ which relates to the mean radius by a moment dependent weighting factor.

$$R_{g,\text{eff}} = [(M_{2+2/D_f}/M_2)^{1/2}/M_{1/D_f}] R_{g,\text{mean}}. \quad (4)$$

To compare sizes of soot samples with significantly different width parameters and fractal dimensions, knowledge of these parameters is crucial. For a TEM (transmission electron microscopy) derived width parameter of 3.5 [18], $R_{g,\text{eff}}$ would be as large as 7.3 times $R_{g,\text{mean}}$.

3. Theoretical background on light scattering

3.1. Relative multi-angle scattering and the Rayleigh–Debye–Gans (RDG) approximation

The theoretical description of scattering by fractal aggregates is demanding due to the complex non-spherical structures. Hence, traditional

Mie theory has substantial shortcomings in correctly predicting the scattering cross sections of these aggregates. Over the last 20 years the Rayleigh–Debye–Gans (RDG) approximation has become the most common theoretical approach to estimate scattering by fractal aggregates [19].

One feature of the RDG approximation is that the differential scattering cross section of the aggregate can be expressed in terms of the cross section of the primary particle

$$C_{\text{sca}}^{\text{agg}}(q) = N^2 S(q) C_{\text{sca}}^{\text{pp}}, \quad (5)$$

with the scattering wave vector $q = (4\pi/\lambda) \sin(\theta/2)$. The differential cross section of the primary particles $C_{\text{sca}}^{\text{pp}}$ is independent of the scattering angle in a plane perpendicular to the direction of polarization of the linearly polarized incident light

$$C_{\text{sca}}^{\text{pp}} = k^4 (d_p/2)^6 F(m). \quad (6)$$

k signifies the wave vector of the incident light, and $F(m)$ is a function of the complex refractive index m with $F(m) = |(m^2 - 1)/(m^2 + 1)|^2$. The structure factor function $S(q)$ in Eq. (5) expresses the angular variation of the scattering intensity with respect to the forward direction, which is caused by interference effects within the aggregate. In this work an analytical form for the structure factor – based on a Gaussian cutoff function [13] was employed

$$S(q) = \exp\left(-\frac{(qR_g)^2}{D_f}\right) {}_1F_1\left(\frac{3-D_f}{2}, \frac{3}{2}, \frac{(qR_g)^2}{D_f}\right). \quad (7)$$

The effective polydisperse structure factor is obtained by a superposition of the monodisperse structure factors of the single size classes within the distribution

$$S_{\text{eff}}(q) = \frac{\int N^2 S[qR_g(N)] p(N) dN}{M_2}, \quad (8)$$

with M_2 being the second moment of the size distribution.

Although Eq. (8) gives the effective structure factor for the complete range of q it is instructive to present some limiting forms that are frequently used to evaluate multi-angle scattering [14]:

$$\begin{aligned} S(q) &= 1, & \text{Rayleigh} & \quad (qR_{g,\text{eff}} < 0.1) \\ &= 1 - (q^2/3)R_{g,\text{eff}}^2, & \text{Guinier} & \quad (0.1 < qR_{g,\text{eff}} < 1). \\ &= C(qR_{g,\text{eff}})^{-D_f}, & \text{Power-Law} & \quad (qR_{g,\text{eff}} > 1) \end{aligned} \quad (9)$$

where $R_{g,\text{eff}}$ is the effective radius of gyration according to Eq. (4).

Most striking is that the functional relationships which allow the measure of R_g in the Guinier regime and D_f in the power-law regime in the monodisperse case remain in principle the same, with $R_{g,\text{eff}}$ replacing the monodisperse R_g .

In the Rayleigh regime the particle is significantly smaller than the wavelength and the structure factor is essentially invariant with q . The Guinier regime shows a prominent linearity of $S(q)/S(0)$ versus q^2 , which is applied to determine $R_{g,\text{eff}}$ from the slope. For sufficiently large $R_{g,\text{eff}}$ -values (the limit depends on the distribution width parameter) a $\log[S(q)]-\log[q]$ representation becomes linear with a slope corresponding to the fractal dimension. A recipe for determining the size and the fractal dimension relies, therefore, on the ability to measure the Guinier and the power-law regime in the scattering experiment.

Khlebtsov et al. have compared the structure factors of monodisperse and polydisperse fractal colloidal aggregates and found that the transition from the Guinier regime to the power-law regime is more extended for polydisperse systems (see Fig. 2 in Ref. [20]). By numerical simulations of the structure factor and its first derivative – in order to identify the slope of the structure factor – we identified the same effect and showed an increase of the transition regime with increasing distribution width. This leads effectively to an increasing separation of the Guinier and the power-law regime, impairing significantly the ability to measure the two regimes and to determine all the desired aggregate parameters D_f , N_g , σ_g , and R_g in one multi-angle experiment.

3.2. Absolute scattering intensity and the differential scattering coefficient

The absolute intensity of light scattered into the direction q (θ , λ) is given by

$$I_{\text{sca}}(q) = c_0 I_0 n^{\text{agg}} C_{\text{sca}}^{\text{agg}}(q) \quad (10)$$

with a constant c_0 , the incident light intensity I_0 , the aggregate number density n^{agg} , and the differential scattering cross section of the aggregate $C_{\text{sca}}^{\text{agg}}(q)$. The aggregate number density corresponds to the soot volume fraction f_v divided by the volume of a single aggregate, which results for a polydisperse distribution with the first moment M_1 in

$$n^{\text{agg}} = (6f_v)/(\pi d_p^3 M_1). \quad (11)$$

The quantity $Q_{\text{sca}}^{\text{agg}}(q) = n^{\text{agg}} C_{\text{sca}}^{\text{agg}}(q)$ is the differential volumetric scattering coefficient. Together with Eqs. (5), (6), and (11) this coefficient can be expressed as

$$Q_{\text{sca}}^{\text{agg}}(q) = (3/32\pi) k^4 f_v F(m) d_p^3 (M_2/M_1) S_{\text{eff}}(q). \quad (12)$$

This shows that the aggregate distribution influences the absolute scattering intensity through the structure factor and a ratio of distribution moments M_2/M_1 .

4. Experimental setup

The light source in the scattering experiment is a pulsed Nd:YLF-laser with an average power of 400 mW at 527 nm when operated at 5 kHz. The laser light polarization is controlled by a polarizer to the vertical direction. A wavelength of 527 nm poses a compromise between the ability to reach large q -values to be sensitive for small aggregates while maintaining size parameters $x_p = \pi d_p / \lambda < 0.3$, which is a prerequisite for the applicability of the RDG approximation. The detection optics are mounted to a high-precision rotation stage (Newport, RV120PP), which is driven by a motion controller (Newport, ESP300 Series), providing an angular resolution of 0.0001° . The rotatable detection arm has a collection lens with a focal length of 20 cm apertured to 17 mm and located 20 cm from the intersection point of the laser propagation axis and the collection axis. This corresponds to an f -number of $1/11.8$ and an acceptance angle in the horizontal plane of 4.9° . A second 20 cm focussing lens images the collected light on to an aperture (2 mm for inverted and premixed flame, 200 μm for the diffusion flame) and photomultiplier (Hamamatsu, H10304 series). Between the lenses, where the light is essentially plane-parallel, there is a polarization analyzer in vertical orientation and a 527 nm bandpass filter. For each angle a 1 s measurement was carried out at an acquisition rate of 10 kHz with the laser firing at 5 kHz, allowing for instantaneous background subtraction. A boxcar integrator (Stanford Research Systems, SR200 Series) was used to average only over the laser pulse duration and thus reject room light contribution. A $\sin(\theta)$ correction factor was applied to account for the change in sample volume with rotation. The volumetric scattering coefficient of the soot sample was measured by comparing the signal at 90° (145° for the diffusion flame) with that of a known Rayleigh scatterer (nitrogen or propane with $1.55 \times 10^{-6} \text{ 1/(m} \cdot \text{sr)}$ or $2.02 \times 10^{-5} \text{ 1/(m} \cdot \text{sr)}$, respectively [21]).

Several soot sources were investigated to explore soot aggregates of different size. The smallest aggregates were obtained with a premixed ethylene/air flame, which was generated with a commercial 60 mm diameter McKenna bronze flat flame burner (Holthuis & Associated), operated at an equivalence ratio of 2.1 at a total gas flow of 10 slpm (20 $^\circ\text{C}$, 101.3 kPa) [22]. A stabilization plate was mounted at 21 mm above the burner and a nitrogen shroud flow of 15 slpm was applied. The second source was a Gülder laminar co-annular diffusion flame (steel fuel tube with 12.7 mm outer diameter and 10.9 mm inner diameter concentrically located in an aluminum air flow tube with 88.4 mm inner diameter), operated with 194 sccm ethylene and an air coflow of 284 slpm [23]. The inverted flame was implemented according to Ref. [24] and run with

1200 sccm methane, 15 slpm air-coflow, and 40 slpm secondary air dilution.

Data was acquired with a multi-angle scattering apparatus over an angular range of 10 – 160° (inverted and diffusion flame) and 20 – 160° (premixed flame). The datasets comprise of 15 (premixed flame), 19 (diffusion flame), and 35 (inverted flame) angular measurements with variable angular intervals, typically between 1° and 5° in the forward direction ($<45^\circ$) and 10° otherwise.

5. Results and discussion

5.1. Relative multi-angle scattering and RDG structure factor fits

Figure 1 shows the normalized multi-angle scattering intensities for three soot samples, namely in-flame soot in the premixed flame at a height of 14 mm and in the diffusion flame at a height of 42 mm, and cooled soot from the inverted flame. The data were compared with the RDG structure factor from Eq. (8). The fit parameters are N_g , σ_g , and D_f . Required input parameters are d_p and k_f , which were taken from reference measurements, mostly performed in our own group or published elsewhere in literature (see Table 1). For the k_f of the diffusion flame a value of 1.94 ± 0.05 was used, which we obtained by reanalyzing TEM images of Tian et al. [25] employing the method of Brasil [26].

Data and fits (solid lines) in Fig. 1 are normalized to the forward direction ($q = 0$). The inception point of the intensity decline in the q -domain is a measure for the effective radius of gyration where earlier inception indicates larger aggregates. It is evident that the cooled soot contains significantly larger aggregates than the diffusion flame, which in turn shows larger aggregates than the premixed flame.

The numerical results of the RDG fits are listed in Table 1a. For the diffusion and inverted flames

Fig. 1. Relative scattering intensities for three samples of polydisperse soot aggregates, namely in-flame soot in a premixed flame (circles $\circ$), in-flame soot in a laminar diffusion flame (squares $\square$), and cooled soot from an inverted flame (triangles Δ). The solid lines indicate RDG structure factor fits.

Table 1

(a) Fits to relative multi-angle scattering

Sample	Fit input parameters		Fit results				
	d_p [nm]	k_f	D_f	N_g	σ_g	$R_{g,mean}$ [nm]	$R_{g,eff}$ [nm]
Premixed flame ^a	19.1 ^[33]	2.4 ^[28]	–	4.2	–	15	35
Diffusion flame	29.0 ^[17]	1.94	1.38	36	1.2	118	127
Inverted flame	39.4 ^[29]	2.4 ^[28]	1.55	138	1.7	294	443

(b) Fits to absolute multi-angle scattering

Sample	Fit input parameters				Fit results				
	d_p [nm]	k_f	f_v	$Q_{sca}(\theta_{ref})$ [m ⁻¹]	D_f	N_g	σ_g	$R_{g,mean}$ [nm]	$R_{g,eff}$ [nm]
Premixed flame ^b	19.1	2.4	0.20 ppm ^[34]	1.5×10^{-3}	–	2.2	2.7	11	37
Diffusion flame	29.0	1.94	3.8 ppm ^[31]	0.20	1.85	32	2.1	72	136
Inverted flame	39.4	2.4	77.6 ppb ^[29]	9.6×10^{-3}	1.65	120	2.1	237	487

Refractive index: $m = 1.57 - 0.56i$ [32]. ^aFits with fixed $D_f = 1.78$ and $\sigma_g = 2.3$. ^bFits with fixed $D_f = 1.78$.

Fig. 2. Contour plots of RDG fit residuals based on relative multi-angle scattering intensities (a–c) and absolute multi-angle scattering intensities (d–f) in the three different flames.

effective radii of gyration of 127 and 443 nm are found, but with surprisingly low D_f values of 1.38 and 1.55, respectively. The fit to the premixed flame data only converges if D_f and σ_g are fixed. For $D_f = 1.78$ and $\sigma_g = 2.3$ the effective radius of gyration is 35 nm.

To investigate the low D_f values and the interplay of D_f and σ_g over a broader range, we created

a grid of (D_f, σ_g) -pairs and generated fits for each (D_f, σ_g) -combination (with free floating N_g , to allow for the best fitting $R_{g,eff}$). The residuals between experimental and fitted intensities are displayed in contour plots Fig. 2a–c, where the color indicates the value of the residual. None of the plots shows a well-defined minimum, indicating the ill-posed nature of the problem. The contour

plots in Fig. 2a and b exhibit pronounced valleys of low residuals. The direction of the valley in the (D_f, σ_g) -plane rotates from a rather diagonal direction for the intermediate sized soot in the diffusion flame to a more horizontal direction for the larger aggregates in the inverted flame. The latter case corresponds to a better defined D_f while σ_g remains ill-defined. The improved resolution of D_f can be explained by a shift towards larger qR_g -values and thus power-law behavior in the scattering measurement. Conversely, the shift sacrifices part of the Guinier-regime which leads to an increased uncertainty in $R_{g,eff}$, a crucial parameter for the σ_g determination. In the case of the premixed flame (Fig. 2c) only the Guinier regime is covered, thus D_f and σ_g are ill-defined, expressed by an extended flat plane of possible D_f and σ_g solutions. It can be concluded that the relative multi-angle scattering approach for an angle range of 10–160° and a single wavelength cannot solve the fractal dimension and the polydispersity of the aggregate sample simultaneously.

5.2. Absolute multi-angle scattering and the differential scattering coefficient

Additional information on the size distribution can be gained by using absolute rather than relative multi-angle scattering intensities and fitting those with the expression for the differential scattering coefficient from Eq. (12). This expression contains the structure factor but also the moment ratio M_2/M_1 , which puts additional constraints on the distribution parameters. A calibration with a reference scatterer (propane or nitrogen) at one angle is sufficient to convert the relative intensities from Fig. 1 into absolute values. In addition to d_p and k_f , the input parameters f_v and $F(m)$ are required for generating scattering coefficients. Table 1b summarizes the fit input and the fit results and Fig. 2d–f show the corresponding contour plots. In all cases a much better confined solution space is obtained than for the pure structure factor fits in Fig. 2a–c.

The best fit for the diffusion flame identifies the global minimum at $D_f = 1.85$ which is in much better agreement with literature values (1.62–1.77 [17,27,28]) and provides a significant improvement over the much lower value found by the relative scatter method (Table 1a). The width parameter of 2.1 is smaller than found with TEM measurements [17]; however, this finding is in agreement with recent scattering investigations in a similar flame [5].

For the inverted flame the absolute scattering fits create a well pronounced global minimum in the contour plot Fig. 2e. The best fitting fractal dimension of 1.65 (Table 1b) is in very good agreement with the TEM reference of 1.68 [29]. The trend to obtain significantly smaller width

parameters holds since the TEM reference was 3.3 in comparison to 2.1.

Besides the drastically improved D_f parameters for the two flames the mean radii of gyration were notably corrected, while the effective radii remained close to their values from Table 1a. The corrected mean radii are 72 nm for the diffusion flame and to 237 nm for the inverted flame, a shift compared to the relative scattering approach by 40% and 20%, respectively.

The situation for the premix flame is more complicated, since the contour plot in Fig. 2c is essentially flat and the additional information from the absolute intensity is still not sufficient to identify a global minimum. However, the space of possible solutions can be significantly narrowed down (Fig. 2f) such that a distinct D_f – σ_g -relationship is established. If a fractal dimension of 1.78 is assumed, a best fit is obtained at $\sigma_g = 2.7$. The corresponding N_g is 2.2, suggesting an early stage of soot formation where pronounced aggregation has not yet occurred.

A potential drawback of the absolute scattering approach is the influence of the input parameters k_f , d_p , f_v , $F(m)$ on the solution. We investigated the propagation of uncertainty from these input parameters to the output parameters exemplarily for the diffusion flame. A deviation of $\pm 10\%$ from the mean value was applied to all four quantities. Interestingly, all of them cause similar uncertainties for D_f , σ_g , and $R_{g,mean}$, namely 4.1–5.1%, 6.7–8.6%, and 8.7–11%, respectively. The effect on N_g differs more strongly, being smallest with 4.1% for 10% changes in $F(m)$ or f_v , and largest with 16% for a 10% change in k_f . Clearly these uncertainties can add up to uncertainties of tens of percents.

Figure 2, however, suggests significant reductions of the uncertainties by going from the relative to the absolute scattering approach. We evaluated the uncertainties in Fig. 2, based on an experimental noise of 10%. This lead to error bars for σ_g and D_f which were 47% and 7% of the mean value in the absolute scattering case but appeared to be 100% and 700% larger in the relative scattering case. This shows that even significant uncertainties introduced by the additional input parameters could still be overcompensated by the considerable improvement in accuracy due to the incorporation of absolute scattering intensities.

A promising way of conveniently providing input parameters for the absolute multi-angle scattering would be the integration with laser-induced incandescence (LII), which has been proven as a reliable technique for the determination of soot volume fraction, effective surface area, and the primary particle size. The integrated techniques would allow measurements with the highest spatial and temporal resolution. First attempts in this direction have been carried out

by Reimann et al. [4] and Bockhorn et al. [30]. The auto-compensating LII technique (AC-LII) [31] measures an effective primary particle diameter along with the soot absorption coefficient. The absorption coefficient replaces soot volume fraction in the calculation and $F(m)/E(m)$ is needed in lieu of $F(m)$. The LII measurement benefits from the simultaneously measured aggregate properties, which can be used for the aggregate correction of the primary particle determination. An iterative evaluation of the integrated LII-scattering experiment should allow for an improved accuracy of the primary particle size and aggregate size, compared to a pure sequential LII-scattering experiment. The combination of these two in-situ non-perturbing optical diagnostics for real-time evaluation of nanoparticle morphology, including (d_p , N_g , σ_g , D_f , $R_{g,eff}$, etc.) holds great potential for process control and environmental monitoring.

6. Conclusion

We have shown that a typical relative multi-angle scattering measurement with one laser wavelength in the visible and an angle range of 10–160° is not capable of determining the fractal dimension and the polydisperse size distribution of soot aggregates simultaneously, but rather establishes a group of possible (D_f , σ_g) combinations. Further, when the effective radius of gyration falls below 100 nm the measurement range does not extend into the power-law regime and no distinct D_f – σ_g -relationship exists in the solution domain. While extension towards smaller angles (e.g. below 10°) would improve the determination of larger aggregates, it would provide no further information for soot aggregates typically found in-flame (i.e. with low or moderate aggregation). Inclusion of an absolute intensity calibration puts additional constraints on the distribution parameters such that the corresponding fits are more likely to converge compared to the relative intensity case. However, the approach is sensitive to the refractive index and depends on the availability of accurate reference data for the soot volume fraction, the primary particle diameter, and the fractal prefactor. We suggest, therefore, the combination of the presented absolute multi-angle scattering method and laser-induced incandescence as a future powerful technique for soot sample characterization.

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