Soot and nanoparticulate optical measurements

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Advanced Measurement Methods

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OUTLINE

- Introduction: soot & diagnostics
- Generality on soot diagnostic techniques
- Extinction technique
- > Scattering/extinction
- Two-color emission technique
- Laser-Induced Incandescence(LII), also applied to other nanoparticles

Nanoparticles produced by combustion processes

Soot particles. Result of non-complete combustion processes.

> Increase of the heat transfer (i.e. in furnaces)

> Particle formation in industrial processes (i.e carbon black to produce rubber, inks, ...)

Reduction of combustion efficiency

> Environmental pollution (i.e. PM10) and health implication.

- 1. Soot presents aromatic molecules adsorbed on the surface, some of which carcinogenic.
- 2. Due to its dimension, it can be easily inhaled and deposit on lungs, resulting in respiratory problems.

Soot characteristics

Soot consists of carbon atoms, at which hydrogen is bounded (C/H = 8). Hydrogen content depends on the combustion residence time (aged particles having lower H_2)

The average density is about 1.8 g/cm³ (lower than the graphite) From TEM analysis



Soot particles parameters are:
✓ f_v: soot volume fraction (cm³/cm³)
✓ N_p (#/cm⁻³): total number of particles / V,
✓ d_p: soot primary particle diameter

• d_p = 10-60 nm

- Cluster of 100 or more primary particles
- Linear chains to fractal-like structures (experimental conditions)

Soot formation mechanims



H. Richter, J.B. Howard, Progress in Energy and Combustion Science 26, 565 (2000)

Challenging topic of the combustion community

understanding of chemical & physical processes responsible for aerosol formation

From a theoretical point of view:

- Developing of a chemical kinetics code able to describe soot formation mechanisms under different experimental conditions

From an experimental approach:

- Measurements of the main parameters of soot particles. Important to validate and improve the previous codes.

Diagnostic techniques (1/2)

To investigate soot formation and growth in practical systems two different kinds of diagnostic techniques can be applied.

Intrusive techniques (e.g. gravimetric analysis, Transmitted
 Electron Microscope analysis (TEM), SMPS).

<u>Advantages</u>: direct information of the system under study (TEM)

<u>disadvantages</u>: possible perturbation of the system (especially in hostile combustion environment).

Example: during soot sampling for TEM analysis a strong perturbation can result from a fast insertion of the probe in the flame. This last can also produce non-controlled chemical effects.

Diagnostic techniques (2/2)

Non-intrusive techniques (optical as laser diagnostics).

Advantages:High spatial and temporal resolutionIn-situ measurementsRemote measurementsNo upper temperature limit

<u>Disadvantages</u>: Optical access needed Complex experiments Sometimes complex models for the interpretation High cost

Aim of experimentalists

To develop and improve a suitable diagnostic tool for:

- Increasing the knowledge on soot formation (basic research) with
 - high sensitivity (e.g. to detect very low soot concentration)
 - dependence on the experimental conditions (e.g. temperature, pressure, equivalence ratio)
- To perform easily measurements in industrial environment (for the implementation of the set-up and to derive soot parameters from the raw signals)

Soot Diagnostic Techniques

- Extinction (1D, 2D):
- Extinction/Scattering:

Two-colour emission (point, 2D):

 f_{ν} , integral line-of-sight (easy to perform in industrial application)

 f_v , d_{p_i} (multiple angles scattering to derive the morphology)

 f_v and T_{soot} (only <u>soot</u> temperature, neglect the contribution of cold gas)

• Laser Induced Incandescence (LII): f_v and d_p (interpretation of LII signal still under study - LII workshop Varenna Aprile 2010)

Point measurements



<u>Probe volume</u>: interception of the laser beam and the image of the detector slit in the flame. Diameter depends on the laser wavelength, the focal lens and the beam diameter.

Line measurements



> Laser-beam mildly focused in the flame

>The signal is collected from different probe volumes along the laser beam and imaged onto pixels of a 1D detector

Two-dimensional measurements



Laser beam: from circular section to a vertical sheet using a cylindrical lens Signal: from each measurements volume imaged on a 2D detector

EXTINCTION TECHNIQUE

Extinction Technique



Homogeneous medium

where TR_{λ} is the monochromatic transmittance and K_{ext} is the extinction coefficient expressed in cm⁻¹.

Extinction Technique

 $K_{ext} = N_p (C_{scatt} + C_{abs}) = K_{scatt} + K_{abs}$

 \checkmark N_p [#/cm3] is the particle number density

 \checkmark C_{abs} and C_{scatt} the cross sections for absorption and scattering.

In most practical cases, the scattering contribution can be assumed to be negligible: $K_{ext} = K_{abs}$.

In the <u>Rayleigh regime</u>: $\frac{\pi d_p}{\lambda} \ll 1$ (particle size much smaller than the wavelength of the incident radiation), the absorption coefficient can be expressed as a function of f_v as:

$$K_{abs} = \frac{6\pi E(m)f_v}{\lambda}$$

Extinction Technique

where E(m) is a function of the refractive index m (m = n - ik):

$$E(m) = \frac{1}{6} \operatorname{Im} \left(\frac{m^2 - 1}{m^2 + 2} \right) = \frac{nk}{\left(n^2 - k^2 + 2 \right)^2 + 4n^2 k^2}$$

The soot volume fraction, f_v , can be expressed in terms of N_p and d_p , as:

$$f_v = \frac{\pi}{6} d_p^{3} N_p$$

and by taking into account the transmittance, f_v can be determined as:

$$f_{v} = \frac{-\ln\left(\frac{I_{L}}{I_{0}}\right)\lambda}{6\pi LE(m)}$$

Typical experimental set-up for extinction



- cw laser (at a given wavelength)
- Focusing and collecting optic systems
- Detector (working in the spectral region of the source)
- Processing signal arrangment (+ mechanical chopper)

Typical extinction measurements



- Each signal = average over a certain number of samples
- Number of samples linked to the signal-to-noise ratio

Extinction: Main characteristics

- Experimentally simple technique
- Line-of-sight: average f_v along the pathway of the medium, no spatial resolution along the laser beam direction. Difficult to apply in non-homogeneous distribution (e.g. turbulence flames)
- To overcome the problem extension of the technique to 2D case 2D distribution of f_{ν} in a single measurement
- Particular laser wavelength used, according to the experimental conditions employed (in terms of the fuel, temperature and pressure)

Abel inversion procedure

Local measurements can be derived in the case of axial-symmetric geometry of the system:

- Chordal profiles of extinction measurements are carried out
- Applying the mathematical procedure local K_{ext} and f_{v} are obtained.



Tomoghraphic deconvolution by 3-point Abel inversion and iterative method for self-absorption correction

C.J. Dasch, One-dimensional tomography: a comparison of Abel, onion-peeling, and filtered backprojection methods, Appl. Opt. 31, 1146-1152 (1992)

Example of optical set-up for 2D measurements



LASER Ar-Kr

- 5 mirror
- 6 burner
- 7 filters (ND and 514 nm)
- 8 objective + CCD (752X582)
- 9 computer

Probe beam Probe+flame Ratio



Dependence of absorption on laser wavelength

- Absorption of the laser light by the species in the probe volume.
- Each species (gas or solid phase) are characterized by a given spectrum of absorption.

To measure f_v care has to be taken in discriminating such contribution from other "non-solid" species.

In laboratory flames, gas species (particularly PAH) exhibit strong absorption spectra in UV-VIS, which can be competitive with soot broad-band grey body absorption.

Dependence of extinction on laser wavelength Examples in two different reactors



SCATTERING/EXTINCTION TECHNIQUE

Scattering/Extinction Technique



- Laser beam: Vertically polarized
- Light scattering: vertically/horizontal polarized, same wavelength of the laser beam
- Dependence on the scattering angle of the scattering signal strictly related to soot structure

Scattering/extinction Technique



 $I_{pp} = I_{0p} \Delta \theta \Delta V N_p C_{pp}^p$ for N_p isolated primary particle /volume:

 $K_{pp} = N_p C_{pp}^p$

 N_p [cm⁻³], K_{pp} [cm⁻¹], C_{pp}^p [cm²]

pp =polarization of source and detected signal



Primary particle polydispersity

In the probe volume particles of different size probability distribution function (PDF)

$$d_{pm}$$
 = geomtric mean
 σ_g = standard deviation

$$p(d_p) = \frac{\exp\left[-\frac{1}{2}\left(\frac{\ln(d_p/d_{p_m})}{\ln(\sigma_g)}\right)^2\right]}{\sqrt{2\pi}N_p\ln(\sigma_g)}$$

$$d_{p_{mn}} = \left[\frac{\int_{0}^{\infty} p(d_{p}) d_{p}^{m} d(d_{p})}{\int_{0}^{\infty} p(d_{p}) d_{p}^{n} d(d_{p})} \right]^{1/(m-n)}$$

$$K_{vv}^{a} = \frac{F(m)}{4} \left(\frac{\pi}{\lambda_{scatt}}\right)^{4} N_{p} \int_{0}^{\infty} p(d_{p}) d_{p}^{6} d(d_{p}) = \frac{F(m)}{4} \left(\frac{\pi}{\lambda_{scatt}}\right)^{4} N_{p} d_{p60}^{6}$$

$$K_{abs} = -\frac{\pi^2}{\lambda_{ext}} \operatorname{Im}\left\{\frac{m^2 - 1}{m^2 + 1}\right\} N_p \int_0^\infty d_p^{-3} p(d_p) d(d_p) = -\frac{\pi^2}{\lambda_{ext}} \operatorname{Im}\left\{\frac{m^2 - 1}{m^2 + 1}\right\} N_p d_{p_{30}}^{-3}$$

$$dp_{63} = \overline{dp} = \left(\frac{\lambda_{abs}^{4}}{\lambda_{ext}}\right)^{1/3} \left(\frac{4 E(m) K_{vv}}{\pi^{2} F(m) K_{abs}}\right)^{1/3}$$

What happens if primary particles are not isolated? (still in the Rayleigh regime)

Dissymmetry ratio technique

$$R_{VV}(\mathcal{G}) = \frac{C_{VV}(\mathcal{G})}{C_{VV}(180 - \mathcal{G})}$$

• Single spheres in the Rayleigh regime $R_{VV}(\mathcal{G}) = 1$

No dependence on the scattering angle

• Linear chain up to fractal like structure: $R_{VV}(\mathcal{G}) > 1$

Dependence of the scattering signal on the scattering angle



 $I_{VV} \alpha F(\theta)$



S. di Stasio, P. Massoli, M. Lazzaro, J.Aerosol Sci. 27, 897-913 (1996)

Dissymmetry ratio vs Np for different soot structure



S. di Stasio, P. Massoli, M. Lazzaro, J.Aerosol Sci. 27, 897-913 (1996)

Dissymmetry ratio technique

<u>Idea</u>: Depending on I_{VV} vs θ , the morphology can be derived with a choice of θ .

More regular the increasing of $R_{\nu\nu}$ with N_p , higher the sensitivity of $R_{\nu\nu}$ to the morphology. $\square R_{\nu\nu}$ (10°/90°) is the most sensitive.

At higher N_p a bending in the trend is detected. $R_{vv}(30^{\circ}/150^{\circ})$ more sensitive than $R_{vv}(45^{\circ}/135^{\circ})$, more than $R_{vv}(90^{\circ}/150^{\circ})$

The choice of a number of angles allows to identify unambiguously soot <u>morphology and aggregation</u>.

According to di Stasio: the selection of three scattering angles is enough to yield such information.

Fractal-like behavior in flames

From TEM analysis in flames:

- PDF for Aggregates (lognormal with σ = 2.1)
- Radius of gyration R_q of each aggregate
- -N primary particles, of diameter d_p , in each cluster.

According to the mass fractal approximation

Douce et al. Proc. C. I., 2000

$$N = k_f \left(R_g \,/\, dp \right)^{D_f}$$

 $R_g^2 = \frac{1}{n} \sum_{i} r_i^2$

- R_g = the radius of gyration
- D_f = the fractal dimension
- k_f = constant fractal prefactor

Fractal-like approach + Rayleigh-Debye-Gans theory

- Each primary particle acts as a dipole for scattering radiation.
- The scattered field is given by the phase difference of the light scattered from separate particles.
 - $C_{vv}^{a} = C_{vv}^{p} N^{2} S(qR_{g})$ $S(qR_{g}) = \text{structure fractor}$ $q = \frac{4\pi}{\lambda} \sin \theta / 2$

 $I_{VV}^{m}(\theta) = \eta I_0 N_a C_{vv}^{p} N^2 S(qR_g) \qquad \qquad N_a = \text{number of aggregates/volume}$

- The scattering coefficient not related directly to d_p
- Dependence of R_g on d_p
- Parameters to be evaluated D_{f} , R_{g} , d_{p} , N

Fractal-like approach + Rayleigh-Debye-Gans theory

<u>In literature</u>: soot parameters are obtained by performing scattering measurements at different scattering angles.

Different expression of the structure factor are proposed in the literature, as for example

$$S(qR_g) = \exp\left(-\frac{q^2R_g^2}{3}\right) \qquad \text{Guinier regime} \qquad q^2R_g^2 <<1$$
$$S(qR_g) = (qR_g)^{D^f} \qquad \text{Power law regime} \qquad q^2R_g^2 >>1$$

From the first Eq. the radius of gyration can be derived
From the power law it can be obtained the fractal dimension

C.M. Sorensen, J. Cai, N. Lu, Langmuir 8, 2064-2069 (1992)

<u>New approach</u>: measurements performed at 3 angles (90°, q°, 180-q°)

Structure factor from Lin

$$S(qRg) = \left[1 + \sum_{s=1}^{4} C_{s} (qR_{g})^{2s}\right]^{-D_{f}}$$

where $C_1 = 8/(3D_f)$, $C_2 = 2.5$, $C_3 = -1.52$ and $C_4 = 1.02$

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> Considering the lognormal PDF for the population of aggretes:

$$\overline{m_q} = \int_0^\infty N^q p(N) dN$$

The scattering from a polydisperse aggregates: $I_{VV}^{p}(\theta) = \eta I_0 C_{vv}^{p} N_a \int N^2 S(qR_g) p(N) dN$

C.M. Sorensen, J. Cai, N. Lu, Langmuir 8, 2064-2069 (1992)

Considering the definition for the average structure factor:

$$\overline{S(qR_g)} = \frac{\int N^2 S(qR_g) p(N) dN}{\int N^2 p(N) dN}$$

$$\int N^2 S(qR_g) p(N) dN = \overline{m_2} \ \overline{S(qR_g)}$$

A mean value of the radius of gyration can be derived with the assumption:

$$\overline{S(qR_g)} = S^*(qR_{gs})$$

A new relationship $S^*(qR_{gs})$, describing the behavior of the integrated polydisperse distribution, <u>must be evaluated</u>: this function has to be written in terms of an averaged radius of gyration R_{qs} for scattering.

Different definitions for the average R_{qs} as:

$$R_{gs} = R_{gm1} = dp \ (\overline{m_1} / k_f)^{(1/Df)}$$

Fixing:

- the structure factor (Lin et al.)
- definition of average Rg
- PDF, σ = 2.1

Building up:

$$\frac{\int N^2 S(qR_{gm1})p(N)dN}{\overline{m_2}} = \overline{S(qR_{gm1})}$$

 R_{gm1} = fixed, obtained with N_p =10 d_p=25 nm N_p =150 d_p=10 nm

as a function of the wave vector q (the scattering angle).



This curve is fitted with a polynomial expression of the structure factor as a function of R_{gm1} :

$$S^{*}(qR_{gm1}) = \frac{1}{1 + P_{1}(qR_{gm1}) + P_{2}(qR_{gm1})^{2} + P_{3}(qRgm1)^{3} + P_{4}(qR_{gm1})^{4}}$$

where P_1 , P_2 , P_3 , P_4 are fitting parameters. This equation is satisfied whatever is the radius of gyration.

Knowing the new polynomial expression for the structure factor, R_{gm1} is evaluated from two-angle scattering measurements.

- Scattering signals at θ and 180°- θ , $I_{VV,1}$ and $I_{VV,2}$
- Ratio of the two signals to derive R_{VV}

$$R_{VV}(\theta_1,\theta_2) = \frac{I_{VV}(\theta_1)}{I_{VV}(\theta_2)} = \frac{I_{VV,1}}{I_{VV,2}} = \frac{\int S(q_1R_g)N^2 p(N)dN}{\int S(q_2R_g)N^2 p(N)dN} = \frac{S^*(q_1R_{gm1})}{S^*(q_2R_{gm1})}$$

 $R_{\rm qm1}$ derived with a numerical inversion procedure



 $R_{vv}(20^{\circ}/160^{\circ})$ $R_{vv}(45^{\circ}/135^{\circ})$ vs $I_{VV,1}/I_{VV,2}$ $R_{vv}(30^{\circ}/150^{\circ})$

Considering $R_{vv}(30^{\circ}/150^{\circ})$ versus $I_{VV,1}/I_{VV,2}$ and fitting with a 6th order polynomial equation, given by the analytical expression

$$R_{gm1} = \sum_{n=0}^{6} C_n (I_{VV,1} / I_{VV,2})^n$$

- Radius of gyration from scattering at 2 angles.
- Other soot parameters: + extinction coefficient

$$K_{vv,pol} = \frac{\pi^4 d_p^6}{4\lambda_{scatt}^4} F(\lambda) N_a \overline{m_2} S^*(qR_{gm1}) \qquad \text{scattering signal at 90}^\circ$$
$$K_{abs,pol} = -\frac{\pi^2}{\lambda_{ext}} E(m) N_a \overline{m_1} d_p^{-3} \qquad \text{extinction coefficient}$$

$$D_{30} = \frac{1}{\pi} \left(\frac{\lambda_{scatt}}{\lambda_{ext}} \right)^{1/3} \left[\frac{4\pi E(m) K_{vv, pol}(90^{\circ})}{F(m) f_n S^* (qR_{gm1}) K_{abs, pol}} \right]^{1/3}$$

$$D_{30} = \overline{m_1} d_p^{3}$$
 + $R_{gm1} = d_p (\overline{m_1} / k_f)^{(1/Df)}$

$$d_p^{3-D_f} = \frac{D_{30}^{3}}{k_f R_{gm1}^{D_f}}$$

- ✓ Structure factor: Lin relationship (Sorensen et al. 1999)
- \checkmark PDF for Na (Lognormal, σ = 2.1)
- \checkmark From Fractal-like approach 2 unknown parameters D_f and K_f



TEM analysis: D_f , K_f -Validation of d_p measurements

Scattering/Extinction Experimental Set-up



TEM measurements - Validation





Koylu et al. Comb.Flame 100, 621 (1995)



Flame	HAB, mm	D _f	K _f	d _p , nm (TEM)	d _p , nm (opt.)
A	14	1.68	6.3	24.7±3	22.5±2.5

Scattering/Extinction: Main characteristics

- In industrial application the implementation of 90° scattering coupled with extinction measurements could be enough to derive information about soot size.
- For the development of the mechanisms of soot formation and growth it could be important to investigate soot morphology. In this case scattering signal collected at different angles could be needed. Anyway it is quite tricky and particular care is required to perform such analysis both from an experimental point of view, and for the procedure to retrieve soot parameters.



- Comparison of the radiation emitted from soot in flame and that of a calibrated lamp.
- >The optical set-up has to be the same, or differing of neutral (independent of wavelength) components

The light intensity emitted from soot can be described as:

- $I_{s} = \varepsilon_{s}(\lambda, f_{v})I_{BB}(\lambda, T_{s})\eta_{s\lambda}$
- $\varepsilon_{s}(\lambda, f_{v})$ is the soot emissivity

 $\begin{bmatrix} \varepsilon_s = 1 & \text{for a blackbody} \\ \varepsilon_s < 1 & \text{dependence on the wavelength and soot volume fraction} \end{bmatrix}$

 $I_{BB}(\lambda,T_s)$ is the spectral blackbody radiation intensity at T_s given by the Planck's law:

$$I_{BB}(\lambda, T_s) = \frac{C_1}{\lambda^5} \frac{1}{\exp\left(\frac{C_2}{\lambda T_s}\right) - 1}$$

For λ <800 and T<2500 K the Wien's law holds:

$$I_{BB}(\lambda, T_s) = \frac{C_1}{\lambda^5} \exp\left(-\frac{C_2}{\lambda T_s}\right)$$

Kirchhoff's law

> At thermodynamic equilibrium, the spectral radiancy of an emitter is proportional to its spectral absorption coefficient (Havrodineau).

For a uniform soot layer of length L and f_{ν} , the emissivity is given by:

$$\varepsilon_{s}(\lambda, f_{V}) = \frac{\Delta I}{I_{0}} = 1 - \exp(-K_{abs}L)$$

where \mathbf{K}_{abs} is the absorption coefficient

$$l_{abs} = \frac{f_v}{K_{abs}} = \frac{\lambda}{36 \,\pi \, E(m)}$$

 I_{abs} is the natural length of absorption: the thickness of pure soot $(f_v=1)$ with a transmittance equals to 1/e

As $f_v L/I_{abs} \ll 1$ an expansion in the Taylor series of ε_s can be applied .

$$\begin{split} I_{s} &= \varepsilon_{s}(\lambda, f_{v})I_{BB}(\lambda, T_{s})\eta_{s\lambda} & \text{Light emitted from soot} \\ I_{L} &= \varepsilon_{L}(\lambda, T_{L})I_{BB}(\lambda, T_{L})\eta_{L\lambda} & \text{Light emitted from a calibrated lamp at } \mathsf{T}_{L} \end{split}$$

written for 2 wavelengths, λ_1 and λ_2

$$\begin{split} \frac{\eta_{S\lambda_1}}{\eta_{S\lambda_2}} &= \frac{\eta_{L\lambda_1}}{\eta_{L\lambda_2}} \\ T_S &= -c_2 \bigg(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \bigg) \bigg[\ln \bigg(\frac{I_S(\lambda_1)}{I_S(\lambda_2)} \frac{I_L(\lambda_2)}{I_L(\lambda_1)} \frac{\varepsilon_L(\lambda_1, T_L)}{\varepsilon_L(\lambda_2, T_L)} \frac{I_{abs1}}{I_{abs2}} \bigg) + \frac{c_2}{T_L} \bigg(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \bigg) \bigg]^{-1} \\ f_V &= -\frac{I_{abs}}{L} \ln \bigg(1 - \varepsilon_L(\lambda, T_L) \frac{I_S(\lambda)}{I_L(\lambda)} \exp \bigg(-\frac{c_2}{\lambda} \bigg(\frac{1}{T_L} - \frac{1}{T_S} \bigg) \bigg) \bigg) \end{split}$$

Example of two colour emission technique



- Same distance quartz-lamp and burner/quartz
- Same optical set-up to collect the radiation
- Quartz plate is the difference in the optics:

> for the flame ,the quartz transmittance has to be considered

> for the lamp, the refrectivity has to be taken into account

F. Cignoli, S. De Iuliis, V. Manta, G. Zizak, Appl.Opt. 40(30), 5370-5378, 2001

Extinction: Main characteristics

- \checkmark The technique is simple and robust, without a laser
- \checkmark It allows to deliver a significant amount of data in a short time (T_s, f_v)
- ✓ Uncertainties due to "cold" soot regions in the flame, different contribution to the overall radiation intensity.
- ✓ <u>Attention for focusing optical system</u>, especially for wide width flames.
 f # large enough: the regions beyond and before the focal length axis give different contribution to the signal.
- ✓ Integral technique. Only for axial symmetric geometry, local values of f_v e T_s are derived through inversion.

2D two-color imaging of soot volume fraction

in diffusion flames



T (left) and f_v (right) - Propane



Application to a diesel engine

basic principle





J.Vattulainen, V. Nummela, R. Hernberg, J. Kytola, Meas. Sci. Technol. 11, 103 (2000)

Final remarks

✓ The application of one or another diagnostic tool is related to:

- the information we are interested in
- the environment where they have to be applied
- the experimental conditions

- ✓ Extinction and emission is almost a classical technique. Anyway, attention has been taken for the application in some experimental conditions.
- ✓ Scattering/exinction technique is quite well assessed, a further development would concern the morphology.
- ✓ LII technique is still under study and many efforts are still needed to gain a complete understanding of the physical phenomena involved.