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Issues with Applying LII to the Measurement of Nonvolatile Particulate Emissions

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International Energy Agency 31st Task Leaders Meeting on Energy Conservation and Emissions Reduction in Combustion
20-24 September 2009 Lake Louise, AB, Canada

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Acknowledgements

- **NRC/ICPET**
  - Oliver Link
  - Francesca Migliorini
  - Robin Devillers
  - Hongsheng Guo
  - Bob Sawchuk
  - Dan Clavel
  - Daniel Gareau
  - Fazil Baksh
  - Ron Jerome
  - Dashan Wang
  - Kyle Daun (now at U Waterloo)
- **Heriot-Watt University**
  - Prof. Doug Greenhalgh
  - Vivien Beyer
- **Carleton University**
  - Prof. Matt Johnson
  - Brian Crosland
  - James McEwen
  - Adam Coderre
- **LII Science Community**
- **Funding**
  - PERD AFTER Program
  - PERD P&E Program
  - PERD UPAIRI Program
  - NRC/NSERC/BDC Program
  - NRC/Helmholtz Program

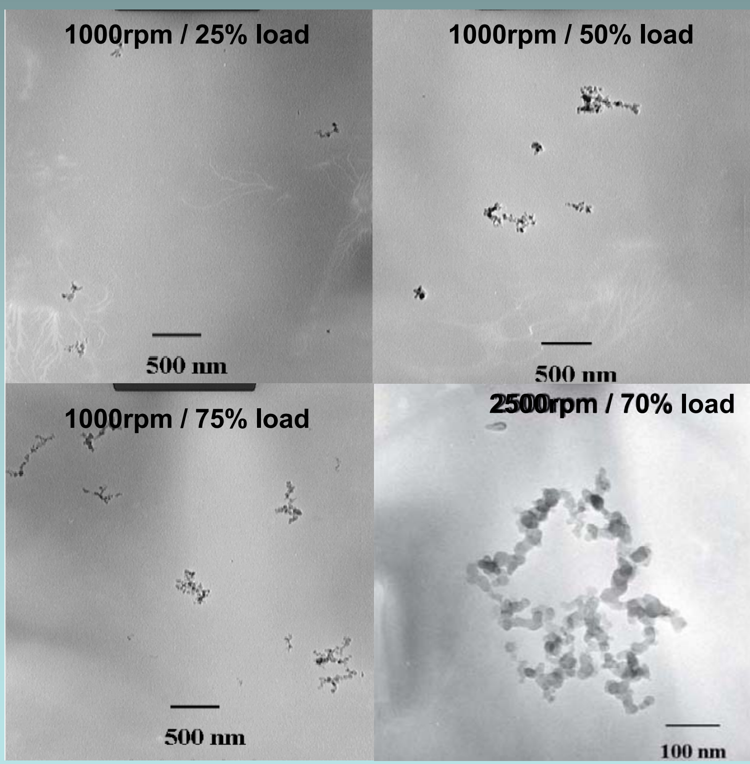
Outline

- Background
- Laser-Induced Incandescence (LII)
  - Autocompensating LII
- Issues
  - Absorption Function
  - Laser Fluence
  - Anomalous Cooling
  - Sizing
- Summary

Why LII?

What is soot?

- dry solid particles produced through incomplete combustion of hydrocarbon fuels
- terminology varies by scientific field
  - elemental carbon, black carbon, refractory carbon, carbon black
- LII can be effective at measuring all of these



[Lee al., SAE Paper No. 2003-01-3169, 2003]

- there is a need for substantially improved instruments to quantify nanoparticle characteristics
- laser-induced incandescence is a technique for the measurement of soot nanoparticles
  - concentration, active surface area, and primary particle diameter
  - species selective technique
  - sensitivity

Objective

- enhance the state of measurements for practical applications
  - nonvolatile particulate matter emissions
  - at or near ambient conditions
- assess and address issues with LII

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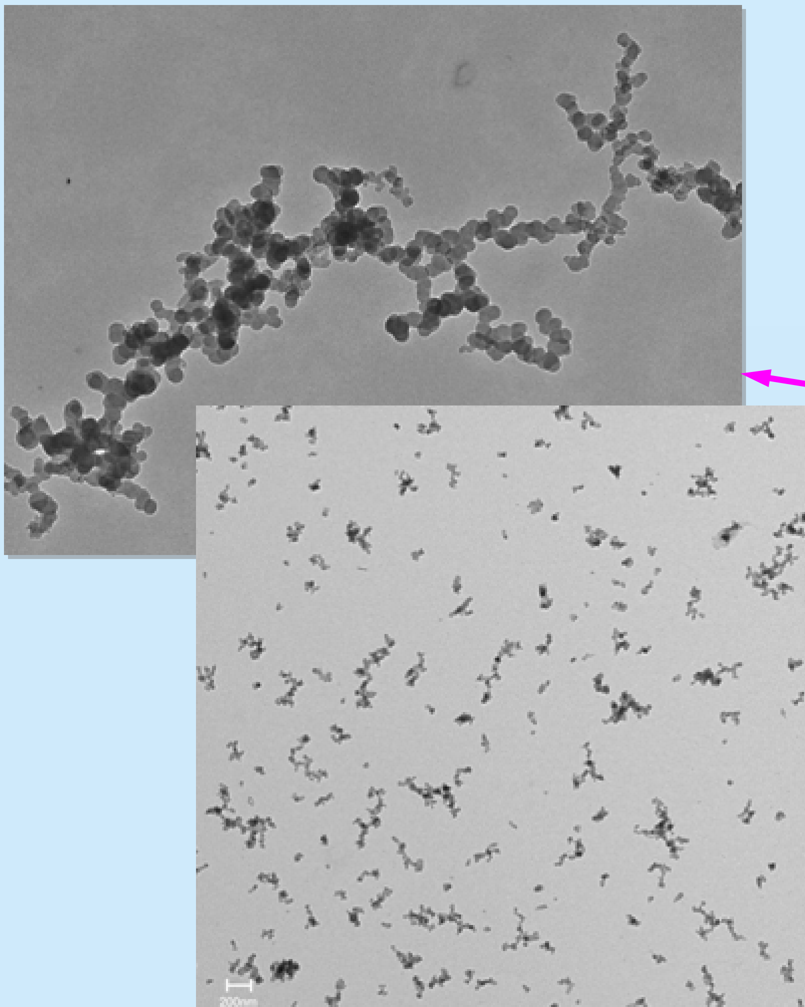
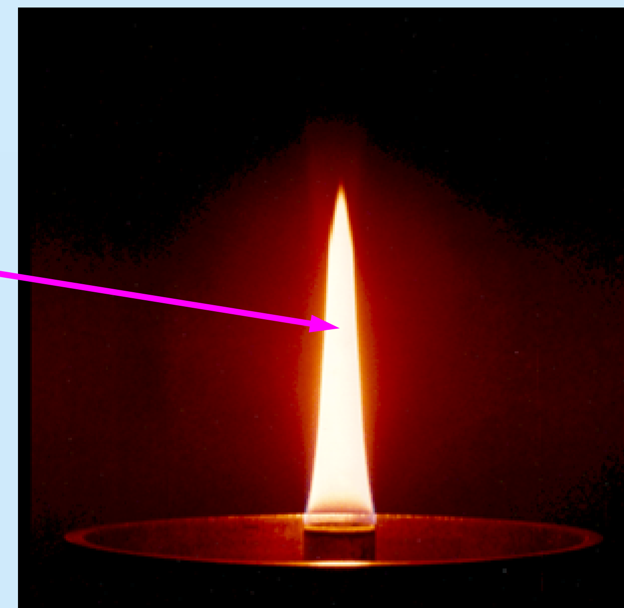
TEM Images of Nanoparticles Sampled From a Flame



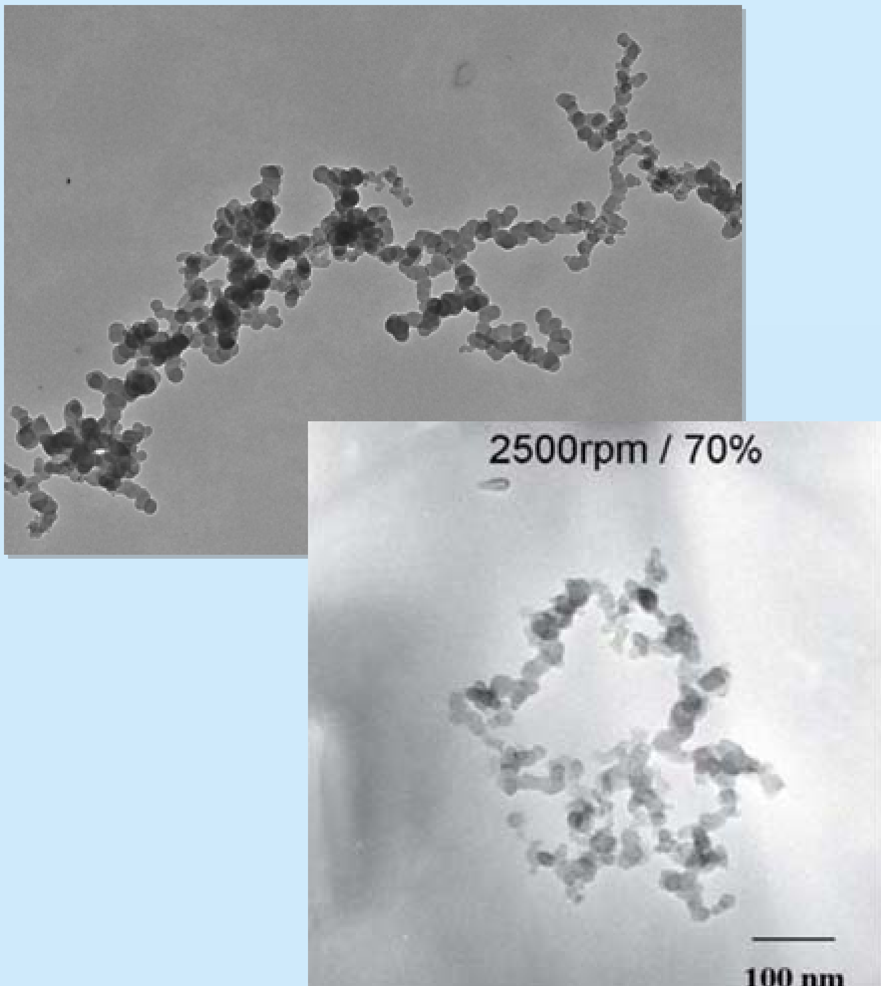
in-flame ethylene

soot



[Schulz *et al*., Applied Physics B **83**, 2006]

TEM Images of Nanoparticles



[Lee al., SAE Paper No. 2003-01-3169, 2003]

Assumption:

in-flame ethylene		in-flame methane		post-flame diesel		oxidized ambient	
soot	**=**	**soot**	**=**	**soot**	**=**	**soot**	**= …**

- particulate matter properties of interest:
  - concentration
  - active surface area
  - primary particle diameter distribution
  - aggregate size distribution
  - optical properties
  - volatile fraction
  - composition

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Auto-Compensating LII (AC-LII)

- traceable calibration procedure
  - absolute intensity, based on spectral radiance
- two-color pyrometry to determine the time-resolved particle temperature
  - permits use of low-fluence
    - particles are kept below the sublimation temperature
- top-hat profile ensures same fluence delivered to all particles
- this new technique is intended to automatically compensate for any changes in the experimental conditions
  - fluctuations in local ambient temperature
  - variation in laser fluence
  - laser beam attenuation by the particulate matter
  - desorption of condensed volatile material

Soot Concentration from Two-Color Pyrometry

- temperature is determined from the spectral radiance signals at two wavelengths
  - varies with relative $E(m)$ at the two wavelengths

$$T_p = \frac{h\,c}{k}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)\left[\ln\left(\frac{V_{\exp_1}\lambda_1{}^6}{\eta_1 E(m_{\lambda_1})}\right) - \ln\left(\frac{V_{\exp_2}\lambda_2{}^6}{\eta_2 E(m_{\lambda_2})}\right)\right]^{-1}$$

- soot volume fraction is determined from the temperature and the spectral radiance signal at either one of the wavelengths
  - depends upon absolute value of $E(m)$ at the selected wavelength

$$f_V = \frac{V_{EXP_\lambda}\,\rho}{\eta_\lambda w_b}\,\frac{\lambda^6\left(e^{\frac{h\,c}{k\,\lambda\,T_p}} - 1\right)}{12\,\pi c^2 h\,E(m_\lambda)} = V_{EXP_\lambda}\,\frac{K_1}{E(m_\lambda)}\left(e^{\frac{K_2}{T_p}} - 1\right)$$

[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

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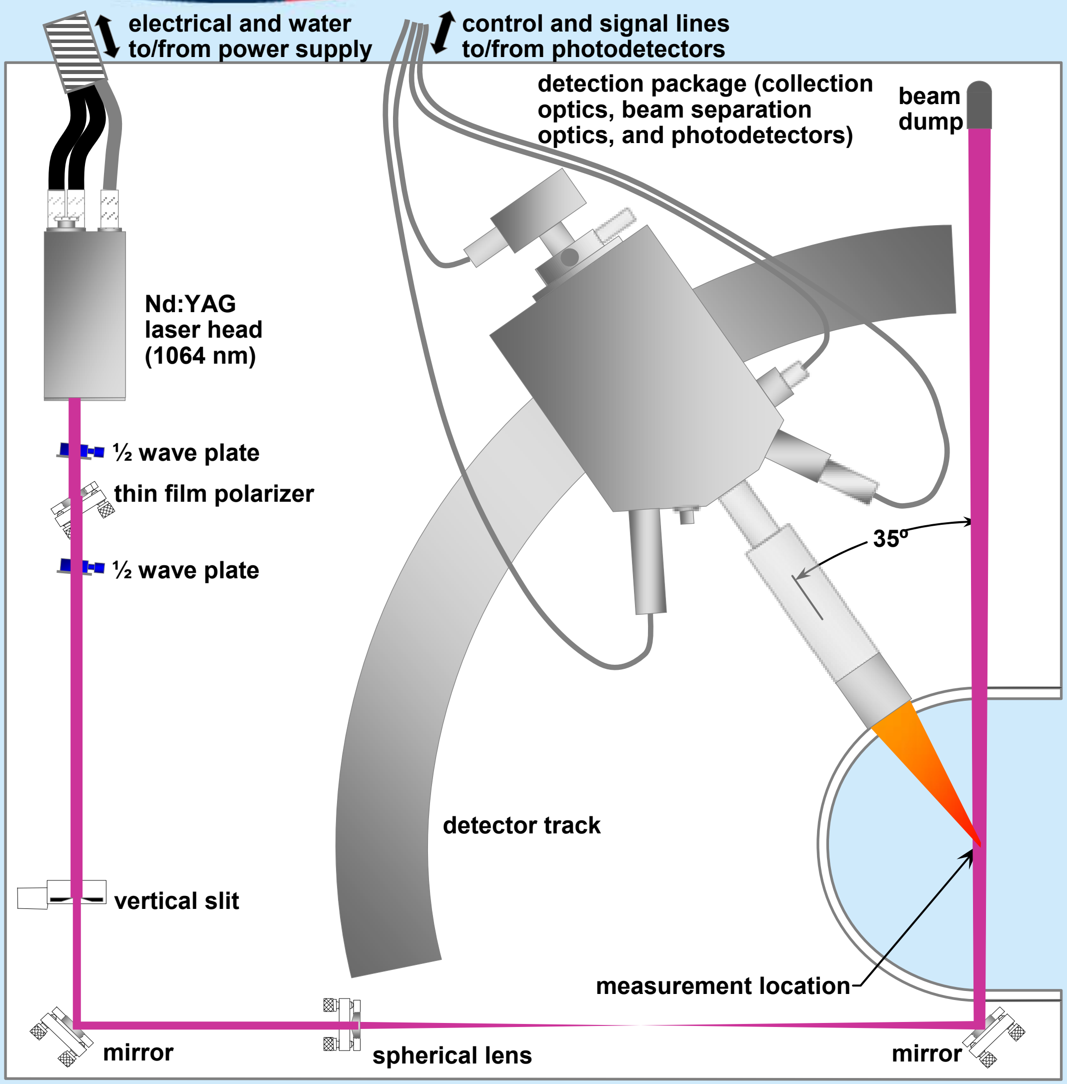
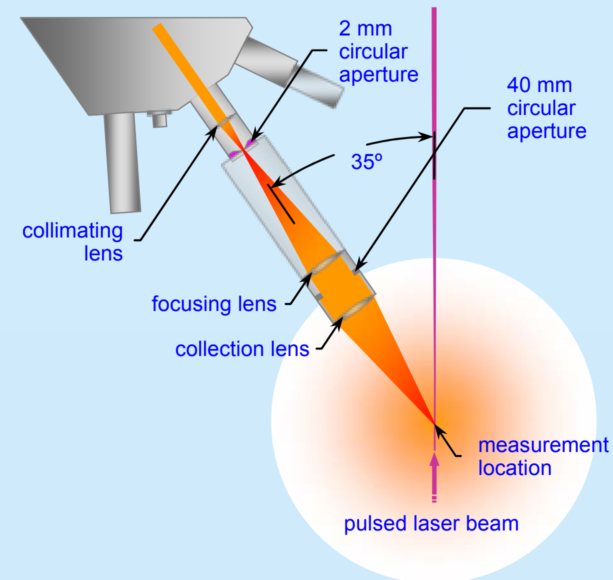
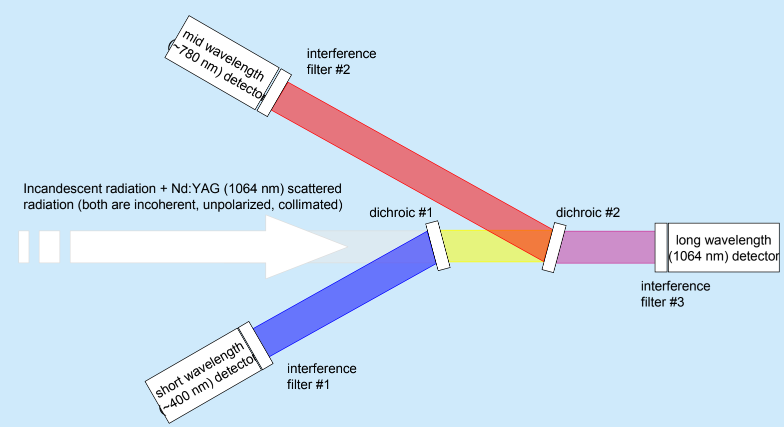
Experiment: LII Optical Apparatus







[Smallwood *et al.*, SAE Paper No. 2001-01-3581, 2001]

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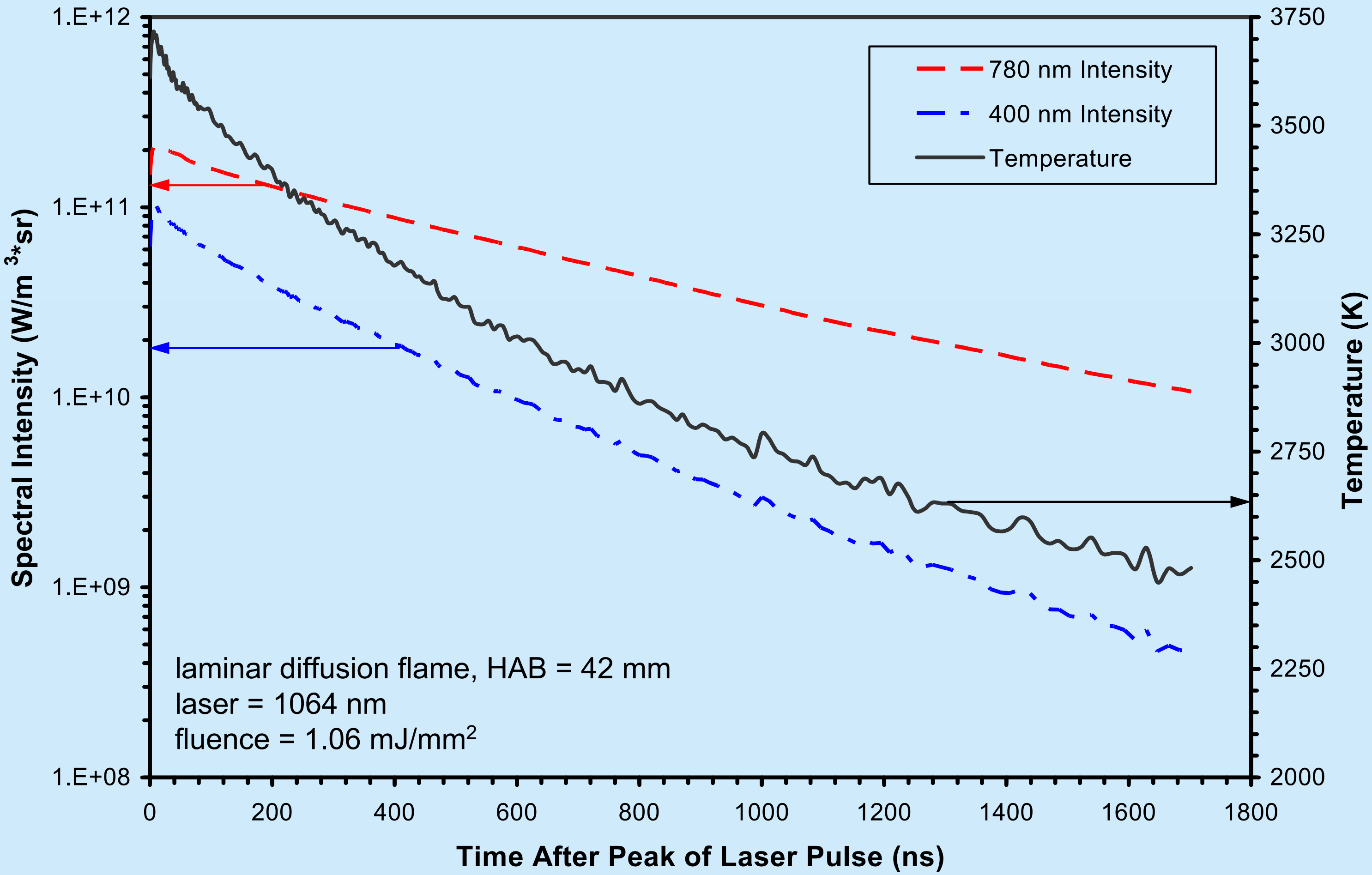
In-Flame – Absolute LII Signals



[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

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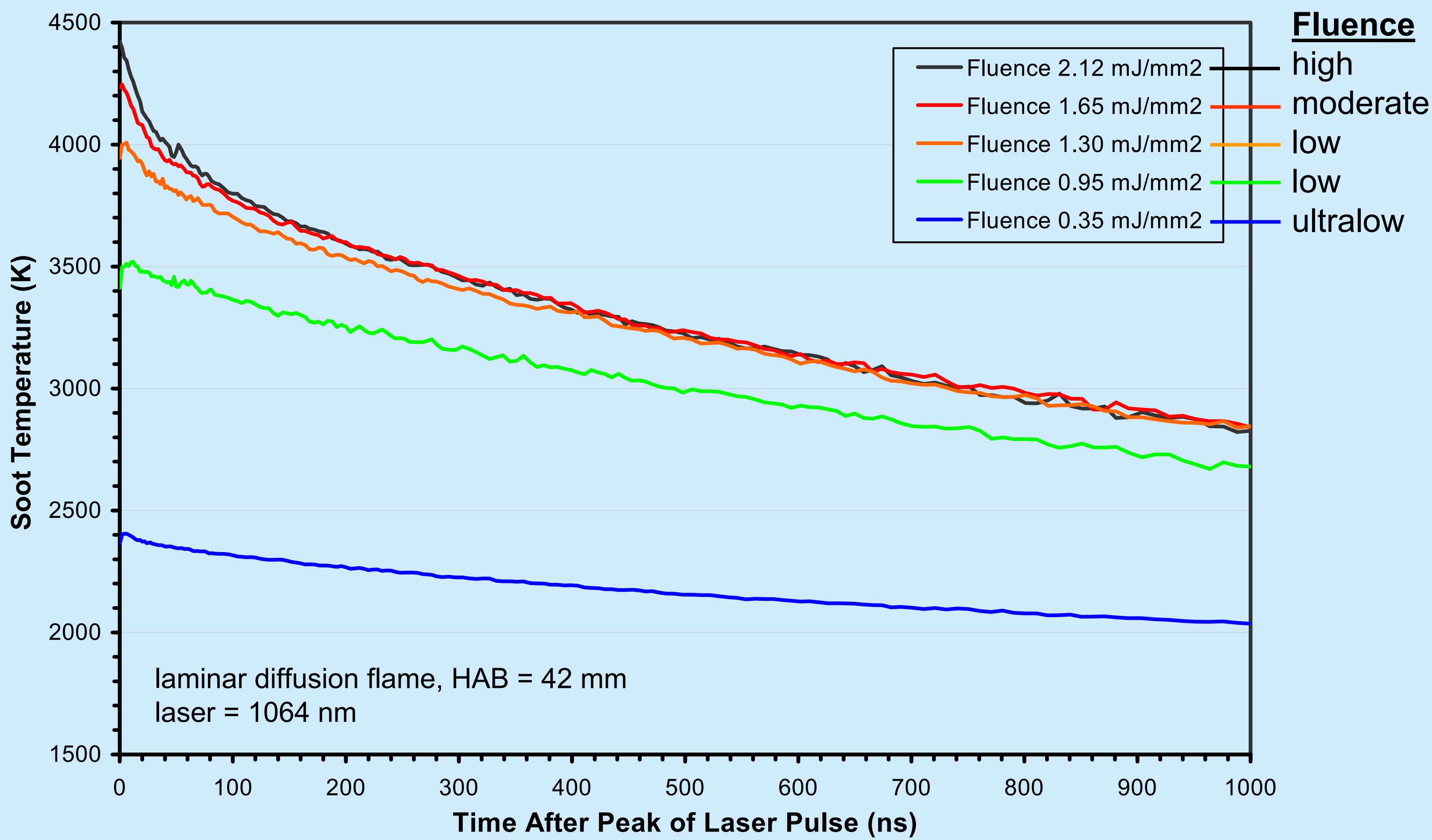
In-Flame – Soot Particle Temperature Decays



[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

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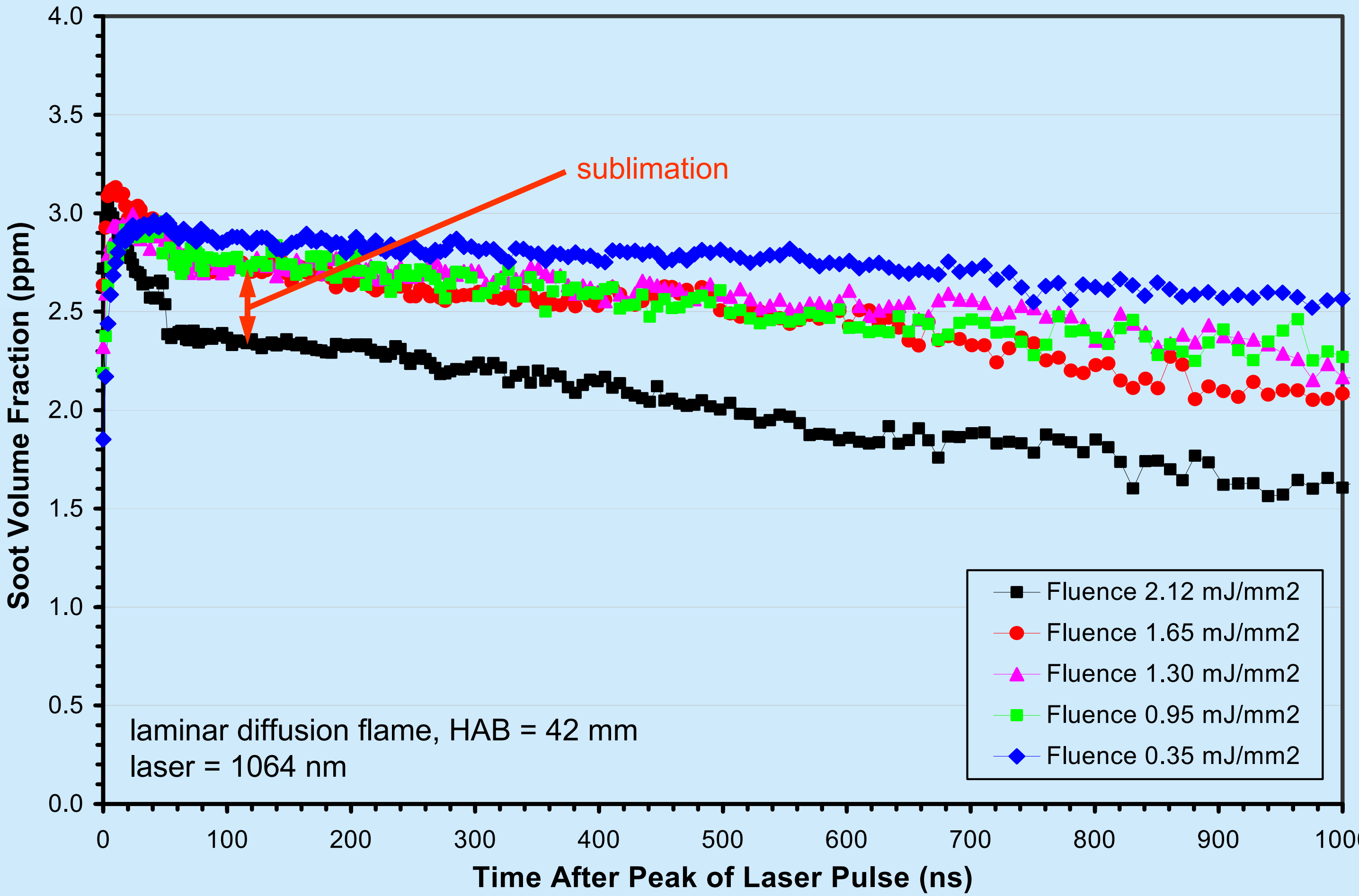
In-Flame – Soot Volume Fraction



[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

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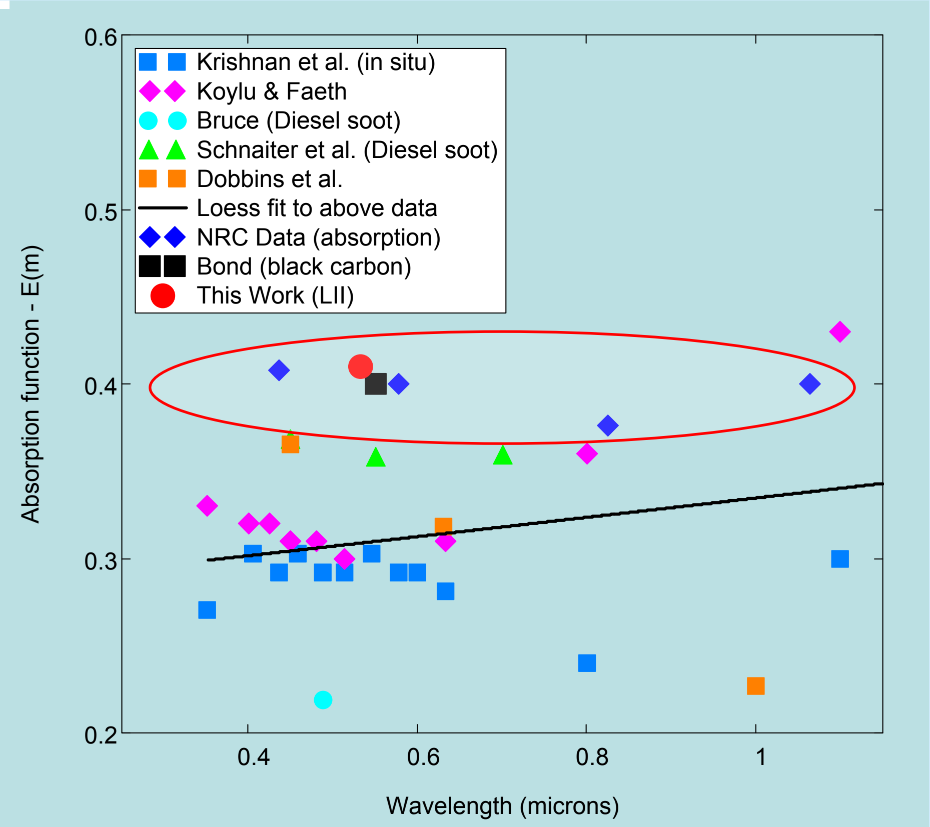
In- and Post-Flame – Soot Absorption Function

- AC-LII does not always agree with gravimetric
  - need improved knowledge of *E*(*m*) as a function of temperature and wavelength
- impact of uncertainty in *E*(*m*) on soot volume fraction

$$\frac{f_{V_1}}{f_{V_0}} = \left(\frac{E(m)_{\lambda_{low}1}}{E(m)_{\lambda_{low}0}}\right)^{\frac{\lambda_{low}}{\lambda_{high}-\lambda_{low}}} \left(\frac{E(m)_{\lambda_{high}1}}{E(m)_{\lambda_{high}0}}\right)^{\frac{-\lambda_{high}}{\lambda_{high}-\lambda_{low}}}$$



[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

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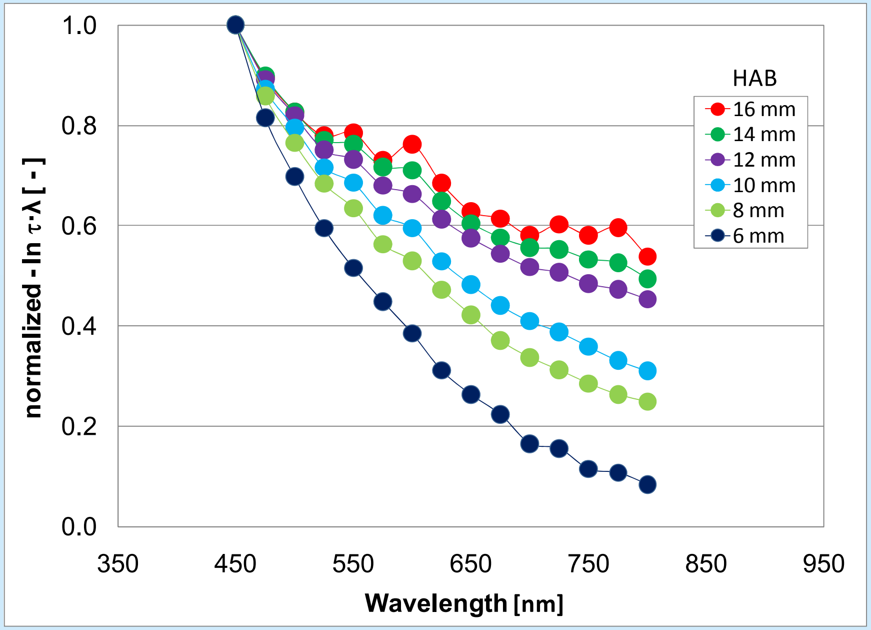
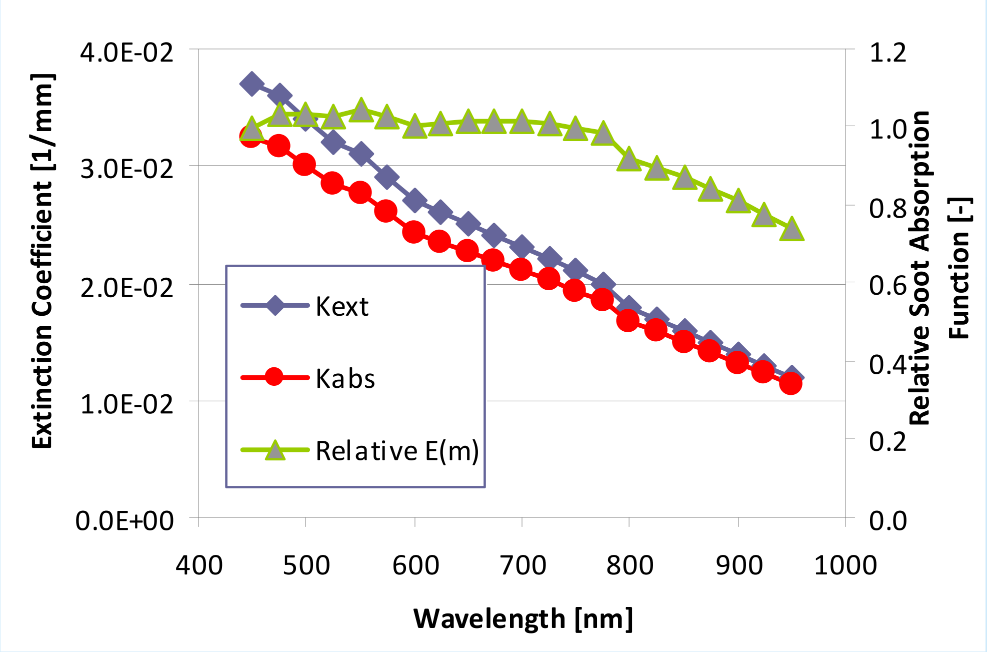
In-Flame – Soot Absorption Function

McKenna Flame



Laminar Diffusion Flame (HAB = 42 mm)



- data acquired with spectral line-of-sight attenuation (Spec-LOSA)
- these results suggest a strong variation of $E(m)_\lambda$ with λ
- could indicate strong variation of soot optical properties with soot age
- could also be absorption of gas or liquid phase species
- if from soot, has significant implications for LII

[Migliorini *et al*., in preparation, 2009]

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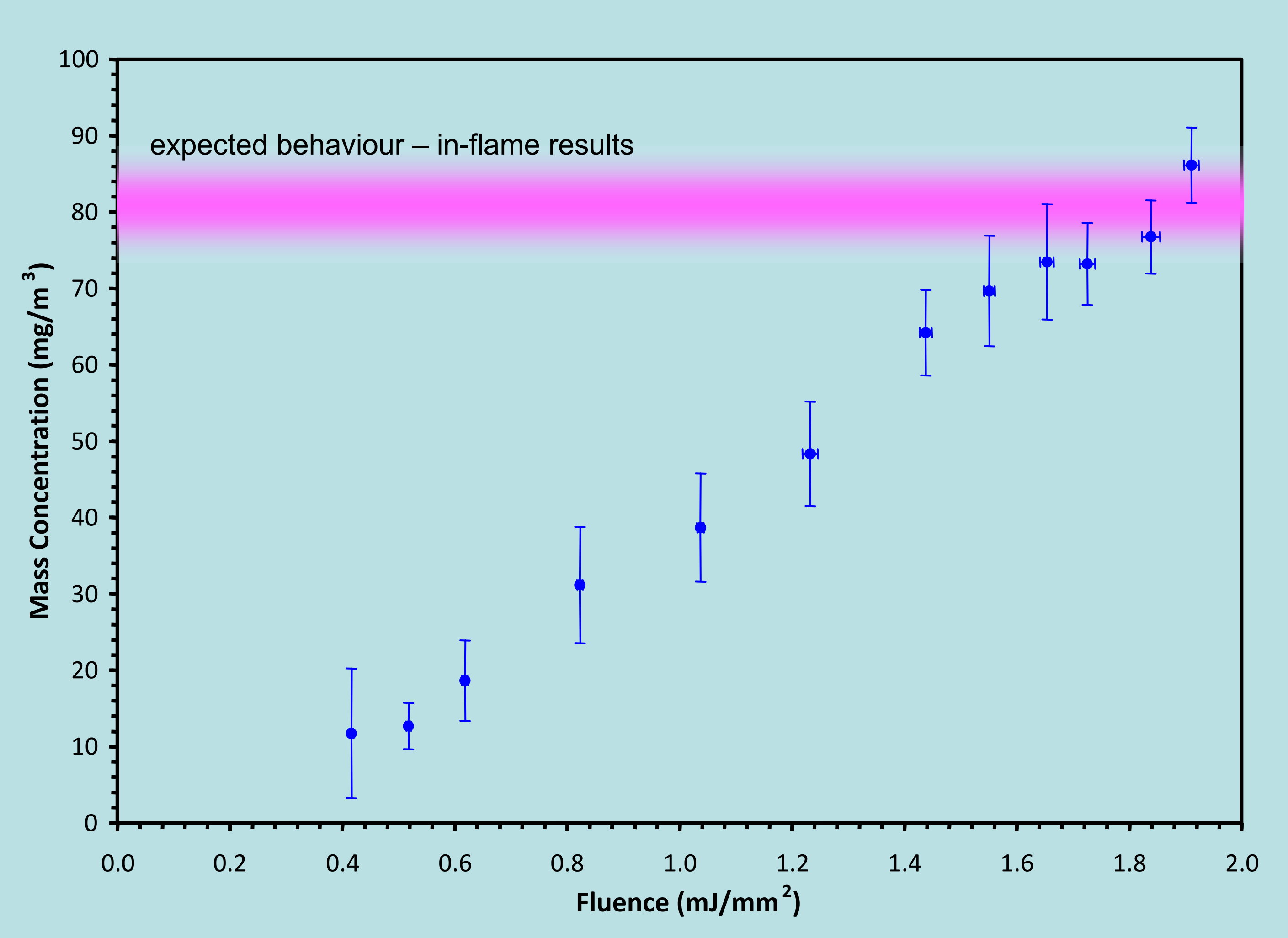
Post-Flame – Variation in Concentration with Fluence



[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

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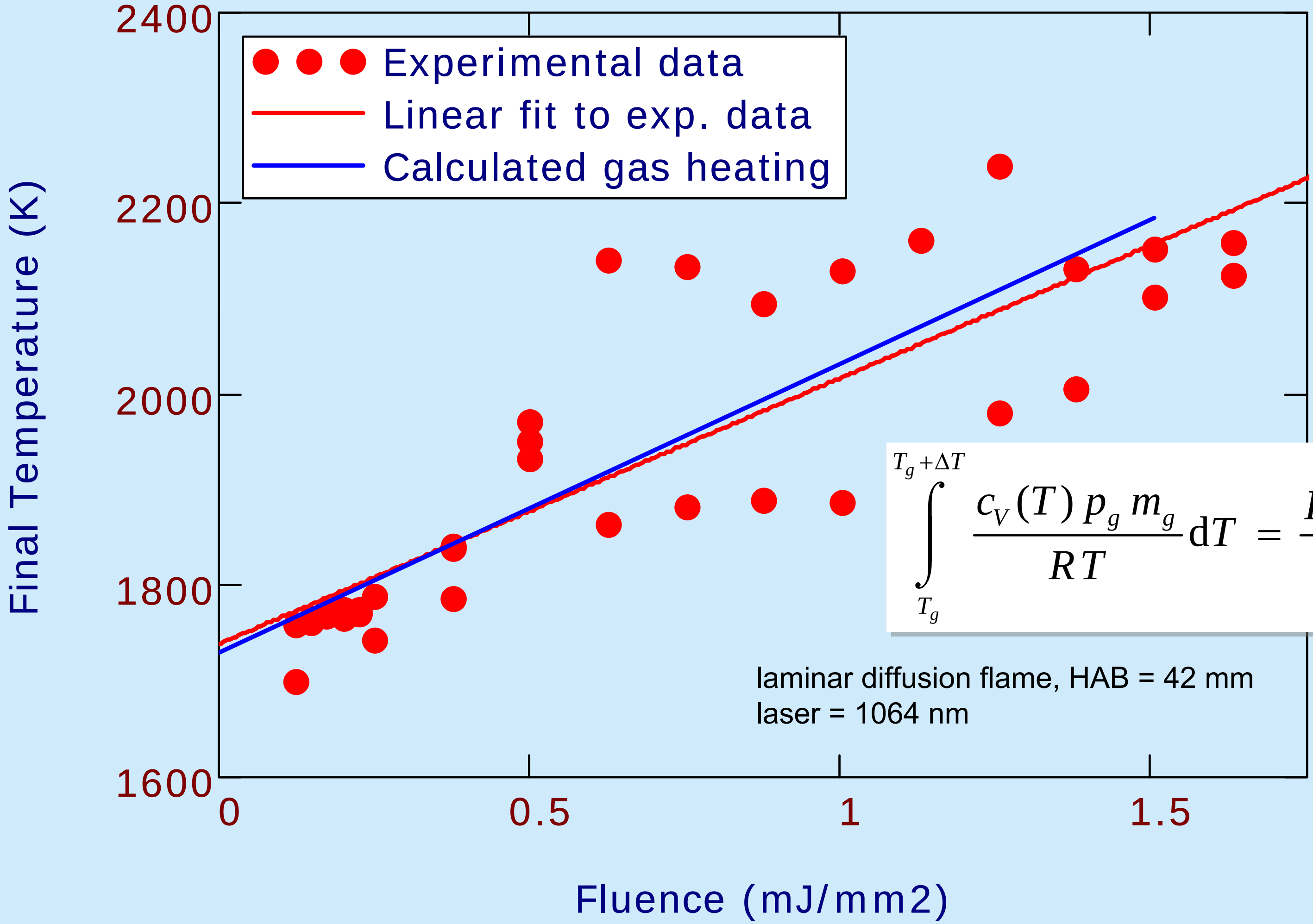
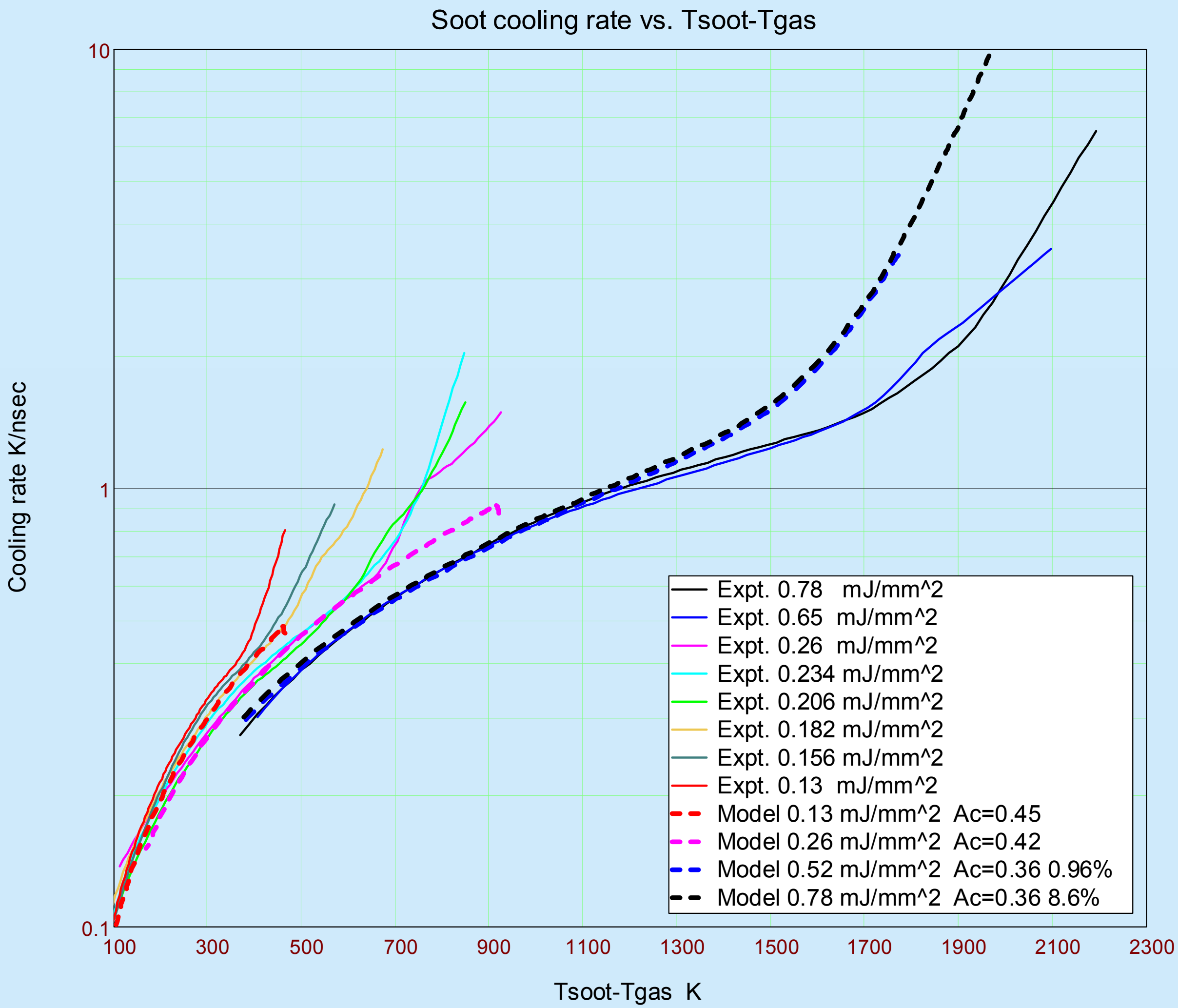
In-Flame – LII is not Noninstrusive



$$\int_{T_g}^{T_g+\Delta T} \frac{c_V(T)\, p_g\, m_g}{R\,T}\,\mathrm{d}T = \frac{F_0\, 6\pi E(m)\, f_V}{\lambda}$$

[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

In-Flame – Anomalous Initial Cooling

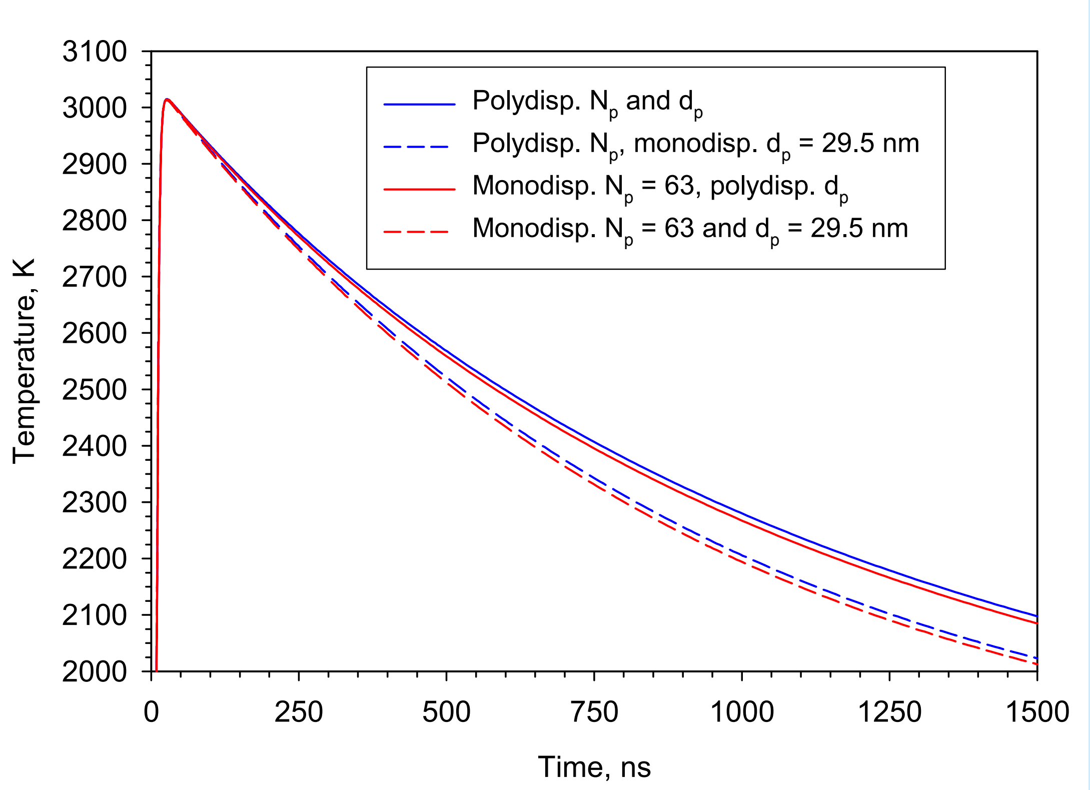


- model seriously underestimates initial cooling rate at low to moderate fluences
- model overpredicts cooling due to sublimation at high fluences

[Snelling *et al*., Applied Physics B **96**, 2009]

Polydisperse Primary Particle Diameters and Aggregate Sizes – In-Flame

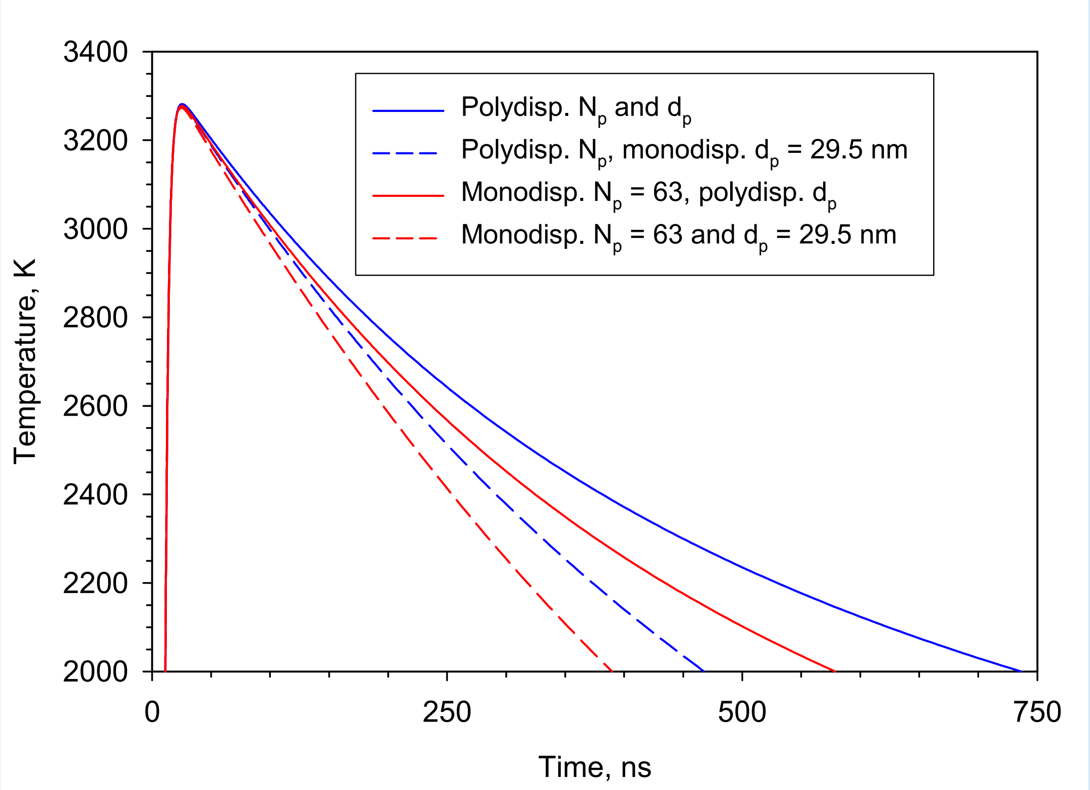
- under flame conditions
  - peak particle temperature is essentially unaffected
  - the decay of the effective temperature is only slightly affected by the N_p distribution
  - the d_p distribution has a significant influence on the effective temperature
  - primary particle diameter can be determined



[Liu *et al.*, Applied Physics B **83**, 2006]

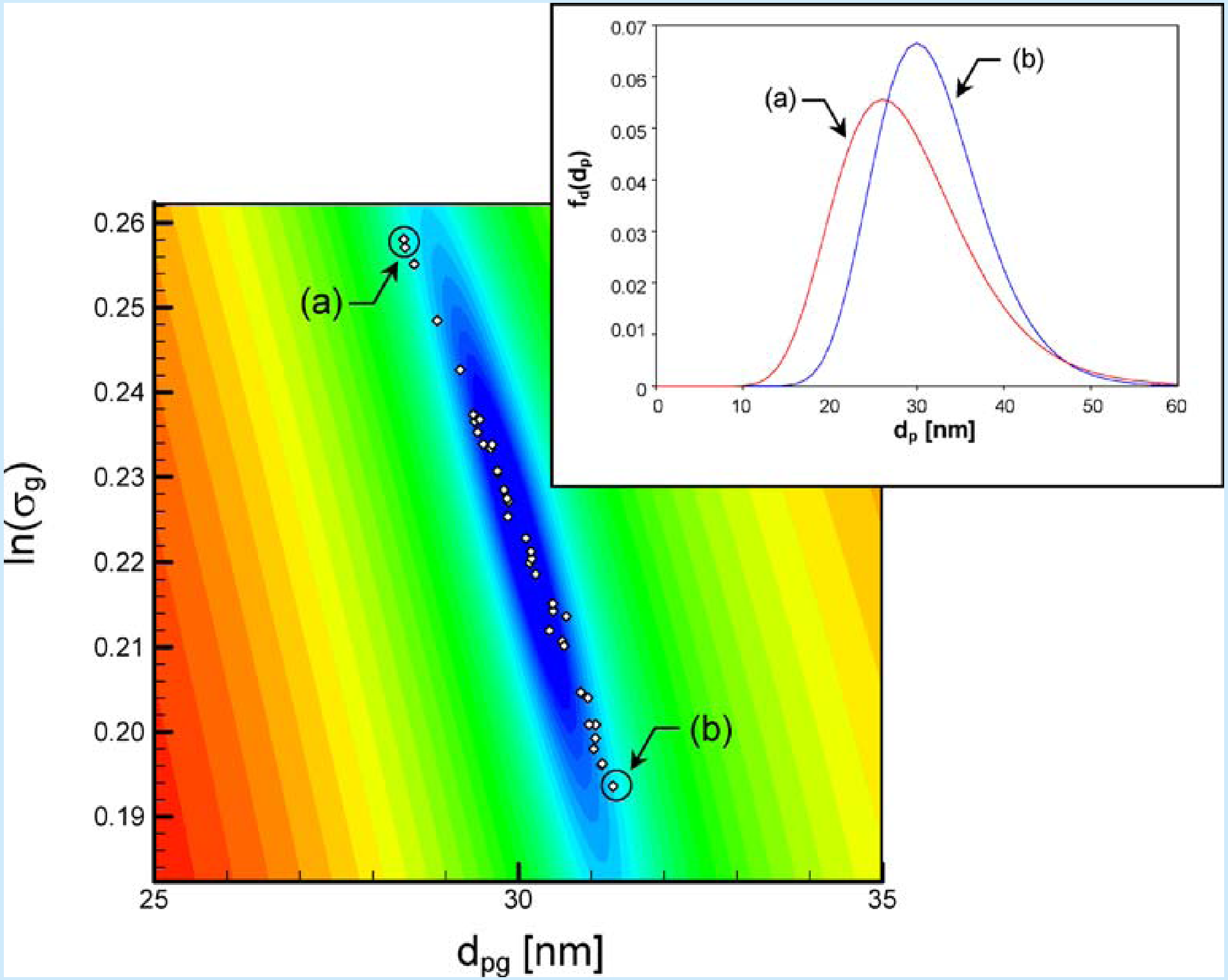
Polydisperse Primary Particle Diameters and Aggregate Sizes – Post-Flame

- at room temperature
  - peak particle temperature unaffected
  - temperature decay is strongly dependent on both the primary particle diameter and the aggregate size distribution function
  - primary particle diameter cannot be adequately retrieved without detailed *a priori* knowledge of the aggregate size distribution



[Liu *et al.*, Applied Physics B **83**, 2006]

Polydisperse Primary Particle Diameters – In-Flame



[Daun *et al.*, Applied Physics B **87**, 2007]

- inverse analysis
- demonstrates range of solutions
- orthogonal data could narrow range of solutions

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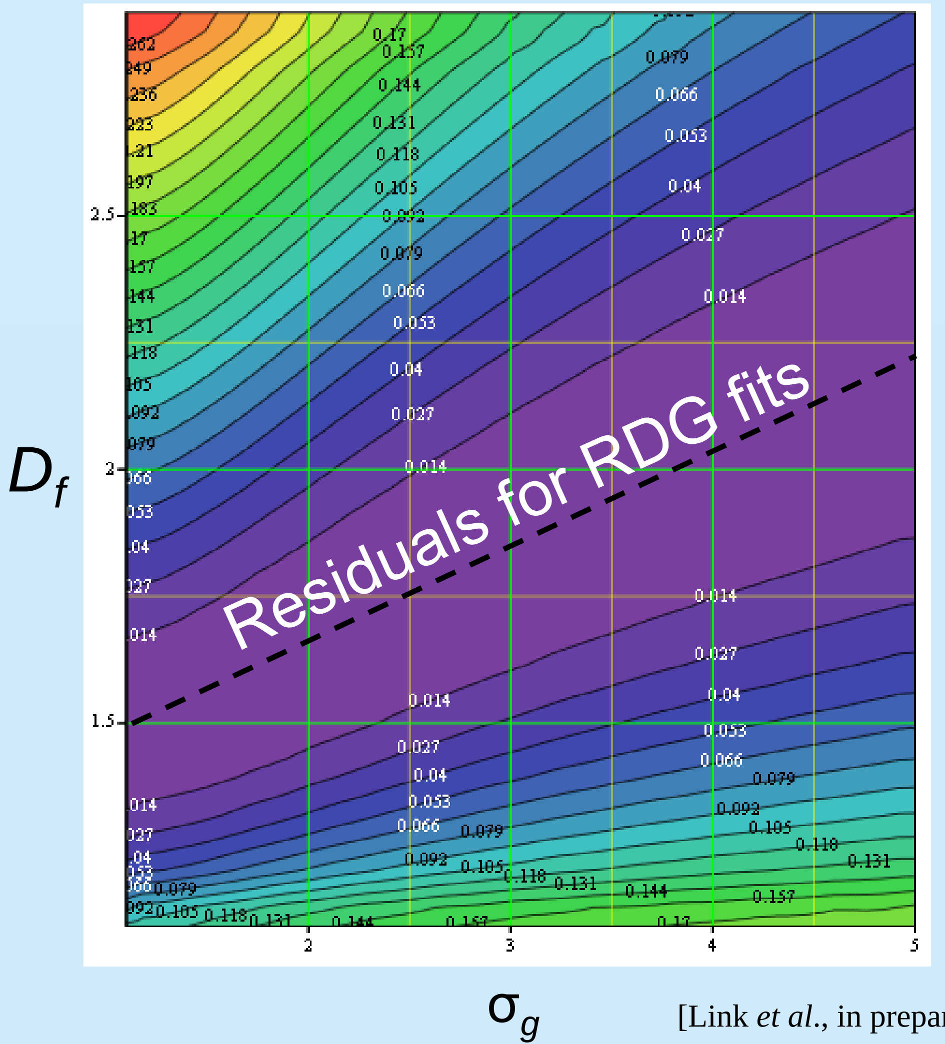
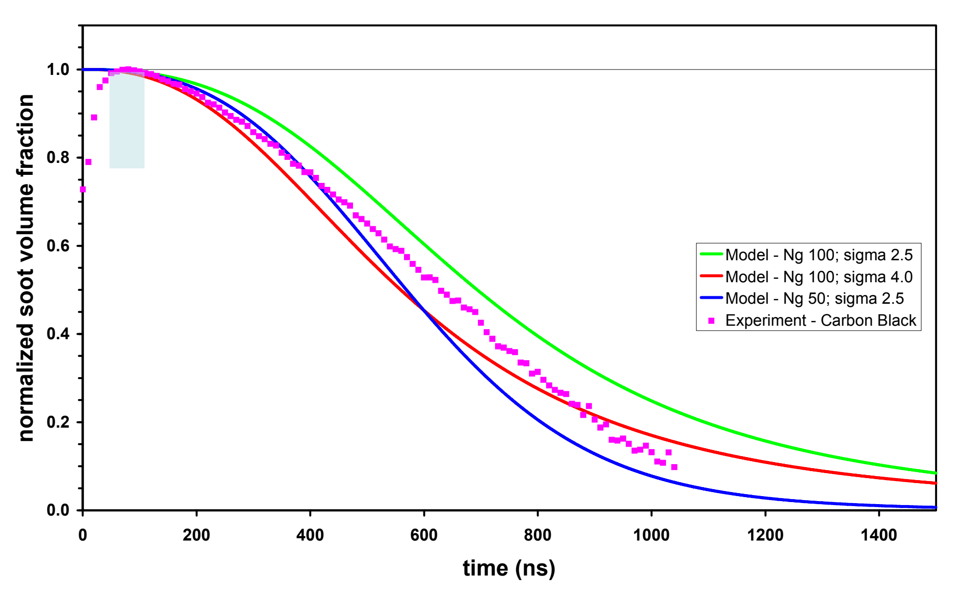
Polydisperse Aggregate Sizes with Elastic Light Scattering

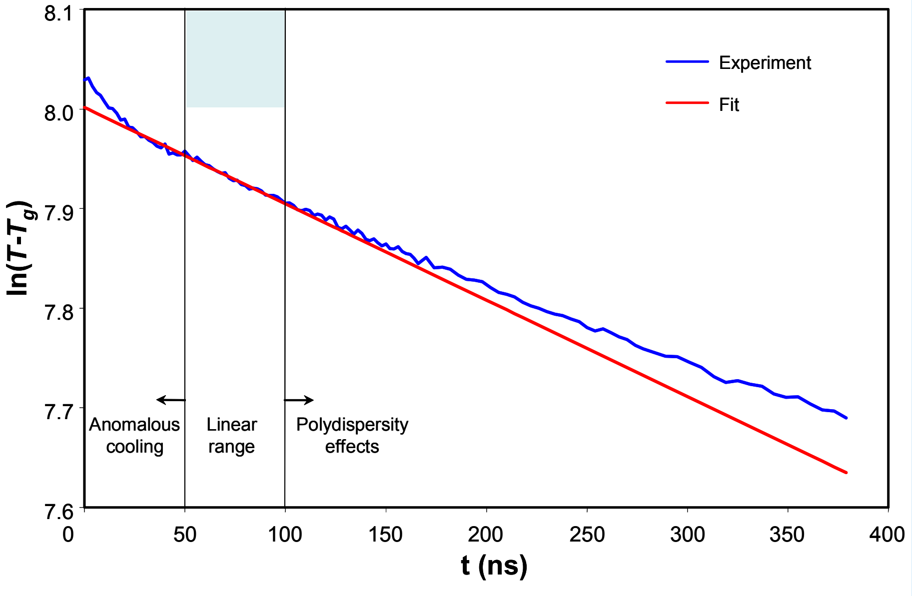


- similar approach to that for primary particle diameter distribution
- assume k_f = 2.3, d_p = 30nm
- fit N_g, D_f, σ_g
- apply Rayleigh-Debye-Gans Polydisperse Fractal Aggregate (RDG-PFA) theory for scattering to experimental data
- both scattering and LII may be required to assess d_p and N_p distributions

[Link *et al.*, in preparation, 2009]

Experiment: Recommended Analysis Interval





[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

- for AC-LII measurements the recommended analysis interval is approximately 50-100 ns after the peak of the laser pulse
  - maximum soot volume fraction and single exponential temperature decay
  - interval is dependent upon experimental conditions

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Summary

- autocompensating laser-induced incandescence (AC-LII) addresses some of the limitations of conventional LII
  - no significant sublimation ✓
  - fluctuations in local ambient temperature ?
  - variation in laser fluence ✗
  - laser beam attenuation by the particulate matter ?
  - desorption of condensed volatile material ?
- LII however has shown uncertainty in the absolute concentration
  - issues with calibration
  - uncertainty in optical properties of the particles
  - variation in concentration with laser fluence

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Summary

- from the perspective of LII

in-flame post-flame
soot ≠ soot

- there is one equality

“constants” = variables

- progress has been made in improving the real-time measurement of soot and nonvolatile particulate matter emissions
- may need to rely on correlation to gravimetric to firmly anchor AC-LII measurements for post-flame soot

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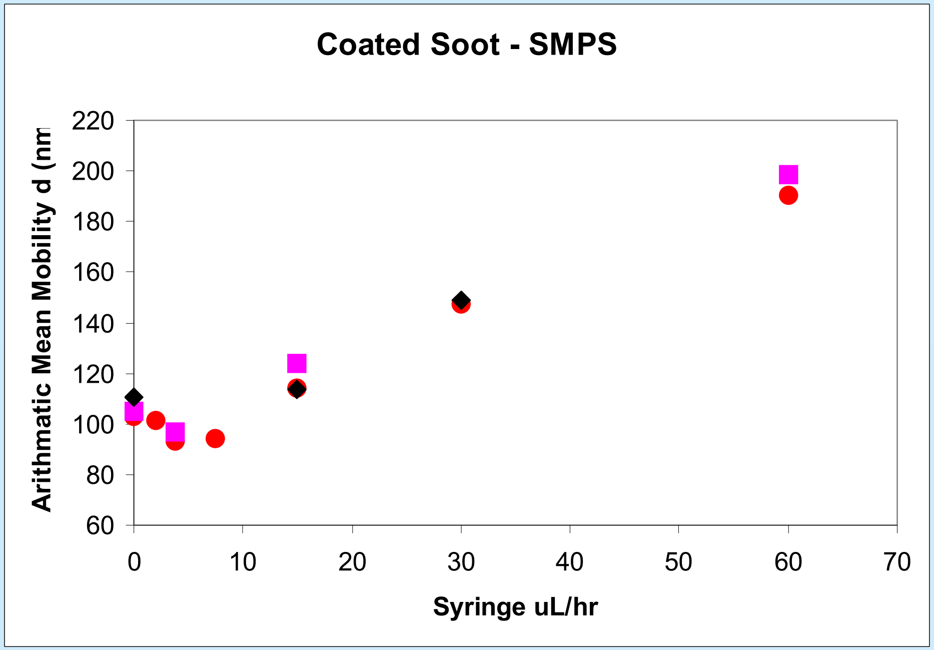
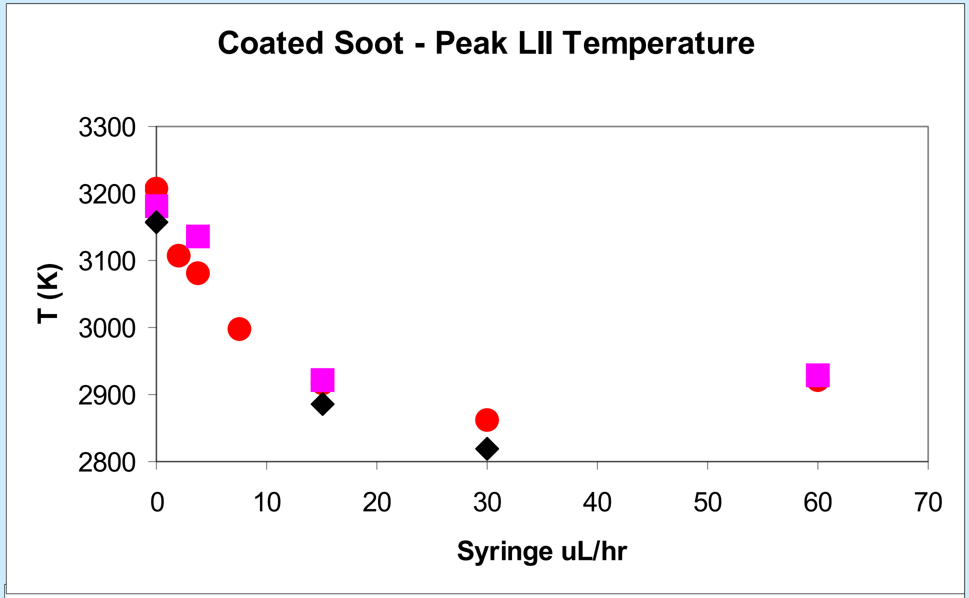
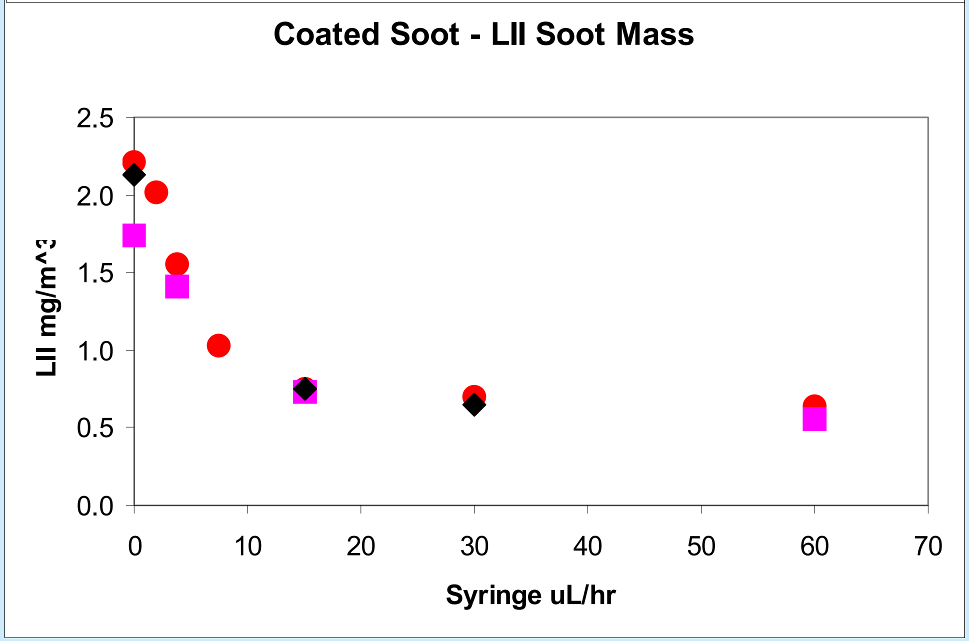
Effect of Condensates







[Smallwood *et al.*, in preparation, 2009]