Laser-induced incandescence (LII) for the measurement of nonvolatile particulate mass

Smallwood, Gregory J.; Bachalo, William D.

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Laser-induced incandescence (LII) for the measurement of nonvolatile particulate mass

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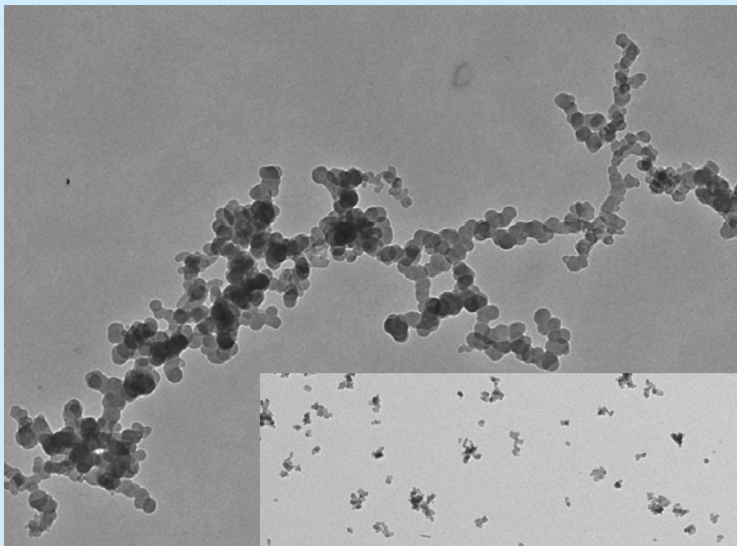
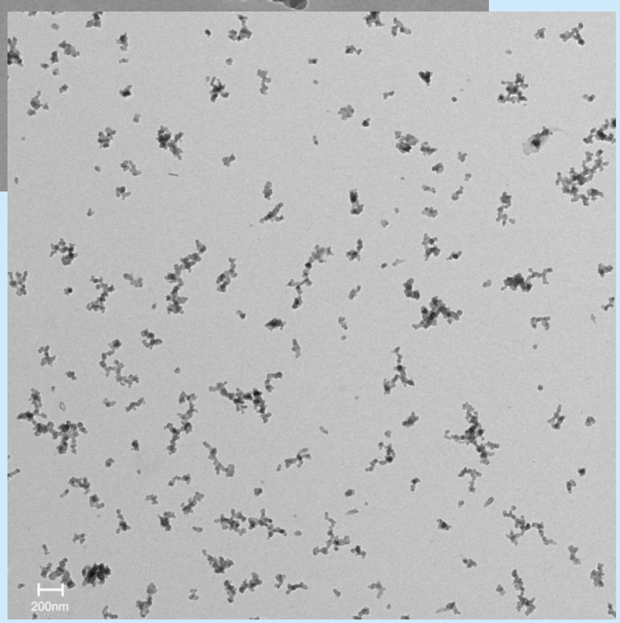
SAE E-31 Committee Annual Meeting
29 June – 2 July 2010 Interlaken, Switzerland

National Research Council Canada | Conseil national de recherches Canada

Canada

TEM Images of Nanoparticles

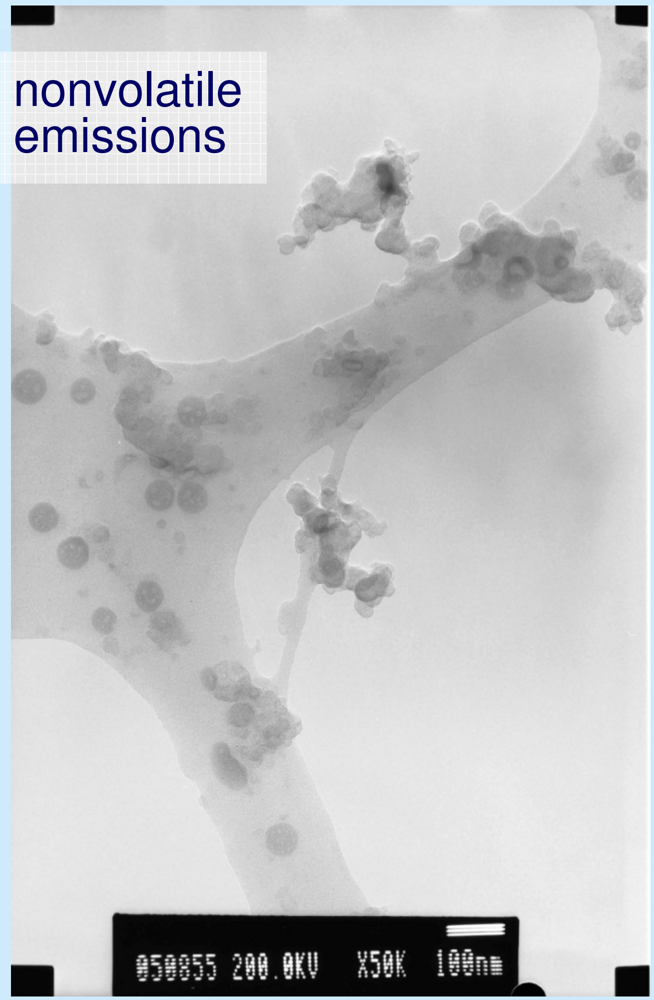




in-flame ethylene soot

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

gas turbine nonvolatile particulate emissions



[Delhaye *et al.*, SAE E-31 Meeting, 2009]

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What is Laser-Induced Incandescence (LII)?

- laser-induced incandescence is a generic name for the physical process of rapidly heating refractory nanoparticles with a laser to the point that the radiative emission from the particles is discernable from the background (in the literature since 1960's)
- 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
- nonvolatile particulate emissions are anticipated to be very similar to soot as defined above

Many Variants of LII Have Appeared

- high fluence (most common)
  - particles are heated to their sublimation temperature
- low fluence
  - particles are heated to lower than sublimation temperature
- remote *in situ* nonintrusive measurements (some instruments)
  - fundamental studies on open flames
- extractive sampling (most instruments)
  - engine and combustor development and emissions measurement
- pulsed laser or cw laser
- time-resolved (TiRe-LII) or gated detection
- single (narrow or broadband), two, or multiple wavelength detection
- 0-D (point measurements); 1-D (line measurements); 2-D (area measurements); or 3-D (volume measurements)
  - "point measurements" refers to imaging sample volume onto a single detector

[Artium LII 300 characteristics in teal]

What Does LII Do?

- quantitative measurement (values are for soot):
  - concentration (0.01 ppt – 10 ppm volume; 20ng/m^3 – 20g/m^3 mass)
  - active surface area (50 – 200 m^2/g)
  - primary particle diameter (typically 5-50 nm)
  - number density of primary particles
- properties are for an ensemble of particles
  - not a single-particle measurement technique
- measurement features:
  - high precision and repeatability
  - transient concentration
  - nonintrusive (dilution unnecessary)
  - wide range of applicability
  - high selectivity
  - measures refractory nanoparticles

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

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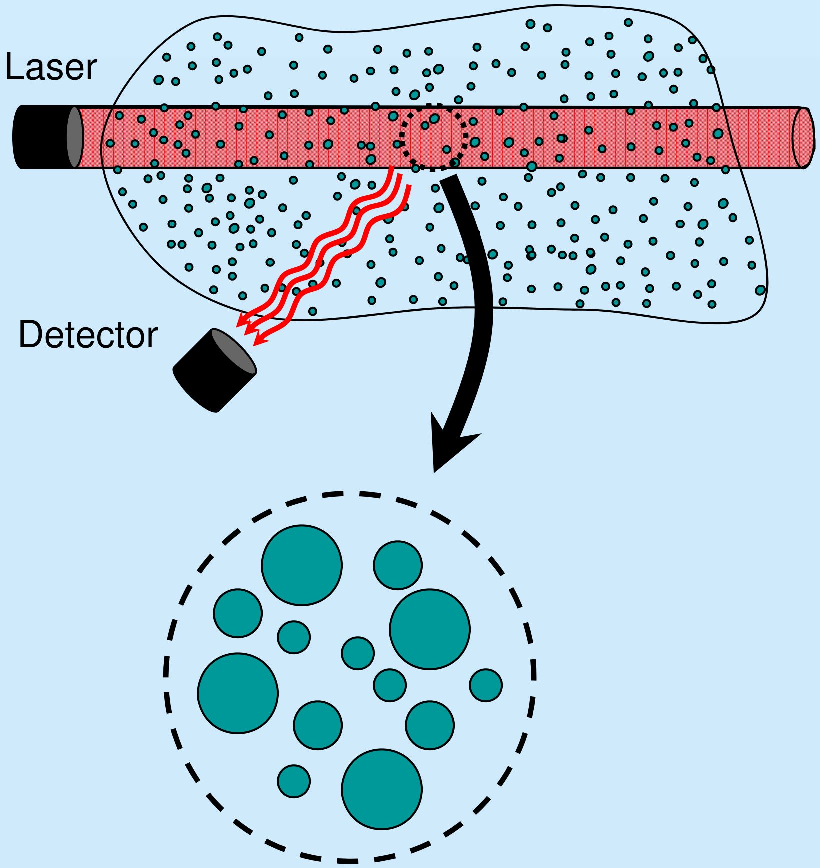
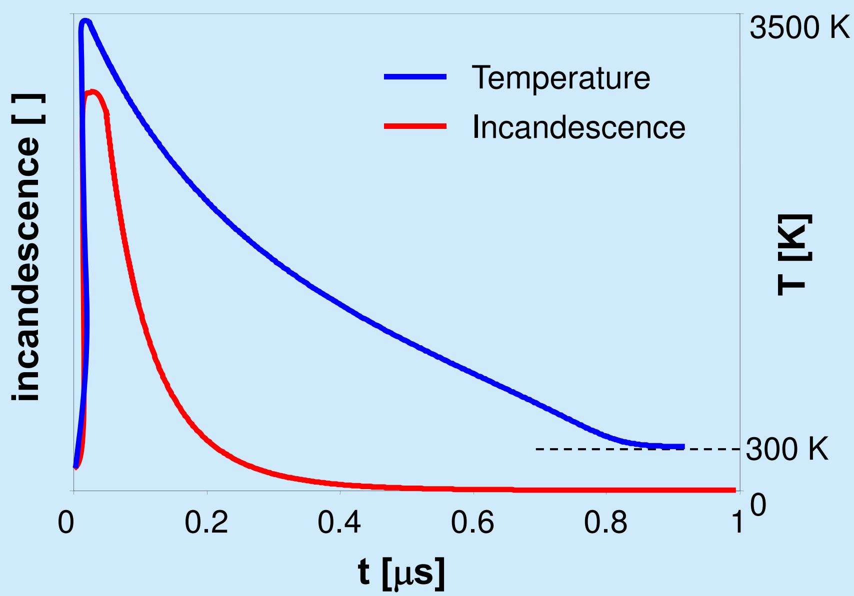
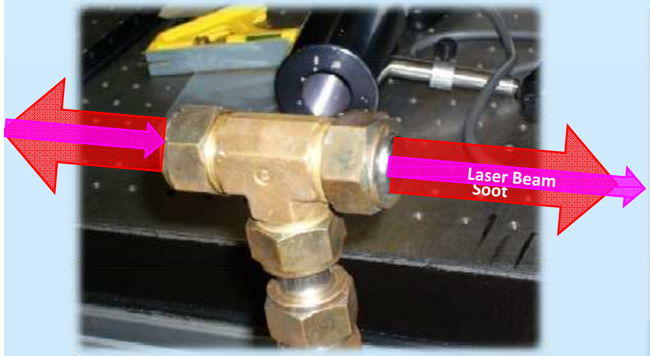
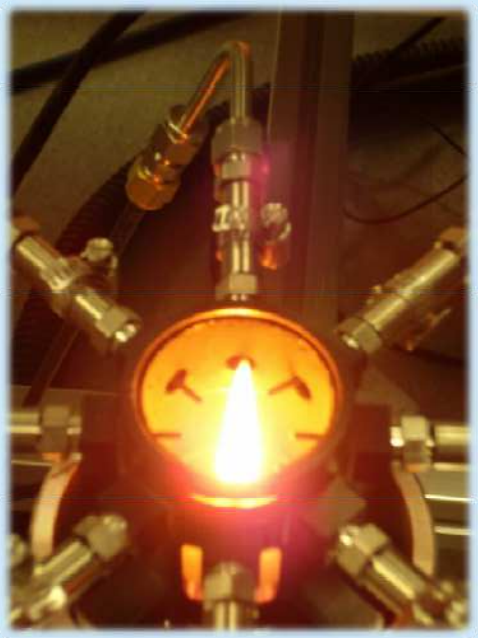
Time-Resolved Laser Induced Incandescence





Demonstration of Fluence Effects in LII





0.50 mJ/mm^2 Peak Fluence

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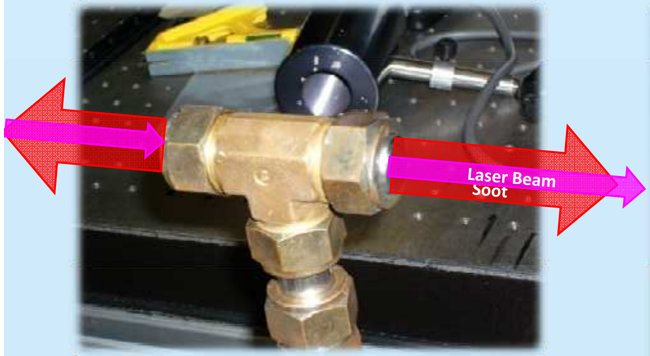
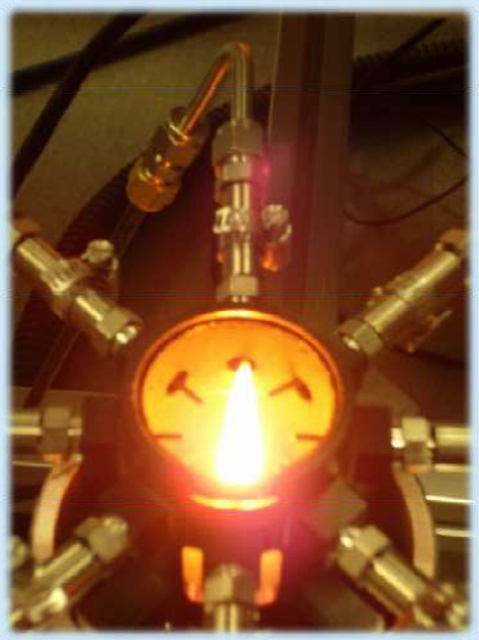
Demonstration of Fluence Effects in LII





0.50 mJ/mm^2
Peak Fluence

0.67 mJ/mm^2

0.83 mJ/mm^2

1.25 mJ/mm^2

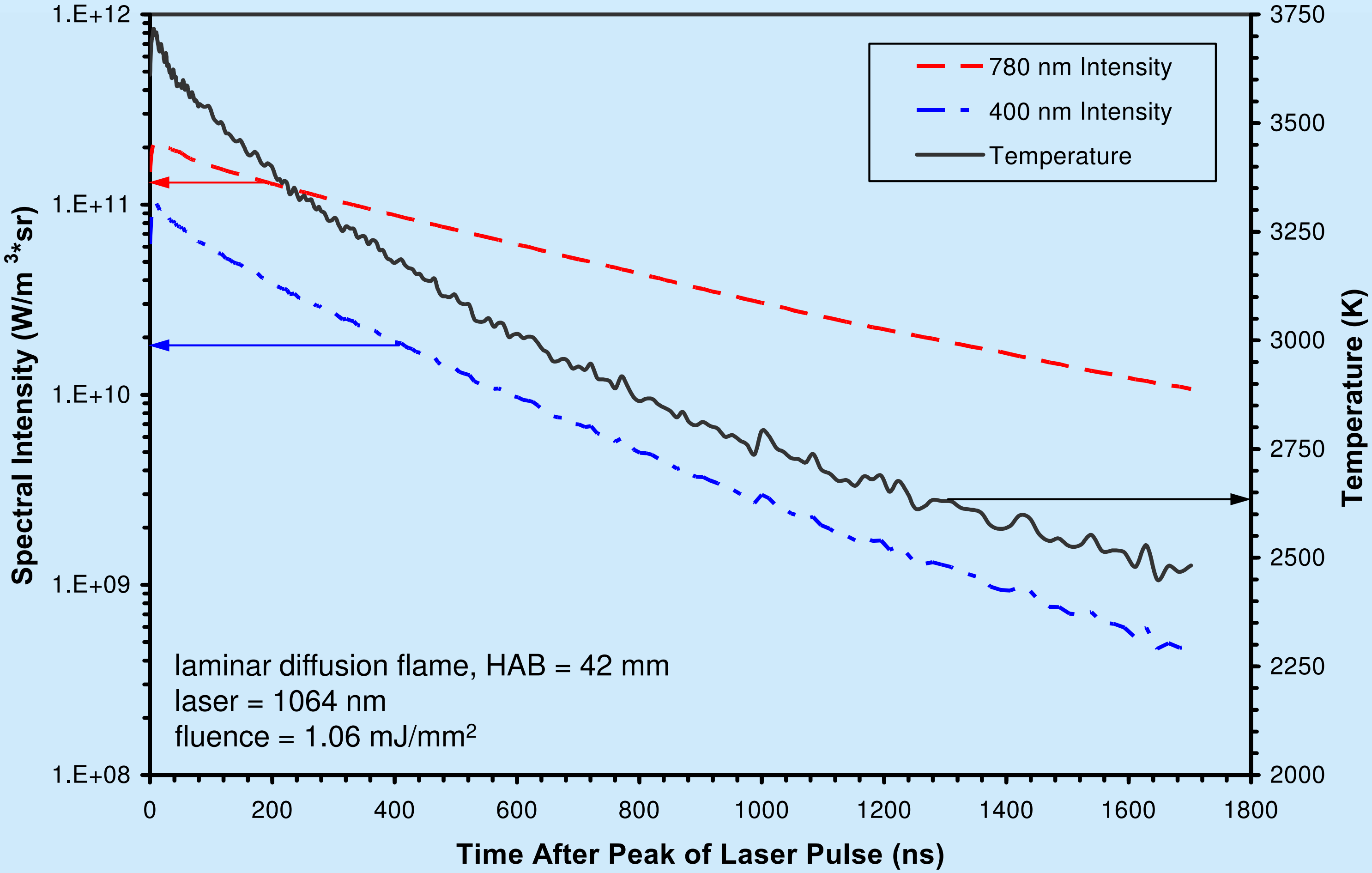
2.50 mJ/mm^2

3.75 mJ/mm^2

Auto-Compensating LII (AC-LII)

- traceable physics-based calibration procedure
  - using calibrated integrating sphere as a spectral radiance source
  - not correlation against another aerosol instrument
- two-color pyrometry coupled with LII to determine the time-resolved particle temperature
  - permits use of low-fluence
  - particles are kept below the sublimation temperature
- this new technique *automatically compensates* 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

Absolute LII Signals



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

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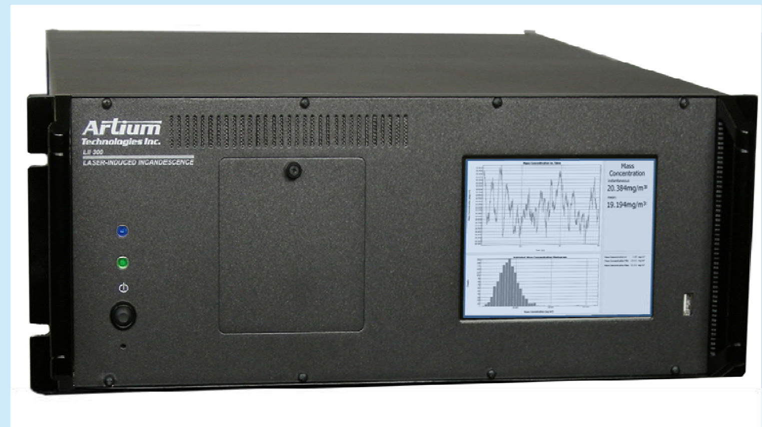
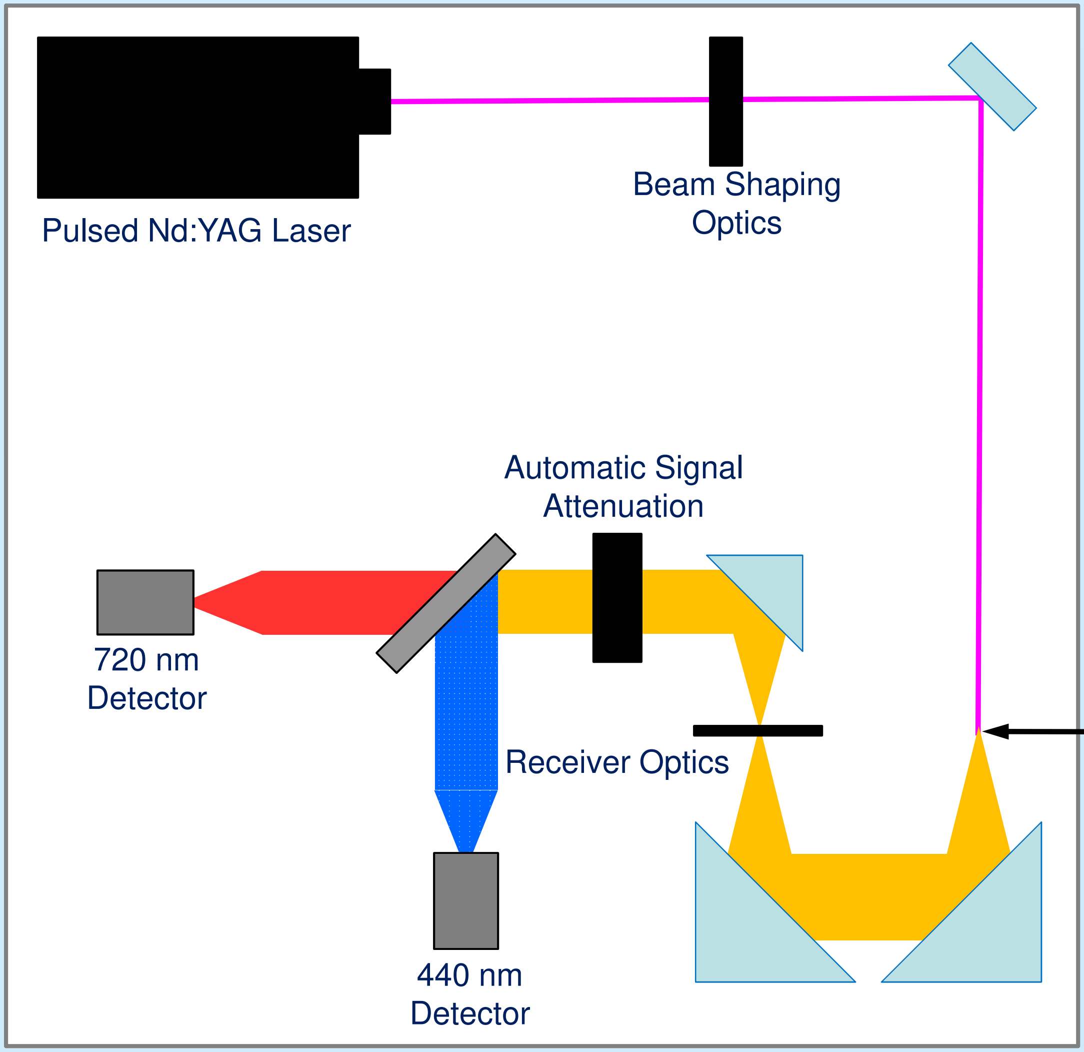
LII Applications: Artium Technologies Instruments

- Artium Technologies takes an active role, with NRC's support, in working with customers who have purchased the LII 300 instrument
  - Easy to use
  - Low maintenance system
  - Low operating costs
  - Very high sensitivity
  - No warm-up time required
  - Compact rugged and portable instrument
  - Built-in computer and display, touchscreen control
  - Built-in pneumatics controller and sampling system
  - Completely enclosed laser, optics, and sampling cell
  - Increased automation features including autosensitivity control
  - Fail safe valve prevents sample from entering cell if purge air or power are off
  - Includes real-time pressure and temperature measurements to reduce data to STP
  - Technologies protected by US Patents 6,154,277 and 6,181,419 under license from National Research Council (NRC) Canada

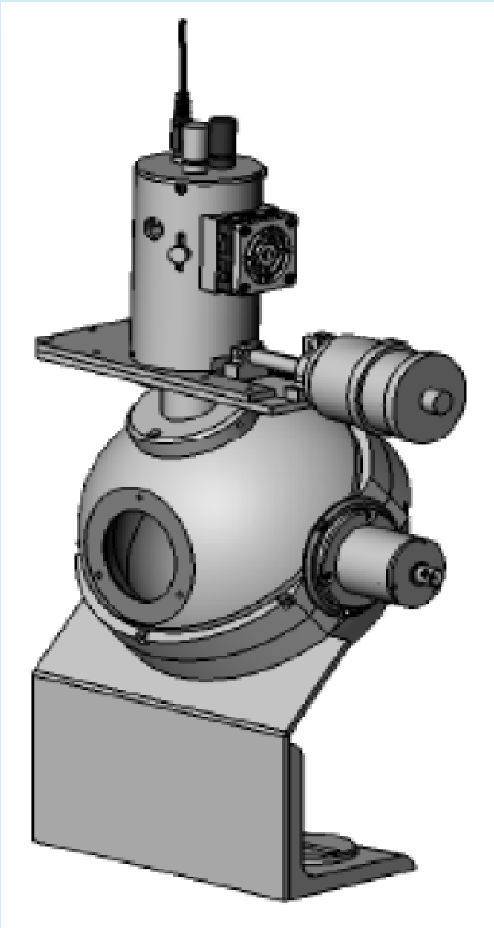


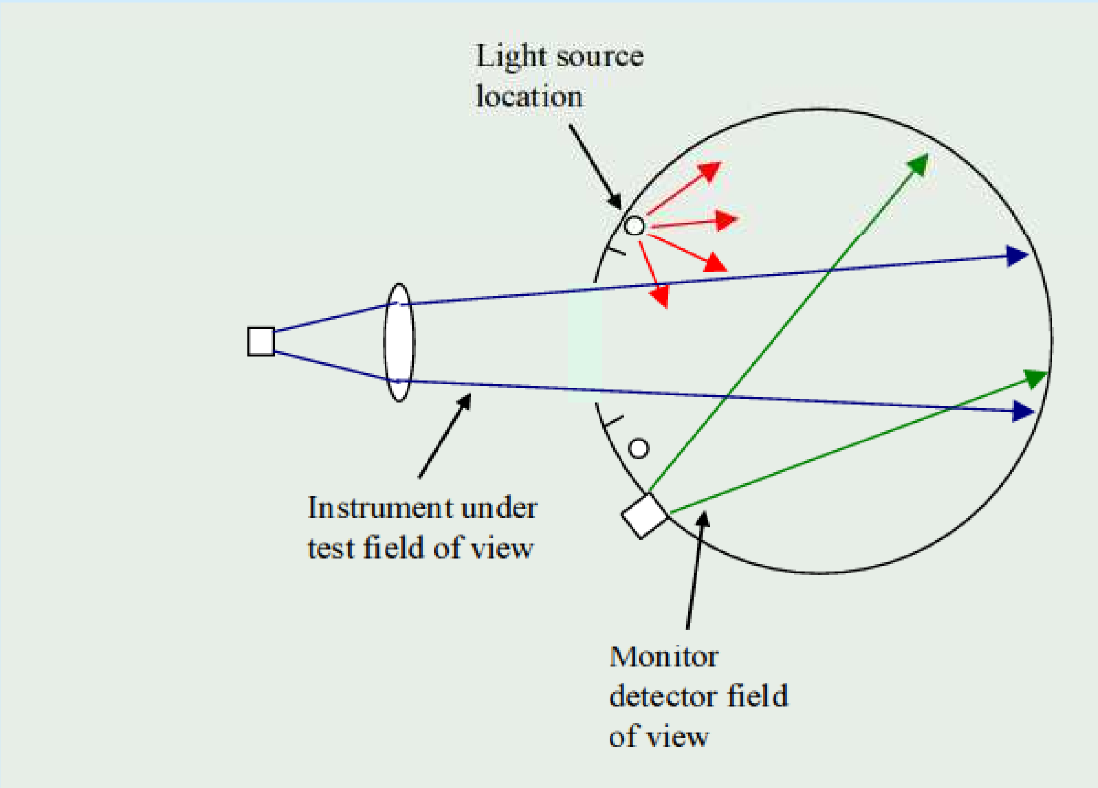
[Artium LII 300 improvements over LII 200 in teal]

Schematic of LII 300 Instrument



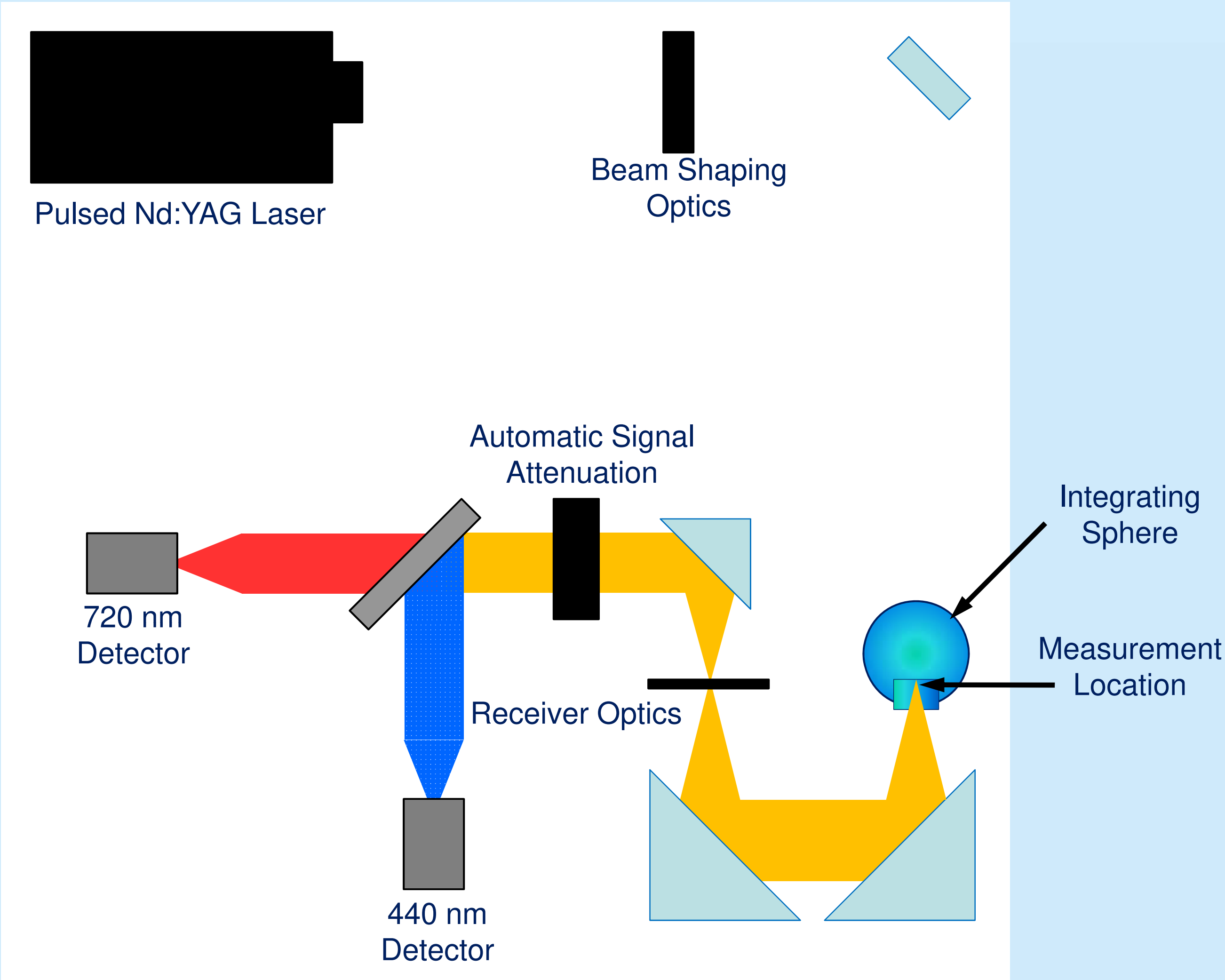
Integrating Sphere Calibration Source





- Spectral radiance is NIST-traceable
- Lamp is monitored by built-in spectrometer

Primary Calibration of LII 300 Instrument



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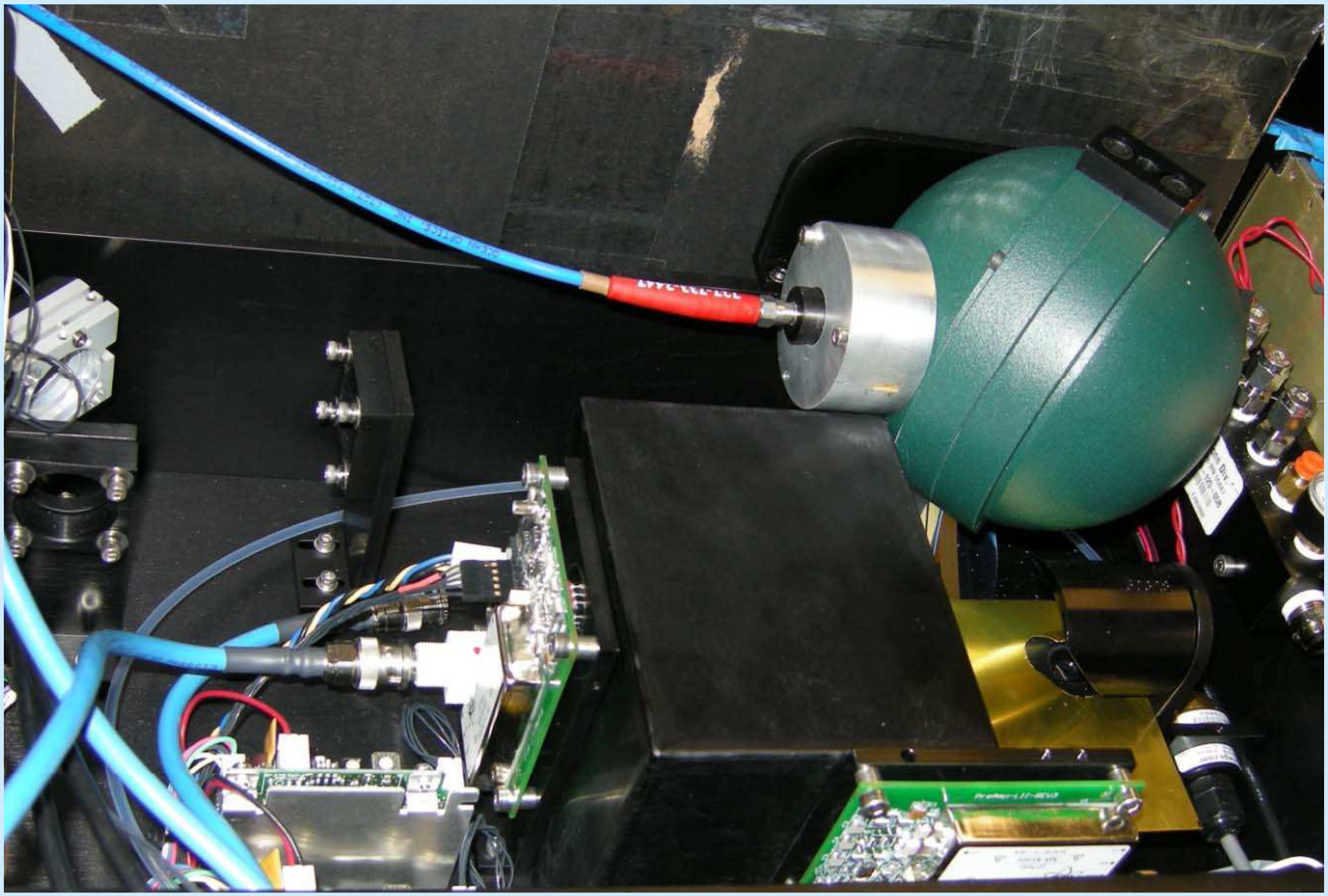
Integrating Sphere Calibration Source



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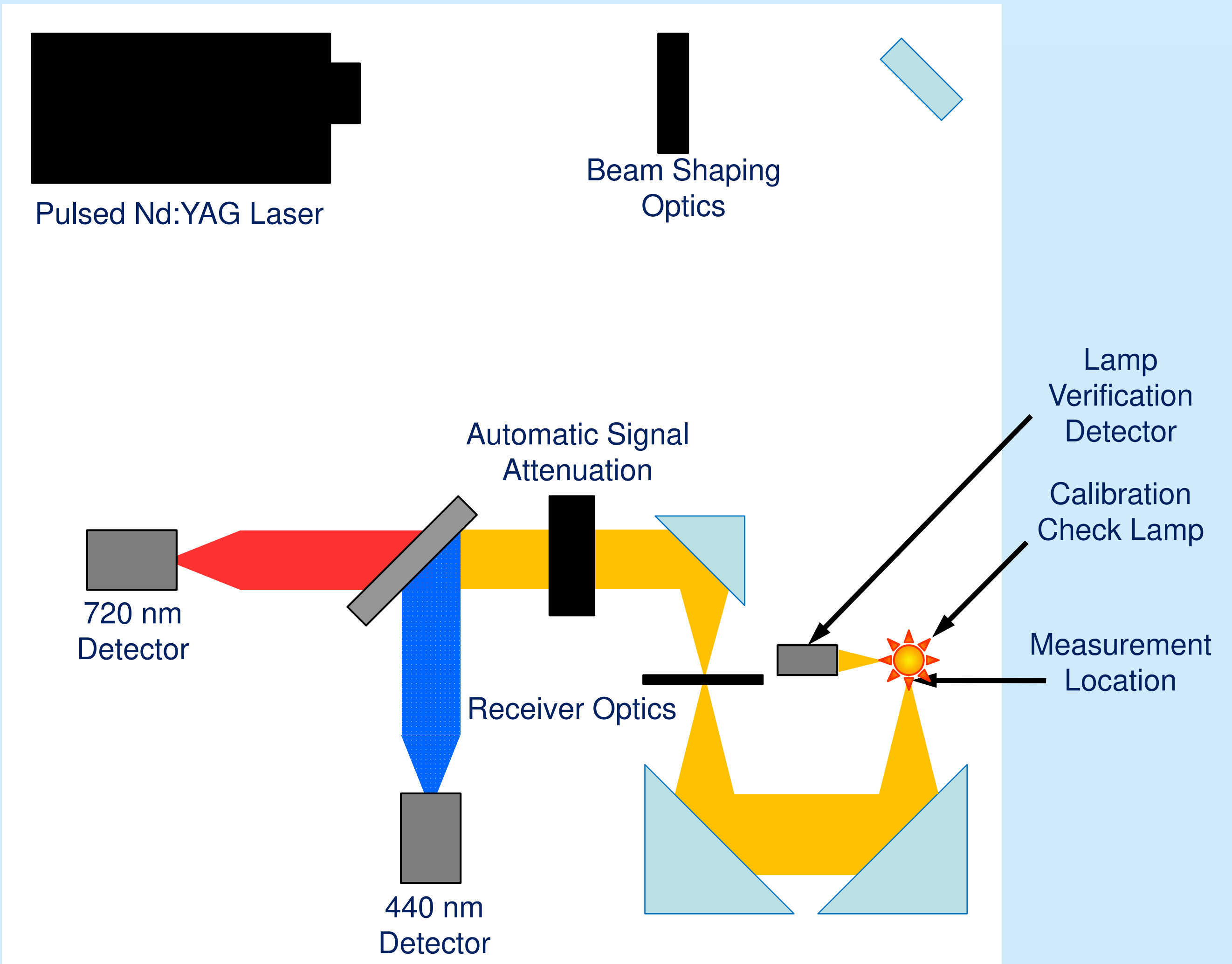
Development of Calibration Check



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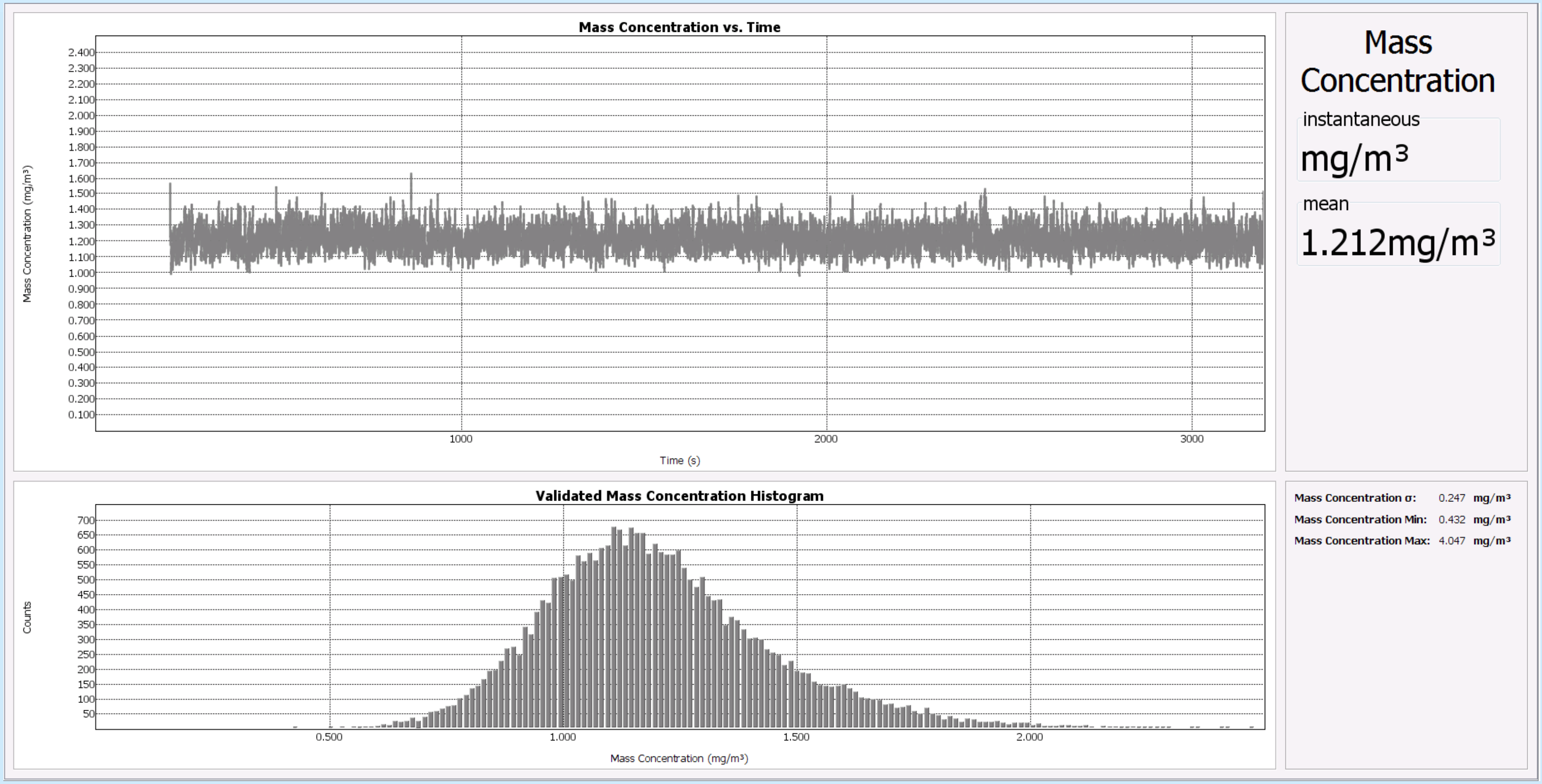
Start-up Device Check Sequence

LII 300 Front Panel Display



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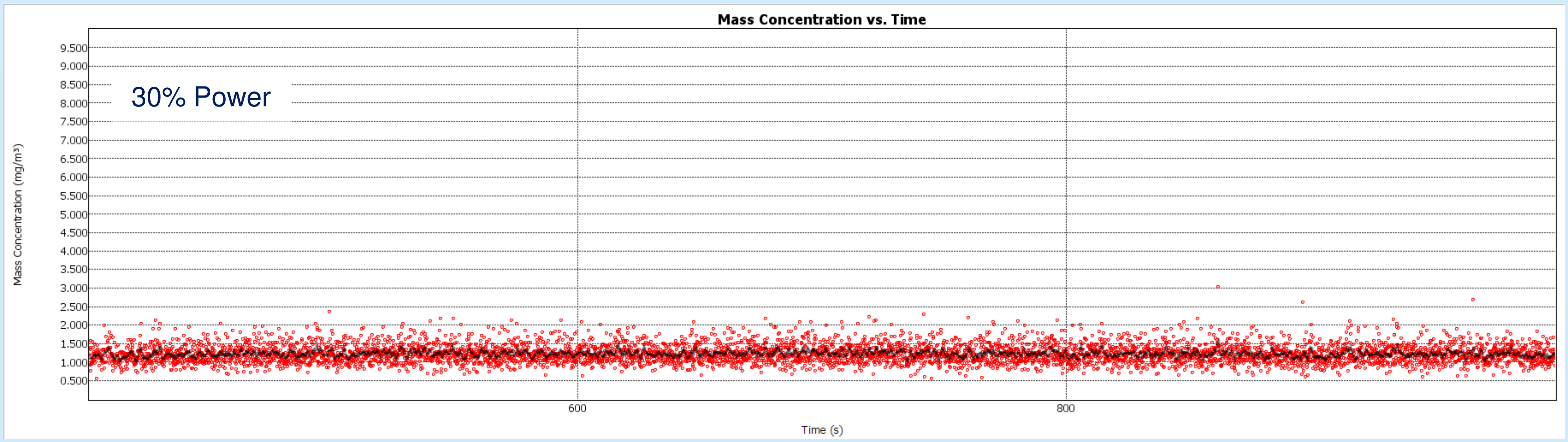
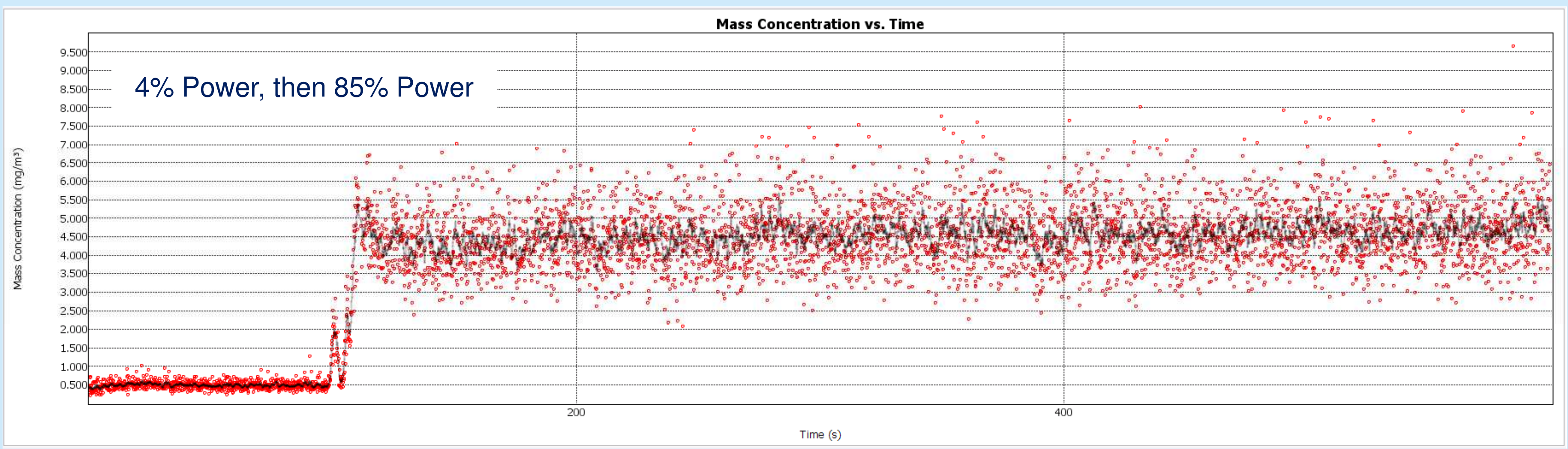
LII 300 Single-Shot Data from WPAFB





[Red dots are single-shot data; Black line is 1 Hz running average]

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Measurement Conditions for LII 300

Organization	Instrument	Test No.	Engine Power	Average Dilution Ratio	Probe	Instrument Location	Sampling Line	Fuel
Artium	LII 300	1	4	0	4	Trailer	75' Long	JP-8
			30	0	4	Trailer	75' Long	JP-8
			85	0	4	Trailer	75' Long	JP-8
			100	0	4	Trailer	75' Long	JP-8
		2	4	0	4	Trailer	75' Long	JP-8
			30	0	4	Trailer	75' Long	JP-8
			30	0	6	Trailer	75' Long	JP-8
			85	0	6	Trailer	75' Long	JP-8
			100	0	6	Trailer	75' Long	JP-8
		3	4	0	6	Trailer	75' Long	JP-8
			30	0	6	Trailer	75' Long	JP-8
			85	0	4	Test Cell	Short	JP-8
			100	0	4	Test Cell	Short	JP-8
		4	30	0	4	Test Cell	Short	JP-8
			85	0	4	Test Cell	Short	JP-8
			100	0	4	Test Cell	Short	JP-8
			4	0	4	Test Cell	Short	JP-8
		5	4	0	4	Trailer	75' Long	F-T
			30	0	4	Trailer	75' Long	F-T
			85	0	4	Trailer	75' Long	F-T
			100	0	4	Trailer	75' Long	F-T

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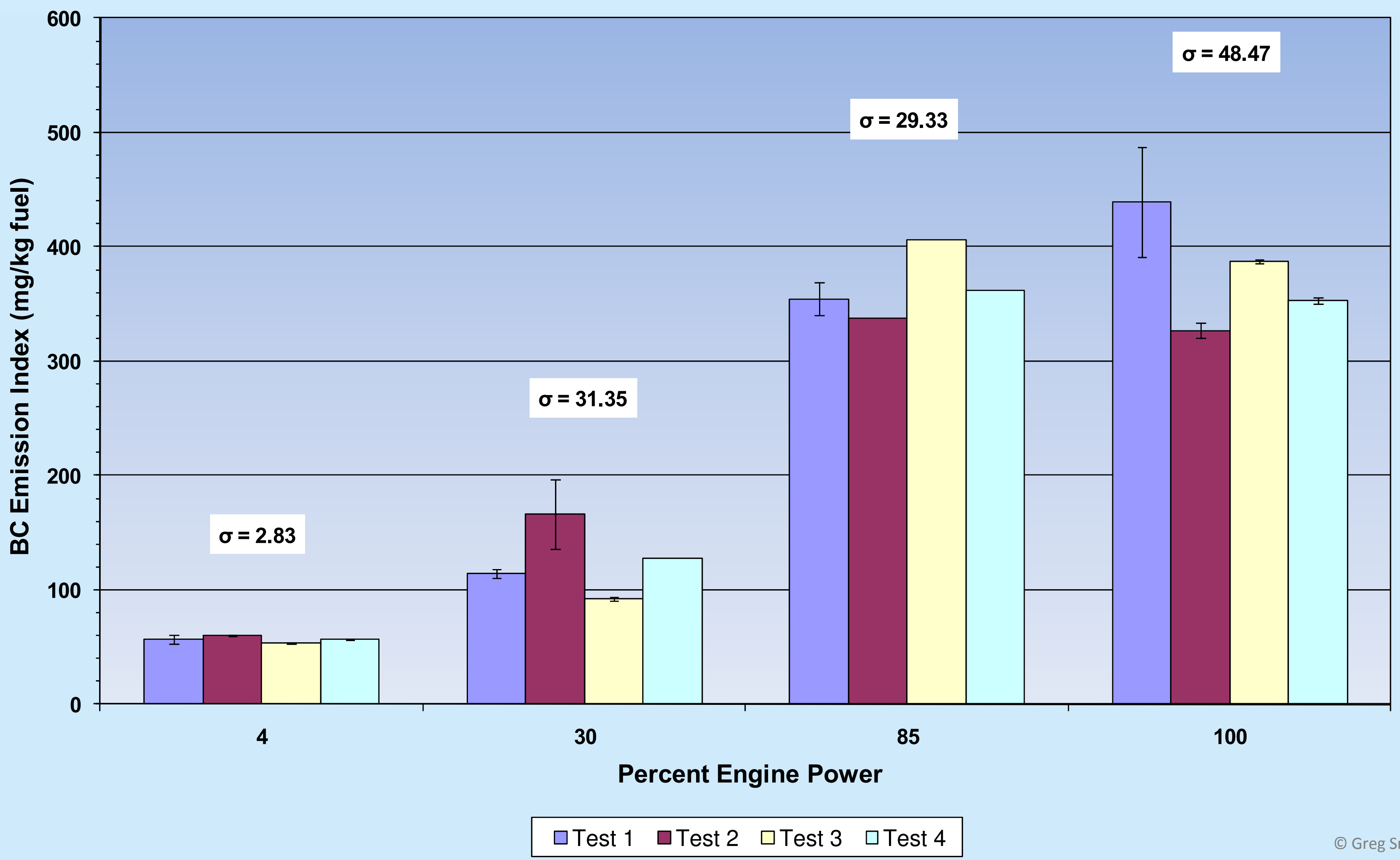
LII Black Carbon Emission Indices for JP-8



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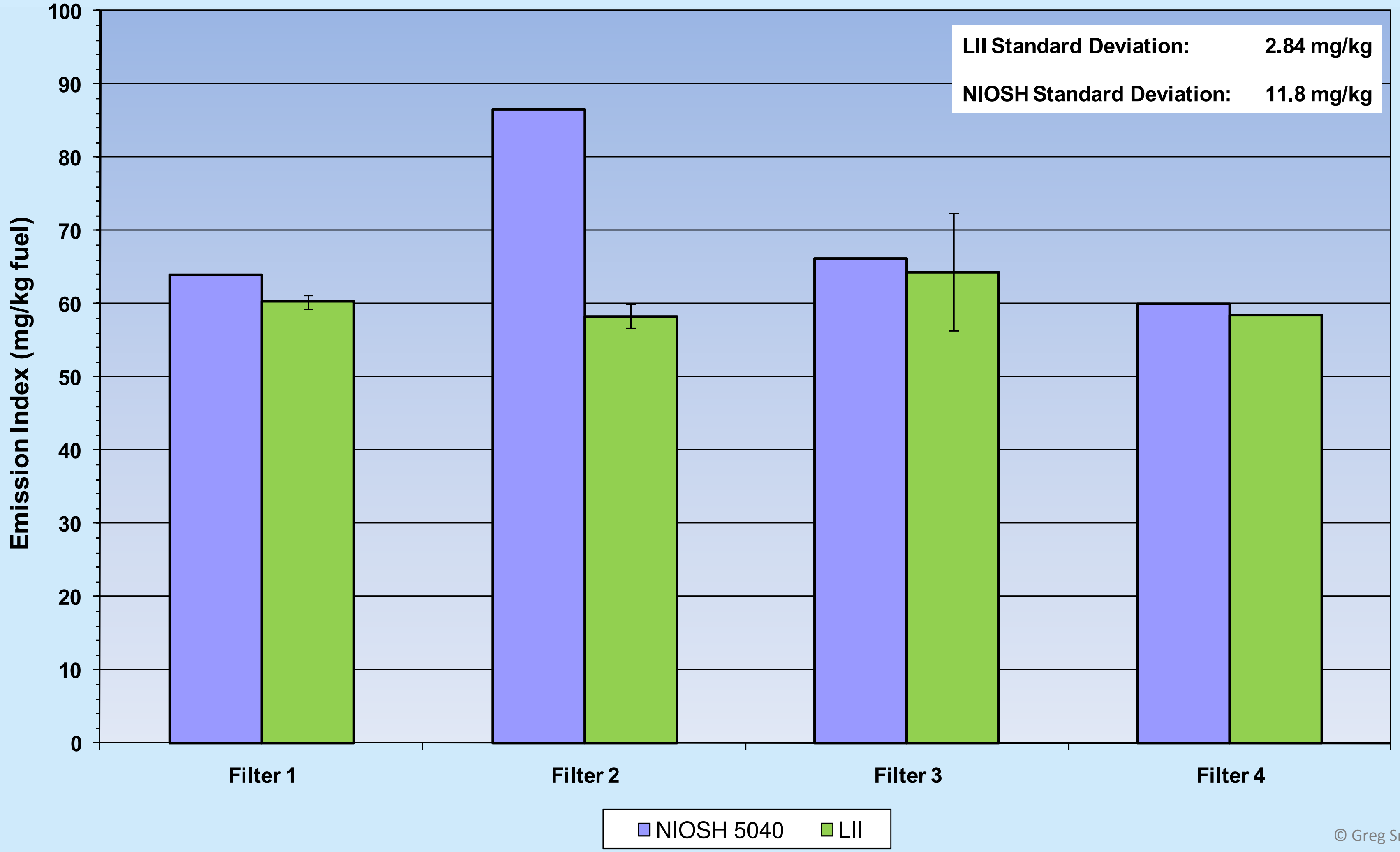
LII vs. NIOSH 5040 for F-T Fuel at 85% Power



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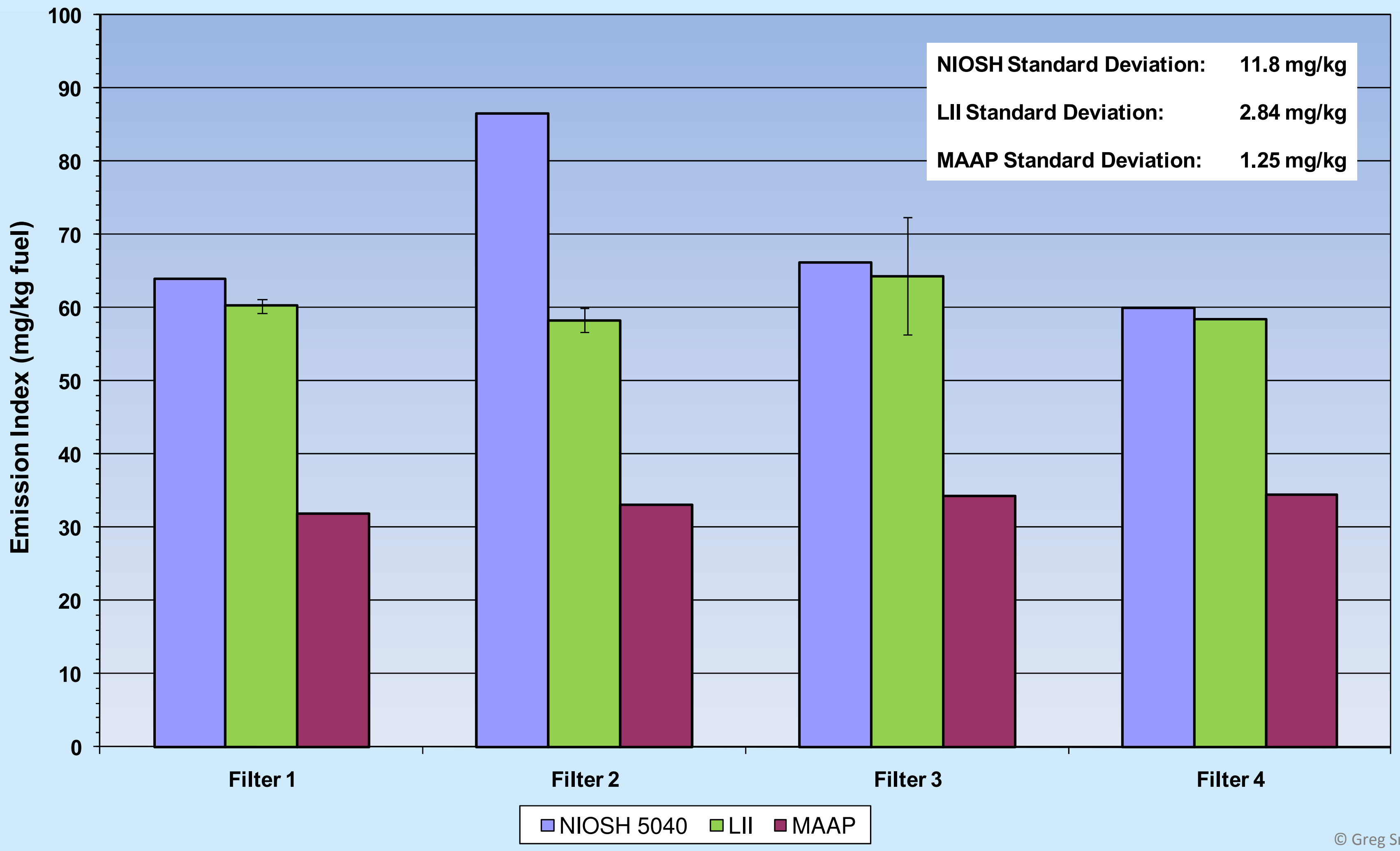
LII and EPA MAAP vs. NIOSH 5040 for F-T Fuel at 85% Power



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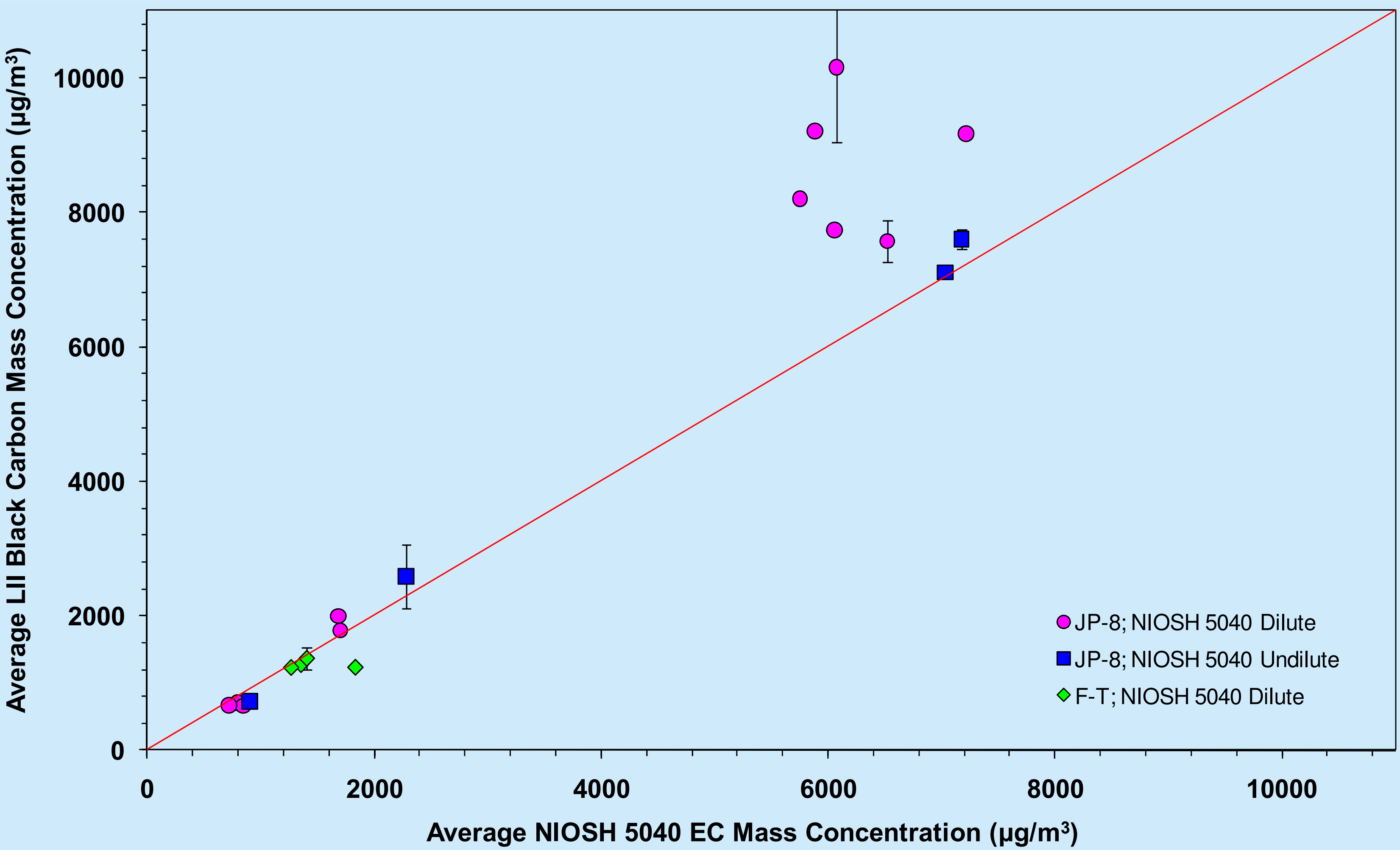
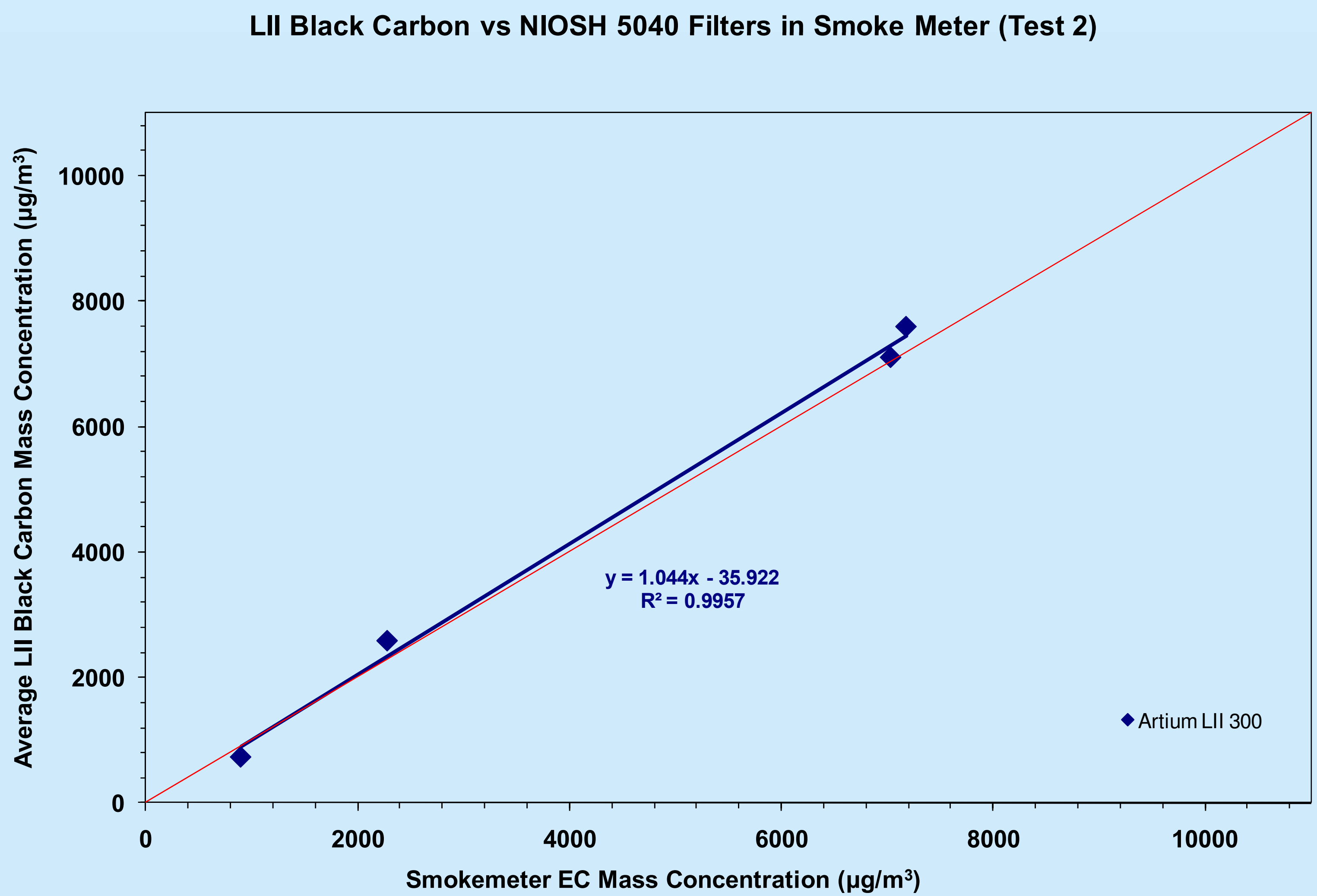
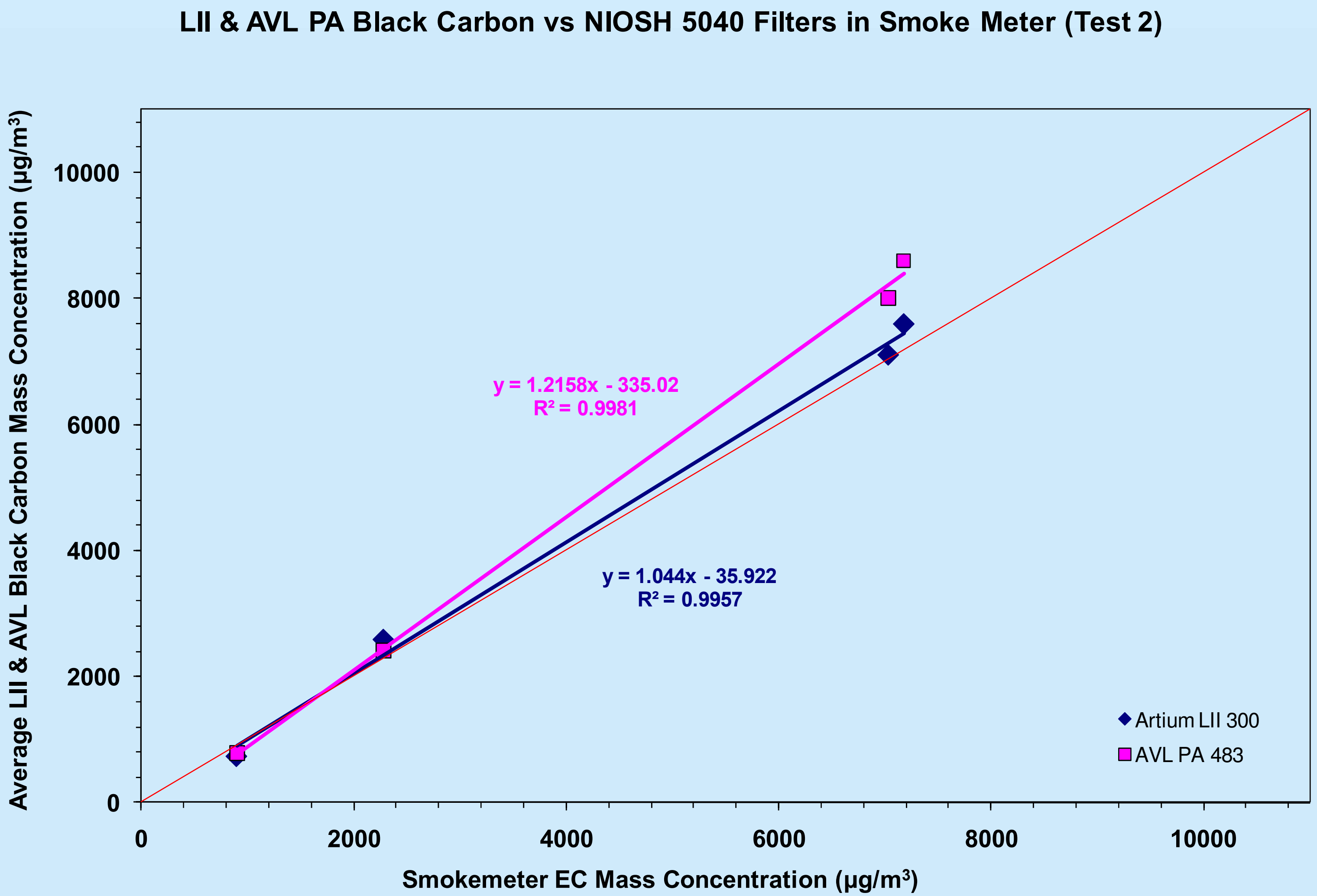
LII Black Carbon vs NIOSH 5040 EC (All Data)



LII vs. Undilute NIOSH 5040



AVL Photoacoustic & LII vs. Undilute NIOSH 5040



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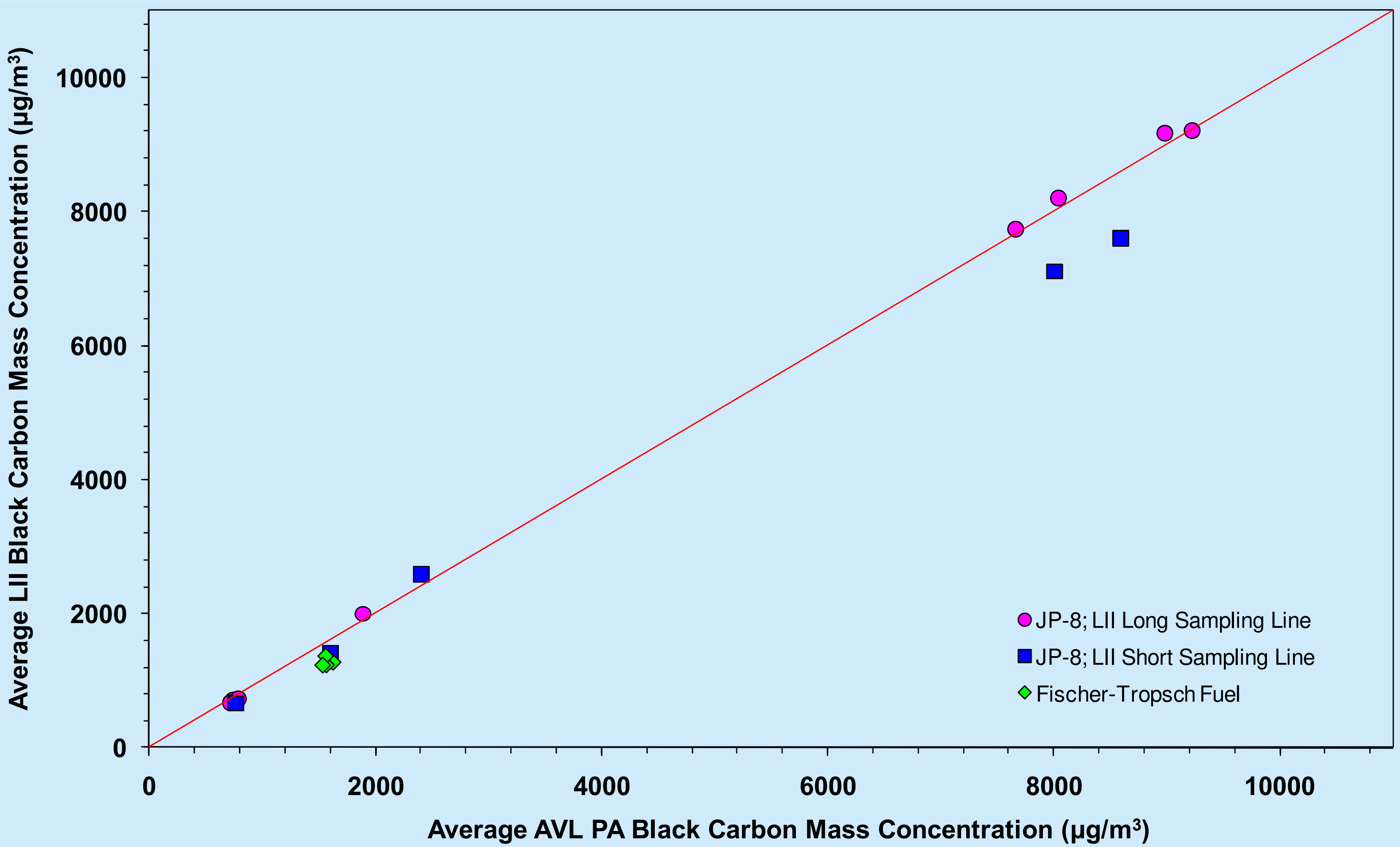
LII Black Carbon vs AVL PA Black Carbon (All Data)



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Summary

- a significant instrument has been developed to improve the real-time measurement of nonvolatile particulate matter
- AC-LII was demonstrated to be highly correlated, repeatable, precise, selective, and linear with respect to some other particle measurement techniques
  - real-time measurements and high sensitivity also achievable
  - easy to operate and maintain
- however, LII has shown differences in the absolute concentration when compared to some other methods

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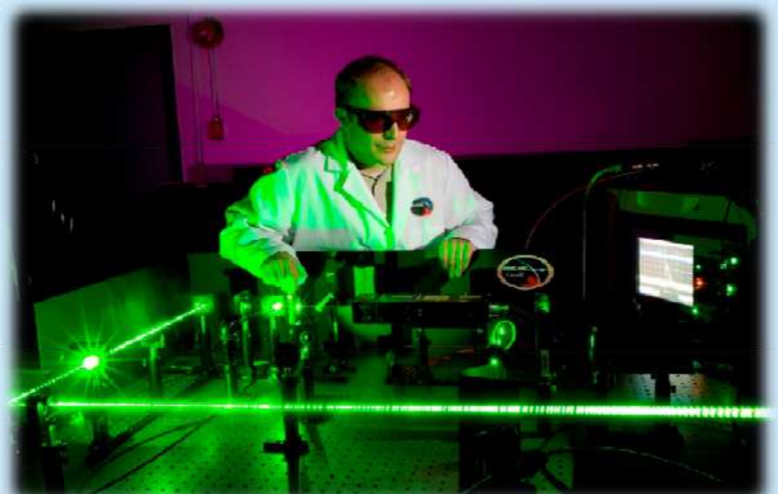
Acknowledgements

- Funding
  - PERD AFTER Project C23.006
  - PERD Particles and Related Emissions Project C11.008
  - NRC/Helmholtz Program (collaboration with DLR)
  - NRC/NSERC/BDC Nanotechnology Initiative Program (collaboration with Canadian universities and industry)



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Science at work for Canada

National Research Council Canada

Conseil national de recherches Canada

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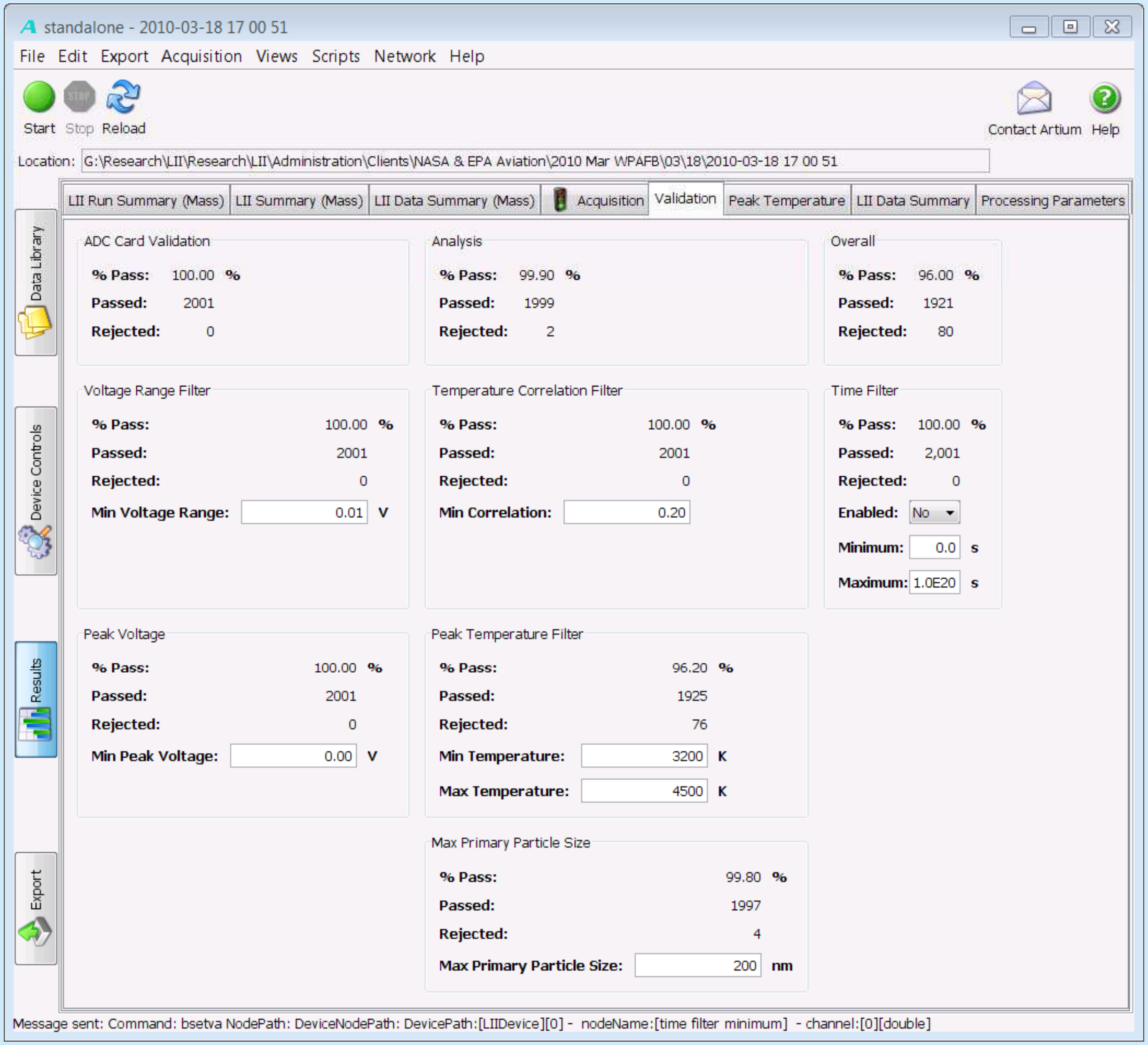
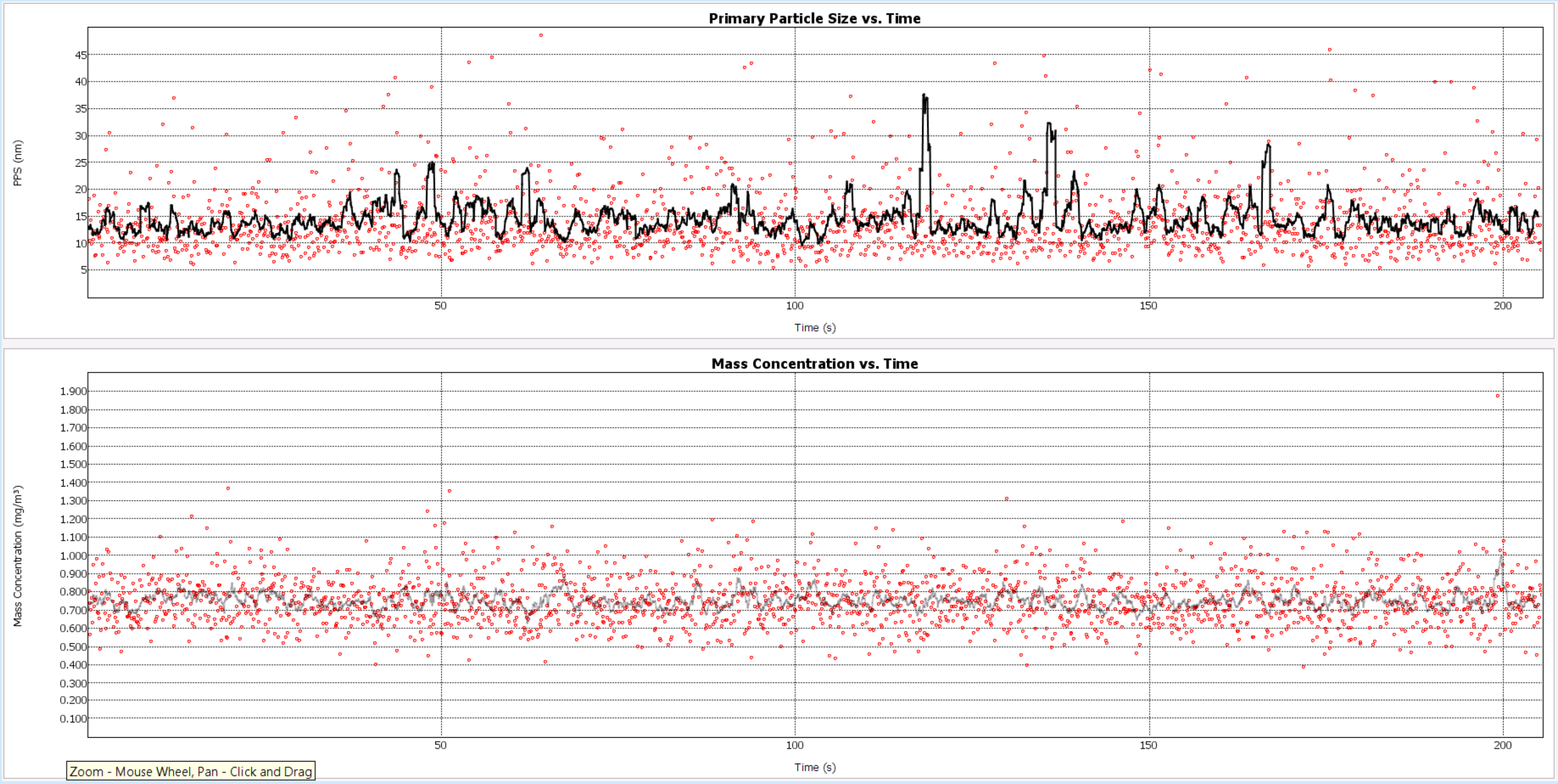
Fischer-Tropsch Fuel at 85% Power (Cruise)



Fischer-Tropsch Fuel at 85% Power (Cruise)



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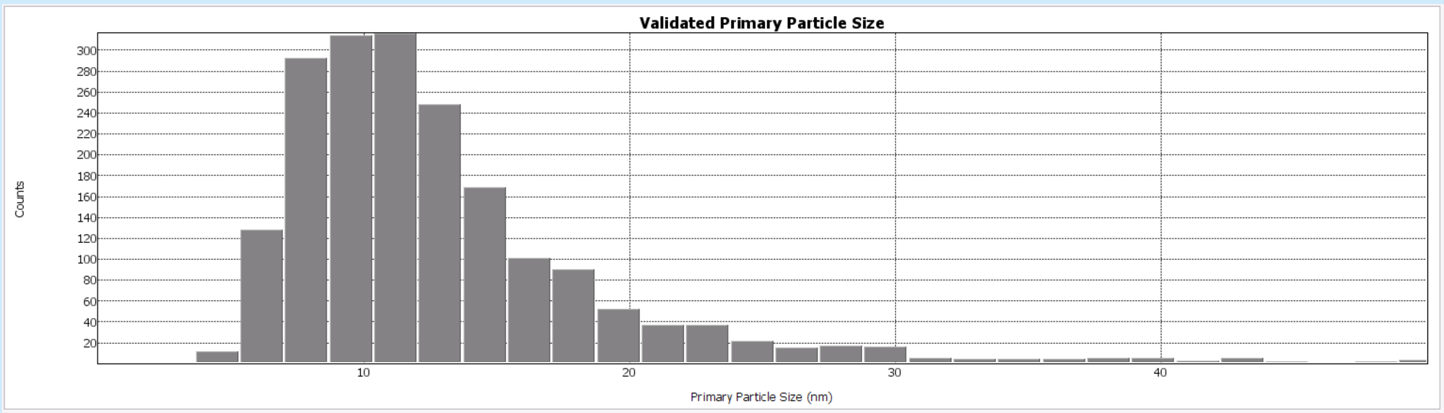
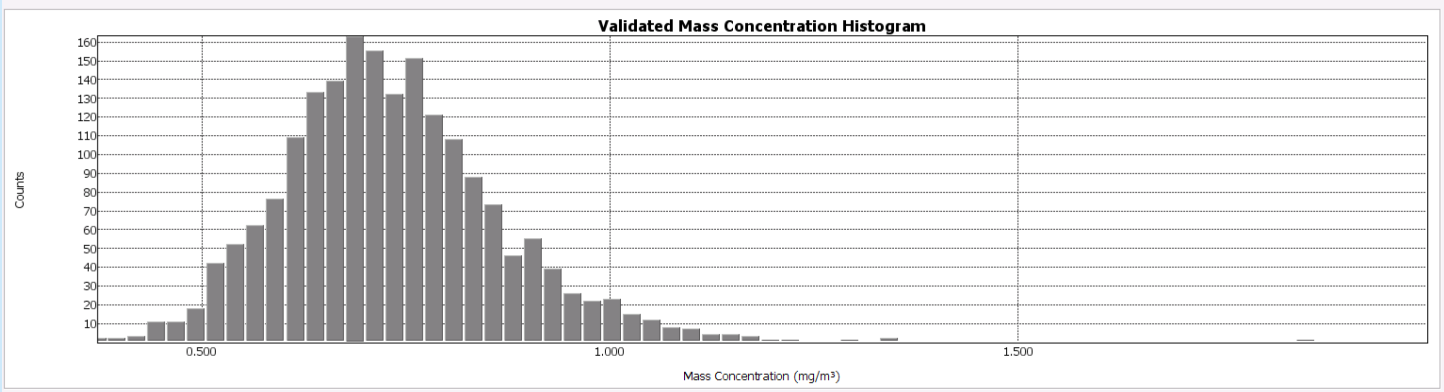
Fischer-Tropsch Fuel at 85% Power (Cruise)



Primary Particle Size Mean: 14.52 nm
Primary Particle Size σ: 9.66 nm
Primary Particle Size Min: 5.35 nm
Primary Particle Size Max: 164.13 nm
Primary Particle Size Counts: 1921

PPS Bins:



Mass Concentration Mean: 0.749 mg/m³
Mass Concentration σ: 0.136 mg/m³
Mass Concentration Min: 0.385 mg/m³
Mass Concentration Max: 1.875 mg/m³

Mass Concentration Bins:

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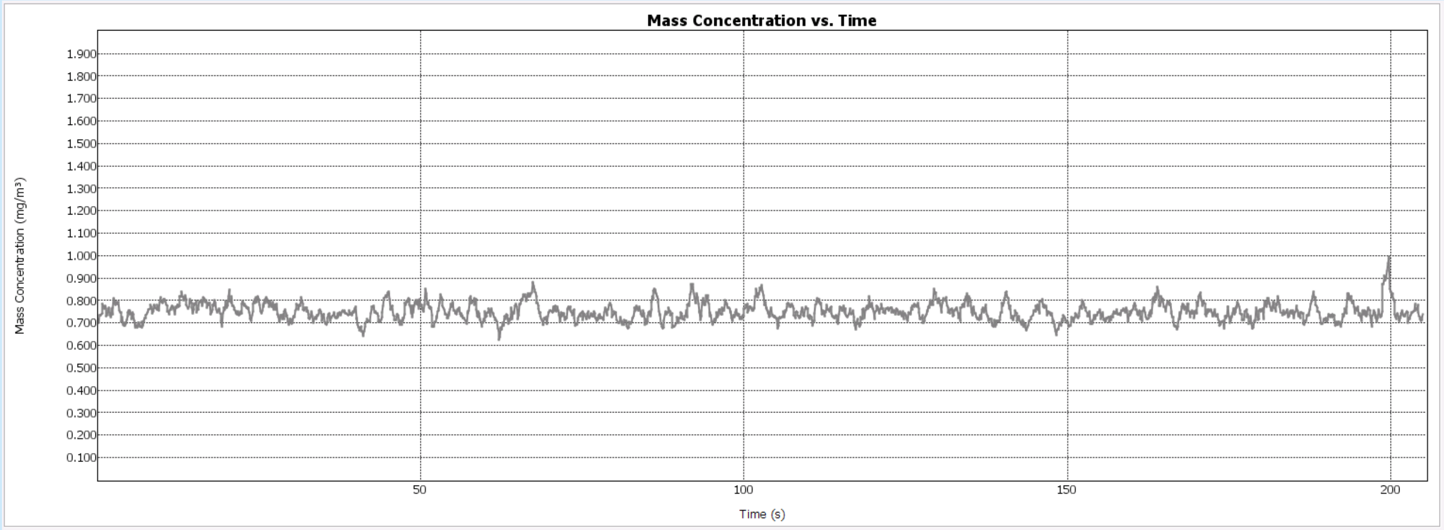
Fischer-Tropsch Fuel at 85% Power (Cruise)



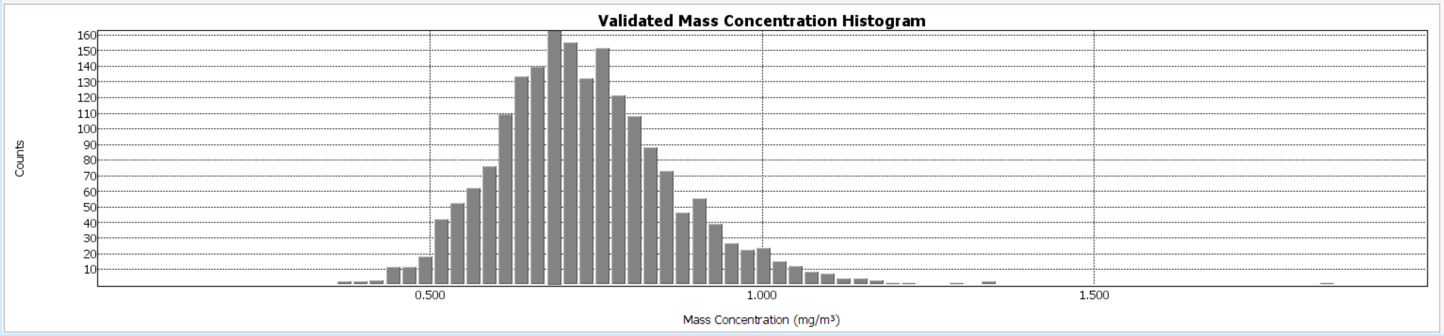
Mass Concentration

instantaneous

0.714mg/m³

mean

0.749mg/m³



Mass Concentration σ:	0.136	mg/m³
Mass Concentration Min:	0.385	mg/m³
Mass Concentration Max:	1.875	mg/m³

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LII Applications: Present and Future

- process control of carbon black:
  - aggregate size distribution
  - higher sensitivity to changes in surface area
- air quality monitoring (urban and global):
  - greater concentration sensitivity
  - 0.05 parts-per-trillion (1 femtogram) detection limit
- engine emissions (manufacturers):
  - single-shot transient response
  - determination of volatile organic compound fraction
- vehicle emissions (regulators)
  - improved repeatability
  - on-road emissions measurements
- manufactured nanomaterials

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Independent Evaluation of LII

"Among the mass-based methods with time resolution, LII and PA would best meet future requirements for legislative purposes. Their signal is directly proportional to soot mass concentration, demonstrated by very good correlation to EC mass concentration of R^2=0.95"

- comparison of 16 different particle mass measurement systems, including mass-related methods (filter methods, laser-induced incandescence, photoacoustic detection, photoelectric charging, combined inertial and mobility sizing, opacity) as well as non-mass-related methods (CPC, diffusion battery, diffusion charger, ELPI, light scattering)
- instruments were compared on the basis of repeatability, limit of detection, sensitivity, time resolution and correlation with the regulated gravimetric filter method, and elemental carbon fraction (EC)
    - Martin Mohr, Urs Lehmann, and Josef Rütter, "*Comparison of Mass-Based and Non-Mass-Based Particle Measurement Systems for Ultra-Low Emissions from Automotive Sources*," Environmental Science & Technology, 39, 2229-2238, 2005

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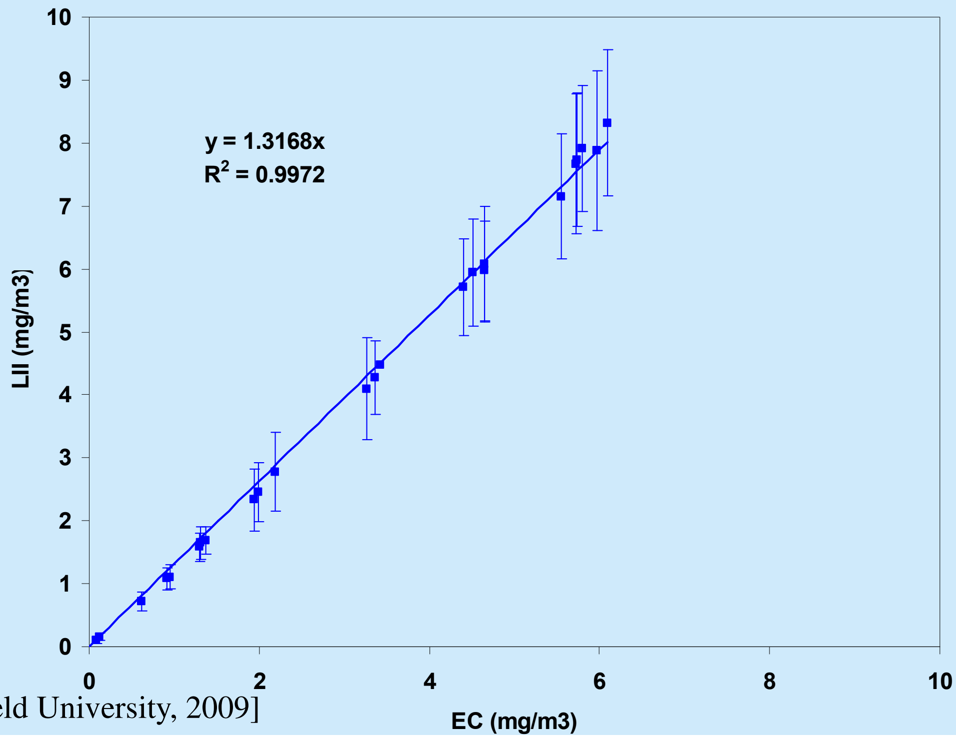
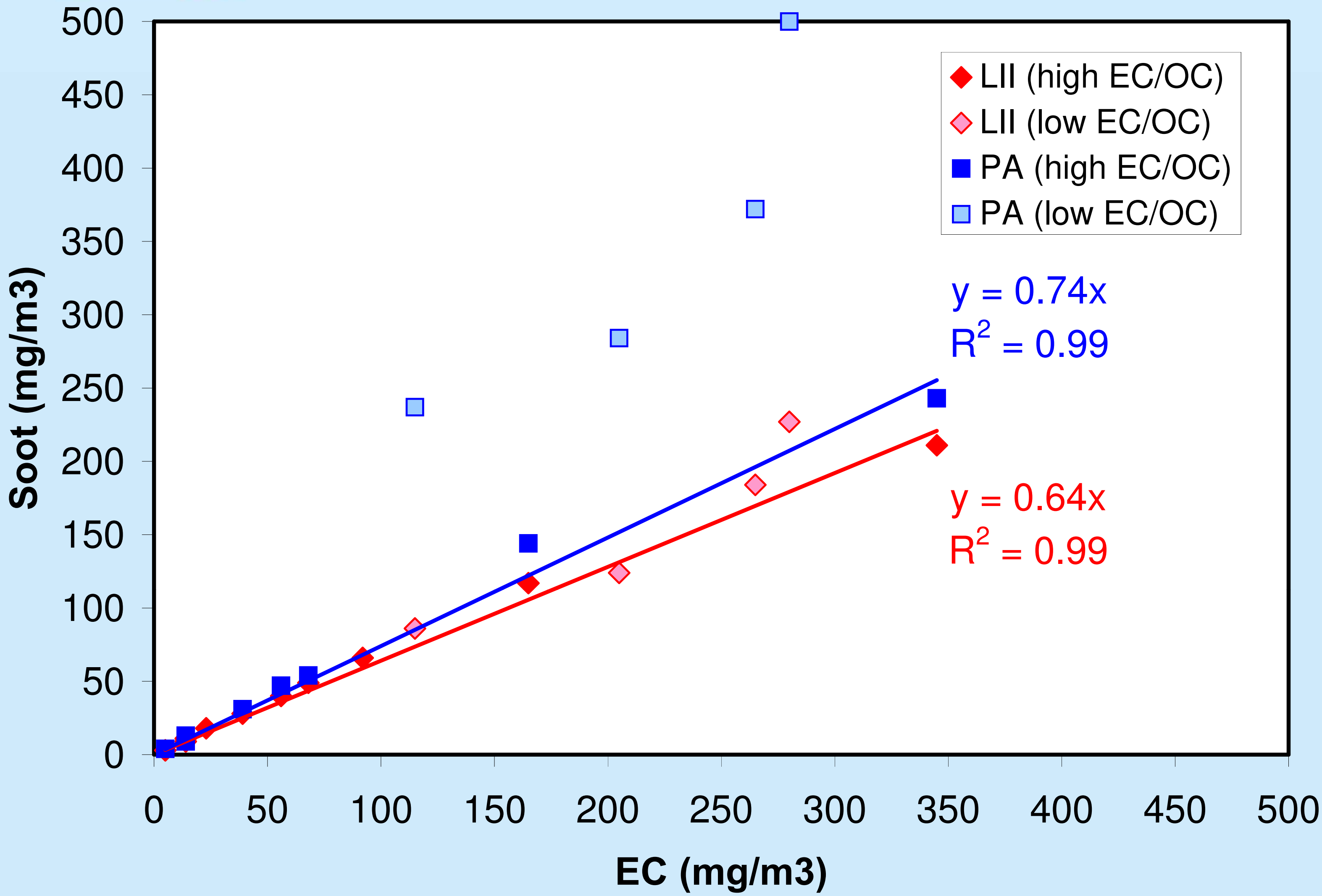
Comparison to Thermo-optical: EC

- AC-LII measurements of soot concentration from miniCAST soot generator compared to elemental carbon concentration determined by the NIOSH 5040 method
  - error bars represent single shot precision



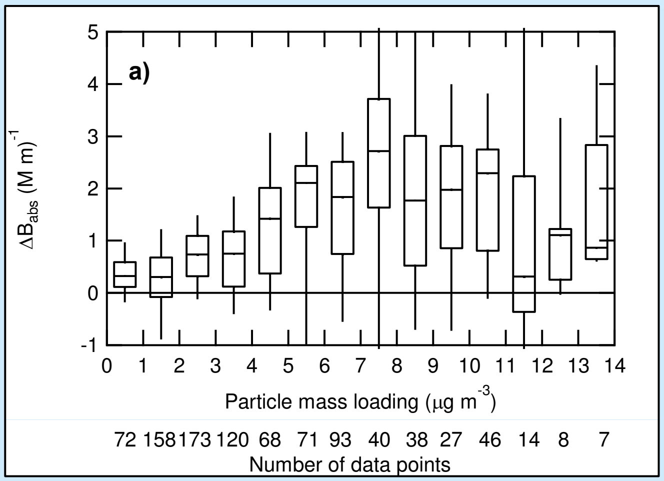
[Smallwood, Ph. D. Thesis, Cranfield University, 2009]

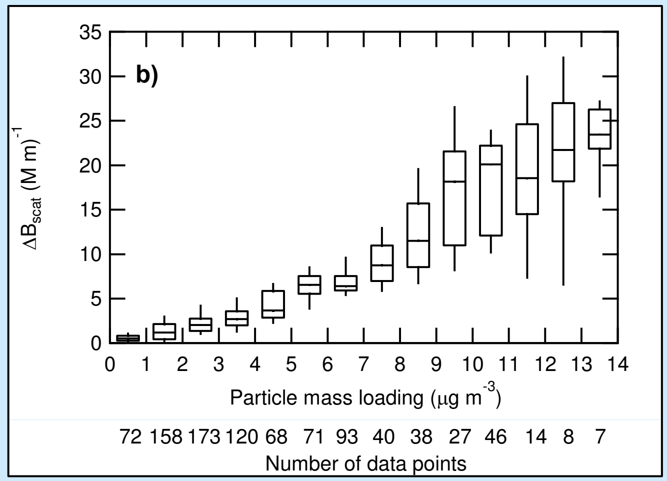
AVL Photoacoustic & LII vs. EC in Diesel Exhaust

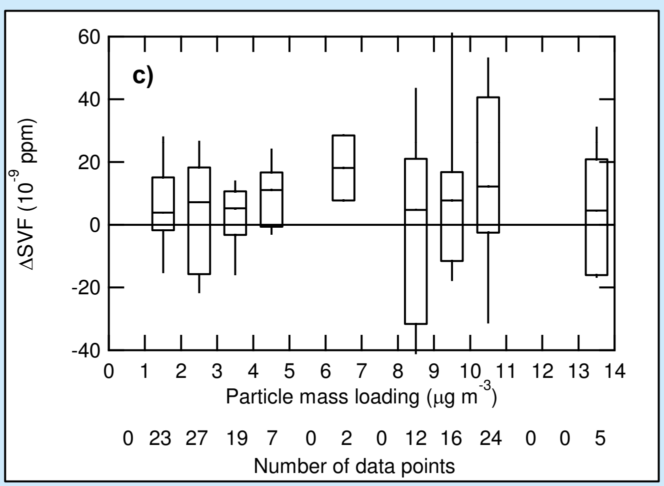


[Krämer *et al.*, 16th CRC On-Road Vehicle Emissions Workshop, 2006]

Effect of Volatile Coating on Photoacoustic and LII Instruments





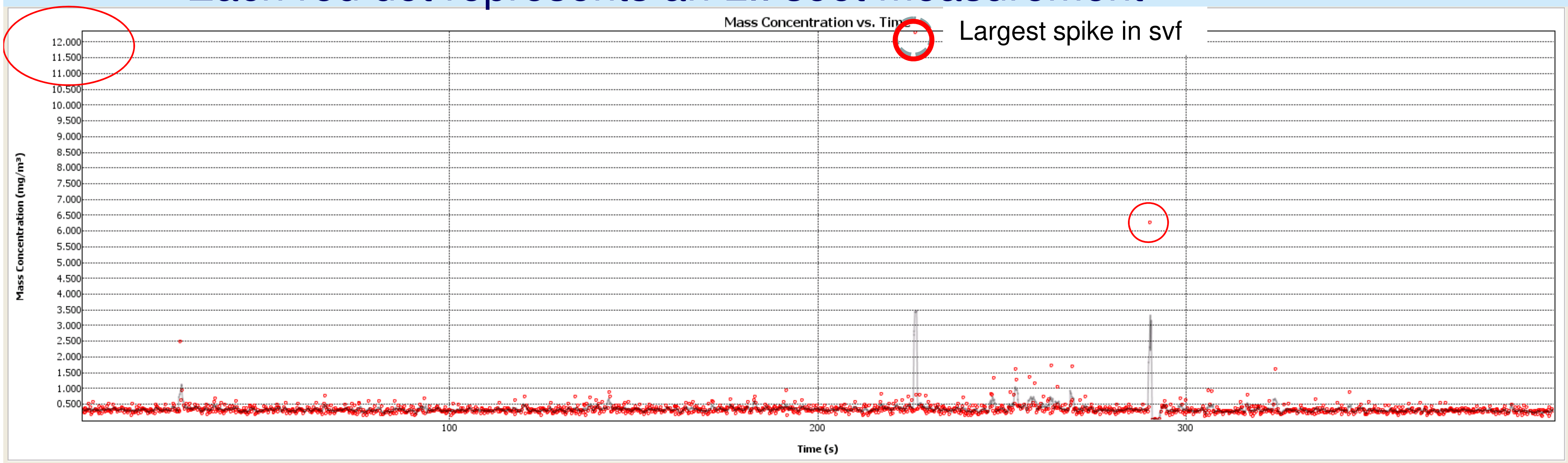


- The variations of (a) the particle light absorption (PA), (b) particle light scattering (PA), and (c) the soot volume fraction (LII), as a function of particle volatile coating mass
- The photoacoustic results are significantly affected by the presence of a volatile coating
- LII shows no significant effect

[Chan *et al.*, Atmospheric Chemistry and Physics (submitted), 2010]

LII Data from SAMPLE I

- Concentration versus time plots show isolated spikes in the concentration values which cannot be accounted for as large numbers of soot aggregates passing the sample volume
- In the turbulent flow, such high concentration gradients do not exist for long
  - Each red dot represents an LII soot measurement



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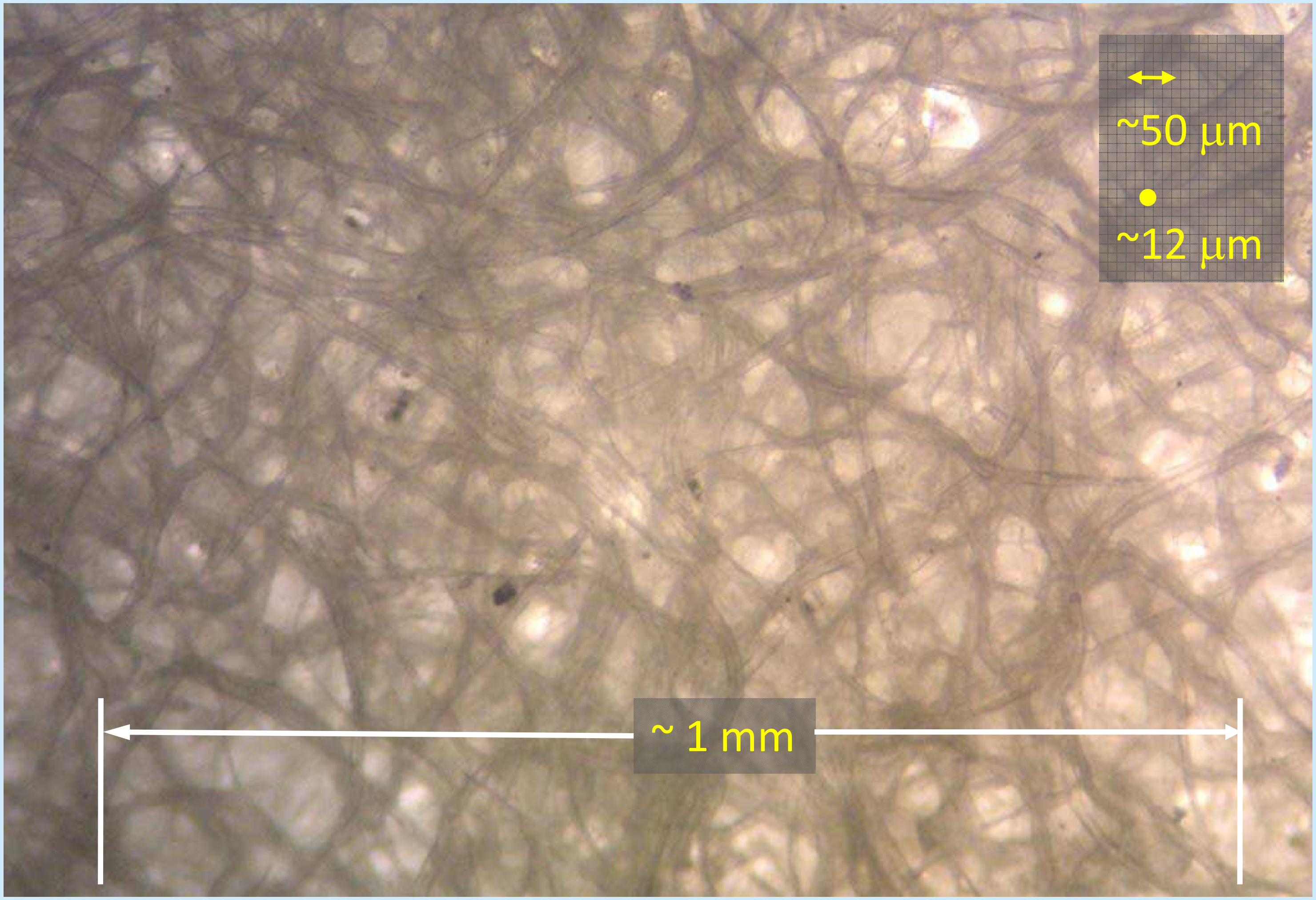
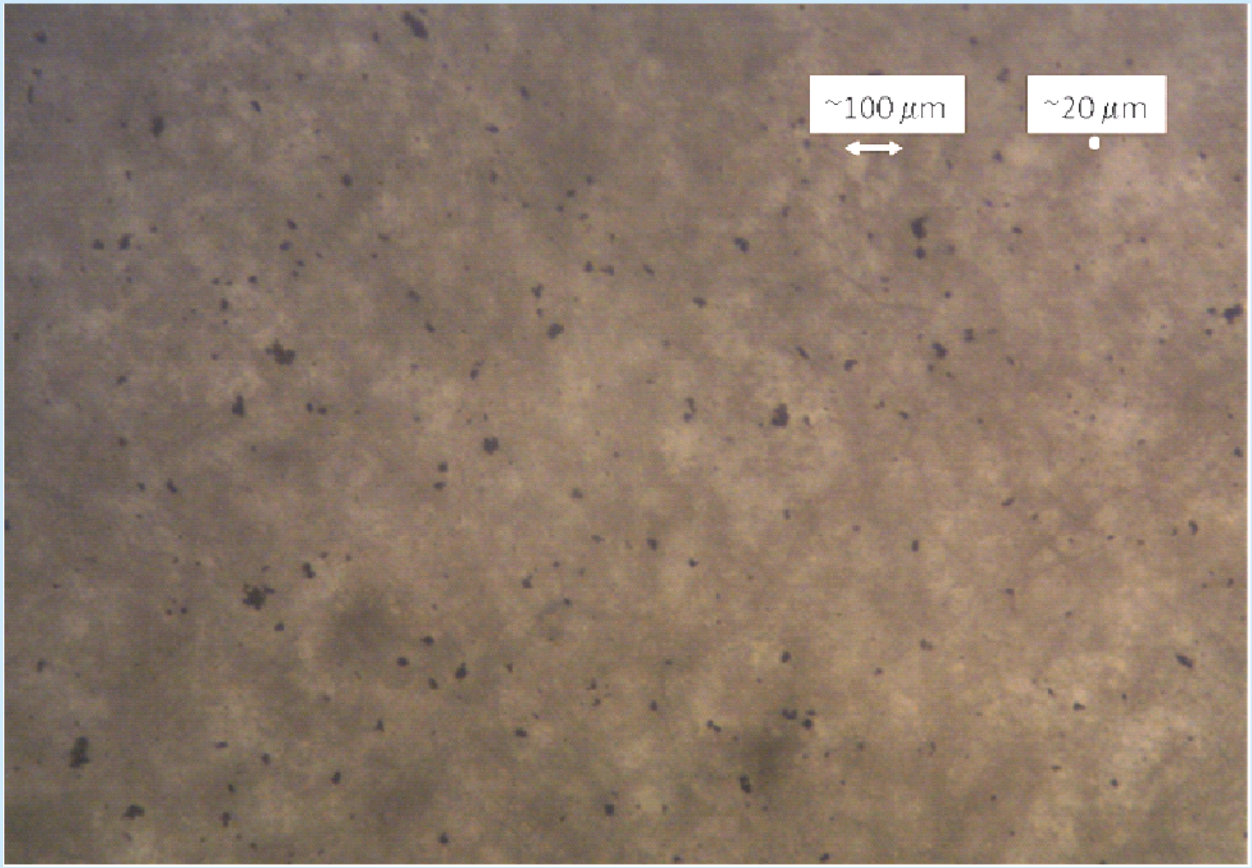
SAMPLE I Filter under an Optical Microscope



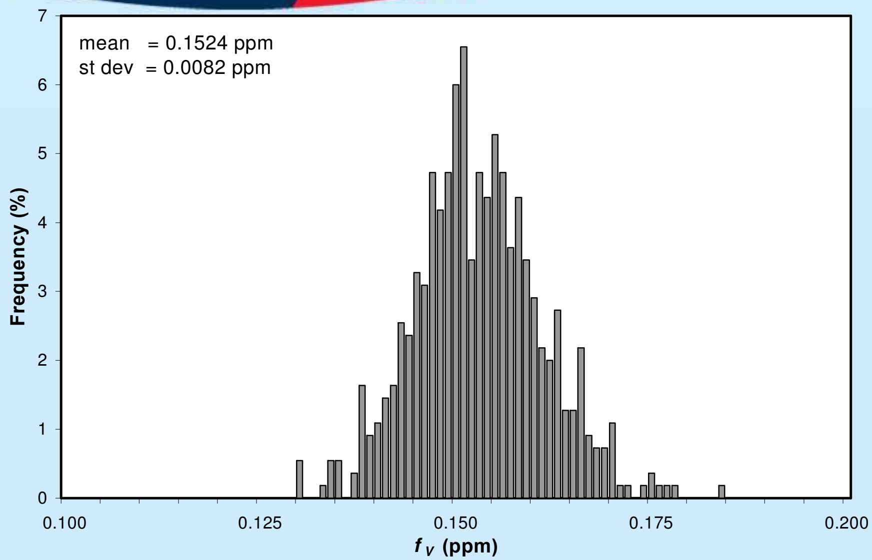
[SAMPLE I - Cardiff Tests 31-3-09 to 1-4-09]

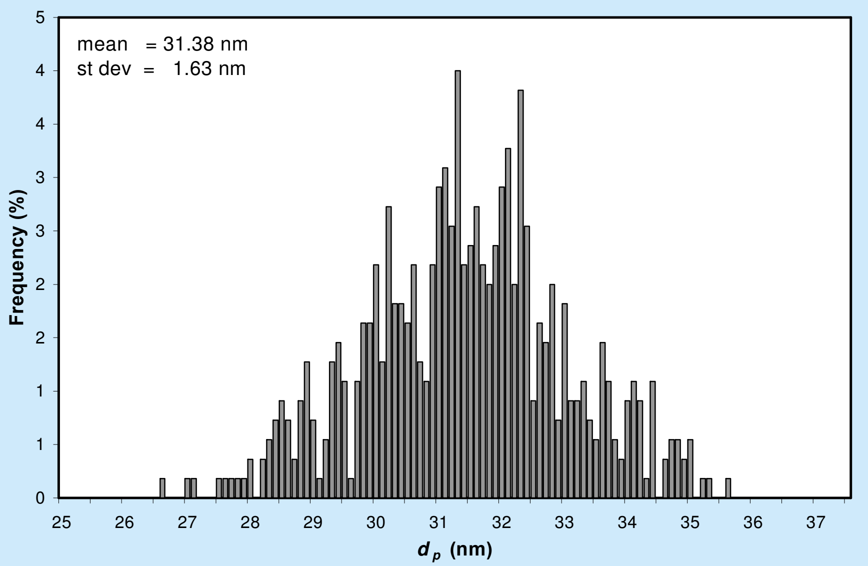
Filter contamination with large agglomerates of soot shed from sampling line surfaces



[From HD Diesel Exhaust]

LII Precision

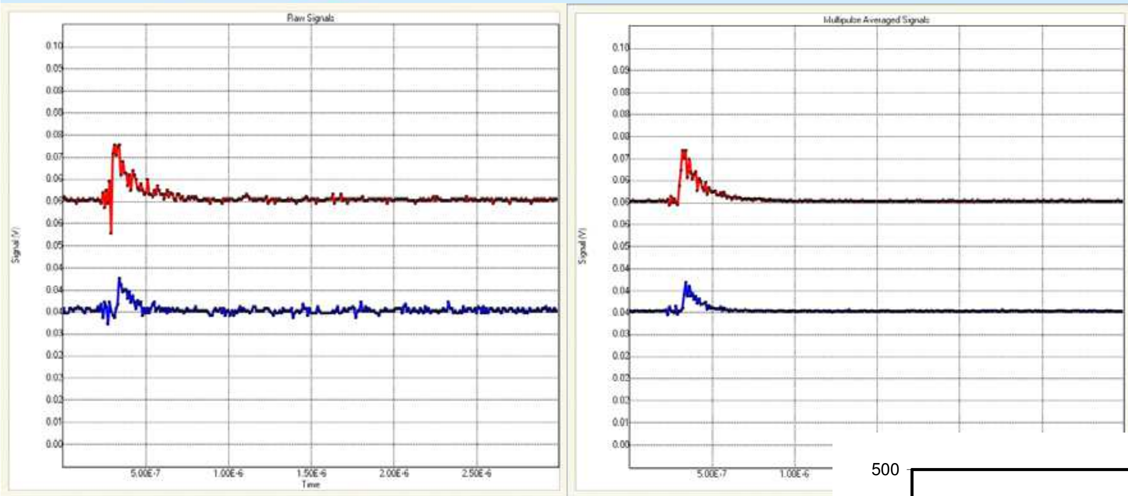




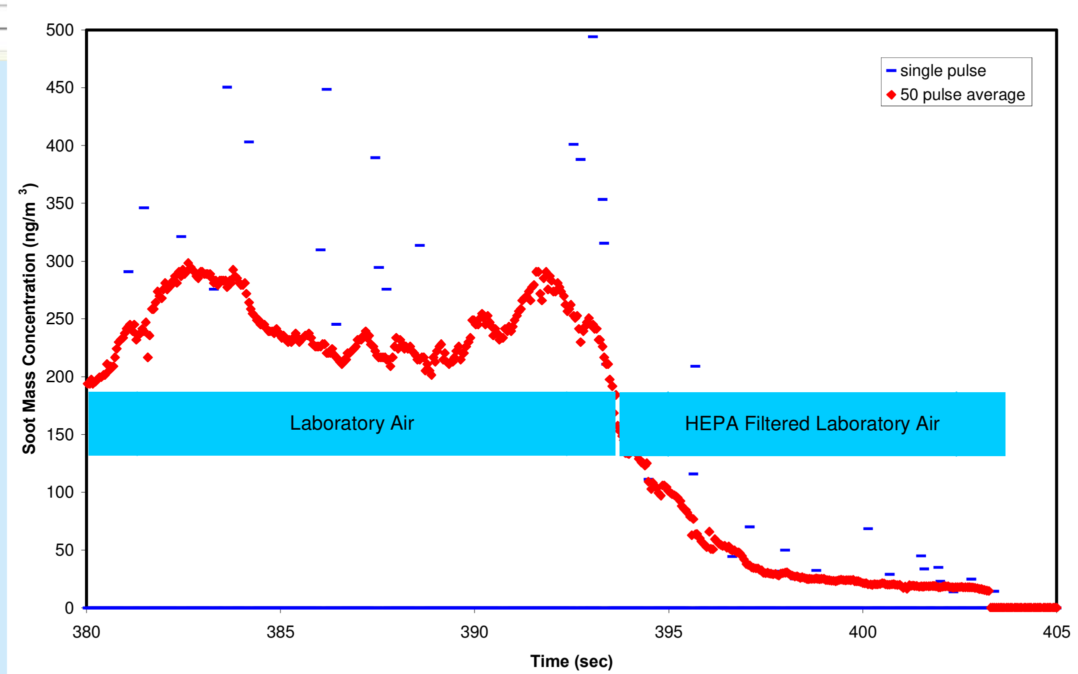
- single-shot precision of LII in measuring soot concentration and primary particle diameter is good
- standard deviation is about 5% for these examples acquired above a quenched laminar diffusion flame at 20 Hz
- precision can be improved with multi-pulse averaging with the sacrifice of time resolution

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

Single-shot vs. Multi-pulse Averaging



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



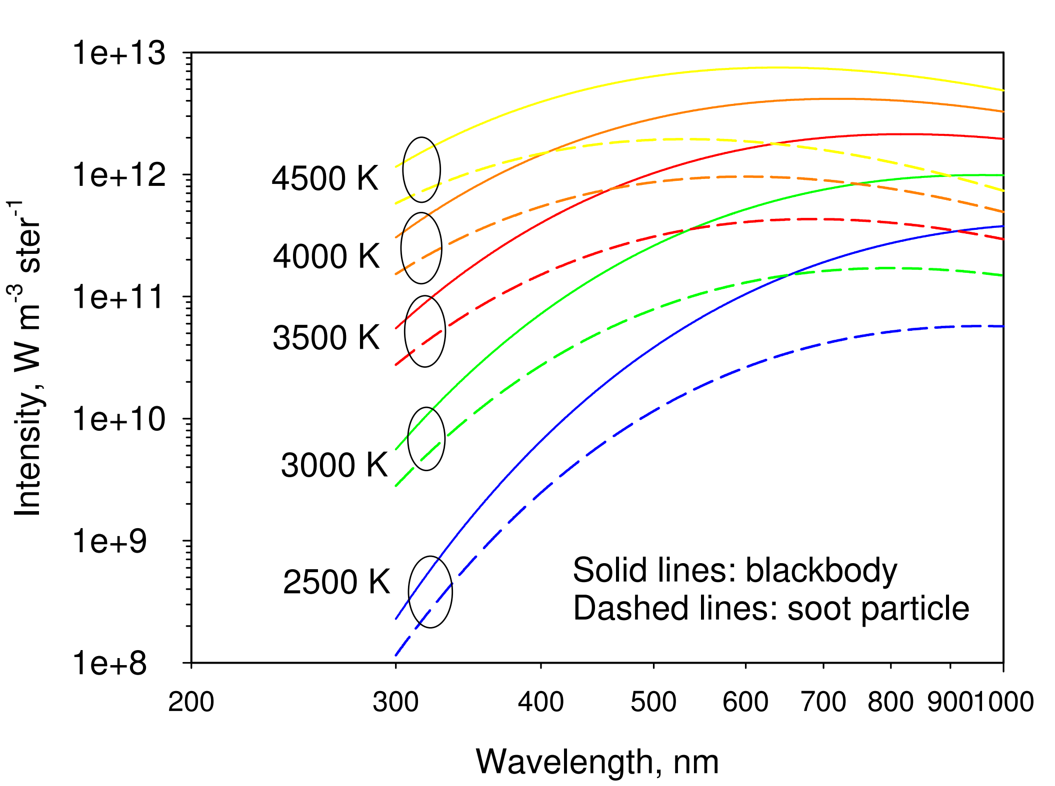
ABOVE

- single-shot (left) and 50-shot average (right)

RIGHT

- effect of averaging on measurement validation rate

Particle Emission Intensities



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

- blackbody and soot particle emission intensity
  - range of temperatures encountered in LII
  - UV-VIS-NIR spectral range
- emissivity

$$\varepsilon_p = \frac{4\pi d_p E(m)}{\lambda}$$

- soot particles are calculated for d_p = 30 nm and $E(m)$ = 0.4

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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

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

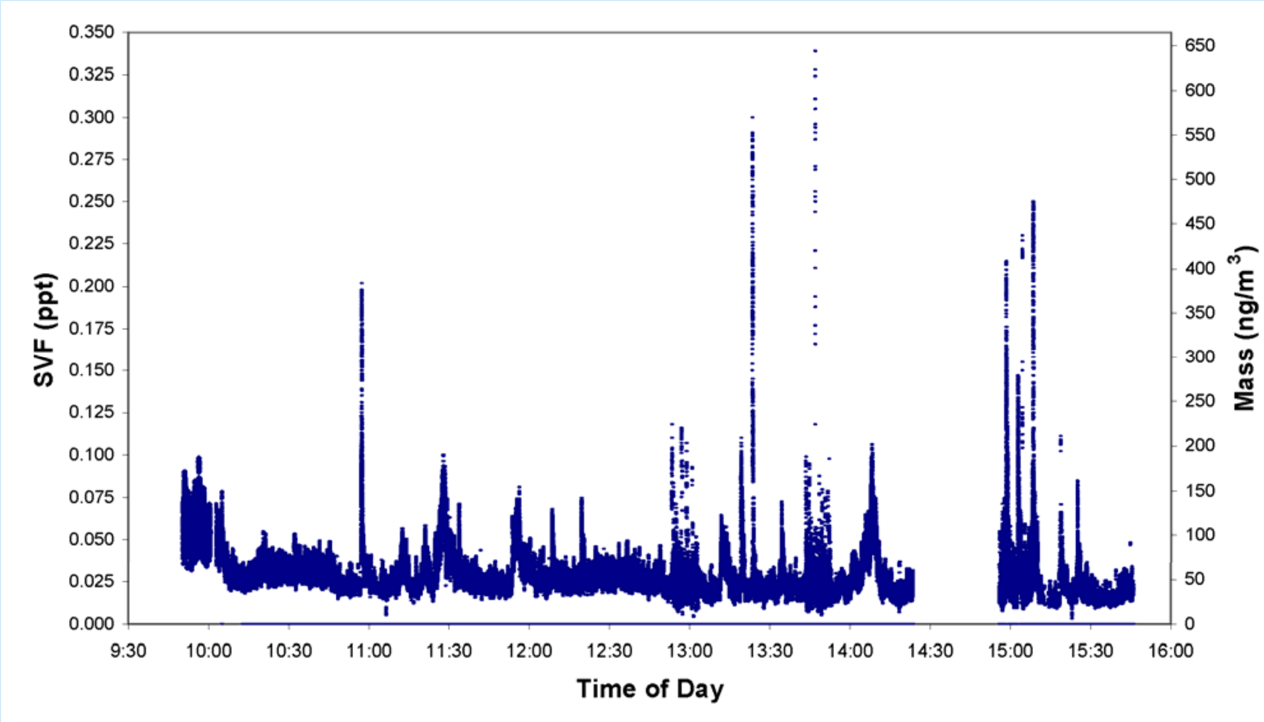
- soot volume fraction is determined from the temperature and the spectral radiance signal at either one of the wavelengths
  - depends upon absolute value of *E*(*m*) at the selected wavelength

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

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

Experiment: High Sensitivity LII

- optimize all aspects of the laser-induced incandescence method
- use Lagrangian invariant principle to constrain design of collection optics and receiver
- resulting design was over 500 times more sensitive (ng/m^3 level)



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

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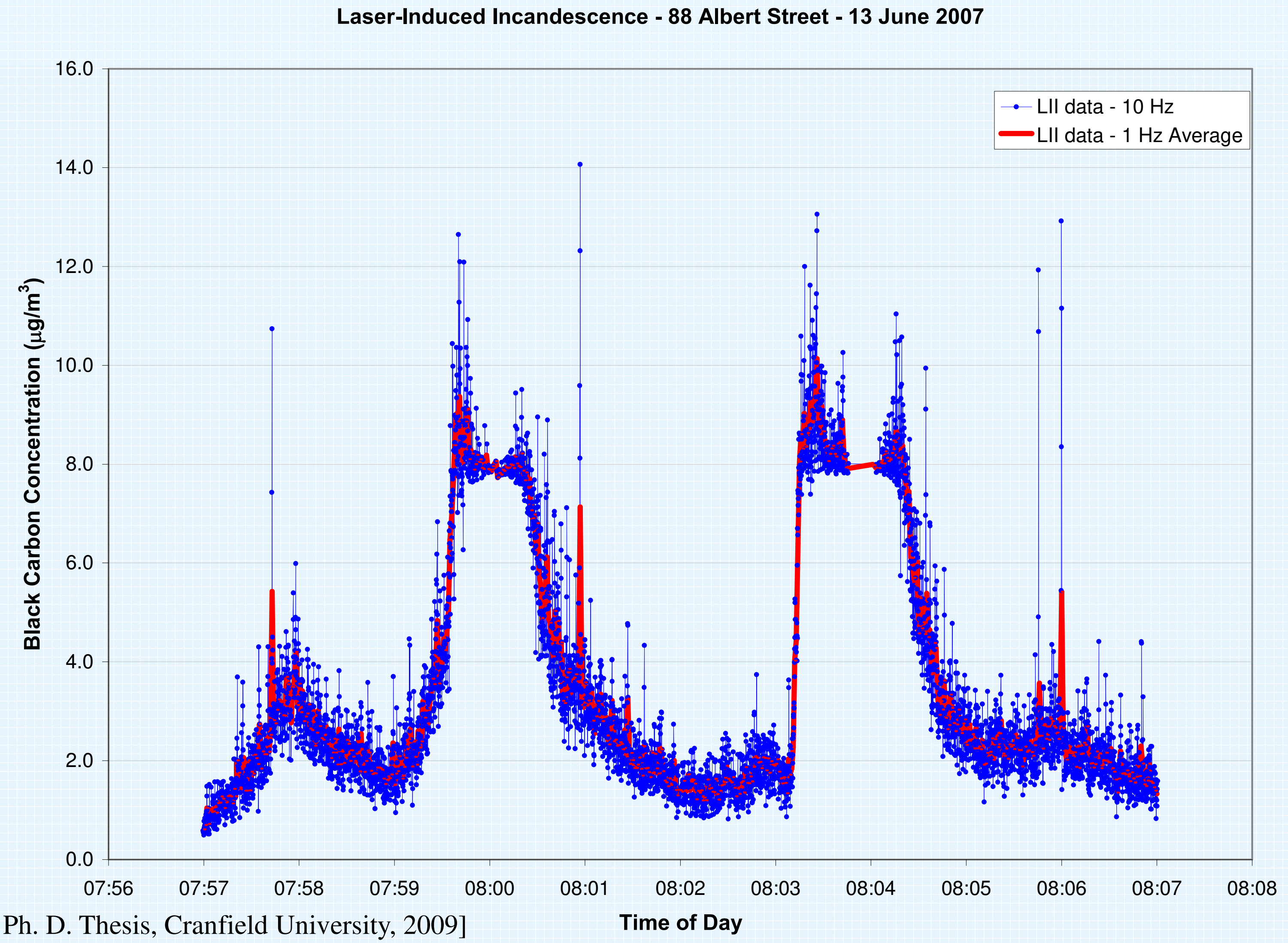
Urban Air Quality – High Sensitivity



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

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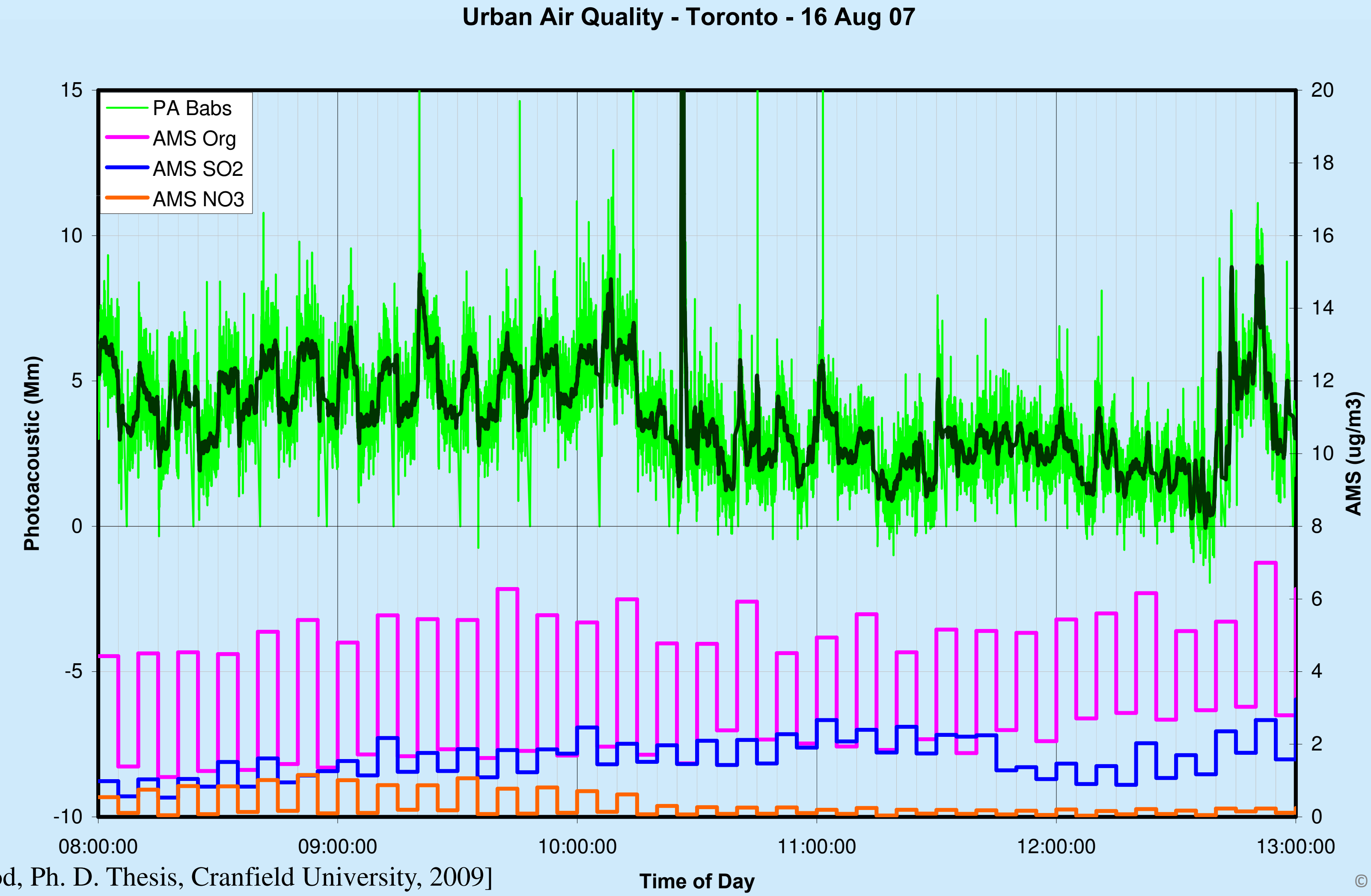
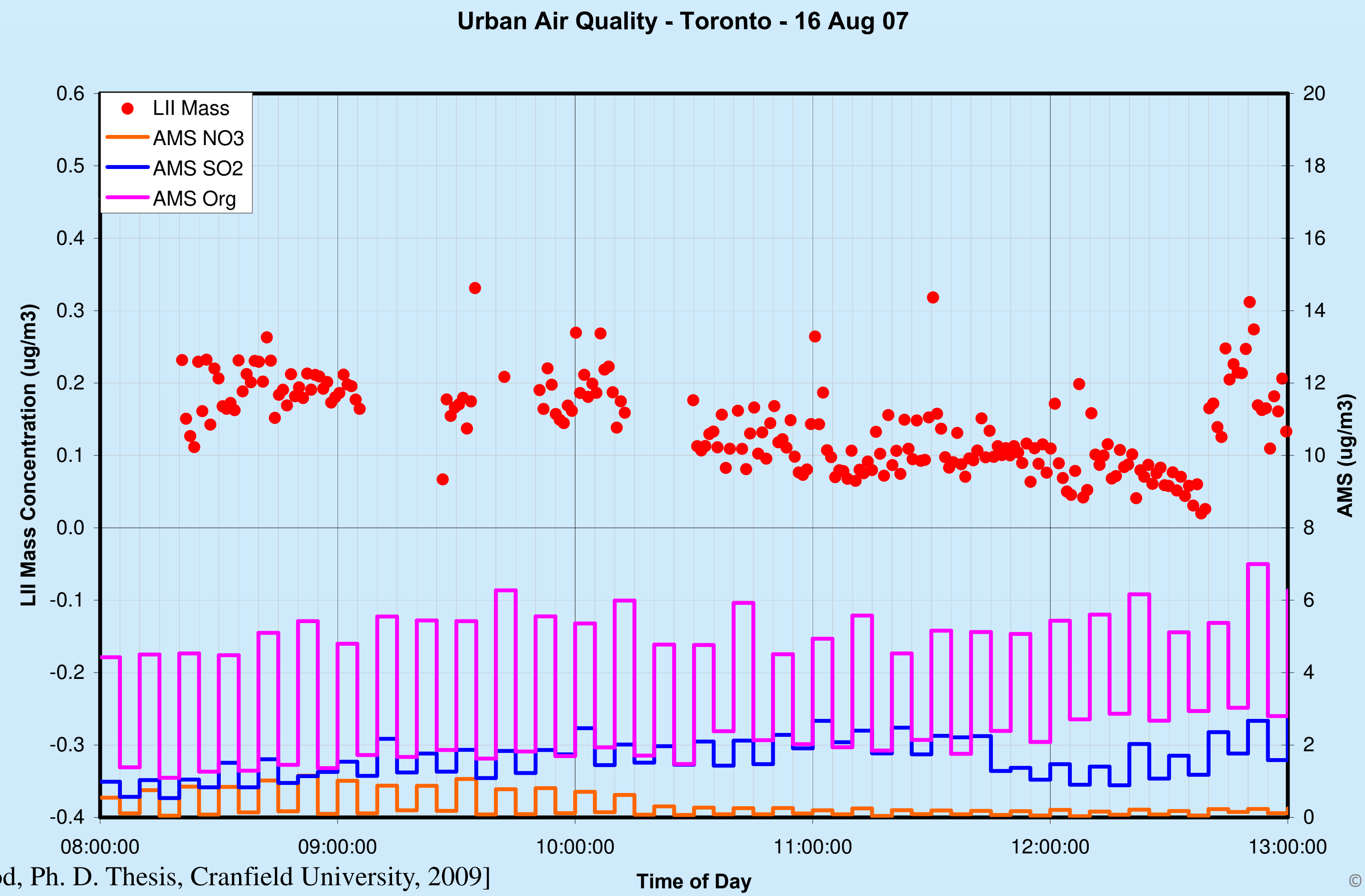
Photoacoustic and AMS – Ambient and Denuded



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

LII and AMS – Ambient and Denuded



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