Advanced Method for Measurement of the Solid Carbonaceous (Soot) Component of Mobile Source Particulate Matter

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LII Technology Licensed from NRC, Canada
Greg Smallwood, Ph.D. and David Snelling, Ph.D.
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Why is soot a serious concern?
- Research indicates soot is implicated directly in numerous health problems
- Microscopic soot particles are among the most harmful components of air pollution
- Black carbon (soot) is a key contributor to radiative forcing, important to climate change
- New regulations in California significantly limit the allowable particulate emissions from diesel engines
- Regulations require means for determining compliance
Outline

• Background
  – introduction
  – reduced PM emissions a problem for gravimetric methods
  – conventional laser-induced incandescence (LII) method

• Auto-compensating laser-induced incandescence (AC-LII) method
  – innovations
  – theory
  – experimental

• Applications
  – engine dyno measurements
  – chassis dyno measurements
  – on-road measurements
  – gas turbine measurements

LII Technology Licensed from NRC, Canada
TEM images of nanoparticles sampled from a Diesel exhaust

- soot
- carbon black
- black carbon
- elemental carbon
- refractory carbon

“Life exists in the universe only because the carbon atom possesses certain exceptional properties”
James Jeans
TEM Imaging of Flame Soot
Morphology

- nearly-spherical primary particles 20–50 nm in diameter
- SOF absorbed onto the surface of the primary particles
- Primary particles cluster into chain-like aggregates
SEM Image of Flame Soot

Others assume an “equivalent sphere diameter”, what’s the density?
What Does LII Do?

- Quantitative measurement for dry soot:
  - concentration (0.5 ppt – 10 ppm volume; 1µg/m³ – 20g/m³ mass)
  - active surface area (50 – 200 m²/g)
  - primary particle diameter (typically 5-50 nm)
  - number density of primary particles

- Measurement features:
  - very high precision and resolution
  - transient concentration
  - nonintrusive (dilution unnecessary)
  - wide range of applicability
  - potential standardized method
  - measures soot
  - uninfluenced by the presence of other species

Technology Licensed from NRC, Canada
NRC Canada LII Innovations

- Absolute intensity (patented)
  - spectral radiance calibration
- Real-time two-color pyrometry (patented)
  - particle temperature
- Laser beam profile (patented)
  - uniform heating
- Low laser fluence (patented)
  - no sublimation
Science Behind LII

International Meeting and Workshop on
Laser-induced incandescence:
Quantitative interpretation, modelling, application
September 25-28, 2005

University of Karlsruhe, Germany
Institut für Technische Chemie und Polymerechemie

Organizers:
- Hansjörg Beckhorn and Klaus-Martin Tschudin
  (TUM, Universitat Karlsruhe)
- Klaas Meier (LRG, Stuttgart)
- Christof Schütz (TH, Universitat Darmstadt)
- Greg Sneddon (NRC, Canada)
- Stéphane Word (UL, Université Libre de Bruxelles)
- Georgi Zonen (CNR-IMM, Italy)

Next Meeting:
4th International Discussion Meeting and Workshop
Laser-Induced Incandescence: Quantitative Interpretation, Modeling, Application
April 18 – 20, 2010, Varenna, Italy
**LII Concepts**

- **LII experiment:**
  - pulsed laser beam
  - rapid heating of soot to evaporation temperature
  - soot radiates incandescence as it cools to ambient temperature
  - incandescence signal is collected to determine soot concentration, surface area, and primary particle diameter

- **LII theory**
  - a state-of-the-art numerical model of nanoscale (time and space) heat transfer to and from the particles
Soot Volume Fraction – Fluence Effects

![Graph showing soot volume fraction over time for low and high fluence, with a peak indicating vaporized soot.](image-url)
Auto-Compensating LII (AC-LII)

- **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
Soot Particle Heat Transfer Equation

\[ \frac{\pi D^3}{6} \rho_s c_s \frac{dT}{dt} = C_a q - \frac{2 k_a (T - T_0) \pi D^2}{(D + G \lambda_{MFP})} + \frac{H_v}{M_v} \frac{dM}{dt} - q_{rad} \]

I. change in internal energy
II. laser heating
III. heat transfer to surrounding gas
IV. soot sublimation
V. radiative heat loss

[Michelsen et al., Third International Discussion Meeting and Workshop on Laser-induced incandescence: Quantitative interpretation, modelling, application, 2008]
Particulate Concentration

- Determine calibration factor
  \[
  \eta(\lambda) = \frac{V_{CAL}(\lambda)}{R_S(\lambda, T)}
  \]

- Measure incandescence, \( P_p(\lambda) \), at two wavelengths and solve for temperature, \( T \)
  \[
  \frac{P_p(\lambda_1)}{P_p(\lambda_2)} = \left( \frac{\lambda_2^6}{\lambda_1^6} \right) \frac{\left( e^{\frac{hc}{k\lambda_2T}} - 1 \right)}{\left( e^{\frac{hc}{k\lambda_1T}} - 1 \right)} \frac{E(m_{\lambda_1})}{E(m_{\lambda_2})}
  \]
Absolute LII Signals

LII signal (watt/m²·steradian)

Time (ns)

0 500 1000 1500 2000

400 nm 780 nm
Two-Color Pyrometry

• relative signal at two wavelengths:

\[
\frac{V_{\text{EXP}}(\lambda_1)}{V_{\text{EXP}}(\lambda_2)} = \frac{\eta(\lambda_1)}{\eta(\lambda_2)} \cdot \frac{\lambda_2^6}{\lambda_1^6} \left( \frac{\frac{hc}{e^{k\lambda_2 T}} - 1}{e^{k\lambda_1 T} - 1} \right) \frac{E(m_{\lambda_1})}{E(m_{\lambda_2})}
\]

• where:
  – \( V_{\text{EXP}} \) is the LII measured signal (volts)
  – \( \lambda_1 \) and \( \lambda_2 \) are the detection wavelengths for each channel
  – \( \eta(\lambda) \) is the calibration factor (relating measured volts to the source radiance)
  – \( h, c, \) and \( k \) are the Planck constant, speed of light, and Boltzmann constant, respectively
  – \( T \) is the temperature (K)
  – \( E(m) \) is the absorption function, an optical property of soot

• the equation is solved to determine temperature

\[
T = \frac{hc}{k} \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \left[ \ln \left( \frac{V_{\text{exp}} \lambda_1^6}{\eta_1 E(m_{\lambda_1})} \right) - \ln \left( \frac{V_{\text{exp}} \lambda_2^6}{\eta_2 E(m_{\lambda_2})} \right) \right]
\]
Real-Time Temperature

![Graph showing temperature vs. time](image)
Primary Particle Size

- The temperature differential between the particle surface and the ambient gas decays steadily in an exponential manner

\[ T - T_g = A \cdot e^{-\Delta t \tau} \]

- The primary particle diameter may be inferred (McCoy and Cha, 1974)

\[ d_p = \frac{12 k_g \alpha}{G \lambda_{MFP} c_p \rho_p \tau} \]

Characteristic decay time
**Soot primary Particle Size at Two Combustion Conditions**

**Carbon Black Production**

- **Dataset 1**
  - Total Points = 287
  - Mean = 65.5
  - 95% Confidence Interval = 0.077

- **Dataset 2**
  - Total Points = 443
  - Mean = 70.5
  - 95% Confidence Interval = 0.057
Primary Particle Size: Discussion

- the number of primary particles is also determined
- primary particle size can also be used to determine active surface area
- aggregate size is of greater interest from the health, environment, and regulation perspectives
- knowledge of primary particle size and number provides insight about aggregate morphology
**Particulate Concentration**

- Particle (soot) volume fraction is known to be

\[ f_v = n_p \cdot \frac{\pi d_p^3}{6} \]

- Combining the above equation with the calibration factor and the particle leads to
Soot Volume Fraction

- soot volume fraction:

\[
 f_v = \frac{V_{EXP}(\lambda)}{\eta(\lambda) w_b} \frac{\lambda^6 \left(e^{k\lambda T} - 1\right)}{12 \pi c^2 h E(m_\lambda)}
\]

- where:
  - \( w_b \) is the laser sheet width, which determines the depth of the measurement volume
  - the other parameters are the same as described previously

- the area of the measurement volume is the same as the area observed with the calibration lamp, and all the optics and electronics (filters, lenses, photomultipliers, amplifiers, etc.) are the same for the calibration and the LII measurement

- note that the soot volume fraction is inversely proportional to \( E(m) \), the soot absorption function

\[\text{Soot Volume Fraction}\]
What Do We Need to Know in Advance?

- calibration source
  - spectral radiance
- optics
  - absolute optical filter transmission
  - relative dichroic mirror reflectivity
  - relative interference filter transmission
- electronics
  - relative photodetector sensitivity
  - photodetector gain
  - amplifier gain
- dimensions of probe volume
- laser spatial fluence profile
Laser Light Beam Spatial Profile

- each fluence level will heat particles to a different temperature
- ideal is a top-hat profile

↑ Gaussian sheet
multimode “tophat” ⇒
**Relay Imaging for Top Hat Profile**

- place rectangular aperture in laser beam
- relay image aperture to probe volume location
Absolute Intensity Calibration

Calibration Factor

$$\eta(\lambda) = \frac{V_{CAL}(\lambda)}{R_S(\lambda, T)}$$

- use two-color pyrometry to determine the filament temperature
- use known filament radiant power incident on the aperture to calibrate the detection system (NIST-traceable spectral radiance calibration)
a) Soot source in measurement volume (sampling cell removed to aid illustration)

b) Lamp replacing soot as source of incandescence

- **NIST – traceable calibration procedure**
  - lamp is a calibrated spectral radiance source, in Watts/m$^3$-steradian
  - tungsten strip filament lamp is used
  - photomultiplier signal is recorded for a number of calibrated filament temperatures to ensure accurate calibration
  - a single calibration factor, $\eta(\lambda)$, is determined for each wavelength channel (400 nm and 780 nm)
  - electronic gain of photomultipliers (PM) are independently calibrated for different PM bias voltages
Luminance / Radiance Standards

- Traceable Luminance & Radiance Standards
- <1” to >24” Port Sizes
- Low-Light Level Calibration (Night Vision)
- CCT/Spectral Monitoring
- Variable Output Levels
- Custom Solution Designs
Radiance Standard Anatomy

Sphere Radiance

\[ \text{Sphere Radiance} = \frac{\phi_i}{\pi A_s} \ast \frac{\rho_0}{1 - \rho} \]
Calibration with Integrating Sphere/Spectrometer
LII TESTING AND VALIDATION

Testing Includes:

• Laboratory diesel engines
• HD Diesels on dynamometers
• On road testing of HD and LD Diesel emissions
• Turbine engine emissions
• Comparisons to Gravimetric and other optical and filter based methods
Applications – Engine dyno measurements

Ricardo Heavy Duty Diesel Engine
AVL 8-Mode Steady-State Simulation
# Single Cylinder Heavy-Duty Diesel Engine

![Engine Image](image)

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
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<tbody>
<tr>
<td><strong>Caterpillar 3401E</strong></td>
<td></td>
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<tr>
<td><strong>(NRC Prototype 2004)</strong></td>
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<tr>
<td>Cylinders</td>
<td>1</td>
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<tr>
<td>Volume</td>
<td>2.44 liters</td>
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<tr>
<td>Comp. Ratio</td>
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<td>Peak Power (@1800 rpm)</td>
<td>74.6 kW</td>
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<td>Valves</td>
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<td>Injection</td>
<td>EUI</td>
</tr>
<tr>
<td>EGR</td>
<td>Cooled</td>
</tr>
</tbody>
</table>
Diesel PM: Soot Concentration

- LII and AVL Smoke Meter correlate well over a wide range of engine conditions
- more than two orders of magnitude variation in concentration
- evidence suggests that SOF plays a role, particularly at mode 1

Ran several EGR rates
LII-200 Instrument Comparison

~ 0.1 to 11 mg/m³
LII-200 Instrument Comparison

LII Comparison

~ 0.1 to 11 mg/m³
LII-200 Instrument Comparison

\[ \sim 0.1 \text{ to } 11 \text{ mg/m}^3 \]
Diesel Cycle Measurement Repeatability
Section of Diesel FTP Cycle from **Dilution Tunnel**, 4 Repeats

~100 to 1 dynamic range
**Raw Exhaust** (600-750s – 2 repeats)
Raw Exhaust (600-750s – 2 repeats)
Raw Exhaust (790-800s – 2 repeats)

Dynamic Range: >100 to 1

Note: Sampling at 10 Hz, could have gone to 20 Hz
LII Optics Subjected to Mil Spec Vibration Testing

MIL-STD-810F Method 516.5 – Shock

Preparation for On road and Helicopter Flight Tests

X Axis  Y Axis  Z Axis
Applications – On-Road Measurements
VW TDI: Stop-Start Urban Driving
NTE cycle 1290 RPM at various loads

PM Concentration, mg/m³

Test time (seconds)
CARB: Heavy-Duty Diesel NTE Summary

\[ y = 0.62x \quad R^2 = 0.50 \]

\[ y = 0.99x \quad R^2 = 0.85 \]
HDDM2 – Steady State – 6 Repeats

Cumulative Mass = 0.583 +/- 0.015 g
HDDM1 – Dilute Exhaust

LII Sampling Dilute Exhaust

PM (gm) 0.00 0.05 0.10 0.15 0.20 0.25 0.30
BS CVS PM Emissions (gm/bhp-hr)

LII PM Emissions (g)
CVS PM Emissions (g)
CVS Dry PM (g)
BS CVS PM Emissions

0.00 0.20 0.40 0.60 0.80 1.00 1.20 1.40 1.60 1.80 2.00

Steady state points

PM (gm) 0.2518 0.0596 0.2513 0.0631 0.00 0.20 0.40 0.60 0.80 1.00 1.20 1.40 1.60 1.80 2.00

BS CVS PM Emissions (gm/bhp-hr)

0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00 1.05 1.10 1.15 1.20 1.25 1.30 1.35 1.40 1.45 1.50 1.55 1.60 1.65 1.70 1.75 1.80 1.85 1.90 1.95 2.00 2.05 2.10 2.15 2.20 2.25 2.30 2.35 2.40 2.45 2.50 2.55 2.60 2.65 2.70 2.75 2.80 2.85 2.90 2.95 3.00 3.05 3.10 3.15 3.20 3.25 3.30 3.35 3.40 3.45 3.50 3.55 3.60 3.65 3.70 3.75 3.80 3.85 3.90 3.95 4.00 4.05 4.10 4.15 4.20 4.25 4.30 4.35 4.40 4.45 4.50 4.55 4.60 4.65 4.70 4.75 4.80 4.85 4.90 4.95 5.00

CVS Dry PM (g) 0.0631 0.0269 0.2269 1.0427 1.0665 0.0045 1.0326 0.0052

CVS PM Emissions (g) 0.0045 0.2369 0.2513 0.0631 0.0045 0.2269 1.0427 1.0665 1.2278 1.0065

BS CVS PM Emissions (g) 1.0065 1.2278 0.0045 0.2269 1.0427 1.0665 0.0045 0.2269 1.0427 1.0665

testing at Cummins
testing at Cummins
SwRI Instrument Comparisons

Comparisons from CAST burner with the Sunset Lab. OC/EC Instrument, Carbon Burnoff

$y = 1.319x$

$R^2 = 0.997$
NASA Glenn Research Center tests conducted on soot from a mini-CAST burner in December 2009 prior to measuring gas turbine particulate emissions

\[ y = 0.8246x - 10.636 \]

\[ R^2 = 0.9982 \]
NASA Glenn measurements of soot generated by the mini-CAST burner and compared to the TSI SMPS measurements.
The Mystery of Inconsistent LII Measurements

Observations:
- During some tests, LII showed variances from run to run
- Poor agreement with gravimetric
- Poor agreement with MAAP and other filter-based instruments
- Large spikes in time svf history
Sampling and Measurement of Aircraft Particulate Emissions (SAMPLE)
Cardiff University, UK
**Observation:** SVF versus time plots show isolated spikes in the SVF values which cannot be accounted for as large concentrations 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.
Photograph of the Filter under an Optical Microscope

Cardiff Tests 31-3-09 to 1-4-09
Sample contamination with large agglomerates of soot shed from sampling line surfaces from HD Diesel
LII was Low in these tests, probably due to large agglomerates of soot.

LII Sampling Dilute Exhaust

PM (gm) 0.00 0.05 0.10 0.15 0.20 0.25 0.30
BS CVS PM Emissions (gm/bhp-hr)

Steady state points

PM Emissions (g)
CVS PM Emissions (g)
CVS Dry PM (g)
BS CVS PM Emissions

testing at Cummins
The Problem of Large Agglomerates

After cleaning the cyclone separator, a close observation of a section of the FTP cycle shows that the LII measurements consistently rise and fall shot to shot indicating that there are no individual spikes in the data. This implies that there are no large particles in the sample and so the results should agree with gravimetric.
Recent Tests at Cummins

Comparisons of LII 300 and Gravimetric

March, 2010

\[ y = 0.7849x - 0.0046 \]

\[ R^2 = 0.9401 \]
Cummins Instrument Comparisons
March 2010

$y = 0.6441x + 0.002$
$R^2 = 0.9676$
Calibration Curve for Conventional LII-to-Mass

LII (high EC/OC) \( y = 0.74x \) \( R^2 = 0.99 \)
LII (low EC/OC)
PA (high EC/OC)
PA (low EC/OC)

Kramer, of IAV, CRC 2006
Field Tests at the Port of Oakland Shipping Yards
LII 300 Setup for Field Testing
Test Location – Port of Oakland Overpass to Shipyards
Sample Data From Oakland Shipyard Tests

Mass Concentration

- instantaneous
- \(0.016 \text{ mg/m}^3\)

Mean

- \(0.012 \text{ mg/m}^3\)
- \(0.003 \text{ mg/m}^3\)
- \(0.053 \text{ mg/m}^3\)

Validated Mass Concentration Histogram
Variation of Soot Volume Fraction with Time (truck transits)
NRC Canada Very High Sensitivity LII

1 ppt = 2 μg/m³

Average Concentration = 1.50 ppt
Turbine Engine (Helicopter) Tests at Wright Patterson AFB

SAE E31

EPA

Filters

MAAP

LII 300
Turbine Engine (Helicopter) Tests at Wright Patterson AFB
SAE E31
Data Acquired at Wright Patterson AFB (SAE E31)

Mass Measurement Comparison Cruise Condition

- AFRI TFOM
- UTRC MAAP
- AFRL MAAP
- Smoke FOA

- LII 300
- AVL 483

FT – Fischer-Tropsch synthetic fuel, gas to liquids technology
Early Breadboard NRC LII Instrument
LII 200 Developed for Lab Use
LII 300 LASER-INDUCED INCANDESCENCE
Instrument for Soot Characterization

Artium Technologies, Inc. provides the LII 300 system, the most advanced laser-induced incandescence instrument available in the market today.

Measures Soot Concentration (mass or volume basis), Specific Surface Area, and Primary Particle Diameter in Real-Time
Summary: LII Features

- *in situ* and nonintrusive
- signal is proportional to soot volume fraction
- spatially resolved measurements
- time resolved
- large measurement range
  - not limited by aggregate size
- high precision and repeatability
- high speed data acquisition and analysis
Summary LII Benefits:

- dilution of sample not required
- stable measurement of elemental carbon
- insensitive to presence of other species
- can operate at very low concentrations
- real-time results
- cycle-resolved measurements possible
- can provide particulate morphology (size, size distribution, number density) when combined with scattering
- little maintenance required over extended periods of operation
LII in Emissions Control Development

- LII provides sensitivity for post-2007 regulations (measures *microgram per cubic metre* concentration)
- Ideal for measuring engine-out / emissions-control-systems-in particulate levels
- Evaluate emissions control system efficiency
Develop, Evaluate, and Commercialize Laser-Induced Incandescence (LII) Systems for Online Exhaust Particulate Material (PM) Monitoring
Thanks for your attention!

Questions or Comments?

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