**Supplemental Information**

**Near-Real Time Measurement of Carbonaceous Aerosol Using Microplasma Spectroscopy: Application to Measurement of Carbon Nanomaterials**

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1*Disclaimer—The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health. Mention of product or company name does not constitute endorsement by the Centers for Disease Control and Prevention.*

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**Table S-1: Description of carbon-containing materials used for calibration**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Material** | **Manufacturer** | **Chemical composition** | **Density, g/cm3** | **Carbon fraction by mass, %** |
| Sucrose | Fisher Chemical | C12H22O11 | 1.58 | 42 |
| EDTA | Aldrich | C10H16N2O8 | 0.86 | 41 |
| Caffeine | Aldrich | C8H10N4O2 | 1.23 | 49 |
| Sodium Carbonate | Fisher Chemical | Na2CO3 | 2.54 | 11 |
| Carbon black | Cabot | C | 1.8 | > 99 |
| CNT (P7-SWNT) | Carbon Solutions | C | 2.1 | > 90 |

**Table S-2 (a): Experimental parameters used in the SES systems**

|  |  |
| --- | --- |
| Spark energy | 200 mJ |
| Delay time | 5 µs |
| Integration time | 1 ms |
| Spectrometer wavelength range | 200–980 nm |
| Aerosol flow rate | 1.5 L min-1 |
| Operating voltage for corona | 5 kV |
| Distance between the electrodes | 5 mm |
| Diameter of corona electrode | 500 µm |
| Diameter of collection electrode | 1500 µm |

**Table S-2 (b): Experimental parameters used in the LIBS systems**

|  |  |
| --- | --- |
| Laser energy | 120 mJ |
| Laser wavelength | 532 nm |
| Delay time (LIBS) | 1.3 µs |
| Integration time | 1 ms |
| Spectrometer wavelength range | 200–980 nm |
| Aerosol flow rate | 1.5 L min-1 |
| Operating voltage for corona | 5 kV |
| Distance between the electrodes | 5 mm |
| Diameter of corona electrode | 500 µm |
| Diameter of collection electrode | 500 µm |

The delay time for LIBS and SES systems was chosen for optimized signal-to-noise ratio. Our previous studies have demonstrated that the optimized signal-to-noise ratio could be obtained at the delay time of 1.3 us for LIBS method and 5 us for SES ([Diwakar et al. 2012](#_ENREF_17); [Diwakar and Kulkarni 2012](#_ENREF_18)). The difference in delay times for the two systems is due to the difference in the spatial and temporal dynamics of the two microplasmas.

**Table S-3: Comparison of different OC/EC thermal analysis methods**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Method** | **OC Analysis** | | | **EC Analysis** | | |
| **Carrier gas** | **Temperature plateaus (**°C**)** | **Residence time (s)** | **Carrier gas** | **Temperature plateaus (**°C**)** | **Residence time (s)** |
| Our method | N/A | N/A | N/A | Ambient air | 300 | 120 |
| NIOSH Method 5040\_TOT† ([Birch 1998](#_ENREF_1)) | He | 250, 500, 600, 850 | 60,60,60, 90 | 2% O2, 98% He | 650, 750, 850, 940 | 30, 30, 60, 120 |
| IMPROVE\_TOR ([Chow et al. 2007](#_ENREF_4)) | He | 120, 250, 450, 550, | 150 – 580 | 2% O2, 98% He | 550, 700, 800 | 150 – 580 |
| STN\_TOR/TOT ([Chow et al. 2005](#_ENREF_3)) | He | 310, 480, 615, 900 | 60, 60, 60, 90 | 2% O2, 98% He | 600, 675, 750, 815, 920 | 45, 45, 45, 45, 120 |
| HKUST-3\_TOT ([Chow et al. 2005](#_ENREF_3)) | He | 250, 550, 650, 850 | 150, 150, 150, 110 | 1% O2, 98% He | 650, 750, 850, 890 | 150, 150, 150, 150 |
| TMO ([Fung et al. 2002](#_ENREF_5)) | He | 120, 525 | 180, 300 | 2.5% O2,  97.5% He | 750 | 180 |
| TGA ([Lapuerta et al. 2007](#_ENREF_7)) | N2 | 450 | Heating rate: 3 °C per min | Ambient air | 500 | 1800 |
| TGA ([Iwatsuki et al. 1998](#_ENREF_6)) | Ambient air | 430 | 3600 | Ambient air | Continuous (430 to 800) | Heating rate: 10 °C per min |
| ACE-Asia\_TOT ([Schauer et al. 2003](#_ENREF_9)) | He | 340, 500, 615, 870, oven off | 60, 60, 60, 90, 45 | 2% O2, 98% He | 550, 625, 700, 775, 850, 900 | 45, 45, 45, 45, 45, 120 |
| EUSAAR\_TOT ([Cavalli et al. 2010](#_ENREF_2)) | He | 200, 300, 450, 650 | 120, 150, 180, 180 | 2% O2, 98% He | 500, 550, 700, 850 | 120, 120, 70, 80 |
| Coulometric method ([ZH1/120.44 1995](#_ENREF_10)) | N2 | 200, 400, 550 | 120, 120, 240 | O2 | 800 | 270 |
| R&P 5400 (continuous analyzer) ([Rupprecht et al. 1995](#_ENREF_8)) | Ambient air | 340 | 600 | Ambient air | 600 | 750 |

†Temperature steps and times may vary but give comparable OC-EC results (as single fractions). Maximum in helium: 650 °C, with 850 °C typical. Maximum in O2/He: 920 °C, but samples can oxidize at higher or lower temperatures. A manual OC-EC split may be required with some applications (NIOSH 2016).

**Table S-4: Composition and liquid concentration of solutions A, B, C, and D used to produce test aerosols.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Samples | Carbon concentration in the solutions, µg/mL | | | | Total atomic carbon concentration, µg/mL | EC/OC |
| CNT | Sucrose | EDTA | Caffeine |
| A | 40 | 1 | 1 | 1 | 43 | 13.3 |
| B | 80 | 5 | 5 | 5 | 95 | 5.3 |
| C | 120 | 15 | 15 | 15 | 165 | 2.7 |
| D | 160 | 50 | 50 | 50 | 310 | 1.1 |

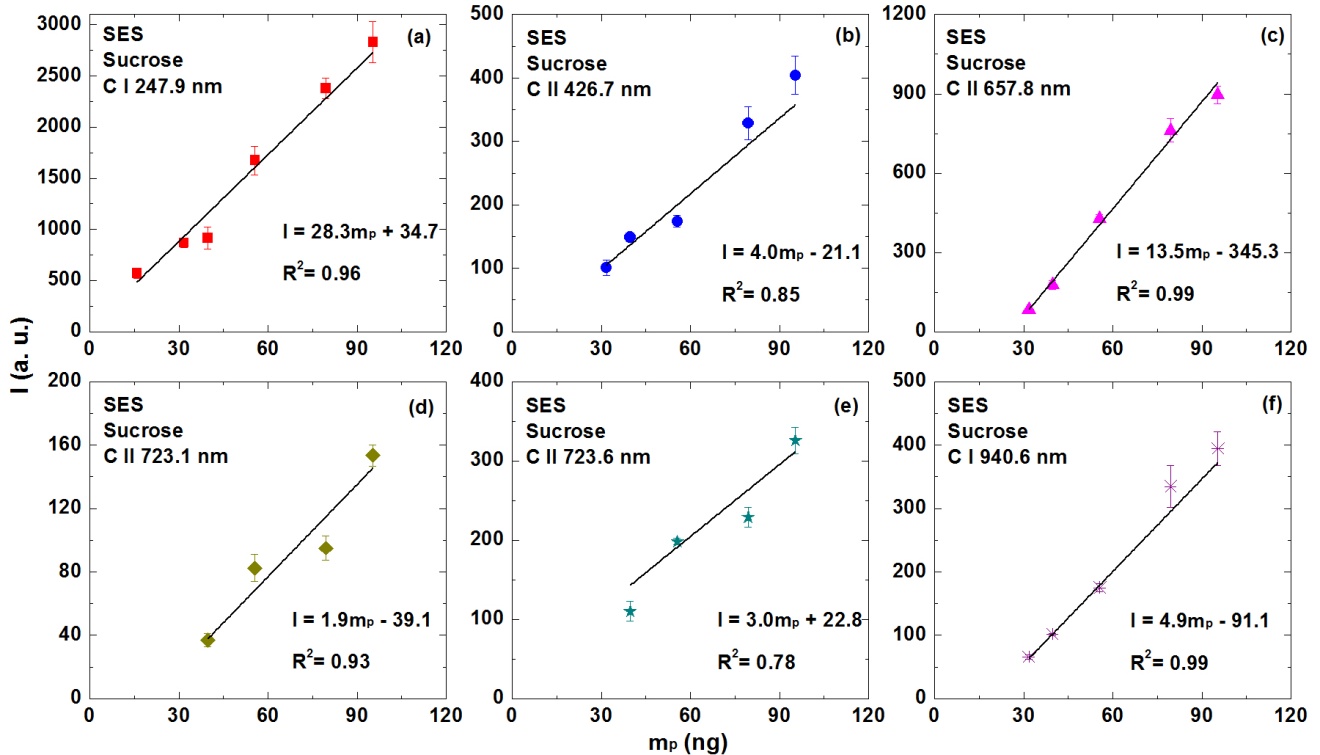


Figure S-1 (a-f). Changes in carbon signal intensity with carbon mass loading using sucrose as analyte, for different emission lines (x-axis represents carbon mass loaded on the collection electrode, ng; y-axis represents carbon signal intensity, arbitrary units [a. u.]).

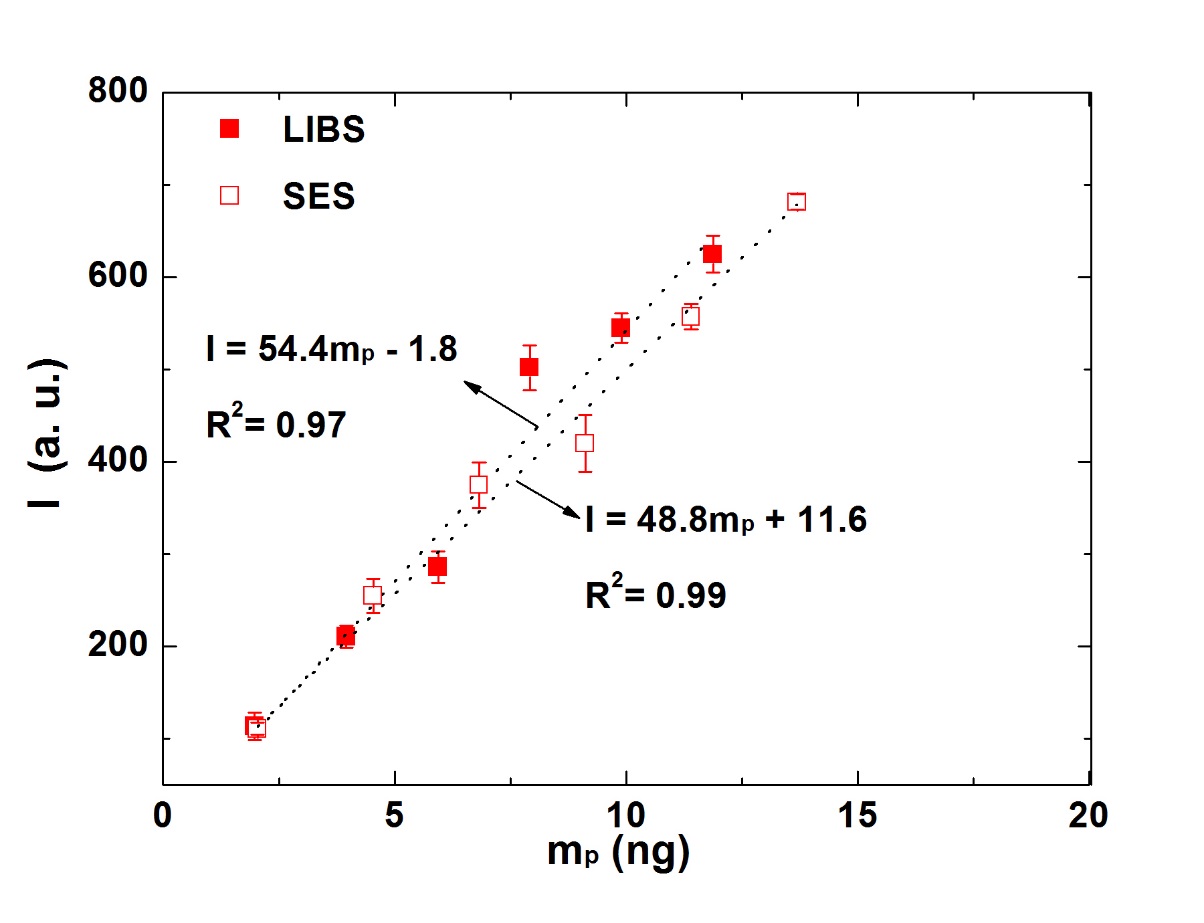


Figure S-2. Calibration curves for carbon black by LIBS and SES using the collection electrode with a diameter of 500 µm.

Figure S-2 shows calibration curves obtained from both microplasma systems, LIBS and SES, for carbon black particles using the 500 µm electrode. As mentioned earlier, the laser beam was oriented perpendicular to the longitudinal axis of the electrode. As discussed elsewhere (Diwakar et al., 2012), this orientation required a correction to account for mass loading in the shadow region. The correction factor was approximately 14% of the total mass collected on the tip ([Diwakar et al. 2012](#_ENREF_17)) in our setup. In the SES system, no such correction was necessary due to the symmetrical nature of the ablation (about the longitudinal axis of the electrode). The sensitivity of LIBS measurements (for carbon black) is about 10% higher than that for SES measurements.

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