DENSITY OF SOOT FOR USE WITH ENGINE EXHAUST PARTICLE SIZER™ (EEPS™) SPECTROMETER MODEL 3090

APPLICATION NOTE EEPS-009 (US)

Contents

Overview

Engine emissions research requires being able to accurately measure particle size, particle number concentration, and also mass concentration. While TSI's "Soot Matrix" brings EEPS Spectrometer's particle size distributions into much better agreement with distribution measurements made by SMPS™ Spectrometer (TSI Inc., 2015), the matrix assumes that soot particles of all sizes exhibit the same density. Published research has provided more insight into the relationships among density, size, and engine conditions.

This application note will discuss these relationships, and show you how to enhance your data quality by bringing research-derived density values into your EEPS software.

The Many Shapes of Soot Particles

Small soot particles can be spherical primary particles, which have the density of carbon. As these smaller spheres aggregate; however, the resulting aggregate is not spherical in shape. Instead, the shape of a larger soot particles can vary anywhere from resembling a small cluster of grapes to resembling long chains of the small, primary particles (Park *et al* 2003). Figure 1 shows a microscope image of such a chain-shaped soot particle.

When these larger aggregate particles are sized according to electrical mobility, the measurement that results is something of a hybrid, due to the fractal nature of these particles. The electrical mobility diameter is smaller than the fullest "diameter" of the aggregate, but also larger than a sphere that would result if all of the primary particles were "melted down" and formed into one big sphere; see Figure 1.

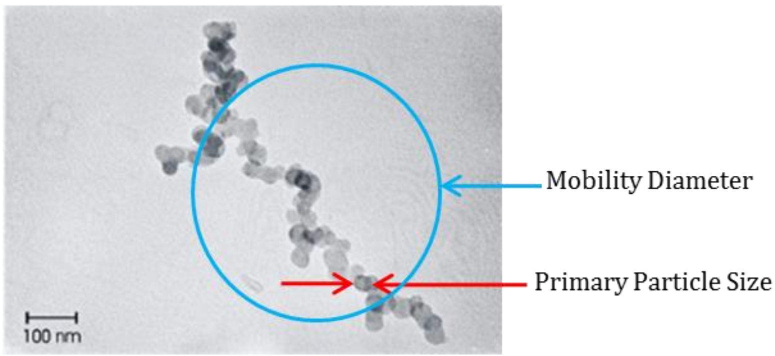

Figure 1: A transmission electron microscope (TEM) image of a soot particle, which is an aggregate of many smaller spherical "primary" particles. The blue circle represents the electrical mobility diameter of the (aggregate) particle.

Since the electrical mobility diameter of an aggregate is midway between these two concepts, it follows that the density of the aggregate is less than the density of the primary particle. Furthermore, as aggregates become larger, their density tends to decrease further, relative to smaller aggregates. The result of all this is that as electrical mobility increases, the effective density of the particles decreases.

Since mass concentrations can often be dominated by a relatively small number of larger-sized particles, having accurate density values for all particles is an important step towards accurate data. Published research has revealed a variety of density values for soot particles, depending upon particle size and engine conditions.

Effective Density Research: Methods

Most aerosol particle density measurement methods follow a "tandem" technique proposed by Kelly & McMurry (1992). This tandem method involves pre-classifying an aerosol using electrical mobility, and then analyzing the classified aerosol using a complementary technique. Two variations on this technique, along with soot density data, are described below.

Mass Mobility Approach

Combining an electrical mobility sizing technique with a mass mobility technique (such as an aerosol particle mass analyzer, APM, or centrifugal particle mass analyzer, CPMA) can allow the calculation of particle density at differing particle masses. This technique was employed by Park *et al* (2003), who found that the effective density of soot particles generated by a diesel engine decreased as particle size increased, ranging from 1.2 g/cm^3 at 50 nm, down to 0.3 g/cm^3 at 300 nm. Aside from particle size, density was also affected by engine load and fuel composition.

Aerodynamic Size Approach

Another experimental method is to combine electrical mobility sizing with aerodynamic sizing. This approach allows the calculation of particle density at different particle (aerodynamic) sizes. This technique was employed by Maricq and Xu in measuring effective densities for particles generated by diesel and gasoline (GDI) vehicles (Maricq & Xu, 2004). Like Park *et al*, their work revealed a decrease in effective particle density with increasing particle size. Similarly to Park *et al*, Maricq & Xu measured effective densities ranging from nearly 1.2 g/cm^3 at D_p = 30 nm to less than 0.3 g/cm^3 at 300 nm.

Based on their data, Maricq & Xu proposed a mathematical relationship to calculate soot particle density:

$$\boldsymbol{\rho_e = \rho_0 \left(\frac{d_m}{d_{0e}}\right)^{(d_f - 3)}}$$

where:

ρ_e = effective density
ρ_o = density of bulk material
d_m = mobility diameter
d_{0e} = effective primary particle diameter
d_f = fractal dimension

The utility of this relationship is explored further below, under "Fitting the Data."

Maricq & Xu's effective density data align well with those of Park *et al*., described above. For particle sizes below approximately 50 nm, Maricq & Xu's density values also align well with values measured by Virtanen and colleagues (2002). While Virtanen *et al* tested only diesel, Maricq & Xu's work found nearly identical soot density values for diesel and gasoline (GDI) exhaust particles.

Fitting the Data

As mentioned above, the density values measured by Park *et al* align well with those measured by Maricq & Xu. The equation above, proposed by Maricq & Xu, may be used to fit the results of Park *et al*.

Figure 2 shows the density values reported by Park *et al* for soot collected from diesel engines at various engine loads, as well as three lines representing theoretical effective density "vectors" (strings of size-specific effective density values). Two of these theoretical vectors are derived from the equation above (from Maricq & Xu), each using slightly different input values for fractal dimension (df) and effective primary particle diameter (d0e). The third line, shown in green, represents the theoretical density vector proposed by Xue *et al* for GDI/LDD vehicles, using parameters from Maricq & Xu.

As is always the case, theory can be very useful, but it has limitations. In the case of soot particle density, a fractal soot particle can only have an "effective" density if it contains more than one primary particle. Thus, below the primary particle size, the density must be held constant. This is visible in Figure 2 in that the fitted lines have a horizontal leg at ρ = 2 g/cm^3, as reported in Maricq & Xu 2004. Xue *et al* opt to take a stair-step approach, setting effective densities for D_p < 30 nm equal to 1.46 g/cm^3, and for 30 < D_p < 55 nm equal to 1.09 g/cm^3.

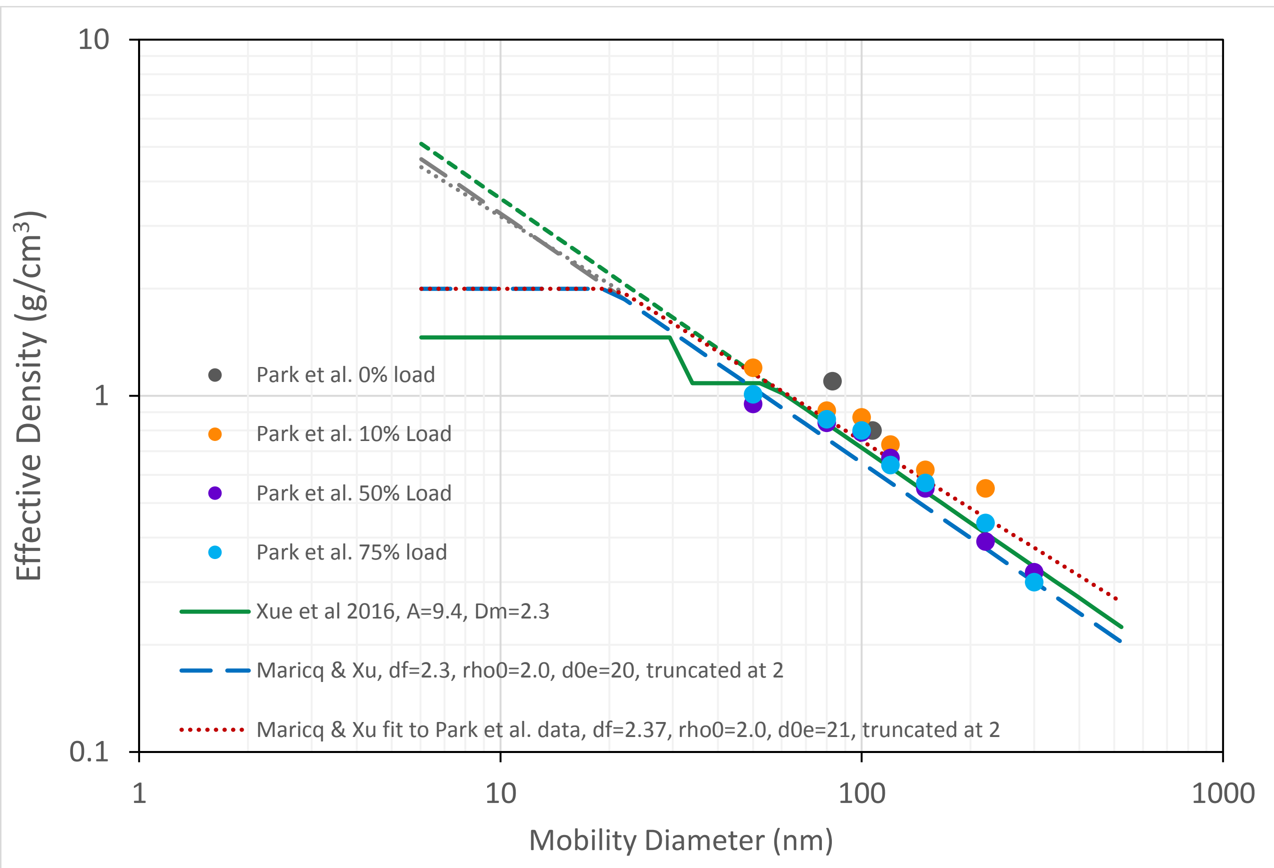

Figure 2: Plot of effective density vs. particle size containing data from Park *et al*. The blue line represents the effective soot density equation from Maricq & Xu using the d_f and d_{0e} values they propose, while the red line modifies these values to better fit the Park *et al* data. Both lines exhibit a "truncation" at a density of 2 g/cm^3 for particle sizes smaller than or equal to the primary particle size. The Xue *et al* density vector truncates in two stages, setting the effective density of particles below 30 nm to 1.46 g/cm^3.

Calculating Density Vectors

By adjusting the input parameters to the equations shown in Figure 2, a best fit for any soot density dataset can be found. Once the best fit is found, a complete density vector can be calculated. Table 1 displays calculated densities for soot particles from several published works.

Column A: The first density column, titled "Maricq & Xu[1]," uses the d_f and d_{0e} parameters presented in Maricq & Xu 2004.

Column B: The column titled "Park *et al*[2]" uses slightly different d_f and d_{0e} values, determined by TSI, to better fit the Park *et al* data using the Maricq & Xu equation.

Column C: These columns display density vectors calculated using an equation in Xue *et al* that uses two dimensionless parameters, as well as EEPS Spectrometer midpoint diameters, as inputs. For the GDI/LDD vector, the dimensionless parameters were taken from Maricq & Xu, and from Quiros *et al* 2015 for PFI.

Column D: The final column demonstrates that the EEPS software's default density vector is fully populated with values of 1.0 g/cm[3], regardless of particle size.

Table 1: Soot density vectors for three published works, as well as the EEPS default density vector.

Electrical Mobility Midpoint (nm)	Effective Densities				
	A	B	C		D
	Maricq & Xu[1]	Park *et al*[2]	Xue *et al*		EEPS Default
	GDI & LDD	Diesel, engine dyno	GDI & LDD[3]	PFI[4]	
6.04	2	2	1.46	1.46	1.00
6.98	2	2	1.46	1.46	1.00
8.06	2	2	1.46	1.46	1.00
9.31	2	2	1.46	1.46	1.00
10.75	2	2	1.46	1.46	1.00
12.41	2	2	1.46	1.46	1.00
14.33	2	2	1.46	1.46	1.00
16.55	2	2	1.46	1.46	1.00
19.11	2	2	1.46	1.46	1.00
22.07	1.87	1.94	1.46	1.46	1.00
25.48	1.69	1.77	1.46	1.46	1.00
29.43	1.53	1.62	1.46	1.46	1.00
33.98	1.38	1.48	1.09	0.63	1.00
39.24	1.25	1.35	1.09	0.63	1.00
45.31	1.13	1.23	1.09	0.63	1.00
52.33	1.02	1.13	1.09	0.63	1.00
60.43	0.92	1.03	1.02	0.61	1.00
69.78	0.83	0.94	0.92	0.58	1.00
80.58	0.75	0.86	0.83	0.55	1.00
93.05	0.68	0.78	0.75	0.53	1.00
107.45	0.62	0.72	0.68	0.50	1.00
124.08	0.56	0.65	0.61	0.48	1.00
143.29	0.50	0.60	0.56	0.46	1.00
165.47	0.46	0.54	0.50	0.44	1.00
191.08	0.41	0.50	0.45	0.42	1.00
220.66	0.37	0.45	0.41	0.40	1.00
254.81	0.34	0.42	0.37	0.38	1.00
294.25	0.31	0.38	0.34	0.36	1.00
339.80	0.28	0.35	0.30	0.34	1.00
392.39	0.25	0.32	0.27	0.33	1.00
453.13	0.23	0.29	0.25	0.31	1.00
523.26	0.20	0.26	0.22	0.30	1.00

[1]Values derived from the fit equation above, using d_f =2.3 and d_{0e} = 20, as proposed by Maricq & Xu.
[2]Values derived from the fit equation above, using d_f =2.37 and d_{0e} = 21, as proposed here in Figure 2.
[3]Values derived using a different fit equation (provided in Xue *et al*) used to fit data from Maricq & Xu 2004.
[4]Values borrowed from Quiros *et al* 2015 from their work on PFI vehicles.

The Impact of the Density Vector

Due in part to uncertainties in soot density, comparison of particle instrument-based estimates with filter-based measurements of total soot mass has generally sowed doubt. By employing both the TSI Soot Matrix for EEPS Spectrometer, as well as a research-supported density vector, this long-sought agreement can finally be obtained.

High-PN Emissions: Excellent Agreement with Filter Measurements

Recent results published by Xue *et al* show the correlation between gravimetric mass and the mass predicted by the integrated size distribution to have a correlation coefficient between 0.76 and 1.01 for GDI vehicles, when both the Soot Matrix and a density vector are employed. Without using either the Soot Matrix or a new density vector, the correlations ranged from 0.45–0.57. Taken together, the Soot Matrix and the use of a research-supported density vector can bring particle instrument-based mass measurements into agreement with filter-based measurements for GDI vehicles.

Low-PN Emissions: Poorer Agreement with Filter Measurements likely due to an Artifact of Filter Sampling

While Xue *et al* saw somewhat poorer agreement with PFI vehicles, it is possible that this is primarily due to vapor adsorption to the filters used to measure the gravimetric mass. For low-particle emissions (such as PFI), this artifact can be significant, and can be as large as 50%, depending upon the type of filter used (Chase *et al* 2004).

Micro Soot Sensor Results Attest to EEPS Spectrometer's Accuracy

While this artifact is a known problem, another tool can be used to demonstrate the accuracy of the EEPS-based measurement. For GDI and PFI engines, the EEPS-based measurement correlates very strongly (within 1% and 9%, respectively) with results from a Micro Soot Sensor. The Micro Soot Sensor measures soot concentration directly, but does not provide particle size information. Excellent agreement between an EEPS Spectrometer-based measurement and the Micro Soot Sensor attests to the accuracy of EEPS Spectrometer-based mass measurements.

To convert the size distribution obtained by the EEPS Spectrometer into a real-time mass measurement, TSI recommends that EEPS Spectrometer users load a research-derived particle density vector into the EEPS software. The following section provides step-by-step instructions to do just that.

How to Load a Density Vector into EEPS Software

The two sets of density values shown in the table above can easily be stored in a text file (contact TSI to have the text files sent to you). The text file(s) of interest should be stored in a selected directory on your computer so you can easily load them into the EEPS software. Density values other than these may be used as well; simply create a text file with the appropriate number of entries, and use that instead. Then, loading the new values into EEPS Spectrometer is very straightforward.

Step 1: Save the Desired Density Vector as a Text File

The text file should simply be a column of density values, with a return following each value, and no delimiters (comma, tab, or otherwise). It must have exactly 32 values to match the 32 size bins measured by the EEPS Spectrometer. An example of such a text file is shown in Figure 3.

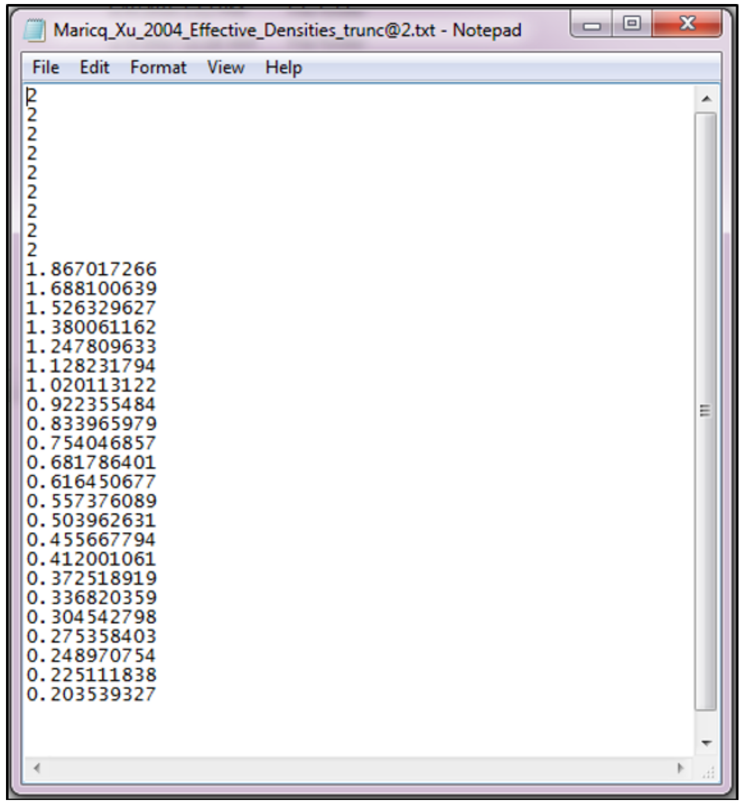

Figure 3: An example text file containing a soot density vector. This text file is loaded into the EEPS software.

Step 2: Load the Desired Density Vector into EEPS Software

Open the EEPS software. As shown in Figure 4, right-click on any cell in the "Density" column within the Particle Table window, and select "Load Density Values…"

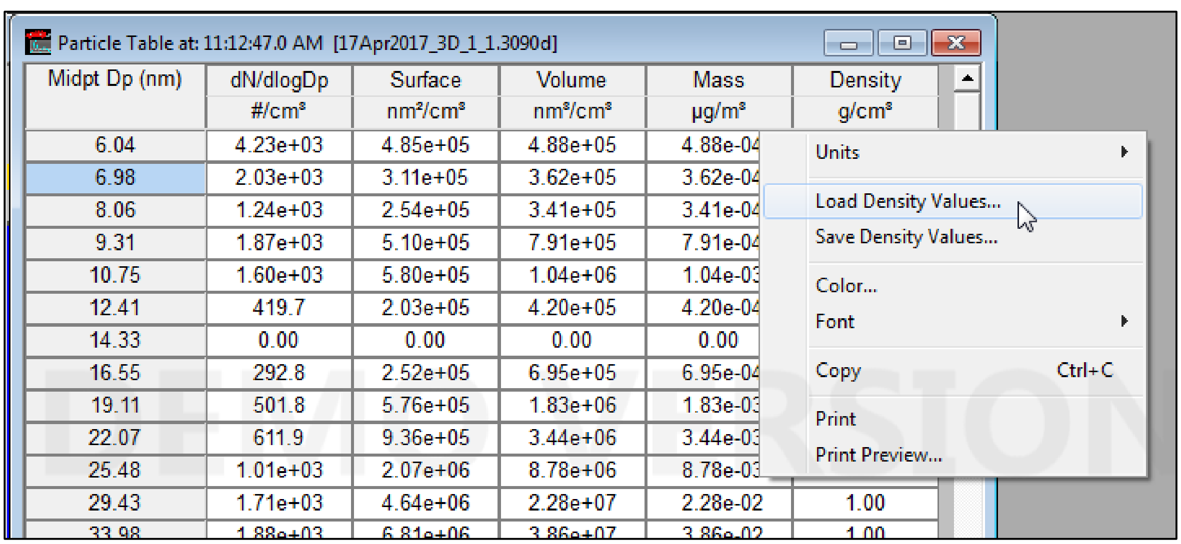

Figure 3: A snapshot of the Particle Table in the EEPS software, and the menu displayed upon right-clicking in one of the cells in the "Density" column. Select "Load Density Values…"

Step 3: Easily Update your Mass Concentration Measurement

Navigate to the text file you prepared that contains the density vector you would like to use. Select the file, click "**Open**," and the density values are immediately brought into the EEPS software. An example is shown in Figure 5. The "Mass" column in the Particle Table is immediately updated to reflect the new density values, including the last cell, the total mass concentration. As a consequence, all mass data in the EEPS file is calculated using the new density vector.

a) Unit density

Particle Table at: 11:12:47.0 AM [17A...

Midpt Dp (nm)	Mass µg/m³	Density g/cm³
80.58	0.00	1.00
93.06	0.00	1.00
107.46	0.00	1.00
124.09	9.36e-03	1.00
143.30	0.135	1.00
165.48	0.283	1.00
191.10	0.280	1.00
220.67	0.00	1.00
254.83	0.00	1.00
294.27	0.00	1.00
339.82	0.00	1.00
392.42	0.00	1.00
453.16	0.00	1.00
523.30	0.00	1.00
Median (nm)	**162.4**	---
Mean (nm)	**138.9**	---
Geo. Mean (nm)	**118.4**	---
Mode (nm)	**165.48**	---
Geo.Std.Dev.	**1.93**	---
Total	**5.85e-02**	---

b) Maricq & Xu 2004 densities

Particle Table at: 11:12:47.0 AM [17A...

Midpt Dp (nm)	Mass µg/m³	Density g/cm³
80.58	0.00	0.754
93.06	0.00	0.682
107.46	0.00	0.616
124.09	5.22e-03	0.557
143.30	6.79e-02	0.504
165.48	0.129	0.456
191.10	0.115	0.412
220.67	0.00	0.373
254.83	0.00	0.337
294.27	0.00	0.305
339.82	0.00	0.275
392.42	0.00	0.249
453.16	0.00	0.225
523.30	0.00	0.204
Median (nm)	**136.3**	---
Mean (nm)	**107.0**	---
Geo. Mean (nm)	**81.6**	---
Mode (nm)	**165.48**	---
Geo.Std.Dev.	**2.22**	---
Total	**3.79e-02**	---

Figure 4: Before and after images of the Particle Table, when updating density values. All non-zero values in the columns for Mass and Density have changed.

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