

2. Materials and Methods

Raman measurement. The DPM samples collected on silver membrane filters (SMF) were analyzed using a portable Raman instrument (i-Raman; B&W Tek, Newark, DE, USA). The field-portable spectrometer has a wavenumber range of 150-3200 cm^{-1} and spectral resolution of 3.5 cm^{-1} . The excitation laser used in this instrument has a wavelength of 785 nm and a maximum power of 420 mW. The laser was focused on the sample using a 20x objective. The spot of the focused laser beam was approximately 105 μm . Raman spectra were collected for an integration time of 1 min at a laser power of 420 mW. The Raman spectra in the range of 800-1800 cm^{-1} (including D mode at $\sim 1322 \text{ cm}^{-1}$ and G mode at $\sim 1595 \text{ cm}^{-1}$) were used for GC identification and quantification. The G band is attributed to the pure graphitic structure of sp²-hybridized carbon micro-domain and the D band is attributed to the defects within the graphitic structure. The Raman signal intensity for GC was calculated as i) the peak intensity (i.e., peak height) at a Raman shift of 1322 cm^{-1} and ii) the integrated intensity (i.e., peak area) in the range of 800-1800 cm^{-1} after baseline correction. The spectra were baseline corrected using a linear fit that connected the signal intensity at 800 and 1800 cm^{-1} .

Calibration methods. Figure 1 shows a scheme for the experimental setup for preparing the calibration samples. Two standard reference materials (SRM) for DPM (SRM 1650 and SRM 2975) were used for calibration in this work. Each DPM material was added to ultra-filtered DI water to obtain a DPM suspension. Test aerosol was generated using a pneumatic atomizer to aerosolize the DPM suspension. The test aerosol was then passed through a diffusion dryer to remove associated water. The resulting dry aerosol was collected on a SMF (25-mm diameter, 0.8- μm pore size, SKC Inc., Eighty Four, PA, USA) at a flowrate of 2 L/min using a personal sampling

pump (GilAir Plus, Sensidyne, LP, St. Petersburg, FL, USA). The SMF was housed in a certified BestChek Asbestos cassette (25-mm diameter, SKC Inc.), designed for uniform particle deposition. Calibration samples with different DPM mass loadings were obtained by varying the collection time, ranging from 1 to 50 min. The test aerosol concentration was kept constant during sampling. The EC mass loading on each filter (silver) sample was calculated based on the EC concentration of the test aerosol, sampling time, and flow rate, where the EC concentration was determined by thermal-optical analysis. For EC measurement, the same test aerosol was collected on a three-piece, 37-mm quartz filter (SKC Inc.) for 30 min at 2 L/min. The quartz filter was then analyzed for EC using an OC-EC analyzer (Sunset Laboratory Inc., Tigard, OR, USA).

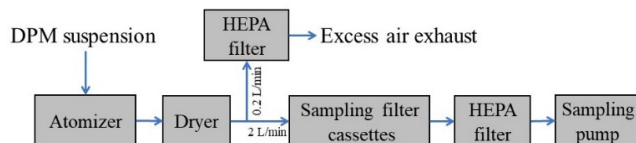


Figure 1. A scheme for the experimental setup for preparing the calibration samples.

For each filter sample, three Raman measurements were obtained at three randomly selected locations on the filter. The average of the three measurements was used to construct the calibration curve. Calibration samples were prepared for each DPM standard. A calibration curve was generated using pooled results for the two sets of calibration samples. The curve was constructed by plotting the Raman signal intensity for GC per unit integration time as a function of EC mass loading on the filter.

Method evaluation. Test samples, used to evaluate the method, were collected from the diesel exhaust generated from idling diesel engines in an ambulance and a fire truck. The filter

media and cassette were the same as those used for collection of the calibration samples. A sampling tubing was placed along the center line of the tailpipe and the tubing inlet was 5 cm away from the tailpipe edge. The flow was split into four flows using a four-way flow splitter (Model 3708; TSI) connected to the sampling tubing. At three of the four split flows downstream of the flow splitter, the diesel exhaust was collected on quartz filters for 8.5 min at 2 L/min, for subsequent determination of EC using NIOSH Method 5040. Diesel exhaust was collected on a SMF at 2 L/min (for Raman measurement) at the fourth split flow. Four SMF samples were collected over collection times of 0.5, 1, 2, and 5 min. The GC mass loading calculated for each SMF measured by the Raman method was compared to EC determined by NIOSH Method 5040.

Field measurements. Field samples were collected over 4 days (April 15-18, 2019) in North Dakota at two well pads during hydraulic fracturing operations. Area air samples were collected at seven locations (Light post, Pumper truck, Down-wind acid, Blender tub, Blender, Pump railing N of blender, and Near blender) for a full shift (approximately 8 hours). Each area sample was collected on a SMF and a 37-mm quartz filter, simultaneously, using two calibrated personal sampling pumps at 2 L/min. The filter cassette was connected to the pump through Tygon[®] tubing (60 cm in length). The cassettes were located in areas of low or high concentrations of DPM, based on previous assessments.¹ After sampling, the collected filter cassettes were stored upright and shipped to the laboratory for analysis. The EC mass loadings on the silver and quartz filters were measured by the Raman and NIOSH 5040 methods, respectively. The time-weighted average EC concentration was calculated by dividing the EC mass on the filter by the volume of air sampled.

[1] Esswein, E. J.; Alexander-Scott, M.; Snawder, J.; Breitenstein, M., Measurement of area and personal breathing zone concentrations of diesel particulate matter (DPM) during oil and gas extraction operations, including hydraulic fracturing. *Journal of occupational and environmental hygiene* 2018, 15 (1), 63-70.