Supplementary Material to: Exposure and Emissions Monitoring During Carbon Nanofiber Production—Part I: Elemental Carbon and Iron-Soot Aerosols

M. Eileen Birch, Bon-Ki Ku, Douglas E. Evans and Toni Ruda-Eberenz.

Appendix A—NIOSH Method 5040

Thermal-Optical Analysis

NIOSH Method 5040 (Birch, 2004; NIOSH, 2003) is based on a thermal-optical analysis technique for organic and elemental carbon (OC and EC) (Birch and Cary, 1996). The analysis quantifies total carbon (TC) in a sample as the sum of OC and EC. Method 5040 was developed for measurement of diesel particulate matter (DPM) in occupational settings, but it is applicable to other types of carbonaceous aerosols and has been widely used for environmental and occupational monitoring.

For the thermal-optical analysis, a portion of a quartz-fiber filter sample is removed (typically a 1.5 square centimeter [cm^2] rectangular punch) and placed on a small quartz spatula. The spatula is inserted into the instrument's sample oven and the oven is tightly sealed. Quartz-fiber filters are required for sample collection because temperatures in excess of 850 °C are employed during the analysis. The thermal-optical analyzer is equipped with a pulsed diode laser and photodetector that permit continuous monitoring of the filter transmittance (and reflectance in some models). This optical feature corrects for the 'char' that forms during the analysis due to carbonization of some materials.

Thermal-optical analysis proceeds in inert and oxidizing atmospheres. In both, the evolved carbon is catalytically oxidized to carbon dioxide (CO_2). The CO_2 is then reduced to methane (CH_4), and CH_4 is quantified with a flame ionization detector (FID). The OC (and carbonate, if present) is first removed in helium, as the temperature is increased to a preset maximum. If sample charring occurs, the filter transmittance (reflectance) decreases as the temperature is stepped to the maximum. After OC is removed in helium, an oxygen-helium mix is introduced to effect combustion of the remaining material, which is light absorbing. The light absorbing fraction may include 'char' (a 'black carbon' [BC]) formed through pyrolysis during the first part of the analysis and EC (or BC) initially in the sample. As light-absorbing carbon is oxidized, the filter transmittance (reflectance) increases. The split between the OC and EC is assigned when the initial (baseline) value of the filter transmittance (reflectance) is reached. All carbon removed prior to the OC-EC split is considered organic, and that removed after the split is considered elemental. If no charring occurs, the split is assigned prior to removal of EC. If the sample chars, the split is not assigned until enough light-absorbing carbon is removed to increase the transmittance to its initial value. Organic and elemental carbon are reported in units of micrograms per square centimeter ($\mu g/cm^2$) of sample deposit. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. Because only a portion of the filter is analyzed, it must be representative of the entire deposit. Thus, a homogeneous deposit is required. Otherwise, the entire sample must be analyzed to determine total OC and EC.

Depending on the sample type and distribution of the deposit, a manual OC-EC split may be required. For example, analysis of multiple punches (simultaneously) from an impaction substrate affects the filter transmittance, and the OC-EC split. In such cases, a manual split can be assigned based on analysis of a single punch from the same substrate. Additional details on the evaluation and use of NIOSH 5040 are provided elsewhere (Birch and Cary, 1996;; Birch, 1998; Birch and Dahman, 1999; Birch, 2002; NIOSH, 2003; Birch, 2003; Birch, 2004; Birch, 2010).

Precision

As mentioned, NIOSH Method 5040 was evaluated for workplace monitoring of DPM, a combustion aerosol. Diesel emissions, and combustion aerosols in general, are composed largely of ultrafine (< 100 nm diameters) particles. Because of its small size, DPM normally deposits evenly across a 37-mm quartz-fiber filter, which is commonly used for sample collection. Deposition of carbonaceous powders such as carbon black or CNFs/CNTs may be more variable because particles in these materials are larger than DPM. As already discussed, even deposition is required because only a portion of the filter is normally analyzed and must therefore be representative of the entire sample deposit.

NIOSH 5040 has been applied to several field studies on CNT/CNF (NIOSH 2010). CNFs/CNTs have negligible (if any) OC content, making EC a good indicator of these materials. When applying NIOSH 5040 to carbonaceous dusts such as CNFs/CNTs, it is important to verify an even filter deposit so that an accurate air concentration (based on a filter portion) can be calculated. Quality assurance procedures should include duplicate measurements of the sample to check precision, especially if the deposit appears uneven. The entire 37-mm filter can be analyzed if the deposit is uneven, but this requires multiple analyses due to the relatively small diameter (about 1 cm) of the analyzer's quartz sample oven. Alternatively, a 25-mm filter can be employed, which also will provide a lower LOD (Birch 2010), but a second analysis is not possible if the entire sample is analyzed.

NIOSH 5040 results for total, thoracic, and respirable dust samples collected on 37-mm filters in different areas of the CNF facility over different survey days are reported in Table S1. Concentrations (µg carbon/m^3) of organic, elemental, and total carbon are reported (with EC as the CNF exposure index), along with the relative percent difference (RPD) or relative standard deviation (RSD) for repeat analyses. The RPD was determined by analyzing either two punches from the same filter (duplicates) or one punch from two different filters (i.e., paired samplers), and the RSD was determined by analyzing a filter in triplicate. The precision for the EC results ranged from about 3% to 14% except for one respirable sample, where the RPD was about 22%. Higher variability for the latter may relate to spatial variation as the two filter punches analyzed were from different samplers. Spatial variation is a likely explanation because two other sets of paired samplers do not show higher variability. The RPDs for these are about 8% and 13%, comparable to results for multiple punches from the same filter.

Table S1. NIOSH 5040 precision for air samples collected in a CNF manufacturing facility with open-face, 37-mm cassettes (total dust) and cyclone samplers (thoracic and respirable dust). Concentrations (µg carbon/m^3) of organic, elemental, and total carbon are reported, with elemental as the CNF exposure index.

Sample	OC[a]	RPD or RSD[b] (%)	EC[c]	RPD or RSD (%)	TC[d]	RPD or RSD (%)	Repeat Type
Respirable	16.42	0.97	[1.87][e]	13.37	18.28	2.19	paired[f]
Respirable	22.19	8.25	3.41	22.29	25.66	10.60	paired
Total	27.17	13.40	21.52	12.04	48.69	12.80	duplicate[g]
Respirable	60.87	0.74	79.59	12.14	140.31	6.36	duplicate
Respirable	25.47	4.46	20.72	8.48	46.09	6.28	duplicate
Total	12.42	6.84	4.14	4.59	16.60	4.88	triplicate[h]
Respirable	19.89	3.22	3.05	4.59	22.93	2.22	triplicate
Total	15.11	1.29	9.89	9.37	25.01	3.63	triplicate
Total	17.80	9.72	11.07	7.97	28.88	9.15	paired
Thoracic	27.16	10.80	11.23	6.79	38.46	6.68	triplicate
Respirable	22.81	2.50	23.67	13.86	46.48	8.26	duplicate
Respirable	18.64	6.77	8.44	3.15	27.14	5.63	duplicate

[a]OC = organic carbon. [b]RPD is relative percent difference. RSD is relative standard deviation. [c]EC = elemental carbon. [d]TC = total carbon; TC = OC + EC. [e]Result in brackets is between LOD and LOQ. [f]Results for two identical, paired samplers. [g]Duplicate analysis of same filter. [h]Triplicate analysis of same filter