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Organic and Elemental Carbon Filter Sets: Preparation Method and Interlaboratory Results

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Carbonaceous aerosols play an important role in climate, visibility, air quality, and human health effects, and they have been routinely monitored in workplace and environmental settings. Different thermal analysis methods have been applied to determine the carbon content of carbonaceous aerosols. Good agreement between results for total carbon (TC) generally has been found, but the organic and elemental carbon (OC and EC) fractions determined by different methods often disagree. Measurement uncertainty is mainly due to pyrolysis and charring of OC sample components. Lack of reference materials has impeded progress on method standardization and understanding method biases. A relatively simple method for generating matched filter sets having known OC–EC contents is reported. After generation and analysis of each set to confirm agreement between filters, the filter sets were distributed to six laboratories for an interlaboratory comparison. Analytical results indicate a uniform carbon distribution for the filter sets and good agreement between the participating laboratories. Relative standard deviations (RSDs) for mean TC (OC + EC), OC, and EC results for seven laboratories were <10, 11, and 12% (respectively). Except for one EC result (RSD = 16%), RSDs reported by individual laboratories for TC, OC, and EC were <12%. The method of filter generation is generally applicable and reproducible. Depending on the application, different filter loadings and types of OC materials can be employed. Matched filter sets prepared by the described approach can be used for determining the accuracy of OC–EC methods and thereby contribute to method standardization.

Keywords: black carbon; carbonaceous aerosol; elemental carbon; organic carbon; particulate matter; ultrafine

INTRODUCTION

Organic and elemental carbon (OC and EC) are major contributors to particulate air pollution. OC emissions have many sources, including forest fires, commercial and home cooking, automobiles, power generation facilities, and many other industrial sources. In the environment, OC is commonly associated with fine and ultrafine particles (aerodynamic diameters less than 2.5 and 0.1 um, respectively), including EC, that are detrimental to human health (Dockery *et al.*, 1993; Samet *et al.*, 2000; Brook *et al.*, 2004; Nel, 2005; Pope and Dockery, 2006). The EC particles originate from combustion processes and are mainly in the ultrafine range.

In 1997, mounting health concerns regarding fine particle air pollution motivated the U.S. Environmental Protection Agency (US EPA) to propose a new National Ambient Air Quality Standard (NAAQS) for particulate matter <2.5 μm in diameter (PM2.5), setting a maximum annual average concentration at 15 μg m^{-3}. Though currently unregulated, OC and EC are important contributors to PM2.5. Over recent years, fine/ultrafine PM, especially ‘black carbon’ (EC and other light-absorbing carbon), has emerged as a serious air quality problem, with on-road vehicles

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being a major source of fine/ultrafine EC and other combustion pollutants (McCarthy *et al.*, 2006). In occupational settings, diesel engines are the main source of ultrafine EC aerosol, exposing workers across many industrial sectors (Lloyd and Cackette, 2001). The EC particles typically carry various metals and thousands of organic compounds, some of which are genotoxic. In addition to adverse effects on human health, EC particles have adverse environmental impacts, such as reduced atmospheric visibility [Intergovernmental Panel on Climate Change (IPCC), 2007].

Thermal–optical analysis (TOA) of airborne PM has been widely applied to environmental and occupational monitoring of OC and EC (Countess, 1990; Chow *et al.*, 2001; Chen *et al.*, 2004). For the analysis, airborne PM is collected on a pre-cleaned quartz–fiber filter. After aerosol collection, a punch (portion) from the sample filter is placed in the analyzer oven and heated in inert and oxidizing atmospheres. In the first part of the analysis, helium is purged through the sample oven as the temperature is increased in steps. The OC on the filter punch is thermally removed, oxidized, reduced, and then quantified as methane by a flame ionization detector. During this heating period in helium, some sample components may pyrolyze to form 'char', causing a decrease in the filter transmittance (and/or reflectance). A correction is made to distinguish the char (also a black or light-absorbing carbon) from EC original to the sample. The correction is accomplished by continuously monitoring the filter transmittance or reflectance (or both) during the analysis. In the second stage of the analysis, any residual char from the pyrolyzed organics is oxidized, along with the original EC, under a mixture of oxygen and helium. As char is removed, the filter transmittance (and reflectance) increases. The instrument defines the split between the OC and EC fractions at the point where the filter transmittance (reflectance) reaches its original value.

Though TOA has been widely applied to OC–EC measurement for many years, there has been inconsistency between different analysis protocols, and between OC and EC methods generally, with differences depending on sample composition (Birch *et al.*, 1999; Chow *et al.*, 2001, 2005; Bae *et al.*, 2009). Good agreement has been reported for samples that have high EC fractions and show little pyrolysis (Birch *et al.*, 1999; Hebisch *et al.*, 2003), which are less challenging analytically. The largest discrepancies have been found with complex carbonaceous aerosols containing components that char during analysis. If uncorrected, char contributes a positive bias in the EC result. The TOA methods apply an optical correction to correct for this bias, and the correction is based on several assumptions regarding the thermal and optical properties of the sample that are not always valid. The OC–EC split also can be affected by certain instrumental factors (e.g. purity of gases, calibration method).

Two widely used TOA methods are the Interagency Monitoring of Protected Visual Environments (IMPROVE) method (Chow *et al.*, 1993) and NIOSH Method 5040 (Birch and Cary, 1996; Birch, 2002, 2003). In IMPROVE, the temperature steps under helium are 120, 250, 450, and 550°C, and the steps under a mixture of 2% oxygen and helium are 550, 700, and 850°C. The NIOSH 5040 temperature steps are 310, 475, 615, and 870°C in helium and 550, 625, 700, 750, 850, and 920°C (final step can be adjusted, depending on sample) in 2% oxygen and 98% helium. The main difference between the two methods is that NIOSH 5040 employs a higher maximum temperature during the first part of the analysis, in helium, when pyrolytically generated EC (char) is formed. Differences in instrument design (NIOSH 5040 employs an instrument from Sunset Laboratories, Inc.) and calibration, as well as the signal (transmittance or reflectance) used to monitor sample pyrolysis, also contribute to the differences that have been reported for these methods (Bae *et al.*, 2004).

Lack of reference materials has impeded progress on OC–EC method standardization and understanding method biases. Well-characterized OC–EC analytical reference filters are needed for improved data quality, methods standardization, and interlaboratory comparisons. Some efforts to fabricate reference filters have been reported, but generation of a matched filter set with known and even deposition of OC–EC aerosol has been problematic (Master, 1991; Iskandar *et al.*, 2001; Lee *et al.*, 2007). A multifilter collection system is needed to generate enough filters for interlaboratory comparisons, but spatial variation in large collection systems can adversely affect homogenous deposition of the OC–EC aerosols onto the filters and thereby reduce precision for the generated set.

This paper describes a relatively simple approach for collection of a matched OC–EC filter set. Four sets of filter samples were collected. Each set contained OC only filters, EC only filters, and OC–EC combination filters. The OC and EC only filters were used to calculate the loadings on the reference (OC–EC combination) filters. The reference filters were analyzed by TOA to evaluate the precision for the set. After establishing the collection method parameters, four batches of reference filters were produced, analyzed, and distributed to six external laboratories to evaluate the interlaboratory agreement for the generated reference filters.

EXPERIMENTAL DESIGN AND METHOD

Solution preparation

Carbon black (Regal 400R; CABOT, Boston, MA, USA) was selected as a material representing EC, while alginic acid (lot #: 60K1443; Sigma, Milwaukee, WI, USA) was selected as an OC material that chars during the TOA (NIOSH, 2003). The carbon black employed was selected because it is a high-purity (negligible OC content) material that is water dispersible, eliminating the need for OC-containing dispersants, such as surfactants (Lee *et al.*, 2007). Dispersions of carbon black were prepared in purified (ultrapure Type I ASTM D1193-91) water and were ~0.05% (weight/volume).

A saturated alginic acid solution was used to generate OC aerosol. Discussion of the choice of alginic acid and solution preparation has been published elsewhere (NIOSH, 2003). Briefly, ~300 mg of alginic acid was mixed with 20 ml of purified water (ultrafiltered, type I) in a glass vial. Several vials of the solution were prepared at one time. The vials were shaken vigorously and allowed to sit for a day at room temperature. The following day, the vials were shaken again and then centrifuged at 500 rpm. The clear supernatant was filtered by 0.45-μm syringe filter (nylon with polypropylene prefiter) before use.

A schematic of the experimental set-up is shown in Fig. 1. For aerosol generation, filtered air was introduced into a Collison nebulizer (model MRE CN24; BGI Inc., Waltham, MA) at 0.7 kgf per cm^2 or 10 pounds psi and a flow rate of 4 liters per minute. Initially, an ultrasonic nebulizer was used to generate aerosol, as reported previously (Lee *et al.*, 2007), but difficulties were encountered with the nebulizer. Specifically, uneven EC deposits were obtained, perhaps due to the rather large size of aerosol droplets generated (~2 μm diameter); the nebulizer overheated after short periods; and the concentration was limited due to clogging of the nebulizer. In contrast, no problems were encountered with the Collision nebulizer. About 50 ml of the alginic acid solution or EC dispersion was used in the nebulizer for generation of OC or EC aerosol.

Before sample sets were collected for a laboratory intercomparison, the particle size distribution was examined. The carbon black has a reported primary particle size of ~30 nm, but the particles are present in agglomerated form. To examine the size distribution for the aerosolized particles, carbon black aerosol was collected on 37-mm polycarbonate filters (stock number 225-1609; SKC Inc., Eighty Four, PA, USA) and observed by scanning electron microscopy (Hitachi model S-3000N, Tokyo, Japan). The diameters of most carbon black particles were between 0.3 and 1.2 μm (Fig. 2) comparable to the size range reported in a similar study (Lee *et al.*, 2007). The small size of the EC aerosol particles provided efficient dispersion and mixing in the sample collection chamber and uniform deposition on the collection media.

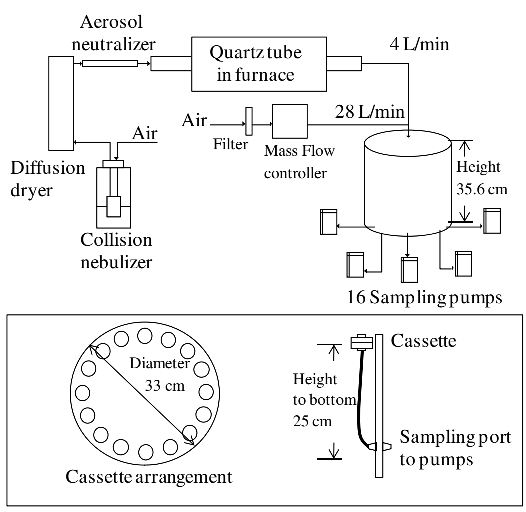

Fig. 1. Schematic of generation system for collection of OC–EC reference filters. Bottom left of figure details the positions of cassettes inside chamber. Bottom right depicts the connection of cassette to a sampling pump (external to chamber) through a port at the base of the chamber wall.

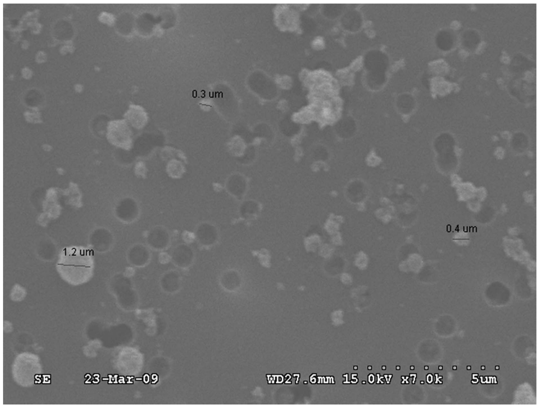

Fig. 2. Scanning electron microscopy image of aerosolized carbon black particles.

Before entering the sample collection chamber, the generated aerosol was passed through a diffusion dryer (model 3062; TSI, Shoreview, MN, USA) to remove moisture and an aerosol neutralizer (model 2U500; NRD LLC, Grand Island, NY, USA). It then entered a quartz tube (1 inch inner diameter × 4 ft long) furnace (model TF55030A; Thermo Scientific www.thermoscientific.com/everylab) held at 150°C to remove any residual moisture. The charge-neutralized dry aerosol was collected on 37-mm quartz filters (2500QAT-UP, product number 7201; Pall Corporation, Ann Arbor, MI, USA) in a metal multi-cassette collection chamber. A Plexiglas plastic chamber had been tested during the initial stages of method development, but the aerosol filter deposits were not even, possibly due to accumulation of static charges on the plastic walls of the chamber.

Prior to sample collection, quartz filters were heated at 600°C for ~2 h. Each filter was placed in a three-piece clear styrene cassette (stock number 225-45A; SKC Inc.) containing a polypropylene support pad (stock number 225-2902; SKC Inc.). The cassettes were connected to separate sampling pumps (mode AirCheck2000; SKC Inc.) calibrated at a flow rate of 2 l min^{-1}. A cassette adapter and Tygon® tubing were used to connect the cassette to a port at the chamber base, which in turn was connected (by Tygon® tubing) to an external sampling pump. Up to 16 samples could be generated during one run. The cassettes were positioned in the collection chamber as shown at the bottom left in Fig. 1.

Before entering the collection chamber, the aerosol flow was diluted with filtered air at a flow rate of ~24 l min^{-1} (adjusted slightly higher to balance pump flow and maintain a small positive pressure in the chamber). An electrometer was used to measure particle charge with and without the neutralizer. With the neutralizer in place, the charged particles were decreased by ~95%. Thus, the neutralizer was necessary to remove excess aerosol charge that can cause an uneven distribution of particles on the filters. The sampling time for EC collection was ~1 h. A fresh carbon black solution was used for each sample set collected. The sampling period for OC aerosol was from 1 to 1.5 h.

Sample analyses

After sample collection, all filters were heated at 120°C for a half hour to remove any volatile organic contaminants. The filters were then analyzed by NIOSH 5040. Some EC loss (from EC only sample) was noted during the maximum temperature step in helium, causing the OC–EC split to be assigned in the helium mode (which had not occurred previously). Trace oxygen contamination due to a spent scrubber was suspected. To prevent this EC loss, the maximum temperature in helium was lowered to 650°C (NIOSH, 2003).

A total of seven laboratories participated in the interlaboratory study: the National Institute for Occupational Safety and Health (Cincinnati and Pittsburgh laboratories), Sunset Laboratory (Hillsborough, NC), theMine Safety and Health Administration (MSHA, Bruceton, PA), Natural Resources Canada, the RPS (the Netherlands), and the University of Stockholm. All laboratories employed NIOSH 5040 and analyzed a sucrose solution as the external standard. The University of Stockholm's laboratory also employed a second protocol ('Eusaar'). Details on laboratory protocols are listed in Table 1.

Table 1. TOA protocols used by participating laboratories ('s' indicates seconds held at specified temperature).

Laboratory	Helium	2% O_2/helium
NIOSH Cincinnati	310°C 80 s, 475°C 60 s, 615°C 60 s, 650°C 100 s	550°C 30 s, 650°C 30 s, 750°C 30 s, 875°C 60 s, 920°C 150 s
NIOSH Pittsburgh	200°C 100 s, 475°C 100 s, 615C 100 s, 870°C 250 s	550°C 45 s, 625°C 45 s, 700°C 45 s, 775°C 45 s, 850°C 45 s, 870°C 190 s
Sunset Lab	310°C 80 s, 475°C 60 s, 615°C 60 s, 870°C 110 s	550°C 45 s, 625°C 45 s, 700°C 45 s, 775°C 45 s, 850°C 45 s, 890°C 110 s
MSHA	250°C 60 s, 500°C 60 s, 650°C 60 s, 870°C 130 s	610°C 30 s, 670°C 20 s, 740°C 20 s, 810°C 20 s, 900°C 150 s
Natural Resources Canada	310°C 60 s, 475°C 60 s, 615°C 60 s, 870°C 100 s	550°C 45 s, 625°C 45 s, 700°C 45 s, 775°C 45 s, 850°C 45 s, 870°C 120 s
RPS	310°C 80 s, 475°C 60 s, 615°C 60 s, 870°C 90 s	550°C 45 s, 625°C 45 s, 700°C 45 s, 775°C 45 s, 850°C 45 s, 870C° 120 s
University of Stockholm NIOSH	310°C 70 s, 475°C 60 s, 615°C 60 s, 870°C 90 s	550°C 45 s, 625°C 45 s, 700°C 45 s, 775°C 45 s, 850°C 45 s, 870°C 120 s
University of Stockholm Eusaar	200°C 120 s, 300°C 150 s, 450°C 180 s, 650°C 180 s	500°C 120 s, 550°C 120 s, 700°C 70 s, 850°C 80 s

As part of this study, we also examined the potential influence of the OC–EC loading order on the OC–EC split because an effect was noted previously (Lee *et al.*, 2007). Filter samples were loaded first with EC then OC, and vice versa. Each sample set consisted of four EC only filters, four OC only filters, and five EC/OC or OC/EC combination filters. One combination filter was used to determine the total carbon (TC) load. It was weighed before sampling and placed in a desiccator for 24 h after sample collection prior to weighing again. The difference between the pre- and post-filter weights was taken as the TC value [though the gravimetrically determined mass is expected to be greater than the actual TC result because the OC component (alginic acid) is not entirely carbon]. The same gravimetric method can be used to determine the EC and OC loads for the EC only and OC only filters. For comparison with the gravimetrically determined weights, three 1.5-cm^2 punches were taken from each filter and analyzed. The sum of the mean EC result for the EC only filters and the mean OC result for the OC only filters was taken as the mean TC result, for comparison with the mean TC value for the combination filters.

For the interlaboratory evaluation, four sample sets were collected, with 10–12 filter samples in each set. All sample sets were heated at 120°C to reduce adsorbed organic vapors. The samples were then placed in plastic PetriSlide™ containers (Millipore PD1504700) and sealed in plastic bags. The bagged samples were stored at room temperature (in a closed box). Prior to shipment to the participating laboratories, one punch (1.5 cm^2) from each EC–OC combination filter was taken and analyzed at the NIOSH Cincinnati Laboratory. The two remaining punches on each filter were analyzed by the study participants. The first punches were analyzed in-house (NIOSH Cincinnati) within a month after sample generation, and two additional punches were analyzed from between 3 and 6 months after generation (some laboratories had instrument problems and other issues that prevented analysis for several months).

Each laboratory except the University of Stockholm was assigned one or two filters from each sample set at random. The University of Stockholm was provided three or four filters from each set because two different analysis protocols (NIOSH 5040 and EUSAAR) were applied. For each protocol, the individual laboratories analyzed a total of two to four filter punches.

RESULTS AND DISCUSSION

Blank filters

Quartz filters readily adsorb vaporous carbon because of their fibrous structure and active surface sites. Even new ultra high-purity filters taken from an unopened package, and also freshly baked filters, can carry some carbon contamination. Typical OC and EC levels on blank quartz filters are listed in Table 2. The average OC was 0.38 μg cm^{-2}, which was reduced to 0.22 μg cm^{-2} after baking at 600°C for 2 h. Because the OC sample loading was ~10 μg cm^{-2}, much higher than the background OC level, the background OC was not significant in this study, even if the filters had not been baked, which resulted in just a modest reduction of the OC contamination. The average EC result was at or close to zero. Unlike OC, quartz filters are not prone to EC contamination if properly handled.

Effect of OC–EC loading order

Results for the study on OC–EC loading order are reported in Table 3. The first set of filters corresponds to filters loaded with EC and then OC, while the second set is for the opposite order (OC first and then EC). The average, standard deviation, and relative standard deviation (RSD) are reported to evaluate the quality of results. All sets have low variation (RSDs $<$ 8%), which indicates an even distribution of OC–EC loadings among filters. For both filter sets, the OC–EC split for the mixed samples was consistent with the results for the filters loaded with OC and EC alone, indicating no influence of loading order. The effect seen in a previous study (Lee *et al.*, 2007) may be due to potassium from potassium hydrogen phthalate (KHP was the OC source), which can catalyze the oxidation of soot and react with quartz at high temperature (Chiao and Friedlander, 1988).

Table 2. Background OC/EC (micrograms per square centimeter).

Sample	Number of measurements	OC		EC	
		Average	Standard deviation	Average	Standard deviation[a]
Unbaked new filter	9	0.38	0.06	0.00	0.01
Baked filter	9	0.22	0.11	−0.02	0.04

[a]Obtained with automatic OC–EC split. Variability (due to lack of sample) may be lower with manual split.

Table 3. Results for two filter sets testing OC–EC loading order (units are micrograms OC, EC, or TC per square centimeter filter).

Sample set	Sample	Analyte	n^a	Average	Standard deviation	RSD (%)
Set 1: deposit EC first and then OC	OC/EC combined	OC	12	9.48	0.31	3.26
		EC	12	8.59	0.59	6.93
		TC	12	**18.06**	0.85	4.71
	OC only	OC	12	9.10	0.53	5.86
	EC only	EC	12	9.35	0.34	3.65
	Average OC only + EC only (n = 12)		**18.45**			
Set 2: deposit OC first and then EC	OC/EC combined	OC	12	12.10	0.91	7.51
		EC	12	11.22	0.59	5.29
		TC	12	**23.32**	1.34	5.75
	OC only	OC	12	11.79	0.42	3.56
	EC only	EC	12	11.79	0.39	3.31
	Average OC only + EC only (n = 12)		**23.58**			

Values in bold are TC averages for mixed-aerosol filters and those determined as the sum of the OC-only and EC-only average results (see discussion in text).
[a]n is number of punches analyzed

The TC value for the EC–OC combination filter is nearly equivalent to the sum of the OC only and EC only filters (combination filter = 18.06 μg and sum = 18.45 μg for Set 1 and combination filter = 23.32 μg and sum = 23.58 μg for Set 2). The TC results calculated as the sum of the two filters (OC only and EC only) are slightly higher (<3%) than the TC results for the combination filters, indicating that the results for the EC only and OC only filters can be used to monitor the value for the OC–EC combination filters. Any small differences (in OC and TC) may be due to the sorption of organic vapors on the quartz filter.

Interlaboratory comparison

Results for all interlaboratory comparison filters are listed in Tables 4–6. Except for Laboratory 1 (NIOSH, Cincinnati), only coded results are reported; individual laboratories are not identified. Laboratories 1–7 used NIOSH 5040 or a comparable method. The 'summary' rows in the Tables report the weighted average results for all seven laboratories. As discussed, the 'Eusaar' results are for a different analytical protocol, as specified in Table 2, and are not included in the summary data.

Average, standard deviation, and RSD are calculated for individual laboratory results based on at least three analyses, while average and relative percent difference (RPD) are reported for results based on two. For the seven laboratories, good agreement between results for all four filter sets was obtained. Excluding Laboratory 4's EC result (RSD = 15.94%) for Sample Set 3 (Table 6) and Laboratory 6's OC result (RPD = 16.88%) for Sample Set 2 (Table 5), the RSDs or RPDs for all TC, OC, and EC results reported by individual laboratories were <12%. The RSDs for the mean (summary) TC results for all four sets are <10%, indicating good agreement among all the filters. Laboratory 1, the NIOSH Cincinnati Laboratory, has lower TC results than the other six laboratories, possibly because the other laboratories analyzed the samples 3–6 months after their generation and OC may have deposited on the filters during transportation and storage (and possibly handling). Nevertheless, good agreement was found, even after several months, demonstrating the validity and ruggedness of the filter generation and analytical methods. Laboratory 2 has the highest TC results, except for Sample Set 2. The TC results for the Eussar protocol are quite similar to the NIOSH 5040 summary results, though additional samples would be needed to perform a valid methods comparison.

The OC results for all filters are listed in Table 5. Again, good agreement between laboratories was obtained. The RSDs (summary results) are <11% for all four filter sets, while RSDs or RPDs for individual laboratories are <12%. Laboratory 1 (NIOSH Cincinnati) reported the lowest OC results for Sample Sets 1 and 2. As mentioned, the other laboratories' results may have been slightly higher due to OC contamination during shipment and storage. The Eusaar protocol has the lowest OC results for Sample Sets 3 and 4, possibly because the protocol utilizes a lower maximum heating temperature in helium (650°C instead of 850°C), as did Laboratory 1 in this study. Laboratory 2 has the highest OC results except for Sample Set 2, probably because its analytical protocol has the longest duration for the maximum heating temperature in helium.

Table 4. Interlaboratory comparison results for TC (micrograms per square centimeter) in four laboratory-generated filter sets.

Laboratory	Set 1				Set 2				Set 3				Set 4			
	n[a]	Average	Standard deviation	RSD ($n > 2$) or RPD ($n = 2$); %	n	Average	Standard deviation	RSD or RPD (%)	n	Average	Standard deviation	RSD or RPD (%)	n	Average	Standard deviation	RSD or RPD (%)
1	12	22.76	0.99	4.34	12	22.82	0.69	3.03	11	18.06	0.85	4.73	10	23.37	1.27	5.42
2	4	26.27	0.69	2.61	3	24.80	1.20	4.85	2	22.12	—	1.72	2	30.43	—	3.55
3	4	25.93	0.68	2.61	4	26.65	0.13	0.49	4	20.44	0.98	4.81	4	26.07	1.66	6.36
4	4	24.61	1.52	6.17	4	24.57	0.52	2.11	4	19.78	1.73	8.74	4	26.98	0.83	3.06
5	4	25.42	0.50	1.97	4	27.56	1.20	4.36	4	20.91	1.05	5.04	2	28.13	—	2.74
6	2	24.15	—	1.20	2	24.68	—	7.19	2	20.06	—	4.75	2	24.80	—	2.90
7	2	24.88	—	2.69	2	25.06	—	1.80	2	20.78	—	1.54	2	26.34	—	1.25
Summary	32	24.38	1.63	6.67	31	24.61	1.87	7.62	29	19.63	1.63	8.33	26	25.53	2.44	9.57
Eusaar[b]	4	26.42	1.34	5.06	4	26.26	0.80	3.05	4	19.90	1.36	6.82	4	25.65	3.13	12.19

[a]n is number of punches analyzed.
[b]Different thermal protocol used (see text for details).

Table 5. Interlaboratory comparison results for OC (micrograms per square centimeter) in four laboratory-generated filter sets.

Laboratory	Set 1				Set 2				Set 3				Set 4			
	n[a]	Average	Standard deviation	RSD ($n > 2$) or RPD ($n = 2$); %	n	Average	Standard deviation	RSD or RPD (%)	n	Average	Standard deviation	RSD or RPD (%)	n	Average	Standard deviation	RSD or RPD (%)
1	12	15.23	0.71	4.67	12	10.35	0.61	5.93	11	8.82	0.74	8.40	10	10.93	0.82	7.48
2	4	18.71	0.75	3.99	3	12.00	0.91	7.57	2	10.90	—	7.80	2	14.79	—	1.15
3	4	17.95	0.80	4.46	4	11.98	0.31	2.61	4	9.34	0.11	1.14	4	12.42	0.43	3.48
4	4	16.78	1.18	7.03	4	10.72	0.34	3.22	4	9.77	0.91	9.33	4	12.37	0.88	7.09
5	4	18.41	0.45	2.45	4	12.79	0.23	1.78	4	10.00	0.43	4.29	2	13.62	—	1.62
6	2	17.39	—	4.09	2	12.45	—	16.88	2	9.08	—	9.14	2	11.98	—	1.03
7	2	16.64	—	0.84	2	11.26	—	5.24	2	9.24	—	0.97	2	12.53	—	3.67
Summary	32	16.82	1.55	9.24	31	11.27	1.10	9.73	29	9.38	0.84	8.94	26	12.09	1.31	10.83
Eusaar[b]	4	17.72	1.10	6.21	4	10.76	0.44	4.11	4	8.74	0.48	5.52	4	11.21	1.28	11.42

[a]n is number of punches analyzed.
[b]Different thermal protocol used (see text for details).

Table 6. Interlaboratory comparison results for EC (micrograms per square centimeter) in four laboratory-generated filter sets.

Laboratory	Set 1				Set 2				Set 3				Set 4			
	n[a]	Average	Standard deviation	RSD ($n > 2$) or RPD ($n = 2$); %	n	Average	Standard deviation	RSD or RPD (%)	n	Average	Standard deviation	RSD or RPD (%)	n	Average	Standard deviation	RSD or RPD (%)
1	12	7.52	0.48	6.40	12	12.48	0.90	7.20	11	9.24	0.74	8.03	10	12.44	0.96	7.74
2	4	7.56	0.52	6.85	3	12.80	0.78	6.08	2	11.23	—	4.19	2	15.65	—	5.82
3	4	7.97	0.41	5.14	4	14.67	0.37	2.49	4	11.10	0.98	8.82	4	13.66	1.38	10.12
4	4	7.82	0.60	7.68	4	13.85	0.26	1.89	4	10.01	1.60	15.94	4	14.61	0.42	2.85
5	4	7.01	0.20	2.86	4	14.77	1.24	8.39	4	10.91	1.00	9.18	2	14.51	—	6.89
6	2	6.76	—	6.24	2	12.23	—	2.67	2	10.98	—	1.11	2	12.11	—	4.92
7	2	8.24	—	9.84	2	13.80	—	1.01	2	11.55	—	3.64	2	13.81	—	0.87
Summary	32	7.55	0.56	7.47	31	13.33	1.22	9.13	29	10.25	1.22	11.89	26	13.45	1.38	10.23
Eusaar[b]	3	8.71	0.62	7.16	4	15.50	0.41	2.63	4	11.16	0.96	8.64	4	14.44	1.87	12.94

[a] n is number of punches analyzed.
[b] Different thermal protocol used (see text for details).

EC results for all filters are listed in Table 6. The summary RSDs for the seven laboratories are <12% for all four samples sets, as were the RSDs or RPDs reported by the individual laboratories, except the previously mentioned result by Laboratory 4 (RSD = 15.94%) for Sample Set 3. One of the results reported by Laboratory 4 for Sample Set 3 is significantly lower than the others and may be an outlier (increasing Laboratory 4's RSD for this particular set). However, the weighted RSD for all filters is quite acceptable (~12%) even if this result is included. Unlike OC, the average EC result for Laboratory 1 is not the lowest among the laboratories, except for Sample Set 3. The good agreement between laboratories also indicates that heating the filters after sample collection does not affect the EC content, as is expected.

CONCLUSIONS

Complex carbonaceous aerosols that form char during thermal analysis are an analytical challenge for OC–EC methods. Method differences have been found for decades, but lack of analytical reference materials has hindered method standardization. Though many interlaboratory comparisons have been conducted, they have not employed filter sets with known OC–EC content and an OC component that chars. We report a relatively simple method to generate matched filter sets with known OC–EC contents, based on aerosolization of an aqueous OC solution and EC suspension. A water-dispersible EC (black carbon) eliminated the need for a surfactant. An OC material that chars was selected because disagreement between methods is greatest for samples that carbonize during analysis. While no single filter set can represent all field samples, the approach used for set generation has general applicability. Different filter loadings and OC types can be employed to suite a particular application (e.g. workplace or environmental monitoring). The intent of this work is to promote development of reference filter sets for use in quality assurance measurements and interlaboratory comparisons. Additional work with different materials, filter loadings, and round robin tests will further progress toward this goal.

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