ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon

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A laboratory intercomparison of organic carbon (OC) and elemental carbon (EC) measurements of atmospheric particulate matter samples collected on quartz filters was conducted among eight participants of the ACE-Asia field experiment. The intercomparison took place in two stages: the first round of the intercomparison was conducted when filter samples collected during the ACE-Asia experiment were being analyzed for OC and EC, and the second round was conducted after the ACE-Asia experiment and included selected samples from the ACE-Asia experiment. Each participant operated ECOC analyzers from the same manufacturer and utilized the same analysis protocol for their measurements. The precision of OC measurements of quartz fiber filters was a function of the filter's carbon loading but was found to be in the range of 4−13% for OC loadings of 1.0−25 μg of C cm^{-2}. For measurements of EC, the precision was found to be in the range of 6−21% for EC loadings in the range of 0.7−8.4 μg of C cm^{-2}. It was demonstrated for three ambient samples, four source samples, and three complex mixtures of organic compounds that the relative amount of total

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evolved carbon allocated as OC and EC (i.e., the ECOC split) is sensitive to the temperature program used for analysis, and the magnitude of the sensitivity is dependent on the types of aerosol particles collected. The fraction of elemental carbon measured in wood smoke and an extract of organic compounds from a wood smoke sample were sensitive to the temperature program used for the ECOC analysis. The ECOC split for the three ambient samples and a coal fly ash sample showed moderate sensitivity to temperature program, while a carbon black sample and a sample of secondary organic aerosol were measured to have the same split of OC and EC with all temperature programs that were examined.

Introduction

Carbonaceous materials influence the optical properties, atmospheric lifetime, and suitability of aerosol particles to act as cloud condensation nuclei (CCN) (*1*). Particulate carbon is often classified into three broad categories: organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC) (*2−4*). OC is carbon associated with organic compounds either directly emitted to the atmosphere (primary OC) or formed by the condensation of products formed via the atmospheric photooxidation of organic species (secondary OC). Typically OC comprises 10−50% of the mass concentration (μg m^{-3}) of atmospheric aerosols in many regions of the world (*1*). EC is formed during thermal degradation of organic material and is essentially nonvolatile at ambient temperature. It has been observed that EC comprises from 1 to 13% and from 2 to 9% of the mass concentration of atmospheric aerosol at U.S. rural and urban sites, respectively (*5*, *6*). CC is present in mineral dust and was found to be an important component of the fine particulate matter in some locations during the ACE-Asia experiment (*7*, *8*).

A series of aerosol characterization experiments (ACE) have been conducted that have integrated ground-, sea-, and aircraft-based measurements with satellite observations and computer modeling to improve the prediction of global climate forcing due to aerosol particles (*9*, *10*). The most recent in this series of experiments is ACE-Asia; the intensive field measurement component of which was conducted from March 31 through May 1, 2001. The area used for aircraft- and ship-based sampling included portions of the Sea of Japan south and east of the Korean Peninsula; the East China Sea between China, Japan, and Korea; and the Philippine Sea south of Japan. Ground-based sampling was conducted at a "supersite" located in Korea (Cheju Island) along with other ground sites located in China (Beijing, Hong Kong, Lin'an, Qingdao, Zhenbeitai), Japan (Hachijo), and Taiwan (Lan Yu).

A major goal of ACE-Asia was to determine the chemical and physical properties of atmospheric aerosol particles originating from the Asian continent. Since carbonaceous material was expected to comprise a significant portion of these aerosols, making directly comparable OC and EC measurements on different platforms was an important objective of the field campaign.

A variety of techniques have been used to measure particulate OC and EC (*2*, *3*, *11−13*). One of the commonly used methods involves the collection of ambient particles onto a quartz fiber filter (QFF). The amount of OC and EC collected on the filter is determined using thermal evolved gas analysis, where a portion of the filter sample is placed into a chamber and heated in the presence of one or more

purge gases through a series of temperature steps. Evolved carbon from the sample is passed over a catalyst that converts the evolved gases to either CO_2 or CH_4, which is quantified using infrared or flame ionization detection, respectively. In most of the thermal evolution ECOC techniques, the split between organic and elemental carbon is based on the temperature and/or the type of purge gas used for analysis (2–4, 11, 14–23). OC is usually defined as the non-carbonate carbon that evolves under a heating cycle in the presence of either He or N_2, and EC is defined as that which evolves in a subsequent heating step in the presence of a gas mixture containing oxygen, such as 98%He + 2%O_2 (2, 3, 14, 17). Importantly, some organic compounds pyrolyze or "char" before they are evolved under the He/O_2 segment of the analysis. The char that is formed in the analysis process, if not properly accounted for, would be incorrectly reported as EC present in the original sample. Thermooptical methods are commonly used techniques in which a laser absorbance procedure is used to correct for charring (2–4, 14, 17). Instruments utilizing a thermooptical method are commercially available.

The char developed during analysis adds to the challenge in measurements of atmospheric aerosol OC and EC levels when determining the amounts of total measured particulate carbon that are OC and EC, i.e., the ECOC split. This split is operationally defined by the analysis method, and a variety of methods have been employed (2–4, 14–18, 21–25). For a given sample, measured EC values have varied significantly among the various analytical methods reported in past interlaboratory comparisons (14, 16, 19, 20). Even when using the same thermooptical ECOC analyzer, different EC and ECOC measurement protocols have been observed to affect the ECOC split (17).

Few laboratory intercomparison studies of OC and EC measurements have been conducted that have directly focused on the ECOC measurement for ambient samples. More importantly, most previous ECOC intercomparison efforts have sought to understand the differences between different ECOC analysis methods and have not directly sought to quantify the precision of a single standardized analytical method among laboratories. Hering et al. (21) conducted a comprehensive carbonaceous aerosol sampling and measurement intercomparison study in 1986 that addressed urban aerosols and compared different ECOC analysis methods. The results of this study showed large deviations in elemental carbon measurements, which were attributed to differences in analytical techniques. More recently, interlaboratory comparison studies have been reported that have focused on higher OC and EC levels, which are typical of occupational exposure and in plumes downside of air pollution sources (14, 19, 20, 26). These results cannot be directly compared to the results of the current study because of the large difference in EC loadings.

In modern thermal-optical methods (2, 3, 14, 17), a sample is heated under a stream of pure He and a laser is used to monitor the reflectance or transmittance of the sample throughout the analysis. As the sample is heated, charring causes the laser absorption of the sample to rise above the initial value. After reaching the maximum operating temperature (selected by the operator and usually between 550 and 900 °C) of the oxygen-free segment of the analysis, the temperature is either reduced or held constant, and the analysis gas is switched to a He/O_2 mixture. The sample is then reheated to near 900 °C, and all remaining carbon evolves with a concomitant decrease in the laser absorption. Carbon evolving from the sample after the sample's laser absorption has returned to the initial value is considered EC. The accuracy of the charring correction can be partially evaluated by analyzing purely organic materials that pyrolyze. Since no EC standard exists that properly represents EC in

atmospheric samples, it is not currently possible to evaluate the accuracy of the EC determination. The precision of the method can be tested by analyzing replicate samples using one or more thermal-optical analyzers.

This paper reports the results of an intercomparison study conducted among participants in ACE-Asia to (i) determine the precision of measurements of OC and EC using the same commercially available thermal-optical ECOC analyzers (Sunset Laboratory, Forest Grove, OR) and the same temperature and purge gas protocols and (ii) evaluate the sensitivity of the ECOC split to the ECOC analysis temperature program and type of sample.

Methods

Sample Collection. The samples used for the ECOC laboratory intercomparison study were collected on quartz fiber filters (Pall-Gelman, Tissuequartz QAO-UP), which were prebaked at 550 °C in air for 12 h prior to sample collection and were stored in Petri dishes lined with baked aluminum foil liners. Table 1A,B lists the samples used for the intercomparison study and the ECOC split study, respectively. The four Milwaukee samples (front and backup filters), the Denver sample, and the two St. Louis samples were collected using a UW–Madison high-volume $PM_{2.5}$ sampler, which operated at 92 L min^{-1}. The sampler was constructed using commercially purchased components and was specifically designed for the collection of atmospheric particulate matter for the analysis and speciation of carbonaceous aerosols. The sampler uses a cyclone (URG, Chapel Hill, NC) to remove particles with aerodynamic diameters greater than 2.5 μm diameter and employs a 90-mm diameter stacked filter pack containing front and back-up filters. Flow through the sampler is controlled using a bank of critical orifices, and the sampler is equipped with a timer to allow the sampler to start and stop at pre-programmed times.

The Bakersfield sample was collected in Bakersfield, CA, as part of the Integrated Monitoring Study (IMS95) in 1995 (27). This 24-h sample was obtained from noon December 8, 1995, through December 9, 1995, using a high-volume dichotomous sampler (28). Details of the sample collection and the study have been previously reported (29).

The three Kosan samples and the aircraft sample were collected during the ACE-Asia experiment using a high-volume particle trap impactor–denuder sampler described by Mader et al. (30). The Kosan samples were collected at the ACE-Asia Kosan supersite located on Cheju Island, South Korea, as described in Table 1A,B. The aircraft sample was collected onboard a modified De Havilland DHC-6 Twin Otter aircraft operated by the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS). The sample was collected over a 4.4-h period on March 31, 2001, at altitudes between 100 and 3000 m and in an area in the Sea of Japan west of Oki Island, Japan.

The secondary organic aerosol (SOA) sample was formed from the reaction of cyclohexene with ozone and was collected on June 7, 2002, from the indoor smog chamber at Caltech. The aerosol sample was taken at a time after all the cyclohexene had been almost completely consumed. The aerosol sample was collected on a prebaked 100-mm-diameter quartz fiber filter (QFF) using an undenuded filter sampler. The flow rate of air through the sampler was controlled by a critical orifice at 30 lpm. There was no size selective inlet present upstream of the filter sampler. From simultaneous measurements of particle number and size distribution performed with a differential mobility analyzer (model 3071, TSI, St. Paul, MN) and a condensation nucleus counter (model 3760, TSI, St. Paul, MN), the particle size distribution was determined to be log-normal with a mean diameter of 500 nm. The details of the Caltech smog chamber have been described by Cocker et al. (31).

TABLE 1. Samples Used for the Study

Section A: Samples Used for the Laboratory Intercomparison Study

sample code	sample description
Round 1 Samples	
Milwaukee 1	24-h average $PM_{2.5}$ sample collected with high-volume sampler operated in Milwaukee, WI, on February 2, 2001
Milwaukee 2	24-h average $PM_{2.5}$ sample collected with high-volume sampler operated in Milwaukee, WI, on February 3, 2001
backup 1	backup filter downstream of sample Milwaukee 1 collected in Milwaukee, WI, on February 2, 2001
backup 2	backup filter downstream of sample Milwaukee 2 collected in Milwaukee, WI, on February 3, 2001
blank 1	intercomparison study blank 1; filter prepared, handled, stored, and shipped in same manner as intercomparison samples
Round 2 Samples	
aircraft	aircraft sample was over a 4.4-h period on March 31, 2001, at altitudes between 100 and 3000 m in an area in the Sea of Japan near Oki Island, Japan[a]
Kosan 1	24-h average $PM_{5.0}$ sample collected with high-volume sampler operated in Kosan, Korea, on March 21−22, 2001, during ACE-Asia
Kosan 2	24-h average $PM_{5.0}$ sample collected with high-volume sampler operated in Kosan, Korea, on March 26−27, 2001, during ACE-Asia
Denver	24-h average $PM_{2.5}$ sample collected with high-volume sampler operated in Denver, CO, on June 10, 2002
St. Louis 1	24-h average $PM_{2.5}$ sample collected with high-volume sampler operated in East St. Louis, IL, on April 25, 2001
blank 2	intercomparison study blank 2; filter prepared, handled, stored, and shipped in same manner as intercomparison samples

Section B: Samples Used for Temperature Program Effect on OC/EC Split Study

sample code	sample description
Round 1 Samples	
St. Louis 2	24-h average $PM_{2.5}$ sample collected with high-volume sampler operated in East St. Louis, IL, on April 27, 2001
Bakersfield	24-h average $PM_{3.5}$ sample collected with high-volume sampler operated in Bakersfield, CA, on December 8, 1995
wood smoke PM	TSP sample of diluted particulate matter emissions from combustion of pinewood logs in a wood stove
Round 2 Samples	
Kosan 3	24-h average $PM_{5.0}$ sample collected with high-volume sampler operated in Kosan, Korea, on March 25−26, 2001, during ACE-Asia
coal fly ash	$PM_{2.5}$ sample of resuspended coal fly ash obtained from the bag house of a stoker boiler
carbon black	$PM_{2.5}$ sample of resuspended carbon black (Fisher Scientific, carbon lampblack)
SOA sample	SOA produced from dark reaction of cyclohexene and ozone in the Caltech smog chamber[a]
wood smoke extract	filter punches spiked with equal volumes of wood smoke extract from particulate matter samples collected with dilution source sampler; samples analyzed after solvent evaporated from filter punch
candle wax	filter punches spiked with equal volumes of commercial candle wax dissolved in dichloromethane; samples analyzed after solvent evaporated from filter punch
motor oil	filter punches spiked with equal volumes of unused motor oil (SAE 10W-30, Havoline) dissolved in dichloromethane; samples analyzed after solvent evaporated from filter punch

[a] See text for details.

The wood smoke PM sample was collected using a dilution source sampler (*32*) while burning pine wood logs during the emissions tests reported by Schauer et al. (*33*). The coal fly ash and carbon black samples were generated by resuspending particulate matter in the University of Wisconsin−Madison dilution source sampler, which is built to closely resemble the Caltech dilution source sampler (*32*). The resuspended coal fly ash sample and the carbon black sample were classified using a cyclone separator and represent fine particulate matter samples ($PM_{2.5}$). The coal fly ash sample was from the University of Wisconsin−Madison Charter Street Power Plant bag house, which burns low sulfur coal in a stoker boiler. The carbon black sample was purchased from Fisher Scientific (carbon lampblack).

The wood smoke extract sample was generated by extracting a composite sample of pine wood smoke and oak wood smoke (*33*) into a mixture of methanol and methylene chloride using a Soxhelet extraction unit. 1.45 cm² punches of prebaked quartz fiber filters were spiked with 10 μL of a clear dilute solution of the wood smoke extract, which was previously filtered using a pasture pipet packed with baked quartz wool. The spiked filter punches were air-dried to remove the volatile solvent mixture. Blank filters, spiked with pure solvent and air-dried using the same drying process, were used to demonstrate that the solvent completely evaporated from the filter punches. The spiked filters were stored in Petri dishes lined with baked aluminum foil in a freezer after preparation until the time of analysis. The motor oil (engine lubricating oil; SAE 10W-30, Havoline) and candle wax (Cake Mate, Signature Brands) samples were prepared using a similar procedure except that motor oil and candle wax samples were dissolved in pure methylene chloride using sonication, and the extract was not concentrated prior to filter spiking.

Sample Preparation and Distribution. Duplicate 1.45-cm² punches from each of the intercomparison study samples were prepared at UW−Madison for each participant in the manner described by Birch and Cary (*2*). Duplicate punches were stored in Petri dishes with prebaked aluminum foil liners. The Petri dishes were wrapped in Teflon tape and stored in Ziploc plastic bags. Samples were shipped cold to the participants with no information on the origin or composition of the samples. The intercomparison samples from round 1 were analyzed for ECOC under identical conditions as the filter samples collected during ACE-Asia. Samples analyzed as part of round 2 of the study, which

TABLE 2. Temperature Programs Used in the Two Studies[a]

			temperature (°C)			
step	gas	hold time (s)	base case	alternate 1	alternate 2	alternate 3
1	He	60	340	275	200	120
2	He	60	500	400	325	250
3	He	60	615	550	500	450
4	He	90	870	750	650	550
	He	45	oven heaters turned off to cool oven			
5	He:O$_2$ [b]	45	550	550	550	550
6	He:O$_2$ [b]	45	625	625	625	625
7	He:O$_2$ [b]	45	700	700	700	700
8	He:O$_2$ [b]	45	775	775	775	775
9	He:O$_2$ [b]	45	850	850	850	850
10	He:O$_2$ [b]	120	900	900	900	900

[a] The base case program was the only program used for the laboratory intercomparison study. [b] Actual gas composition: 98% He + 2% O$_2$. Lab H used 99%He + 1% O$_2$.

included samples from the ACE-Asia project, were analyzed about 1 year after the ACE-Asia field experiment. Participants who operated their instruments in the field during ACE-Asia also analyzed the round 1 intercomparison samples while in the field. Intercomparison study participants agreed not to discuss the samples or analysis results with anyone until all of the results were reported to the UW−Madison group. Table 1A,B shows the distribution of samples between round 1 and round 2 of the intercomparison.

In addition to participating in the intercomparison discussed above, the groups at Caltech and UW−Madison analyzed additional samples to examine the effect of the ECOC analysis temperature program on the ECOC split. Both groups received a basic description of the samples but did not share results until the analyses were complete.

ECOC Analysis. The amounts of OC and EC on the filter punches were determined using a thermal-optical ECOC analyzer (Sunset Laboratory Inc., Forest Grove, OR) (2). Briefly, the 1.45-cm^2 filter punches were individually placed in the ECOC analyzer oven. The operating conditions for the ECOC intercomparison study are shown in Table 2 as the base case ECOC program and were chosen to provide a gradual carbon evolution and maximum peak oven temperatures that would not lead to premature degradation of the instruments oxidation catalyst. OC and EC were determined as follows: OC was evolved under a stream of ultrahigh purity He (99.999% minimum) while heating the sample in four temperature steps to a final temperature of 870 °C. To

evolve EC and pyrolyzed OC, the sample was first cooled to 550 °C and then heated under a mixture of 2% O$_2$ + 98% He in six temperature steps as shown in Table 2. The analyzer utilized laser transmission to correct for sample charring. EC was determined as the carbon evolved after the filter transmittance returned to its initial value. All study participants followed the protocol described in Table 2 and calibrated and operated their instruments as described by Birch and Cary (2) and NIOSH 5040 (22).

The operating conditions used in the study of the effect of the ECOC analysis temperature program on the ECOC split are shown in Table 2. Alternative 3 (Table 2) has the same overall temperature profile as the IMPROVE ECOC method, commonly described as the TOR ECOC method (3). It is important to recognize, however, that alternative 3 is not exactly the IMPROVE ECOC method since (i) it does not utilize the TOR instrument, (ii) it does not use reflectance to monitor pyrolysis, and (iii) the amount of time spent at a given analysis temperature is not identical to that in the IMPROVE method.

Results

Precision of OC and EC Values among Laboratories. Table 3 summarizes the OC results in the ACE-Asia ECOC laboratory intercomparison study, and Table 4 summarizes the associated EC results. The data presented in Tables 3 and 4 are average values for the duplicate measurements of each laboratory, except in a few cases where the duplicate sample was not analyzed because of handling problems. In Figure 1a,b is shown the individual Z scores for each laboratory's OC and EC analysis of the intercomparison samples, respectively. The Z score represents deviation from the consensus value normalized to the standard deviation of the consensus value. Of the 72 OC and 72 EC measurements, only one OC measurement and three EC measurements deviate from consensus value by more than two standard deviation of the consensus value. Only the OC and EC measurements of Lab H and the EC measurement of Lab E have average Z scores outside ±1.0, the rest of the labs average within ±0.5. As a result of the intercomparison study, Lab H has determined that their instrument calibration has a systematic bias in the set-volumes of the pipet used for spiking. A systematic lower EC measurement could result from oxygen contamination in the instrument during the helium only analysis portion of method, but this does not appear to be the case for any of the laboratories participating in the intercomparison. Lab H has been able to correct their ACE-Asia ECOC results, but their reported results for this

TABLE 3. Organic Carbon (OC) Results for Individual Laboratories (μg of C cm^{-2}) of Filter

sample description	avg OC	STD OC[a]	Lab A[b]	Lab B[b]	Lab C[b]	Lab D[b]	Lab E[b]	Lab F[b]	Lab G[b]	Lab H[b]
				ACE-Asia Samples						
aircraft	0.81	0.25	0.82	1.30	0.85	0.75	0.82	0.76	0.75	0.43
Kosan 1	24.78	2.81	24.45	24.59	23.87	27.68	26.27	24.09	26.61	20.23
Kosan 2	5.02	0.56	5.39	5.36	5.32	5.43	4.91	4.89	5.08	3.83
				Urban Smples						
Milwaukee 1	10.13	0.37	9.91	9.97	10.36	9.76	10.46	10.59	10.57	9.66
Milwaukee 2	7.10	0.31	6.72	6.97	7.44	7.03	7.39	7.36	7.23	6.56
Denver	10.47	0.87	9.78	10.43	10.43	11.43	11.73	9.94	10.30	9.05
St. Louis 1	15.35	1.08	14.70	15.76	15.52	17.29	15.15	15.72	15.34	13.38
				Backup Filters						
backup 1	1.76	0.23	1.74	1.71	1.92	1.91	2.04	1.72	1.70	1.37
backup 2	1.54	0.17	1.52	1.60	1.63	1.60	1.78	1.38	1.53	1.28
				Blanks						
blank 1	0.41	0.22	NR[c]	0.30	0.72	0.67	0.55	0.17	0.21	0.25
blank 2	0.44	0.15	0.59	0.44	0.48	0.54	0.53	0.28	0.41	0.25

[a] Standard deviation of all individual measurements from all laboratories. [b] Average of duplicate measurement. [c] NR, not reported.

TABLE 4. Elemental Carbon (EC) Results for Individual Laboratories (μg of C cm^{-2}) of Filter

sample description	avg EC	STD EC[a]	Lab A[b]	Lab B[b]	Lab C[b]	Lab D[b]	Lab E[b]	Lab F[b]	Lab G[b]	Lab H[b]
				ACE-Asia Samples						
aircraft	0.13	0.08	0.13	0.21	0.07	0.26	0.08	0.18	0.13	0.02
Kosan 1	8.41	1.77	8.01	8.08	7.46	7.73	12.35	7.26	7.34	8.57
Kosan 2	1.40	0.21	1.31	1.35	1.51	1.41	1.80	1.26	1.38	1.15
				Urban Samples						
Milwaukee 1	1.09	0.14	1.29	1.15	1.12	1.03	1.24	0.92	0.97	0.92
Milwaukee 2	0.69	0.11	0.81	0.68	0.75	0.65	0.80	0.61	0.59	0.46
Denver	0.90	0.19	0.98	1.03	0.89	0.93	1.11	0.76	0.85	0.36
St. Louis 1	2.96	0.55	3.06	2.97	2.46	2.88	4.24	2.92	2.70	2.46
				Backup Filters						
backup 1	0.12	0.12	0.21	0.00	0.00	0.27	0.24	0.19	0.05	0.06
backup 2	0.06	0.06	0.07	0.02	0.00	0.08	0.16	0.03	0.06	0.05
				Blanks						
blank 1	0.05	0.08	NR[c]	0.03	0.00	0.13	0.12	0.01	0.00	0.09
blank 2	0.04	0.05	0.04	0.00	0.00	0.13	0.02	0.02	0.00	0.11

[a] Standard deviation of all individual measurements from all laboratories. [b] Average of duplicate measurement. [c] NR, not reported.
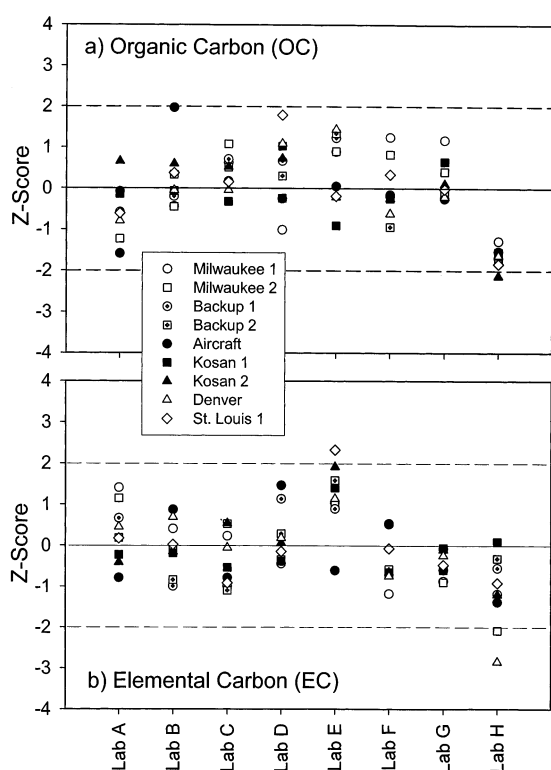

FIGURE 1. Z scores (individual deviation from the consensus value normalized to the standard deviation of the consensus value) for each laboratory's OC and EC measurements of the intercomparison samples used in the ECOC laboratory intercomparison study. Panel a shows the OC results, and panel b shows the EC results.
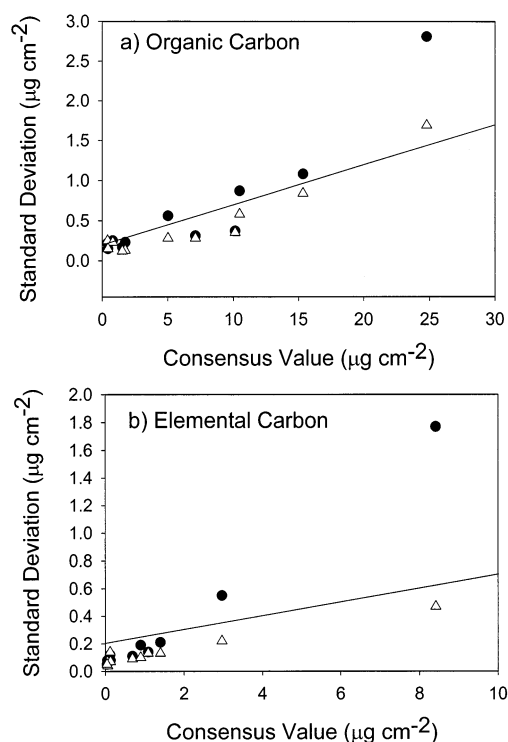

FIGURE 2. Comparison of the standard deviation of each intercomparison sample results as a function of consensus sample loading. Panel a shows the OC results, and panel b shows the EC results. Solid circles are standard deviations of data from all laboratories, open triangles are standard deviation of the measurements from all laboratories except Labs E and H, and the solid line is the uncertainty calculated by the Sunset Labs ECOC instrument.

ACE-Asia intercomparison study have not been revised from their original report. The cause of the higher EC results from Lab E has not yet been identified.

Figure 2a,b presents the standard deviations of the OC and EC measurements of each intercomparison sample as a function of the sample's consensus value, respectively. The solid circles represent the standard deviation of all individual measurements by all labs as shown in Tables 3 and 4. The open triangles are the standard deviation of all of the measurements from all laboratories except Labs E and H. The solid lines shown in Figure 2a,b are the reported uncertainties of the OC and EC measurements by the commercial Sunset Laboratory ECOC instrument. Except for the heavily loaded Kosan 1 samples, the uncertainty in the

OC measurements determined for all laboratories shows good agreement with the instrument reported uncertainty. Of significance is the excellent agreement for the minimum uncertainty of 0.2 μg cm^{-2} as the OC loading approaches zero. The exclusion of the results from Labs E and H yield a standard deviation for the Kosan 1 sample that is consistent with the other samples and is consistent with the reported uncertainty of the Sunset Laboratory ECOC instrument.

The uncertainties in the EC measurements show an important deviation from the reported EC uncertainties of the Sunset Laboratory instrument. The threshold uncertainty of EC measurements as the EC level approaches zero is around 0.05 μg cm^{-2}, which is a factor of 4 lower than the

TABLE 5. Fraction of Total Carbon That Is Elemental Carbon As Determined Using Different Temperature Programs in the ECOC Analysis of Selected Ambient, Source, and Organic Matrix Samples

	absorbs light at 660 nm	pyrolysis during ECOC analysis	total carbon loading (μg cm^{-2})	% elemental carbon of total carbon (avg $\pm$ SE)			
				base ECOC method	alternative 1 method	alternative 2 method	alternative 3 method
			Atmospheric Samples				
Kosan 3	yes	yes	7.9	19.5 $\pm$ 1.3	25.4 $\pm$ 2.0	27.1 $\pm$ 1.5	29.4 $\pm$ 1.7
St. Louis 2	yes	yes	9.8	16.4 $\pm$ 1.3	20.3 $\pm$ 0.6	24.0 $\pm$ 0.6	24.7 $\pm$ 0.9
Bakersfield	yes	yes	24.2	12.6 $\pm$ 0.4	16.4 $\pm$ 0.4	19.2 $\pm$ 0.6	18.3 $\pm$ 1.0
			Source Samples				
wood smoke PM	yes	yes	186	17.0 $\pm$ 0.2	17.6 $\pm$ 0.2	20.7 $\pm$ 0.6	36.7 $\pm$ 0.4
coal fly ash	yes	no	33.8	86.6 $\pm$ 1.5	89.9 $\pm$ 0.5	91.6 $\pm$ 0.5	94.1 $\pm$ 0.7
carbon black	yes	no	13.8	98.0 $\pm$ 0.2	97.5 $\pm$ 0.3	98.0 $\pm$ 0.4	98.2 $\pm$ 0.4
SOA sample	no	yes	16.9	1.6 $\pm$ 0.8	2.3 $\pm$ 1.1	1.7 $\pm$ 0.8	2.2 $\pm$ 1.0
			Organic Matrixes				
wood smoke extract	no	yes	5.4	5.1 $\pm$ 0.9	12.9 $\pm$ 3.6	21.6 $\pm$ 7.1	21.3 $\pm$ 6.0
candle wax	no	no	15.7	0.3 $\pm$ 0.2	0.6 $\pm$ 0.2	1.3 $\pm$ 0.4	1.7 $\pm$ 0.2
motor oil	no	no	14.1	0.3 $\pm$ 0.1	0.8 $\pm$ 0.0	1.3 $\pm$ 0.3	3.2 $\pm$ 0.8

reported threshold value for the Sunset Laboratory instrument. In addition, the slope of the uncertainty curve for EC is close to 20% when results from all of the laboratories are included. If the results from Labs E and H are excluded, the relative standard deviation (RSD) of the measurements from the other six labs is close to the instrument reported level of 5%. It is important to note that most of the EC levels measured by participants in the intercomparison study during the ACE-Asia experiment were in the range of $0-2$ μg cm^{-2}. The exception being the 24-h integrated land-based samples that were collected at Kosan during Asian dust storms. These samples correspond to the two high EC samples shown in Figure 2b. The relative standard deviations of the both the OC and EC measurements from this study are in reasonably good agreement with three of the five samples reported for a subset of five labs that participated in the intercomparison study by Birch (*14*) and used the Sunset Laboratory instrument and NIOSH 5040 (*22*) protocol. The two other samples from that study that showed poorer precisions were wood smoke samples.

Sensitivity of ECOC Split to the ECOC Analysis Temperature Program and Type of Sample. Previous studies (*16, 17*) have shown that the total evolved carbon allocated as OC and EC (i.e., the ECOC split) is sensitive to both the temperature program used for analysis and the purge gas used during the different stages of analysis and that the magnitude of the sensitivity is dependent on the type of aerosol particles analyzed. To examine this issue, 10 different filter samples (see Table 1B) were analyzed using four different temperature programs. Analysis of the filter samples was conducted at Caltech and UW−Madison. Duplicate analyses of each filter sample were carried out using each temperature program; each laboratory conducted a total of 80 sample analyses plus standards calibrations. The temperature programs used for ECOC analysis are summarized in Table 2.

The four temperature programs differed only in the temperatures used during the first four analysis steps when the sample was heated under a He environment (Table 1). The analysis temperatures used during steps $1-4$ were progressively lower from the base case program to alternative 1, alternative 2, and alternative 3. Table 5 presents the average ratio of EC to total carbon for each of the analysis conditions for each sample along with the standard error of the four replicate measurements (i.e., two analyses by Caltech and two analyses by UW−Madison). In Table 5, the total carbon loading for the samples as well as an indication if the samples absorb light at 660 nm or pyrolyze during analysis is presented. If the initial absorbance of the sample before

analysis was significantly less than the absorbance of the filter after the completion of the analysis, the sample was determined to absorb light with a wavelength of 660 nm. It is interesting to note that all of the atmospheric samples and the three combustion-derived source samples absorbed light, but the SOA sample and the organic matrixes did not absorb light as indicated by this measurement. As expected, the atmospheric samples pyrolyzed during analysis, but the only source samples that pyrolyzed were the wood smoke and SOA sample. The only organic extract that pyrolyzed was the wood smoke extract. The absence of pyrolysis for the motor oil extract is consistent with absence of pyrolysis observed by Chow et al. (*17*) for the ECOC analysis of motor vehicle exhaust samples.

The fraction of TC in the ambient samples that is EC as determined by the four different temperature programs is presented in Figure 3. Although the absolute levels of EC are different, the sensitivity to the temperature program is similar for all three atmospheric samples. The three source samples presented in Figure 4 each show very different behavior. Figure 5 summarizes the difference in the fraction of EC measured for each sample for the base case and alternative 3 temperature programs. Since only filtered air was used to fill the chamber and no combustion occurred during the SOA formation, it was expected that no significant EC be measured for the SOA sample for any temperature program. The relatively high fraction of EC measured for the wood smoke extract for both conditions and the statistically significant fraction of EC measured by alternative 3 for all three organic matrixes demonstrate that both measurements of EC can be biased by some organic compounds. Clearly, alternative 3 is significantly more biased for these three organic matrixes than the base case temperature program. It is interesting to note that the fraction of OC measured by base case that is reported as EC by the alternative 3 analysis is similar for both the wood smoke extract and the wood smoke sample of around 20%.

Thermograms for the analysis of the Bakersfield sample are shown in Figure 6a,b. The thermograms were obtained using the base case and alternative 3 temperature programs, respectively. As a consequence of the lower temperatures used in steps $1-4$ of the alternative 3 temperature program as compared to the base case program, significantly less carbon is evolved under steps $1-4$. The laser transmittance decreases during steps $1-4$ of both programs; however, in the base case program the laser transmittance reaches a minimum in step 4 and remains nearly constant until step 5, when the gas is switched to 98%He:2%O$_2$, and the laser
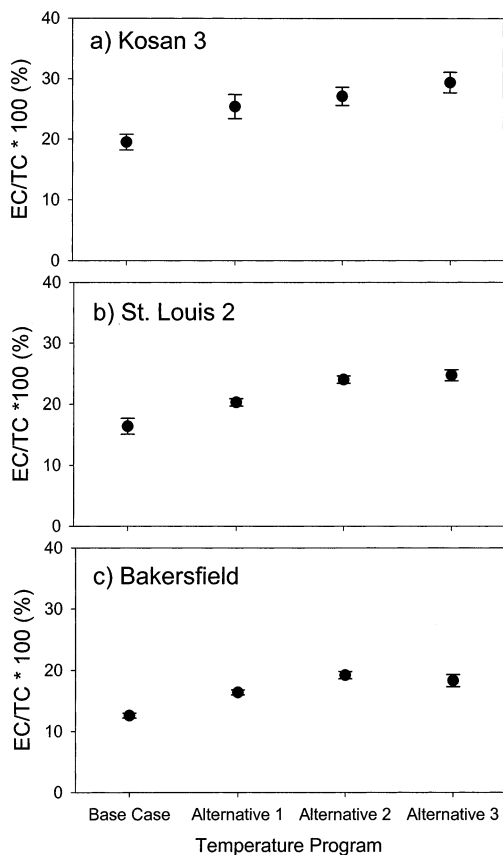
FIGURE 3. Pooled (Caltech and UW—Madison) elemental carbon (EC) levels as measured for the ambient particulate matter samples using the four different temperature programs for ECOC analysis. Panel a is for Kosan 3, panel b is for St. Louis 2, and panel c is for Bakersfield.

FIGURE 4. Pooled (Caltech and UW—Madison) elemental carbon (EC) levels as measured for the selected source samples using the four different temperature programs for ECOC analysis. Panel a is for wood smoke PM, panel b is for coal fly ash, and panel c is for carbon black.

FIGURE 5. Comparison of the fraction of total carbon that is measured as elemental carbon (EC) for the base case and alternative 3 ECOC analysis protocol. Uncertainty bars represent standard errors.

transmittance increases as the char and native EC are evolved. In alternative 3, the laser transmittance continues to decrease during steps 5 and 6, suggesting the formation of char despite the presence of 2% O_2 in the purge gas. Cadle and Mulawa (16) show that significant charring occurs when wood smoke aerosol samples are heated to 950 °C in pure He. To reduce charring, these authors heated the wood smoke aerosol samples in air at 350 °C prior to switching to pure He atmosphere and raising the temperature to 950 °C. The O_2 present in air is thought to enhance the oxidation of OC to CO_2 and reduce the formation of char. Since significantly more carbon remains on the filter after steps 1—4 in alternative 3 than in the base case program, one possibility is that the rate of diffusion of O_2 into the filter-bound PM is insufficient during steps 5—6 to oxidize all the OC, and additional char is formed even though oxygen is present. In thermal-optical methods, the split between OC and EC is determined as the point in the thermogram at which the laser absorbance (after increasing due to the charring of OC) returns to the initial value; the amount of EC measured for the given sample should not be affected by the temperature or purge gas composition at which charring occurs. However, as shown in Figure 5, the amount of EC measured using the alternative 3 temperature profile was 1.6—2.1 times greater than the amount measured using the base case temperature program for the ambient and wood smoke samples, respectively. These results are consistent with the method comparisons observed by Birch (12) and Chow et al. (17). The reason the EC content varies between the different temperature programs is not immediately clear; however, one possible explanation is that organic compounds are present
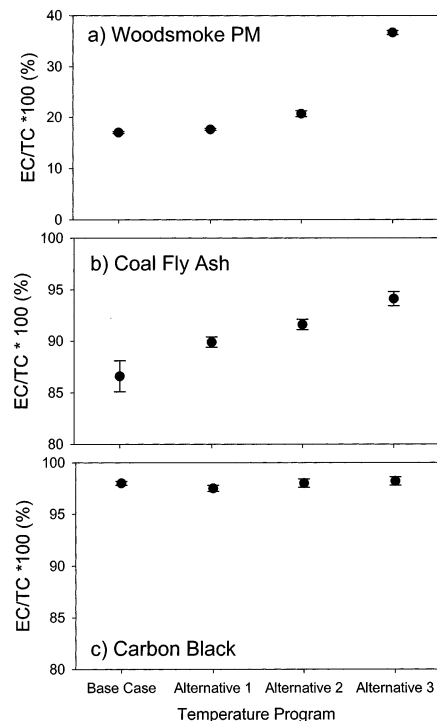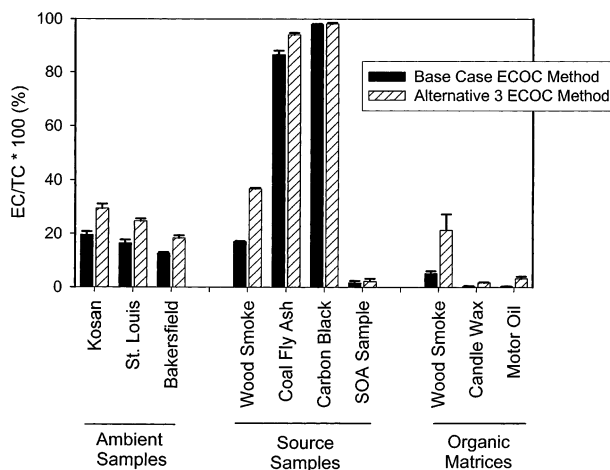
that do not pyrolyze or volatilize at the lower temperatures steps (steps 1—4) of the alternative temperature programs. Under such conditions, these organic compounds would be measured as EC. This hypothesis is supported by the fact that the initial and final laser transmission values are nearly equal for the different protocols, suggesting that (i) the initial levels of light absorbing species on the two filters were similar and (ii) both temperature programs removed similar amounts of light-absorbing species, which were originally present in the sample.

Implications for ACE-Asia and Other Field Studies

Because of the increased concern over the impact of carbonaceous aerosols on climate forcing, regional haze, and
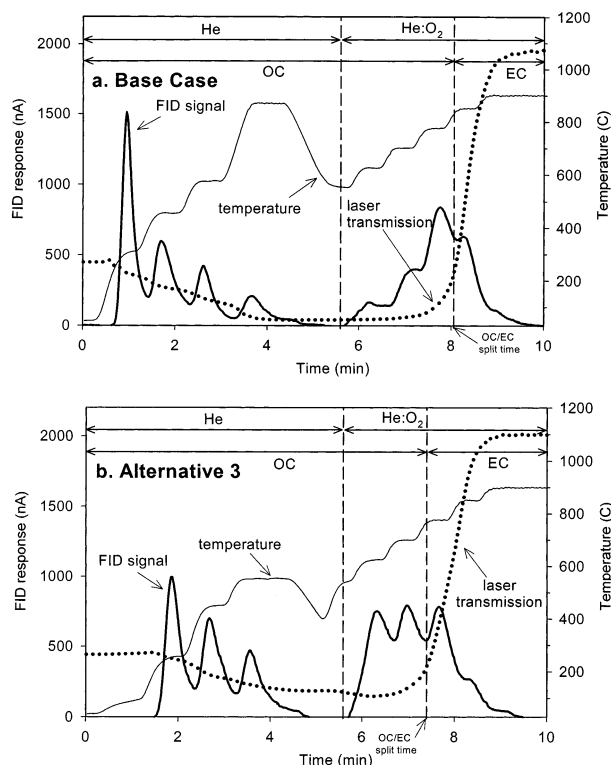
FIGURE 6. Thermograms of the analysis of the PM$_{3.5}$ sample collected in Bakersfield, CA, on December 8, 1995. Panel a shows the thermogram of the ECOC analysis using the base temperature program for the ECOC analysis. Panel b shows the thermogram of the ECOC analysis using the alternative 3 temperature program.

human health issues, there are a considerable number of large field studies and modeling efforts that are currently underway or commence in the next few years. The ability to understand the origin, distribution, and role of carbonaceous aerosols requires the integration of OC and EC measurements by different research groups. The results of this study demonstrate that adoption of standardized protocols for the analysis of carbonaceous aerosols (as was done for the ACE-Asia experiment) enables a direct comparison of measurements from different participating groups to answer important questions concerning the sampling, distribution, and impact of carbonaceous aerosols. This has not been possible in past field studies of this nature since several different ECOC analysis methods were used. The precision of OC and EC measurements determined by participants during ACE-Asia are likely to be within the precision of the measurements of the current laboratory intercomparison. These results demonstrate the benefits and importance of standardized protocols for the analysis of OC and EC in large multi-investigator field studies that are addressing the distribution of carbonaceous aerosols and their impacts on air quality and health related issues.

It is important to recognize that differences observed among the alternative ECOC methods are of great significance to the understanding and development of control strategies to mitigate anthropogenically induced climate forcing, since source emission inventories could vary by as much as a factor of 2 only because of differences in the analysis methods alone. The results of this study further emphasize the need to develop a fundamental understanding of the relationship between the optical and the chemical properties of atmospheric aerosols.

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