

Analysis of carbonaceous aerosols: interlaboratory comparison

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Carbonaceous aerosols are present in many workplace and environmental settings. Some of these aerosols are known or suspect human carcinogens and have been linked to other adverse health effects. Exposure to diesel exhaust is of particular concern because it has been classified as a probable human carcinogen and use of diesel-powered equipment is widespread in industry. Because previously used methods for monitoring exposures to particulate diesel exhaust lack adequate sensitivity and selectivity, a new method was needed. A carbon analysis technique called the 'thermal-optical method' was evaluated for this purpose. In thermal-optical analysis, carbon in a filter sample is speciated as organic and elemental (OC and EC, respectively). When the thermal-optical method was initially evaluated, only one instrument was available, so interlaboratory variability could not be examined. More recently, additional instruments were constructed and an interlaboratory comparison was completed. Eleven laboratories participated in the study, including four in Europe that employ an alternative thermal technique based on coulometric detection of CO₂. Good agreement (RSDs ≤ 15%) between the total carbon results reported by all laboratories was obtained. Reasonable within-method agreement was seen for EC results, but the EC content found by the two methods differed significantly. Disagreement between the OC–EC results found by the two methods was expected because organic and elemental carbon are operationally defined. With all filter samples, results obtained with the coulometric method were positively biased relative to thermal-optical results. In addition, the alternative method gave a positive bias in the analysis of two OC standard solutions. About 52% and 70% of the carbon found in two aqueous solutions containing OC only (sucrose and EDTA, respectively) was quantified as elemental, while EC contents of about 1% and 0.1% (respectively) were found by the thermal-optical method. The positive bias in the analysis of the OC standards is attributed largely to inadequate removal of OC during the first part of the analysis; lack of correction for pyrolytically formed carbon (char) also is a factor. Results obtained with a different thermal program having a higher maximum temperature were in better agreement with the thermal-optical method.

Keywords: Carbon analysis; elemental carbon; black carbon; soot; carbonaceous aerosol; diesel exhaust; diesel emissions; diesel particulate; combustion aerosol

Many workplace and environmental settings contain aerosols composed primarily of carbon. Carbonaceous aerosols encountered in these settings include asphalt fumes, oil mists, cigarette and wood smokes, carbon black, and diesel exhaust. Some of these aerosols are known or suspect human carcinogens (*e.g.*, cigarette smoke and diesel exhaust, respectively) and have been

linked to other adverse health effects (*e.g.*, asthma, heart disease). Exposure to diesel exhaust is of particular concern because it has been classified a probable human carcinogen^{1,2} and diesel equipment use is widespread in industry (*e.g.*, trucking, transit, mining, railroads, agriculture). An estimated² 1.35 million workers are routinely exposed to diesel engine exhaust, and exposures in some industries are relatively high (*e.g.*, >0.5 mg m⁻³). Unfortunately, health-based exposure criteria for diesel particulate have not yet been established. A Threshold Limit Value (TLV) of 150 µg/m⁻³ has been proposed³ but has not yet been adopted.

Particulate diesel exhaust, like fine particulate air pollution in general, also is of concern with respect to noncancer health effects. The US Environmental Protection Agency (EPA) has proposed an inhalation Reference Concentration (RfC) of 5 µg m⁻³ for the noncancer health effects of diesel exhaust,⁴ and the State of California Office of Environmental Health Hazard Assessment (OEHHA) has proposed adoption of this value for the chronic inhalation reference exposure level in California.⁵ The RfC for a substance is an estimate of a daily exposure of humans, including sensitive subgroups, that is 'likely to be without appreciable risk of deleterious effects during a lifetime of exposure'.⁵ Comprehensive reviews of the potential health effects of exposure to diesel exhaust exposure have been recently published.^{6,7}

Because diesel exhaust is a chemically complex mixture containing thousands of compounds, some measure of exposure must be selected. Given the high carbon content of diesel particulate, a carbon-based method was investigated. The method, recently published as National Institute for Occupational Safety and Health (NIOSH) Method 5040,⁸ is based on an evolved gas analysis technique called the 'thermal-optical method'. With this technique, speciation of organic and elemental carbon (OC and EC, respectively) is accomplished through temperature and atmosphere control and by an optical feature that corrects for pyrolytically generated carbon, or 'char', formed during the analysis of some materials. Although both organic and elemental carbon are determined in the analysis, EC is the superior marker of diesel particulate because it constitutes a large fraction of the particulate mass, it can be quantified at background (*i.e.*, environmental) levels, and its only significant source in most workplaces is the diesel engine. Different approaches can be applied for OC–EC analysis, but a thermal-optical method was selected because the instrumentation has desirable design features not present in other carbon analyzers. An in-depth discussion on Method 5040, including both technical and exposure-related issues, has been published elsewhere.⁹

In a previous study,¹⁰ different methods gave widely varying results in the speciation of organic and elemental carbon. For this reason, OC–EC methods are considered *operational*, in the sense that the method itself defines the analyte. Given its operational nature, it is important to examine interlaboratory variability of the method; however, when the thermal-optical method was initially evaluated, only one instrument was available, so interlaboratory variability could not be examined.

More recently, additional instruments were constructed by a commercial laboratory¹¹ and an interlaboratory comparison was conducted. Seven laboratories that perform thermal-optical analysis participated in the comparison. Six of these used NIOSH Method 5040 (*i.e.*, they used identical instrumentation and thermal program), while the seventh used a variation on the method. Another thermal technique based on coulometric detection of CO₂ is being used in Europe for occupational monitoring of diesel particulate. Four laboratories employing the coulometric method also participated in the interlaboratory comparison, giving a total of eleven laboratories (seven thermal-optical and four coulometric). Discussion of the methods and a summary of the results of the intercomparison are reported in this paper.

Experimental

Reagents and materials

All air samples were collected in the field with the exception of a mixed sample of urban particulate and cigarette smoke, where cigarette smoke was collected in the laboratory on 25 mm diameter portions taken from a field sample. In addition to the mixed sample, the sample set included an urban particulate sample collected at a construction site (diesel-powered compressors were used) near a downtown area, a sample collected in a loading dock area (diesel trucks used) of a building, one collected in the bay of a fire engine house, and two wood smoke samples. A high-volume sampler loaded with quartz-fiber filters (8 × 10 inch QM-A, Whatman, Clifton, NJ, USA) was used for sample collection. To remove possible carbon contamination, the filters were precleaned in a muffle furnace at 800 °C for approximately 2 h. After sample collection, rectangular portions of the filters were distributed to the participating laboratories for analysis in triplicate. To ensure matched sample sets, multiple analyses were performed across all filters prior to distribution of the portions. Two aqueous standard solutions containing only OC were also included in the sample sets. Reagent grade sucrose and a 0.05 M calibrated standard solution (both from Aldrich, Milwaukee, WI, USA) of the disodium salt of ethylenediaminetetraacetic acid (EDTA) were used for preparation of the OC standards. These standards provided a check on the accuracy of the total carbon (TC) data as well as a check on the pyrolysis correction feature of the thermal-optical method (both standards char during analysis).

Analytical methods

Six laboratories analyzed samples by a thermal-optical method,⁸ (*i.e.*, 5040), one used a similar method¹² (TOR) having an optical correction feature based on filter reflectance rather than transmittance, while four others used an alternative

thermal technique¹³ with detection based on coulometric titration of CO₂. All Method 5040 laboratories (TOM1 through TOM6) employed the same thermal program (or parameter file), while users of the coulometric technique employed different protocols. The different thermal protocols used by the participating laboratories are listed in Table 1.

One coulometric laboratory (C2) reported two sets of results for each sample. One set (C2A) corresponds to results obtained with the thermal program normally used by the laboratory, while the second set (C2B) corresponds to results obtained by the protocol used by laboratories C3 and C4. This protocol (see Table 1) is specified in an official method¹³ currently being used in Germany (Method No. 44) for occupational monitoring of diesel particulate. The two sets of data were obtained simply by reading the integrator counts at different times (see Results and discussion: Thermal treatment).

Briefly, in NIOSH Method 5040,⁸ speciation of organic and elemental carbon is accomplished through temperature and atmosphere control, and by an optical feature that corrects for pyrolytically generated 'EC' (or 'char') formed during the analysis of some materials (*e.g.*, cigarette and wood smoke). Light from a pulsed diode laser is passed through the filter to allow continuous monitoring of filter transmittance. The analysis proceeds essentially in two stages. In the first, organic carbon and carbonate carbon (if present) are volatilized from the sample in a pure helium atmosphere as the temperature is stepped to a maximum (about 860 °C in Method 5040). Evolved carbon is catalytically oxidized to CO₂ in a bed of granular MnO₂, reduced to CH₄ in a Ni-firebrick methanator, and quantified as CH₄ by a flame ionization detector (FID). During the second stage of the analysis, a pyrolysis correction (if needed) and the EC measurement are made. The oven temperature is reduced, an oxygen (2%)–helium mix is introduced, and the oven temperature is again raised. As oxygen enters the oven, pyrolytically generated EC is oxidized and a concurrent increase in filter transmittance occurs. Correction for the char contribution to EC is accomplished by identifying the time at which the filter transmittance reaches its initial value. This point is defined as the 'split' between organic and elemental carbon. Carbon evolved prior to the split is considered 'organic' (including carbonate), and carbon volatilized after the split and prior to the peak used for instrument calibration (final peak) is considered 'elemental'. If desired, the presence of carbonate can be verified through analysis of a second portion (punch) of the filter after its exposure to HCl vapor. In the second analysis, the absence or diminished size of the suspect peak (typically the fourth 'OC' peak) is indicative of carbonate in the original sample. Normally, a 1.5 cm² rectangular portion (taken with a punch) of the filter deposit is analyzed. Organic and elemental carbon are reported as µg C per cm² of deposit area. The total EC and OC on the filter are calculated by multiplying reported values by the sample deposit

Table 1 Thermal Protocols

Laboratory	OC determination	EC determination
TOM1–TOM6*	In helium: 250 °C, 1 min; 500 °C, 1 min; 650 °C, 1 min, 850 °C, 1.5 min; reduce to 650 °C, switch to oxygen mode	In 2% oxygen in helium: 650 °C, 30 s; 750 °C, 30 s; 850 °C, 1 min; 940 °C 2 min (or more)
TOR†	In helium: 120 °C, 4.5 min; 250 °C, 3.5 min; 450 °C, 4–5 min; 550 °C, 8–10 min, switch to oxygen mode	In 2% oxygen in helium: 550 °C, 6–7 min; 720 °C, 2.5 min; 820 °C, 2.5 min
C1	In nitrogen: 800 °C, 10 min	In oxygen: 800 °C, 7 min
C2A‡	In nitrogen: 200 °C, 2 min; 400 °C, 4 min; 560 °C, 6 min (or until stable)	In oxygen: 800 °C, 4.5 min; 1000 °C, 2 min (or until stable)
C2B‡, C3, C4 (Method No. 44)	In nitrogen: 200 °C, 2 min; 400 °C, 2 min; 550 °C, 4 min	In oxygen: 800 °C, 4.5 min

* TOM is thermal-optical method detailed in NMAM 5040.⁸ † Times specified for thermal-optical reflectance (TOR) method are estimates based on scale shown in thermograms; different parameter files were used for analysis. ‡ Laboratory reported two sets of data. One set obtained with specified protocol (C2A) and second set (C2B) obtained with Method No. 44¹³ protocol.

area. In this approach, a homogeneous filter deposit is assumed. Instrument calibration is achieved through injection of a known volume of methane into the sample oven. The thermal-optical reflectance method¹² (TOR) is similar to Method 5040, but a different thermal program is applied and filter reflectance is monitored instead of filter transmittance. Additional details on these methods have been described elsewhere.^{8,9,12}

An alternative OC-EC Method¹³ currently in use in Europe for analysis of diesel particulate is based on a slightly modified version of a commercial instrument called a 'Coulomat' (Ströhlein GmbH, Koarst, Germany). Unmodified, the Coulomat is used for total carbon or sulfur analysis, depending on the configuration. The instrument was modified slightly (valve added) to allow gas switching between nitrogen and oxygen so that both OC and EC (respectively) could be determined. Data acquisition and instrument control must be done manually because the instrument is not computer-interfaced. During the analysis, a potentiometer is used to adjust the temperature manually, which is sensed by an internal thermocouple. Thermally evolved carbon is oxidized to CO₂ (in a CuO furnace) and CO₂ is then determined by coulometric titration. As the CO₂ is absorbed by the electrochemical cell solution, the resulting decrease in pH is sensed by a pH electrode. Back-titration occurs automatically (to the initial pH of 10) through an electrolytically generated reagent (dissociation of water). The integrated signal (*i.e.*, the current integral), is displayed in 'counts' and is directly proportional to the amount of carbon in the sample. A single count corresponds to 0.1 µg of carbon.

Normally, all samples are acidified before analysis to remove carbonates, which interfere in the coulometric determination of EC. Other potential interferences in the sample gas stream, including halogens, oxides of sulfur and nitrogen, water, and any titratable acid, must be scrubbed or trapped. Interfering halogens are removed by heated silver wool in an oven (maintained at 400 °C) that is continuous with and immediately downstream of the oxidizer oven. Further downstream are a scrubber for removal of interfering sulfur constituents and a trap for removal of water vapor.

Results and discussion

Total carbon

As seen in a previous study,¹⁰ good agreement (RSDs ≤ 15%) between the total carbon (TC) values reported by all laboratories was obtained (Table 2). Mean results of thermal-optical analysis show good precision for all samples, with relative standard deviations (RSDs) ranging from 3 to 6% for the seven sample types. The between-laboratory (thermal-optical) variability seen with the filter samples is only slightly higher (≤ 2% higher) than the within-laboratory variability (Table 2) determined by analyzing portions ($n \geq 10$) of the filter at different locations (*i.e.*, across the filter). RSDs of coulometric results are more variable, ranging from 5 to 23%. The relatively wide range in precision may indicate that the variability of the coulometric method is sample-dependent (*i.e.*, depends on sample composition).

Elemental carbon

In contrast to the TC results, the EC results (Fig. 1 and Table 3) found by the two methods were highly variable. Laboratory C1 results are reported separately because it employed a relatively different thermal program (see Table 1) than that used by the other coulometric labs. The TOR method is similar to Method 5040, but this laboratory's results also are reported separately because the method defines three types of 'EC' based on the temperature at which the carbon is evolved during the second stage of the analysis. EC1 is carbon evolved at 550 °C, EC2 is that evolved at 700 °C, and EC3 is carbon evolved after 800 °C. Only total EC is reported, which corresponds to EC1 + EC2 in this case because no EC3 was found in any of the samples. EC2 results were generally much lower than EC1, so these were not reported separately.

With all filter samples, coulometric results were positively biased *relative* to thermal-optical results. In addition, the coulometric method gave a true positive bias in the analysis of OC standard solutions. About 52% and 70% of the carbon found

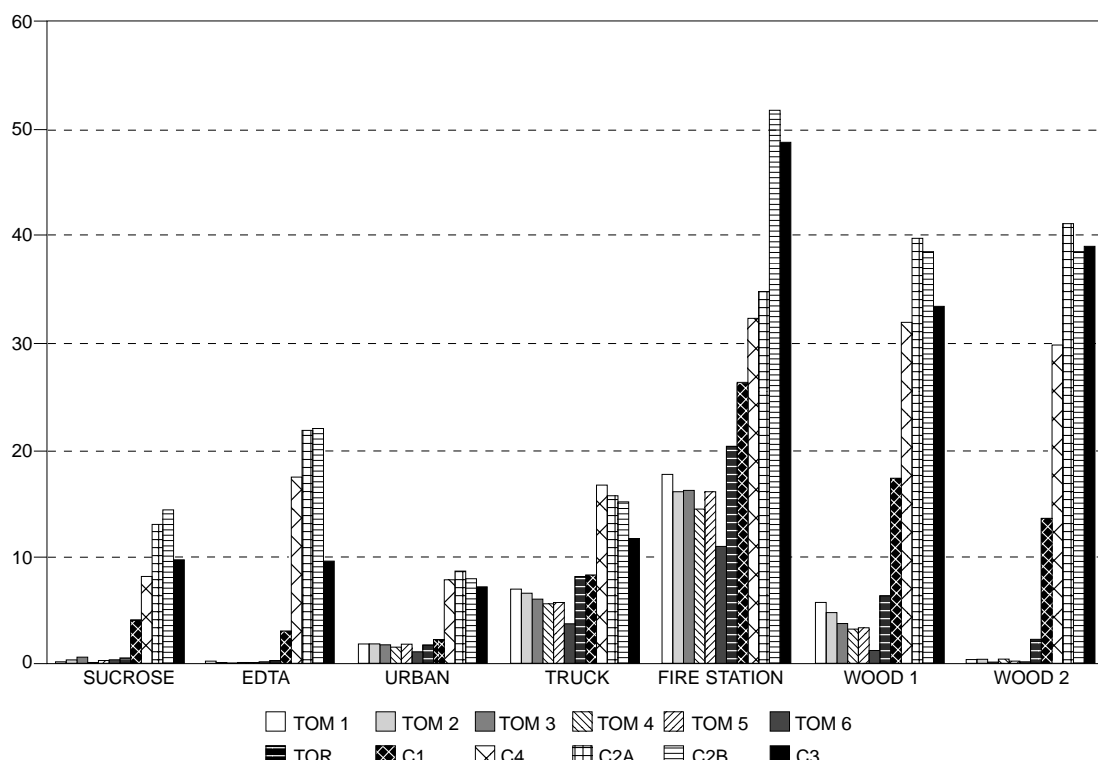


Fig. 1 Histogram of EC results ($\mu\text{g m}^{-3}$) obtained by all laboratories.

in two aqueous solutions (sucrose and EDTA, respectively) was quantified as elemental, while EC contents of about 1% and 0.1% (respectively) were found by Method 5040. The TOR method found less than 3% and 1% (respectively) for these standards, and laboratory C1 found about 22% and 11% (respectively).

In the analysis of samples containing diesel particulate (Table 2; urban, truck, and fire station samples), reasonable within-method agreement was seen (variability of thermal-optical Method 5040 ranged from 6 to 9% compared with from 9 to 23% for the coulometric method), but the between-method variability was quite high (RSDs of EC grand means ranged from 44 to 72%). Significant between-method differences also were seen with the wood smoke samples, wood1 and wood2. Only a relatively small EC fraction was found by Method 5040 (6% and 0.3%, respectively), while over half (59% and 55%, respectively) of the carbon in these samples was quantified as elemental by three of the coulometric labs. The TOR method found about 9% and 3% EC (respectively) in these samples. The EC fractions found by coulometric lab C1 were higher (24% and 17%, respectively) than those found by the thermal-optical methods, but were about 30% lower than those found by the other coulometric labs.

Mixed sample

To examine the methods' ability to discriminate against cigarette smoke, which contains very little EC, a sample containing both diesel particulate and cigarette smoke was prepared. Because the actual EC content of the sample cannot be measured directly, an indirect approach was taken. From the same filter used to collect urban particulate, 25 mm diameter portions were removed with a punch and placed into 25 mm cassettes; cassettes were then used for collection of cigarette smoke. The urban particulate sample was selected for prepara-

tion of the mixed sample because the EC loading on it was relatively low, which is when the potential interference of cigarette smoke has significance. Based on the analysis of a sample simultaneously collected on a clean filter, the carbon loading from cigarette smoke was about $90 \mu\text{g cm}^{-2}$. Loadings of this magnitude (and higher) have been found in samples collected in the trucking industry. Estimated loadings based on the differences between the TC values reported for the urban sample and the mixed sample ranged from about 47 to $107 \mu\text{g cm}^{-2}$.

If a given method effectively discriminates against cigarette smoke, the EC results pre- and post-loading (with smoke) should show reasonable agreement. Results of the analysis of the mixed samples are reported in Table 4 and are illustrated in Fig. 2. As reported previously,^{9,14} only about 2% of the carbon in cigarette smoke was measured as elemental by the thermal-optical method (5040). In contrast, a mean EC fraction of 40% was found by the coulometric method (labs C2-C4). Again, the EC content (14%) found by laboratory C1 was lower than that found by the other coulometric laboratories. No results are reported for TOR or TOM2 because samples were not available for these laboratories.

Thermal treatment

Aside from the atmosphere used (*i.e.*, helium instead of nitrogen) and optical correction feature, the thermal-optical methods' temperature programs differ from those used in the coulometric approach. This includes not only the maximum temperature reached, but also the manner in which the temperature is elevated. Specifically, the heating rate and time spent at a given temperature are different and these parameters can be critical, especially when samples are heavily loaded.

Although thermal treatments specified (Table 1) for the coulometric method imply temperature steps (*i.e.*, 2 min at 200 °C, *etc.*), when OC standards were analyzed in our laboratory with a parameter file containing the same time-temperature settings specified in Method No. 44, lower EC results (see Results and discussion, Bias) were obtained even though an optical correction was intentionally not made. This result brought into question the actual thermal profile obtained with the Coulomat instrument, so the actual temperature data were requested from one of the laboratories (C2). These data indicate that the temperature actually increases linearly from about 25 °C to about 550 °C (at $\approx 100 \text{ }^\circ\text{C min}$). In contrast, the thermal-optical techniques employ a stepped temperature profile where the time spent at each temperature is the time specified (Table 1) minus the rise time ($\approx 30 \text{ s}$) of the step.

As mentioned earlier, laboratory C2 reported results corresponding to its own protocol (results C2A) and that used by laboratories C3 and C4 (results C2B; Method No. 44 used). This was done simply by reading integrator counts at different times. To quantify OC with Method No. 44, the temperature was raised

Table 2 Round robin results: total carbon

Sample	Mean* TC (RSD)		TC grand mean† (RSD)	Variability across filter‡
	Coulometric	Thermal-optical		
Sucrose	21.95 (0.12)	21.74 (0.05)	21.82 (0.08)	—
EDTA	25.72 (0.08)	23.44 (0.05)	24.39 (0.08)	—
Urban	13.34 (0.23)	12.37 (0.06)	12.80 (0.15)	0.05
Diesel truck	24.45 (0.05)	25.11 (0.04)	24.84 (0.05)	0.02
Fire station	153 (0.06)	158 (0.03)	156 (0.05)	0.03
Wood1	61 (0.14)	68 (0.04)	65 (0.10)	0.03
Wood2	67 (0.12)	73 (0.04)	71 (0.08)	0.02

* $n = 5$ for coulometric method; $n = 7$ for thermal-optical. Filter samples reported as μg of C per cm^2 ; OC standards reported as μg C. † All labs. ‡ Within-laboratory variability (RSD) determined by thermal-optical analysis of filter portions (≥ 10) taken at different locations on the filter.

Table 3 Round robin results: elemental carbon

Sample	Mean* EC (RSD)				EC grand mean*† (RSD)
	Coulometric‡	TOM§	TOR¶	C1	
Sucrose	11.36 (0.25)	0.26 (0.80)	0.57 (0.67)	4.10 (0.24)	4.31 (1.28)
EDTA	17.69 (0.33)	0.02 (1.44)	0.20 (1.73)	3.10 (0.14)	6.74 (1.38)
Urban	7.92 (0.09)	1.80 (0.08)	3.00 (0.03)	2.30 (0.27)	4.18 (0.72)
Diesel truck	14.82 (0.15)	6.25 (0.09)	8.20 (0.02)	8.32 (0.20)	9.73 (0.44)
Fire station	42 (0.23)	16.10 (0.06)	20.27 (0.02)	26.27 (0.02)	26.77 (0.50)
Wood1	36 (0.11)	4.42 (0.26)	6.20 (0.04)	17.23 (0.20)	16.12 (0.94)
Wood2	37 (0.14)	0.30 (1.24)	2.17 (0.21)	13.43 (0.06)	13.75 (1.29)

* Filter samples reported as μg of EC per cm^2 ; OC standards reported as μg EC. TOM6 results excluded because of laser problem. † $n = 11$. ‡ Three laboratories; 4 results. § Five laboratories; NIOSH Method 5040. ¶ EC is carbon evolved after 550 °C (includes EC1 and EC2; see text).

and held at about 560 °C and the integrator counts were read at 8 min. Because about 5 min is required to reach 560 °C, only about 3 min is actually spent at 560 °C with this (Method No. 44) protocol; however, C2's protocol requires attainment of a stable signal, which was not observed with one of the samples until 22 min had elapsed (*i.e.*, 22 min since beginning the analysis). At 22 min the counts were read again, the gas was switched to oxygen and the temperature was increased (through adjustment of the knob pot) to 800 °C; about 4.5 min was required to reach 800 °C. Upon reaching 800 °C, the TC counts were read (27 min elapsed time) and the corresponding EC values (TC-OC) were listed as those obtained by Method No. 44 (C3 and C4 protocol). For the C2 protocol, the oven temperature was then increased from 800 °C to a final temperature of 1000 °C, where the temperature was held until a stable count was obtained (a total of 70 min was required for the same sample).

Laboratory C2 uses a different thermal program than laboratories C3 and C4 because 4 min at 550 °C has not been

adequate for the removal of all OC from the samples it has analyzed, particularly with high filter loadings. For the same reason, it raises the temperature to 1000 °C for removal of EC. Results obtained by our laboratory (NIOSH), and by other laboratories using NIOSH Method 5040, demonstrate that this is the case. Samples collected in mining environments in particular have typically required about 4 min at 940 °C for removal of all EC; however, no sample has required 40 min at 1000 °C. The amount of time required at this temperature is suspect, especially in view of the 100% oxygen atmosphere employed (coulometric method) and the fact that comparable results (except for fire station sample) were obtained by the two different protocols (C2A and Method No. 44). Instrument noise/drift rather than analyte evolution may have been responsible for a nonconstant signal.

Bias

The positive bias in the EC results obtained by the coulometric method in the analysis of the OC standards is largely attributed to incomplete removal of OC; lack of an optical correction for char also is a factor. With respect to the thermal treatment, the higher results are not exclusively due to the lower maximum temperature used (≈ 550 °C) relative to Method 5040 (≈ 850 °C). For example, lower results were obtained by our laboratory when analyzing a sucrose standard solution with the temperature program specified for laboratory C3 (Table 1). Although more time was spent at each temperature (TOM program is stepped), a lower EC result (≈ 3 μg) was obtained even when all of the carbon evolving after 400 °C (as opposed to 550 °C) was *defined* as elemental (EC redefined by overriding the transmittance-based OC-EC split). This result is comparable to that obtained by laboratory C1 (≈ 4 μg), which reportedly raised the temperature to 800 °C during the first part of the analysis. Further, as do laboratories C3 and C4 (Method No. 44), the TOR laboratory also raises the temperature to 550 °C in the first part of the analysis, and it was held at 550 °C for about 10 min (as opposed to ≈ 17 min with the C2 protocol), yet EC results obtained by TOR analysis also were much lower than those obtained by the coulometric method. The duration of the first part of the analysis was similar with the two methods (about 22 min with C2 protocol; about 23 min with TOR protocol), so differences cannot be explained by time alone.

Because no increase in filter transmittance was seen during the first stage (helium only) of the thermal-optical analysis of the filter samples, use of a higher maximum temperature during this stage did not appear to cause loss of EC. This implies that the EC results obtained with the coulometric method are positively biased. Elevating the maximum temperature of the thermal program (C1 protocol) gave better agreement with the thermal-optical methods.

Precision

Organic and elemental carbon results for the three filter samples containing diesel particulate are listed in Table 5. In general, good precision was obtained with the thermal-optical methods (TOR and TOM). The RSDs of the OC and EC results are less than 6% in all cases (34 results total) except for two TOM4 results (9% for OC in fire station sample; 11% for EC in truck sample) and one TOM2 result (11% for OC in truck sample). Results obtained by laboratories using the alternative method are more variable. The RSDs of 19 results (out of 30 total) range from 2–10%, seven results are between 10% and 25%, and four results have RSDs above 25%. In the last group (*i.e.*, RSDs > 25%), outliers may be responsible for the high variability seen in two instances (C3 and C4 results for EC in urban sample) as one of the results reported was much higher than the others; however, no explanation for the odd (high) value was provided.

Table 4 Round robin results: urban particulate and cigarette smoke

Laboratory	Carbon loading*/ $\mu\text{g cm}^{-2}$						EC fraction of CSC† (%)
	TC1	TC2	CSTC	EC1	EC2	CSEC	
C3‡	14.75	91.30	76.55	7.20	49.90	42.70	56
C4§	17.53	64.00	46.47	7.83	28.00	20.17	43
C2A¶	12.93	82.53	69.60	8.68	29.03	20.35	29
C2B¶	11.94	74.44	62.50	7.96	28.94	20.98	34
C1	9.53	95.90	86.37	2.30	14.70	12.40	14
TOM1	12.94	99.64	86.70	1.94	3.31	1.37	1.6
TOM3	12.14	96.93	84.79	1.80	3.75	1.95	2.3
TOM4	10.97	82.42	71.45	1.57	2.78	1.21	1.7
TOM5	12.06	113	101	1.83	3.86	2.03	2.0
TOM6	13.61	121	107	1.18	1.52	0.34	0.3

* TC1 and TC2 are total carbon loadings before and after collection of cigarette smoke onto the urban sample. CSTC is the cigarette smoke total carbon estimated as TC2 - TC1. EC1, EC2 and CSEC are defined similarly but apply to elemental carbon. † EC fraction of cigarette smoke carbon.

‡ TC1 and EC1 values based on two of three results reported. § TC1 and EC1 values based on three of four results reported. ¶ Laboratory C2 reported two sets of data; C2A data obtained with its analytical protocol, C2B data obtained with Method No. 44¹³ protocol (see Table 1 and text).

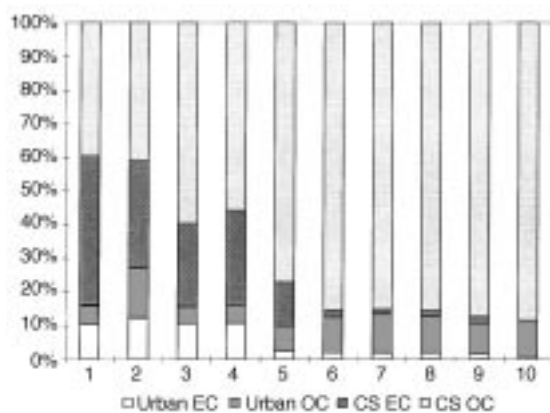


Fig. 2 Plot of EC-OC data for urban sample loaded with cigarette smoke. Urban EC and OC percentages are based on analysis of a separate (unloaded) portion of the same filter. Cigarette smoke EC and OC were calculated as discussed in Table 5 and related text. Results 1–4 obtained by the coulometric method [laboratories C3, C4, C2 (A and B), respectively]. Results 5 obtained by laboratory C1 (coulometric instrument, different thermal program). Results 6–10 obtained by thermal-optical method (TOM laboratories 1, 3, 4, 5, 6).

Table 5 EC and OC results* for three filter samples containing diesel particulate

	Mean carbon/ $\mu\text{g cm}^{-2}$ (RSD) [†]					
	Urban		Truck		Fire station	
	OC	EC	OC	EC	OC	EC
C3	8.50 (0.21)	9.60 (0.43)	14.77 (0.16)	11.70 (0.23)	107 (0.04)	48.73 (0.05)
C4	9.60 (0.28)	11.25 (0.61)	8.03 (0.13)	16.70 (0.10)	111 (0.12)	32.27 (0.02)
C2A [‡]	4.25 (0.08)	8.68 (0.08)	8.38 (0.03)	15.73 (0.08)	115 (0.04)	34.88 (0.02)
C2B [‡]	3.97 (0.03)	7.96 (0.10)	8.04 (0.09)	15.14 (0.03)	96 (0.02)	51.57 (0.06)
C1	7.23 (0.11)	2.30 (0.27)	15.17 (0.07)	8.32 (0.20)	141 (0.05)	26.27 (0.02)
TOR	9.70 (0.03)	3.00 (0.03)	17.33 (0.02)	8.20 (0.02)	136 (0.02)	20.27 (0.02)
TOM1	11.00 (0.06)	1.94 (0.05)	17.84 (0.02)	7.05 (0.06)	144 (0.02)	17.05 (0.02)
TOM2	11.12 (0.03)	1.85 (0.04)	19.28 (0.11)	6.66 (0.02)	139 (0.02)	16.17 (0.04)
TOM3	10.34 (0.05)	1.80 (0.03)	17.15 (0.06)	6.10 (0.05)	136 (0.02)	16.17 (0.01)
TOM4	9.40 (0.06)	1.57 (0.05)	19.47 (0.04)	5.64 (0.11)	145 [§] (0.09)	14.41 [§] (0.04)
TOM5	10.23 (0.03)	1.83 (0.06)	18.64 —	5.81 —	135 (0.01)	16.68 (0.06)

* TOM6 data excluded because of laser problem. [†] All samples analyzed in triplicate except laboratory C4, which performed four analyses on filter portions. [‡] Laboratory C2 reported two sets of data; C2A data obtained with its analytical protocol, C2B data obtained with Method No. 441³ protocol (see Table 1 and text). [§] Excludes one of three results because sample portion was dropped.

Conclusion

The primary objective of this interlaboratory comparison was to further evaluate NIOSH Method 5040. A round robin on Method 5040 was not conducted when the method initially was evaluated because only one instrument was available. More recently, additional instrumentation was constructed by a private laboratory,¹¹ and this made further evaluation of the method possible. Because the method can be applied not only for the analysis of diesel particulate samples, but also for other complex carbonaceous aerosols, a variety of materials were analyzed. In spite of the complex nature of the samples, good interlaboratory agreement was seen.

A comparison also was made between the thermal-optical method (includes Method 5040 and a similar method) and another thermal (coulometric) technique being used in Europe for analysis of diesel particulate. The higher EC results obtained by the coulometric method were expected for some samples (*e.g.*, smokes) because a different thermal program is employed, but significant disagreement in the results obtained for two of the diesel particulate samples (fire station and diesel truck) was not expected. The samples were collected at work sites where diesel equipment was operating. No obvious nondiesel sources of OC were present at the fire station or the loading dock area where the truck sample was collected. The urban sample contained diesel exhaust (from trucks and air compressors) and other vehicular exhausts, as well as a small amount of carbonate, so between-method differences were expected for this sample. In the case of the former two samples, evolution of OC after 560 °C was observed during thermal-optical analysis. This OC profile differs from that usually observed with diesel particulate samples collected in mining environments, which typically have relatively little OC that is evolved after 550 °C. Better agreement may be obtained in the analysis of samples from mining environments, where diesel engines are often the major contributor to airborne carbon. Obviously, this will not be the case in some mines (*e.g.*, coal mines) unless an appropriate sampler is used to exclude other carbon sources. Sampling requirements in the mining industry are discussed elsewhere.¹⁵

Although better between-method agreement may be found with some sample types (*e.g.*, laboratory-generated diesel soot) and in some occupational settings, it is important to examine a variety of workplaces because no single one is representative of all. Differences between the two methods can be expected whenever a sample contains organic material that requires high temperature for removal (*e.g.*, cigarette smoke, oil mists). This can occur often in occupational settings because the delineation

between workplace and environmental sources is not always a clear one. Further, even when no other sources of OC are present, differences in the equipment type, engine operation mode (speed, load), fuels, additives used (*e.g.*, biocides), maintenance schedules all contribute to the nature of the exhaust particulate.

In principle, any reliable OC-EC method should not indicate a significant amount of EC in a purely OC standard. Whether or not a positive bias (relative to a thermal-optical approach) is seen with an alternative (*e.g.*, coulometric) technique will depend on the nature of the sample. With respect to occupational monitoring of diesel particulate in particular, it is important to have as specific an exposure marker as possible. In this regard, thermal-optical methods are superior because the temperature program and optical feature maximize selectivity in the analysis. Further, the analysis procedure and data reduction are automated, so manual recordings and adjustments (*e.g.*, integrator counts, temperature settings) are unnecessary.

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References

- 1 IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Diesel and Gasoline Exhausts and Some Nitroarenes. International Agency for Research on Cancer, Lyon, France, World Health Organization, 1989, vol. 46.
- 2 NIOSH Current Intelligence Bulletin No. 50: Carcinogenic Effects of Exposure to Diesel Exhaust, National Institute for Occupational Safety and Health, Cincinnati, OH, DHHS (NIOSH) Publication No. 88-116, 1988.
- 3 American Conference of Governmental Industrial Hygienists (ACGIH), Notice of Intended Changes, 1996-1997 (also see draft TLV document).
- 4 US Environmental Protection Agency, Health Assessment Document for Diesel Emission, EPA/600/8-90/057A (External Review Draft, 1993), Office of Health and Environmental Assessment, Environ-

- mental Criteria Assessment Office, Research Triangle Park, NC, 1993.
- 5 California Environmental Protection Agency, *Health Risk Assessment for Diesel Exhaust (Draft)*, Office of Environmental Health Hazard Assessment, Sacramento, CA, 1994.
 - 6 World Health Organization, *Environmental Health Criteria 171: Diesel Fuel and Exhaust Emissions*, World Health Organization, Geneva, 1996.
 - 7 Health Effects Institute, *Diesel Exhaust: A Critical Analysis of Emissions, Exposure, and Health Effects*, A Special Report of the Institute's Diesel Working Group, Health Effects Institute (HEI), Cambridge, MA, 1995.
 - 8 NIOSH, Elemental Carbon (Diesel Particulate): Method 5040. in *NIOSH Manual of Analytical Methods, 4th ed. (1st Supplement)*, ed. Eller, P. M., and Cassinelli, M. E., National Institute for Occupational Safety and Health, DHHS (NIOSH), Cincinnati, OH; Publication No. 96-135, 1996.
 - 9 Birch, M. E., and Cary, R. A., *Aerosol Sci. Technol.*, 1996, **25**, 221.
 - 10 Countess, R. J., *Aerosol Sci. Technol.*, 1990, **12**(1), 114.
 - 11 Sunset Laboratory, Forest Grove, OR, USA.
 - 12 Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G., *Atmos. Environ.*, **27A**, 1185.
 - 13 ZH 1/120.44 (1995) Von der Berufsgenossenschaften anerkannte Analysenverfahren zur Feststellung der Konzentrationen krebserzeugender Arbeitstoffe in der Luft in Arbeitsbereichen. Method No. 44: Diesel Engine Emission. Carl Heymanns Verlag, Köln.
 - 14 Zaebst, D. D., Clapp, D. E., Blade, L. M., Marlow, D. A., Steenland, K., Hornung, R. W., Scheutle, D., and Butler, J., *Am. Ind. Hyg. Assoc. J.*, 1991, **52**(12), 529.
 - 15 NIOSH, Elemental Carbon (Diesel Particulate): Method 5040, in: *NIOSH Manual of Analytical Methods, 4th ed. (2nd Supplement)*, ed. Eller, P. M., and Cassinelli, M. E., National Institute for Occupational Safety and Health, DHHS (NIOSH), Cincinnati, OH; 1998 (pre-publication copy of method available from this paper's author).

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