Q. MONITORING OF DIESEL PARTICULATE EXHAUST IN THE WORKPLACE

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1. INTRODUCTION

a. Health Effects

In the United States alone, over a million workers (e.g., trucking, mining, railroad, agriculture) are occupationally exposed to diesel exhaust [1]. The widespread and growing use of diesel-powered equipment has raised concern because workers exposed to diesel exhaust show an elevated (20% to 50%) risk of lung cancer [2]. While environmental exposure is a concern, occupational exposure is a greater one because workplace exposures to diesel exhaust are generally much higher. The National Institute for Occupational Safety and Health (NIOSH) considers diesel exhaust a potential occupational carcinogen and recommends that employers reduce workers' exposures [1]. This [1988] recommendation was based on five independent animal studies in which rats exposed to unfiltered exhaust showed an increased incidence of benign and malignant lung tumors [3]. Other organizations, including the International Agency for Research on Cancer (IARC) [3], the World Health Organization (WHO) [4], the California Environmental Protection Agency [5], the U.S. Environmental Protection Agency (U.S. EPA) [6], and the National Toxicology Program [7] have reviewed the animal and human evidence, and each has classified diesel exhaust as a probable human carcinogen or similar designation.

Noncancer health effects have also been associated with diesel exhaust exposure, including immunologic, respiratory, and cardiovascular effects. Diesel exhaust particles can act as nonspecific airway irritants at relatively high exposures. At lower levels, they can trigger release of mediators (cytokines, chemokines, immunoglobulins, and oxidants) of allergic and inflammatory responses [8]. Diesel particles may promote expression of the immunologic response phenotype (Th2) associated with asthma and allergic disease and appear to have greater immunologic effects in the presence of environmental allergens. Internationally, the prevalence of asthma (and related hospitalizations and mortality) continues to rise in adults and children. Children may be more vulnerable than adults [9-12]. Studies indicate children living along major trucking thoroughfares are at increased risk for asthmatic and allergic symptoms. In the United States, the number of individuals with self-reported asthma increased by 75% from 1980 to 1994 [13]. The immunologic evidence is consistent with results of epidemiologic studies that associate traffic-related air pollution, especially diesel exhaust particles, to an increase in respiratory diseases.

Studies have consistently found positive associations between particulate air pollution and daily mortality [14–23]. The traditional U.S. air quality standard for particulate matter is based on particles having diameters $\leq$ 10 µm (PM_{10}) [24]. In 1997, EPA proposed a new standard (see http://www.epa.gov/airlinks/airlinks4.html) based on particles having diameters $\leq$ 2.5 µm ($PM_{2.5}$). These smaller particles originate mainly from combustion sources. The new standard was proposed because recent studies show higher correlation between fine particle pollution and adverse health effects. In an analysis [19] of data from six U.S. cities, fine particles were consistently associated with increased risk of death from chronic obstructive pulmonary disease, pneumonia, and ischemic heart disease. Positive associations between fine particle pollution and hospital admissions due to respiratory and cardiovascular illness also have been found [25–27]. Particles produced by combustion sources have been implicated in these findings. In addition to asthma, chronic inhalation of diesel exhaust particles may play a role in these adverse health outcomes. Comprehensive reviews on the health effects of diesel exhaust can be found elsewhere [1-7, 28, 29].

b. Composition

Diesel engine exhaust is a highly complex and variable mixture of gases, vapors and fine particles. The amount and composition of the exhaust vary greatly, depending on factors such as fuel and engine type, maintenance schedule, tuning, workload, and exhaust gas treatment. The gaseous constituents include hydrocarbons and oxides of carbon, sulphur, and nitrogen. Particulate components consist of liquid droplets and soot particles bearing organic compounds, sulfates, metals and other trace elements. The organic fraction (droplets and particle adsorbed) is mainly unburned fuel and oil, but also contains thousands of compounds (e.g., aldehydes; polycyclic aromatic hydrocarbons [PAH])—some of which are genotoxic. Detailed information on the composition of diesel exhaust has been published previously [1-4, 28].

c. Analyte Choice

Because diesel exhaust is a highly complex mixture, a surrogate of exposure must be selected. In the early nineteen-nineties, NIOSH researchers considering potential surrogates sought an overall measure of the particulate fraction because animal studies linked lung tumor induction to unfiltered diesel exhaust [1,3], and most (90% in one study) [30] of the exhaust's mutagenic potency was associated with the particulate fraction. At the time, gravimetric methods for respirable combustible and submicrometer dusts were being used in mines, but gravimetric methods lack selectivity and are not suitable for low-level (e.g., < 200 µg/m^3) measurements. Methods for characterization of the soluble organic fraction of diesel particulate matter also were available; others have since been developed. Although measurement of specific organic compounds, particularly genotoxins, may be relevant in characterizing the potential toxicity of diesel exhaust, a single compound or compound class would not reflect exposure to the particulate fraction—even if unique markers are found—because the composition of the exhaust is highly variable.

Carbon is a logical exposure surrogate to monitor because diesel particulate matter is predominantly (typically more than 80%) carbon [31-33], but carbon in the organic fraction (i.e., *organic carbon,* or OC) of diesel particulate matter is not a selective measure because other sources of OC (e.g. cigarette smoke and other combustion aerosols, asphalt fumes) are present in many workplaces.

Elemental carbon (i.e., carbon in the soot particle core, or EC) is a better surrogate [34] to monitor because it is a more selective measure of particulate diesel exhaust and still constitutes a sizable fraction (30%–90%) (see reference [28], Part I, Section 1) of the particulate mass. Fine EC particles are derived primarily from the combustion of fossil fuels, and diesel engines are major sources of these particles. Carbonaceous aerosols such as cigarette and wood smokes contain little, if any, EC [34, 35]. Gasoline engines emit far less EC than diesels, so the contribution of this source is relatively small. Other sources such as coal combustion, incinerators, and tire debris can contribute to the background (environmental) levels of EC, but diesel engines are the primary emitters (see reference [2]: Sawyer and Johnson; Cass and Gray). In occupational settings, where diesel equipment is used in relatively close proximity to workers, the contribution of these remote sources is negligible, especially when EC levels are well above background. Environmental EC concentrations typically range from about 1–3 µg/m^3 [34]; workplace levels are generally much higher [36–43]. Although higher background levels (near 5 µg/m^3) have been reported for more polluted U.S. cities (e.g., Los Angeles), the higher levels were attributed to diesel vehicles [44, 45] (see also reference [2], Cass and Gray). At one monitoring site (Glendora, CA), examination of the data collected at 1-minute intervals revealed that emission plumes from diesel vehicles located 50 meters from the site contributed up to 5 µg/m^3 above the background level [46].

Materials such as coal dust contain EC (content depends on coal rank), but mechanically generated particles are larger (generally > 1 µm diameter) than combustion-based particles. Therefore, coal dust, and other mechanically generated dusts, can be effectively excluded from the diesel sample on the basis of size. Only low levels of EC ($\leq$ 15 µg/m^3) were found in electric-powered (i.e., nondieselized) coal mines when impactors with submicrometer cutpoints were used for air sampling [47]. Guidance on air sampling is discussed in a following section.

In addition to selectivity, potential health effects were considered when an EC surrogate was proposed [34, 48, 49]. Diesel particles and other types of insoluble fine particles are inhaled deeply into the lungs, where they can induce an inflammatory response. Further, EC particles increase the long-term retention [50, 51] of adsorbed genotoxins and other chemical toxins because the particles have a high affinity for them [52]. The adsorbed organic fraction results from rapid cooling of the exhaust mixture, which causes enrichment of some species on the particle surface [53–55]. Enrichment by this mechanism is associated with compounds of moderate to low volatility [54, 55]. For example, PAHs having four or more rings are generally associated with particulate matter [56]; this is important because these higher-ring condensates are expected to be the most carcinogenic or mutagenic [57, 58]. In combination with an inflammatory response induced by the particles, genotoxic agents may promote tumorigenesis. Ultrafine particles (< 0.10 µm) may pose an even greater health risk. Results of toxicological studies on solid particles having aerodynamic diameters in this size range indicate ultrafine particles are especially toxic, even those not having an organic fraction and consisting of materials considered relatively nontoxic (e.g., carbon black, titanium dioxide). In a recent study (see reference [23], Donaldson et al.) of rats, a 10-fold increase in inflammation was seen with exposures to ultrafine particles, relative to the same mass of fine particles. This is significant because, by mass, the majority of diesel particles are in the fine particle range, and most are in the ultrafine range by number (see reference [28], Kittleson et al.). Given the physical and chemical nature of EC particles emitted by diesel engines, monitoring and controlling exposures to these particles is prudent.

2. ANALYTICAL METHOD

a. Background

A monitoring method for diesel particulate matter was published as Method 5040 in the NIOSH Manual of Analytical Methods (NMAM). The method is based on a thermal-optical analysis technique for particulate carbon. Both OC and EC are determined by the method, but EC is a better surrogate of exposure. Rationale for use of an EC surrogate is summarized in the previous section (see Analyte Choice). Method updates have been published [59, 60] to include data (e.g., round robin results) obtained since the initial publication (1996) of the method. NMAM 5040 has been used in numerous industrial hygiene surveys, [36–43] and it was recently applied to an ongoing epidemiological study (NIOSH/National Cancer Institute [NCI]) of miners. Details on method operation and performance are provided in this chapter. Recently proposed exposure criteria also are discussed.

b. Instrumentation

Of the possible approaches for OC-EC analysis, a thermal-optical technique was investigated because it offers greater selectivity (a pyrolysis correction for char) and flexibility (automated analysis, programmable parameter files) than previously used methods. While thermal-optical methods have not been widely used in the industrial hygiene field prior to its proposed use for diesel exhaust monitoring, they have been routinely applied to environmental monitoring of particulate carbon air pollution.

The thermal-optical analyzer has been described previously [34, 59]. Design improvements have since been made, but the operation principle remains unchanged. The analyzer (Figure 1) is equipped with a pulsed diode laser and photodetector that permit continuous monitoring of the sample filter transmittance. This optical feature corrects for the char formed during the analysis of some materials. As in samples where EC is initially present, char strongly absorbs light, particularly in the red/infrared region. Char is formed through pyrolysis, which is a thermal decomposition process. When some organic substances are heated to elevated temperatures in an inert (non-oxidizing) atmosphere, carbonization (conversion to carbon) occurs. Both volatile products and char (decomposition product containing mostly carbon) are formed in the process, which can begin at temperatures as low as 300 °C.

In the thermal-optical analysis, a filter portion (punch) of known area (typically 1.5 cm^2) is placed in the sample oven, and the oven is tightly sealed. Quartz-fiber filters are required because temperatures in excess of 850 °C are employed. The analysis proceeds in inert and oxidizing atmospheres. In both, the evolved carbon is catalytically oxidized to carbon dioxide (CO_2). The CO_2 is then reduced to methane (CH_4), and CH_4 is quantified with a flame ionization detector (FID).

OC (and carbonate, if present) is first removed in helium, as the temperature is increased to a preset maximum (about 870 °C, NMAM 5040). If charring occurs, the filter transmittance decreases as the temperature is stepped to the maximum. After OC is removed, an oxygen-helium mix is introduced to effect combustion of the remaining material. As light-absorbing carbon is oxidized from the filter, the filter transmittance increases. The split (Figure 2) between the OC and EC is assigned when the initial (baseline) value of the filter transmittance is reached. All carbon removed before the OC-EC split is considered organic, and that removed after the split is considered elemental. If no charring occurs, the split is assigned prior to removal of light-absorbing carbon. If the sample chars, the split is not assigned until enough light-absorbing carbon is removed to bring the transmittance back up to its initial value. In general, char is more readily oxidized than diesel-particle EC. The delay (i.e., the transit time from sample to FID) between the laser and FID signals is considered in the split assignment. Ordinarily, the split is assigned in the oxidative mode of the analysis.

EC and OC results are reported in micrograms per square centimeter ($\mu g/cm^2$) of the sample deposit. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous deposit is assumed. For triplicate analyses, the precision (relative standard deviation) is normally under 5%, and it is typically

2% or better [60]. The total carbon (TC) in the sample is the sum of OC and EC. If carbonate is present, the carbon in it is quantified as OC, unless a carbonate-subtracted value is requested by the client. Additional details about carbonates are given in a following section.

c. Standards

Currently, a reference material is not available for determining the OC and EC content of a complex carbonaceous aerosol. For this reason, only the accuracy of the method in the determination of TC could be examined. No discernable differences in the responses of five different organic compounds were noted. Linear regression of the data (43 analyses total) for all five compounds gave a slope and correlation coefficient (r) near unity [slope = 0.99 (± 0.01), $r^2 = 0.999$, $n = 43$]. In addition to the OC standards, eight different carbonaceous materials were analyzed. Three different methods (including the thermal-optical method) were used, and laboratories reported the TC contents of the samples. The samples analyzed included diesel particulate matter and other types of carbonaceous matter (coals, urban dust, humic acid). Thermal-optical results agreed well with those reported by the two other laboratories. The variability in TC results for the three laboratories ranged from about 1%–7%. These findings [34, 59] indicate that the carbon in a sample is accurately quantified, irrespective of sample type.

To estimate the method's limit of detection (LOD), a set of low-level calibration standards (ethylenediaminetetraacetic acid [EDTA]) was analyzed [34, 59]. The standards covered a loading range from 0.23 to 2.82 µg C (or from 0.15 to 1.83 µg C per cm^2 of filter). Results of linear regression of the low-level calibration data were then used to calculate a LOD as $3\ \sigma_y/m$, where σ_y is the standard error of the regression and m is the slope of the regression line. The LOD estimated through the linear regression results was 0.24 µg C, or 0.15 µg/cm^2. This value showed good agreement with the LOD estimated as $3\sigma_{blank}$ (three times the standard deviation for blanks), which gave a value of about 0.3 µg C. The mean ($n = 40$) instrumental blank was 0.03 ± 0.1 µg C. With a 960-L air sample collected on a 37-mm filter and use of a 1.5 cm^2 sample portion, this LOD translates to an air concentration of about 2 µg/m^3. As with all analytical methods, the LOD is a varying number. Other values can be expected, depending on the individual instrument and means by which the LOD is calculated.

d. Air Sampling

In the initial evaluation of the thermal-optical method, a set of laboratory-generated air samples was analyzed. A dilution tunnel equipped with a dynamometer was used for generation of diesel particulate samples. Four EC concentrations, ranging from 23 to 240 µg/m^3 (EC loadings from 2.7 to 27 µg/cm^2), were generated. The analytical results [59] indicated that the method met the NIOSH accuracy criterion [61]. The variance was roughly proportional to the mean concentration; therefore, the relative standard deviation (RSD) decreased with increasing concentration. The accuracy was calculated accordingly. The accuracy was ± 16.7% at the lowest loading (2.7 µg/cm^2), with an overall precision (RSD) of 8.5%. On the basis of a method evaluation, the NIOSH accuracy criterion requires a confidence limit on the accuracy less than 25% at the 95% confidence level. Restated, the criterion dictates that greater than 95% of the measurements fall within ± 25% of the true value at 95% confidence in the method's validation experiments. The method was considered unbiased (i.e., considered the reference method), and the overall precision reflected method accuracy. Sample generation and collection, not analysis, was the main source of variability.

When only combustion-source EC is present, different samplers can be expected to give comparable EC results because particles from combustion sources are generally less than 1 µm (diameter). As such, the particles are evenly deposited on the filter and collected with the same efficiency (near 100%). To confirm this assumption, seven different sampler types (open-faced 25-mm and 37-mm cassettes; 298 personal cascade impactor [7 stages, 0.9-µm cutpoint]; 4 prototype impactors) were used to collect diesel aerosol at the loading dock of an express mail facility. The RSD for the mean EC concentration was 5.6% [39]. Based on the 95% confidence limit (19%; 13 degrees of freedom, n =14) on the accuracy, results of this experiment also indicated that the NIOSH accuracy criterion [61] was fulfilled. The amount of EC collected (240 µg per sample) would have been equivalent to sampling an air concentration of 250 µg/m^3 for 8 h at 2 L/min. Variability in the OC results was higher (RSD = 12.3%), which is to be expected when different samplers are used to collect aerosols that contain semivolatile (and volatile) components because these can have a filter face velocity dependence.

Similar performance was obtained from collected samples in an underground molybdenum mine. Five different sampler types were used (closed-face 25-mm and 37-mm cassettes; 298 cascade impactor [7 stages, 0.9-µm cutpoint]; cyclone with filter; in-house impactor). The RSD for the EC results (mean EC = 297 µg/m^3) was 7%. The EC deposits obtained with all five sampler types were homogeneous, even when the ore deposit was visually heavier in the center of the filter (e.g., with the closed-face 37-mm cassette). Although the dust loading was higher in the center of the filter, portions taken from the center gave equivalent EC results, indicating the ore contained no EC component. The TC results for the center portions were only slightly higher, so this particular ore was mostly inorganic. EC concentrations found with three different sampler types (nylon cyclone, open-faced cassette, and impactor with sub-micrometer cut) also were comparable in a study of railroad workers [42].

If high levels of other dusts are present, a size classifier (e.g., impactor and/or cyclone) should be used to prevent filter overloading, particularly if the dust is carbonaceous. In the latter case, a size classifier provides a more selective measure of the diesel-source OC. It also provides a better measure of the diesel-source EC if the dust contains an EC component, which is less common. A finely ground sample of the bulk material can be analyzed to determine whether a specific dust poses potential interference [34]. Depending on the dust concentration, size distribution, and target analyte, an impactor may be required.

For mines, the Mine Safety and Health Administration (MSHA) recommends a specialized impactor to minimize collection of carbonates and other carbonaceous dusts [62]. An impactor can greatly improve the selectivity of the TC measurement in some cases, but it may exclude a small amount of the diesel particulate matter. Then, too, some OC interferences cannot be excluded on the basis of size (e.g., condensation aerosols, fumes, wood and cigarette smokes). If present in the sampling environment, these materials can positively bias the OC (TC) results to some degree, depending on their relative concentrations and the sampling location. Although a 37-mm cassette is often suitable for general industry, the sampler required must be dictated by the sampling environment.

e. Carbonates

The presence of carbonate is indicated by a narrow peak during the fourth temperature step in helium (Figure 2). Its presence is verified by exposing a second portion of the filter to hydrogen chloride (HCl) vapor prior to analysis. When the acidified portion is analyzed, a diminished (or absent) peak during the fourth temperature step is indicative of carbonate in the original sample. (Note: Acid treatment may sometimes alter the appearance of the EC profile in the thermogram [output signal of thermal-optical instrument], but the EC result itself should not be affected significantly.)

A desiccator containing concentrated HCl (added to the desiccator or a petri dish placed at the bottom of it) can be used to acidify the sample portions. The desiccator, or alternative vessel, should be used in a well-ventilated hood. The filter portions are placed on the desiccator tray, and the tray is placed in the desiccator. A wetted pH indicator stick can be used to check acidity. A wetted indicator stick inserted between the desiccator lid and base should give a pH near 2. Portions should be exposed to the acid vapor for about 1 hour (large particles can require more time). After acidification, the tray is placed on a clean, inert surface inside the hood. The residual acid on the portions should be allowed to volatilize in the hood for at least an hour prior to analysis.

Environmental samples typically contain little (if any) carbonate, but levels in some occupational samples can be quite high. For example, respirable dust samples collected in limestone and trona mines can contain high levels of calcium carbonate and sodium sesquicarbonate, respectively. In such cases, acidified samples give a better measure of the diesel-source OC (TC). If the carbonate loading is relatively high (e.g., carbonate carbon > 10% of the TC), the difference between the TC results (before and after acidification) gives an estimate of carbonate carbon (CC). Estimation of CC by difference assumes the carbonate is evenly deposited on the filter, which may not always be the case. It also assumes that OC loss through acidification is negligible. The latter assumption is generally true for workplace samples, but depends on sample composition and loading.

Alternatively, a carbonate-subtracted OC (TC) result can be obtained through separate integration of the carbonate peak. This applies only to carbonates (e.g., calcium carbonate) that can be removed as a single peak during the fourth temperature step in helium. The carbonate of interest should be analyzed to ensure this is the case. A minor adjustment (lower) to the third temperature step may be necessary to prevent partial loss during this step. Sodium sesquicarbonate (trona) is removed over multiple temperature steps. Samples containing trona should be acidified if a carbonate-subtracted result is desired. (Note: *At elevated temperature, trona and other compounds containing sodium can etch the quartz oven wall and sample holder. An etched surface can reduce laser throughput. Avoid direct contact of these materials with the oven wall and sample holder.)*

The presence of a small ‘peak’ during the fourth temperature step is not necessarily due to carbonate. Other carbonaceous matter (e.g., char) is sometimes removed during the fourth step. Unlike carbonates, which produce a relatively sharp peak, other materials typically evolve as a small, broad peak. If determination of relatively low (e.g., CC < 10% of TC) amounts of CC is desired, a second portion of the sample should be acidified and analyzed to verify the presence of carbonate and reveal any underlying baseline features contributed by other materials. A more accurate estimate of CC can then be obtained by integrating the first (non-acidified) sample over the missing peak area (i.e., area removed through acidification).

f. Sampling Artifacts: Organic Aerosol

Face velocity. Quartz-fiber filters are routinely used to collect airborne particulate matter for carbon determination. Quartz filters have high collection efficiency for particulate carbon, but collection of organic aerosol is artifact prone [63–67]. Particulate carbon (EC and nonvolatile OC) results should not depend on filter face velocity. This is true for EC, but OC (and TC) results can have a face velocity dependence due to sampling artifacts. Namely, adsorption of organic vapor can positively bias the results, while evaporative losses have the opposite effect. Although both processes may occur, recent studies indicate vapor adsorption is the dominant artifact [65, 67]. In one study [65], the OC (TC) results for air samples collected at face velocities of 20, 40, and 80 cm/sec had a face velocity dependence before, but not after, correction for adsorbed vapor. Lack of dependence after correction supports adsorption as the dominant artifact. At the much lower face velocities typical of occupational monitoring (e.g., about 4 cm/sec with a 37-mm filter and 2 L/min flow rate), OC losses induced by pressure drop across the filter are expected to be minor relative to adsorption. OC sampling artifacts were acknowledged when the thermal-optical method was proposed [48, 49], but this issue was not investigated prior to publication of NMAM 5040 because an EC surrogate was recommended. In view of the MSHA-proposed air standard for TC, and the fact that both OC and EC are determined by the method, the issue has since been addressed.

Adsorbed OC. Correction for adsorbed organic vapor through use of traditional blanks (media or field) may not be accurate because the amount of vapor adsorbed by them is variable [68]. More importantly, traditional blanks collect vapor passively, while the samples collect it actively (during sampling). A more representative correction for adsorbed organic vapor can be made through use of two filters in tandem [65, 67]. The air sample is collected with a sampler containing a Teflon or quartz upper filter and a bottom quartz filter. After sampling, the bottom filter is used to correct for adsorbed vapor. The vapor adsorbed on the bottom filter more closely represents that adsorbed on the sample filter (quartz) because both are collected actively. Use of two quartz filters is preferable to Teflon and quartz because the filter used to correct for adsorbed vapor is in the same sampler; however, the second (bottom) quartz filter may underestimate the amount of adsorbed OC relative to a quartz filter under Teflon [65, 67]. These results have been attributed to depletion of the vapor concentration by the top quartz filter, which presents a lower concentration to the bottom one. A shorter equilibration time (for partitioning between gas phase and adsorbed state) is expected with Teflon filters because they have less surface area and are more inert than quartz. Thus, less adsorption is expected on Teflon relative to quartz. Because differences in the amount of adsorbed OC have been reported for the two sampling configurations, both were examined.

Six sets of air samples were collected. Two precleaned quartz-fiber filters were loaded into each of eight 37-mm cassettes. In four of the these, a Teflon filter was then placed on top. The bottom quartz filters in all eight cassettes, as well as the four directly under the Teflon filters, provided measures of adsorbed OC. Filters in four additional cassettes served as passive field blanks, which meant that no air was pulled through them. The second (bottom) quartz filter in the cassettes with the Teflon filters were compared to the bottom quartz filters in those having only a quartz pair. If negligible adsorption occurs on Teflon, the bottom quartz filters in the two different sampling configurations should give equivalent results. To avoid possible variability due to lot-to-lot differences [67], filters from the same lot were used to collect a given sample set.

Portable dust chamber. A portable dust chamber [69] designed for sampling in mines was used for sample collection. The chamber allowed simultaneous collection of up to eighteen samples. Twelve cassettes were mounted inside the chamber in a symmetrical fashion. Samples were collected on six different days, five days in a loading dock area and a sixth near an outside smokers' shelter. A diesel truck was operating in the loading dock, over different periods, on three of the days. Personal air pumps were programmed to run at 2 L/min over an 8-hour period. In one case, the pumps were stopped after 23 minutes. The short sampling period provided a low loading of diesel exhaust (a light deposit was visible) and was of interest with respect to the amount of adsorbed carbon collected in the short time frame.

Results for the six sample sets are shown in Table 1 and Figure 3. The QQ2 results correspond to the bottom quartz filters in the four cassettes containing quartz pairs only. The TQQ1 results are for the four filters directly beneath Teflon filters; TQQ2 results are for quartz filters beneath the TQQ1 filters (i.e., top Teflon, middle TQQ1, bottom TQQ2). The mean carbon on the bottom quartz filters ranged from 1.35 to 3.44 $\mu g/cm^2$, and the variability (RSD) ranged from about 4% to 12% on a given day. The loading found on the two sets of bottom filters (QQ2 and TQQ2) was not statistically different, so all bottom filters were pooled in the calculation of the mean. The pooled means for the bottom quartz filters (BQ), the means for the quartz under Teflon (TQQ1), and the corresponding OC and EC loadings are plotted in Figure 3. Results for the TQQ1 filters were only slightly higher than those for the bottom quartz filters, even with the 23-minute sampling period (set 4). Thus, using a separate cassette that has a top Teflon filter appears unnecessary. Although differences between the amount of carbon adsorbed on a quartz filter under another quartz and on one beneath a Teflon filter reportedly can be significant [65, 67], these studies concerned environmental monitoring at much higher flow rates. The negligible differences reported here most likely relate to the lower flow rates and filter face velocities used.

TABLE 1. RESULTS FOR SIX SETS OF AIR SAMPLES COLLECTED IN TWO OUTDOOR LOCATIONS. SEE TEXT FOR DETAILS.

		TC, µg/cm²								
Set	Location	QQ1		TQQ1		Bottom quartz mean				Adsorbed fraction (%)
		mean, SD	RSD %	mean, SD	RSD %	QQ2	TQQ2	pooled, SD	RSD %	
1	shelter	4.81, 0.47	9.77	3.66, 0.43	11.75	3.46	3.41	3.44, 0.30	8.80	76
2	dock	3.52, 0.25	7.10	2.82, 0.36	12.77	2.48	2.33	2.43, 0.23	9.57	80
3	dock	3.61, 0.05	1.39	2.89, 0.04	1.38	2.41	2.42	2.41, 0.18	7.45	80
4	dock	4.59, 0.18	3.92	1.79, 0.24	13.40	1.41	1.36	1.38, 0.09	6.46	30
5	dock	8.43, 0.33	3.91	1.84, 0.35	19.02	1.35	1.36	1.35, 0.16	12.03	22
6	dock	22.78, 0.35	1.54	3.62, 0.18	4.97	3.10	3.18	3.14, 0.13	4.09	16

The mean carbon loading (Table 1) on the sample filters (QQ1) was about 4 μg/cm^2 on four different days (sample sets 1-4). A diesel truck was operating briefly on one of these days (set 4). On two other days (sets 5 and 6), the truck was running for longer periods, as evidenced by the higher EC loadings (Figure 3). The corresponding TC loadings on these two days were about 8 μg/cm^2 and 23 μg/cm^2. Over the loading range, the amount of adsorbed OC had no dependence on the TC loading, and the OC results for the bottom quartz filters (1.35 to 3.44 μg/cm^2) were higher than those for the passive field blanks (0.17 to 0.74 μg/cm^2). Two of the results (sets 4 and 5) were slightly lower than the others. In one case (set 4), the sampling period (23 minutes) was shorter, but the adsorbed OC results for the bottom filters in both sampling configurations (i.e., QQ2 and TQQ2) were equivalent and comparable to the upper quartz filters (TQQ1), below the Teflon. This implied that partitioning [65] (between gas and adsorbed states) on the sample filters (QQ1) had reached equilibrium; thus, the lower result was not due to lack of equilibration. In large part, the results for passive blanks provided a likely explanation for the lower value. The mean blank (passive) for this set was 0.17 (± 0.10) μg/cm^2, which was the lowest value obtained. Passive blank results for the other sets (excluding set 5) ranged from 0.25 (± 0.07) to 0.74 (± 0.14) μg/cm^2. It is not known whether the same explanation applied to set 5 because passive blanks for this set were accidentally contaminated (results voided). As in sets 1–3 and 6, set 5 was collected for an 8-hour period, but it was collected during the spring, while the other sets were collected during mid-summer. Changed weather conditions may explain the lower value.

On three days, the adsorbed OC fraction (calculated as the TQQ1 TC mean divided by QQ1 TC mean) constituted about 80% of the TC on the sample filters (QQ1). On three other days (sets 4, 5, and 6), the adsorbed OC fraction was 39%, 22%, and 16% of the total. A backup quartz filter provided a better correction for adsorbed carbon than a traditional blank would have. Traditional blanks (media and field) underestimated the adsorbed OC, causing overestimation of the true particulate OC (TC) concentration. The need for this correction, and the number of backup filters analyzed, depends on the sampling strategy and environment. The lower the OC loading, the greater the influence of adsorbed vapor on the particulate OC measurement. If the EC loading also is low, the same holds true for the TC result. Thus, when carbon loadings are low, correction for adsorbed OC is important for accurate measurement of particulate OC and TC concentrations. However, the correction addresses adsorbed vapor only—not interference of less volatile materials (e.g., components in cigarette and wood smokes, oils) collected primarily on the top filter. Depending on vapor pressure, sampling conditions (temperature, flow rate, sampling period), and filter loading, these materials also collect on the bottom filter to some extent. The bottom filter cannot correct for this interference. If high OC loadings are found on the bottom filter, less volatile OC interferences should be suspected.

g. EC Oxidation in Helium

In the NMAM 5040 analysis, oxidation of original EC (as opposed to char) is sometimes seen during the last temperature step in helium, but this is generally not common. If early removal occurs, it is important to ensure that oxygen contamination is not responsible. This check can be performed by analyzing a sucrose standard solution applied to a clean, unused filter punch. Although char loss is sometimes observed with sucrose, the filter transmittance normally does not reach its initial value until after oxygen is introduced. If oxygen contamination can be ruled out, the early EC loss is most likely due to oxidants in the sample. In our laboratory, EC loss in helium has been observed with samples from a few mines [70]. With these samples, the filter transmittance exceeded its baseline (initial) value during the last temperature step in helium. No sample pyrolysis was apparent, so the increase in transmittance was not caused by char loss. Moreover, analysis of sucrose standards revealed only a minor increase in transmittance in helium, and no increase was seen with samples from other mines. For these reasons, oxygen contamination was ruled out. On average, about 10% of the EC was removed at 870 °C in helium, but the carbon removed was included in the EC result because the OC-EC split was assigned when the initial transmittance was reached (in helium). Reducing the maximum temperature to 750 °C was recommended [59] for these types of samples (i.e., *no sample charring and early splits in helium*). Early EC loss was not seen at this temperature. A lower (< 750 °C) temperature may be required, depending on the type and amount of internal oxidant present. Our analytical result and precision were not affected by the early splits, but a reduced temperature was recommended in the interest of interlaboratory precision, which might be adversely affected. Interlaboratory testing was not conducted to determine if this is indeed the case, and, if so, whether a lower temperature would improve precision.

h. Reference Materials

Unfortunately, a suitable reference material for OC and EC is not yet available. A new Certified Value (17.68% g/g) for the TC mass fraction of an urban dust standard (SRM 1649a, formerly SRM 1649) was recently reported by the National Institute of Standards and Technology (NIST), but only Information (not Certified) Values are provided for the EC content. The EC content (as EC:TC fractions) was determined by a variety of methods. As expected from past studies [35, 71–74], the results were quite variable. The EC:TC fractions found by 13 methods ranged from about 7% to 52%, and the data were distributed in three clusters. Method bias was not evaluated. The reported range is obviously too broad to use this material as an analytical standard. According to the Certificate of Analysis (1649a), the reported values may be useful for comparison with results obtained by similar methods, but this may not be the case for methods with optical corrections because filter samples are not available. Depending on its placement, bulk dust on a filter can present different optical properties, which may increase variability. Preparation of a reference material deposited on quartz filters is being investigated at NIST.

Sample composition is an important consideration in the production of an analytical reference material. As is true with many standards, no single OC-EC material can be representative of all samples because there are many sources of particulate carbon and many different monitoring sites—both occupational and environmental. Production of an OC-EC reference material is further complicated by the variability between methods (SRM 1649a provides only Information Values for different methods), and the need of a filter-based material for thermal-optical methods.

Because sample components that char pose a potential interference in the determination of EC, and interlaboratory variability is greater when samples contain them, analysis of organic materials that char provides an important quality assurance check. Sucrose serves as both an analytical standard and a check of the method's char correction, but sucrose is a simple carbohydrate (a disaccharide). Air samples can contain complex particulate matter, such as wood and cigarette smokes, plant debris (cellulose), and products of biomass burning. In some cases, the biomass may contribute a sizable fraction of the sample carbon. About 38% of the particulate carbon in SRM 1649a (an urban dust) is derived from biomass (see Certificate of Analysis and related publication [J. Res. Natl. Inst. Stand. Technol., 107:279-298, 2002] available at http://www.nist.gov/jres). For these reasons, a material more representative of the plant-derived components in air samples was sought.

Various plant-derived materials were examined to determine whether any would be useful as laboratory control samples. A well-characterized, stable material that chars also would be useful for proficiency testing, and it could potentially be used to produce a standard reference material. After a preliminary screening of candidate materials (e.g., agarose, alginic acid, starch, and cellulose), alginic acid was selected for further study. Alginic acid is a polysaccharide derived from sea kelp [76], it has adequate solubility in water, and it forms a significant amount of char during the analysis.

To prepare a solution, about 150 mg of alginic acid (Sigma, St. Louis, MO) was added to a test tube containing 10 mL of purified water (ultrafiltered, type I). The tube was shaken vigorously and allowed to sit overnight at room temperature. The following day, the tube was shaken again and then centrifuged to settle the suspended material. The clear supernatant was removed and syringe filtered. Aliquots of the alginic acid solution were applied to clean filter punches. The solution was analyzed over a seven-week period. Results of these analyses are plotted in Figure 4. No evidence of solution degradation was observed. A mean carbon loading of 13.98 µg /cm^2 (RSD = 3.06%, n = 22) was obtained for 10-µL aliquots of the solution. This translates to a carbon concentration of 2.06 µg /µL. About half of the carbon in alginic acid remained on the filter as char before oxygen was introduced, but the mean EC result (0.04 ±0.06 µg /cm^2) was not statistically different from that for the media blanks (0.06 ±0.03). Therefore, the pyrolysis correction was accurate.

Sets of diesel soot samples spiked with the alginic acid solution also were examined. Multiple punches (1.5 cm^2) were taken from a soot sample collected on an 8” x 10” filter. The punches were then analyzed before and after spiking with a 10-µL aliquot of the solution. Punches in a given set were taken from the same area of the filter to minimize variability, and the solution was applied in a consistent manner (dispersed evenly on one end of the punch where the laser penetrates it). Mean TC results for the unspiked and spiked samples are provided in Table 2. Results for three sample sets (A, B and C) are reported. For each set, the difference between the mean results for the unspiked and spiked samples is reported; this difference is the alginic acid carbon. Based on the mean (13.98 µg/cm^2) for 22 spiked blanks, recoveries of alginic acid carbon from the soot samples were 96%, 101% and 110% (sets A, B, and C, respectively). The pooled recovery for all spiked samples was 97%.

TABLE 2. RECOVERY OF ALGINIC ACID CARBON FROM DIESEL PARTICULATE SAMPLES SPIKED WITH 10-µL ALGINIC ACID SOLUTION.

Sample Set	Mean Carbon[a], micrograms/cm^2 (SD)			
	unspiked	spiked	difference[b]	Recovery[c] (%)
A	22.94 (1.49)	34.90 (0.66)	13.47	96
B	22.25 (0.28)	36.38 (0.65)	14.14	101
C	22.61 (0.33)	38.01 (0.80)	15.39	110
All	22.56 (0.84)	36.06 (1.32)	13.49	97

[a] Three unspiked samples per set. Seven spiked samples in sets A and B, and 3 in set C. [b] Spiked minus unspiked result. [c] Recovery based on mean result (13.98 µg/cm^2) for 22 analyses of blank punches spiked with 10-µL aliquot of alginic acid solution. Analyses done over a 7-week period.

EC results for the three sample sets are listed in Table 3. Spiked sample results for two sets (A and C) were slightly higher, while those for a third set (B) were slightly lower. Differences between the mean EC loadings on the unspiked and spiked samples were not statistically different. Thus, an accurate correction was again made for the char formed through pyrolysis of alginic acid. Additional tests on spiked samples are ongoing.

TABLE 3. EC RESULTS FOR SPIKED AND UNSPIKED DIESEL PARTICULATE SAMPLES.

Sample Set	Mean EC[a], micrograms/cm^2 (SD)		
	unspiked	spiked	difference[b]
A	4.24 (0.20)	4.36 (0.42)	0.12 (0.47)
B	3.88 (0.01)	3.78 (0.12)	-0.10 (0.12)
C	4.32 (0.14)	4.43 (0.12)	0.11 (0.18)

[a] Three unspiked samples per set. Seven spiked samples in sets A and B; three spiked samples in set C. [b] Spiked minus unspiked results.

i. Quality Assurance

Quality assurance (QA) procedures followed at NIOSH and NIOSH contract laboratories have included repeat analyses, analysis of OC standards, and analysis of media and field blanks. Results for repeat analyses of over 200 filter samples at a contract laboratory (DataChem Laboratories, Inc., Salt Lake City, UT) gave a pooled RSD (95% confidence) of about 4% for EC and TC, and 5% for OC [68]. The samples were collected in mines, and some contained other carbonaceous matter such as limestone. In the analysis of OC standards, recovery was typically within 6% of the expected value [68]. For example, the mean recovery for more than 400 sucrose standards analyzed at DataChem over a one-year period was 99.97 % ±6.07%. Nearly identical results (100.33 % ± 5.15%, n = 462) were obtained by Clayton Laboratory Services (Novi, MI). Different sets of field blanks (41 at DataChem and 129 at Clayton) analyzed by the two laboratories also gave comparable results [68]. Mean blank results (µg carbon per filter) were as follows: DataChem OC = 9.96 ± 7.05, Clayton OC = 12.80 ±5.76; DataChem EC = -0.54 ±1.89, Clayton EC = -0.08 ±2.14; DataChem TC = 9.26 ±7.30, Clayton TC = 12.70 ±6.18.

In lieu of an OC-EC reference material, a limited confirmation of results by a second laboratory is advisable. Our laboratory (NIOSH, Cincinnati, OH) has routinely performed repeat analyses on samples previously analyzed at a contract laboratory. As an added check, subsets of representative field samples also have been analyzed by a third laboratory. In the analysis of fifty samples (analyzed at DataChem, NIOSH, and Clayton) from mines, the pooled RSD (95% confidence) was about 6% for TC, 10% for EC, and 12% for OC [68]. These results are consistent with those found in a previous round robin [35].

EPA. The EPA recently conducted a special study [75] as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network (STN). Samples collected as part of this network were removed from refrigerated storage eight months after they were analyzed at Research Triangle Institute (RTI, Research Triangle Park, NC). The samples were then shipped to the EPA New England Regional Laboratory (NERL, Lexington, MA) for re-analysis. Good interlaboratory agreement was reported. The acceptance criteria for the archived samples were based on filter loading ($\mu g/cm^2$). The three acceptance criteria are the following: a difference $\leq$ 1 $\mu g/cm^2$ for loadings less than 5 $\mu g/cm^2$, a relative percent difference (RPD) $\leq$ 20% for loadings from 5 to 10 $\mu g/cm^2$, and an RPD $\leq$ 15% for loadings above 10 $\mu g/cm^2$. The OC, EC, and TC data had 85%, 96%, and 93% of the inter-laboratory results, respectively, within the acceptance criteria. The lower percentages for OC and TC are thought to reflect contamination of lightly loaded samples from adsorbed vapors and handling. An OC blank (passive) correction was applied, but it most likely was not representative of the entire sample set. Additional interlaboratory comparison results are discussed in a following section (see Section 3).

3. INTERLABORATORY COMPARISONS

a. NMAM 5040

When results of the initial method evaluation were published [34], an interlaboratory comparison was not possible because the thermal-optical instrument was available in only one laboratory. Interlaboratory comparisons are especially important in this type of analysis because variable results have been obtained by different OC-EC methods [35, 71–74], and a reference material is not yet available. After additional laboratories acquired thermal-optical instruments, a round robin comparison [35] was conducted. Matched sets of filter samples containing different types of complex carbonaceous aerosols were distributed to eleven laboratories. Six of the eleven analyzed the samples according to NMAM 5040, while five used purely thermal (i.e., no char correction) methods. Good interlaboratory agreement was obtained among the six laboratories that used NMAM 5040. In the analysis of samples containing diesel particulate matter, the variability (RSD) for the EC results ranged from 6% to 9%. Only low EC fractions were found in wood and cigarette smokes. Thus, these materials pose minimal interference in the analysis of diesel-source EC. In addition, only minor amounts of EC were found in two OC standards that char: about 1% and 0.1% for sucrose and the disodium salt of ethylenediaminetetraacetic acid (EDTA), respectively. Two aqueous solutions of OC standards were included in the comparison as a check on the validity of the char correction and accuracy of the TC results. Variability (RSD) of the TC results for the two standard solutions and five filter samples ranged from 3% to 6%.

Another interlaboratory comparison using NMAM 5040 was conducted more recently [77]. Seven environmental aerosol samples were analyzed in duplicate by eight laboratories. Four samples were collected in U.S. cities, and three were collected in Asia. Variability of the EC results ranged from 6% to 21% for six samples having EC loadings from 0.7 to 8.4 $\mu g/cm^2$. Four of the six had low EC loadings (0.7 $\mu g/cm^2$ to 1.4 $\mu g/cm^2$). The variability of the OC results ranged from 4% to 13% (OC loadings ranged from about 1 to 25 $\mu g/cm^2$). Results for TC were not reported, but the variability reported for the OC results should be representative of that for TC because the samples were mostly OC (75% to 92%).

b. Other Methods

Thermal methods. Different thermal methods have given consistent agreement for TC, but OC-EC results have been quite variable [35, 71–74]. The degree of variability depends on the sample type. In general, there is greater disagreement among methods when samples contain materials that char [35, 71, 72] (e.g., wood and cigarette smokes). Methods that employ a lower maximum temperature and/or do not correct for char obtain results that are positively biased relative to NMAM 5040 [35]. When a lower temperature (typically 550 °C) is used, less thermal breakdown of refractory organic components (and possibly carbonates) may occur. This, as well as lack of char correction, can positively bias the EC results. In the round robin study [35] discussed above, three laboratories employed four purely thermal methods that specified a maximum in nitrogen (not helium) of about 550 °C. Unlike the

NMAM 5040 results, these laboratories reported high EC contents for the two OC standards (about 52% for sucrose and 70% for EDTA). Similar findings (i.e., positive bias) for thermal methods having no char correction were obtained recently in another international round robin [72].

In contrast to round robin results obtained previously [35], relatively good agreement was seen in a recent comparison [78] between NMAM 5040 and a thermal method (ZH 1/120.44) used in Germany. The comparison was limited to two laboratories. Method ZH 1/120.44 specifies a 550 °C maximum in nitrogen. The other European laboratories that participated in the previous round robin [35] used variations of this method. In the European laboratories, nitrogen is used as the inert gas, and carbon determination is based on coulometric titration of carbon dioxide. For the comparison [78], samples were obtained in a mine where diesel equipment was being operated. The samples had a much higher EC content (about 50%) than did the round robin samples. No charring was noted in the thermograms, and only a minor amount of carbon was removed above 550 °C. Although differences in the OC-EC results were again seen, they were minor relative to those obtained in the round robin [35]. The mean EC fractions (EC:TC) found with methods ZH 1/120.44 and NMAM 5040 were 0.53 ($\sigma = 0.19$) and 0.46 ($\sigma = 0.15$), respectively. The relatively minor difference in the reported fractions was attributed to the different thermal programs employed.

IMPROVE method. Another thermal-optical method, called the IMPROVE (Interagency Monitoring of Protected Visual Environments) method [79], also was included in the NMAM 5040 round robin [35]. Relatively good agreement between NMAM 5040 and the IMPROVE method was obtained, although the IMPROVE EC was consistently a bit higher. The carbon analyzers used for the two methods are based on similar measurement principles, but they differ with respect to design and operation. For example, the optical correction in NMAM 5040 is based on filter transmittance, whereas that for the IMPROVE method is reflectance based. Different components are used to monitor these signals. The instrument (Sunset Laboratory, Inc., Forest Grove, OR) used for NMAM 5040 incorporates a pulsed diode laser (670 nm) and photodetector positioned on opposite sides of the filter. The instrument (Desert Research Institute, Reno [DRI], NV) for the IMPROVE method uses a quartz tube and fiber optic to measure helium–neon laser light (632.8 nm, unmodulated) reflected from the filter surface. In addition to instrumental differences, NMAM 5040 specifies a higher maximum temperature (870 °C) in helium than the IMPROVE method (550 °C). As discussed in the preceding section, a higher temperature is used to better remove refractory OC components and carbonates. In the NMAM 5040 analysis, the transmittance of some samples continues to decrease as the temperature is stepped to 870 °C, which indicates charring is not complete at 550 °C. More exhaustive charring results in a lower EC result because the correction for it is larger, and volatile pyrolysis products can evolve to a greater extent. Although environmental samples contain only small amounts (if any) of carbonate, levels in some workplaces (e.g., mines, construction sites) can be relatively high. Collection of carbonate can be prevented (or minimized) through use of an impactor [62].

Two comparisons [73, 74] between the NMAM 5040 and IMPROVE methods were conducted recently. In one [73], the NMAM 5040 EC was typically less than half the IMPROVE EC, but a Sunset Laboratory instrument was not used. Instead, samples were analyzed on a prototype instrument by running two different thermal programs [73]. The results reported for NMAM 5040 (emulated on DRI instrument) may not be representative of those obtained with a Sunset Laboratory instrument because, depending on the sample type, differences in instrument design can affect the results to varying degrees. Adjustment of the temperature program, according to another method's specifications, does not necessarily produce the same results as that method. For example, lower EC results [35] were obtained with a Sunset Laboratory instrument when a sucrose standard was analyzed according to the temperature program specified for a method used in Europe. No pyrolysis correction was made, and the total analysis time was shorter, yet the EC result was much lower (about 3 µg with the Sunset instrument and 11 µg with a different instrument).

When the NMAM 5040 thermal program was used on a DRI instrument, the filter transmittance reportedly exceeded its initial value before the addition of oxygen [73]. In a recent audit by CARB (California Air Resources Board), the same problem was seen with a DRI instrument, but not a Sunset Laboratory instrument (report [*2003 Performance Evaluation Evaluation Sample Audit of the CARB Lab*] available at http://www.epa.gov/ttnamti1/pmspec.html). Char loss was extensive when the NMAM 5040 program was used on a DRI instrument. Again, the filter transmittance exceeded its initial value in helium, but the split point was not assigned until after oxygen was introduced. These results contrast with those obtained by our laboratory and others, and such behavior was not seen in another comparison [74]; however, that comparison (and the CARB audit) was a direct comparison of the two methods (samples were analyzed with Sunset and DRI instruments). Only 2 of 52 samples analyzed by Sunset Laboratory showed an increase in transmittance before the addition of oxygen, and the OC-EC split was near the point where oxygen was added [74]. Both samples had low carbon loadings (OC = 4.0 µg/cm^2, EC = 0.6 µg/cm^2, OC = 3.3 µg/cm^2, EC = 0.5 µg/cm^2) and were thought to be wood-smoke dominated. As pyrolysis was evident, the increase in filter transmittance was attributed to char removal. Comparable EC results would have been obtained if the char had not been removed until after oxygen was added, because char is assigned to the OC fraction. In the NMAM 5040 analysis of organic compounds (e.g., sucrose), partial char loss in helium sometimes occurs. The varying degree of loss may relate to differences in filter purity.

4. OCCUPATIONAL EXPOSURE CRITERIA (U.S.)

In 1995, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed a Threshold Limit Value (TLV®) for diesel exhaust (see Notice of Intended Changes for 1995–1996). A TLV of 150 µg of submicrometer particulate matter per cubic meter of air was proposed. Four years later, a value of 50 µg/m^3 was proposed [80]. Because EC is a demonstrated exposure marker for diesel particulate exhaust and can be accurately quantified at low levels [81], the standard was recast in terms of an equivalent elemental carbon measurement in 2001 [81]. A TLV-TWA (time-weighted average) of 20 µg EC per cubic meter of air was recommended [82]. By comparison, the proposed TLV is high relative to an environmental standard supported by the California Office of Environmental Health Hazard Assessment (OEHHA). The California OEHHA has classified particulate emissions from diesel-fueled engines as a toxic air contaminant (TAC) and supports 5 µg/m^3 as the chronic inhalation reference exposure level (REL) [5]. Because EC is a fraction of the diesel particulate emissions, the difference between the two air standards is greater than four fold, and the magnitude of the difference is dependent on the EC mass fraction of the diesel particulate. For example, if EC constituted 40% of the diesel particulate mass, the proposed

TLV would be ten times higher than the OEHHA REL. The ACGIH withdrew diesel exhaust particulate, as EC, from the 2002 Notice of Intended Changes (NIC) and placed it under study [86].

An EC (or TC) standard, rather than submicrometer particulate mass, would simplify interpretation of the analytical results because the target analyte and exposure standard would be the same. This would eliminate the problem of extrapolation (to submicrometer mass), which is not straightforward and introduces unacceptable analytical error. As discussed previously, OC interferences are an issue when making TC measurements; variable EC content is a problem when measuring EC. If EC concentrations are high and samples are relatively free of OC contaminates, the TC concentration is a reasonable measure of the diesel particulate mass, and the EC:TC ratio is representative of the EC fraction of the mass. Unfortunately, this situation is uncommon outside of mines. In general industry, EC and OC levels are normally much lower. When EC levels are low, the EC:TC ratios are not reliable estimates of the EC fraction of diesel particulate matter because OC interferences can skew the ratios low and increase variability in the apparent ratio. In such cases, TC is an inaccurate measure of the diesel particulate concentration.

Exposures in the mining industry are of particular concern because diesel particulate concentrations in mines [62, 83, 84] sometimes exceed 2 mg/m^3, which is one thousand times higher than a typical environmental level. In its final rule [62] on metal and nonmetal mines, MSHA proposed an interim exposure standard of 400 µg TC per cubic meter of air. Five years after publication of the rule, a final standard of 150 µg TC per cubic meter was to apply. In response to a legal challenge, MSHA recently initiated limited new rulemaking [85] to revise certain provisions of the final rule. Among other amendments, MSHA agreed to propose a change of exposure surrogate from TC to EC. Comments on appropriate interim and final limits for EC were requested in the new rulemaking. MSHA exposure standards consider health risks and technical and economic feasibility, based on available engineering controls and their cost.

5. SUMMARY

NMAM 5040 is based on a thermal-optical analysis technique for particulate carbon. Its intended application is assessment of workplace exposure to particulate diesel exhaust, but thermal-optical analysis has been routinely applied to particulate carbon measurement in general. Both OC and EC (and TC as OC + EC) are determined by the method. For reasons discussed in this chapter, EC is a better exposure surrogate than TC. Over 30 epidemiological studies are consistent in finding a positive association between exposure to diesel exhaust and lung cancer, but quantitative exposure data are lacking. Accurate monitoring methods are necessary in quantifying the risks of exposure.

The thermal-optical instrument incorporates an optical feature that corrects for the char formed during the analysis of some materials. EC results of purely thermal methods show positive bias when samples contain materials that char. Although minimal charring has been observed with most diesel soot samples from mines, workplace (and environmental) air often contains components that char. Depending on the workplace and thermal protocol, these components can be significant contributors to the measured EC. For this reason, an analytical protocol that maximizes removal of refractory OC components (and carbonates) and corrects for the char formed through thermal decomposition is important. In the NMAM 5040 analysis, the transmittance of some samples continues to decrease as the temperature is stepped to 870 °C in helium, which indicates charring is not always complete at the lower temperatures used in some methods. Partial char loss is sometimes observed (at 870 °C), but loss of original EC is uncommon.

Good interlaboratory agreement between OC-EC results has been obtained by laboratories using NMAM 5040. Because a certified reference material is not currently available, confirmation of results in a second laboratory using NMAM 5040 is advisable, particularly when samples char during the analysis because interlaboratory results for these are typically more variable. Organic materials that char are useful as quality control samples. Accurate pyrolysis correction was obtained in the NMAM 5040 analysis of an alginic acid solution spiked onto blank filters and diesel soot samples. Sucrose has traditionally been used as a check on the method's char correction, but alginic acid is more representative of complex, plant-derived components present in some air samples.

To ensure data quality, participation in proficiency testing among laboratories involved in major studies also is advised. At present, seven commercial laboratories (six in the United States and one in Canada) offer the NMAM 5040 analysis, and over 60 instruments are available globally for environmental and occupational monitoring. Method standardization is critical if results obtained by different laboratories are to be compared. Interlaboratory studies are useful in exposing differences among methods, but results of such comparisons must be interpreted with a clear understanding of each method's limitations (e.g., in dealing with interferences).

Additional research is necessary to address the potential health effects of diesel exhaust and other types of fine particle air pollution. Although the organic compounds associated with diesel particulate matter have potential health effects, those traditionally measured are not unique to diesel exhaust. Nevertheless, characterization of this fraction may be useful in assessment of exposure risks, particularly if compounds enriched in diesel relative to other particulate emissions can be used as indicators of mutagenic potency (e.g., specific nitro-PAH). This information also may reveal engine types or operating conditions that produce higher emission rates of genotoxic compounds.

Undoubtedly, much will be learned through additional research. As reasoned previously [34], regardless of whether the potential adverse health effects of diesel particles are due to the carbonaceous cores, adsorbed compounds, or a combination of both, monitoring and control of the particulate component are necessary if effects exist that are particle related. In most workplaces, diesel engines are the primary source of fine-particle EC. Other combustion sources may contribute to environmental levels of EC. These sources may be relevant from an emission control perspective, but if the potential toxicity of these particles is similar, their origin is not relevant from a health perspective.

6. FIGURES.

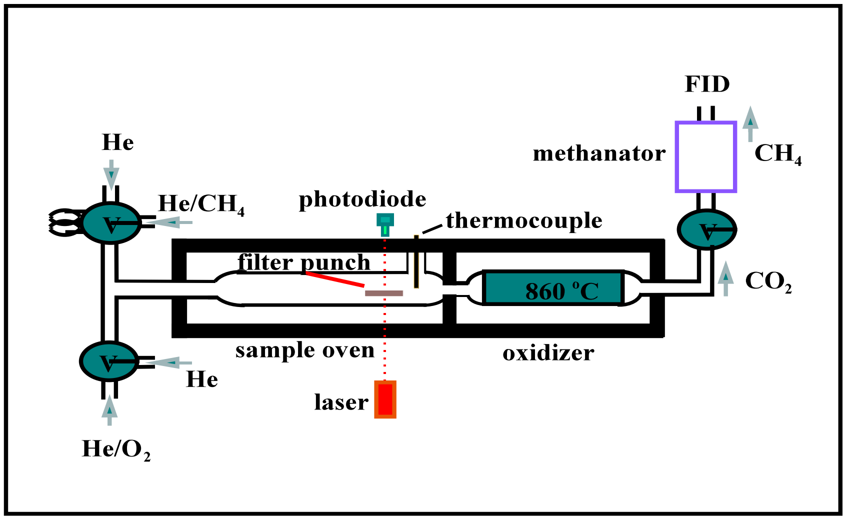

Figure 1. Schematic of thermal-optical instrument (*V* = valve) for determination of OC and EC in diesel particulate exhaust and other carbonaceous aerosols.

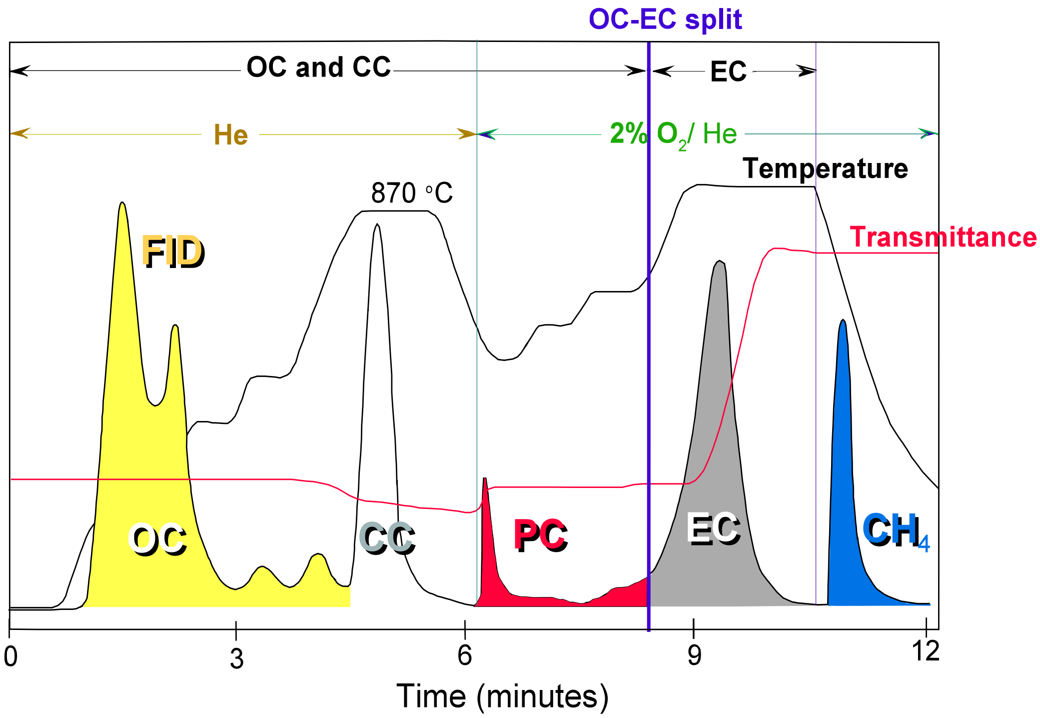

Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.

Note: In the round robin study [35] discussed earlier, the actual maximum temperature in helium ranged from about 850 °C to 900 °C. Laboratories were asked to use the same maximum, but not all did. Comparable results were obtained because some differences in the thermal program do not affect the results significantly. For the purpose of standardization, use of the same maximum is recommended. An 870 °C maximum is near the middle of the range used by participants in the study.

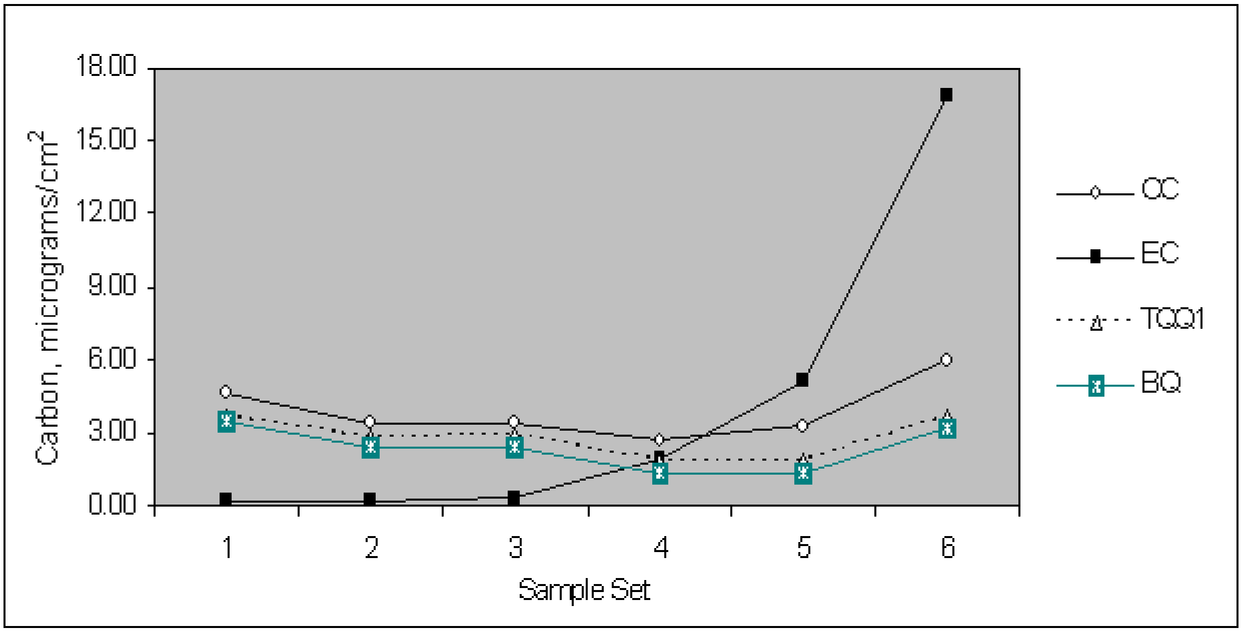

Figure 3. Results for six sets of air samples collected in two outdoor locations. OC and EC results are the means for the top quartz filters (QQ1) of quartz-filter pairs. TQQ1 is the mean carbon (total) result for quartz filters placed directly beneath Teflon. BQ is the mean carbon result for all bottom quartz filters (i.e., QQ2 and TQQ2). See text for additional details.

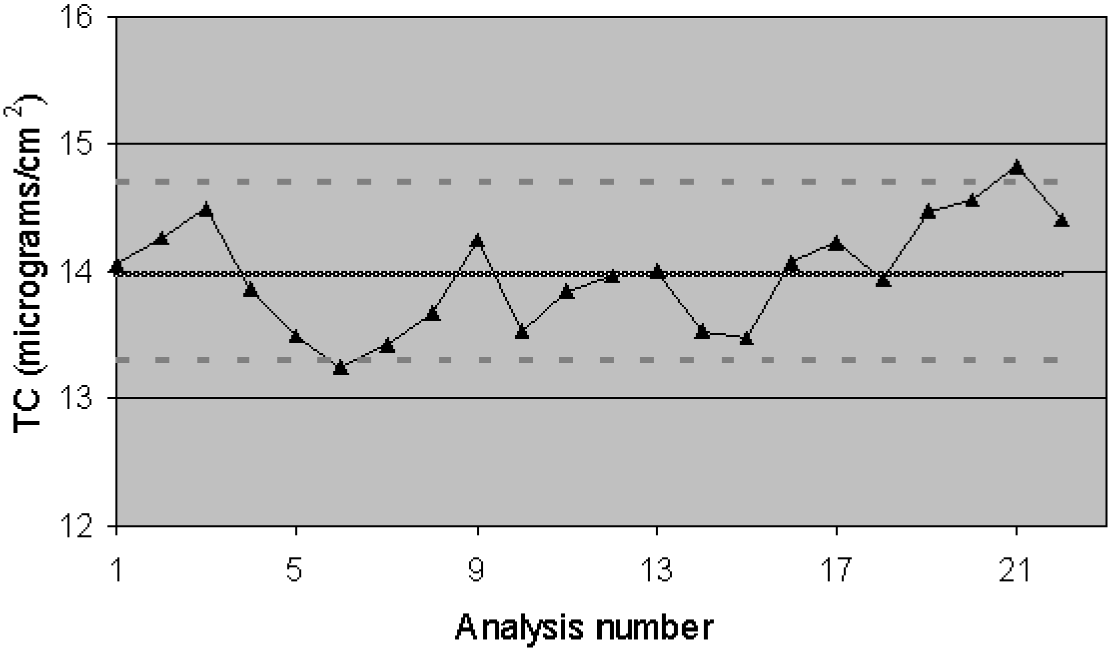

Figure 4. Results for clean punches (blanks) spiked with 10-µL aliquots of alginic acid solution. Analyses done over a 7-week period. The middle horizontal line is the mean result (13.98 µg/cm^2). The upper and lower dashed lines are ±5% of the mean.

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