Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust†

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ABSTRACT. Diesel exhaust has been classified a probable human carcinogen, and the National Institute for Occupational Safety and Health (NIOSH) has recommended that employers reduce workers' exposures. Because diesel exhaust is a chemically complex mixture containing thousands of compounds, some measure of exposure must be selected. Previously used methods involving gravimetry or analysis of the soluble organic fraction of diesel soot lack adequate sensitivity and selectivity for low-level determination of particulate diesel exhaust; a new analytical approach was therefore needed. In this paper, results of investigation of a thermal–optical technique for analysis of the carbonaceous fraction of particulate diesel exhaust are reported. With this technique, speciation of organic and elemental carbon is accomplished through temperature and atmosphere control, and by an optical feature that corrects for pyrolytically generated carbon, or "char," which is formed during the analysis of some materials. The thermal–optical method was selected because the instrument has desirable design features not present in other carbon analyzers. Although various carbon types are determined, elemental carbon is the superior marker of diesel particulate matter because elemental carbon constitutes a large fraction of the particulate mass, it can be quantified at low levels, and its only significant source in most workplaces is the diesel engine. Exposure-related issues and results of investigation of various sampling methods for particulate diesel exhaust also are discussed. AEROSOL SCIENCE AND TECHNOLOGY 25:221–241 (1996).

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Aerosol Science and Technology 25:221–241 (1996)

Published by Elsevier Science Inc.

0278-6826/96/$15.00
PII S0278-6826(96)00077-3

INTRODUCTION

The widespread use of diesel equipment has generated concern about occupational exposures to diesel engine exhaust, which has been classified as a probable human carcinogen (IARC, 1989). The National Institute for Occupational Safety and Health (NIOSH) considers diesel exhaust a potential occupational carcinogen, and has recommended that employers reduce workers' exposures (NIOSH, 1988). This recommendation was based on results of five independent animal studies in which rats exposed to unfiltered diesel exhaust showed an increased incidence of benign and malignant lung tumors (IARC, 1989). An increased incidence of lung tumors was observed in one study of mice exposed to filtered diesel exhaust, but the total incidence of lung tumors in this particular study was comparable to that for historical controls (IARC, 1989).

Various estimates of unit cancer risk [defined as the lifetime risk per unit of lifetime exposure (in $\mu g/m^3$)] associated with exposure to diesel exhaust have been summarized by Mauderly (1993). In their calculation, adjustments were made so estimates could be based on similar assumptions and expressed in common units. Three estimates were derived by comparative potency, three were derived using data from a rat inhalation bioassay, and two were based on epidemiological studies. Risk estimates derived by the former two means are similar, ranging from $0.3–1.6 \times 10^{-4}$ per $\mu g/m^3$. Estimates based on the epidemiological data are higher, and range from $2.6–11.6 \times 10^{-4}$ per $\mu g/m^3$. A more recent estimate (Pepelko and Chen, 1993) of unit risk was derived from lung tumor data from three chronic bioassays of Fischer 344 rats. In the assessment, both inhaled particulate matter (mg/kg/day) and lung burden of carbonaceous particulate per unit lung surface area (mg/cm^2) were used to estimate human dose, but the latter dose estimate was considered the most appropriate dose equivalence parameter. Unit risks (95% upper confidence limits) based on carbon particulate matter per unit lung surface area ranged from $1.0–4.6 \times 10^{-5}$ for the three data sets, with a geometric mean of 1.7×10^{-5}. The geometric mean reportedly is thought to be the most reasonable estimate. In a draft quantitative risk assessment conducted by the State of California Office of Environmental Health Hazard Assessment (OEHHA), carcinogenicity data from one animal bioassay (Mauderly et al., 1987) and one human study (Garshick et al., 1988) were used to predict risks of cancer in humans exposed to ambient levels of diesel exhaust. The calculated risk range based on the animal (rat) data was $3 \times 10^{-5}–3 \times 10^{-4}$ per $\mu g/m^3$. Different models of carcinogenicity and different measures of exposure were used in the calculation of the range of estimates. Based on results of the human study by Garshick et al. (1988) and two different measures of cumulative exposure, lifetime unit risks (95% upper confidence level) of 3.4×10^{-4} and 2.3×10^{-3} were calculated. Of these two estimates, the rounded value of 3×10^{-4} was proposed as the lifetime unit risk of exposure, and this value reportedly is "consistent with the current evidence" (California Environmental Protection Agency, 1994).

Particulate diesel exhaust, like particulate air pollution in general, also is of concern with respect to noncancer health effects. The U.S. EPA has proposed an inhalation Reference Concentration (RfC) of 5 $\mu g/m^3$ for the noncancer health effects of diesel exhaust, and the California OEHHA has proposed to adopt this value for the chronic inhalation reference exposure level (REL) in California (California Environmental Protection Agency, 1994). 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" (California Environmental Protection Agency, 1994). A comprehensive review of the potential health effects of diesel exhaust recently has been published (Health Effects Institute, 1995).

Because diesel exhaust is a highly complex mixture containing thousands of compounds (NIOSH, 1988; IARC, 1989), some measure(s) of exposure must be selected. As tumor induction in animals is associated with exposure to unfiltered diesel exhaust, a measure of exposure to the particulate fraction of the exhaust was sought. Previously, specific soot-borne organic compounds have been targeted; however, this approach is limited in that selected compounds usually are present only at low (often nondetectable) levels (Blade and Savery, 1989). Furthermore, although considerable research effort has been devoted to chemical characterization of the solvent-extractable fraction of diesel soot, a unique marker for diesel exhaust has not been found. Even if a unique marker(s) could be identified, the exhaust composition is highly variable (Schuetzle, 1983; SAE, 1992), so any single compound or compound class likely would not reflect exposure to the diesel aerosol mass concentration. A review of analytical methods for chemical characterization of the organic fraction of particulate diesel exhaust has been published previously (Levsen, 1988).

Gravimetric methods for diesel particulate matter have been employed for exposure monitoring. A respirable combustible dust (RCD) method (Gangal and Dainty, 1993) is being applied in Canada for estimation of diesel particulate concentrations in the mining industry (coal mines excluded). In this approach, combustible material in a respirable aerosol sample is determined as the difference in filter weight before and after combustion at 500°C. Similarly, a low-temperature ashing (LTA) method has been used in a survey of a U.S. silver mine to estimate the diesel fraction of respirable dust (Cornwell and Knutti, 1992). Other gravimetric methods have involved direct determination of either "fine particulate material" (Fowler, 1985) or submicrometer aerosol. Impactors with optimized cutpoints (submicrometer) have been developed for application in coal mines to minimize interference of coal dust (McCawley and Cocalis, 1986; Burkhart et al., 1987; Haney, 1990; McCartney and Cantrell, 1992). These size-selective sampling devices affect separation of particles according to their aerodynamic diameter through inertial impaction. Because diesel exhaust particles are essentially submicrometer (Dolan et al., 1975; Vuk et al., 1976; Groblicki and Begeman, 1979; Lipkea et al., 1979; Amann, 1982; Kittleson et al., 1988; Baumgard and Johnson, 1992; Johnson et al., 1994), their separation from larger, mechanically generated dust is possible. In other (i.e., noncoal) mines, a similar approach would be necessary for gravimetric determination of diesel particulate.

Although size-selective sampling can improve the selectivity of gravimetric analysis, significant amounts of submicrometer aerosol can arise from nondiesel sources (e.g., mists, cigarette smoke, fuels). Thus, even if very low masses could be precisely determined, the presence of other submicrometer aerosols could make the accuracy of such measurements highly questionable, especially when determining low levels (e.g., < 200 $\mu g/m^3$) of particulate diesel exhaust. Aside from the potential interference problem, a small portion of diesel aerosol may be excluded in some cases if a submicrometer size fraction is collected. Choice of a 0.8 μm cutpoint was based on size distribution data collected in coal mines, where vehicles normally are equipped with water scrubbers that tend to collect larger (i.e., > 1 μm) particles. In other workplaces, larger diesel particles could be present, and these will be excluded if an impactor with a submicrometer cutpoint is employed.

Because previously used methods for measuring occupational exposures to particulate diesel exhaust lack adequate sensitivity and selectivity, a new approach was needed. As diesel exhaust is primarily organic and elemental carbon, carbon measurement is a logical approach, but the many nondiesel sources of organic carbon make a total carbon measurement interference-prone. For this reason, use of an elemental carbon marker was proposed (Birch, 1992). Elemental carbon is the superior

measure of exposure to particulate diesel exhaust because elemental carbon constitutes a large portion of the particulate mass, it can be quantified at low levels, and its only significant source in many workplaces is the diesel engine. Selection of an elemental carbon marker also was based on previous work by Fowler (1985), who evaluated various analytes as indices of "overall diesel exposure." Included in the evaluation were CO_2, CO, SO_2, NO, NO_2, total and fine particulate material, volatilizable carbon (organic), and elemental carbon. Of these constituents, elemental carbon was reportedly the most reliable measure of "diesel exhaust as an entity" (i.e., it reflected exposures to the largest number of exhaust components examined).

In addition to being a specific and sensitive measure of particulate diesel exhaust, use of an elemental carbon marker was proposed in view of preliminary results of an animal study (Mauderly et al., 1988; Mauderly, 1992 communication) involving groups of rats exposed to unfiltered diesel exhaust or carbon black containing very little organic content. In this study, tumor incidence was similar in the two groups, which reportedly indicates that fine particulate carbon itself may play a primary role in the formation of malignant tumors in rats exposed to high levels of diesel particulate (Mauderly et al., 1994). The relevance of this finding with respect to humans exposed to much lower levels of diesel particulate is uncertain (see Uncertainties in Human Risk). A full report on the study has been published (Mauderly et al., 1994).

Various methods, most of which involve thermal separation, have been used for the determination of organic and elemental carbon (OC and EC, respectively) in carbonaceous aerosols. Thermally evolved OC and EC are oxidized to CO_2, which is quantified either by a nondispersive infrared detector or electrochemically. Alternatively, the CO_2 can be reduced to CH_4, which is then quantified by a flame ionization detector (FID). Although various techniques have been used for analysis of carbonaceous aerosols, different analytical methods generally give similar results for total carbon (TC). In an interlaboratory comparison of methods for analysis of carbonaceous aerosols (Countess, 1990), good agreement among 11 laboratories (pooled CV = 9.0%) was obtained analyzing a wide variety of "reference" samples (e.g., organic aerosol, soot, wood smoke, diesel exhaust). In contrast, large disagreement was seen in the EC and OC results reported by ten laboratories (pooled CVs for OC and EC were 25.8 and 52.3%, respectively). Unlike the case with TC, there are no reference standards for speciation of different carbon types in complex carbonaceous aerosols. For this reason, methods that speciate EC and OC are considered operational (Cadle and Groblicki, 1980) in the sense that the method itself defines the analyte. Results of laboratories performing such analyses can be compared on a relative basis, but it is not possible to assess the accuracy of results. Although a standard reference material (SRM 1650) for diesel particulate matter is available from the National Institute of Standards and Technology (NIST), this standard applies only to specific soot-borne organic compounds.

Other (i.e., nonthermal) methods have been employed for the analysis of carbonaceous aerosols, but were not considered practical for occupational monitoring of particulate diesel exhaust. For example, a method based on the optical absorption of a filter sample was used by a laboratory participating in the methods comparison study (Countess, 1990); however, this approach requires use of empirically derived, optical absorption coefficients to calculate EC loadings, which makes accurate analysis of unknowns unlikely. Also, the method is limited to relatively low EC loadings (typically $< 10\ \mu g/cm^2$ of filter). Laser Raman and a forward alpha scattering technique (FAST) have been applied for the analysis of carbonaceous particulate. Drawbacks to Raman analysis include the lack of suitable calibration standards and poor performance at low filter loadings (i.e., $< 100\ \mu g/cm^2$); drawbacks to FAST include instrumental cost and complexity, re-

stricted beam time on the limited number of accelerators available (requires high-energy, ion-producing capability), and the requirement of analysis in vacuum.

In this paper, an elemental carbon-based approach for occupational monitoring of particulate diesel exhaust is described. A thermal–optical analysis technique was investigated for this purpose. This particular technique was investigated because the instrumentation has desirable design and performance features (e.g., flame ionization detector, pyrolysis correction, minimal undesired oxidation of EC, no carbonate interference) that afford it greater sensitivity and selectivity than other methods for OC–EC determination. Selectivity is especially important when analyzing complex carbonaceous aerosols, as is evident from results of the methods comparison study (Countess, 1990). In the study, four laboratories took measures to minimize or correct for pyrolytically generated EC, but only the thermal–optical method's EC results were lower than those reported by laboratories that did not correct for pyrolysis. In addition to sample pyrolysis, the higher EC results reported by these labs may be due to the presence of carbonate-source carbon (CC), which was found in wood smoke and automotive exhaust samples. A discussion of the thermal–optical instrument's design, operation, and performance is provided in this paper. Exposure-related issues and results of investigation of various sampling strategies also are discussed.

EXPERIMENTAL

Reagents and Materials

Standard solutions (Supelco, Inc., Bellefonte, PA) of polycyclic aromatic hydrocarbons (PAHs) were $\geq 96\%$ pure as determined by capillary gas chromatography coupled with flame ionization detection (GC–FID). All chemicals (Aldrich, Inc., Milwaukee, WI) used for the preparation of aqueous solutions were reagent grade or better. Coarsely ground (-20 mesh) coal samples were obtained from the Penn State Coal Sample Bank at the Energy and Fuels Research Center, Pennsylvania State University. Coals were sieved to 50 mesh prior to use. Pallflex 2500QAT-UP quartz-fiber filters (Pallflex, Inc., Putnam, CT) were used for all samples (air and spiked filter punches). To remove possible carbon contamination, quartz-fiber filters were precleaned either in a muffle furnace or a low-temperature asher. Both commercial and prototype samplers were used for collection of diesel aerosol. A description of the sampling devices employed is given in a following section (see Sampler Comparison).

Instrumentation

In the thermal–optical method, speciation of organic, carbonate, and elemental carbon is accomplished through temperature and atmosphere control. A schematic of the instrument is shown in Fig. 1. The instrument is a modified version of a design previously described in the literature (Johnson et al., 1981). An optical feature corrects for pyrolytically generated EC, or "char," which is formed during the analysis of some materials (e.g., cigarette smoke, pollen). He–Ne laser light passed through the filter allows continuous monitoring of filter transmittance. Because of the high temperatures employed during the analysis, quartz-fiber filters are required for sample collection. Normally, a 1.54 cm^2 rectangular portion (taken with a punch) of the filter deposit is analyzed, and organic and elemental carbon are reported as $\mu g \cdot C/cm^2$ of deposit area. Total EC and OC on the filter are calculated by multiplying reported values by the sample deposit area. In this approach, a homogeneous filter deposit is assumed. A flame ionization detector (FID) is used for quantification (as CH_4) of evolved carbon, and instrument calibration is achieved through injection of a known volume of methane into the sample oven. Additional details on the analytical procedure and a description of the instru-

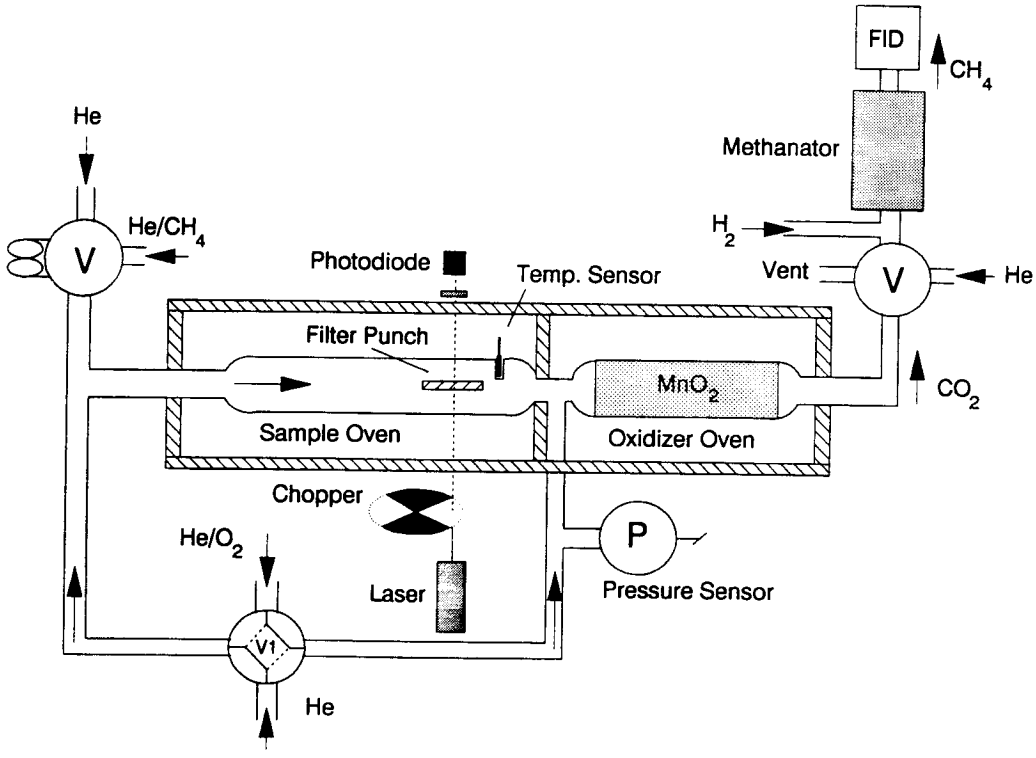

FIGURE 1. Schematic of thermal–optical instrumentation. Gas stream selected by four-port switching valve (V1). Pure He used during first stage of analysis; O_2 (2%)–He mix used during second stage (see text for details).

ment output are given below (see Carbon Speciation).

RESULTS AND DISCUSSION

Carbon Speciation

An example of the instrument output, called a "thermogram," is shown in Fig. 2. The three traces appearing in the thermogram correspond to temperature, filter transmittance, and detector response (FID). The analysis proceeds essentially in two stages. In the first, organic and carbonate carbon (if present) are volatilized from the sample in a pure helium atmosphere as the temperature is stepped to about 820°C. Evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2 (held at about 900°C), reduced to CH_4 in an Ni/firebrick methanator (at 450°C), and quantified as CH_4 by an FID. During the second stage of the analysis, pyrolysis correction and EC measurement are made. The oven temperature is reduced, an oxygen (10%)–helium mix is introduced, and the oven temperature is then raised to about 860°C. As oxygen enters the oven, pyrolytically generated EC is oxidized and a concurrent increase in filter transmittance occurs (Fig. 2). Correction for the char contribution to EC is accomplished by measuring the amount of char oxidation required to return the filter to its initial transmittance value. The point at which the filter transmittance reaches its initial value (vertical solid line) is defined as the "split" between organic and elemental carbon. Carbon evolved prior to the split is considered "organic" (including car-

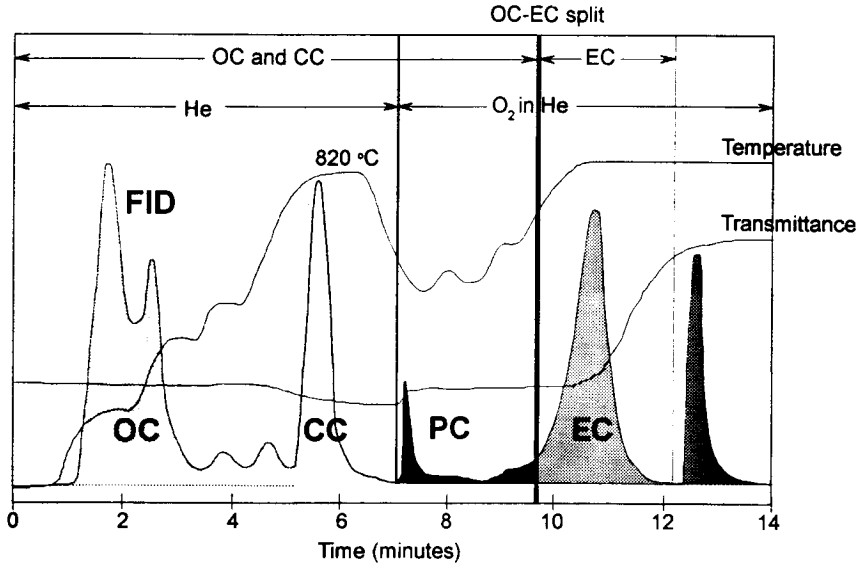

FIGURE 2. Example thermogram for sample containing rock dust (carbonate source) and diesel exhaust. Three traces correspond to temperature, filter transmittance, and detector (FID) response. Peaks correspond to organic (OC), carbonate (CC), pyrolytic (PC), and elemental (EC) carbon. The final peak is a methane calibration peak.

bonate), 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 of the suspect peak (typically the fourth peak) is indicative of carbonate in the original sample.

Instrument Calibration

Because a standard for OC, EC, and CC in carbonaceous aerosol samples is not currently available, OC standards must be used for instrument calibration. In this approach, accurate determination of carbon in samples of unknown composition requires an instrument response that is independent of the compound and matrix type.

To investigate whether the efficiency of the thermal–optical method's catalytic oxidation–reduction process is independent of sample type, various carbonaceous materials were examined. Standard solutions containing polynuclear aromatic hydrocarbons (PAHs) and solutions of various water-soluble organic compounds were analyzed. An aliquot of solution was applied to a 1.5 cm^2 filter (quartz) punch. Prior to application of the standard solution, the punch was precleaned in the analyzer to remove possible carbon contamination. Results of linear regression of the OC data (i.e., μg carbon reported versus μg carbon actual) are given in Table 1. Two of the PAHs selected (naphthalene and acenaphthylene) were too volatile to be reliably analyzed, and results for these compounds are not reported. Response of each of the other PAHs examined appeared linear ($r^2 \geq 0.996$, $3 \leq n \leq 13$), but results for two PAHs (benzo(a)pyrene and benzo(k)fluoranthene) were higher than predicted. Higher results are attributed to the presence of residual solvent (acetone), which did not completely volatilize from the filter punch. No discernible difference between the responses of dimethylbenz(a)anthracene and fluoran-

TABLE I. Linear Regression Results for Organic Carbon Standards

Analyte(s)	n	r^2	Slope[a], CL[b]	Intercept	SE[c] y Estimate
DMB(a)anthracene[d]	3	> 0.999	0.98, 0.01	0.11	3.02
Benzo(a)pyrene	13	0.999	1.15, 0.02	0.60	0.67
Benzo(k)fluoranthene	4	0.999	1.08, 0.07	0.25	0.69
Fluoranthene	3	> 0.999	0.97, 0.01	1.59	0.08
Sucrose	7	0.998	0.98, 0.04	0.94	1.06
Caffeine	4	> 0.999	0.98, 0.10	0.85	0.63
Glycine	4	0.999	0.96, 0.09	1.45	1.03
EDTA	19	> 0.999	0.99, 0.01	0.15	0.35
KHP	9	> 0.999	1.01, 0.01	−0.21	0.28
All nonaqueous	23	0.991	1.00, 0.04	2.35	3.02
All aqueous	43	0.999	0.99, 0.01	0.30	0.89

[a] μg·C reported/μg·C actual.
[b] 95% confidence limits of slope.
[c] Standard error of y estimate.
[d] Dimethylbenz(a)anthracene.

thene was seen. Results for all four PAHs are plotted in Fig. 3.

Better agreement between actual and reported values was obtained with the aqueous standard solutions, where interference of residual organic solvent was not a problem. Based on the confidence intervals of the slopes (Table 1), no compound dependence was noted with the five compounds examined. Response of individual compounds was linear ($r^2 \geq 0.999$, $3 \leq n \leq 19$), and slopes of the regression lines were all

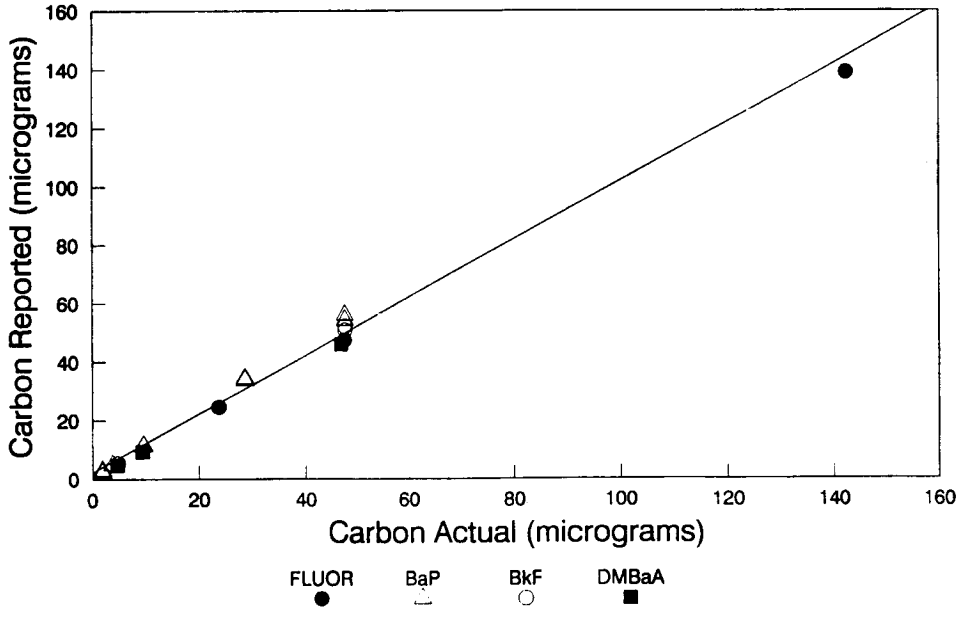

FIGURE 3. Plot of amount of carbon reported versus actual. Results obtained for four different PAHs: fluoranthene (FLUOR), benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF), and dimethylbenz(a)anthracene (DMBaA).

near unity, indicating that the efficiency of the method's oxidation–reduction process (i.e., conversion of analyte carbon to CH_4) was near 100%. Results of linear regression of data (i.e., $\mu g \cdot C$ reported versus μg actual) for all aqueous standards also are listed in Table 1, and these data are plotted in Fig. 4.

In addition to the OC standard solutions, a variety of carbonaceous dusts was analyzed by the thermal–optical method and by two other independent laboratories (Galbraith Laboratories, Inc., Knoxville, TN; M-H-W Laboratories, Phoenix, AZ). Materials examined and analytical results are given in Table 2. Good interlaboratory agreement was seen in results reported by the three laboratories. The relative standard deviation (RSD) of the mean percent carbon found in the samples was under 7% for all materials examined. Good reproducibility also was obtained by individual labs; variability in the mean carbon reported was less than 2%.

Analytical Range and Limit of Detection

The analytical range and limit of detection (LOD) of the thermal–optical method were determined with aqueous solutions of OC standards. An upper filter loading of about 50 $\mu g \cdot C/cm^2$ was obtained when the carbon was evolved as a narrow peak, which occurred with caffeine. In general, when a given peak in the thermogram represents more than about 50 $\mu g \cdot C/cm^2$ a smaller sample punch should be analyzed because an offscale response results. Alternatively, the gas flow through the instrument can be lowered to prevent an offscale response, but this approach is generally not recommended because the instrument parame-

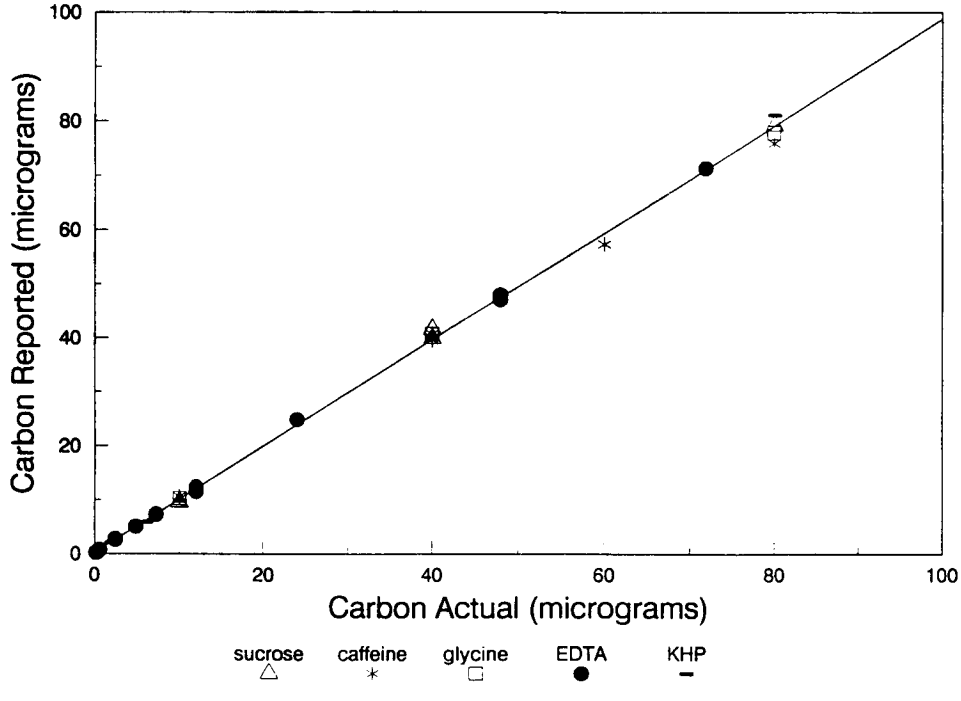

FIGURE 4. Plot of amount of carbon reported versus actual. Results obtained for aqueous solutions containing sucrose, caffeine, glycine, EDTA, and KHP. One analyte per solution.

TABLE 2. Analysis of Carbonaceous Materials: Interlaboratory Comparison

Sample	C Reported (%)			Mean C, RSD (%)
	Galbraith	M-H-W	Thermal–Optical	
Lignite	51.51	55.40	53.27	53.39, 2.98
subB[a]	60.17[b]	63.34	57.12[c]	60.21, 4.22
hvAa[a]	61.04	62.04[d]	70.40	64.49, 6.51
lvb[a]	75.46	77.01	75.72	76.06, 0.89
Anthracite	77.98	80.64	79.76[e]	79.46, 1.39
SRM 1649	17.55	18.95	17.60	18.03, 3.60
SRM 1650	77.19	77.01	74.60	76.27, 1.55
Humic acid	41.84	44.44	41.05	42.44, 3.41

[a]American Society for Testing and Materials (ASTM) coal rank: subbituminous (subB) and bituminous (hvAb, lvb) coals.
[b]Mean, $n = 2$, RSD = 0.26%.
[c]Mean, $n = 3$, RSD = 1.90%.
[d]Mean, $n = 2$, RSD = 0.14%.
[e]Mean, $n = 2$, RSD = 6.97%; second sample analyzed six months after first analysis.

ters must be altered once again prior to analysis of lightly loaded samples.

In contrast to the OC standards examined, various types of carbon are usually present in field samples, and the different types are evolved over different temperature ranges. In this case, much higher carbon loadings (e.g., 200–300 $\mu g/cm^2$) are possible. Although carbon loadings as high as 300 $\mu g/cm^2$ can be analyzed, the split between OC and EC can be affected if the filter is so heavily loaded with EC that changes in transmittance cannot be monitored. The loading at which this occurs depends on the optical properties of the sample; however, in general, EC loadings less than 20 $\mu g/cm^2$ are recommended. For an 8 h sample collected at 2 L/min on a 37 mm filter, this translates to a maximum EC concentration of about 180 $\mu g/m^3$. In practice, pyrolysis correction is unnecessary when EC loadings are this high because the char contribution to the measured EC is only minor [note: an impactor with appropriate design specifications must be used in coal mines (Birch and Stanevich, 1996)]. In such cases, the OC–EC split can simply be designated prior to the EC peak, and a maximum EC concentration of about 0.5 mg/m^3 can be determined when collecting 8 h samples at 2 L/min on 37 mm filters, or an upper EC loading of about 50 $\mu g/cm^2$. If measurement of higher concentrations is desired, lower sampling rates or shorter sampling times should be used. In many workplaces, EC concentrations are well below this upper limit, a notable exception being the mining industry. Requirements for application of the thermal–optical method in the mining industry will appear elsewhere (Birch and Stanevich, in preparation).

The LOD of the thermal–optical method was calculated following a Standard Operating Procedure (Eller, 1995). Accordingly, low-level calibration standards covering a range from less than the expected LOD to no greater than ten times that expected were prepared and analyzed. A 0.05 M volumetric standard solution (Aldrich) of the disodium salt of ethylenediaminetetraacetic acid (EDTA) was diluted with distilled–deionized water, and aliquots of the solution were applied directly to 1.54 cm^2 quartz-fiber filter punches, which is the punch size normally taken from the filter sample for analysis. As with all standards, punches were precleaned in the analyzer prior to application of the standard solution to ensure that they were carbon-free. Loadings on the punches covered a range from 0.19–4.79 μg carbon, and five levels were examined. The three lowest carbon levels were analyzed in duplicate and the two

highest were analyzed once, giving a total of eight analyses.

Results of linear regression of the low-level calibration data (i.e., $\mu g \cdot C$ reported versus $\mu g \cdot C$ actual) were used to calculate the analytical LOD as follows:

$$LOD = 3s_y/m$$

where s_y is the standard error of the regression and m is the slope of the regression line. Using this procedure, an LOD of about 0.23 μg carbon (or about 0.15 $\mu g \cdot C/cm^2$ of filter) was calculated [intercept = 0.02, standard error (SE) of y estimate = 0.08, $r^2 = 0.998$, $m = 1.05 \pm 0.02$]. In terms of concentration, if air samples were collected for 8 h at 2 L/min on 37 mm filters, an LOD of about 2 $\mu g \cdot C/m^3$ of air could be expected. Thus, the method is capable of EC determination at the background (i.e., environmental) level. Measured background EC levels are discussed in a following section.

Sampler Comparison

When interference of other dusts is not a problem, which is often the case in general (i.e., nonmining) industry, size-selective samplers are not required. In this situation, any of a variety of samplers can be expected to give equivalent results because submicrometer diesel particles will be collected by different samplers with the same efficiency (near 100%). To confirm this assumption, a sampler comparison study was conducted at an express-mail facility that uses diesel-powered trucks for package transport. Included in the comparison were open-face, 35 and 25 mm cassettes; the "298" personal cascade impactor (Graseby/Andersen, Atlanta, GA); the IOM inhalable dust sampler (Mark and Vincent, 1986); and four different prototype impactors designed by researchers at the University of Minnesota and the U.S. Bureau of Mines (BOM) (McCartney and Cantrell, 1992), the Mine Safety and Health Administration (MSHA) (Haney, 1990), and NIOSH (McCawley and Cocalis, 1986). The prototype impactors were designed for use in coal mines and are not required in general industry, but they were included in the evaluation so results obtained with these devices could be compared with those found using commercially available samplers.

Two each of the eight sampler types were used, and all samplers were operated at 2 L/min. The prototype impactors were modified to accommodate quartz-fiber filters, which are necessary for thermal–optical analysis. The samplers were hung in the base of a chamber, which was placed in the loading dock area of the facility where diesel-powered trucks were operating while being loaded prior to their departure from the facility. For the purpose of randomization, the samplers were arranged inside the chamber in a circular fashion, and samplers of a given type were diametrically opposed. Large-diameter (ca. 14 in) flexible duct was used to transport diesel aerosol from a truck's above-cab exhaust pipe to the sampling chamber. The duct preserved a high aerosol concentration and facilitated mixing of the exhaust.

Results of thermal–optical analysis of diesel exhaust samples collected with the eight different sampler types are given in Table 3. Because the precision of the mean EC concentration determined with the IOM sampler was poor (RSD = 31%), results obtained with this sampler were not included in the statistical comparison of samplers. The RSD of the mean EC concentration found using results for the other seven sampler types was 5.6% (mean EC = 4.01 mg/m^3, $n = 14$). To compare differences between means for different samplers, estimates of the between- and within-sampler variances were calculated (0.0516 and 0.0507, respectively). Based on results of a one-tailed F test ($F_{6,7} = 1.02$), differences between sampler means were not significant [critical value of $F \approx 3.87$ ($P = 0.05$)]. Higher intersampler variability was seen in the OC concentration (mean OC = 8.63 mg/m^3, RSD = 12.3%, $n = 14$), which can be expected when filters are used

TABLE 3. Sampler Comparison Study: Thermal–Optical Analysis of Carbon in Diesel Particulate Samples

Sampler	Cutpoint[a], μm	Mean[b] EC, mg/m^3 (RSD)	Mean[b] OC, mg/m^3 (RSD)
25 mm cassette[c]	—	3.95 (0.08)	8.99 (0.00)
37 mm cassette[c]	—	4.16 (0.02)	9.74 (0.04)
298 cascade impactor[d]	0.9	3.72 (0.03)	6.88 (0.08)
IOM sampler	—	4.34 (0.31)	8.38 (0.04)
BOM impactor	0.8	4.20 (0.05)	9.58 (0.00)
University impactor[e]	0.8	4.09 (0.04)	9.27 (0.03)
MSHA impactor	0.8	3.96 (0.10)	8.44 (0.01)
NIOSH impactor	1	4.02 (0.02)	7.54 (0.04)

[a]Approximate 50% cutpoint.
[b]$n = 2$.
[c]Open-face configuration.
[d]Seven stages loaded to give 0.93 μm cutpoint.
[e]Developed jointly by the University of Minnesota and BOM.

for collection of organic aerosol containing volatile or semivolatile components.

Interferences

A variety of carbonaceous aerosols are present in the workplace; however, most of these aerosols are primarily OC and do not pose an interference in the determination of EC. Unlike other thermal methods, char generated during thermal–optical analysis of some materials (e.g., cigarette smoke, spores, pollen, plant debris) does not interfere because the method optically corrects for carbonization.

The potential contribution of EC by cigarette smoke was examined. Filter samples of cigarette smoke were collected for analysis. The mean EC found was only 0.86% ($\sigma_{n-1} = 0.48\%$, $n = 6$) of the total carbon content. This result is in good agreement with that previously obtained in an industrial hygiene study by other NIOSH investigators (Zaebst et al., 1991), where less than 2% of the carbon found in cigarette smoke was elemental. The EC fraction reported here may be slightly lower than that found previously because the current temperature program differs slightly from the program used previously. It is important to recognize that the temperature program employed in the analysis was optimized for specificity against cigarette smoke, and other temperature programs could produce different results. For example, when a different temperature program was used for analysis of cigarette smoke, the evolution of high-temperature carbon and a concomitant increase in filter transmittance happened too quickly, and the OC–EC split occurred earlier than it did with the optimized program. Consequently, 20–30% of the carbon in cigarette smoke was designated elemental when a less than optimal temperature program was used. Depending on the thermal program employed, EC fractions in this range could potentially be found with other carbon analysis methods.

Various inorganic materials may be present in some workplaces. Colored inorganics (e.g., iron oxide) ordinarily do not present a problem with respect to the OC–EC split because their absorbance is usually negligible (relative to EC) and is constant during the analysis. Although metals that form black oxides could affect the OC–EC split, this situation can be remedied through manual assignment of the split. Nonabsorbing inorganics (e.g., ammonium sulfate or nitrate) that scatter light and vaporize during the analysis also do not affect the determination of EC unless they are present at high loadings (e.g., > 100 μg/cm^2) and the amount of EC is low (background levels).

Other airborne materials that could be encountered include wood smoke, welding fumes, automotive (gasoline) exhaust,

and soils. Because wood smoke is largely ($\geq 95\%$) OC, its EC contribution should be relatively minor in most situations. Welding fumes consist mostly of organic and metallic (e.g., manganese, iron) species, which ordinarily do not interfere in the analysis. Gasoline-powered vehicles emit much less soot than do diesel vehicles (Zweidinger, 1982), so their contribution to the measured EC should be negligible. Finally, because soils are composed largely of inorganic matter, they also do not present an interference (soils high in humic acid may be an exception if present at high levels).

Although interferences in most workplaces are not anticipated, it is not possible to predict all possible scenarios. Obviously, the method should not be applied for monitoring particulate diesel exhaust when other major sources of EC (e.g., carbon black) are present. In general, the best means of determining whether the EC contribution from a particular airborne material could be significant is through analysis of the bulk material. If the dust is mechanically generated, as is coal dust, a size-selective sampling approach can be used to minimize its collection. Only low levels ($\leq 15\ \mu g/m^3$) of EC were found in electric-powered (i.e., nondieselized) underground coal mines when impactors with submicrometer cutpoints were used (Birch, 1992; Birch and Stanevich, in preparation). If the material is a combustion aerosol that cannot be excluded on the basis of size (e.g., cigarette smoke), its EC contribution will depend on the concentration and EC content of the aerosol.

OCCUPATIONAL EXPOSURE LEVELS

Workplace exposures to particulate diesel exhaust have been assessed by both gravimetric and thermal–optical analysis methods. Results of gravimetric determination of submicrometer aerosol indicate that miners' exposures to diesel exhaust are higher than those typical of nonmining industries. In a study of five dieselized coal mines (Watts et al., 1992), mean concentrations of submicrometer aerosol collected with personal diesel aerosol samplers (0.8 μm cutpoint) ranged from 0.89–1.43 mg/m^3, depending on location. In other surveys (McCawley and Cocalis, 1986) of two coal mines equipped with diesel shuttle cars, levels of submicrometer particulate collected with 298 cascade impactors ranged from 0.1 (at a section intake) to 0.8 mg/m^3 (operator of continuous mining equipment). Thermal–optical analysis results also indicate that diesel exhaust levels in mines are relatively high. In preliminary investigations of dieselized mines (Stanevich and Birch, 1991), EC levels typically ranged from 150–500 $\mu g/m^3$, and sometimes exceeded 800 $\mu g/m^3$. A detailed discussion of miners' exposures to diesel exhaust will appear elsewhere (Birch and Stanevich, in preparation).

As stated earlier, gravimetric methods lack adequate sensitivity and selectivity for determination of low levels of diesel exhaust. For this reason, carbon analysis methods have been used for environmental measurements and for monitoring exposure to diesel aerosol in general (i.e., nonmining) industry. In a study of the trucking industry (Zaebst et al., 1991), an overall mean EC exposure of about 14 $\mu g/m^3$ was found. Mean EC exposures ranged from about 2–44 $\mu g/m^3$ and were highest for mechanics and dock workers. In the dock area, where there reportedly were no other (i.e., nondiesel) obvious sources of OC except sidestream tobacco smoke, about 47% ($n = 29$, RSD = 4.0%) of the carbon content of the samples was elemental.

Elemental carbon exposures ranged from about 4–52 $\mu g/m^3$ in surveys of four fire stations (Ferrara, T., Occupational Health and Safety Section, Bureau of Health Risk Assessment, Division of Public Health Services, Department of Health and Human Services, Concord, NH, personal communication, 1995). The two highest exposure levels were 23 and 53 $\mu g/m^3$, and EC was 71 and 89%, respectively, of the total carbon content of these samples. In contrast, samples collected in an area where portable gasoline-powered equipment (e.g., chain saws, jaws of life) was being tested had

relatively high levels of OC (273 $\mu g/m^3$), but only about 3% of the carbon was elemental. In other investigations of fire engine houses (Echt et al., 1993), firefighters' personal exposures (i.e., breathing zone samples) to EC ranged from about 20–79 $\mu g/m^3$. In certain locations of the engine houses, maximum levels found through area sampling were higher than those found with personal samples. For example, EC concentrations in the apparatus bays ranged from about 86–683 $\mu g/m^3$ on one day of the survey.

In surveys of automotive repair shops (Olesen, A., Urban Engineers, Philadelphia, PA, personal communication, 1995), EC levels in shops dedicated to the repair of diesel vehicles ranged from about 7–70 $\mu g/m^3$, and approximately 38% of the carbon in a sample that was thought to be mostly diesel exhaust (i.e., the 70 $\mu g/m^3$ sample) was elemental. In contrast, EC levels found in shops responsible for repair of gasoline-powered vehicles were lower, ranging from about 3–7 $\mu g/m^3$. In these areas, OC levels were typically about 200 $\mu g/m^3$, but less than 4% of the carbon found was elemental.

During an industrial hygiene survey of a public transit system (Wilson, K., Division of Safety and Hygiene, Ohio Bureau of Workers' Compensation, Dayton, OH, personal communication, 1995), the highest EC exposures occurred in a service bay area for buses. In this area, a personal exposure of 98 $\mu g/m^3$ was found, and about 55% of the sample carbon was elemental (80 $\mu g/m^3$ OC exposure). Elemental carbon exposures in other areas ranged from about 15–30 $\mu g/m^3$, and in these areas about 31% of the sample carbon was elemental. The lower EC fractions seen in the other areas are not surprising because the influence of adsorbed vapor and nondiesel OC on the apparent EC fraction of the diesel-source carbon is greater when diesel particulate levels are relatively low.

Other workplaces examined include a timber processing facility, a commercial airline, and a beverage distribution warehouse. At the timber facility, a front-end loader equipped with a grappler was being used for lifting and placing logs into a steam vat for "cooking." The loader was operating in a poorly ventilated, enclosed area, and its exhaust stack height is approximately at operator level. EC concentrations (breathing zone samples) near 200 $\mu g/m^3$ were found (Jefferies, D., Corporate Safety Director, Plum Creek Manufacturing, LP, personal communication, 1995). EC exposures of aircraft ground crew at a Houston airport ranged from about 7–15 $\mu g/m^3$ (Decker and Donovan, 1994). OC exposures, which ranged from about 46–292 $\mu g/m^3$, were considerably higher because the crew also was exposed to gasoline engine exhaust and fuels. Finally, breathing zone EC levels found in beverage distributor's warehouse ranged from about 5–17 $\mu g/m^3$; OC exposures ranged from 25–40 $\mu g/m^3$ (Kiefer, 1992). Cigarette smoking reportedly took place throughout the warehouse and contributed to the OC levels present.

EXPOSURE ISSUES

Uncertainties in Human Risk

Although various methods for detecting potential human carcinogens have been developed, elucidation of a causal relationship between exposure to a suspect agent and human cancer ultimately requires epidemiological evidence (Cohen and Ellwein, 1992). Often, results of epidemiologic studies are equivocal unless strong relationships exist, and they are not specific when exposures involve a wide variety of agents (Cohen and Ellwein, 1992). Current epidemiological evidence suggests that long-term employment in occupations where significant exposure to diesel exhaust occurs is associated with a "modest" increase in risk (relative risk 1.2–1.5) for lung cancer (Mauderly, 1992) relative to workers categorized as unexposed. Because the apparent increase in risk is small, it is sensitive to misclassification of subjects [e.g., smoker versus nonsmoker (Mauderly, 1992)] and other potential confounding factors.

Animal studies provide evidence that unfiltered diesel exhaust is a pulmonary carcinogen in rats when high concentrations are inhaled chronically (Mauderly, 1992); evidence for exposed mice and Syrian hamsters is questionable and negative, respectively. Although rat bioassay data have been used to calculate human carcinogenic risk estimates, the validity of the extrapolation has been questioned (Mauderly et al., 1994; Health Effects Institute, 1995). Risk assessments based on studies of high-dose animal exposure rely on two important assumptions (Cohen and Ellwein, 1992). Namely, it is assumed that a substance causing cancer in animals likely will do so in humans, and that a substance causing cancer at high doses also will at low doses. Although standard bioassay protocols are widely used for the evaluation of chemical carcinogenicity in rats and mice, their initial development for use in human risk assessment was based on the evaluation of agents such as radiation and potent chemical genotoxins (e.g., N-nitrosodi-ethylamine, benzo[a]pyrene), where there is considerable evidence that species and dose extrapolations are appropriate (Cohen and Ellwein, 1992). In the case of nongenotoxic agents, standard protocols based on these assumptions may be inappropriate. Unlike genotoxic agents, nongenotoxic agents do not interact directly with DNA; rather, they are thought to produce their effects by increasing cell proliferation (Cohen and Ellwein, 1992). Under these circumstances, dose and mechanistic factors could be important in the estimation of human risk because the dose to which humans are exposed may be below a threshold level required for carcinogenesis or the mechanisms responsible for tumor formation in rodents may not occur in humans (Cohen and Ellwein, 1992). The high diesel particulate concentrations to which rats were exposed are thought to effect a "lung overload" (Morrow, 1988) response involving inflammation and cell proliferation (Mauderly et al., 1992, 1994). This response, which is induced by the insoluble carbon core of the diesel particle, has been proposed as the dominant factor in carcinogenesis in rats, and reportedly may be required for tumor formation (Pepelko and Chen, 1993). Whether such a mechanism occurs in humans exposed to much lower levels of particulate diesel exhaust is uncertain.

If diesel exhaust causes lung cancer in humans and impaired particle clearance is involved in the mechanism(s) of carcinogenicity, it is important to assess the particulate lung burdens at which particle clearance is impaired. In a retention model (Yu et al., 1991) of diesel exhaust particles in humans and rats, the predicted level of diesel soot affecting reduced alveolar clearance in humans is much lower than that for rats. For ten years of continuous exposure, *no clearance impairment* is predicted if exposure concentrations are below about 50 $\mu g/m^3$. For ten years of intermittent exposure (i.e., 8 h/day, 5 days/week), impairment of particle clearance is not predicted at concentrations below about 200 $\mu g/m^3$. The apparently higher sensitivity of humans (relative to rats) to diesel particulate matter also is suggested by the cancer risk estimates based on epidemiology data, and by results of a study of monkeys and rats exposed to diesel exhaust (Bond et al., 1989), where levels of DNA adducts found in the lungs of monkeys were higher than those found in the lungs of similarly exposed rats.

Both genotoxic and nongenotoxic mechanisms may be responsible for the elevated lung cancer risks found in some epidemiological studies. The presence of trace levels of genotoxic chemicals may be acting synergistically with the effects of accumulated particulate in the lung to further increase the probability of DNA damage. Future research is necessary to establish whether the mechanisms responsible for malignancies in rats are operative in humans.

Exposure Criteria: Current Status

As is apparent from the discussion of carcinogenic risk, many uncertainties and complex issues are involved in the quantitative assessment of human cancer risk asso-

ciated with exposure to diesel exhaust. At present, health-based exposure criteria have not been established, but the American Conference of Governmental Industrial Hygienists (ACGIH) has proposed an exposure standard of 150 μg of submicrometer particulate per m^3 air (see 1995–1996 Notice of Intended Changes list).

Standards based on technical feasibility have been set in British Columbia and Germany. British Columbia limits respirable combustible dust (RCD) levels in mines (coal mines excepted because of coal dust interference) to 1.5 mg/m^3 (Dainty and Gangal, 1991). Based on an estimated 33% contribution to the RCD by nondiesel sources (e.g., oil mist), this standard corresponds to an average diesel particulate level of about 1 mg/m^3. Reportedly (Watts, 1995), reduction of the RCD standard to 0.75 mg/m^3 has been recommended.

Germany has established carbon-based exposure criteria for diesel particulate matter (TRK-Wert, 1992; Lehmann, E., Bundesanstalt für Arbeitsschutz, Dortmund, Germany, personal communication, 1993). TRK values (based on technical feasibility) were set at 200 μg carbon per m^3 air in nonmining industries and 600 μg carbon per m^3 air in noncoal mines and other underground worksites. A carbon analysis method involving combustion and coulometric determination of CO_2 initially was employed (Lehmann et al., 1989), and this method was later modified to permit speciation of OC and EC (Auffarth, 1991). Although an EC exposure standard for diesel particulate has not yet been established in Germany, an EC standard is expected to be set in 1996 (Dahmann, D., Technical Director, Institut für Gefahrstoff-Forschung der Bergbau-Berufsgenossenschaft, Bochum, Germany, personal communication, 1995).

Submicrometer Particulate or EC?

As detailed earlier, many interferences can be expected in the gravimetric determination of submicrometer particulate concentrations at (and certainly below) the proposed TLV (150 μg/m^3). Alternatively, the proposed TLV could be cast in terms of EC, which is the most specific measure of diesel particulate, by estimating the EC fraction of diesel particulate. Because this fraction is variable, an approximation must be made. Based on the EC fraction of the carbon found in field samples, a fraction of 50% appears reasonable. Assuming that carbon constitutes about 88% of the diesel particulate mass (Volkswagen, 1989), an EC fraction of about 44% could be used as an estimate. Although an estimated value contributes added uncertainty in the standard development process, this contribution is minor relative to the uncertainties in the assumptions made in arriving at the proposed TLV.

An EC exposure standard also could be proposed through reference to a previously conducted risk assessment (Smith and Stayner, 1991). In the assessment, the dose equivalence term used to extrapolate unit risk for humans from rat carcinogenicity data was the mass concentration of diesel aerosol; however, the most appropriate term for extrapolation is uncertain (Smith and Stayner, 1991; Mauderly, 1992). Risk also could be expressed in terms of EC because the exhaust to which animals were exposed was characterized. During most of the study, the particulate fraction averaged about 85% nonextractable material (Mauderly et al., 1987; Mauderly, 1992 communication). Presuming that about half of the other elements (e.g., metals, oxygen) found (Volkswagen, 1989) in diesel particulate are present in the nonextractable fraction, one could assume that about 6% of this fraction is contributed by other (i.e., noncarbon) elements. Thus, approximately 79% of the particulate to which the animals were exposed was EC. Knowing this percentage, a risk-based EC exposure standard could be expressed. For example, if a 50 μg/m^3 standard for particulate diesel exhaust was considered protective, this level would translate to an EC standard of about 40 μg/m^3 (0.79×50).

Because the validity of using animal data for estimating human cancer risk has been

questioned, reference to epidemiologic studies of railroad workers may be the preferred approach to setting an EC-based exposure standard. As part of these studies, respirable samples from the locomotive repair shops were collected and characterized. Approximately 30–40% of the particulate mass was extractable in dichloromethane. If the nonextractable portion is used as an estimate of the EC fraction of the particulate, about 60–70% of the particulate mass was EC. This range agrees well with that found in other studies, where EC constituted approximately 64–71% of the diesel particulate mass (Gray, 1986; Volkswagen, 1989).

If an EC-based occupational exposure standard ultimately is established for particulate diesel exhaust, background (i.e., environmental) levels should be considered. Numerous sources of carbonaceous matter (e.g., diesel and nondiesel vehicles, incinerators, tire debris) contribute to varying extents to the ambient background levels of EC, and various environmental EC levels have been reported. Mean EC concentrations from 4.97–6.38 $\mu g/m^3$ were found (Cadle and Mulawa, 1990) in Glendora, CA, during an intercomparison study of analytical methods for carbonaceous aerosols. During the same study, average (6 h) EC concentrations from about 2–6 $\mu g/m^3$ were found using a real-time technique. Examination of the data at 1 min intervals revealed that emission plumes from diesel vehicles located 50 m from the study site contributed up to 5 $\mu g/m^3$ above the background level (Hansen and Novakov, 1990).

In downtown Los Angeles, where ambient aerosol concentrations are generally the highest in Southern California because of heavy motor vehicle traffic, an annual mean EC concentration of 4.9 $\mu g/m^3$ has been reported (Gray et al., 1984). The EC constituted about 38% of the total fine (< 2 μm particle diameter) aerosol carbon, and diesel engine exhaust was the dominant source of the airborne EC. Higher EC concentrations were observed during winter months, which reportedly was the case for other pollutants (e.g., CO and Pb) emitted by motor vehicles. In other U.S. cities, mean background concentrations measured at eight different sites were 3.4 $\mu g/m^3$ ($n = 21$, SE = 0.5) and 1.4 $\mu g/m^3$ ($n = 23$, SE = 0.2) near major highways and in residential areas, respectively (Zaebst et al., 1991). In contrast to the EC levels found in urban areas, environmental levels of EC (or "soot carbon") found in nonindustrialized locations (e.g., Ivory Coast, Congo, costal Corsica) seldom exceeded 1 $\mu g/m^3$ (Cachier et al., 1989).

SUMMARY AND CONCLUSIONS

Because animal studies link the carcinogenic effects of exposure to diesel engine exhaust emissions to the particulate fraction of the exhaust, a sampling and analytical method for carbonaceous aerosols was investigated. Of the various methods that have been used for carbon analysis, a thermal–optical technique that speciates different carbon types in a filter sample was examined because this approach offers maximum selectivity relative to other methods. Neither carbonate nor carbonized material interfere in the determination of EC, which is the most specific measure of particulate diesel exhaust. In addition to its selectivity advantage, the thermal–optical method is capable of the determination of EC at environmental background levels. The method is both practical and inexpensive (currently about $30 per analysis), making it well suited for routine exposure monitoring and evaluation of control technology for diesel particulate matter.

In this study, the EC results obtained when collecting diesel aerosol samples with a variety of samplers were not statistically different. Because open-face cassettes are inexpensive, easy to use, require no modification, give homogeneous deposits, and are readily available, these samplers are recommended unless the sampling environment dictates otherwise. In some instances (e.g., when other dust is present at levels that could overload the filter), collection of a respirable dust fraction should be consid-

ered. In coal mines, an impactor with a submicrometer cutpoint is necessary to minimize collection of coal-source EC. Sampling requirements for this particular workplace appear elsewhere (Birch and Stanevich, 1996).

Although an EC-based method (5040) for particulate diesel exhaust has been submitted for inclusion in the *NIOSH Manual of Analytical Methods* (*NMAM*) and industrial hygienists both within and outside the Institute have been using the method for occupational monitoring, exposure criteria for particulate diesel exhaust have not yet been established in the U.S. A TLV of 150 $\mu g/m^3$ air has been proposed, but this value applies to submicrometer particulate, and there is much uncertainty in its basis. Many interferences can be expected when determining diesel particulate by gravimetric means. Interferences also are expected if total carbon is used as a measure of the diesel particulate concentration.

Environmental background EC levels can be used as a reference point for determining the extent to which workplace EC concentrations are elevated, but the risks associated with these elevated levels are uncertain. Typically, background levels of EC are about 2–3 $\mu g/m^3$ air. For comparison, an overall mean EC exposure of 14 $\mu g/m^3$ was seen in the trucking industry. In the mining industry, EC concentrations often exceeded 100 times environmental levels, and typically range from about 150–500 $\mu g/m^3$. In other workplaces, EC concentrations ranged from about 5–200 $\mu g/m^3$, but levels below 100 $\mu g/m^3$ were more common. Until health-based exposure criteria are established, reference to epidemiological studies as an indicator of potential health effects may be a prudent approach when considering whether elevated levels of diesel particulate warrant remedial action (e.g., exhaust filters, increased ventilation). To date, the weight of epidemiological evidence indicates that the increased risk of lung cancer for workers exposed to diesel exhaust is comparable to that for environmental tobacco smoke. In a widely cited retrospective cohort study of diesel-exposed railroad workers (Garshick et al., 1988), a relative lung cancer risk of 1.4 (95% CI = 1.11, 1.89) was found. Geometric mean exposures to respirable particulate (after correction for cigarette smoke) ranged from 17 $\mu g/m^3$ for clerks to 134 $\mu g/m^3$ for locomotive shop workers. In general, the average levels of diesel exhaust found in most occupational settings (mining industry excepted) are estimated to be less than 100 $\mu g/m^3$ (Health Effects Institute, 1995). Taken in the aggregate, these findings suggest that occupational exposure to relatively low concentrations (e.g., 100 $\mu g/m^3$) of diesel exhaust may pose an elevated risk for lung cancer. At present, actual (i.e., measured) exposure data are lacking, and the accuracy of past human exposure estimates is uncertain. An ongoing epidemiological study (by NIOSH and the National Cancer Institute) of miners exposed to diesel exhaust may help resolve some of the uncertainties involved in the assessment of the potential carcinogenic risk for humans.

Additional research is necessary to address the potential adverse health effects of fine particulate matter, especially carbonaceous material bearing trace levels of adsorbed carcinogens, as does diesel particulate. Such particles have a high affinity for organic compounds, and have been shown to increase the long-term retention of known carcinogens. Although it appears that tumor induction in animals may be caused primarily by excessive lung burdens of particulate carbon, it has not been determined whether the mechanisms responsible for tumorigenesis in rats are operative in humans. Regardless of whether potential adverse health effects in humans originate largely from the particles themselves, their adsorbed genotoxins, or from a combination of the two, monitoring and control of the particulate component are necessary if effects exist that are particle-related.

Aside from its potential carcinogenicity, it is important to recognize that other principal components of diesel exhaust, including carbon monoxide and oxides of nitrogen and sulfur, also are associated with

adverse health effects. Exposure criteria already exist for these gas-phase species, and adoption of an EC standard would not obviate the need to monitor their concentrations as well.

M.E.B. thanks Karen McCabe for assistance in arranging the survey conducted at an express-mail facility, Paul Baron (NIOSH) for assistance with figure preparation and loan of a diesel automobile used for generation of some samples, and Dennis Zaebst (NIOSH), who provided preliminary results of surveys conducted in the trucking industry. The cooperation of Annette Olesen, Theresa Ferrara, Ken Wilson, and Dana Jefferies also is appreciated.

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Received February 21, 1995.