NIOSH Comments to DOL

COMMENTS FROM THE
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ON THE
MINE SAFETY AND HEALTH ADMINISTRATION
PROPOSED RULE ON
PERMISSIBLE EXPOSURE LIMIT FOR DIESEL PARTICULATE

30 CFR Parts 58 and 72

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

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INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) has reviewed the advance notice of proposed rulemaking (ANPR) of the Mine Safety and Health Administration (MSHA) entitled "Permissible exposure limit for diesel particulate published in the Federal Register on January 6, 1992 [57 FR 500]. NIOSH supports MSHA in its effort to establish a permissible exposure limit (PEL) for diesel particulate to control miner's exposure to diesel exhaust in the mining industry.

NIOSH continues to recommend that diesel exhaust be regarded as a potential occupational carcinogen and that efforts be made to reduce exposure to the lowest feasible concentration [NIOSH 1990a]. The NIOSH Current Intelligence Bulletin #50 titled "Carcinogenic effects of diesel exhaust" [NIOSH 1988] has a detailed discussion on this subject.

NIOSH has comments on the following topics related to the ANPR: risk assessment, sampling and monitoring methods, genotoxicity, and specific issues raised by MSHA for public comment.

RISK ASSESSMENT

As noted in the ANPR, NIOSH has submitted to MSHA the risk assessment entitled "An exploratory risk assessment of the risk of lung cancer associated with exposure to diesel exhaust based on a study of rats." In addition, we have attached for consideration by MSHA two recently completed risk assessments on contaminants from diesel exhaust:

> "*Assessment of risk from exposure to diesel exhaust emissions*," prepared by Crump and Lambert (Clements International Corporation) and Chen (U.S. Environmental Protection Agency), July 1991 [Crump et al. 1991]
>
> "*Projection of human lung cancer risks for diesel particulates from animal data - effects of using measures of internal dose, and possible interactions with smoking*," prepared by Hattis and Silver (Ashford Associates), April 1, 1992 [Hattis and Silver 1992]

SAMPLING AND MONITORING METHODS

At the request of MSHA, NIOSH is in the process of developing a sampling and analytical method for airborne diesel exhaust particles. NIOSH will forward the method to MSHA when it is finalized. Attachment 1 is the plan detailing the proposed research which was transmitted previously to MSHA on June 4, 1991.

NIOSH has proposed in Attachment 1 the use of elemental carbon as a surrogate measure of particulate diesel exhaust. In this plan, a thermal-optical method for determination of elemental carbon is described. Use of this method, in combination with a size-selective sampling approach, is proposed for monitoring worker exposure to particulate diesel exhaust because it is more accurate at low concentrations of diesel particulate than the gravimetric method.

The evaluation of the thermal-optical method has proceeded as outlined in the research plan. Size-selective sampling will be necessary in coal mines to minimize interference of elemental carbon from coal. Attachment 2 is a discussion of the current status of this project. Investigations should be completed by the end of the fiscal year and the research results will be transmitted to MSHA at that time.

GENOTOXICITY

Many reports in the scientific peer-reviewed literature show that diesel soot can express genotoxic activity to cells *in vitro*. This determination has been made frequently by extracting soot samples with organic solvents such as dichloromethane and dimethylsulfoxide, and then assaying *in vitro* the mutagenic or clastogenic potential of the extracts. The salmonella histidine reversion assay [Maron and Ames 1983], a bacterial gene mutation test system, is frequently used, followed by other tests for genotoxic potential using mammalian cells.

Concern has been expressed that the procedure for extracting soot with organic solvents is not analogous to the physiological environment of the lung, and that active genotoxic materials associated with respired soot particles might not be biologically available in the lung.

In addressing the mechanism of bioavailability, research by NIOSH has shown that diesel soot expresses genotoxic activity in vitro when the soot is dispersed in the primary component of the pulmonary surfactant which coats the surface of the lung air spaces. Therefore, this research demonstrates the biological availability of active genotoxic materials without organic solvent interaction. NIOSH has reported the following research that summarizes these results:

> **"*Mutagenicity of diesel exhaust particles and oil shale particles dispersed in lecithin surfactant,*" by Wallace et al. [1987]**
>
> This paper reported that diesel soot particles dispersed in dipalmitoyl phosphatidylcholine surfactant in saline were active in the Ames assay. That is, the NIOSH study indicates that surfactant dispersed soot particles can express mutagenic activity.

"Genotoxicity of diesel-exhaust particles dispersed in simulated pulmonary surfactant" by Keane et al. [1991]

This paper extends the above finding to sister chromatid exchange activity in an eucaryotic cell line which is derived from the Chinese hamster pulmonary fibroblasts. This indicates surfactant-dispersed diesel soot can also express clastogenic potential in mammalian cells.

"Induction of unscheduled DNA synthesis in V79 cells by diesel particles dispersed in simulated pulmonary surfactant" by Gu et al. [1991]

This paper demonstrates that repair of deoxyribonucleic acid (DNA), an indicator of DNA damage, is increased in mammalian cells following exposure to surfactant-dispersed diesel soot.

"Micronucleus induction and phagocytosis in mammalian cells treated with diesel emission particles," by Gu et al. [1992]

This paper reports the *in vitro* induction of micronucleus formation in V79 cells by exposure to surfactant-dispersed diesel soot. NIOSH is currently reviewing data for the induction of chromosomal aberration and induction of the 6-thioguanine-resistant forward mutation assay in V79 cells for solvent extracted, surfactant extracted, and surfactant dispersed diesel soot [Gu et al. (unpublished)]. The diesel soot used in most of these experiments was generated by a commercial automotive engine operated on a test stand. NIOSH is in the process of acquiring soots generated by diesel engines used in some representative mining operations. NIOSH is also developing protocols for testing complex exposures of diesel exhaust in combination with respirable mineral particulate matter. NIOSH will forward to MSHA the results of these studies when they are completed.

In summary, the solvent extract of diesel soot and the surfactant dispersion of diesel soot particles were found to be active in procaryotic cell and eucaryotic cell *in vitro* genotoxicity assays. These data indicate that respired diesel soot particles on the surface of the lung alveoli and respiratory bronchioles can be dispersed in the surfactant-rich aqueous phase lining the surfaces, and that genotoxic material associated with such dispersed soot particles is biologically available and genotoxically active.

SPECIFIC ISSUES

Issue - What effect does the environmental background level of diesel particulate have on diesel particulate exposure?

Response - Environmental background levels of diesel particulate will add to the exposure attributable to in-mine diesel operations. The observed levels are dependent upon nearby industrial activity, and the amount of ancillary diesel activity proximate to the surface air intakes. Generally, ambient levels of diesel particulate will be significantly lower than in-mine concentrations. For example, at the Young Mine of ASARCO, Inc. [NIOSH 1986], the submicrometer-sized particulate concentration that was measured outdoors was 0.04 mg/m^3. The average concentration underground at that mine was 0.70 mg/m^3. On this survey submicrometer particulate was used as the surrogate for diesel exhaust exposure. Regardless of the diesel activity at the surface, however, the amount of diesel particulate entering the mine will become a part of the miners' overall diesel exposure concentration.

Issue - Are there other health effects that result from exposure to diesel particulate?

Response - A paper by Glenn et al. [1983] summarized findings from several NIOSH studies of nonmalignant respiratory disease effects of diesel exhaust in underground miners. Elevated prevalences of chronic symptoms (cough and phlegm) were seen among diesel exposed miners in all four studies (coal, potash, trona, and salt). The cause of these elevated symptom rates was not established by the studies, though the authors concluded that inhalation of diesel exhaust or mineral dust may have been a factor. In terms of pulmonary function, data from these studies provided little indication that exposure to diesel exhaust at the observed levels leads to permanent deleterious effects on lung function.

Issue - What methods are available to measure diesel particulate exposure in underground mines? Are there any surrogate methods available that can be used to monitor diesel particulate levels? What are the advantages and disadvantages, and relative costs for these methods?

Response - The submicrometer elemental carbon method that was previously discussed under the Sampling and Monitoring Methods section and in Attachment 2, was used in a NIOSH study of diesel exhaust exposures in the trucking industry. As reported by Zaebst et al. [1991], the method is approximately 100 times as sensitive as gravimetric determinations and is more specific (because it effectively excludes many contaminants such as tobacco smoke, which has a content of about 3% elemental carbon of the total carbon present), and has a high level of precision, especially at low filter loadings (below 100-200 μg), when compared to gravimetric determinations. In the trucking industry study, only submicrometer-sized particles were collected on the filter via a single-stage personal impactor [Zaebst et al. 1991], further enhancing specificity of the method to diesel exhaust. The cost for the thermal optical analysis is approximately \$20 to \$25 per analysis. It may be noted that coal dust contains some elemental carbon, and may interfere in the determination if collected on the same filter. Use of a personal impactor sampler should greatly reduce this potential interference, or eliminate it -- depending on the content of the mining environment. NIOSH is conducting tests specifically to determine the level of the potential interference.

Issue - **What after-treatment devices currently being developed for over-the-road vehicles would be applicable...and what diesel particulate reduction can be achieved...?**

Response - The equipping of fork-lift truck exhausts with high-efficiency filters is described in the attached Health Hazard Evaluation Report (HETA 90-088-2110) [NIOSH 1990b]. These filters were found to be effective in reducing the exposure of diesel exhaust for dock workers. Dock workers' exposures to submicrometer elemental carbon while using filtered diesel-powered forklifts (geometric mean = 1.9 $\mu g/m^3$) were significantly reduced (essentially to background concentrations) when compared with exposures during use of identical forklift trucks without filtered exhausts (geometric mean = 24 $\mu g/m^3$). The geometric mean exposure during use of the filtered diesel forklifts could not be distinguished from background levels of elemental carbon (geometric mean = 1.6 $\mu g/m^3$) in the same area. In addition, frequencies of some respiratory symptoms were greatly reduced as measured by questionnaires among dock workers. These studies were not done in the mining industry; however, technology used to reduce exposure may be applicable to the mining industry.

Subsequent to the NIOSH submittal of July 5, 1990 [NIOSH 1990a], a number of publications have become available that pertain to this ANPR. Below is a list and summary of the enclosed publications:

Blade LM and Zaebst DD [1990]. Characterization of exposures to fifteen substances or classes of substances in diesel exhaust emissions. Orlando, FL: **Presented at AIHA Conference.**

This report summarizes four health hazard evaluations that were previously submitted to MSHA.

- **RDHETA 88-104 ASARCO/Troy Unit Mine - Montana [NIOSH 1991a]**
  This report presents results of an environmental and medical health hazard evaluation of a silver mine for exposures to diesel exhaust, silica, and noise. NIOSH determined that a health hazard existed due to worker exposure to respirable silica, noise, and products of diesel combustion.

- **RDHETA 88-108-2146 New Market/Young Mines - Tennessee [NIOSH 1991b]**
  This report presents results of an environmental and medical health hazard evaluation of two zinc mines and mills for exposures to diesel exhaust, silica, and asbestos. NIOSH determined that a health hazard existed due to worker exposure to products of diesel combustion.

- **RDHETA 88-388-2155** Morton Salt Company - Texas [NIOSH 1991c]
- **RDHETA 88-389-2147** International Salt Company - Louisiana [NIOSH 1991d]
- **RDHETA 88-390-2148** American Salt Company - Kansas [NIOSH 1991e]
- **RDHETA 88-391-2156** Morton Salt Company - Louisiana [NIOSH 1991f]

These four reports present results of environmental and medical health hazard evaluations of four salt mines for exposures to diesel exhaust and asbestos. NIOSH determined that a health hazard existed due to worker exposure to products of diesel combustion in all four mines.

Enclosures and/or attachments that are not included are available free of charge from the NIOSH Docket Office (513/533-8450).

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Attachment 1

RESEARCH PLAN

A SAMPLING AND ANALYTICAL METHOD FOR AIRBORNE DIESEL-EXHAUST PARTICLES

February 21, 1991

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Overview: Health Effects

The National Institute for Occupational Safety and Health (NIOSH) concluded in 1986 (1) that a causal association between exposure to "whole diesel exhaust" and human lung cancer was not documented, although an association is plausible based on results of animal studies. In July, 1986, the Department of Occupational Health and Safety, United Mine Workers of America (UMWA), requested that the Secretary of Labor form an Advisory Committee to provide the Department guidance on this issue (2). In its final report (3) of July, 1988, the Committee concluded that "whole diesel exhaust represents a probable risk for causing human lung cancer" (p 22, p 64) and recommended that "the Secretary [should] set in motion a mechanism whereby a diesel particulate standard can be set" (p 64). The conclusion regarding the potential carcinogenicity of diesel-engine exhaust emissions (hereafter referred to as "diesel exhaust") was reached by a majority of Committee members and was based on results of five independent animal studies (4-8) reported after NIOSH reached its 1986 conclusion.

Most of the animal studies on carcinogenic and mutagenic effects of diesel-exhaust exposure link these effects to the carbonaceous particulate fraction of the exhaust. Although not explicitly proven, particle-borne organic compounds are thought to be responsible for, or contribute to, formation of lung tumors in animals. Shortly after release of the Advisory Committee's report, NIOSH published the Current Intelligence Bulletin (CIB) 50--Carcinogenic Effects of Exposure to Diesel Exhaust (9). In the CIB 50, NIOSH recommended that "whole diesel exhaust be regarded as a potential occupational carcinogen" and that employers reduce worker exposures to the "lowest feasible limit."

In response to the Advisory Committee's recommendations, MSHA requested research assistance from NIOSH (and the Bureau of Mines) in the "development of a device to measure diesel particulate and a sampling strategy" (10). Development of a sensitive, selective, sampling and analytical method for airborne diesel exhaust has therefore become a "high-priority issue both within and outside the Institute" (11).

BACKGROUND

Information relevant to development of the research plan proposed herein is discussed in the following sections. Included are a physical description of diesel soot, a synopsis of the substantial amount of research devoted to chemical characterization of the solvent-extractable fraction of particulate diesel exhaust, and discussions of combustion-based, gravimetric, and other techniques used for analysis of the particulate fraction. In addition, issues related to selection of a surrogate measure of worker exposure to diesel exhaust are discussed.

Diesel Soot: Origin, Morphology, and Composition

Combustion-generated, carbonaceous particles (soot) constitute the main portion of particulate diesel-exhaust. A soluble organic fraction, which largely consists of unburned hydrocarbons deposited through sorption and condensation processes, is associated with diesel soot.

Soot formation occurs when fuel is combusted without an adequate oxygen supply. The heterogeneous combustion process characteristic of the diesel engine (12) makes soot formation an inherent aspect of its operation. Most of the soot production occurs during the last of three combustion stages; net soot output will depend on the amount formed and subsequently oxidized (13). Because oxidation (by both hydroxy radicals and oxygen) is the major path of soot mass reduction in the cylinder, elevated temperatures and long residence times favor reduction of soot-emission factors. These conditions also favor lower hydrocarbon emissions, since they promote complete combustion (13).

Processes responsible for formation of soot nuclei are not completely understood--at least eight different nucleation theories have been proposed (12). Surface growth on nuclei results in soot "spherules." Continued growth on spherules, which reportedly results from gas-phase deposition of hydrocarbon intermediates (12), increases soot mass and is responsible for most of the final soot volume.

Based on lattice images of diesel particles, a concentric lamellate structure similar to carbon black, which structurally resembles graphite, has been suggested (12). Diesel particles are reportedly "mesomorphic" (i.e., neither amorphous nor crystalline) in structure (12).

Agglomeration of spherules upon collision results in particles having a chain- or cluster-like appearance. Agglomeration is completed (essentially) during the expansion stroke (12). A bimodal size distribution consisting of nuclei and accumulation modes has been reported (14). Load-dependent, number-mean particle diameters of 10 and 20 nm were reported for the nuclei mode, and 100 and 150 nm for the accumulation mode, which results from spherule agglomeration (14). The nuclei mode is believed to be composed of liquid hydrocarbon droplets and/or individual spherules (12).

Other size distributions have been reported by different workers employing a variety of particle-sizing instrumentation (12, 15-18). Although size distributions have been measured under widely varying experimental conditions (e.g., engine and fuel type, fuel additives, engine load, dilution ratio), all studies indicate that particulate diesel exhaust is largely sub-micron in size. In fact, Vuk et al. (15) found that even at exhaust temperatures as low as 150 °C, greater than 80% by mass of the particles had aerodynamic diameters less than 1 μm. At exhaust temperatures above 300 °C, approximately 95% (by mass) of the particles had sub-micron aerodynamic diameters. Larger particle diameters at lower exhaust temperatures possibly result from condensation and adsorption of gas phase hydrocarbons on the solid agglomerates and aggregates (15). These processes occur mainly in the exhaust system and in dilution tunnels used in laboratory experiments (12).

Solvent-extractable fractions of particulate diesel exhaust in the 10-30% (12) and 15-30% range (14) have been reported. Extractable fractions from 10-90% were obtained in a study of various diesel passenger cars (19); however, this range is less typical. In recent work conducted by Schuetzle and Butler of Ford Motor Co. (20), particulate diesel-exhaust samples were analyzed for organic and "elemental" (i.e., graphite-like) carbon by an evolved-gas-analysis technique (see pp 8-9). In these experiments, organic carbon composed 20-40% of the total carbon measured (i.e., 60-80% was elemental). In similar studies, organic carbon composed 20-25% of the total carbon content (21).

Some of the variability in the solvent-extractable mass percent may be a dilution ratio effect (22). Dilution ratios from 5-20 and exhaust residence times from 1-5 s maximize the possibility of condensation and adsorption processes. By comparison, ratios greater than 1,000 are normally obtained in less than one second under roadway conditions. Although the effect of dilution ratio on the extractable fraction remains uncertain (contradictory results have been reported), results of studies conducted at moderate dilution ratios should be "interpreted with care" (22). Other explanations for highly variable extractable fractions include sampling artifacts and impure dilution air.

The extractable fraction of particulate diesel exhaust largely consists of unburned hydrocarbons (12); both fuel and oil were primary contributors to this fraction (23). Because mechanisms (e.g., hydrocarbon pyrolysis and incomplete combustion) responsible for generation of the extractable fraction are influenced by many factors--including engine type, speed and load, engine maintenance, temperature, air-to-fuel ratio, fuel composition, oil consumption, exhaust-gas treatment, meteorological conditions, etc.--the chemical composition of diesel-soot extracts is extremely complex and variable. Number estimates of particle-adsorbed compounds as high as 18,000 have been reported (9).

In a comparison of HPLC/fluorescence profiles for extracts of particulate emissions from several diesel-engine types, Schuetzle et al. noted a compositional similarity between extracts; however, concentrations of individual components were highly variable (24). Extracts of particulate exhaust from two diesel engines were fractionated by HPLC into non-polar, moderately polar, and polar fractions. These fractions accounted for 57%, 9%, and 32% (% weight recovered), respectively, of the extractable mass.

Gas chromatography/mass spectrometry was employed for analysis of the three fractions. A detailed list of individual compounds identified and quantified can be found elsewhere (24). A general description of each fraction's composition follows:

> Non-polar 90% (by weight) consisted of C_{14}-C_{35} aliphatic hydrocarbons and alkyl benzenes and naphthalenes. PAHs and alkyl PAHs (C_{14}-C_{24}) accounted for the remaining mass. Alkyl-substituted PAHs were more abundant than their PAH analogs.
>
> Moderately Polar PAH ketones (3 and 4 rings), PAH carboxaldehydes (2-5 rings), hydroxy PAHs and PAH quinones (both 3 and 4 rings), PAH anhydrides (e.g., of naphthalic and methyl naphthalic acids), nitro PAHs (including nitropyrene and dinitropyrene). This fraction accounted for more than 50% of the total particulate extract mutagenicity.
>
> Polar PAH and alkyl-substituted PAH carboxylic acids and dicarboxylic acids, N-containing heterocycles (e.g., acridine).

Methodology for Chemical Characterization of Solvent Extracts of Particulate Diesel Exhaust

Because particle-borne organic compounds may be responsible for, or contribute to, tumor formation in animals (4-8), much work has been devoted to chemical characterization of the solvent-extractable fraction of particulate diesel exhaust, most of which has focused on speciation of polycyclic aromatic hydrocarbons (PAHs), nitro PAHs, and oxy PAHs. A summary of sample collection, extraction, fractionation, and analysis techniques is provided below. A more detailed discussion of these topics can be found in a recent review (25).

Laboratory Sample Generation/Collection

Various systems have been devised for exhaust generation and particle sampling. A dilution tube method (26), where exhaust is diluted by filtered air in a dilution tunnel prior to sample collection, is used most often. Samples are collected on Teflon-coated, glass-fiber filters (27) and should be refrigerated to minimize volatile-compound losses, which have been reported for filter samples stored at room temperature for periods longer than two weeks (27, 28).

Extraction

Removal of PAHs from particulate diesel exhaust most often is accomplished through Soxhlet extraction. About 8 h is required to extract 99% of the soluble organic fraction; extraction of the remaining 1% required an additional 16 h (27). Other extraction methods include refluxing, sublimation, and ultrasonic agitation. Although conflicting results exist regarding efficiencies of extracting solvents, aromatic solvents (e.g., toluene) or mixtures of aromatic solvents and alcohols are reportedly preferred for extraction of PAHs. Absolute recoveries of 75-100% were obtained for benzo(a)pyrene (BaP). Recently, supercritical fluids were employed for quantitative extraction of PAH from particulate diesel exhaust in as little as 30 min (29).

Fractionation

Because of the complexity of diesel-soot extracts, fractionation into various compound classes is required prior to analysis. Fractionation methods include liquid-liquid extraction, open column liquid chromatography, high performance liquid chromatography (HPLC), and solid phase extraction. In spite of the

disadvantages of low speed and poor reproducibility (27), open column liquid chromatography is most frequently employed. HPLC fractionation is mainly applied when oxy PAHs or nitro PAHs are being determined.
Solid-phase-extraction methods are gaining popularity due to the shorter fractionation times afforded by this approach.

Analytical Methods

PAHs. PAHs in the soluble organic fraction of particulate diesel exhaust have been determined by a number of techniques including thin layer chromatography (TLC) with fluorescence detection, gas chromatography with flame ionization detection (GC/FID), and gas chromatography with detection by mass spectrometry (GC/MS). Although analysis of PAHs in other environmental matrices is usually achieved by HPLC with ultraviolet or fluorescence detection (HPLC/UV or HPLC/FL), the large number of interfering alkyl PAHs in diesel-soot extracts (27) normally precludes use of these methods. However, with proper choice of excitation and emission wavelengths, an HPLC/FL method for determination of PAHs in diesel-soot extracts can be employed (30, 31). Instruments permitting wavelength variation during chromatographic runs (31) eliminate the need for multiple sample injections, which are otherwise required to optimize for individual PAHs (30). Supercritical fluid chromatography (SFC) with photodiode array detection has been employed for separation and determination of four- and five-ring PAHs (32).

Nitro and Oxy PAHs. A variety of nitro and oxy PAHs are present in diesel-soot extracts. Because oxy compounds commonly found in extracts show less toxicity than PAHs or nitro PAHs, fewer studies on oxy PAHs have been conducted. Detailed studies identifying a large number of oxy PAHs have been published by Schulze et al. (33), Schuetzle et al. (34) and Tong et al. (35). Some of the identified oxy-PAH compounds resulted from artifact formation during sampling (34).

Nitro PAHs show extremely high mutagenicity--especially the dinitro compounds (36)--and are reportedly carcinogenic (37, 38). Analytical methods for these compounds are therefore especially important. Because nitro PAHs are present only at trace levels in diesel-soot extracts, their identification in this matrix is difficult. Nitro PAHs have been determined by GC techniques using various detectors (electron capture (ECD), nitrogen sensitive (NSD), and thermionic (TID)); however, identification requires available reference compounds, since conventional detectors also respond to nitrogen heterocycles. A new GC detector that is especially sensitive to nitro compounds has been described (39). Other methods include GC/ECD and HPLC/FL after reduction of nitro PAHs to their corresponding amines, HPLC with electrochemical detection, and a chemiluminescence method based on NO reaction with ozone. In addition, SFC with thermionic detection was applied for determination of nitro PAHs of low volatility (e.g., hydroxynitro PAHs) (40). GC/MS methods (using various ionization modes) have been especially instrumental in the identification of nitro PAHs. In terms of numbers of nitro PAHs detected (>200) and positively identified (>20) (41), GC/MS is the technique of choice.

Artifact Formation

Results of investigations of artifactual formation of nitro PAHs during sampling are contradictory. In studies involving re-exposure of filter samples of diesel particles to gas-phase diesel exhaust (42), or to dilution air containing NO_2 levels near 100 ppm (43), significant elevations in mutagenic activity (due to increased levels of nitro PAHs) were observed. In contrast, in recent work by Levsen et al. (44), only 13% of the 1-nitropyrene content was attributed to artifact formation. One explanation for these apparently conflicting results may involve the variable NO_2 concentrations in the gases to which the filter samples were subsequently exposed. According to recent work by Bradow (45), NO_2 levels above about 5 ppm are necessary to produce an artifact effect.

Combustion-Based Methods for Particulate Diesel Exhaust

CARB Study

Various combustion-based methods have been used for analysis of carbonaceous particles. These methods employ thermal programming for speciation of organic and elemental carbon. Recently, the California Air Resources Board (CARB) sponsored a nine-day field study for comparison of various measurement techniques for carbonaceous aerosols. During the Third International Conference on Carbonaceous Particles in the Atmosphere (Lawrence Berkeley Laboratory (LBL), Berkeley, CA, October 5-8, 1987), a special session entitled "Symposium on the Carbonaceous Species Methods Comparison Study" was held to present results of the CARB field study. In presentations involving the "round robin" portion of this study, analytical results of a number of laboratories (including LBL, GM research, EPA (RTP), Sunset Laboratory (see below)) using various combustion-based methods were compared. These laboratories were given a set of "reference" carbonaceous aerosol samples for analysis of their organic- and elemental-carbon content. The reference samples were distributed by Environmental Monitoring & Services, Inc. (EMSI), which served as the quality assurance manager for the study.

Although the organic-to-nonvolatile carbon ratios obtained by laboratories were internally consistent, large interlaboratory differences were noted. Of the sample types distributed by EMSI (including ambient samples collected in the Los Angeles Basin area, automotive exhaust samples, wood-smoke-dominated samples, and "soot" and organic aerosol samples), the largest discrepancies in results were obtained for the organic content of automotive exhaust and wood smoke samples (46), which differed by the factor of 2-3. In general, agreement between laboratories was within 20% for total carbon. Considering that the analytical definitions of elemental and organic carbon are "operational" (47) (i.e., analytes are defined by the method), interlaboratory differences are expected.

Because Sunset Laboratory's "thermal-optical method" was recommended to NIOSH by a number of the study's participants (including LBL and GM) (48), this method was used in NIOSH field studies (pp 15-16). Sunset's instrument incorporates desirable features not present in other instrumentation; a description of the thermal-optical method is provided below. In addition, a brief description of another combustion-based technique (not used in the CARB study) is provided, since it is planned for use (within the next year) in Germany (FRG) for monitoring worker exposures to particulate diesel exhaust. Because previous research involving LBL's method is directly related to the alternative analytical approach proposed in this plan, this method is discussed in a later section (pp 22-23).

The Thermal-Optical Method

The instrument used by Sunset Laboratory (Forest Grove, OR), which is a modified version of one previously described in the literature (49), employs thermal programming and optical measurements for analysis of carbonaceous aerosols. In Sunset's method, speciation between organic (volatile and nonvolatile), inorganic (carbonate), and elemental carbon is temperature-based. Sunset's instrument overcomes limitations associated with many of the existing combustion-based techniques in that it allows for correction of pyrolytically generated elemental carbon, or "char." Correction for the char contribution to elemental carbon is accomplished in the second stage of analysis by measuring the amount of elemental carbon oxidation required to return the sample filter to its initial transmittance value. Laser light (He/Ne) is passed through a quartz-fiber filter punch and filter transmittance is continuously monitored. Sunset's instrument also is preferred because the combustion chamber's temperature program and gas composition have been optimized to prevent undesired oxidation of original elemental carbon, and to allow speciation of carbonate carbon, which can interfere with determination of elemental carbon by other methods. Details of the modified instrument's design have been described elsewhere (50).

Operationally, the thermal-optical method involves three stages. In the first stage, volatilization of organic and carbonate carbon from a 1.0 x 1.5-cm portion of a quartz-fiber filter occurs in a pure He atmosphere. The temperature program begins at room temperature and proceeds through four temperature steps (250 °C, 385 °C, 580 °C and 680 °C). Temperature steps were chosen such that the carbonate peak appears as the fourth of four peaks observed in the "thermogram" (plot of detector response as function of temperature) during this stage of the analysis. Volatilized carbon is oxidized to CO_2 (in a bed of granular MnO_2 at 950 °C) and subsequently reduced to CH_4 (in a Ni/firebrick (450 °C) methanator), which is then quantified with a flame ionization detector. The second stage of analysis begins after reducing the temperature of the combustion chamber to 525 °C. At this point, oxygen (2%) is introduced and two additional temperature steps (to 600 °C and 750 °C) are made. It is during this second stage that char correction and elemental carbon measurement are achieved. In the third (final) stage of analysis, a known amount of methane is injected into the oven for calibration and quality assurance purposes. Areas of individual peaks in the thermogram correspond to the amount of each carbon type in the sample.

According to Sunset, the best range for filter-sample loadings is 5-200 $\mu g/cm^2$ for organic carbon and 1-15 $\mu g/cm^2$ for elemental carbon. In cases where elemental carbon is present at levels greater than about 15 $\mu g/cm^2$, analysis is complicated by low filter transmittance, which makes results difficult to interpret. In addition, when organic-carbon levels are above 200 $\mu g/cm^2$, organic carbon may interfere in the determination of elemental carbon if the amount of elemental carbon present is small.

BIA Method

The Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA) in Sankt Augustin, Federal Republic of Germany (FRG) plans to use a combustion-based method for analysis of particulate diesel-exhaust samples for total carbon. National toxicologists (FRG) advised BIA to measure "elementary carbon plus adsorbed substances" (i.e., organic species) (51). In the BIA method for personal sampling, respirable dust (BMRC) is collected on glass-fiber filters. The CO_2 content formed during ashing of the sample in an oven is considered "diesel soot by definition." Evolved CO_2 is determined coulometrically. At a flow rate of 2 L/min for an 8-h sampling period, a "relative measuring limit" of 66 $\mu g/m^3$ was reported (52).

Gravimetric and Other Techniques

BOM/MSHA

The Bureau of Mines (BOM) and the Mine Safety and Health Administration (MSHA) are investigating size-selective sampling techniques for measurement of particulate diesel exhaust in underground coal mines. In a BOM-sponsored research project, the University of Minnesota developed a personal aerosol sampler for use in a gravimetric method for analysis of particulate diesel exhaust in underground coal-mine air. Research by NIOSH's Division of Respiratory Disease Studies (DRDS) on development of a size-selective sampling device also was sponsored in part by the Bureau (53). Such gravimetric techniques are premised on the assumption that size-selective sampling effects separation of airborne diesel particles (which are largely sub-micrometer) from non-diesel coal-mine aerosol (which is largely super-micrometer). The separated particulate diesel exhaust is collected on the sampler's final filter and its mass determined gravimetrically.

Based on size-distribution data from studies of eight coal mines (six with diesel-powered hauling equipment and two with only electric-powered hauling equipment), Cantrell et al. of BOM chose a 0.8-μm diameter (mass mean aerodynamic diameter (MMAD)) cut point for separating most of the diesel particles from most of the coal-mine dust (54). Based on NIOSH size-distribution data, a 1-μm (MMAD) cut point was selected (55).

Although sampler cut points were selected to achieve optimal separation of diesel-exhaust and other coal-mine aerosols, in field studies conducted in underground coal mines where no diesel-powered equipment was used, concentrations of sub-micrometer particles reportedly ranged from 80-170 $\mu g/m^3$, depending on sampling location (55). Concentrations in the 20-100-$\mu g/m^3$ range also have been reported (54). Obviously, interference by sub-micrometer coal-mine dust places serious limitations on a gravimetric-based method for analysis of diesel-exhaust aerosol when low-level concentrations are sought.

In this research proposal for the development of a sampling and analytical method for airborne diesel-exhaust particles, a probable NIOSH recommended exposure level (REL) must be addressed. In view of NIOSH's carcinogen policy, it has been speculated that a standard in the tens of $\mu g/m^3$ (or less) is likely (56). Demand for quantification at these low levels would preclude use of BOM's currently proposed gravimetric method, since a lower limit of detection near 300 $\mu g/m^3$ has been estimated (54).

Other Techniques

BOM-sponsored research on a laser Raman spectroscopic method for determination of percent composition of mixtures of particulate diesel exhaust and coal dust has been conducted at Michigan Technological University, Houghton, MI. Aside from poor performance at low filter loadings (under 100 $\mu g/cm^2$), this method suffers from the lack of reliable calibration standards. These problems are currently being addressed by researchers at Michigan Tech.

Fourier transform infrared (FTIR) techniques have been applied for analysis of particulate samples. Spectral complexity and lack of suitable calibration standards hinder an FTIR approach to analysis of particulate diesel-exhaust/coal mixtures.

A Forward Alpha Scattering Technique (FAST) for determination of total nonvolatile carbon has been investigated. Because the sample must be analyzed in vacuum, volatile losses occur. Instrumental complexity, restricted beam time, and a limited number of accelerators with the required high-energy-ion-producing capability (e.g., 30-MeV alpha particles) are additional problems making this approach impractical. A more detailed discussion of FAST and FTIR methods can be found elsewhere (see Aerosol Sci. Technol. 1989, 10(2), pp 390-407).

Surrogates

Because diesel-exhaust aerosol contains thousands of compounds, development of a sampling and analytical method for all its constituents is not feasible. A surrogate measure of diesel-exhaust exposure is therefore necessary.

Rationale for selection of elemental carbon as a surrogate measure of exposure to airborne diesel exhaust particles is offered in the following discussions on phase distribution of genotoxic substances and elemental carbon's potential role as a promoter of lung-tumor formation. Other issues relating to selection of this surrogate are addressed as well. Finally, conclusions regarding these topics and previously discussed analytical options are presented.

Particulate Versus Gas Phase

As pointed out by Bradow (57), the question of whether the carcinogenic/mutagenic materials are associated with the particulate phase or gas phase of diesel exhaust (or both) may be "immaterial"--the significant issue concerns the phase distribution of these materials. As discussed earlier, adsorption and condensation processes that occur principally in the exhaust system are responsible for the soluble organic fraction of diesel soot. Rapid cooling of the exhaust mixture exiting the combustion zone results in enrichment of species on the surface of particles through condensation (58). At ambient temperatures, surface enrichment by this mechanism is essentially associated with compounds of moderate-to-low volatility (59, 60), which is especially significant because four-, five-, and six-ring PAHs are reportedly the most carcinogenic or mutagenic substances (61, 62). Furthermore, PAHs possess a strong binding affinity for the surface of carbonaceous particles. In fact, in in-situ, sorption-desorption studies of various PAHs on the surfaces of different monodisperse ultrafine particles (19-nm diameter), PAHs showed the greatest affinity for carbon particles (63).

Another important consideration in selecting specific analytes as a surrogate measure of worker exposure to airborne diesel exhaust concerns their concentrations. In a recent NIOSH Health Hazard Evaluation (HHE) involving exposures to diesel exhaust in the trucking industry (64), a number of gas and particulate phase contaminants were targeted. Gas-phase species examined included CO, CO_2, SO_2, NO_2, H_2SO_4, total NO_x, formaldehyde, and volatile hydrocarbons (aliphatic and aromatic). All selected component's concentrations were significantly below recognized occupational exposure evaluation criteria, yet levels of elemental carbon (which represented about 60% of the carbonaceous particulate fraction) ranged from 33-94 $\mu g/m^3$. Furthermore, the presence of non-diesel sources of these components may result in unreliable measures of occupational exposures to diesel exhaust. Because solvent extracts of particulate diesel exhaust accounted for 90% of the mutagenic potency of diesel-exhaust aerosol in studies conducted by Schuetzle et al. (24), a sampling and analytical method for monitoring worker exposures to the particulate phase of airborne diesel exhaust currently seems most appropriate.

Elemental Carbon

Because of the compositional variability and chromatographic complexity of diesel-soot extracts, uncertainty about the compounds responsible for mutagenic and carcinogenic activity, and presence of interfering species, selection of a soot-associated organic compound or class of compounds as a surrogate measure of exposure to airborne diesel-exhaust particles is a difficult task. Based on a Coordinating Research Council supported study by Fowler et al. (65), method development solely targeting species in the soluble organic fraction of particulate diesel exhaust may be inappropriate as well.

Fowler et al. evaluated a number of species as indices of "overall diesel exposure." Included in the evaluation were CO_2, CO, SO_2, NO, NO_2, volatilizable carbon (organic), and elemental carbon. Of these constituents, elemental carbon was found to be the most reliable measure of exposure to "diesel exhaust as an entity" (i.e., reflected exposures to the largest number of exhaust components examined).

When considering exposure indices for particulate diesel exhaust, workplace concentrations and interferences must be addressed. In the above-discussed HHE, concentrations of individual PAHs and total PAHs in the solvent- (benzene or acetonitrile) extractable fraction of the particulate mass also were measured and none exceeded the evaluation criteria employed (coal-tar pitch components in benzene- or cyclohexane-soluble fraction); however, elemental-carbon levels ranged from 33-94 $\mu g/m^3$. Furthermore, the ubiquity of PAHs in the environment may cause inaccuracies in PAH-based exposure assessments.

Although not currently established, evaluation criteria based on elemental-carbon exposure may be more appropriate. Elemental carbon's suspect role in potential health effects also makes it a logical choice of surrogate. In a recent study by Mauderly et al. (66), laboratory rats were exposed to diesel-exhaust or carbon-black particles. The carbon-black material contained no mutagenic organic content. At 12 weeks, the measured lung burdens and inflammatory responses for both materials were nearly identical, however, DNA-adduct levels were 3-fold higher in the diesel-particle-exposed animals. It was concluded that "repeated inhalation of carbonaceous particles causes lung inflammation regardless of organic content, but that the level of DNA damage is primarily related to the organic content." According to Mauderly et al., these results are consistent with the hypothesis that diesel-soot-associated organic compounds and/or their metabolites are responsible for initiating chemical carcinogenesis, and that cell transformation and progression to lung tumors is promoted by the inflammatory and proliferative (epithelial proliferation) responses caused by accumulation of soot in the lung. Lastly, it was observed that heavy exposures to "materials" (unspecified) with little or no organic content also elicit the above-mentioned responses. These results reportedly suggest that "large accumulations of diesel-exhaust soot in the lung might have caused tumors independently from chemical carcinogens" (66).

In animal (rats) studies by Sun et al. (67), the deposition, retention, and biological fate of benzo(a)pyrene (BaP) inhaled as pure aerosol and as BaP adsorbed onto ultrafine particles were compared. Particle adsorption significantly increased the retention of BaP in the respiratory tract. In experiments by Wolff et al. (68) involving inhalation (by rats) of pure BaP and diesel-particle-adsorbed BaP aerosols, the particle-adsorbed BaP showed an approximately 200-fold increase in long-term lung retention (percentage retained after 7 days) relative to pure BaP (68).

One of the possible factors responsible for prolonged retention of particle-adsorbed PAHs may be their altered metabolic fate (e.g., after ingestion by macrophages) relative to pure PAHs, which are more rapidly cleared by absorption into the blood (68). Because prolonged retention and slow release of PAHs in the lung are correlated with increased tumor incidence (68), the role of elemental carbon should not be trivialized.

FRG's Selection of Surrogate

As discussed earlier, the Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA) in Sankt Augustin, Federal Republic of Germany (FRG) has recently elected to use a combustion-based method for analysis of particulate diesel-exhaust samples. National toxicologists (FRG) advised BIA to measure "elementary carbon plus adsorbed substances" (i.e., organic species) (51) in the respirable particulate fraction of an air sample. Total carbon in the particulate sample is being considered "diesel soot by definition" (51).

Obviously, this method is less selective than the thermal-optical method, which is capable of distinguishing organic (volatile and nonvolatile), carbonate-type, and elemental carbon. In addition, severe interference problems will be encountered in some workplaces (e.g., coal mines) when a total respirable particulate fraction is collected. The BIA method also requires scrubbing other titratable acidic gases (e.g., NO_x, SO_x) from the combustion gas stream. In addition, inorganic carbonates will likely interfere in the analysis.

Conclusions

A number of approaches to the analysis of particulate diesel exhaust have been employed--including gravimetric- and combustion-based methods, and chemical characterization of the soluble organic fraction of the particulate sample. Although carcinogenic/mutagenic species have been found in this fraction, methods based solely on analysis of the soluble organic phase ignore the possible role of elemental carbon in potential health effects. In view of the significantly increased biological retention times of particle-adsorbed PAHs, elemental carbon may be involved in mechanisms responsible for these effects.

Thus, methods providing information on both organic and elemental carbon are preferred, since exposures essentially can be stated "in terms of the total mass of diesel particulates" (56), which NIOSH has recommended. Because the thermal-optical method corrects for pyrolytically generated elemental carbon and speciates various carbon types (including carbonate carbon), it appears to be the most promising technique currently available. Elemental carbon likely will be a more reliable indicator of workplace exposures to particulate diesel exhaust, however, since many potential sources of non-diesel organic aerosol exist. In contrast, there are relatively few sources of environmental elemental carbon.

In summary, elemental carbon constitutes a large fraction of diesel-exhaust particulate mass, serves as a carrier of carcinogenic/mutagenic organic species, is a suspect lung-tumor promoter, is reportedly the most suitable index (of indices examined) of "overall diesel exposure," serves as a unique marker for diesel exhaust in many workplaces, and can be precisely quantified at low levels by the thermal-optical method (approximate lower limit of detection is 2 $\mu g/m^3$ for an 8-h sampling period using a 2-L/min flow rate and 37-mm filter). For these reasons, and the fact that levels of organic compounds targeted in the above-mentioned field surveys were typically well below established exposure criteria, elemental carbon appears to be the most suitable exposure index for particulate diesel exhaust at present. A discussion of some results obtained with the thermal-optical method in a recent NIOSH (Division of Surveillance, Hazards Evaluations, and Field Studies (DSHEFS)) industrial-hygiene study of the trucking industry is provided below.

NIOSH Field Studies: The Thermal Optical Method

Sunset Laboratory's thermal-optical method (see pp 8-9) was employed by Dennis Zaebst and co-workers in DSHEFS's industrial-hygiene study on worker exposures to diesel-exhaust aerosol in the trucking industry. Selection of this method was based on the previously mentioned work of Fowler et al. (see p 16) and recommendations by a number of participants in the CARB-sponsored, nine-day field study for comparison of various measurement techniques for carbonaceous aerosols (see pp 7-8). In the DSHEFS study, a dichotomous sampler with a calculated 1-μm (MMAD) cut point at a flow rate of 4 L/min was employed. The sampler is a single-jet, single-stage impactor containing an impaction plate constructed from a cellulose support pad; it is a modified version of a design used by DRDS (69), which was based on earlier work by Jones et al. (70). Four off-center holes were punched in the support pad in a symmetric fashion and the center portion of the pad, which served as the impaction surface, was greased to minimize particle bounce. A pre-fired, quartz-fiber after filter supported by a stainless steel support screen was used for collection of the sub-micrometer particulate fraction of an air sample. Although collected filter samples were analyzed for organic and elemental carbon, elemental carbon data were used as a surrogate measure of exposures to airborne diesel-exhaust particles.

Data resulting from Sunset Laboratory's analyses of filter samples collected during DSHEFS's industrial-hygiene survey of the Yellow Freight truck terminal (St. Louis, MO, February, 1988) were obtained from Dennis Zaebst, DSHEFS, and levels of organic and elemental carbon associated with various job categories were calculated. Upon examination of calculated exposure levels, expected trends were noted. For example, dock workers' exposures to elemental carbon were higher than road drivers', and smokers' exposures to organic carbon were elevated relative to nonsmokers'. Exposure levels for dock and repair shop workers, and for mechanics ranged from 20-40 $\mu g/m^3$ for elemental carbon, although levels from 30-35 $\mu g/m^3$ were more typical. As anticipated, city and long-haul drivers' exposures to elemental carbon, which ranged from about 2-4 $\mu g/m^3$, were much lower than the above-mentioned job categories.

Exposures to organic carbon were highly variable, ranging from 40-264 $\mu g/m^3$. In general, higher levels of organic carbon were observed for smokers than for nonsmokers. For one smoker, exposure levels of 140 $\mu g/m^3$ for organic carbon and 63 $\mu g/m^3$ for elemental carbon were calculated. The higher level of elemental carbon is not believed to originate from cigarette smoke, since an elemental-carbon exposure level of only 20 $\mu g/m^3$ was calculated for another smoker whose exposure to organic carbon was almost twice as high (264 $\mu g/m^3$). Moreover, results of Zaebst and co-workers (20) indicate that only about 2% of cigarette smoke is elemental carbon.

In addition to tobacco smoke, another interference problem regarding organic carbon was noted. Typical background (i.e., highways and residential parks) levels of organic and elemental carbon found during this survey were less than 20 and 4 $\mu g/m^3$, respectively; however, an organic carbon concentration of 478 $\mu g/m^3$ was calculated for one background sample collected in a residential park. Most likely, terpenes were collected in this case, since the sampler reportedly was hung in a pine tree.

Adsorption of organic carbon on quartz-fiber filters (Pallflex QAO) has been observed by other workers (71, 72). Negative sampling artifacts (e.g., volatile-compound losses) also have been reported (73), however, positive artifacts are predominant. These results further illustrate problems associated with meaningful interpretation of organic carbon data (74, 75).

RESEARCH PLAN

Goal

Development/evaluation of potential sampling and analytical methodology for monitoring worker exposure to airborne diesel exhaust particles is the intended goal of this research. An existing thermal desorption/pyrolysis/combustion technique, the "thermal-optical method," will be evaluated. This method employs thermal programming and optical measurements for analysis of carbonaceous samples. In the analysis, temperature-based speciation between organic (volatile and nonvolatile), inorganic (carbonate-type), and elemental carbon is achieved. Because elemental carbon is the most reliable marker for particulate diesel exhaust and plays a suspect role in potential human health effects, its use as an exposure index is being recommended. Effects of various sampling strategies on analytical results will be investigated. Should the thermal-optical method prove unsatisfactory for the intended application, investigation of an alternative analytical approach employing instrumentation with multielemental detection capability will be considered. This alternative approach (see pp 23-25) should afford greater selectivity and sensitivity, which may be required in some workplaces.

Coal Mines: Potential Problems and Solutions

Coal-Source Elemental Carbon: Discussion and Preliminary Results

The assumption that diesel-powered equipment is the only significant source of elemental carbon in the sub-micrometer particulate fraction of air samples may be invalid in a coal-mine environment. As mentioned previously (p 13), in NIOSH field studies conducted in coal mines where no diesel-powered equipment was used, sub-micrometer particle concentrations reportedly ranged from 80-170 $\mu g/m^3$ (55). Concentrations from 20-100 $\mu g/m^3$ also have been observed (54). If most of the non-diesel sub-micrometer particulate material found in coal mines is coal dust, the high-temperature carbon residue contributed by coal could pose an interference problem in the determination of diesel-source elemental carbon by thermal-optical analysis. The extent to which coal-source elemental carbon will interfere in the analysis of a sample's diesel component will not only depend on the amount and rank of coal present in the sample, but also on the temperature windows over which the two materials are combusted. Because the coal component will be generated under different conditions and have significant organic nitrogen and sulfur content relative to diesel elemental carbon, it may be less graphitic and more easily oxidized (i.e., combusted at a lower temperature); however, peak positions likely will be matrix- and particle-size dependent and deconvolution of the two signals may not always be possible. In this situation, an alternative analytical approach would be required. Alternative analytical methodology is discussed in a following section.

Preliminary results of thermal-optical analysis of particulate samples collected in various locations in non-diesel-equipped coal mines indicate that sub-micrometer levels of elemental carbon are low. In these surveys, as well as in surveys conducted in diesel-equipped mines, Sierra 298 cascade impactors containing quartz-fiber final filters were used to collect various size fractions of coal-mine dust. Lower stages were removed from the impactors for collection of these fractions. Samples were collected using paired impactors containing 8, 7, and 6 stages, which provided 0.52-, 0.93-, and 1.55-μm cut points, respectively, at a flow rate of 2 L/min.

Although an average respirable dust concentration (BMRC) of 2.27 mg/m^3 (%RSD=2.08, n=2) was calculated using data from impactors placed at a face location of an underground coal mine employing longwall equipment, elemental carbon concentrations less than 6 μg/m^3 were calculated using results of thermal-optical analysis of filters from six-stage impactors. In this particular survey, paired four-stage impactors having a 6-μm cut also were used. Even when collecting this relatively large size fraction, an average elemental carbon concentration less than 30 μg/m^3 was calculated. These results can be explained by examining the means by which the thermal-optical method speciates carbon types. In the method, correction for pyrolytically generated carbon is achieved by monitoring filter transmittance, which decreases as filter-borne carbonaceous matter is pyrolyzed during the first stage of analysis. During the second stage of the analysis, where oxygen is introduced, the "split" between organic and elemental carbon is defined as the point at which the filter transmittance reaches its initial value. Because extensive pyrolysis occurred during thermal-optical analysis of coal-dust samples collected during this survey (high-volatile bituminous, 50% fixed carbon), significant attenuation of filter transmittance was observed. Consequently, most of the sample (>95% of the total carbon) was not reported as elemental carbon since the designated split occurred <u>after</u> the majority of the high-temperature carbon component was combusted. It also was of interest to note that the peak position of this component occurred at a temperature that was about 100 °C <u>lower</u> than that typically observed for diesel-source elemental carbon. Possible reasons for this behavior were discussed above.

To provide a better indication of the potential interference posed by coal dust in environments where high-rank, low-volatile coals are mined, a second survey of a non-diesel-equipped underground coal mine was conducted. The coal rank in this study was a low-volatile bituminous with 75% fixed carbon. Cascade impactors located at a beltline entry were again employed in the manner discussed above. As anticipated, higher levels of elemental carbon were observed in this survey. Results from the six-stage (1.55 μm cut) impactors indicate elemental carbon concentrations from 17-20 $\mu g/m^3$; a concentration of about 8 $\mu g/m^3$ was calculated from the seven-stage (0.93 μm cut) impactor results. Because total respirable dust levels found in this particular mine were fairly low (about 0.7 mg/m^3, (BMRC)), higher concentrations of elemental carbon are expected in similar mining workplaces when higher respirable dust levels are present. For this reason, preselection of a sub-micrometer size fraction may be necessary in this type mining environment (i.e., mines containing low-volatile, high fixed carbon coals).

Coal Mine Sampling Requirements

As stated earlier, Cantrell et al. (BOM) found that a 0.8-μm cut point was optimal for separation of most of the diesel particles from most of the coal-mine dust (54). Based on NIOSH (DRDS) size-distribution data, a 1-μm cut point was selected (55). For more effective exclusion of coal-mine dust, a 0.8-μm cut (or smaller) is preferred to a 1-μm cut provided that diesel exhaust is not excluded as well, which should be the case when water scrubbers are implemented (i.e., in underground coal mines). If analytical selectivity can be achieved, establishing an optimal sampler cut point for separation of diesel and non-diesel aerosols will not be necessary.

The contribution of coal-source elemental carbon will depend on the coal's rank and size distribution, as well as sampler cut point. Size fractions of coal dust of known rank will be collected on preweighed quartz-fiber filters. Sample mass will be determined by reweighing filters after sample collection. Eight different types of minus 20-mesh coal samples obtained from the Department of Energy's Sample Bank at Penn State University will be examined. Coal types were selected to be representative (albeit not exhaustively) of those mined in the U.S. and range from lignite to anthracite. Collected fractions will be analyzed by the thermal-optical method. This work will provide an indication of the magnitude of elemental-carbon interference expected from a given mass of coal dust of specific rank and particle size. Sub-micrometer particulate samples having low (e.g., 20-100 μg) mass loadings will be included to determine whether their thermograms show any unique features (e.g., pyrolysis) that could "flag" the presence of small amounts of coal dust.

In cooperation with Dr. Bruce Cantrell of BOM, size distribution data and various size fractions of particulate diesel exhaust will be collected using a diesel test cell and dust chamber located at the Twin Cities Research Center (BOM), Minneapolis, MN. According to Dr. Cantrell, the necessary facilities should be ready for use by 4Q91. The engine will be operated using one or more representative duty cycles, and with and without a water scrubber. Samples collected on quartz-fiber filters will be analyzed by the thermal optical method. Various samplers will be employed and their performance evaluated. Coal and coal/diesel aerosols also will be collected and analyzed by the thermal-optical method.

Thermal-Optical Method Evaluation

Standards Preparation/Method Evaluation

Techniques for standards preparation will be established and analytical range, precision, accuracy, and selectivity of the thermal-optical method will be determined. To date, preparation of organic-carbon standards has been partially successful (76). Initial results of analysis of potassium hydrogen phthalate (KHP) standards prepared in-house (by Dr. Eller, DPSE) show a 12-14% RSD (between-filter precision, n=3). Filter-deposit inhomogeneity and possible sample contamination likely were responsible for imprecision in results. Initial attempts to prepare elemental-carbon standards using graphite were unsuccessful (76). Because graphite exhibits distinctly different thermal behavior than diesel-source elemental carbon, its use as a standard for diesel-source elemental carbon does not seem appropriate.

Currently, Sunset laboratory uses both a sucrose solution and methane (in a gas sample loop) as calibration standards. Sunset's results for analysis of these materials show better than 2% RSD. When analyzing the carbon content of other materials, it is assumed that all carbon-containing species in the samples are oxidized and reduced with the same efficiency as Sunset's calibration standards. The validity of this assumption will be investigated by analyzing a variety of materials (including PAHs and commercially available polymeric carbons (e.g., NIST SRM 1650 (diesel soot)) to ensure that total-carbon results are in agreement with those expected. Elemental analysis of selected polymeric carbon materials will be performed by an independent laboratory.

Provided that thermal-optical measurements of total carbon show good agreement with expected results, an operational definition of diesel-source elemental carbon will be established. Particulate emissions from commonly used diesel equipment will be examined in order to bracket the temperature window over which diesel-source elemental carbon is combusted so that materials evolved outside of the established window will not be recognized as diesel-source elemental carbon. This approach is considered "operational" in that diesel elemental carbon is being defined as material evolved over a given temperature window in an oxidizing atmosphere after desorption of organic material in a high-temperature inert atmosphere.

Potential interferences by carbon-containing inorganic materials also should be addressed. In some work environments, carbonate-containing materials (e.g., limestone) will be encountered. Although carbonate-type carbon reportedly does not interfere with the determination of elemental carbon (50), a 60% lower result for elemental carbon was reported (by Sunset Laboratory) for an untreated, carbonate-containing, filter-punch sample relative to an acid-treated (to remove carbonate) punch from the same filter. Because results of analysis of punches from the same filter are normally very reproducible (%RSD < 2, n=2) when filter deposits appear homogeneous, which reportedly was the case, filter-sample inhomogeneity is not believed to be responsible for this result. The effect of carbonate carbon's presence on analytical results will be examined.

The presence of materials that form black oxides during the combustion stage of analysis pose potential interference problems as well. These materials may be encountered in ore-producing industries. In general, however, neither colored inorganic compounds (e.g., iron oxide) nor colored organic materials usually present interference problems (50). Because non-diesel sources of elemental carbon likely will be negligible in these industries, the diesel-source elemental carbon should be obvious in the thermograms. Thus, if oxide formation results in an inaccurate split time, the appropriate split time could be entered (post-analysis) and raw date reintegrated. Because oxide formation is not expected to pose an interference problem, potential interference by oxide-forming materials will not be examined unless a reason for doing so becomes apparent.

Pyrolytic Carbon Correction

The instrument's pyrolysis correction feature will be examined by analyzing samples containing organic materials susceptible to charring (e.g., sugars). Char resulting from pyrolysis of organic materials during sample analysis should not be recognized as elemental carbon. Pyrolytic correction may be necessary for determination of diesel-source elemental carbon in ambient aerosol samples, which often contain significant amounts of pyrolyzable organic materials (e.g., cigarette smoke).

The extent of charring in the analysis of uncontaminated particulate diesel exhaust will be examined further. Preliminary results indicate that compounds responsible for extensive charring may largely arise from non-diesel sources. If so, high pyrolytically generated carbon values could be used to flag the presence of non-diesel sources of organic aerosol.

The need for accurate pyrolytic correction for coal-source elemental carbon will depend on the sampling strategy adopted. If coal dust can be excluded by size-selective sampling without compromising collection of diesel aerosol, interference by coal-source elemental carbon should be negligible. Otherwise, the accuracy of the pyrolysis correction feature must be determined using diesel, coal, and diesel/coal samples of known composition (mass and coal rank).

Field Surveys

In workplaces where the only significant source of elemental carbon is the diesel engine, selection of a 1-μm cut point should not be necessary. Even in workplaces containing other airborne dusts (e.g., construction sites, railroads), full-shift sampling of the total respirable fraction should be possible. If so, commercially available sampling equipment (e.g., cyclone plus quartz-fiber filter) could be employed and method users would not be forced to fabricate samplers in-house.

A large amount of thermal-optical data was collected during previous NIOSH field surveys of the trucking industry. These results (i.e., data and corresponding thermograms) will be closely examined before deciding whether additional surveys outside the coal-mining industry are warrented.

Because interference in the analysis of diesel-source elemental carbon is expected to occur in underground coal mines, field work will be conducted in this environment. If possible, non-diesel-equipped coal mines known to have relatively high concentrations of sub-micrometer aerosol will be surveyed. Various aerosol size fractions will be collected in diesel-equipped mines as well. Sierra 298 personal cascade impactors and Andersen series 220 cascade impactors containing quartz-fiber after filters will be used to collect different aerosol size fractions. In addition, samplers developed at the University of Minnesota will be employed by BOM researchers, who will be conducting the field trips that are currently scheduled (tentatively).

Filters will be analyzed by the thermal-optical method to examine the effect of sampler cut point on measured levels of elemental carbon.

Alternative Approach

Should elemental-carbon interference from coal preclude use of the thermal-optical method for analysis of samples from some mining environments, an alternative approach would be required. Although elemental-carbon interference by coal dust will not likely occur in many situations if small-sized dust fractions (e.g., < 1 μm) are collected, interference by coal dust may preclude use of the thermal-optical approach for determination of diesel-source elemental carbon when larger size fractions (e.g., total respirable) are collected. For this reason, collection of a sub-micrometer size fraction is recommended.

In order to distinguish coal char from diesel soot in the event that significant interference by the former occurs, a specific and quantitative marker for coal char is necessary. In view of the biological origin of coal (carbonized vegetation), nitrogen will likely be the most suitable elemental marker. In the ultimate analysis of seven bituminous coals ranging in volatile matter from low to high, an average nitrogen content (by weight) of 1.31% (SD= 0.24%) was reported (77). Additionally, an average value of 1.31% (SD=0.17%) was reported (78) in recent work involving the analysis of three standard reference coals obtained from widely varying origins (NIST, South African Bureau of Standards, and the Commission of the European Communities, Community Bureau of Reference). Considering that the presence of mineral matter not native to the original plant material influences the reported nitrogen content of bulk samples, variation in these results is surprisingly low; an even smaller variation is predicted when percent nitrogen in coal <u>char</u> is determined. Results of analyses of coal samples by a combustion-based evolved gas analysis (EGA) technique developed by T. Novakov's Atmospheric Aerosol Group at Lawrence Berkeley Laboratory (LBL, University of California, Berkeley) support this prediction.

In LBL's EGA technique, the sample (a punch from a quartz-fiber filter) is heated at a pre-determined rate in an oxidizing or neutral carrier gas. Evolved C-, N-, and H-containing gases (resulting from volatilization, pyrolysis, decomposition, and combustion) are converted to CO_2, NO_x, and H_2O by an oxidizing catalyst and these species are then determined by CO_2, NO_x, and H_2O detectors, respectively. The integrated area under each thermogram trace corresponds to total C, N, and H content of the sample.

In CO_2 thermograms of coal-dust samples analyzed by EGA, two main components are observed. Novakov designates the low-temperature component "aliphatic" carbon and the high-temperature component "aromatic" carbon. In nitrogen thermograms of coal-dust samples, a distinct high-temperature peak appears at the same temperature as the aromatic peak in the CO_2 thermogram. Novakov claims (79) that the ratio of the nitrogen and aromatic carbon responses was essentially constant for all coal-dust samples examined. Furthermore, because nitrogen species in diesel particulate samples (e.g., nitrate) will be evolved at much lower temperatures (< 300 °C), a diesel-source nitrogen interference is not expected. For these reasons, it should be possible to use the high-temperature nitrogen peak as a specific and quantitative marker for coal-source elemental carbon.

A Hewlett-Packard (HP) Atomic Emission Detector (AED) with multielement detection capability is available within NIOSH (MRB/DPSE) for investigation of the above-described analytical approach. For these investigations, a thermal desorption/pyrolysis/combustion unit interfaced to the AED (HP 5921) would be required. Elemental fingerprints (C, N, and S) will be obtained for diesel soot and coals of ranging rank in an attempt to distinguish these two materials. Relative to the thermal-optical method, this approach should provide improved sensitivity (specified elemental detection limits are typically below 50 pg/sec) and selectivity. The AED also should afford greater selectivity and sensitivity in the analysis of a sample's organic fraction; however, it may not be possible to select components in the organic fraction for accurate assessment of occupational exposures to particulate diesel exhaust as many of the compounds present can originate from numerous non-diesel sources.

Instrumentally, the AED has other desirable features as well. Because atomic emission is monitored, a CO_2-to-CH_4 conversion step (required in the thermal-optical method) is not required. In addition, the AED's multielemental detection capability enables investigation of a subtractive approach (using nitrogen as a marker for coal-source elemental carbon) without the need for multiple detectors. Furthermore, elemental detection is simultaneous, which is not the case in a multiple-detector instrument such as that used by LBL. Should the thermal-optical method prove unsatisfactory for the intended application, investigation of the above-described approach will be considered.

Emission-Source Variations in Exhaust Composition

Elemental carbon (C_e) composed 60-80% of the total carbon (C_t) found in particulate diesel-exhaust samples collected in a dilution tube (20).

Similarly, more than 60% of the total carbon found in sub-micrometer particulate samples collected during surveys of diesel-equipped mines (coal and metal/nonmetal) was elemental carbon. In eight NIOSH surveys of the trucking industry (includes road drivers and dock workers), particulate samples contained an average of 41% elemental carbon. Sampling artifacts (e.g., adsorption of organic compounds), in combination with relatively low filter loadings, may be responsible for the apparently lower proportion of elemental carbon in these particulate samples. Lower C_e/C_t ratios also may reflect actual source-to-source variations in exhaust composition.

Aside from inter-source variability in the elemental-carbon content of diesel-exhaust particulate emissions, variation in emission factors for a given engine exists. For "mode sensitive" engines (i.e., exhaust composition changes significantly with, e.g., rpm and load), the composition of the particulate sample collected will depend on (among other factors) the proportion of time spent in different operational modes. Because emission factors for heavy-duty engines are reportedly more dependent on driving cycle and engine load and rpm than light-duty engines (80), heavy-duty engine exhaust composition may show greater variability than that of light-duty engines.

When using elemental carbon as an exposure index for particulate diesel exhaust, widely varying elemental-carbon content may result in an inaccurate estimation of actual differences between worker exposures. For example, if the elemental-carbon fraction of a given diesel particulate mass ranged from 24-64%, an apparent exposure difference up to 2.7-fold could be indicated if elemental carbon were used to estimate total particulate mass. However, if less variation in the mass fraction of elemental carbon is obtained when full-shift samples are collected, and if true exposure differences are large relative to errors caused by this variation, elemental carbon should be a fairly accurate reflection of differences in particulate diesel exhaust exposures.

Highly variable inter- and intra-source exhaust compositions do not necessarily render a problem intractable from a relative-exposure standpoint. It may be possible to <u>characterize</u> emission sources by collecting particulate samples at area locations near/at the emission source(s). C_e/C_t ratios for "exhaust-source" samples can then be compared with those for personal samples. If the C_e/C_t ratio obtained for a personal sample is systematically lower than that for the emission source (or average of contributing sources), sampling interferences are likely responsible (e.g., adsorption of organic species or collection of non-diesel organic aerosol), since in the <u>absence</u> of such interferences C_e/C_t ratios for samples collected near the emission source are expected to be less than or equal to those for samples collected at locations remote from the source (81). In fact, in a study involving atmospheric carbon particles, C_e/C_t ratios obtained at sampling sites were used to indicate the extent of atmospheric formation of secondary organic aerosol (i.e., condensation aerosol formed in the atmosphere by gas phase reaction of hydrocarbon vapors) that had occurred since movement of the air mass from the emission sources (82). In making the above-stated conclusion regarding expected C_e/C_t ratios, it is assumed that condensation and adsorption processes responsible for the diesel-source organic fraction of the particulate material are essentially complete at the selected area location, and that relatively low interference levels exist at this location.

Because many organic-carbon interferences could be present, measurement of a particulate sample's total carbon for compliance purposes is a flawed approach; however, measurement of total carbon (as organic and elemental) should provide useful data for future epidemiological studies. Rationale for selecting elemental carbon as a surrogate measure of exposure to particulate diesel exhaust is provided at length in this protocol. Based on a conservative estimate of the elemental-carbon mass fraction of particulate diesel exhaust, an elemental-carbon standard could be recommended at the desired margin of safety. Although C_e/C_t ratios reportedly depend on many factors, including engine type, speed, and load, ratios obtained in my work generally ranged from 0.70-0.80 for sub-micrometer particulate from underground dieselized coal mines. In DSHEFS's studies of the trucking industry, ratios ranged from 0.33-0.47. In this case, actual ratios may be higher than measured, since sample loadings were light and interfering organics could have resulted in apparently lower ratios. Because no source sampling was conducted in these studies, actual ratios are uncertain.

In the event that NIOSH recommends exposures be expressed in terms of the total diesel particulate mass, which for all practical purposes can be represented by total carbon, an estimate of diesel particulate exposure could be calculated from the elemental carbon result (personal sample) and the C_e/C_t ratio (presuming that source sampling is a valid means of establishing workplace C_e/C_t ratios). Because the accuracy of calculated results would be questionable, this approach is not recommended for regulatory use. Instead, establishing an elemental-carbon standard based on a conservative estimate of its fraction of the total particulate mass (see above discussion) is recommended, since low levels of elemental carbon can be precisely determined and the diesel engine is its only significant source in many workplaces.

Statistical Design

Before a study design for evaluation of the overall (i.e., sampling and analytical) performance of the method is prepared, two preliminary investigations will be conducted. These investigations will address the thermal-optical method's performance in the determination of total carbon (see pp 20-21), and the potential interference by coal dust.

The thermal-optical method is being used by NIOSH researchers for analysis of particulate diesel exhaust, but has not yet been evaluated using carbon standards. This work is necessary to ensure that measurement of total carbon is accurate and precise. If so, an operational definition (see p 21) of diesel-source elemental carbon will be established as part of the analytical method.

To provide an indication of the interference expected from coal dust in the determination of diesel-source elemental carbon, size fractions of a variety of coals obtained from the DOE Sample Bank will be collected and analyzed by the thermal-optical method. This work will assist in selection of factors (e.g., coal type) to be implemented in the study design.

After completion of the above-described preliminary work, a study design will be prepared in cooperation with DPSE statisticians and submitted to the NIOSH Statistical Peer Review Group (SPRG). Elements of the design will include number and types of sampling devices, aerosol composition (e.g., coal type and size distribution), and levels examined. A diesel test cell and dust chamber being assembled by BOM researchers will be used for collection of coal, diesel, and coal/diesel aerosols (p 20). Because candidate sampling devices are currently being developed, the number and types of sampling devices to be evaluated cannot be specified at this time. It is anticipated that BOM facilities for this work will be functional by 4Q91. Overall success of the method will be evaluated using the NIOSH "Standards Completion Program (SCP) Statistical Protocol" when applicable. Strict adherence to the SCP protocol is not possible, since no OSHA standard exists for diesel-source elemental carbon and it is being defined operationally.

Safety

Guidelines regarding laboratory and field health and safety will be observed in accord with those outlined in the NIOSH/DPSE safety manual. No experiments with human or animal subjects are involved in the conduct of this research.

NIOSH personnel conducting field surveys of mines are certified (by MSHA) to do so. DRDS personnel have extensive field experience, both in mining and other workplaces.

PROJECT PERIOD

3Q90:
Complete preliminary studies and project peer review.

1Q91:
Revise peer-reviewed project protocol and submit to Director, DPSE and Assistant Director of Science, OD, NIOSH.

Prepare sampling media for field surveys (if scheduled) of coal and/or metal/nonmetal mines. Analyze samples by thermal-optical method (TOM) and enter results into Lotus worksheets.

2Q91:
Establish techniques for preparation of carbon standards and analyze standards. Examine different diesel soots to determine temperature window for elemental-carbon response. Examine potential non-coal interferences.

Analyze various coal ranks and size fractions of DOE coal samples by thermal-optical method.

3Q91:
Prepare study design on instrument performance in determination of total carbon and comparison of various samplers.

Determine TOM sensitivity, selectivity, precision, analytical range, and accuracy in determination of total carbon.

If TOM not satisfactory and alternative approach pursued, select commercially available thermal desorption/pyrolysis/combustion unit or decide on in-house furnace design. If TOM acceptable, arrange/plan for laboratory collection of diesel, coal, and diesel/coal particulate samples at BOM (or elsewhere).

4Q91:
Collect diesel, coal, and diesel/coal particulate samples at BOM and analyze by TOM (note: presumes method results found acceptable). Different sampling devices will be examined.

Complete data reduction work and evaluation of TOM.

If alternative analytical approach pursued, procure necessary components for investigation.

1Q92:
Submit report on TOM to NIOSH peer review. Pursue alternative approach, depending on results obtained during FY91. Effort on alternative approach during FY91 will be conducted on a time-available basis, with priority being given to milestones for TOM work; however, project emphasis may change as dictated by experimental results.

2Q92:
Disseminate information to DSDTT. Submit paper (TOM work) to an appropriate technical journal. If appropriate, submit method description to NIOSH Methods Manual.

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Attachment 2

SUMMARY AND STATUS REPORT ON PROJECT TO DEVELOP A SAMPLING AND ANALYTICAL METHOD FOR AIRBORNE DIESEL EXHAUST PARTICLES

Background

In its Current Intelligence Bulletin 50, "Carcinogenic Effects of Exposure to Diesel Exhaust," the National Institute for Occupational Safety and Health (NIOSH) recommended that "whole diesel exhaust be regarded as a potential occupational carcinogen." In response to this recommendation, researchers at NIOSH have been exploring various approaches for monitoring worker exposure to diesel engine exhaust. Because diesel exhaust contains thousands of compounds, a surrogate measure of its exposure must be selected. Gravimetric methods targeting the mass of the particulate fraction have been developed. To reduce interference on non-diesel aerosol, size-selective sampling devices have been employed. Because particulate diesel exhaust is largely submicrometer in size, its separation from larger-sized aerosols is possible. Size-selective samplers for use in underground coal mines have been developed by NIOSH researchers, the Bureau of Mines (BOM), the Mine Safety and Health Administration (MSHA), and the University of Minnesota [Cantrell and Rubow 1991; McCawley et al. 1986].

Although size-selective sampling can improve the selectivity of a gravimetric analysis, significant amounts of submicrometer aerosol may arise from non-diesel sources. Thus, even if very low masses could be determined precisely, the presence of submicrometer background aerosol could make the accuracy of such measurements highly questionable. In field studies conducted in underground coal mines where no diesel-powered equipment was used, concentrations of submicrometer whole dust were reported to range from 20-100 $\mu g/m^3$ [Cantrell and Rubow 1991]. In workplaces where smoking is permitted, cigarette smoke could pose a major interference to a gravimetric method.

NIOSH researchers have selected the use of elemental carbon as a surrogate measure of exposure to particulate diesel exhaust because it is more sensitive than the gravimetric approach. An evolved gas analysis technique, called the "thermal-optical method," is being investigated for its determination. This work is being conducted in cooperation with a contract laboratory. The instrument being evaluated is similar to a design previously described in the literature [Johnson et al. 1981]. This method was used by NIOSH researchers in an industrial hygiene study of the trucking industry [Zaebst et al. 1991]. Selection of elemental carbon as a marker for diesel exhaust exposure was based on the work of Fowler [1985], who evaluated a number of species as indices of "overall diesel exposure." Included in the evaluation were CO_2, CO, SO_2, NO, NO_2, total and fine particulate material (determined gravimetrically), volatilizable carbon (organic), and elemental carbon. Of these constituents, elemental carbon was the most reliable measure of "diesel exhaust as an entity" (i.e., it reflected exposures to the largest number of exhaust components examined) [Fowler et al. 1985]. Elemental carbon constitutes a large fraction of the diesel particulate mass, serves as a carrier of polycyclic aromatic compounds, can be quantified at low levels, and its only significant source in many workplaces is the diesel engine. Sources of elemental carbon that may interfere are 1) commercial polymeric carbons, such as lamp black or carbon black; 2) anthracite and low-volatile bituminous coal with a high percent of fixed carbon. However, a size-selective sampling approach should minimize this interference. Other interferences include pyrolyzable materials and combustion aerosols such as cigarette smoke which contributes high-temperature carbon. However, only 2% to 3% of total carbon in cigarette smoke is defined as elevated. Inorganic carbon (carbonate) is not an interference because it is evoked during the first stage of analysis. For these reasons, its use as a surrogate measure of particulate diesel-exhaust exposure is proposed.

Analysis Method

In the thermal-optical method, speciation of organic, carbonate, and elemental carbon is accomplished through temperature/atmosphere control and optical measurements. Quartz-fiber filters are used for sample collection and punches are taken from the filters for analysis. An optical feature corrects for pyrolytically generated elemental carbon, or "char," formed during the analysis of some materials. Operationally, the thermal-optical method involves three stages. In the first, organic and carbonate carbon are volatilized from the quartz filter punch in a helium atmosphere as the sample oven's temperature is stepped to 680°C. Evolved carbon is catalytically oxidized to CO_2 and subsequently reduced to methane, which is then quantified by a flame ionization detector (FID). Temperature steps were chosen such that carbonate carbon appears as the fourth of four peaks typically observed in the "thermogram" (plot of detector response vs. temperature). The second stage of the analysis begins after reducing the oven temperature to 525°C. At this point, an oxygen/helium mix is introduced and the oven temperature is raised to 750°C. It is during this stage that pyrolysis correction and elemental carbon measurement are made. In the final stage of the analysis, calibration is achieved through injection of a known amount of methane into the oven.

Method Evaluation

Standard solutions containing polynuclear aromatic hydrocarbons (PAHs), and solutions of various water-soluble organic compounds were analyzed. Different analytes were examined to investigate whether the efficiency of the method's catalytic oxidation/reduction process is compound-dependent. 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 "analyzed to remove possible carbon contamination. Two of the PAHs (naphthalene and acenaphthylene) were partially lost from the filter punch and could not be reliably analyzed. Response of the other PAHs examined was linear ($r^2 \geq 0.996$ for individual compounds) and did not appear to be compound-dependent ($r^2 = 0.994$ for four compounds). Better agreement between actual and reported values was seen with the aqueous samples, where interference of residual organic solvent was not a problem. Response of individual compounds was linear ($r^2 \geq 0.999$) and no compound-dependence was noted for the five compounds examined ($r^2 = 0.998$).

The analytical range and limit of detection (LOD) of the thermal-optical method were determined. Detector (flame ionization detection - FID) response was offscale when organic carbon was present at about 50 $\mu g/cm^2$. The 200-$\mu g/cm^2$ upper value quoted by the contract laboratory assumes that the organic carbon in the sample will be evolved in stages as the temperature is stepped, which is normally the case when real-world samples are analyzed. The maximum loading was lower when individual compounds were analyzed because each was volatilized as a single peak. When a peak in the thermogram represents more than about 50 μg carbon/cm^2, the sensitivity of the FID response must be decreased. To determine the LOD of the thermal-optical method, a set of low-level calibration standards was analyzed. Using the results of linear regression of the mass of carbon reported vs. the amount present, an LOD of about 0.4 $\mu g/cm^2$ was calculated.

Although the thermal-optical method is intended for use in a variety of workplaces, the greatest interference in the determination of diesel-source elemental carbon is expected when analyzing samples from underground coal mines. To determine whether the thermal-optical method was suitable for application in this environment, a preliminary field evaluation was conducted in an electric-powered underground coal mine as part of the NIOSH method development. In order to exclude most of the coal dust, size-selective samplers were employed. Only low levels (0.6 - 7.5 $\mu g/m^3$) of elemental carbon were found in sub-micrometer dust samples collected in two electric-powered underground coal mines.

To further investigate the potential interference of coal dust, different ranks of submicrometer coal dust were collected on quartz-fiber filters and analyzed by the thermal-optical method. Coarsely ground (-20 mesh) coal samples obtained from the Department of Energy Sample Bank at the Pennsylvania State University were sieved to ≤ 53 μm and placed in a fluidized bed. Dust from the fluidized bed was directed through a MOUDI impactor. The last three stages and the after filter of the impactor were removed in order to collect the sub-micrometer size fraction. A 37-mm cassette containing a quartz-fiber filter was located downstream of the impactor for sample collection. As anticipated, the extent of interference was rank-dependent. The greatest interference occurred with anthracite, where about 80% of the total carbon found was elemental. In contrast, only about 14% of the carbon found in two sub-bituminous coals, and a high volatile bituminous coal was elemental. In practice, the degree of interference will depend on the coal type, respirable dust (coal) concentration and size distribution, and the aerosol size fraction sampled. Before recommendations regarding a sampling device can be made, a sampler comparison study must be completed to evaluate the performance of various samplers. Currently, NIOSH researchers plan to conduct this study jointly with the Bureau of Mines (BOM), which has been assembling the required aerosol generation system. According to BOM staff, the system should be operational in early August. Should its completion be delayed beyond this date, other arrangements will be made. Additional investigations by NIOSH researchers will be completed by the end of this fiscal year. When complete, research results will be transmitted to MSHA and published in the NIOSH Manual of Analytical Methods.