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REVIEW OF SAMPLING AND EVALUATION TECHNIQUES FOR DIESEL EXHAUST PARTICULATE MATTER IN THE MINING INDUSTRY AND THE APPLICATION OF A VAPOR PHASE ORGANIC CARBON CORRECTION FACTOR

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by

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Abstract

The health effects associated with diesel exhaust exposure have been documented for decades. However, methods used to assess diesel exhaust have experienced considerable revision over the past twenty years. The latest sampling methodology considers particulate matter elemental carbon (EC) and organic carbon (OC) analysis along with the vapor phase OC analysis. The objective of this study was to evaluate the influence of vapor phase OC on the current National Institute for Occupational Safety and Health (NIOSH) method 5040 sampling and evaluation techniques for diesel exhaust particulate matter.

A pilot study was conducted as part of a larger study evaluation biodiesel exhaust particulate matter in an underground metal/non-metal mine in the northwest United States. Seventeen area samples were collected and analyzed via the NIOSH 5040 method for EC and OC. In addition to the primary quartz filter, the backup filter was also analyzed in accordance with the NIOSH method 5040 for OC concentrations.

A regression analysis revealed no correlation between the top filter and backup filter in terms of OC concentrations (R^2=0.005) (P=0.017). In addition, no correlation was observed in OC concentrations on the top and backup filter when a mean medium sample blank concentration of 17.8 µg/sample was subtracted from the backup filter (R^2=0.005) (P=0.000).

These data suggest that when analyzing for biodiesel particulate matter via the NIOSH 5040 method, there is no correlated contribution of OC from the top filter to the backup filter, which implies that the OC collected on the backup filter is not derived from gas phase OC vapors from the active sampling, but from the quartz filters themselves.

Keywords: DPM, organic carbon, elemental carbon, total carbon, diesel health effect, NIOSH 5040 method, sampling methods, underground mining

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Glossary of Terms (acronyms)

Term	Definition
ACGIH	American Conference of Governmental Industrial Hygienists
DE	Diesel Exhaust
DPM	Diesel Particulate Matter
EGA	Evolved Gas Analysis
EC	Elemental Carbon
FID	Flame Ionization Detector
IARC	International Agency for Research on Cancer
IDLH	Immediately Dangerous to Life and Health
MSHA	Mining Safety and Health Administration
OC	Organic Carbon
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
QQ	Quartz-Quartz
RCD	Respirable Combustible Dust
REL	Recommended Exposure Limit
TC	Total Carbon
TLV	Threshold Limit Value
VOF	Volatile Organic Fraction

1. Introduction

In the U.S. underground mining industry, diesel powered equipment comprises the majority of transportation fleets. The use of diesel-powered equipment by the underground mining community has continuously increased since its inception in a German coal mine in 1927. In the United States approximately 3,000 pieces of diesel equipment were being operated in underground coal mines by 1995 and over 4,000 units were operated in underground metal/non-metal mines by 2001 (Brune, 2010). Diesel is used primarily in the underground operations for machine power and to reduce the engine emissions and associated health effects. Diesel engines emit less carbon monoxide and other gases, which make them more attractive in underground mining. While diesel engines can operate with less highly refined fuel and consume less fuel per unit of work (high power output), they typically emit more particulate mass than gasoline powered engines.

Diesel engine exhaust is a highly complex and variable mixture of gases, vapors and fine particles (Birch, 2003). The major components of diesel exhaust (DE) are particulate matter, carbon monoxide, carbon dioxide, nitrogen dioxide, nitric oxide and sulfur dioxide. The amount and composition of the exhaust vary greatly, depending on factors such as fuel and engine type, maintenance schedule, tuning, workload, and exhaust gas treatment. Particulate components consist of liquid droplets and soot particles bearing organic compounds, sulfates, metals and other trace elements (Birch, 2003).

Although the use of diesel engines is common in the mining industry, there are negative effects that can result from the combustion of diesel. Recent studies have shown that exposure to diesel particulate matter (DPM) in DE can have severe adverse health effects. Workers exposed to DE show an elevated (20-50%) risk of lung cancer (Birch, 2003). DE has also been linked to

health effects such as eye and nose irritation, headaches, nausea, and asthma (J. Noll, 2005). Based on sufficient evidence that DE increases the risk of lung cancer, the International Agency for Research on Cancer (IARC) classified DE as a group 1 human carcinogen in June of 2012 (WHO, 2012). In 1988 it was classified as a probable carcinogen.

In the United States alone, over a million workers (e.g. trucking, mining, railroad, agriculture) are occupationally exposed to DE. Since diesel is so commonly used in the mining industry, many people are exposed to these harmful effects every day. Two hundred thousand people are employed in the mining industry in the United States according to the Bureau of Labor Statistics (U.S. Department of Labor, 2015). There have been many strides to reduce the widespread presence in occupational settings, primarily because of the number of people that are exposed to DE and the harmful effects associated with it.

The first diesel engine emission standards in the U.S. were published under the Clean Air Amendments of 1990 and were referred to as Tier 1 -3 standards (EPA, 2012). These standards were met primarily through advanced engine design, with limited use of exhaust gas after treatments. Tier 4 standards were phased in from 2008-2015 and require substantial reductions (90%) in oxides of nitrogen and particulate matter which will be achieved primarily through exhaust gas after treatments. Non-road (or off-road) engines are addressed as a separate category in the Tier standards. However, the off-road engines used in underground mining equipment are exempt since diesel emissions and air quality in mines are regulated by the Mine Safety and Health Administration (MSHA) (EPA, 2012).

MSHA developed a total carbon (TC) air exposure limit of 160 micron per meter cubed (160_{TC} $\mu g/m^3$) as a surrogate for diesel exhaust constituents in order to minimize exposure to

DPM. Total carbon is defined as both the elemental carbon & organic carbon components (MSHA, 2008).

There have been several occupational exposure limits and sampling and analytical techniques developed over the years to evaluate diesel exhaust exposures. The objective of this thesis is to investigate these techniques and to evaluate the impact of gas phase organic compounds on current sampling & analytical techniques.

2.0 Background

2.1 Health Effects

The National Institute for Occupational Safety and Health (NIOSH) considers diesel exhaust a potential occupational carcinogen and recommends that employers reduce workers exposure. This 1988 recommendation was based on five independent animal studies in which rats exposed to unfiltered exhaust showed an increased incidence of benign and malignant lung tumors. Other organizations, including the World Health Organization (WHO), the California Environmental Protection Agency, the U.S. Environmental Protection Agency (U.S. EPA), and the National Toxicology Program have reviewed the animal and human evidence, and each has classified diesel exhaust as a probable human carcinogen (Birch, 2003). As previously discussed IARC classified DE as a group 1 human carcinogen in 2012.

Experimental studies of diesel particulate that aided the results were *in vitro* models, animal *in vivo* models, studies of healthy humans and occasional observations in patients. Respiratory, immunological and systemic effects have been documented (Sydbom, et al., 2001).

Exposure to diesel exhaust can have acute health effects. Diesel exhaust can irritate the eyes, nose, throat and lungs, and it can cause coughs, headaches, lightheadedness and nausea (acute effects). In studies with human volunteers, DE made people with allergies more susceptible to the materials to which they are allergic, such as dust and pollen. Exposure to DE also causes inflammation in the lungs, which may aggravate chronic respiratory symptoms and increase the frequency or intensity of asthma attacks (CA.gov, 2007)

Chronic exposure to DE induces cough, sputum production and lung function decrements. Pathological and histological findings in the lungs of rats after exposure to diesel particulate matter (DPM) include increases in lung weight, increased numbers of particles in the

lung and an increased burden of soot, associated with alveolar infiltration of macrophages, macrophage aggregation, chronic inflammatory responses, proliferation and hyperplasia of alveolar epithelium and type 2 cells, thickening of alveolar septa and wall fibrosis (Sydbom, et al., 2001).

Due to the complexity of DE, it is likely that some effects are caused by the gaseous components whereas other effects relate to the particle content. The suggested mechanisms of detrimental actions of particulate matter include oxidative stress and actions of particulate matter content such as metals, hydrocarbons, acids and carbon core. The ultrafine particles are currently suspected of being the most aggressive particulate component of DPM. Comparison of DPM and carbon black in animal inhalation studies show that both induce a reduction in lung function and accumulation of macrophages, suggesting that the toxic effects of DPM are, in part, coupled to the carbon core (Sydbom, et al., 2001).

2.2 Diesel Particulate Matter Occupational Exposure Limits

There have been numerous proposed and published occupational exposure limits (OELs) for DPM as illustrated in Table 1. Analytical techniques have evolved over the years along with sampling techniques for DPM. The Occupational Safety and Health Administration (OSHA) to date does not have an established permissible exposure limit (PEL) for diesel exhaust. The American Conference of Governmental Industrial Hygienists (ACGIH), however, has had several proposed threshold limit values (TLV's) for the DE. The recommended TLV's were based on three parameters:

- the relative risk of lung cancer in the exposed cohorts;
- the diesel exhaust exposures in those cohorts; and
- an "acceptable value" for a relative risk (TLV, 1998)

The 1996 ACGIH TLV publication proposed a TLV of 0.15 milligrams per cubic meter (mg/m^3) for diesel exhaust in the notice of intended changes (ACGIH, 1996). This proposed TLV consisted of total carbon concentration, both organic carbon (OC) and elemental carbon (EC).

The TLV was changed in 1998 to a level of 0.05 mg/m^3 because it was found that the particulate fraction of the exhaust might present a risk of causing lung cancer (TLV, 1998). The mechanism of action and the causative agents involved in the adverse health effects are not specifically known.

Since DE is primarily composed of OC and EC, it was considered to be the most logical marker for measuring DPM. However, the many non-diesel sources of OC found in the environment make OC prone to interferences from non-diesel sources. Because it was shown that EC could be used as a marker for DPM, and OC has many sources, which could lead to interferences with the results, ACGIH modified the proposed TLV again in 2001 to 0.02 mg/m^3 with an EC designation (ACGIH, 2001). The proposed TLV was revised from 0.05 mg/m^3 to 0.02 mg/m^3 based on the assumption that 88% of DPM is carbon, and that 50% or the total carbon is represented by EC.

NIOSH has not yet established a recommended exposure limit (REL) or an immediately dangerous to life and health (IDLH) concentration for DE. However, NIOSH has recommended that whole DE be regarded as a potential occupational carcinogen, and DE exposures should be limited to avoid possible health effects.

In addition to regulatory and best practices of OELs in the U.S., there have been several other countries with established exposure limits:

- Australia – 100 $\mu g/m^3$ 8 hour time weighted average (TWA); and

- Germany – 100 mg/m^3

Table I: Chronology of Occupational Exposure Limits for DPM

Year	Source	DPM Concentration Considered	OEL Concentration	DE Component
1988 **1995** **1999** **2000** **2001** **2002** **2003**	IARC ACGIH	Probable carcinogen A2 (suspected human carcinogen) A2 A2 A2 (elemental carbon) A2 Withdrawn; ACGIH TLV for DPM – under notice of intended change	 0.15 mg/m^3 0.05 mg/m^3 0.05 mg/m^3 0.02 mg/m^3 0.02 mg/m^3	 EC
2001	MSHA	MSHA (USA) Risk Assessment with respect to health effects was: "Exposure to DPM can materially impair miner health or function capacity. These material impairments include acute sensory irritations and respiratory symptoms (including allergic responses); premature death from cardiovascular, cardiopulmonary, or respiratory cause; and lung cancer." Fed. Reg. 5853-5855 (Jan. 19, 2001)		
2001	MSHA	Mean concentration of 0.64 mg/m^3 TC for a period of 45 years of occupational exposure results in a relative risk of lung cancer 2.0		TC
2006	MSHA	- This established an interim concentration limit - Took effect on Jan. 6, 2006	400 µg/m^3 160 µg/m^3	TC as surrogate TC final limit
2001-2005	MSHA	The American Mine Study		
2005	MSHA	(TC/EC ratio of 1.3 for 90% of the valid samples ~ 464)	400 µg/m^3 308 µg/m^3	TC EC
2007	MSHA	The DPM limit was reduced	350 µg/m^3 270 µg/m^3	TC EC
2008	MSHA	Final limit	160 µg/m^3 123 µg/m^3	TC EC

2.3 Organic, Elemental, and Total Carbon

2.3.1 Elemental Carbon

Diesel exhaust is a complex mixture of gases, vapors, and particulate matter (PM) generated under high pressure and temperature during the engine combustion cycle. Diesel particulate matter has a carbonaceous core (defined as EC) with adsorbed organic compounds [described as organic carbon (OC)] and small amounts of sulfates, metals, and other compounds

as illustrated in Figures 1 & 2. The gaseous constituents include carbon oxides (CO_x), nitrogen oxides (NO_x), aldehydes, and low-molecular weight hydrocarbons (Roel Vermeulen, 2010).

All fuel combustion within diesel engines is not always complete. If temperatures are not hot enough, fuel will burn without the presence of oxygen, creating a black charred waste, or solid carbon soot (EC). Once the EC is formed, most of it will combine with oxygen and burn during later stages of the combustion process. The remainder of the carbon will be emitted from the engine exhaust as solid particulate matter, forming the core of a typical diesel-particle aggregate. The formation EC during combustion and expulsion are driven by the three factors of temperature, resistance time, and availability of oxidants (Bugarski, Janisko, Cauda, Noll, & Mischler, 2011).

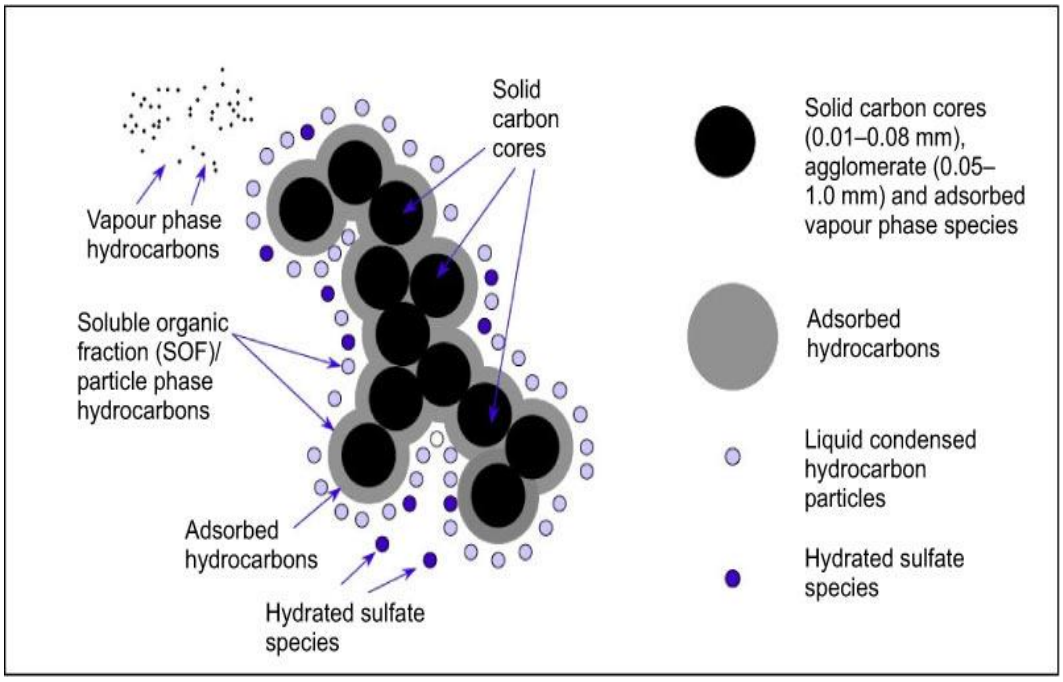

Figure 1: Composition of Diesel Particulate Matter (Twigg & Phillips, 2015)

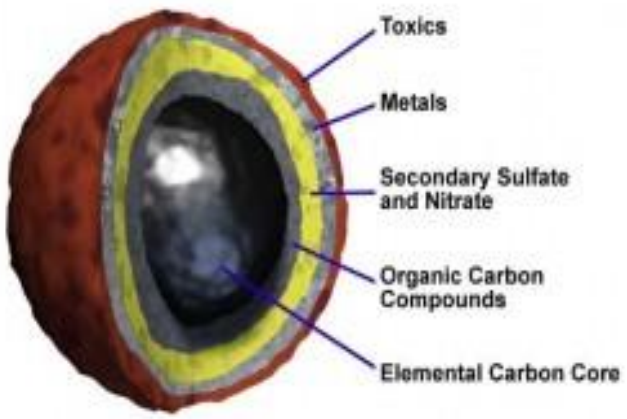

Figure 2: DPM Particle (Force, 2015)

2.3.2 Organic Carbon

The particulate components of DE consist of liquid droplets and soot particles bearing organic compounds, sulfates, metals and other trace elements. The organic fraction (droplets and adsorbed particles) is mainly unburned fuel and oil, but also contains thousands of compounds (Birch, 2003).

Organic carbon (OC) compounds are formed when hydrocarbons (in fuel and lubricating oil) are consumed but not fully oxidized during the combustion process. Sources of OC emissions include fuel that is present in overly lean regions (where the ratio of fuel to air is too low to support efficient combustion), fuel that leaked into the chamber too late during combustion, or oils that get introduced in the combustion chamber from other sources (Bugarski, et al., 2011). In these instances the high temperatures may be enough to vaporize the hydrocarbons but not high enough to convert them to CO_2 and water vapor.

Organic carbon compounds are partially composed of volatile material rather than nonreactive elemental carbon, and will react and change in both composition and phase during emission. These compounds are considered a component of DPM if not in the gas phase (Bugarski, et al., 2011). If OC remains in the gas phase, it is often referred to as an "HC" or "Vapor-phase OC" emission. Organic carbon in the non-gas phase is often referred to as the volatile organic fraction (VOF) or soluble organic fraction (SOF). In the mining industry, the term OC almost always refers to non-gas-phase organics or substances that have mass and, therefore, contribute to total DPM mass (Bugarski, et al., 2011).

When sampling for DPM and considering OC and TC, some OC interferences cannot be excluded. If compounds such as cigarette smoke, wood smoke, condensation aerosols, and fumes are present, these materials can bias the OC, and therefore the TC results, depending on their relative concentrations and where sampling is taking place. The interfering aerosols, which are OC aerosols, belong to the same size category as diesel aerosols. This means that the interfering aerosols can be adsorbed by the sampling equipment just as easily as DPM (Birch, 2003). Although interferences in most work places are not anticipated, it is not possible to predict all possible scenarios. In general, the best way of determining whether the OC contribution from a particular airborne material could be significant is through analysis of the bulk material (Birch & Cary, 1996).

3.0 Organic Carbon Interferences Related to DPM

There have been studies performed to evaluate the organic carbon interferences related to DPM measurement. Two previous studies (Huntzicker, 1994; Kirchstetter, 2000) primarily focused on with the adsorption of gaseous organic compounds onto backup quartz filters. The first study was done in the Los Angeles Basin and was an investigation of organic aerosol sampling artifacts in that area. The purpose of these measurements was to evaluate the relative particulate and filter surface areas available for adsorption of gas-phase compounds during sampling (Huntzicker, 1994). Filter collection of particulate organic carbon is complicated by adsorption and volatilization sampling artifacts. Adsorption of organic vapors on the sampling filter comprises a positive artifact, and volatilization, which removes material from the filter, is a negative artifact; which obstructs attempts to accurately assess aerosol concentrations (Huntzicker, 1994).

Huntzicker (1994) reported that significant adsorption of gas-phase organic compounds occurs on quartz fiber filters, and the presence of typical DPM on the sampling filter does not significantly affect the magnitude of the adsorption artifact. Organic carbon sampled from the atmosphere is unlikely to attain equilibrium between that in the gas phase and that absorbed on the quartz fiber sampling filter (Huntzicker, 1994).

As a result, a quartz fiber filter behind a quartz fiber filter is exposed to a lower gas-phase concentration. Under typical sampling conditions adsorption is the dominant artifact in the sampling of particulate organic carbon, and longer sampling periods reduce the percentage of collected material that is adsorbed vapor (Huntzicker, 1994).

Kirchstetter (2000) performed a laboratory and field study of gaseous organic compounds being absorbed onto quartz filters. Adsorption of organic gases onto quartz filters (and possibly

the collected material) and the evaporation of collected DPM during sampling may lead to inaccurate results if not properly taken into account. The adsorption of organic gases may result in the overestimation of particulate OC concentrations because the adsorbed organics contribute to the total carbon measured during filter analysis. On the other hand, the evaporation of collected particles may result in the underestimation of organic carbon concentrations (Kirchstetter, 2000).

In the Kirchstetter (2000) study, a tandem quartz filter method was used to collect samples in Berkeley, California. The tandem method is simply sampling with two quartz filters, one on top of the other. The top, or front, quartz filter removes all particles, and gas-phase organics adsorbed onto both front and back filters. The measured carbon content of the backup filter can be subtracted from that of the front filter to give an improved estimate of the organic particulate mass collected on the front filter (Kirchstetter, 2000). The major findings of this study of the positive sampling artifact were: the tandem filter method can be used to correct for the adsorption of OC on the filter. If, however, only a quartz-quartz (QQ) pair is used (not a Teflon filter), the accuracy of the method improved with increased sampling time. It is also noted that all quartz filters should be cut from the same lot (batch) because of the variation in the adsorption capacity of filters from different lots (Kirchstetter, 2000). These two studies suggest further that adsorbed organic carbon vapors on quartz backup filters can more accurately depict the TC concentration because of the corrected adsorbed vapor.

3.1 Total Carbon

Total carbon (TC) is the term used to describe the sum of the OC and EC fractions of DPM (TC = EC + OC). There have been several studies that evaluated the different components of carbon with fuel sources, engine loads, etc.

The type of engine, engine operating conditions, fuel type, work load, running time, and a number of other factors effect EC and OC fractions. Because EC and OC make up over 80% of the total DPM mass, the EC/TC ratio helps to describe the general composition of DPM as well as the condition under which the DPM is formed (Bugarski, et al., 2011). When heavy-duty diesel engines are using a petroleum diesel fuel, and in low-speed and load conditions (typical operating mode approximation), high OC formation is the outcome. The result is a low EC/TC ratio if the aerosol contains more organic carbon (Bugarski, et al., 2011).

3.1.2 Diesel Fuel Used in the Mining Industry

The mining industry today is heavily dependent on the use of diesel and diesel products, including biodiesel. As an alternative control measure, some underground mine operators have turned to biodiesel/diesel fuel blends, ranging from 20/80% (B20) to 80/20% (B80) to reduce respirable DPM exposures. Using biodiesel instead of regular petroleum diesel significantly reduces the EC, CO, and hydrocarbons but fails to reduce NO_x and OC emissions (Lutz, et al., 2014). Another fuel alternative being considered is a natural gas/diesel blend (GD). In the diesel engine, the diesel acts as an igniter to facilitate the gas to ignite inside the combustion chamber. As the engine is started with pure diesel fuel and the inlet air temperature rises, natural gas is injected into the cylinder from an additional intake valve. As the natural gas is injected, the amount of diesel being consumed is reduced. Natural gas/diesel blend referenced from the Lutz et al. (2014) study showed that GD fuel use resulted in decreased exposures for every analyte measured in the study, with the exception of CO, suggesting that its use would likely reduce adverse health effects as compared with use of diesel and biodiesel fuels (Lutz, et al., 2014). Both biodiesel and GD significantly reduce the DPM, but GD shows an advantage over a

biodiesel blend. This suggests that the use of alternative fuels has the possibility to reduce harmful emissions from diesel engines.

Alternative fuels (biodiesel/biodiesel blends/GD) serve an important control for DE. The use of biodiesel reduces tailpipe PM, hydrocarbons (HC) and CO emissions. These benefits occur because biodiesel contains 11% oxygen by weight. The presence of O_2 allows the fuel to burn more completely, resulting in fewer emissions from unburned fuel (M. Bowman, 2006). This same principle also reduces air toxicity, which is associated with the unburned or partially burned HC and PM emissions (M. Bowman, 2006). The toxicity of biodiesel as diesel DPM is still out for debate.

3.2 Sampling and Analytical Techniques for Diesel Exhaust Exposure in Mining

Since the inception of exposure limits for DPM, there have been several sampling and analytical techniques used in the mining industry. These include gravimetric DPM monitoring, elemental carbon based methods, and total carbon methods. This section summarizes those methods used to assess the DPM.

3.2.1 Gravimetric Method

Gravimetric methods for DPM were initially employed for exposure monitoring. A respirable combustible dust (RCD) method was being used for estimation of diesel particulate concentrations in the mining industry (coal mines excluded). This method was acquired from the Proceedings of the 6th U.S. Mine Ventilation Symposium, Society for Mining, Metallurgy, and Exploration (Gandal, 1993). In this approach, combustible material in a respirable aerosol sample was determined as the difference in filter weight before and after combustion at 500°C (Birch & Cary, 1996).

The sampling train consisted of a 37 or 25mm glass fiber filter to collect respirable dust. Before the filter, a 10mm Dorr-Oliver cyclone with a 4.0µm cut point was used. A personal sampling pump was used to maintain a constant air flow rate of 1.7 lpm (DEEP, October 2001). Oil mists, EC, and OC were collected on the filter along with other combustable materials that are present in the sampling air. Therefore, it was concluded that the RCD method collects more than EC and is not the best sampling method for DPM (DEEP, October 2001). A limitation to gravimetric method is that it lacks specificity and sensitivity because it does not accurately measure low DPM concentrations (< 200 µg/m^3) (Birch & Cary, 1996).

3.2.2 Elemental Carbon Used As Surrogate for DPM

Elemental carbon has been reported as a superior measure of exposure to particulate diesel exhaust because elemental carbon constitutes a large portion of the particulate mass (around 50%), it can be quantified at low levels, its only significant source in many workplaces is the diesel engine (Birch & Cary, 1996), and it does not require a complicated sampling strategy to avoid or correct for interferences. Samples for EC are collected with or without an inertial impactor that removes particles greater than 0.8µm.

The sampling train typically consists of a 10mm Dorr-Oliver cyclone, an inertial impactor, and a 37mm quarts filter. In this method (NIOSH 5040, 1996), the DPM passes through the impactor and only the particles less than 0.8µm deposit on the filter. Because the large non-diesel aerosols cannot deposit on the filter they will not interfere with the analysis (DEEP, October 2001).

One potential limitation with using EC as a surrogate for DPM is that the EC fraction of DPM may change depending upon factors such as engine duty cycle and fuel type, etc. The

portion of EC in DPM in underground mining atmospheres could potentially vary, depending on how much engine conditions vary from day to day and mine to mine (Noll, 2005).

3.2.3 Total Carbon as a Surrogate for DPM

In the United States, TC is used as surrogate for determining DPM compliance exposures in underground metal/non-metal mines. Since TC can be affected by interferences and EC is not, one method used to estimate the TC concentration is to multiply the EC concentration from the personal sample by a conversion factor to avoid the influence of potential interferences. Since there is no accepted single conversion factor for all metal/non-metal mines, one is determined every time an exposure sample is taken by collecting an area sample that represents the TC/EC ratio in the miner's breathing zone and is away from potential interferences (Noll, et al., 2015). Initially, MSHA employed TC as the surrogate because it consistently represented over 80% of DPM and could be measured at concentrations well below the final limit. However, a 31-mine joint study by industry and government revealed that aerosols such as dust, cigarette smoke, and oil mist as well as sampling artifacts could interfere with the TC measurements (Noll, et al., 2015). Unfortunatly, no methods to correct for cigarette smoke or oil mist have been developed to date.

Another interference to TC is the adsorption of vapor-phase OC on quartz filters (see section 3.0). Quartz filters are used to collect DPM samples because they are highly efficient in collecting pariculate matter and can withstand the temperautes required for NIOSH Method 5040 analysis. However, quartz filters can also adsorb some vapor-phase OC, which is not traditionally recognized as part of the DPM. This adsorption can contribute a positive bias in DPM TC results. To account for the bias, one method (section 3.3.2) places a second quartz filter behind the initial sample filter, resulting in two filters positioned in series. In theory, all of the

DPM will collect on the first filter, and both the first and second filters will adsorb the same amount of vapor-phase OC. The results from the second filter, which is only exposed to vapor-phase OC, can then be subtracted from the results from the first filter to correct for the adsorbed vapor-phase OC. This correction is referred to as the tandem filter correction. The accuracy of the correction seems to depend upon flow rate, filter size, sampling time, and concentration of vapor-phase OC.

3.3 Analytical Method for Diesel Exhaust

MSHA requires DPM sample analysis according to the NIOSH 5040 analytical method (refer to appendix C). A thermal-optical analysis along with a flame ionization detector (FID) is used in the NIOSH 5040 method for an evolved gas analysis. Thermal-optical analysis determines speciation of elemental and organic carbon through temperature and atmosphere control, along with continuous monitoring of the filter transmittance (Birch, NIOSH 5040, 2003). Because of the high temperatures needed at 850°C, a quartz fiber filter is used for the sample media. A 1.5cm^2 punch (1) is taken from the filter for analysis and both EC and OC are reported in µg/cm^2. Concentrations of EC and OC are calculated by a simple equation; the total carbon content on a filter is obtained by adding EC and OC (Noll, 2005).

3.3.1 NOISH 5040 Method (1996)

The first issue of the NIOSH 5040 method for sampling of diesel particulate matter was published in May 15, 1996; this was then revised to issue 3 by September 30, 1999 (Interim – using total carbon). This initial method used a technique of an evolved gas analysis (EGA) by thermal-optical analyzer, an analyte of elemental carbon, a filter punch size of 1.5cm^2, calibration by methane injection, range of 1 to 105µg per filter portion, estimated LOD of 0.3µg per filter portion, and a precision of 0.19 @ 1 µg C, 0.01 @ 10 to 72 µg C (Birch, NIOSH 5040,

1999). Equipment is relatively straight forward with a sampler with a precleaned quartz-fiber filter (37mm) in a three piece cassette with filter support (stainless steel screen or cellulose pad), along with personal sampling pump (2-4L/min) with flexible tubing (Birch, 1999).

3.3.2 NIOSH 5040 Method (2003)

The latest NIOSH 5040 method was published in March 15, 2003. This issue is a revised and updated method from the 1999 issue and is relatively the same except for few new techniques, which involves using a thermal-optical analysis; flame ionization detector (FID) instead of the evolved gas analysis (EGA) by thermal-optical analysis, equipment notes that go into filter support (stainless steel screen, cellulose pad, or a second quartz filter), and other small changes/additions related to sample preparation, calibration and quality control, measurement, and evaluation of the method.

Another revision noted in the 2003 edition involves a secondary filter beneath the quartz filter. An important factor for the filter support instead of a stainless steel screen or cellulose pad is using a second quartz filter. This second quartz filter, or backup filter, can be used to correct for adsorbed vapor as it can provide a better estimate of the adsorbed OC as OC vapors readily adsorb onto clean filters (Birch, 2003b).

This final method has had inter-laboratory comparison work conducted since the initial publication of the method. Background information and guidance on method use, including sampling requirements have all been updated.

3.3 Ratio of EC/TC Reported in Literature

Previous studies have reported EC/TC ratios found during sampling and these ratios have varied greatly. Noll (2005) reported the EC/TC ratio from values approaching 100% to below 45%. Another previous study reported the EC/TC ratio values nearing 80% to below 30% and

can vary even greater (Zaebst, Clapp, & Blade, 1991). According to ACGIH, elemental carbon comprises approximately 50% of the total carbon of diesel exhaust (TLV, 2001). In this pilot study, the organic carbon interferences can alter the results of a sampling experiment and have a direct impact of the EC/TC ratio. With OC generated from cigarette smoke, multiple aerosols, and the backup filter itself, this would significantly lower the EC/TC ratio. If EC comprises 50% of the TC in DPM, then this pilot study futher illustrates the potential for organic interference from sources other than diesel exhaust.

Fuel sources such as regular gasoline have produced EC/TC ratios that differ from ratios observed with petroleum diesel. The oxygen content in biodiesel leads to more complete combustion, resulting in increased CO_2. In addition, biodiesel decreases the solid carbon fraction (EC) of particulate matter in emissions. With less elemental carbon in the atmoshphere, a lower EC/TC ratio would be expected. Obtained from the larger study (Evans 2015), explained in section 4.0, a mean of 9.71 $\mu g/m^3$ for EC and a mean of 15.56 $\mu g/m^3$ OC was observed.

The EC/TC ratios are not reliable estimates of the EC fraction of DPM because OC interferences can skew the ratios low and increase variability in the ratio. In such cases, TC is an inaccurate measure of the diesel particulate concentration (Birch, 2003a).

4.0 Methods

A study was conducted in an underground metal/ non-metal mine in the south central region of Montana. Members of Montana Tech, Boise State, and the University of Washington collaborated on a large research project in which the primary objective was to evaluate potential mine worker exposures to biodiesel exhaust. Real time and integrated sampling for DPM was conducted. In addition, biological monitoring was performed for the biomarker nitropyrene.

Four sampling tours were performed in the months of February, June, August, and October, 2014 for four days at specific locations where low, medium, and high DPM exposure was anticipated. Job tasks and areas within the mine associated with potential high exposure (e.g. vehicle maintenance shops and ore dump locations), or low exposure (areas with little or no diesel emissions, whose ambient air is continuously diluted with outside supply air such as those areas located near ventilation and elevator shafts, and above ground office locations), were identified. Twenty subjects were recruited as part of a cohort group for the study. The cohort represented a wide range of job tasks and locations (both above and below ground) to ensure a wide range of potential DPM exposures.

With all four tours, ten of the twenty workers were monitored the first day and the next ten the following day. This cycle continued with the following two days of monitoring and the other sampling tours. The mine employed a B70 biofuel source in its fleet (70% biodiesel, 30% petroleum blend).

4.1 Personal and Area Sampling

In addition to integrated and area sampling for DPM and nitropyrene, real-time data was collected using direct reading instrumentation for particle count, particle mass, NO_x, CO, CO_2 and environmental data such as temperature and humidity. Area sampling was performed in four

locations within the mine. The four locations were chosen strategically to characterize areas where specific study subjects were working, and to capture a wide range of DPM concentrations.

Personal sampling was performed on each subject participating in the study. To assess personal exposures to DPM, an SKC GS-1 respirable cyclone (1 µm cut point) (a 10-mm Dorr-Oliver equivalent design but comprised of conductive material to eliminate the electrostatic effects and safe for underground mine use) was fitted to the collar/vest of each worker in a location representative of his/her breathing zone. Subsequently, the filter element from the impactor was analyzed for EC and OC (and thus TC) using NIOSH method 5040. In addition, a personal 8 stage Sioutas Cascade impactor was placed at a strategic location in the breathing zone of a subset of miners, to measure the size distribution of the DPM aerosol. Media field blanks (10%) were also submitted to the laboratory for the data collected during the larger study.

As part of this large study described above, in an effort to evaluate the impact of gas-phased organic compounds on DPM sampling results, a pilot study was conducted at the same mine. Seventeen area samples for DPM were collected in the same locations (four), as well as sample duration as were previously sampled in the larger study. In addition to the primary quartz filter, the backup filter was analyzed. The analysis was done in accordance to the NIOSH 5040 method and was measuring OC concentrations. Results of this pilot study are presented below.

5.0 Results and Discussion

Results of the 17 additional samples in which organic carbon was measured are presented in Table I and Table III. Table II represents the concentration of OC on the sample filter (µg/sample) and Table III represents the concentration of OC in µg/m^3. The organic carbon concentrations on both the top filter and backup filters are reported as filter 1 and filter 2, respectively. The mean concentration of OC for the top filter was 42.95 µg/m^3 and the mean concentration of OC for the backup filter was 36.57 µg/m^3. A regression correlation analysis was performed to evaluate the relationship between the top and backup filters. As illustrated in Figure 3, an R^2 value of -1.745 (P=0.019) was obtained. These results imply that there was no correlation between the top and backup filter OC concentrations obtained in this pilot study.

Since no correlation was observed between the top and backup filter in this pilot study, an analysis was performed on the media blank filters (n=20) obtained from former sampling campaigns and reported in the larger study (Evans, 2015). In the Evans (2015) study, the top filter only was analyzed for elemental & organic carbon, and in addition, 10% field blanks were submitted. As noted in section 3.0, filters can be a source of organic interference and thus samples should be corrected based on the OC concentration found on media blanks.

The OC concentrations for media field blanks for the four sampling campaigns, in addition to field blanks submitted through this pilot study, are reported in Table IV. The mean OC concentration for all media field blanks was 17.8 µg/sample. This mean OC concentration of 17.8 µg/sample was subtracted from the backup filter (filter 2) results reported in this pilot study. The blank corrected sample results are reported in Table V. A regression analysis was performed on the media filter blank corrected data to determine if there was a correlation between OC concentrations observed on the top and backup filters. As illustrated in Figure 4, there was no

correlation (R^2= -0.069) (P=0.000) observed. As a result, there was no correlation between OC concentration collected on the top filter and backup filter when considering either original data or media blank corrected data. This suggests there is no correlated contribution of OC from Filter #1 to Filter #2. Thus, the blank correction for all data was a simple subtraction of the average OC mass (17.8 µg/sample) contained on submitted blanks over all field campaigns, including the pilot study.

On average, the media blanks comprised 69-81 percent of the OC measured on the top and backup filters, respectively. This implies that the filter itself contributes substantially to the measured OC concentration. The NIOSH Manual of Analytical Methods for Monitoring of Diesel Particulate gives artifacts of absorbed OC and how traditional blanks collect vapor passively, while the samples collect it actively (while sampling). The vapor adsorbed on the backup filter more closely represents that absorbed on the sample filter because both are collected actively. These results have been attributed to depletion of the vapor concentration by the top filter, which represents a lower concentration than the bottom filter (Birch, 2003). Considering this pilot study, 64.7% (11 of 17) of the samples revealed higher OC concentrations on the top filter than the backup filter. This means that our pilot study follows the NIOSH Analytical Methods relatively well in explaining that the organic fraction on particulate matter is contributing more (in most cases) to the overall OC measured than the vapor. This data implies that the OC contribution was most frequently associated with DPM than the vapor phase OC constituents.

Table II: 17 Pilot Study Organic Carbon Sample Results for Top and Backup Filters

ID	Analyte	Filter #1 Results	Filter #2 Results	Units
032715A01	OC	36	22	µg/sample
032715A02	OC	27	20	µg/sample
032715A03	OC	30	21	µg/sample
032715A04	OC	36	19	µg/sample
032715A05	OC	25	25	µg/sample
032715A06	OC	22	21	µg/sample
032715A08	OC	22	23	µg/sample
032715A09	OC	21	20	µg/sample
032715A010	OC	21	21	µg/sample
032715A011	OC	25	29	µg/sample
032715A012	OC	24	24	µg/sample
032715A013	OC	21	19	µg/sample
032715A014	OC	25	19	µg/sample
032715A015	OC	25	19	µg/sample
032715A016	OC	26	20	µg/sample
032715P01	OC	24	20	µg/sample
032715A01	OC	25	32	µg/sample
		25.6	22.0	
		Mean		

Table III: 17 Pilot Study Organic Carbon Sample Results for Top and Backup Filters

ID	Analyte	Filter #1 Results	Filter #2 Results	Units
032715A01	OC	64.17	39.22	µg/m^3
032715A02	OC	46.15	34.19	µg/m^3
032715A03	OC	50.42	35.29	µg/m^3
032715A04	OC	61.75	32.59	µg/m^3
032715A05	OC	41.32	41.32	µg/m^3
032715A06	OC	38.87	37.10	µg/m^3
032715A08	OC	36.73	38.40	µg/m^3
032715A09	OC	38.25	36.43	µg/m^3
032715A010	OC	38.74	38.74	µg/m^3
032715A011	OC	43.63	50.61	µg/m^3
032715A012	OC	42.63	42.63	µg/m^3
032715A013	OC	37.43	33.87	µg/m^3
032715A014	OC	44.33	33.69	µg/m^3
032715A015	OC	41.88	31.83	µg/m^3
032715A016	OC	46.18	35.52	µg/m^3
032715P01	OC	30.97	25.97	µg/m^3
032715A01	OC	26.77	34.26	µg/m^3
		42.95	36.57	
		Mean		

Table IV: Campaign Blanks Along with Pilot Study Blanks Analyzed to Develop a Blanks Correction Concentration

OC – Blanks (µg/sample)	
Blanks Campaign 1	**18**
	28
	18
	14
	20
Blanks Campaign 2	**22**
	18
	38
	24
	23
Blanks Campaign 3	**16**
	12
	13
	10
	11
Blanks Campaign 4	**11**
	15
	11
	11
	13
Blanks Pilot Study 5	**23**
	22
	19
Mean	**17.8**
Median	**18.0**
SD	**6.6**
95% CI = mean ±	**2.7**
Note: BC (Blank correction) = 17.8 µg/sample OC_{F1}	

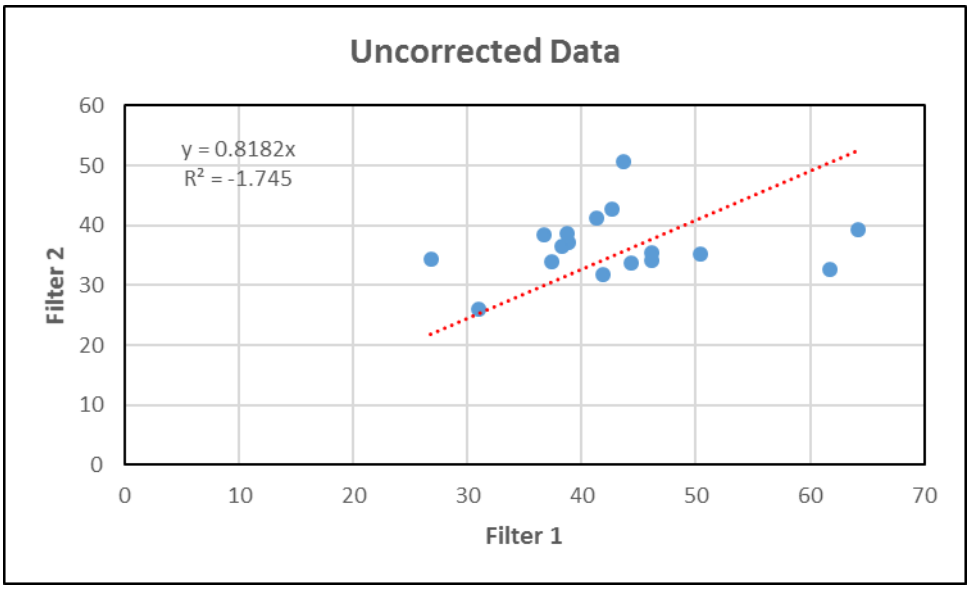

Figure 3: Original Uncorrected Pilot Study Sampling Results

Table V: 17 Pilot Study Sample Results Corrected

Filter #1 Result	Filter #2 Result
36	4.2
27	2.2
30	3.2
36	1.2
25	7.2
22	3.2
22	5.2
21	2.2
21	3.2
25	11.2
24	6.2
21	1.2
25	1.2
25	1.2
26	2.2
24	2.2
25	14.2
25.6	4.2
Mean	

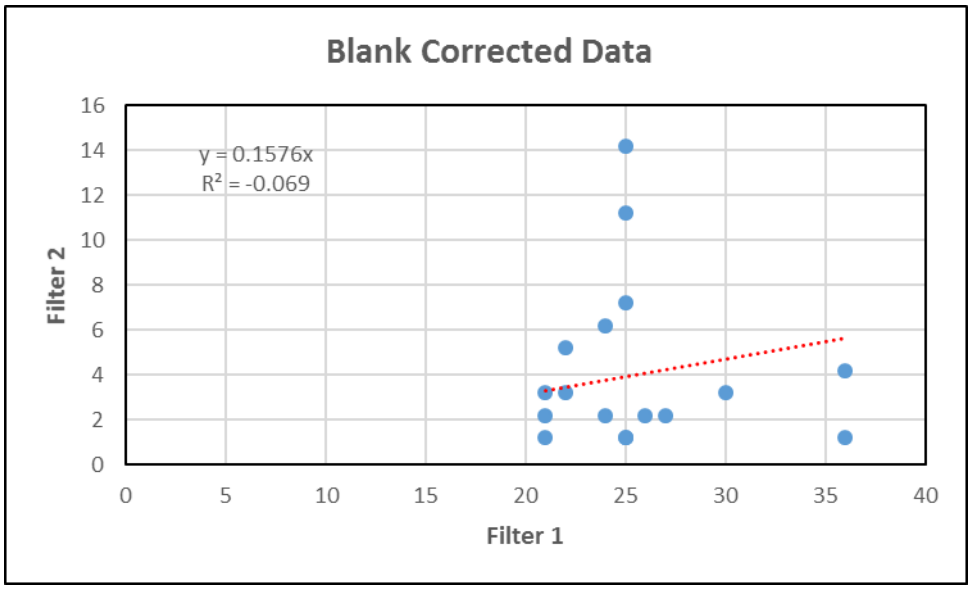

Figure 4:Corrected Pilot Study Sampling Results

6.0 Conclusion

As our knowledge of the health effects related to diesel exhaust exposure has expanded over the past several decades, techniques to monitor miners' exposures have also experienced significant revision. Initially, EC was considered as the surrogate for measuring DPM as it made up the majority of the particulate mass and the main source of the EC coming from DE. The next technique involved carbon analysis in which the elemental carbon core as well as organic constituents were considered. The latest sampling methodology considers carbon analysis (EC + OC) of DPM, as well as the vapor phase OC constituents. This method is complicated due to recognized organic interferences as mentioned previously. It is however, a more specific way that can be used to correct for adsorbed vapor as it can provide an improved estimate of the adsorbed OC.

This pilot study revealed that OC concentrations on the tandem quartz filters, specifically the backup filter, contained lower OC concentrations than the top filter. The analysis showed there was no correlation between OC concentration collected on the top filter and backup filter when considering either original data or blank corrected data. This suggests there is no correlated contribution of OC from the top filter to the backup filter, which indicated that OC collected on the backup filter are not gas phase OC vapors from the active sampling but from the quartz filters themselves.

The media blank is an important factor in the sampling of DE in that the filter allows for a more accurate concentration of DPM and therefore OC. With the media blank being a source of OC itself, this would change the EC/TC ratio. The ratio would rise due to the increase of OC from the media blank. Media blanks underestimate the adsorbed OC, causing overestimation of the true particulate OC (TC) concentration. The lower the OC, the greater the effect of adsorbed

vapor on the particulate OC measurement. If EC is also low, the same holds true for the TC result. Thus, when carbon concentrations are low, correction for adsorbed OC is important for accurate measurement of particulate OC and TC concentrations.

6.1 Recommendations for Future Research

Based on the results of this study, and the results from the larger study, a future recommendation would be to have all backup filters analyzed when sent in for analysis. This would improve the accuracy of the sample concentrations and used to correct for absorbed vapors. Another recommendation would be to have additional sampling according the MSHA, where additional samples are put upstream of impending interferences. One major limitation in this study is having a short number of additional samples in the pilot study. Having more samples broadens the range of possible data and forms a better picture for analysis.

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Appendix A: NIOSH 5040 Analytical #1

ELEMENTAL CARBON (DIESEL PARTICULATE) 5040

C AW: 12.01 CAS: none RTECS: none

METHOD: 5040: Issue 3 (Interim) **EVALUATION: FULL** **Issue 1: 15 May 1996**
Issue 3: 30 September 1999 (Interim)

OSHA : no REL
NIOSH: no PEL
ACGIH: see APPENDIX A

PROPERTIES: nonvolatile solid; MP >350 • C

SYNONYMS (related terms): soot, black carbon, diesel emissions, diesel exhaust particles, diesel particulate matter

SAMPLING

SAMPLER: FILTER (quartz fiber, 37-mm; size-selective sampler may be required, see APPENDIX B)

FLOW RATE: 2 to 4 L/min (see APPENDIX B)

VOL-MIN: 142 L @ 40 µg/m^3
-MAX: 19 m^3 (for filter load of ~ 90 µg/cm^2)

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 23 to 240 µg/m^3 (see EVALUATION OF METHOD)

BIAS: none (see EVALUATION OF METHOD)

OVERALL PRECISION ($\hat{S}_{rT}$): 0.085 at 23 µg/m^3 (see EVALUATION OF METHOD)

ACCURACY: ± 16.7% at 23 µg/m^3 (see EVALUATION OF METHOD)

MEASUREMENT

TECHNIQUE: EVOLVED GAS ANALYSIS (EGA) by thermal-optical analyzer

ANALYTE: elemental carbon (EC)

FILTER PUNCH SIZE: 1.5 cm^2 (see APPENDIX C)

CALIBRATION: methane injection [1]

RANGE: 1 to 105 µg per filter portion (see EVALUATION OF METHOD)

ESTIMATED LOD: 0.3 µg per filter portion

PRECISION ($\hat{S}_r$): 0.19 @ 1 µg C, 0.01 @ 10 to 72 µg C

APPLICABILITY: The working range is approximately 6 to 630 µg/m^3, with an LOD of ~ 2 µg/m^3 for a 960-L air sample collected on a 37-mm filter with a 1.5 cm^2 punch from the sample filter. If a lower LOD is desired, a larger sample volume and/or 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.4 µg/m^3). The split between organic-based carbon (OC) and EC may be inaccurate if the sample transmittance is too low. The EC loading at which this occurs depends on laser intensity. In general, the OC-EC split may be inaccurate when EC loadings are above 20 µg/cm^2 of filter. High loadings can give low (and variable) EC results because the transmittance remains low and relatively constant until some of the EC is oxidized from the filter. The split should be reassigned (prior to EC peak) in such cases [1]. An upper EC limit of 800 µg/m^3 (90 µg/cm^2) can be determined.

INTERFERENCES: As defined by the thermal-optical method, EC is the carbon determined during the second stage of the analysis (after pyrolysis correction). If the sample contains no pyrolyzable material, all the carbon evolved during this stage is considered elemental. Cigarette smoke and carbonates ordinarily do not interfere, but if heavy loadings of carbonate are anticipated, a cyclone should be used (see APPENDIX B). For measurement of diesel-source EC in coal mines, an impactor with submicrometer cutpoint [2,3] must be used to minimize collection of coal dust.

OTHER METHODS: Other methods for determination of EC and OC have been described in the literature [4], but alternative instrumentation is currently not commercially available.

REAGENTS:

1. Aqueous organic-based carbon (OC) solutions (e.g., sucrose), 0.1 to 3 mg C per mL solution (ensure range brackets that for samples).
2. Helium, prepurified.
3. Hydrogen, purified.
4. Oxygen (10%) in helium, premixed, purified.
5. Methane (5%) in helium, premixed, purified.

EQUIPMENT:

1. Sampler: Quartz-fiber filter, precleaned (Clean in low temperature asher 2 to 3 h, or muffle furnace for 1 to 2 h at ~ 800 •C), 37-mm, in a 3-piece, 37-mm, cassette with support (stainless steel screen or cellulose pad). See also alternative samplers (APPENDIX B).
   NOTE: Cellulose supports give higher OC blanks than stainless.
2. Personal sampling pump, 2 to 4 L/min, with flexible tubing.
3. Thermal-optical analyzer (see APPENDIX C) or other analyzer capable of EC speciation.
4. Punch for removal of 1.5 cm^2 rectangular portion of filter.
   NOTE: Smaller portion may be taken (e.g., with cork borer), but portion • 0.5 cm^2 with diameter or width • 1 cm is recommended.
5. Syringe, 10-µL.
6. Aluminum foil.
7. Needle (for lifting filter punch portion).

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Open-faced cassettes give even deposits over the entire flow-rate range specified, but are not practical in some workplaces (e.g., mining). Alternative samplers also can be used (see APPENDIX B) provided that an even deposit of diesel particulate results. An even deposit is necessary because the sample portion analyzed must be representative of the entire deposit. If the deposit is not homogeneous, the entire sample must be analyzed.
2. Attach sampler outlet to personal sampling pump with flexible tubing. Remove top piece of cassette, unless sampling environment dictates otherwise (i.e., closed-face or other type sampler is required).
3. Sample at an accurately known flow rate (see APPENDIX B).
4. After sampling, replace top piece of cassette, if removed, and pack securely for shipment to laboratory.

SAMPLE PREPARATION:

5. Place sample filter on a freshly cleaned aluminum foil surface. Punch out a representative portion of the filter. Take care not to disturb deposited material and avoid hand contact with sample. A needle inserted at an angle is useful for removal of the filter portion from the punch body.

CALIBRATION AND QUALITY CONTROL:

6. Analyze at least one replicate sample. For sets of up to 50 samples, replicate 10% of the samples. For sets over 50 samples, replicate 5% of the samples. If a particular filter deposit appears uneven, take a duplicate portion (step 5) for analysis to check evenness of deposition.
   NOTE: Precision of replicate analyses of a filter is usually better than 5% (1 to 3% is typical).
7. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
   a. With 10-µL (or other) syringe, apply an aliquot of OC standard solution directly to filter portion taken

(step 5) from a precleaned filter. For best results, the precleaned filter punch should be cleaned again in the sample oven prior to application.

NOTE: With small aliquots (e.g., • 10 µL), disperse standard solution over one end of filter portion to ensure standard is in laser beam. To prevent possible solution loss to surface, hold the portion off the surface. Larger volumes can easily penetrate to the underside of the filter portion.

b. Allow water to evaporate and analyze spikes with samples and blanks (steps 9 and 10).

NOTE: A decrease in filter transmittance during the first temperature step of the analysis indicates water loss. Allow portions to dry longer if this occurs.

8. Determine instrument blank (results of analysis with freshly cleaned filter portion) for each sample set.

MEASUREMENT:

9. Set analyzer according to manufacturer's recommendations (see APPENDIX C). Place sample portion into sample oven.

NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require a longer period and higher temperature during the 2nd part of the analysis to ensure that all EC is removed (the EC peak should never merge with the calibration peak). Adjust time and temperature accordingly. A maximum temperature above 940 • C should not be required.

10. Determine EC (and OC) mass, µg. Analyzer results are reported in units µg/cm^2 of C. The reported values are based on a sample portion of 1.5 cm^2, which is the area of the punch provided by the manufacturer. If the portion area differs from this value, multiply the reported result by 1.5 and divide the product by the actual area of the portion analyzed to obtain correct result (i.e., reported result x 1.5/actual punch area = corrected result in µg/cm^2).

CALCULATIONS:

11. Multiply the reported (or area-corrected) EC result (µg/cm^2) by filter *deposit area*, cm^2, (typically 8.55 cm^2 for a 37-mm filter) to calculate total mass, µg, of EC on each filter sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b).

12. Calculate EC concentration (C_{EC}) in the air volume sampled, V (L):

$$C_{EC} \cdot \frac{W_{EC} \cdot W_b}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Diesel exhaust is a chemically complex mixture containing thousands of compounds; therefore, some measure of exposure must be selected (See APPENDIX A). Rationale for selection of EC has been discussed elsewhere [1].

Because a suitable reference material is not available for determining the organic and elemental carbon content of a complex carbonaceous aerosol, only the accuracy of the method in the determination of total carbon (TC) could be examined. No discernable differences in the responses of five different organic compounds were noted. Linear regression of the data (43 analyses total) for all five compounds gave a slope and correlation coefficient (*r*) near unity [slope = 0.99 (± 0.01), r^2 = 0.999, n = 43]. Based on results for individual compounds, reported carbon values are expected to be from 98 to 100% of the actual amount present. In addition to the OC standards, eight different carbonaceous materials were analyzed by the thermal-optical method and the results were in good agreement with those reported by two other independent laboratories. These findings [1] indicate that instrumental response appears to be compound- and matrix-independent (i.e., carbon in a sample is accurately quantified irrespective of compound and matrix type). Such a response is required for accurate determination of carbon in samples of unknown composition.

To calculate the estimated limit of detection (LOD) of the method (i.e.,• 0.24 µg C, or 0.15 µg/cm^2),

ethylenediaminetetraacetic acid (EDTA) calibration standards covering a range from 0.23 to 2.82 µg C (or from 0.15 to 1.83 µg C per cm^2 of filter) were analyzed. Results of linear regression of the low-level calibration data (i.e., µg C reported vs. actual) were then used to calculate the LOD as 3 s_y/**m** (where s_y is the standard error of the regression and **m** is the slope of the regression line). The calculated LOD shows good agreement with that estimated as LOD = $3s_{blank}$, which gives a value of • 0.3 µg C. The mean (n = 40) *instrumental* blank was 0.03 (± 0.1) µg C.

Like all OC-EC methods, the thermal-optical method is an *operational* method in the sense that the analytical procedure itself defines the analyte. Of the possible approaches for OC-EC analysis, this particular technique was investigated because it offers greater selectivity (pyrolysis correction) and flexibility (automated analysis, programmable parameter files) than previously used methods. The method is considered unbiased (i.e., it is the reference method), and the overall precision reflects method accuracy. The S_r of the mean EC concentration found with fourteen samplers (two each of seven types) for collection of diesel exhaust in a loading dock area where a diesel truck was operating was 5.6% [1]. Although pumps were used for sample collection, a 5% pump error was added in the calculation of the overall precision of the method because of the relatively small sample taken (0.5 h, 60 L). Based on the 95% confidence limit (19%; 13 degrees of freedom, n =14) on the accuracy, results of this experiment indicate that the NIOSH accuracy criterion [5] is fulfilled. The amount of EC collected (240 µg per sample) would be equivalent to sampling an EC level of 250 $µg/m^3$ for 8 h at 2 L/min.

In addition to this initial field test, laboratory-generated diesel particulate samples were analyzed. A dilution tunnel equipped with a dynamometer was used for generation of the samples. Four EC concentrations ranging from 23 to 240 $µg/m^3$ (EC loadings from 2.7 $µg/cm^2$ to 27 $µg/cm^2$) were generated. Again, analytical results indicate that the method meets the NIOSH accuracy criterion. The variance was roughly proportional to mean concentration; therefore, the S_r decreased with increasing concentration. The accuracy was calculated accordingly. The pointwise accuracy was ± 16.7% at the lowest loading (2.7 $µg/cm^2$) and the overall precision (• $_{rT}$) was 0.085.

When the thermal-optical method was evaluated [1] only one instrument existed. More recently, a private laboratory [6] built additional instruments (14 total:10 in the U.S., 1 in Canada, 1 in Australia, 1 in Hong Kong, 1 in Belgium). An interlaboratory comparison [7] was undertaken. Nine laboratories participated in the study, including four in Europe that employ an alternative thermal technique based on coulometric detection of CO_2. For the comparison, carbonaceous aerosols were collected on quartz-fiber filters (8" x 10") and portions of the filters were distributed to the participating laboratories for analysis in triplicate. Prior to distribution of the filter portions, multiple analyses were performed across all filters to ensure matched sample sets. Two aqueous solutions containing OC standards also were included in the sample sets. These standards provided a check on the accuracy of the TC data as well as a check on the pyrolysis correction feature of the thermal-optical method (both standards char during analysis).

As seen in a previous study [4], good agreement (within 15%) between TC values reported by all laboratories was obtained. In the analysis of samples containing diesel particulate, reasonable agreement was seen between the EC results obtained by each method (variability of the thermal-optical method was about 8% and variability for the coulometric method ranged from 9 to 23%). However, the EC content found by the two methods differed significantly. Given the operational nature of such methods, significant between-method variability was expected. Significant differences in the OC-EC results obtained by different methods also were reported previously [4].

With all filter samples, coulometric results were positively biased *relative* to thermal-optical results. In addition, the coulometric method gave a true positive bias in the analysis of the OC standard solutions. About 52% and 70% of the carbon found in two aqueous solutions (sucrose and EDTA, respectively) were quantified as elemental, while EC contents of about 1% and 0.1% (respectively) were found by the thermal-optical method. The positive bias in the results for OC standards is attributed largely to inadequate removal of all OC during the first part of the analysis (maximum temperature ~ 550 • C); lack of correction for pyrolysis (char) also is a factor. Because no increase in transmittance was seen during the first stage (helium only) of thermal-optical analysis, use of a higher maximum temperature during this stage did not appear to cause loss of light-absorbing carbon. This implies that the EC results (filter samples) obtained with the coulometric method are positively biased. Elevating the maximum temperature of the thermal program

gave better agreement with the thermal-optical method.

When a diesel particulate sample contains no other type of carbonaceous particulate and the OC fraction is essentially removed below about 500 •C, better agreement between methods is expected. Good correlation [8] was seen between results of thermal-optical and coulometric methods in the analysis of 22 samples collected in a simulated mining environment. The two methods gave essentially equivalent results for TC, with the coulometric method finding about 6% less than the thermal-optical. The small differences between TC results obtained by the two methods, even after shipping and handling by three laboratories, indicates TC measurement is accurate. Based on a previous comparison [7], this result was expected. Differences in the EC and OC results were again seen, but were much smaller than those obtained previously [7]. Mean EC fractions (i.e., EC/TC) of 0.53 and 0.46 were obtained by the coulometric and thermal-optical methods, respectively. The relatively minor difference is attributed to the different thermal programs used. Neither charring nor loss of a significant amount of carbon above 500 •C (and up to 850 •C in helium) were noted in the thermograms (i.e., output signal of thermal-optical instrument), which was not the case in the previous comparison [7].

The thermal-optical method is applicable to nonvolatile, carbon-containing species only. The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection. A complete discussion on the evaluation of this method for monitoring occupational exposures to particulate diesel exhaust in general industry can be found in the literature [1]. Different sampling requirements usually are required in the mining industry (see APPENDIX B).

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APPENDIX A. GENERAL

Diesel exhaust has been classified by IARC as a probable human carcinogen [9]. NIOSH has recommended "...that whole diesel exhaust be regarded as a potential occupational carcinogen..." and that workers' exposures be reduced [10,11]. Because diesel exhaust is a chemically complex mixture containing thousands of compounds, some measure of exposure must be selected. Rationale for selection of EC has been provided elsewhere [1].

The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed a TWA of 0.15 mg/m^3 for diesel particulate [12]. The TLV is expressed in terms of submicrometer particulate matter, which includes the solid carbon core of diesel particulate and particle-adsorbed components. Other submicrometer aerosols will be collected as well (see APPENDIX B).

In general, three methods have been used for monitoring exposures to DPM: submicrometer particulate mass (gravimetric), respirable combustible dust (RCD; also gravimetric), and EC. These methods are mentioned in the draft TLV documentation, but the latter two (RCD and EC) do not give a direct measure of the stated analyte (submicrometer particulate). The RCD method targets the *respirable* fraction, not just submicrometer, and it is not a specific measure of DPM. The EC method is highly selective for diesel particulate, but the EC fraction of diesel particulate is variable, so a single constant cannot be used for extrapolation to submicrometer mass. Use of TC as a measure of diesel particulate has been considered because there is less variability in the carbon content of DPM. Although the TC fraction of DPM is relatively constant (typically 85% or more), other OC sources can interfere with the determination of the diesel-source carbon. A discussion of analytical methods is provided in the next appendix (APPENDIX B).

APPENDIX B. GUIDELINES ON METHODS

Gravimetric methods for DPM target submicrometer aerosol because diesel particulate is largely submicrometer and interference of larger dusts is minimized; however, if other submicrometer aerosols are present (e.g., cigarette smoke or other combustion aerosols, condensation aerosols) they will interfere in the gravimetric determination of diesel particulate. With personal monitoring, this approach is limited to relatively high concentrations because of poor sensitivity. This applies to the traditional gravimetric approach, as well as a "respirable combustible dust" (RCD) method used in the Canadian mining industry. RCD involves gravimetric determination of the combustible material on a silver membrane (or quartz-fiber) filter. The filter is weighed pre- and post-combustion, and the difference is considered RCD. This method is subject to interferences from non-diesel, respirable combustible matter and other potential problems (e.g., hygroscopic materials, negative bias with metal oxide formation).
A suitable impactor for personal monitoring of submicrometer particulate mass concentrations is not commercially available. A specialized impactor with a 0.8-µm cutpoint has been applied for the gravimetric determination of diesel particulate in underground coal mines. The cutpoint was based on bimodal particle size distributions found in dieselized underground coal mines, which is the only environment where the impactor must be used. Although it excludes most of the coal dust while collecting most of the diesel particulate, some sub-0.8-µm coal dust is collected. To determine the potential contribution of sub-0.8-µm, coal-source EC, laboratory studies and surveys of underground coal mines were conducted. When sampling a laboratory-generated, respirable coal dust concentration of 1.5 mg/m^3, a submicrometer TC concentration of about 54 $\mu g/m^3$ was found, but the corresponding EC concentration was only about 8 $\mu g/m^3$. Even when

the concentration of respirable coal dust was as high as 5 mg/m^3, which is more than 2.5 times the US compliance level, only a relatively low EC concentration was seen (EC = 30 µg/m^3; TC concentration = 156 µg/m^3). These results are in good agreement with those found in preliminary field studies. Only low levels (• 15 µg/m^3) of EC were found in non-dieselized underground coal mines when a submicrometer cutpoint was used [13], indicating that the thermal-optical method could be applied in coal mines with only a minor contribution of coal-source EC if an impactor with appropriate design specifications is used. It is important to emphasize that the cutpoint of the prototype impactor was based on particle size distributions found in *coal mines.* Size distributions (of both diesel and non-diesel particles) found in coal mines may differ from those found in metal/nonmetal mines. With respect to diesel particles in particular, distributions might differ because water scrubbers are used in coal mines and these may affect particle size (e.g., by trapping larger respirable particles). If larger (e.g., 1 to 2 µm) diameter particles are present, these will be excluded if an impactor with a submicrometer cutpoint is used.

Unlike submicrometer particulate, RCD and TC, EC is a specific marker of occupational exposure to diesel particulate, so use of an impactor is unnecessary (except in coal mines). In some workplaces, a preclassifier (e.g., cyclone) should be used with a 37-mm cassette (or alternative cassette giving an even deposit) as a "sample cleanup" step (e.g., to reduce loadings of inorganic dusts), but a submicrometer cut is not necessary. Although uneven deposition of larger particles (i.e., non-diesel) can occur, an even deposit of DPM is ordinarily found. If an uneven deposit should form, the entire filter must be analyzed (in portions) to quantify the total OC and EC.

Different samplers can be expected to give equivalent results for EC because diesel exhaust is a combustion aerosol (particle diameters generally • 1 µm). As such, particles will be evenly deposited on the filter and collected with the same efficiency (near 100%). To confirm this assumption, seven different sampler types (open-faced, 25-mm and 37-mm cassettes; 298 personal cascade impactor (7 stages, 0.9 µm cutpoint); 4 prototype impactors) were used to collect diesel aerosol at the loading dock of an express mail facility. The S_r of the mean EC concentration found was only 5.6% [1]. Higher variability (about 12%) was seen in the OC result, which is expected when using filters to collect aerosol containing volatile and semivolatile components. Similar results were obtained when collecting samples in an underground molybdenum mine, where non-diesel particulate also was present. Five different sampler types were used (closed-face, 25-mm and 37-mm cassettes; 298 (7 stages, 0.9 µm cutpoint); cyclone with filter; in-house impactor). The S_r of the mean EC concentration found (297 µg/m^3) was only 7%. An even deposition of EC was obtained with all five sampler types, even when the deposit of other mine particulate was visually heavier in the center of the filter (e.g., with the closed-face 37-mm cassette). These results indicate that any of a variety of samplers can be used in some environments. In trona and limestone mines, a cyclone should be used to reduce the amount of carbonate collected (non-respirable-sized particles in particular). Specificity of the OC (and TC) determination can be further improved by removal of carbonate through acidification of the sample portion (see APPENDIX C). In the case of carbonates and other types of carbonaceous dusts, an impactor can improve the selectivity of the OC (and TC) measurement, but it could exclude a portion of the diesel particles. Some OC interferences cannot be excluded on the basis of size (e.g., condensation aerosols, fumes, wood and cigarette smokes).

APPENDIX C. THERMAL-OPTICAL ANALYZER DESIGN AND OPERATION

In the thermal-optical analysis of carbonaceous aerosols, speciation of organic and elemental carbon is accomplished through temperature and atmosphere control, and by continuous monitoring of filter transmittance. A schematic of the instrument is given below (Figure 1). The instrument is a modified version of a design previously described in the literature [14]. An optical feature corrects for pyrolytically generated elemental carbon (EC), or "char," which is formed during the analysis of some materials (e.g., cigarette and wood smokes, pollen). Laser light passed through the filter allows continuous monitoring of filter transmittance. Because temperatures in excess of 850 • C are employed during the analysis, quartz-fiber filters are required. A punch from the sample filter is taken for analysis, and organic and elemental carbon are reported in terms of µg per cm^2 of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. In this approach, a homogeneous sample deposit is assumed. Just prior to the end of the analysis (i.e., after EC is evolved), calibration is achieved through injection of a known volume of methane into the sample oven.

Thermal-optical analysis proceeds essentially in two stages. In the first, organic and carbonate (if present) carbon are evolved in a helium atmosphere as the temperature is stepped to about 850 •C (750 •C if EC loss is evident). The evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2, then reduced to CH_4 in a Ni/firebrick methanator. CH_4 is quantified by an FID. In the second stage, the sample oven temperature is reduced, an oxygen-helium mix is introduced, and the temperature is stepped (to about 940 •C). As oxygen enters the oven, pyrolytically generated carbon (PC) is oxidized and a concurrent increase in filter transmittance occurs (see Figure 2). The point at which the filter transmittance reaches its initial value is defined as the "split" between OC and EC. Carbon evolved prior to the split is considered OC (including carbonate), and carbon volatilized after the split is considered elemental (EC).

The presence of carbonate is verified by exposing a second punch from the filter to HCl vapor prior to analysis. A dessicator containing concentrated HCl (added to dessicator or a petri dish placed at the bottom of it) can be used to acidify the punches. The dessicator, or alternative vessel, should be used in a well-ventilated hood. Place punches on the dessicator tray, put tray in dessicator and cover with lid. A wetted pH indicator stick can be used to check acidity. A wetted indicator stick inserted between the dessicator lid and base should give a pH near 2. Expose punches to vapor for about 1 h (large particles can require more time). After acidification, remove the tray and place it on a clean surface inside a hood. Allow the residual acid on the punches to volatilize in hood for at least one hour before analyzing. When the acidified sample is analyzed, a much-reduced (or absent) peak is indicative of carbonate in the original sample. The difference between the TC results obtained for the two punches (i.e., before and after acidification) gives an estimate of carbonate-source carbon (presuming it is evenly deposited on the filter). The acidified sample results provide a better measure of the diesel-source OC (and TC) if the sample contains carbonates. Acid treatment may change the appearance of the carbon profile, but the EC result itself should not be affected significantly. More recent versions of the calculation software allow estimation of carbonate carbon through integration, but this applies only in cases where the carbonate can be removed as a single peak during the fourth temperature step (e.g., calcium carbonate). If the integration feature is used, always verify that the carbonate of interest is removed as a single, unique peak.

Currently, three laboratories [6,15,16] perform thermal-optical analysis on a commercial basis. The commercial availability of the instrument is limited to a single supplier [6] and its design continues to be improved. An evaluation of a newer design is planned.

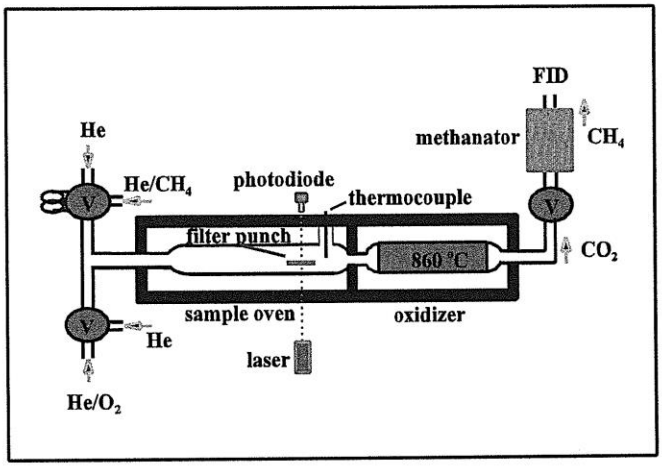

Figure 1. Schematic of Thermal-Optical Instrument (V=valve)

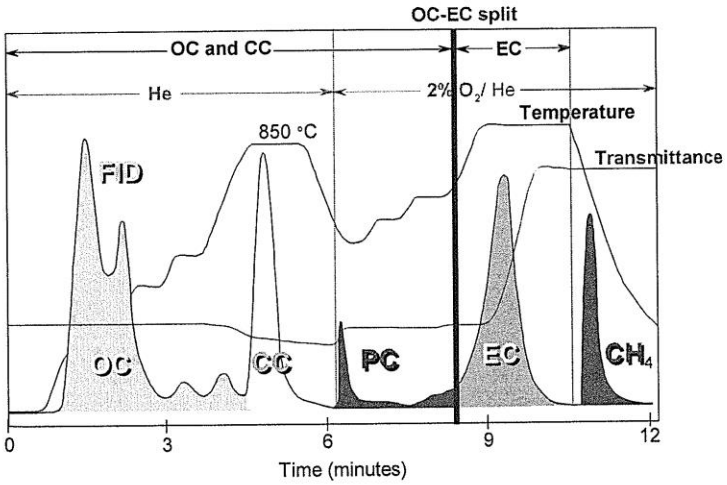

Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.

Appendix B: NIOSH 5040 Analytical #2

DIESEL PARTICULATE MATTER (as Elemental Carbon) 5040

C AW: 12.01 CAS: none RTECS: none

METHOD: 5040: Issue 3 **EVALUATION: FULL** **Issue 1: 15 May 1996**
Issue 3: 15 March 2003

OSHA: no PEL
NIOSH: no REL
ACGIH: 20 µg/m³ as elemental carbon (proposed [1])

PROPERTIES: nonvolatile solid

SYNONYMS (related terms): diesel particulate matter, diesel exhaust, diesel soot, diesel emissions

SAMPLING

SAMPLER:	FILTER: quartz-fiber, 37-mm; size-selective sampler may be required [2].
FLOW RATE:	2 to 4 L/min (typical)
VOL-MIN:	142 L @ 40 µg/m³
-MAX:	19 m³ (for filter load of ~ 90 µg/cm²)
SHIPMENT:	Routine
SAMPLE STABILITY:	Stable
BLANKS:	2 to 10 field blanks per set

ACCURACY

RANGE STUDIED:	23 to 240 µg/m³ (See also ref. [2].)
BIAS:	None (See also ref. [2].)
OVERALL PRECISION ($\hat{S}_{rT}$):	0.085 at 23 µg/m³ (See also ref. [2].)
ACCURACY:	± 16.7% at 23 µg/m³ (See also ref. [2].)

MEASUREMENT

TECHNIQUE:	Thermal-optical analysis; flame ionization detector (FID)
ANALYTE:	Elemental carbon (EC). Total carbon is determined, but an EC exposure marker was proposed. See [2] for details.
FILTER PUNCH SIZE:	1.5 cm² (or other [2])
CALIBRATION:	Methane injection
RANGE:	1 to 105 µg per filter portion (See also [2].)
ESTIMATED LOD:	0.3 µg per filter portion
PRECISION ($\hat{S}_r$):	0.19 @ 1 µg C, 0.01 @ 10 to 72 µg C

APPLICABILITY: The working range is approximately 6 to 630 µg/m³, with an LOD of ~ 2 µg/m³ for a 960-L air sample collected on a 37-mm filter with a 1.5 cm² punch from the sample filter. If a lower LOD is desired, a larger sample volume and/or 25-mm filter may be used (e.g., a 1920-L sample on 25-mm filter gives an LOD of 0.4 µg/m³). The split between organic carbon (OC) and EC may be inaccurate if the sample transmittance is too low. The EC loading at which this occurs depends on laser intensity. In general, the OC-EC split may be inaccurate when EC loadings are above 20 µg/cm². High loadings can give low (and variable) EC results because the transmittance remains low and relatively constant until some of the EC is oxidized. The split should be reassigned (prior to EC peak) in such cases [3]. An upper EC limit of 800 µg/m³ (90 µg/cm²) can be determined.

INTERFERENCES: Total carbon (as OC and EC) is determined by the method, but EC was recommended as a measure of workplace exposure because OC interferences may be present [2, 3]. Cigarette smoke and carbonates ordinarily do not interfere in the EC determination. Less than 1% of the carbon in cigarette smoke is elemental. If heavy loadings of carbonate are anticipated, a size-selective sampler (impactor and/or cyclone) should be used [2]. For measurement of diesel-source EC in coal mines, a cyclone and impactor with a submicrometer cutpoint are required to minimize collection of coal dust. A cyclone and/or impactor may be necessary in other workplaces if EC-containing dusts are present.

OTHER METHODS: Other methods for determination of EC and OC have been employed, but these are not equivalent to the method described herein. Information on other methods is summarized elsewhere [2].

REAGENTS:

1. Aqueous solutions of reagent grade (99+%) sucrose, 0.1 to 3 mg C per mL solution. Ensure filter spike loading range brackets that of samples.
2. Ultra pure H_20, Type I, or equivalent.
3. UHP helium (99.999%), scrubber also required for removal of oxygen.
4. Hydrogen, purified (99.995%), cylinder or hydrogen generator source.
5. Ultra Zero air (low hydrocarbon).
6. 10% oxygen in helium balance, both gases UHP, certified mix.
7. 5% methane in helium balance, both gases UHP, certified mix.

EQUIPMENT:

1. Sampler: Quartz-fiber filter, precleaned (in low temperature asher 2 to 3 h, or muffle furnace for 1 to 2 h at ~ 800 °C), 37-mm, in a 3-piece cassette with filter support (stainless steel screen, cellulose pad, or a second quartz filter). Alternative samplers may be required in dusty environments. See ref. [2] for details.
   NOTE 1: High purity, high efficiency, binder-free quartz-fiber filters must be used (e.g., Pall Gelman Sciences Pallflex Tissuequartz 2500QAT-UP. Precleaned filters are available from several laboratories. Filters also can be purchased and cleaned in-house. Filters should be cleaned in a muffle furnace operated at 800-900°C for 1-2 hours. Check (analyze) filters to ensure removal of OC contaminants. A shorter cleaning period may be effective. OC results immediately after cleaning should be below 0.1 $\mu g/cm^2$. OC vapors readily adsorb onto clean filters. Even when stored in closed containers, OC loadings may range from 0.5 $\mu g/cm^2$ after several weeks.
   NOTE 2: Cellulose supports give higher OC blanks than screens and quartz filters. Bottom quartz filters can be used to correct for adsorbed vapor; see ref. [2].
2. Personal sampling pump with flexible tubing.
3. Thermal-optical analyzer; see ref. [2].
4. Metal punch for removal of 1.5 cm^2 rectangular portion of filter.
   NOTE: A smaller portion (e.g., taken with cork borer) may be used, but the area must be large enough to accommodate the entire laser beam (i.e., beam should pass through the sample, not around it). The area of the portion must be accurately known, and the sample must be carefully positioned (the filter transmittance will decrease dramatically when the sample is properly aligned). A filter portion ≥ 0.5 cm^2 with diameter or width $\leq$ 1 cm is recommended.
5. Syringe, 10-µL.
6. Aluminum foil.
7. Needle (for lifting filter punch portion).
8. Forceps
9. Volumetric flasks, Class A.
10. Analytical balance.

SPECIAL PRECAUTIONS: Hydrogen is a flammable gas. Users must be familiar with the proper use of flammable and nonflammable gases, cylinders, and regulators. According to the instrument manufacturer, the instrument is a Class I Laser Product. This designation means there is no laser radiation exposure during normal operation. Weakly scattered laser light is visible during operation, but does not pose a hazard to the user. The internal laser source is a Class IIIb product, which poses a possible hazard to the eye if viewed directly or from a mirror-like surface (i.e., specular reflections). Class IIIb lasers normally do not produce a hazardous diffuse reflection. Repairs to the optical system, and other repairs requiring removal of the instrument housing, should be performed only by a qualified service technician.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
   NOTE: Both open- and closed-faced cassettes have been used. Both configurations generally give even deposits. At higher flow rates (e.g., 4 L/min), small spots occasionally have been observed in the center of the filters when closed-faced cassettes are used. This material likely consisted of impacted diesel agglomerates and/or non-diesel particulate matter. EC results for multiple portions of the filters were in good agreement, so the spots had little analytical impact. Other samplers also can be used (see ref. [2]) provided an even deposit of diesel particulate results. An even deposit is necessary because the sample portion analyzed must be representative of the entire deposit. If the deposit is not homogeneous, the entire sample must be analyzed. An impactor/cyclone may be needed in some cases. [2]
2. Attach sampler outlet to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate. Typical rates are 2-4 L/min (note: Lower flows (e.g., 1 L/min) have been used in mines to prevent overloading).
4. After sampling, replace top piece of cassette, if removed, and pack securely for shipment to laboratory.
   NOTE: Diesel particulate samples from occupational settings generally do not require refrigerated shipment unless there is potential for exposure to elevated temperatures (that is, well above collection temperature). Filter samples normally are stable under laboratory conditions. Some OC loss may occur over time if samples contain OC from other sources (for example, cigarette smoke). Sorption of OC vapor after sample collection has not occurred, even with samples having high (e.g., 80%) EC content.

SAMPLE PREPARATION:

5. Place sample filter on a freshly cleaned aluminum foil surface. Isopropyl alcohol or acetone can be used to clean the foil. Allow residual solvent to vaporize from the surface prior to use. Punch out a representative portion of the filter. Take care not to disturb deposited material and avoid hand contact with sample. A needle inserted at an angle is useful for removal of the filter portion from the punch body. Newer instruments have an externally mounted bracket to support the quartz sample holder while the previous sample is removed and a new one is loaded. Through a hole in the side of the standard punch, a needle can be used to push the filter portion from the punch onto the sample holder. Alternative approaches also can be used, depending on the user's preference, as long as contamination is avoided.

CALIBRATION AND QUALITY CONTROL:

6. Analyze at least one replicate sample. For sets of up to 50 samples, replicate 10% of the samples. For sets over 50 samples, replicate 5% of the samples. If a filter deposit appears uneven (this should not be the case if the cassette is sealed properly), take a second portion (step 5) for analysis to check evenness of deposition.
   NOTE: Precision of replicate analyses of a filter is usually better than 5% (1 to 3% is typical).

7. Analyze three quality control blind spikes and three analyst spikes to ensure that instrument calibration is in control. Prepare spike as follows:
   a. With 10-µL (or other) syringe, apply an aliquot of OC standard solution directly to filter portion taken (step 5) from a precleaned filter. For best results, the precleaned filter punch should be cleaned again in the sample oven prior to application of the aliquot.
      NOTE: With small aliquots (e.g., ≤ 10 µL), disperse standard solution over one end of filter portion to ensure standard is in laser beam. To prevent possible solution loss to surface, hold the portion off the surface. Larger volumes can easily penetrate to the underside of the filter portion.
   b. Allow water to evaporate and analyze spikes with samples and blanks (steps 9 and 10).
      NOTE: A pronounced decrease in filter transmittance during the *first* temperature step of the analysis indicates water loss. Allow portions to dry longer if this occurs. Spiked punches also can be dried in the oven, if desired. For quick drying, the 'clean oven' command on the menu can be selected and canceled after about 4 seconds. The time allowed may depend on instrument, but oven temperatures should be below 100 °C to avoid boiling the solution. This approach is convenient and prevents potential adsorption of organic vapors in laboratory air.
8. Determine instrument blank (results of analysis with freshly cleaned filter portion) for each sample set.

MEASUREMENT:

9. Adjust analyzer settings according to manufacturer's recommendations (see instrument operation manual and background information in ref. [2]). Place sample portion into sample oven.
   NOTE: Forms of carbon that are difficult to oxidize (e.g., graphite) may require a longer period and higher temperature during the oxidative mode to ensure that all EC is removed (the EC peak should never merge with the calibration peak). Adjust time and temperature accordingly. A maximum temperature above 940 °C should not be required.
10. Determine EC (and OC) mass, µg. Analyzer results are reported in units µg/cm^2 of C. The reported values are normally based on a sample portion of about 1.5 cm^2, which is the area of the standard punch provided by the manufacturer. If the portion area used differs from the value entered in the ocecpar.txt file, multiply the result by 1.5 (or value in ocecpar.txt file) and divide the product by the actual area analyzed to obtain the area-corrected result (i.e., reported result x 1.5/portion area = corrected result in µg/cm^2). This is most easily done in the data spreadsheet. Alternatively, the correct results will be obtained with the data calculation program if the portion area is entered in the parameter file (ocecpar.txt), but this approach is cumbersome when punches of different areas are used because correct results will not be obtained for all punch sizes.

CALCULATIONS:

11. Multiply the reported (or area-corrected) EC result (µg/cm^2) by filter *deposit area*, cm^2, (typically 8.5 cm^2 for a 37-mm filter) to calculate total mass, µg, of EC on each filter sample (W_{EC}). Do the same for the blanks and calculate the mass found in the average field blank (W_b). The mass of OC is calculated similarly, but the mean OC field blank may underestimate the amount of OC contributed by adsorbed vapor. A quartz filter placed beneath the sample filter can provide a better estimate of the adsorbed OC. [2]
12. Calculate the EC concentration (C_{EC}) in the air volume sampled, V (L):

$$C_{EC} = \frac{W_{EC} - W_b}{V}, mg / m^3$$

EVALUATION OF METHOD:

Details on the evaluation of this method are provided in a chapter of this NMAM Supplement. [2] The chapter includes a summary of interlaboratory comparison work conducted since the initial publication of the method. Background information and guidance on method use, including sampling requirements, also are provided. In general industry, 37-mm cassettes are normally suitable for air sampling, but there are exceptions. A cyclone in series with an impactor having a submicrometer cutpoint must be used in coal mines, and the Mine Safety and Health Administration (MSHA) has recommended use of a cyclone-impactor sampler in metal and nonmetal mines. [5] The impactor is commercially available [6]. A size-selective sampler (either impactor and/or cyclone) also may be required in other dusty environments [2], particularly if the dust is carbonaceous. If a sample contains carbonate, the carbonate carbon (CC) will be quantified as OC. A carbonate-subtracted result can be obtained through acidification of the sample portion or through separate integration of the carbonate peak [2] (*note: Trona and other compounds containing sodium can etch the quartz oven wall at elevated temperatures. Avoid spillage of these materials in the sample oven.*) These procedures are described in a Chapter of this Supplement. [2] The thermal-optical method is applicable to nonvolatile carbon species (i.e., particulate OC, CC and EC). The method is not appropriate for volatile or semivolatiles, which require sorbents for efficient collection.

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[1] ACGIH [2001]. Cincinnati, OH: American Conference of Environmental Industrial Hygienists. Diesel Exhaust (Particulate and Particulate Adsorbed Components), Draft TLV-TWA Document, 2001.
NOTE: Recently, diesel exhaust has been taken off the ACGIH Notice of Intended Changes list. See reference [2].
[2] NIOSH [2003]. Manual of Analytical Methods (NMAM). O'Connor PF, Schlecht, PC, Monitoring of Diesel Particulate Exhaust in the Workplace, *Chapter Q*, Third Supplement to NMAM, 4th Edition, NIOSH, Cincinnati, OH. DHHS (NIOSH) Publication No. 2003-154.
[3] Birch, ME, Cary, RA [1996]. Elemental Carbon-based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust Aerosol Sci Technol *25*:221-241.
[4] Birch, ME [1998]. Analysis of carbonaceous aerosols: interlaboratory comparison, Analyst, 123:851-857.
[5] Mine Safety and Health Administration (MSHA) [2001]. Department of Labor, 30 CFR Part 57, Diesel Particulate Matter Exposure of Underground Metal and Nonmetal Miners; Final Rule, Federal Register *Vol. 66*, No. 13, January 19.
[6] SKC, Eight Sixty Three Valley View Road, Eighty Four, PA 15330.

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SIGNATURE PAGE

This is to certify that the thesis prepared by Ryley Bosch entitled "Review of Sampling & Evaluation Techniques for Diesel Exhaust Particulate Matter in the Mining Industry and the Application of a Vapor Phase Organic Carbon Correction Factor" has been examined and approved for acceptance by the Department of Philosophical Musings, Montana Tech of The University of Montana, on this 29th day of December, 2015.

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