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Standard Test Method for Monitoring Diesel Particulate Exhaust in the Workplace¹

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1. Scope

1.1 This test method covers determination of organic and elemental carbon (*OC* and *EC*) in the particulate fraction of diesel engine exhaust, hereafter referred to as diesel particulate matter (*DPM*). Samples of workplace atmospheres are collected on quartz-fiber filters. The method also is suitable for other types of carbonaceous aerosols and has been widely applied to environmental monitoring. It is not appropriate for sampling volatile or semi-volatile components. These components require sorbents for efficient collection.

NOTE 1—Sample collection and handling procedures for environmental samples differ from occupational samples. This standard addresses occupational monitoring of *DPM* in workplaces where diesel-powered equipment is used.

1.2 The method is based on a thermal-optical technique (1, 2).² Speciation of *OC* and *EC* is achieved through temperature and atmosphere control, and an optical feature that corrects for sample charring (carbonization).

1.3 A portion of a 37-mm, quartz-fiber filter sample is analyzed. Results for the portion are used to calculate the total mass of *OC* and *EC* on the filter. The portion must be representative of the entire filter deposit. If the deposit is uneven, two or more representative portions should be analyzed for an average. Alternatively, the entire filter can be analyzed, in multiple portions, to determine the total mass. Open-faced cassettes give even deposits but may not be practical. At 2 L/min, closed-face cassettes generally give results equivalent to open-face cassettes if other dusts are absent. Higher flow rates may be employed, but closed-faced cassettes operated at higher flow rates (for example, 5 L/min) sometimes have uneven deposits due to particle impaction at the center of the filter. Other samplers may be required, depending on the sampling environment (2-5).

1.4 The calculated limit of detection (*LOD*) depends on the level of contamination of the media blanks (5). A *LOD* of

approximately 0.2- μg carbon per cm^2 of filter was estimated when analyzing a sucrose standard solution applied to filter portions cleaned immediately before analysis. *LODs* based on media blanks stored after cleaning are usually higher. *LODs* based on a set of media blanks analyzed over a six month period at a commercial laboratory were *OC* = 1.2 $\mu\text{g}/\text{cm}^2$, *EC* = 0.4 $\mu\text{g}/\text{cm}^2$, and *TC* = 1.3 $\mu\text{g}/\text{cm}^2$, where *TC* refers to total carbon (*TC* = *OC* + *EC*). In practice, the *LOD* estimate provided by a laboratory is based on results for a set of media blanks submitted with the samples. To reduce blank variability (due to lack of loading), a manual *OC-EC* split is assigned at the time when oxygen is introduced. With manual splits, the *SD* for media blanks is typically about 0.02–0.03 $\mu\text{g EC}/\text{cm}^2$, giving *LODs* ($3 \times \text{SD blank}$) from about 0.06–0.09 $\mu\text{g EC}/\text{cm}^2$. The corresponding air concentration depends on the deposit area (filter size) and air volume.

1.5 *OC-EC* methods are operational, which means the analytical procedure defines the analyte. The test method offers greater selectivity and precision than thermal techniques that do not correct for charring of organic components. The analysis method is simple and relatively quick (about 15 min). The analysis and data reduction are automated, and the instrument is programmable (different methods can be saved as methods for other applications).

1.6 A method (5040) for *DPM* based on thermal-optical analysis has been published by the National Institute for Occupational Safety and Health (NIOSH). Method updates (3, 4) have been published since its initial (1996) publication in the NIOSH Manual of Analytical Methods (*NMAM*). Both *OC* and *EC* are determined by *NMAM* 5040. An *EC* exposure marker (for *DPM*) was recommended because *EC* is a more selective measure of exposure. A comprehensive review of the method and rationale for selection of an *EC* marker are provided in a Chapter of *NMAM* (5).

1.7 The thermal-optical instrument required for the analysis is manufactured by a private laboratory.³ As with most

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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² The boldface numbers in parentheses refer to references at the end of this test method.

³ The carbon analyzer used in the development and performance evaluation of this test method was manufactured by Sunset Laboratory, 2017 19th Avenue, Forest Grove, Oregon 97116, which is the sole source of supply of the instrument known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

instrumentation, design improvements continue to be made. Different laboratories may be using different instrument models.

1.8 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.9 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 7.1.5, 8.3, and 12.12.2.

1.10 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards*:⁴

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D1356**.

3.1.1 *limit of detection (LOD), n*—a value for which exceedence by measured mass indicates the presence of a substance at given false-positive rate: $3 \times$ estimated standard deviation of estimated mass of a blank.

3.2 *Definitions of Terms Specific to This Standard*:

3.2.1 *elemental carbon (EC), n*—excluding char, light-absorbing carbon that is not removed from a filter sample heated to 870°C in an inert atmosphere.

3.2.2 *organic carbon (OC), n*—carbon volatilized in helium while heating a quartz-fiber filter sample to 870°C. Includes carbonates, if present, unless quantified separately. Also includes char formed during pyrolysis of some materials.

3.2.3 *thermogram, n*—digitized output signal of thermal-optical instrument. Shows detector and filter transmittance signals at different temperatures in nonoxidizing and oxidizing atmospheres.

3.2.4 *total carbon (TC), n*—sum of organic and elemental carbon.

3.3 *Symbols and Abbreviations*:

3.3.1 *DPM*—diesel particulate matter

3.3.2 *LOD* ($\mu\text{g}/\text{cm}^2$)—limit of detection: $3 \times s_w$

3.3.3 *s_w* ($\mu\text{g}/\text{cm}^2$)—estimate of σ_w

3.3.4 *σ_w* ($\mu\text{g}/\text{cm}^2$)—standard deviation in collected mass loading determination

3.3.5 *OC, EC, TC* ($\mu\text{g}/\text{cm}^2$ or μg)—organic, elemental, and total carbon

3.3.6 *RSD*—relative standard deviation

3.3.7 *V* (*L*)—sampled volume

3.3.8 *W_b* (μg)—field blank filter's EC mass reading

3.3.9 *W_{EC}* (μg)—active filter's EC mass reading

4. Summary of Test Method

4.1 The thermal-optical analyzer has been described previously (1-5). Design improvements have been made over time, but the operation principle remains unchanged. *OC-EC* quantification is accomplished through temperature and atmosphere control. In addition, the analyzer is equipped with an optical feature that corrects for the char formed during the analysis of some materials. Optical correction is made with a pulsed diode laser and photodetector that permit continuous monitoring of the filter transmittance/reflectance.

4.2 The main instrument components (transmittance instrument) are illustrated in Fig. 1. The instrument output, called a *thermogram*, is shown in Fig. 2. For analysis, a known area (normally 1.5 cm²) of the quartz-fiber filter sample is removed with a sharp metal punch. Quartz-fiber filters are required because temperatures in excess of 850°C are employed. The portion is inserted into the sample oven, and the oven is tightly sealed. The analysis proceeds in inert and oxidizing atmospheres. First, *OC* (and carbonate, if present) is removed in helium as the temperature is stepped to a preset maximum (usually $\geq 850^\circ\text{C}$ in *NMAM 5040*; see 4.4). Evolved carbon is catalytically oxidized to CO₂ in a bed of granular MnO₂. The CO₂ is then reduced to CH₄ in a Ni/firebrick methanator, and CH₄ is quantified by a *FID*. Next, the sample oven temperature is lowered, an oxygen-helium mix (2 % oxygen after dilution of the 10 % oxygen in helium supply) is introduced, and the temperature is increased to 900°C (or higher) to remove (oxidize) the remaining carbon, some or all of which is *EC*, depending on whether char is formed during the first part of the analysis (a char correction is made if so). At the end of each analysis, calibration is made through automatic injection of a fixed volume of methane.

4.3 Some samples contain components (for example, cigarette and wood smokes) that carbonize (convert to carbon) to form *char* in helium during the first part of the analysis. Like *EC* typical of fine particle pollution, char strongly absorbs light, particularly in the red/infrared region. The char formed through pyrolysis (thermal decomposition) of these components causes the filter transmittance/reflectance to decrease. Charring can begin at 300°C; the process may continue until the maximum temperature is reached. After *OC* removal, an oxygen-helium mix is introduced to effect combustion of residual carbon, which includes char and any *EC* originally present. As oxygen enters the oven, light-absorbing carbon is oxidized and a concurrent increase in filter transmittance occurs. The *split* (vertical line prior to *EC* peak in Fig. 2) between *OC* and *EC* is assigned when the initial (baseline)

⁴ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

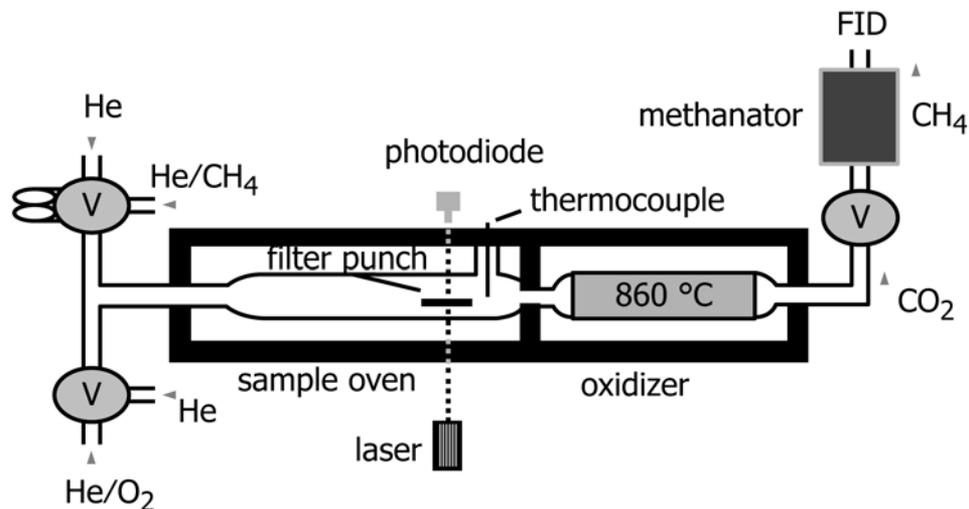
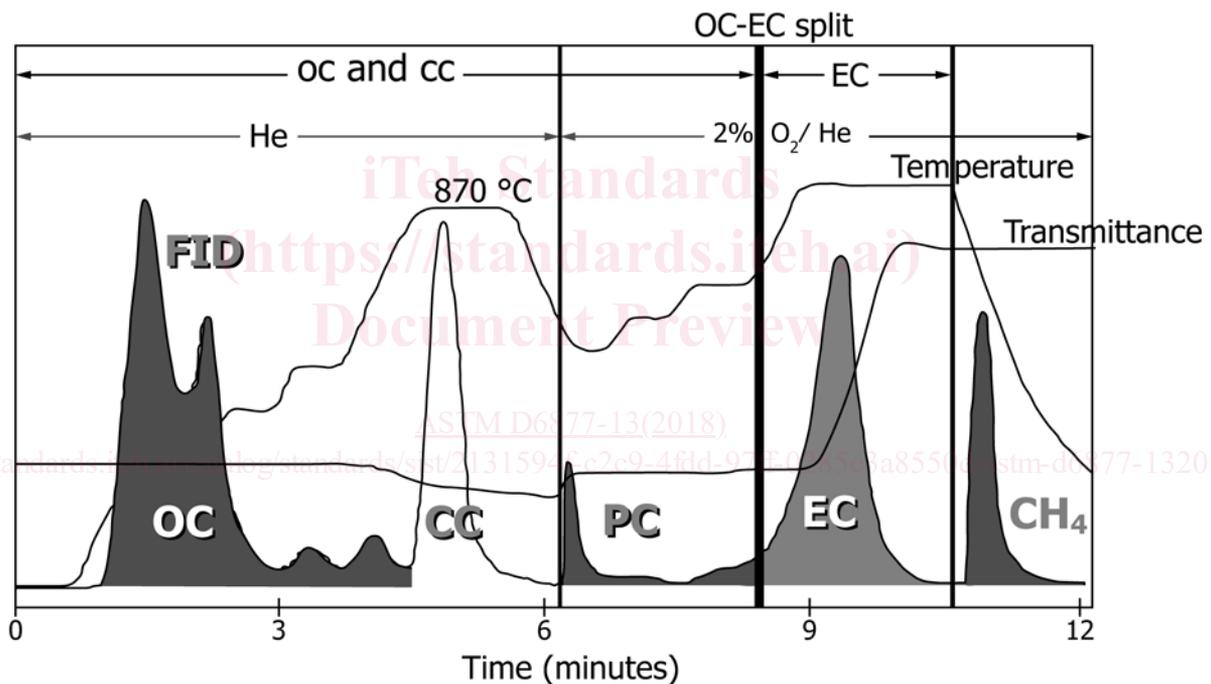


FIG. 1 Schematic of Thermal-Optical Instrument (V = Valve) for Determination of Organic and Elemental Carbon in DPM and Other Carbonaceous Aerosols



NOTE 1—PC is pyrolytically generated carbon (char). Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate matter.

NOTE 2—In the comparative test reported by Birch (6), participants used different maximum temperatures in helium (5). The actual maximum ranged from about 850–900°C. NMAM 5040 specifies 870°C, which is near the middle of this range.

FIG. 2 Thermogram for Filter Sample Containing OC, Carbonate (CC), and EC

value of the filter transmittance is reached. All carbon removed before the OC-EC split is considered organic; that removed after the split is considered elemental. If no char is formed, the split is assigned prior to removal of EC. Ordinarily, the split is assigned in the oxidative mode of the analysis.

4.4 Occasionally, the sample EC (along with any char formed) is lost during the fourth temperature step in helium. Loss of EC in helium is uncommon but sometimes occurs, possibly due to oxidants in the sample. In cases when loss is to an extent where the filter transmittance reaches/exceeds its

initial (baseline) value during the first part of the analysis (in helium), the OC-EC split is automatically assigned earlier, in helium mode (5). A lower preset maximum (for example, 650°C) can be used to reduce EC/char loss in helium so that the split occurs during the oxidative mode (5).

4.5 OC and EC results are reported in units μg per cm^2 of filter deposit. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area (slightly less than the filter area). A homogeneous deposit is assumed. The TC in the sample is the sum of OC and EC. If carbonate

is present, the carbon in it is quantified as *OC* unless correction is made. Additional details about carbonates are given in a following section.

5. Significance and Use

5.1 The test method supports previously proposed occupational exposure standards (7, 8) for *DPM*. A *DPM* exposure limit has since been promulgated for metal and nonmetal mines, but there currently are no limits for general occupational settings (a proposed limit (7) was withdrawn from the ACGIH Notice of Intended Changes (NIC) list in 2003). In the United States alone, over a million workers are occupationally exposed (9). An exposure standard for mines is especially important because miners' exposures are often quite high. NIOSH (9), the International Agency for Research on Cancer (10) (IARC), the World Health Organization (11) (WHO), the California Environmental Protection Agency (12), the U.S. Environmental Protection Agency (13) (EPA), and the National Toxicology Program (14) reviewed the animal and human evidence on *DPM* and all classified diesel exhaust as a probable human carcinogen or similar designation. In 2012, the WHO reclassified diesel exhaust as carcinogenic to humans (Group 1) (15). In addition, in a study of miners, the National Cancer Institute (NCI) and NIOSH reported increased risk of death from lung cancer in exposed workers (16, 17).

5.2 The test method provides a measure of occupational exposure to *DPM*. Given the economic and public health impact of epidemiological studies, accurate risk assessment is critical. The NIOSH/NCI study of miners exposed to diesel exhaust provides quantitative estimates of lung cancer risk (16, 17). The test method was used for exposure monitoring. Since publication (in 1996) as *NMAM* 5040, the method has been routinely used for occupational monitoring (5).

5.3 Studies indicate a positive association between airborne levels of fine particles and respiratory illness and mortality (18-26). The test method and others have been used for EPA air monitoring networks and air pollution studies. Because different methods produce different results, method standardization is essential for regulatory compliance determinations and valid comparisons of interlaboratory data.

5.4 The test method is being applied for emission-control testing.

6. Interferences

6.1 *EC* is a more selective marker of occupational exposure than other measures of *DPM* (for example, particulate mass, total carbon). As defined by the test method, *EC* is the carbon determined during the second stage of the analysis (after pyrolysis correction). If the sample contains no pyrolyzable material, all carbon evolved during this stage is considered elemental. Inorganic dusts, carbonates, and wood and cigarette smokes ordinarily do not interfere in the *EC* determination (2-5). *OC* can be contributed by smokes, fumes and other sources.

6.2 If high levels of other dusts are present, a size classifier (for example, impactor, or cyclone, or both) should be used. If the dust is carbonaceous, a size classifier provides a more

selective measure of the diesel-source *OC*. It also provides a better measure of the diesel-source *EC* if the dust contains *EC* (for example, carbon black, coal), which is less common. A finely ground sample of the bulk material can be analyzed to determine whether a dust poses potential interference. Depending on the dust concentration, size distribution, and target analyte (*EC* or *TC*), an impactor/cyclone may be required. Additional details can be found elsewhere (5). Some *OC* interferences cannot be excluded on the basis of size (for example, cigarette smoke and other combustion aerosols, condensation aerosol).

6.3 In metal and nonmetal mines, the Mine Safety and Health Administration (MSHA) recommended use of a specialized impactor (with cyclone) to minimize collection of carbonates and other carbonaceous dusts (6, 8, 27-31).

6.4 For measurement of diesel-source *EC* in coal mines, an impactor with sub-micrometer cutpoint (6, 8, 27-31) must be used to minimize collection of coal dust. Only low levels of *EC* were found in non-dieselized coal mines when an impactor with a sub-micrometer cutpoint was used (6).

6.5 Environmental samples usually contain little (if any) carbonate. Levels in some occupational settings (for example, trona mines) may be quite high. Depending on the carbonate type, a carbonate-subtracted value for *OC* (and *TC*) can be obtained through acidification of the sample or separate integration of the carbonate peak (see 12.12). If carbonate is not of interest but present, a size-selective sampler can be used to exclude carbonate-containing dusts (see 6.3, 6.4, and 12.12).

7. Apparatus

7.1 The main components of the thermal-optical analyzer (transmittance instrument) used in the test method are illustrated in Fig. 1. The principal components are:

- 7.1.1 *Sample oven*, temperature programmable.
- 7.1.2 *Oxidizer oven*, packed with MnO_2 and heated to 860°C.
- 7.1.3 *Methanator*, packed with catalyst (Ni-coated firebrick) and heated to 500°C.
- 7.1.4 *Flame ionization detector (FID)*.
- 7.1.5 *Pulsed diode laser and photo detector*, for continuous monitoring of filter transmittance. (**Warning**—In accordance with the manufacturer, the instrument is a Class I Laser Product. Weakly scattered laser light is visible during operation, but does not pose a hazard. 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 (that is, 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.)
- 7.1.6 *Valve box/calibration loop*, for control of gas flow and automatic injection of methane internal standard.

8. Reagents and Materials

8.1 *Organic Carbon (OC) Standards*—Sucrose stock solution having carbon concentration of 25 mg/mL. Working standards (dilutions of stock) with concentrations of 0.1 to 3