Designation: D6877 – 13$^{\varepsilon 1}$

Standard Test Method for Monitoring Diesel Particulate Exhaust in the Workplace[1]

This standard is issued under the fixed designation D6877; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε^1 NOTE—Editorial changes were submitted after publication in October 2013.

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. *LOD*s based on media blanks stored after cleaning are usually higher. *LOD*s based on a set of media blanks analyzed over a six month period at a commercial laboratory were *OC* = 1.2 µg/cm^2, *EC* = 0.4 µg/cm^2, and *TC* = 1.3 µg/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 µg EC/cm^2, giving LODs (3 × SD blank) from about 0.06-0.09 µg EC/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**).

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Qualityand 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.

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

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

3. Terminology

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

3.2 *Definitions:*

3.2.1 *limit of detection, LOD*—A value for which exceedence by measured mass indicates the presence of a substance at given false-positive rate: 3 × estimated standard deviation of estimated mass of a blank.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *organic carbon (OC)*—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.

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

3.3.3 *total carbon (TC)*—Sum of organic and elemental carbon.

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

3.4 *Symbols and Abbreviations:*

3.4.1 *DPM*—diesel particulate matter

3.4.2 *LOD* ($\mu g/cm^2$)—limit of detection: 3 × s_w

3.4.3 s_w ($\mu g/cm^2$)—estimate of σ_w

3.4.4 σ_w ($\mu g/cm^2$)—standard deviation in collected mass loading determination

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

3.4.6 *RSD*—relative standard deviation

3.4.7 *V (L)*—sampled volume

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

3.4.9 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 cm^2) 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 ≥850°C in *NMAM* 5040; see 4.4). Evolved carbon is catalytically oxidized to CO_2 in a bed of granular MnO_2. The CO_2 is then reduced to CH_4 in a Ni/firebrick methanator, and CH_4 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)

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[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 Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.

[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.

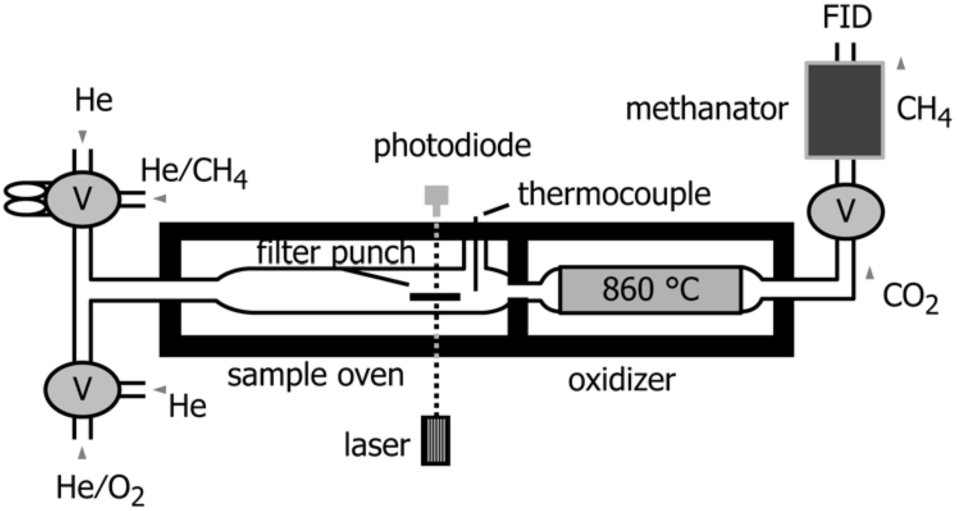
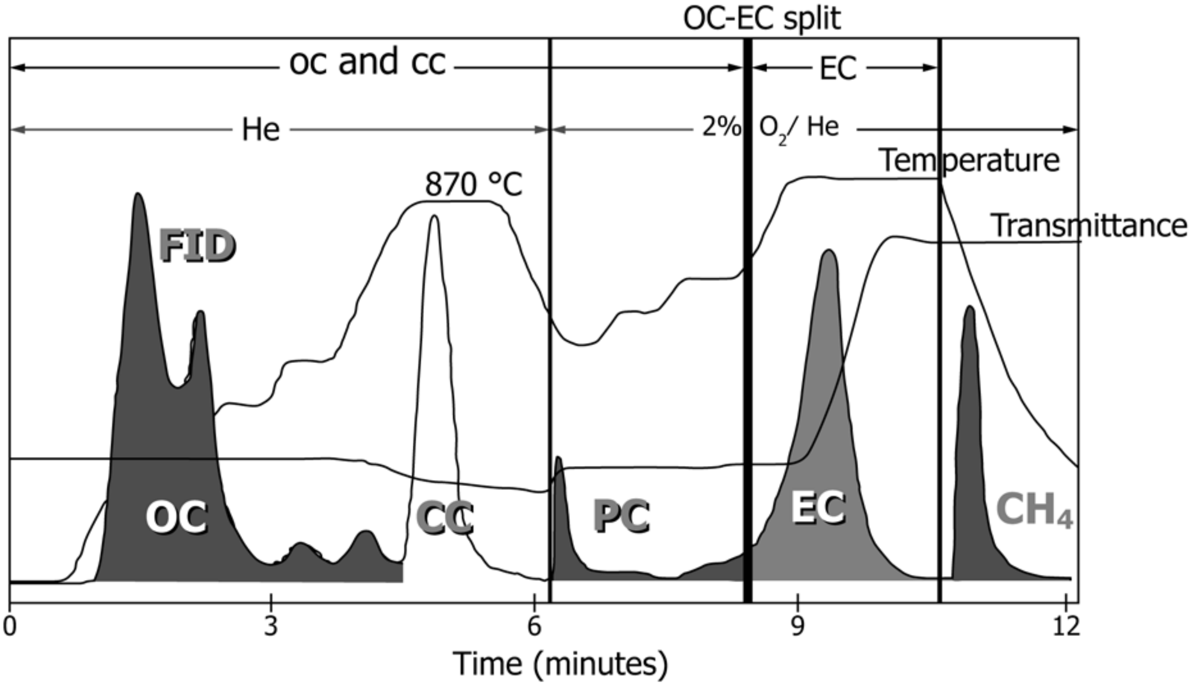


FIG. 1 Schematic of Thermal-Optical Instrument (*V* = valve) for Determination of Organic and Elemental Carbon in DPM and Other Carbonaceous Aerosols



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

between *OC* and *EC* is assigned when the initial (baseline) value of the filter transmittance is reached. All carbon removed before the *OC-EC* split is considered organic; 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 mg C per mL solution. Ensure carbon loadings of standards spiked onto filter punches bracket the range of the samples.

8.2 *Ultrapure water, Type I,* (for preparation of sucrose standard solution).

8.3 *Sucrose,* reagent grade (99+ %).

8.4 *Helium-UHP (99.999%)*—Scrubber also required for removal of trace oxygen.

8.5 *Hydrogen,* purified (99.995%). Cylinder or hydrogen generator source. (**Warning—**Hydrogen is a flammable gas. Users must be familiar with proper use of flammable and nonflammable gases, cylinders, and regulators.)

8.6 *Air*—Ultra zero (low hydrocarbon).

8.7 *Oxygen (10 %) in helium,* both gases UHP, certified mix.

8.8 *Methane (5 %) in helium,* both gases UHP, certified mix.

8.9 *37-mm cassettes or alternative sampler.*

8.10 *Personal sampling pumps.*

8.11 *High-purity, quartz-fiber filters,* pre-cleaned. High-purity, binder-free, high efficiency filters must be used.[5] Pre-cleaned 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. The filters should be checked (analyzed) to ensure that *OC* contaminants have been removed. A shorter cleaning period may be effective. *OC* results immediately after cleaning should be below 0.1 µg/cm^2. *OC* vapors readily adsorb onto clean filters. Even when stored in closed containers, *OC* loadings may range from 0.5 µg/cm^2-0.8 µg/cm^2 after several weeks.

8.12 *Aluminum foil.*

8.13 *10-µL syringe,* (and other sizes, depending on volume of standard applied).

8.14 *Metal punch,* for removal of 1.5 cm^2 filter portions.

NOTE 2—A smaller portion (for example, taken with cork borer) may be used, but the area must be large enough to accommodate the laser (that is, 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 (filter transmittance will decrease dramatically when the sample is properly aligned). A filter portion ≥0.5 cm^2 with diameter or width ≤1 cm is recommended.

8.15 *Tweezers,* to handle filters.

8.16 *Volumetric flasks*—Class A (for preparation of sucrose stock solutions).

8.17 *Analytical balance.*

9. Sampling

9.1 Calibrate each personal sampling pump at 1-4 L/min with a representative sampler in line.

9.2 Use tweezers to insert filter supports (a second quartz filter, cellulose pads or clean stainless steel screens) and pre-cleaned, quartz-fiber filters into sampling cassettes. Seal cassettes. A second quartz filter permits correction for adsorbed vapor (**5**, **30**).

NOTE 3—Cellulose support pads give higher *OC* blanks than quartz filters or stainless steel screens. Filters are less expensive than screens.

9.3 Attach sampler outlet to personal sampling pump with flexible tubing. Remove plug from cassette inlet, if present.

9.4 Sample at an accurately known flow rate.

9.5 After sampling, replace top piece of cassette (or otherwise protect sample), if removed, and pack securely for shipment to laboratory.

NOTE 4—*DPM* 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). *DPM* 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 (for example, 80 %) *EC* content.

10. Calibration and Standardization

10.1 Analyze aliquots of *OC* standard solution spiked onto freshly cleaned filter portions. Remove portions from clean filters with metal punch. Clean portions in sample oven before spiking. Apply aliquots with syringe. Include carbon loadings representative of samples.

10.2 When applying small aliquots (for example, 10 µL), disperse standard solution at one end of the 1.5 cm^2 filter portion to ensure it can be positioned in laser beam. To prevent possible solution loss to surface, hold portion off the surface (larger volumes can penetrate to the underside). Allow water to evaporate before analyzing. A decrease in filter transmittance during the first temperature step of the analysis indicates water loss. Allow samples to dry longer if this occurs. About 20 minutes should be adequate. Filter portions also can be dried in the sample oven. For quick drying, the "clean oven" command on the menu can be selected and canceled after about 4 seconds (time may depend on instrument). The oven temperatures should not exceed 100°C to avoid boiling the solution. As the sample is heated, a rapid decrease in filter transmittance should occur if the sample is properly aligned in the laser beam. The sample is dry when the transmittance reaches a constant. This drying approach is convenient and prevents potential adsorption of organic vapors in laboratory air.

10.3 Analyze blanks with each sample set. Instrument blanks are based on analysis of freshly cleaned filter portions.

11. Quality Control

11.1 Analyze three blind spikes and three analyst spikes (sucrose solution) to ensure that instrument calibration is in control.

11.2 Analyze at least one replicate sample per sample set. For sets of up to 50, replicate 10 % of the samples. For sets

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[5] High filtration efficiency and filter purity are essential to the performance of the test method. Certain impurities (alkali metals) can react with quartz at elevated temperature. Impure quartz also may cause EC removal in helium. The following product was used in the evaluation of this test method: Pall Gelman Sciences Pallflex Tissuquartz 2500QAT-UP quartz-fiber filters. An equivalent product is not known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.

over 50, replicate 5 %. If a filter deposit appears uneven, reanalyze to check evenness. The relative standard deviation (*RSD*) of triplicate analyses of a 37-mm filter is normally below 5 %.

12. Procedure

12.1 Set analyzer in accordance with manufacturer's recommendations. Except for hydrogen, turn gas flow valves counter clockwise to set flows. Adjust hydrogen (H_2) after other flows are set. Settings within the following ranges are typical: Air, 280-300 mL/min; H_2, 42-80 mL/min; CalGas (5 % methane), 10-25 mL/min; helium 1 (He 1), 55-65 mL/min; He 2, 10-15 mL/min; He 3, 65-80 mL/min; helium/oxygen (He/O_2) 10-15 mL/min. Settings depend on the instrument model. See instrument operating manual for specifics.

12.2 Temporarily increase H_2 flow (for example, to 80 mL/min or flow required to light detector easily). Light FID with lighter held over top of exhaust chimney. Check to ensure flame is lit (condensation should appear on a mirror held at an angle over chimney). Reduce H_2 flow to normal operating flow. Check flame again.

12.3 Recheck all gas flows; adjust if necessary. Do not adjust flows during an analysis.

12.4 Place new quartz-fiber filter on a clean aluminum foil surface and remove a portion with a clean, sharp metal punch of known area. A 1.5-cm^2 rectangular metal punch provided with the instrument is normally used. Multiple sheets of foil taped (at foil edge) to the lab bench work well as a cutting surface. The cutting area should be cleaned before use. Isopropyl alcohol can be used for cleaning. Allow residual alcohol to vaporize from the surface prior to use. Cover area when not in use.

12.5 Place blank filter portion in sample oven and close oven with clamp. Make sure the o-ring seals securely; oven pressure is typically between 2-3 psi. Clean blank portion by selecting clean oven command from the options menu. Several punches can be cleaned simultaneously if multiple standards are to be analyzed.

12.6 Load method file if not already loaded. Enter sample name and file name for raw data file.

12.7 Press Start Analysis button to run blank(s). Post-analysis, a message informs the user when the instrument is ready for the next sample. When ready, remove freshly cleaned portion(s), apply sucrose standard solution and allow it to dry (see section 10.2). Check results for accuracy before beginning sample analyses.

NOTE 5—Avoid application of large volumes (for example, >50 µL) that saturate the punch. Apply larger volumes in stages, with drying between aliquots. For higher loadings, a smaller volume (for example, 10 µL) of a more concentrated solution should be used.

12.8 Place sample filter on clean aluminum foil surface. Avoid hand contact with sample. Do not scrape or otherwise disturb deposit. Punch out a representative portion of known area (normally 1.5 cm^2).

12.9 Remove sample portion from punch body. A needle inserted at an angle into a corner of the portion can be used. Avoid poking a hole in area where laser penetrates the portion. Transfer sample to quartz filter holder. The 1.5 cm^2 metal punch has a small hole in its side. A needle or wire inserted into the hole can be used to push out the sample onto the foil, if preferred. If the instrument has an external bracket to support the quartz sample holder, the punch can be pushed onto the holder. Other approaches can be used, provided contamination and disruption of the sample are avoided.

12.10 Use tweezers to insert quartz sample holder with filter portion into sample oven.

12.11 Enter sample and data file names. Start the analysis.

NOTE 6—Forms of carbon that are difficult to oxidize (for example, graphite) may require a longer period and higher temperature in the oxidative mode. Ensure 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.

12.12 *Carbonate:*

12.12.1 *Carbonate Peak*—High levels of carbonate are present in some occupational settings (for example, limestone and trona mines). Carbonate is indicated by a relatively narrow peak during the fourth temperature step in helium. Its presence is verified by exposing a second punch from the filter to HCl vapor prior to analysis. A much-reduced (or absent) peak after acidification is indicative of carbonate in the sample. Depending on the carbonate type, a carbonate-subtracted *OC* (and *TC*) result can be obtained through acidification of the sample or separate integration of the peak (**5**). Commercial laboratories may not report carbonate carbon separately (it is quantified as *OC*) unless a client requests it. A size classifier can be used to minimize collection of carbonate. In metal and nonmetal mines, MSHA recommends use of a specialized impactor (with cyclone) to exclude carbonates and other carbonaceous dusts (**8**).

12.12.2 *Acidification*—A dessicator or alternative vessel can be used to acidify punches. Add concentrated HCl to petri dish and place uncovered dish at bottom of dessicator to produce acid vapor inside. (**Warning—**Avoid inhalation and skin contact with concentrated HCl.) Acidify samples in a well-ventilated hood. Place sample portions on dessicator tray (acid resistant), place tray in dessicator, and cover with lid. A wetted pH indicator stick can be used to check acidity. A wetted stick inserted between the dessicator lid and base should give a pH near 2. Expose sample portions to acid vapor for about one hour. Large (for example, non-respirable) particles may require more time. After acidification, place tray on a clean surface inside hood. Allow the residual acid on samples to volatilize in hood for at least one hour before analyzing.

12.12.3 *Measurement*—Analyze the acidified sample portion. The acidified portion provides a better measure of the diesel-source *OC* (and *TC*), especially if the carbonate loading is relatively high. Acid treatment sometimes changes the appearance of the carbon profile, but *EC* results are normally comparable. The difference between *TC* results for the two portions (before and after acidification) gives an estimate of carbonate-source carbon (presuming carbonate deposit is even). The data calculation program can be used as an alternative to acidification if the carbonate can be removed as a single peak during the fourth temperature step (for example, calcium carbonate). If so, carbonate can be estimated through separate integration of the carbonate peak. Additional details regarding carbonates are provided elsewhere (**5**).

13. Calculation

13.1 Run data analysis program on raw data file to obtain carbon results in units μg/cm^2. A spreadsheet with results is automatically generated. The reported results assume a 1.5 cm^2 sample area. If the area differs, multiply the reported result by 1.5 and divide the product by the actual area analyzed to obtain the correct result (that is, reported result × 1.5/actual punch area = corrected result in μg/cm^2). The correction can be done in the results spreadsheet. Alternatively, the actual punch area can be entered into the external parameter file (ocecpar) associated with the data analysis program before running the program. If the data file contains results for samples having different areas, the area correction should be made in the results spreadsheet.

13.2 Multiply the reported (or area-corrected) *EC* result (μg/cm^2) by the 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 blank (W_b). The mass of *OC* is calculated similarly.

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

$$C_{EC} = \frac{W_{EC} - W_b}{V}, \ mg/m^3 \quad (1)$$

The *OC* concentration is calculated similarly.

NOTE 7—The mean *OC* blank may underestimate the *OC* contributed by adsorbed vapor. A more accurate correction can be made through use of two quartz filters in the cassette. The *OC* result for the bottom filter gives a better measure of adsorbed *OC* because it collects vapor actively (that is, during sampling), rather than passively. Bottom filters typically give higher *OC* results than traditional blanks. Details on *OC* sampling artifacts are summarized elsewhere (**5**).

14. Precision and Bias

14.1 Three sets of air samples were collected in a loading dock area on three separate days. A diesel truck was operating in the area for different durations each day. Personal pumps were programmed to run at 2 L/min. Two samples (days 2 and 3) were collected for 8 hours; a third (day 1) was collected for 23 minutes. A portable dust chamber (**32**) designed for simultaneous collection of air samples was used. Four, 37-mm cassettes (2-piece, closed-face) containing quartz-fiber filters were mounted inside the chamber. The following results (mean [s_w], μg/cm^2) were obtained by the test method: Day 1-*OC* = 2.65 [±0.26], *EC* = 1.95 [±0.12], *TC* = 4.60 [±0.18]; Day 2-*OC* = 3.29 [±0.17], *EC* = 5.15 [±0.22], *TC* = 8.44 [±0.33]; Day 3-*OC* = 5.97 [±0.16], *EC* = 16.81 [±0.50], *TC* = 22.78 [±0.35]. These results (**5**) correspond to average RSDs (single laboratory) of 6 % for *OC* (range = 3-10 %), 4 % for *EC* (range = 3-6 %), and 3 % for *TC* (range = 2-4 %).

14.2 Fifty *DPM* samples collected in different types of mines were analyzed by the test method. Thirty-six were analyzed once at three different laboratories; the remaining 14 were analyzed by two of the three laboratories. The filter loadings (μg C per 37-mm filter) ranged from 29-531 μg *OC*, 32-404 μg *EC* and 71-776 μg *TC*. The pooled RSD (95 % confidence level [CL]) for *EC* was 10 %. The pooled RSDs (95 % CL) for *OC* and *TC* were 12 % and 6 %, respectively. These results (**5**) are consistent with those found in a collaborative test (see 14.3).

14.3 A collaborative test (**33**) of this test method was conducted. A high volume air sampler containing a precleaned, quartz-fiber filter (8 × 10 inch) was used for collection of air samples containing *DPM*. Two samples were collected in workplaces where diesel trucks were being used; a third was collected at an urban location. Prior to distribution of the sample sets, multiple analyses across the filters were performed to ensure matched (RSD for *TC* < 5 %) sets. Portions of the filters were then distributed to eleven laboratories for analysis in triplicate. Six laboratories analyzed the samples in accordance with the test method; five used purely thermal (no char correction) methods. The following results (mean [s_w], μg/cm^2) were obtained by the test method: urban sample- *OC* = 10.42 [±0.69], *EC* = 1.80 [±0.14], *TC* = 12.37 [±0.83]; *truck 1-OC* = 18.47 [±0.98], *EC* = 6.25 [±0.59], *TC* = 25.05 [±1.18]; *truck 2-OC* = 140 [±5], *EC* = 16.10 [±1.01], *TC* = 158 [±6]. These results correspond to average, between-laboratory RSDs of 5 % for *OC* (range = 3 %-7 %); 8 % for *EC* (range = 6 %-9 %), and 5 % for *TC* (range = 4-7 %). Results of the collaborative test and other tests of repeatability and reproducibility have been reported previously (**2-5**, **30**, **33-35**).

NOTE 8—*OC-EC* results reported by one of the six test laboratories that participated in the collaborative test (**30**) were excluded because of a laser problem. *TC* results were included because they were not affected by the problem.

14.4 A reference material is not available for determining the accuracy of *OC-EC* measurements on filters. Different methods normally give equivalent *TC* results (for example, within 15 %), but *OC-EC* results are method dependent (**33**, **36**, **37**) (see also NIST SRM 1649a Certificate of Analysis, Issue Date: 01/31/01). Variability between methods depends on sample type. In general, there is greater disagreement when samples contain materials that char. With these, *EC* results of methods that use a lower maximum temperature (typically 550°C) in inert gas and do not correct for char were more variable and positively biased relative to the test method (**30**, **33**, **37**). *DPM* samples from mines often have high *EC* contents (for example, > 50%) and *OC* fractions that are essentially removed below 500 °C (**5**, **30**). Better agreement between methods can be expected for these types of samples because all the *OC* can be removed by the thermal protocols in use. In the analysis of 22 samples collected in a simulated mining environment, good correlation between the test method and a purely thermal method was reported (**38**). The relatively small difference was attributed to the different thermal programs used. Unlike the samples in the collaborative test (**33**), only a minor amount of carbon was removed above 500°C and the samples did not char.

14.5 A method for generating matched filter sets with known *OC–EC* contents was reported (**39**). Generated filter sets were distributed to six laboratories for an interlaboratory comparison. Analytical results indicate uniform carbon distribution for the sets and good agreement between the participating laboratories. Relative standard deviations (RSDs) for mean *TC*, *OC*, and *EC* results for seven laboratories were <10, 11, and 12% (respectively). Except for one *EC* result (RSD = 16 %), RSDs reported by individual laboratories for *TC*, *OC*, and *EC* were <12 %. The method of filter generation is generally applicable and reproducible. Depending on the application, different filter loadings and types of *OC* materials can be employed. Matched filter sets can be used for determining the accuracy of *OC–EC* methods, which are operational.

14.6 Preparation of a reference material deposited on quartz filters has been investigated by NIST, but a suitable *OC-EC* reference material is lacking. A limited confirmation of results by a second laboratory is advised (**5**).

15. Keywords

15.1 air pollution; carbonaceous aerosols; carbon analysis; diesel exhaust; diesel particulate matter; diesel soot; elemental carbon; $PM_{2.5}$; sampling and analysis; ultra-fine particles

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