



DIESEL PARTICULATE MATTER (as Elemental Carbon)

5040

C

MW: 12.01

CAS: none

RTECS: none

METHOD: 5040, Issue 4

EVALUATION: FULL

Issue 1: 15 May 1996

Issue 2: 10 March 2016

OSHA: None

NIOSH: None

PROPERTIES: nonvolatile solid

SYNONYMS: diesel particulate matter, diesel exhaust, diesel soot, diesel emissions

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER: quartz-fiber, 37-mm or 25-mm; size-selective sampler may be required [1]</p> <p>FLOW RATE: 2 to 4 L/min (typical)</p> <p>VOL-MIN: 142 L @ 40 µg/m³ -MAX: 19 m³ (for filter load of ~ 90 µg/cm²)</p> <p>SHIPMENT: Routine.</p> <p>SAMPLE STABILITY: Stable.</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: Thermal-optical analysis; flame ionization detector (FID)</p> <p>ANALYTE: Elemental carbon (EC). Total carbon is determined, but an EC exposure marker was proposed. See [1] for details.</p> <p>FILTER PUNCH SIZE: 1.5 cm² (or other [1])</p> <p>CALIBRATION: Methane injection</p> <p>RANGE: 1 to 105 µg per filter portion (See also [1].)</p> <p>ESTIMATED LOD: 0.3 µg per filter portion</p> <p>PRECISION (\bar{S}_r): 0.19 @ 1 µg C, 0.01 @ 10 to 72 µg C</p>
ACCURACY	
<p>RANGE STUDIED: 23 to 240 µg/m³ (See also ref. [1].)</p> <p>BIAS: None (See also ref. [1].)</p> <p>OVERALL PRECISION (\hat{S}_{rT}): 0.07</p> <p>ACCURACY: ± 16.7% at 23 µg/m³ (See also ref. [1].)</p>	

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 [2]. An upper EC limit of 800 µg/m³ (90 µg/cm²) can be determined. Low EC loadings (e.g., near the LOD) also may require a manual split to improve accuracy [1].

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 [1,2]. 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 or organic dusts are anticipated, a size-selective sampler (impactor and/or cyclone) should be used [1]. 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 [1]. The method procedures are unchanged from the 4th edition supplement to NMAM, but the corresponding diesel guidance chapter was updated for the 5th edition.

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. Ultrapure H₂O, 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. [1] 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 µg/cm². OC vapors readily adsorb on to clean filters. Even when stored in closed containers, OC loadings may range from 0.5 µg/cm² 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. [1].

2. Personal sampling pump with flexible tubing.
3. Thermal-optical analyzer; see ref. [1].
4. Metal punch for removal of 1.5 cm² 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 cm² with diameter or width ≤ 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. [1]) 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 [1].

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- μ L (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., $\leq 10 \mu\text{L}$), 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. Some software versions may not have this feature.
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. [1]). 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 $\mu\text{g}/\text{cm}^2$ 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 ocepar.txt file, multiply the result by 1.5 (or value in ocepar.txt file) and divide the product by the actual area analyzed to obtain the area-corrected result (i.e., reported result $\times 1.5 / \text{portion area} = \text{corrected result in } \mu\text{g}/\text{cm}^2$). 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 (ocepar.txt), but this approach is error prone and tedious when punches of different areas are used for a sample set because correct results will not be obtained for all punch sizes. Updated software avoids this potential problem by prompting entry of the sample punch area prior to the analysis.

CALCULATIONS

11. Multiply the reported (or area-corrected) EC result ($\mu\text{g}/\text{cm}^2$) 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 [1].
12. Calculate the EC concentration (C_{EC}) in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Details on the evaluation of this method are provided in an NMAM guidance chapter on diesel [1]. 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 or 25-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 [3]. The impactor is commercially available through SKC, Inc. A size-selective sampler (either impactor and/or cyclone) also may be required in other dusty environments [1], 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 [1] (Note: Trona and other compounds containing sodium can etch the quartz oven wall during the analysis. Avoid spillage in the sample oven and frequent analysis of these materials.) These procedures are described in a Chapter of this Manual [1]. 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.

REFERENCES:

- [1] NIOSH [2016]. Chapter DE: Monitoring of diesel particulate exhaust in the workplace. In: O'Connor PF, Ashley K, eds. NIOSH manual of analytical methods. 5th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2014-151.
- [2] Birch ME, Cary RA [1996]. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci Tech* 25:221-241.
- [3] 66 Fed. Reg. 13 [2001]. Department of Labor, Mine Safety and Health Administration: Diesel particulate matter exposure of underground metal and nonmetal miners; final rule. (To be codified at 30 CFR Part 57).

METHOD REVISED BY:

M. Eileen Birch, Ph.D., NIOSH

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