



Method no.:	ID-196
Control number:	T-ID196-PV-02-0709-ASD
Matrix:	Air
OSHA PEL:	3.5 mg/m ³
Procedure:	Samples are collected by drawing a known volume of air through pre-weighed 37-mm diameter low-ash polyvinyl chloride (PVC) filters. Sample filters with gravimetric results greater than the PEL are dissolved in tetrahydrofuran (THF). The residue is redeposited on THF-rinsed quartz fiber filters. The quartz fiber filters are heated at 150 °C and then cooled and weighed. The filters are reheated at 600 °C and then cooled and reweighed. Weight lost after heating at 600 °C is reported as carbon black.
Recommended sample volume:	480 to 960 L
Recommended sampling rate:	2 L/min
Analytical procedure:	Gravimetric
Status of method:	Partially validated. This method is presented for information and trial use.
Detection limit:	0.1 mg (administrative)

January 1982
Revised September 2007

Alan Peck
Robert Douglas

Analytical Services Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

1. Introduction

1.1. Scope

This method is used for the measurement of airborne carbon black particulates to assess carbon black exposure in workplaces where carbon black is known to be used.

1.2. History of the method

- 1.2.1. A previous method for the analysis of carbon black was gravimetric. All dust present in an atmosphere known to contain carbon black was reported as carbon black (Ref. 6.1.).
- 1.2.2. In 1975, ignition was used at the OSHA Laboratory to eliminate interference from particulates that do not lose significant weight upon ignition, i.e. minerals.
- 1.2.3. In 1979, scanning electron microscopy was used to distinguish between carbon black and other organic substances. With the current procedure, scanning electron microscopic analysis is no longer required.
- 1.2.4. The method was tested at the OSHA Salt Lake Technical Center (SLTC) in 2007 and the currently available glass fiber filters were found to have high and somewhat inconsistent gravimetric blank levels after heating at 600 °C. This rendered them unsatisfactory for use in the method. Quartz fiber filters were tested, but were found to also have high blank levels. The material causing high blanks was not identified, but it was found to be soluble in tetrahydrofuran (THF). Quartz fiber filters were selected for use in this method because glass fiber filters were observed to have melted after heating at 600 °C. The blank issue was circumvented by prerinsing the filters with THF. Evaluation data to support these changes are presented in Appendix 1.

1.3. Principle

Organic chemicals and the filter are dissolved with THF and carbon black is re-deposited on a quartz fiber filter. Carbon black is determined as weight difference after heating at 150 °C and then reheating at 600 °C.

1.4. Classification and properties

Carbon black may also be classified as lampblack, channel black, furnace combustion black, and thermal black. Each form is produced by the partial combustion or thermal decomposition of liquid or gaseous hydrocarbons. It is composed of more than 85% elemental carbon in the form of near-spherical colloidal aggregates. The properties of carbon black commonly evaluated for control and classification purposes are usually based on particle size, surface area, structure, and surface chemistry.

1.5. Uses

Carbon black is used as a reinforcing agent in rubber and as a black pigment in printers ink, coatings, paper, and plastics. Ninety-five percent of carbon black is used in the rubber industry, predominantly as a pigment and reinforcing agent in tires.

2. Recovery

The average recovery of carbon black based on weight loss after heating at 150 °C and then reheating at 600 °C was 104.4% (Appendix 1). This recovery was within acceptable limits of uncertainty.

3. Interferences

3.1. Source

- 3.1.1. The most probable sources of interferences are chemicals used in the rubber-processing industries that are released as dusts with carbon black during the weighing, conveying, and mixing operation. These airborne particulates will contribute to the total weight of carbon black samples. Particulates (other than carbon black) that are insoluble in THF and that lose weight after heating at 600 °C are interferences in this method.
- 3.1.2. Rubber-processing chemicals are usually grouped into accelerators, antioxidants and stabilizers, antiozonants, and miscellaneous materials (Ref. 6.2.). These chemicals are defined by the U.S. Tariff Commission as "organic compounds that are added to natural and synthetic rubbers to give them qualities necessary for their conversion into finished rubber goods" (Ref. 6.3.). Most of the commercial organic chemicals used in the rubber industry are listed in Tables of the Encyclopedia of Chemical Technology (Ref. 6.4.).

3.2. Controlling interferences

Chemicals or substances are eliminated as potential interferences in this method according to the following physical constants:

1. Those that vaporize at 150 °C.
2. Those that are soluble in THF.
3. Those that are weight stable at 600 °C.

THF is the preferred solvent extractant because of its unique solvent properties and wide miscibility. It is a saturated cyclic ether (CH₂)₄O and is a good solvent for high-molecular weight polyvinyl chloride, polyvinylidene, resins, and other organic materials. THF is miscible with most organic solvents and with water in all proportions (Ref. 6.5.).

Other solvents can be used for the removal of organic chemicals insoluble in THF. The efficacy of each should be pre-determined in tests with bulk samples.

4. Sampling

Note Some carbon blacks may contain significant amounts of polynuclear aromatic hydrocarbons (PAH) such as:

Anthracene/Phenanthrene
Pyrene
Chrysene
Benzo [a] Pyrene

If PAHs are suspected to be present, the following additional steps and analyses can be performed:

- A. Provide a bulk sample.
- B. Take separate personal air samples on glass fiber filters following OSHA Method 58 (Ref. 6.6.) or other suitable method.
- C. Take area samples on glass fiber filters following OSHA Method 58 (Ref. 6.6.) or other suitable method.

The bulk sample and glass fiber filters can be analyzed for PAH content using parameters established in OSHA Method 58 (Ref. 6.6.) or other suitable method.

4.1 Apparatus

- 4.1.1. Pre-weighed (tared) 37-mm diameter low-ash 5- μ m polyvinyl chloride filter contained in a polystyrene cassette. OSHA personnel can obtain this filter and cassette from SLTC.
- 4.1.2. Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. The pump must be calibrated with a filter holder and filter in the line.

4.2. Procedure

- 4.2.1. Immediately before sampling, remove the top and bottom plugs from the cassette.
- 4.2.2. Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing down during sampling near the worker's breathing zone. Position the sampling pump, cassette, and tubing so it does not impede work performance or safety.
- 4.2.3. Air being sampled should not pass through any hose or tubing before entering the cassette.
- 4.2.4. After sampling for the appropriate time, remove the sampler, and replace the top and end plugs. Wrap each sample end-to-end with a Form OSHA-21 seal.
- 4.2.5. Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.
- 4.2.6. Record sample volume (in liters of air) for each sample, identify the type of operation, and identify any potential interference.

5. Analytical Procedure

Samples are first gravimetrically screened for carbon black following OSHA Method PV2121 (Ref. 6.7.) or other suitable method. Samples with results greater than 3.5 mg/m³ (the PEL for carbon black) are then further analyzed as described below.

5.1. Apparatus

- 5.1.1. Muffle furnace capable of maintaining temperature at 600 °C.
- 5.1.2. Drying oven capable of maintaining temperature at 150 °C.
- 5.1.3. Balance accurate to at least 0.1 mg.
- 5.1.4. Filtering assembly and vacuum system.
- 5.1.5. Quartz fiber filters (37-mm) without organic binder. Millipore quartz fiber filters (lot R6MN83955) were used to gather additional evaluation data. These filters are rinsed by placing them in a small beaker containing about 10 mL of THF for about 10 min. The beakers are swirled several times. The filters are air dried in a hood before use. See Section 5.3., Safety Precautions, for handling THF.
- 5.1.6. Centrifuge tubes (50 mL).

- 5.1.7. Ultrasonic bath.
- 5.1.8. Filter holder (for quartz fiber filters) and accessories with a vacuum source and a cold trap for collection of THF.
- 5.1.9. Quartz crucibles. Fisher Scientific Fisherbrand Self-Sealing 10-mL Quartz Crucibles (catalog 10-490-4) were used to gather additional evaluation data.

5.2. Reagents

- 5.2.1. Tetrahydrofuran [CAS no. 109-99-9]. Sigma-Aldrich tetrahydrofuran, 99+%, A.C.S. reagent (lot 17769T0) stabilized with 250 ppm BHT was used to gather additional evaluation data.
- 5.2.2. Carbon, Lampblack [CAS 1333-86-4]. Fisher Scientific, 100% (lot 061965) was used to gather additional evaluation data.

5.3. Safety precautions

- 5.3.1. Care should be exercised in using THF. It is extremely flammable and the vapor is harmful. It should be used only with adequate ventilation and contact with the skin should be avoided. Other dangers are listed on the reagent label.

When using THF, work in a well ventilated hood and wear protective gloves to avoid skin contact.

- 5.3.2. Usual precautions in working near high temperature furnaces or ovens and fumes should be observed. Protective gloves and tongs should be used in the transfer of samples to and from the high temperature apparatus.

5.4. Laboratory quality control samples

Quality control samples are prepared by placing weighed portions of carbon black, PVC filters, and 15 mL of THF into a 50-mL centrifuge tube. The carbon black is weighed to the nearest 0.1 mg. The weighed amounts of carbon black corresponding to 0.5, 1.0, and 2.0 times the PEL are 1.7, 3.4, and 6.8 mg based on a 960 L air sample.

5.5. Sample analysis

- 5.5.1. The air sample filters and 15 mL of THF are placed in a 50 mL centrifuge tube and sonicated for 10 minutes to dissolve the PVC filter and organic interferences.
- 5.5.2. The samples are transferred (filtered) onto rinsed quartz fiber filters. The filtered THF is captured with a cold trap. The quartz fiber filters are washed 3 times with 2 to 3 mL of THF.

Occasionally, a carbon black sample has a very large amount of material that will not allow the THF to pass through the filter. To facilitate filtration, the pre-filtrate sample material can be portioned onto one or more additional filters (as many as needed) so as to allow for smaller amounts of sample material per each filter. The result for each of the filters for that sample is added together to obtain the correct level of carbon black in the original heavily loaded sample.

After the final wash, immediately remove the quartz fiber filter from the filtering assembly in order to prevent its adherence to the assembly. Place each filter in a separate quartz crucible.

- 5.5.4. The crucibles with the filters are dried in an oven at 150 °C for 30 minutes, cooled to room temperature in a desiccator and weighed (W1) to 0.1 mg.
- 5.5.5. The crucibles with the filters are placed in a muffle furnace at 600 °C for one hour.
- 5.5.6. The filters are cooled to room temperature in a desiccator and reweighed (W2).

5.6. Calculations

The amount of carbon black is determined by subtracting W2 from W1. Average the results for blank samples and identify the average as W3. Subtract the average blank result, W3, from the carbon black result. This value in milligrams is divided by the sample air volume in m³ and reported as mg/m³.

$$\text{carbon black, mg/m}^3 = \frac{[(W1 - W2) - W3]}{m^3}$$

where: W1 is the weight after heating at 150 °C
W2 is the weight after heating at 600 °C
W3 is the average weight loss for the blanks
m³ is the sample air volume in cubic meters

6. References

- 6.1. NIOSH Criteria Publication No. 78 - 204, U.S. Dept. Of Health, Education, and Welfare, 55 - 56, 72 (1978).
- 6.2. Kirk, Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Vol. 17, 509 (1968).
- 6.3. U.S. Tariff Commission, U.S. Production and Sales of Synthetic Organic Chemicals for 1966, Aug. 11, (1967).
- 6.4. Kirk, Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Vol. 17, p. 512 - 539 (1966).
- 6.5. Kirk, Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Vol. 10, p. 249, (1966).
- 6.6. Burright D., Coal Tar Pitch Volatiles (CTPV), Coke Oven Emissions (COE), Selected Polynuclear Aromatic Hydrocarbons (PAHs), <http://www.osha.gov/dts/sltc/methods/organic/org058/org058.html> (accessed 9/21/2007).
- 6.7. Methods Development Team, Gravimetric Determination, <http://www.osha.gov/dts/sltc/methods/partial/pv2121/pv2121.html> (accessed 9/21/2007).

Appendix 1
Additional Evaluation Data

Three samples were prepared by weighing aliquots of carbon black (Section 5.2.2.) into 50-mL centrifuge tubes, and adding 15 mL of THF (Section 5.2.1.) and a PVC filter (Section 4.1.1.) into each of the tubes. The centrifuge tubes were sonicated for 10 min and each sample was filtered separately through a THF-rinsed quartz fiber filter (Section 5.1.5.) as described in Section 5.5.2. of this method. The quartz fiber filters were heated to 150 °C for 30 min and then placed in a desiccator to cool to room temperature. The filters were weighed to 0.1 mg and then heated to 600 °C for one hour. The filters were returned to the desiccator to cool and again weighed to 0.1 mg. The weight difference was divided by the sample weight and then multiplied by 100 to calculate percent loss which is defined as percent carbon black. The data show that the blank issue was resolved and that carbon black recovery was excellent.

sample	carbon black (mg)	crucible weight (g)	weight after 150 °C (g)	weight after 600 °C (g)	weight loss after 600 °C (mg)	blank corrected (mg)	carbon black (%)
cb	9.6	6.8551	6.9546	6.9446	10	9.9	103.1
cb	3.1	7.1915	7.2838	7.2804	3.4	3.3	106.4
cb	5.4	6.8894	6.9815	6.9758	5.7	5.6	103.7
blk	0.0	7.1980	7.2885	7.2883	0.2		
blk	0.0	7.0736	7.1622	7.1621	0.1		
blk	0.0	7.1769	7.2676	7.2676	0.0		