



## *Project Summary*

# Method for Measuring Carbon Fiber Emissions from Stationary Sources

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Carbon fibers are small, highly conductive, and lightweight. When released as emissions from production, manufacturing, processing and disposal sources, they are readily airborne and can be dispersed over wide areas. Because of their high electrical conductivity, carbon fibers settling out of the atmosphere onto electronic or electrical components can cause malfunctions and damage. This research program was initiated to develop techniques to identify and measure carbon fiber concentrations emitted from manufacturing, processing, fabricating and incinerating sources. The overall objective of the research was to develop a measurement method to meet possible emission source regulations.

Because fiber count, fiber size range, and total fiber mass concentration were required, a method based on light microscopy was selected for test and development.

Experimental work, carried out on laboratory and field site samples, showed that carbon fibers could be readily recognized and counted without extensive separation from other particulate "debris" collected during source sampling. Although fibers were reduced in diameter during oxidative and thermal processes such as incineration, the size reductions were not beyond the resolution power of light microscopy.

The method was tested on samples collected from various stationary

emission sources and on samples collected from a pilot-scale in-house incineration facility and the results of these emission measurements are reported.

*This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

The rapidly developing use of carbon or graphite\* fibers incorporated into resin matrix composites is a potential environmental problem. Present generation fibers are small in diameter (typically 5 to 15  $\mu\text{m}$ ), and very lightweight (1.5 to 2  $\text{g}/\text{cm}^3$ ); they are chemically inert and are excellent electrical conductors. Therefore, when the fiber filaments are separated from their composite forms, they are readily airborne and can be transported long distances by normal atmospheric motion. The principal environmental concern is the potential of released fibers to settle out of the atmosphere onto electrical and electronic

\*The term "carbon fibers" is used in this report to include both carbon and graphite fibers resulting from pyrolysis of fibrous materials which have been heat treated to temperatures higher than the decomposition temperature of the precursor polymer (typically 1,000 to 1,200°C for carbon fibers and above 2,000°C for graphite fibers)

components, causing short circuits and arcing and damaging or destroying equipment. Manufacturers, processors, and fabricators of carbon fibers and composites are aware of these potential hazards and take measures to minimize fiber emissions. Despite these control measures, fibers are released during fiber manufacture, composite formation machining and grinding, and other fabrication and processing operations. Additional fiber contamination hazards can occur during waste disposal of consumer goods by incineration, which can thermally decompose the matrix material and release fibers into the atmosphere via stack emissions.

While current production and use of carbon fiber composites (estimated as less than 500 T in 1980) may present only a limited hazard, large increases in demand are foreseen for these lightweight, high-strength materials, especially in the automotive and aircraft industries to achieve fuel savings via weight reductions. For this reason, the Federal government has instituted various programs to study all aspects of carbon fiber production, usage, and disposal. The research project described herein is one of several initiated by the U.S. Environmental Protection Agency (EPA). The risk potential for carbon fibers released to the atmosphere is related to the size range, number, and mass of fibers emitted. In this study, fibers with a length-to-diameter ratio of 5:1 were of primary concern, although the research showed that particles of lower length-to-diameter ratios could be identified and counted readily.

## Conclusions and Recommendations

Studies of available analytical techniques for measuring carbon fiber emissions from stationary sources indicate that light microscopy will provide the necessary fiber mass, number, and size range data.

Since extraneous particulate matter collected with carbon fibers does not interfere with the carbon fiber identification measurements, rigorous separation procedures are not required. Still, separating the carbon fibers from other particulate matter might reduce the time required for analysis and improve the accuracy and precision of the method; for that reason, the use of cyclones preceding a filter backup sampling system warrants further investigation.

Although sampling methodology was not explored in depth, the use of membrane filters as a collection medium may be warranted. The membrane filter can be readily removed from the collected particulate prior to microscopy with the use of simple nitric acid digestion treatment. For sampling at incineration sites, where a membrane filter is not thermally stable, the use of cyclones preceding a quartz or glass filter results in most of the carbon fiber emissions being collected in the cyclones and in the probe portion of the sampling systems, thus simplifying the measurement procedure.

If necessary to support regulatory actions on carbon fiber emissions, the methodology is compatible with the personnel skills and equipment available at most Federal and local regulatory and industrial testing laboratories. As with any new analytical technique based on microscopy (even light microscopy), the skill and experience of the operator is paramount in obtaining reliable data. To establish precision and accuracy data, the method should be evaluated by intercomparisons among several laboratories.

The field site and incinerator emission data in the final report are among the first such data available, and should be useful in guiding control practices and risk evaluations of carbon fiber emissions.

## Procedure and Results

The field sampling procedure involved drawing the fiber-laden air through high-efficiency filters with a vacuum pump. A cellulose acetate (Millipore)

filter (pore size = 5.0  $\mu\text{m}$ ; diameter = 47 mm) was used.

Light microscopic analyses were performed over a selected radial filter area; typically, one-eighth of the 47-mm filter area was analyzed. All carbon fibers observed in the radial section being analyzed were counted, and individual lengths and widths were measured. These data were combined with the known sampling times and flow rates to calculate fiber number concentrations. The corresponding mass concentrations were calculated as follows: mass concentration = (number concentration)  $\cdot$  (average fiber volume [determined by length and width measurements])  $\cdot$  (an assumed density of 1.85 g/cm<sup>3</sup>).

Table 1 summarizes the data obtained from the various field samples. The carbon fiber concentrations ranged from 100 ng/m<sup>3</sup> to 5500 ng/m<sup>3</sup>.

In all samples the fiber width was relatively constant, but the fiber length varied greatly from process-to-process and was widely distributed within a given sample.

For the field samples analyzed, no treatment to remove extraneous particulates was required, a result which can be expected for most emission samples from noncombustion processes. Treating the specimen in boiling HNO<sub>3</sub> (or another appropriate treatment) would be necessary only when the NIOSH clearing method does not produce a specimen suitable for light microscopy. The NIOSH clearing method is a standard procedure for asbestos analysis and involves dissolving the Millipore filter in a 1:1 mixture of diethyl oxalate and dimethyl phthalate.

Table 1 Carbon Fiber Analyses of Field Collections

Operation	Average Length ( $\mu\text{m}$ )	Average Width ( $\mu\text{m}$ )	Number Concentration (fibers/m <sup>3</sup> )	Mass Concentration (ng/m <sup>3</sup> )
Winding <sup>(a)</sup>	69.5	6.5	46	482
Prepregging <sup>(b)</sup>	213.1	6.1	24	356
Shuttle Loom Weaving	749.4	6.7	88	5,497
Machining <sup>(c)</sup>	30.9	6.6	823	2,062
Machining	32.8	6.2	1,212	2,812
Rapier Weaving <sup>(d)</sup>	706.0	3.9	340	6,831

<sup>(a)</sup> Average of four samples taken in work area.

<sup>(b)</sup> Unless otherwise noted, all samples are of outside emissions.

<sup>(c)</sup> Work area sample.

<sup>(d)</sup> Outside ambient, downstream of baghouse. Some fibers appeared damaged.

A stoker-boiler designed and constructed to study combustion processes was used to simulate combustion conditions likely to occur in a municipal incinerator. After reaching a steady-state combustion rate of 75 lb/h of refuse, 1 lb of carbon fiber composite was fed onto the burning hearth over a 1-min period and the combustion continued for 60 min.

Sampling employed two simultaneous modes of collection: a Source Assessment Sampling System (SASS) train using three cyclones preceding a filter, and a Method 17 (in-stack) filter sampling system. The Method 17 filter was changed every 15 min in order to provide information on the rate of carbon fiber emissions with time. Care was taken to maintain an isokinetic sampling period.

The samples consisted of three types: (1) bulk particulate brushed from the cyclone catches, (2) cyclone and probe washings deposited on DM-450 (Gelman) filters, and (3) Method 17 samples and the SASS train collections on quartz (2500 QAST) filters. For analyses of the incineration samples, the basic sample preparation consisted of sonicating the weighed bulk sample and/or filter in a measured volume ( $\approx 10$  ml) of filtered deionized water for 15 min. Twenty-five milliliters of hot (180°F) concentrated nitric acid were added to destroy extraneous organic materials in the sample that might interfere with the microscopic analysis. After cooling to room temperature (25°C), the nitric acid mixture was diluted to 1000 ml and redeposited in aliquots of 100, 200, and 700 ml on SM Millipore filters (pore size = 5.0  $\mu\text{m}$ ; diameter = 47 mm). When thoroughly dry, each deposit-bearing filter was transferred to a glass slide (2 x 3 in). The sample was then cleared using the standard NIOSH solution (dimethyl phthalate and diethyl oxalate at 1:1 plus 0.5 g/ml Millipore filter) and covered with either glass cover slips or slides.

Analysis was performed by screening samples and original quartz filters at 250 to 400X magnification on a Leitz Orthoplan microscope with transmission objectives.

The analysis showed that fibers are oxidized during incineration and that the widths are reduced, resulting in width variations. When they are not oxidized (as in the aforementioned field samples), fiber widths are quite uniform. Oxidation of carbon fibers during incineration occurs nonuniformly,

producing dimples or notches in the fibers. In the laboratory, it was noted that as oxidation proceeds, each notched fiber is cut in two at the site of the notch, leaving fibers of relatively short length and pointed ends. Thus, most oxidized fibers of small diameter also are relatively short.

Table 2 shows the results of the incineration study in terms of emission rates. The total emission rates measured by the SASS train (55.6 mg/dscm particulate; 0.998 mg/dscm carbon fiber) agree quite well with those measured by Method 17 (73.0 mg/dscm particulate; 0.840 mg/dscm carbon fiber), given the nature of the experiment. Inspection of the Method 17 emission rate data also reveals a decay in fiber emission rate with time as would be expected considering the single-point (with respect to time) introduction of the fiber composite into the stoker. This phenomenon is shown graphically in Figure 1. The carbon fiber emission rates display a nearly exponential decay in time, whereas the total particulate emission rate is constant within normal operating bounds.

Table 3 is a breakdown of the results by individual sample. It is interesting to note that nearly all of the carbon fibers (99.6%) were captured in the first two cyclones, whereas only a relatively small portion (17.1%) of the total particulate matter was collected by these cyclones. This pattern is not surprising, given the aerodynamic diameter of these carbon fibers (approximately twice the physical diameter given in Table 1, or 10  $\mu\text{m}$ ). This observation suggests that cyclones may be used to separate the carbon fibers from extraneous particulate material, thus facilitating analysis.

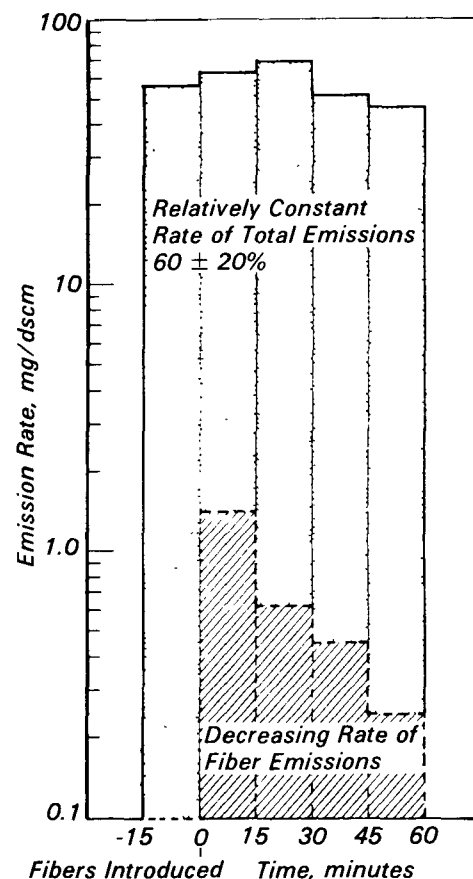


Figure 1. Rates of carbon fiber and total particulate emissions.

Table 2. Incineration Test Emissions Rates

Sample	Sample Volume (dscm)	Total Particulate (mg/dscm)	Carbon Fiber	
			(mg/dscm)	(fibers/dscm)
SASS Train	7.88	55.6	0.998	4310
Method 17				
Pretest	0.295	57.6	0.003	---
0-15 min	0.293	63.8	1.40	---
15-30 min	0.291	70.1	0.62	---
30-45 min	0.287	52.6	0.45	---
45-60 min	0.286	47.7	0.24	---
Nozzle Rinse	1.452	14.6	0.30	---
Total Method 17	1.452	73.0	0.84	---

**Table 3. Results of Incineration Stack Sampling**

Sample	Total Particulate (mg)	Carbon Fiber (mg)	% Carbon Fiber	% of Total Carbon Fiber Sample	Carbon Fiber	
					Average Length (μm)	Average Width (μm)
<i>SASS Train</i>						
10 μm Cyclone	58.3	6.33	10.9	80.5	5534	4.98
3 μm Cyclone	16.7	1.50	9.0	19.1	1320	3.45
1 μm Cyclone	0.4	0	0	0	----	----
Probe	13.3	0.03	0.23	0.4	108	2.94
Filter	391.8	0.0005	0	0	55	5.6
<i>Total SASS</i>	438.2	7.86	1.79			
<i>Method 17</i>						
Pretest	17.0	0.001	----	0.1	----	----
0-15 min	18.7	0.41	2.19	33.6	----	----
15-30 min	20.4	0.18	0.88	14.8	----	----
30-45 min	15.1	0.13	0.86	10.7	----	----
45-60 min	13.6	0.07	0.51	5.7	----	----
Nozzle Rinse	21.2	0.43	0.20	35.2	----	----
<i>Total Method 17</i>	106.0	1.22	1.15			

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*Roy L. Bennett is the EPA Project Officer (see below).*

*The complete report, entitled "Method for Measuring Carbon Fiber Emissions from Stationary Sources," (Order No. PB 83-118 760; Cost: \$8.50, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
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*The EPA Project Officer can be contacted at:*

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