Lawrence Berkeley National Laboratory

Title
SIZE FRACTIONATION OF BLACK AND ORGANIC PARTICULATE CARBON FROM FIRES: FINAL REPORT

Permalink
https://escholarship.org/uc/item/0bj626zf

Author
Dod, R.L.

Publication Date
1985-11-01

Lawrence Berkeley Laboratory
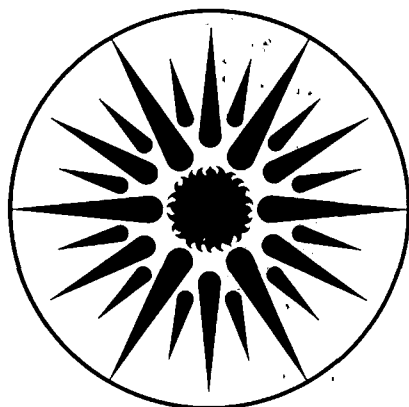## UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

SIZE FRACTIONATION OF BLACK AND ORGANIC
PARTICULATE CARBON FROM FIRES: FINAL REPORT

R.L. Dod, F. Mowrer, L.A. Gundel,
R.B. Williamson, and T. Novakov

November 1985

APPLIED SCIENCE DIVISION

DISCLAIMER

SIZE FRACTIONATION OF BLACK AND ORGANIC PARTICULATE CARBON FROM FIRES: FINAL REPORT

R.L. Dod, F. Mowrer, L.A. Gundel,
R.B. Williamson, and T. Novakov
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

November 1985

SIZE FRACTIONATION OF BLACK AND ORGANIC PARTICULATE CARBON

FROM FIRES: FINAL REPORT*

R.L. Dod, F. Mowrer, L.A. Gundel, R.B. Williamson, and T. Novakov

Lawrence Berkeley Laboratory

University of California

Berkeley, California 94720

Abstract

Emission factors to total smoke particulates as well as organic and black carbon have been measured as a function of size for a set of building materials typical of those used in urban construction. Black carbon emissions (mass per fuel mass) were similar among the wood fuels studied, although the dominant form of combustion varied from flaming to smoldering. Black carbon was found predominantly in the finest size ranges (≤ 0.20 μm). Polyurethane foam produced a greater emission of black carbon, and the particle size distribution of that carbon extended to much larger aerodynamic diameters than did those of the wood samples. For the fuels tested, total smoke particle emissions ranged from 0.3 to 2.3 percent of fuel mass; black carbon emissions were 0.03 to 0.3 percent of fuel mass.

Introduction

The concept of "nuclear winter" has been postulated with a number of assumptions regarding the smoke produced by post-nuclear secondary fires.[1] The general premise is that sufficient smoke may be generated and deposited in the stratosphere to cause a decrease in the incident solar energy reaching the earth's surface. Such a change in the

net energy balance could potentially cause global cooling. Whether nuclear winter would occur in the aftermath of a nuclear exchange depends largely on the quantity of smoke generated, its distribution in the atmosphere, and the optical characteristics of the smoke produced.

Chemical kinetics during combustion are not understood in the detail necessary to predict smoke production. It has therefore been necessary to develop and use empirical methods to measure smoke generation.[2] Most of these methods have used optical techniques to quantify smoke production, with attenuation of light the principal measured parameter. None of the methods measured directly the size distribution or optical characteristics of smoke particles. A set of measurements of the black ("elemental") and organic carbon content of smoke particles from model forest fires has been reported.[3] The fuels were largely limited to pine needles, and no size segregation of the smoke particles was carried out.

We report here on a series of small-scale fire experiments that were conducted to measure the black carbon, total carbon, and total mass of smoke particles produced in the burning of building materials such as those found in urban environments.

Experimental Apparatus

Sample holders. Samples were tested in one of two orientations, depending on the nature of the product. The rigid building materials, including the Douglas fir, birch, and plywood samples, were tested in the parallel plate geometry; the flexible polyurethane samples were burned in the upward facing horizontal geometry.

The sample holder for the parallel plate geometry was adapted from the sample holder used for the proposed ASTM "Ease of Ignition" test apparatus.[4] The sample holders, constructed of brass bar stock, hold samples approximately 15 cm x 15 cm in face area. Two sample holders face each other across a 25.4-mm (1-in.) gap. Samples of varying thicknesses are accommodated and secured in the apparatus by four set screws at the back face of each holder that is used to hold test specimens in place. The

specimen holders are bolted to the load cell platform.

Specimens tested in the horizontal orientation had their edges and bottom face wrapped in aluminum foil. These specimens were then placed on the load cell platform.

Burner. The source of ignition use for these experiments varied with the geometry being considered. The horizontal samples, which consisted solely of flexible polyurethane foam, were readily ignited by touching a match to the center of the exposed top sample face. The wood-based building materials tested in the parallel plate geometry were more difficult to ignite so a more severe ignition source, a methane burner, was used.

The methane burner consists of a 13-mm (1/2-in.) stainless steel tube, which has 21 1.5-mm diameter holes bored along its length at intervals of about 6.5 mm. Methane from a gas cylinder is introduced into the tube at both ends to provide a flow rate of approximately 200-cm^3/s (25-SCFH). The burner tube is located centrally between the two sample holders at a distance of about 25-mm below the bottom of the two samples. The burner ports are located in the top of the tube so that the ignition flame extends up between the two samples. Smoke particle sampling was not conducted during the ignition phase.

Weight loss measurement instrumentation. Mass loss measurements were made during each experiment. The samples and sample holders were placed on top of a weighing cell (Automatic Timing and Controls, Model 6005C, 1-lb dynamic range), which transmits a signal proportional to load to a chart recorder.

Exhaust system assembly. The sample holder/weighing cell assembly is mounted on a platform, which was placed within a three-sided enclosure. This enclosure, constructed of sheet metal and measuring 0.91 m x 0.91 m x 1.22 m high (3 ft x 3 ft x 4 ft high), is topped by a pyramid-shaped reducer that terminates at the exhaust stack.

The exhaust stack is 100-mm (4-in.) diameter aluminum pipe. The length of the aluminum stack is 2.1 m. A 1.9-m length of 100-mm flexible duct connects the exhaust stack to the exhaust fan. This centrifugal blower produced flow rates of approximately

5.38 m^3/min (190 cfm) under test conditions, as determined by an orifice plate located in the aluminum stack.

Smoke sampling equipment. Two ports were milled opposite each other in the aluminum exhaust stack at a distance of 0.25 m below the top and approximately 3 m above the flame position. Sampling tubes of 6-mm (1/4-in.) diameter stainless steel were introduced into the exhaust duct through these ports. Total filter samples were withdrawn isokinetically through one of the sampling tubes and impactor samples through the other, each with a flow rate of 14.2 L/min (0.50 cfm). Samples were withdrawn by two rotary vane pumps connected with 13-mm i.d. nylon-braid vinyl tubing.

The impactor (Pilat Mark 5 Source Test Cascade Impactor) (University of Washington) was fitted with aluminum foil collection plate inserts on the impaction plates. These inserts were cleaned before use by sonication in reagent grade acetone, followed by two rinses in the same solvent. The foils were then allowed to dry and equilibrate in a humidity-controlled atmosphere (51% R.H.) before their tare weights were determined. The afterfilter was quartz fiber (Pallflex 2500QAO) that had been fired in air at 800 °C for 4 hours to remove all combustible carbon. The filters were humidity equilibrated as the foils before tare weights were determined. Following collection of a sample, the collection plate insert foils and afterfilter were removed from the impactor and returned to the humidity-controlled chamber. They were allowed to equilibrate for 24 hours before the weights were measured. The quartz and aluminum substrates used in this study are not optimum for mass determinations, but both are suitable for combustion carbon analyses. Replicate weighings showed that sample masses on the foils can be determined with a 1 σ error of 12 μg, and those on quartz with a 1 σ error of 20 μg.

The second sampling port was fitted with a filter stack unit composed of two stainless steel in-line 47-mm filter holders (Gelman Sciences Inc.). Each filter holder was loaded with a quartz fiber filter that had been treated as had the impactor afterfilter. Since we have shown that under ambient conditions the second (back-up) filter can

contain carbon loadings equal to 10% of the loading (total) filter,[5] presumptively from adsorbed gaseous hydrocarbons, it was decided that this technique would allow a realistic correction for nonparticulate organic carbon in the filter samples.

Sample Analyses

The samples were analyzed by CO_2 evolved gas analysis, a thermal technique that has been shown to quantitatively determine the total carbon content of ambient aerosol particles. The apparatus used is shown schematically in Fig. 1. The sample is heated in a linear temperature ramp programmed furnace in a stream of purified oxygen. The oxygen, together with any sample decomposition or combustion products, is then drawn immediately into a second furnace containing a platinum catalyst at 900 °C where all carbon-containing gases are converted to CO_2. The CO_2 concentration is continuously monitored in the gas stream by a nondispersive infrared analyzer (MSA, LIRA 202S). Oxygen that has been purified by passing over CuO at 900 °C and then through a bed of Ascarite is supplied to the combustion tube. The flow through the tube and CO_2 analyzer is maintained at a constant value by the critical orifice at the exhaust of the CO_2 analyzer. Thus, the sample carbon evolved during any part of the analysis can be calculated as the integral of the CO_2 signal during that time interval. Additionally, the blackness of the sample can be monitored for samples on quartz filters using the transmitted laser light intensity. This information can be used to confirm the temperature at which CO_2 from the combustion of black carbon is evolved. We have further shown that for ambient and combustion source samples on quartz filters, black carbon can be determined by measurement of the change in laser light transmission as the sample is burned.[6] Black carbon from combustion sources has an extinction coefficient for visible light large enough to totally absorb incident light in less than 1 μm. To the extent that particles of black carbon exceed this physical (not aerodynamic) particle size, the content reported by this technique will be less than that actually present.

For some samples, the black carbon peak in the CO_2 thermogram cannot be estimated unambiguously because of the simultaneous combustion of organic carbon. We have shown that for ambient particle samples on quartz filters, much of this organic material can be removed by solvent extraction without significantly affecting the black carbon.[6] Deposits on the foil collection plate inserts, however, are more readily disturbed during the extraction process; thus this procedure is not appropriate for them.

For each of the impactor and filter samples, total carbon was measured from the integrated area of the CO_2 thermogram, and black carbon was estimated from the area of the high temperature peak (e.g., Figs. 2-7). The high temperature peaks for these samples were identified as black carbon for the total and after filters by the laser optical technique. For each of the thermograms, blank values were subtracted equal to either the CO_2 thermogram of a blank aluminum foil or the thermogram for the backup filter in the filter stack as appropriate. Solvent extraction followed by evolved gas analysis was carried out on some of the filter samples to confirm the black carbon determination.

The black carbon content of each of the filter samples was also calculated from the change in transmission of incident laser light during the analysis. We applied an empirically determined relationship that we have determined to apply to aerosol particles collected in ambient air and from combustion sources. We have defined the term "attenuation," ATN, as

$$ATN = -100 \ln I/I_0 \, ,$$

where I and I_0 are the transmitted light intensities through the loaded and fully burned filter respectively. We have shown that for our fired quartz fiber filters, the relationship

$$ATN = -100 \ln (\alpha + (1-\alpha)\exp(-\sigma[BlC]) \, ,$$

gives the black carbon concentration [BlC] as a function of attenuation where the constants α and σ are 0.0172 and 0.239$\pm$0.020 respectively.[6]

Results

The summarized results from four test materials are shown in Tables 1-4. For each particle size fraction, the total mass of collected smoke particles, as well as the total carbon and black carbon content of those particles, is shown. Organic carbon is in each example equal to the difference between total and black carbon. The same information is shown graphically in Figs. 8-11. For each of the wood fuels, the preponderance of black carbon is present among the smallest size fraction collected, although organic carbon and non-carbon mass in the smoke particles may have a broader size distribution. Polyurethane foam also produces the majority of its black carbon smoke particles in the smallest size fractions, although it does show a broader size range for particles containing black carbon.

Agreement of the laser optical determined black carbon content with that determined by CO_2 evolved gas analysis is generally within 15% for the wood samples but differs by a factor of 2 for the polyurethane foam. The source of this relatively large disagreement may lie in the black carbon particle size distribution or in particle morphology. Assumptions regarding particle size and shape were made in the development of the laser transmission method; while these assumptions have proven valid for ambient particles and many combustion sources, they may not hold for fuels such as polyurethane. Observation during individual tests are listed in Table 6.

Replicate combustion tests were carried out on all materials reported here, for a total of 18 test fires. Complete analyses were carried out only as reported above; however, visual observations and weighings indicate that the results of these four complete tests are typical.

References

1. R.P. Turco, O.B. Toon, T.P. Ackerman, J.B. Pollack, and C. Sagan, "Nuclear winter: Global consequences of multiple nuclear explosions," Science *222*, 1283-1292 (1983).

2. S. Bard and P.J. Pagni, "Carbon particulate in small pool fire flames," J. Heat Trans.*103*, 357-362 (1981).

3. E.M. Patterson and C.K. McMahon, "Absorption characteristics of forest fire particulate matter," Atmos. Environ. *18*, 2541-2551 (1984).

4. ASTM Committee E5, *Draft Standard Method of Test for Time to Ignition of Solid Materials by Flame Exposure* (1980).

5. R. Dod, et al., "Investigation of sampling artifacts in filtration collection of carbonaceous aerosol particles," Lawrence Berkeley Laboratory report LBL-10735, pp. 8-35 to 8-37 (1980).

6. L.A. Gundel, R.L. Dod, H. Rosen, and T. Novakov, "The relationship between optical attenuation and black carbon concentration for ambient and source particles," Sci. Total Environ. *36*, 197-202 (1984).

Table 1. Run 2 - Douglas fir plywood.

Particle diameter (μm)	Total mass		Carbon mass		Black carbon mass	
	μg/sample	μg/g fuel	μg/sample	μg/g fuel	μg/sample	μg/g fuel
16-34	-	-	-	-	-	-
5.8-16	18 ±12	180 ±120	-	-	-	-
2.9-5.8	12 ±12	120 ±120	-	-	-	-
0.94-2.9	55 ±12	530 ±120	24 ±3	230 ±30	-	-
0.74-0.94	33 ±12	320 ±120	28 ±3	280 ±30	5 ±2	50 ±20
0.59-0.74	58 ±12	560 ±120	30 ±3	300 ±30	8 ±1	80 ±10
0.42-0.59	73 ±12	710 ±120	37 ±3	360 ±30	6 ±1	60 ±10
0.33-0.42	102 ±12	990 ±120	43 ±3	420 ±30	4 ±1	40 ±10
0.27-0.33	28 ±12	270 ±120	11 ±3	110 ±30	3 ±1	20 ±10
0.11-0.27	112 ±12	1090 ±120	95 ±5	920 ±50	34 ±3	330 ±30
<0.11	150 ±20	1460 ±190	103 ±5	1000 ±50	27 ±3	260 ±30
Total		6230 ±400		3620 ±100		840 ±50

Fuel mass lost during sampling = 39.0 g; or since 0.50/190 of the smoke was sampled, 0.103 g of fuel per sample.

Table 2. Run 13 - Douglas fir, solid wood.

Particle diameter (μm)	Total mass		Carbon mass		Black carbon mass	
	μg/sample	μg/g fuel	μg/sample	μg/g fuel	μg/sample	μg/g fuel
16-34	40 ±12	240 ± 70	-	-	-	-
5.8-16	48 ±12	280 ± 70	23 ± 3	130 ± 20	-	-
2.9-5.8	97 ±12	570 ± 70	32 ± 3	190 ± 20	-	-
0.94-2.9	205 ±12	1210 ± 70	83 ± 4	490 ± 20	-	-
0.74-0.94	139 ±12	820 ± 70	49 ± 3	290 ± 20	-	-
0.59-0.74	108 ±12	640 ± 70	71 ± 4	420 ± 20	-	-
0.42-0.59	382 ±12	2260 ± 70	210 ±10	1240 ± 60	4 ±1	20 ± 6
0.33-0.42	614 ±12	3630 ± 70	292 ±15	1730 ± 90	4 ±1	30 ± 6
0.22-0.33	187 ±12	1110 ± 70	90 ± 5	530 ± 30	-	-
0.11-0.20	569 ±12	3370 ± 70	276 ±14	1630 ± 80	2 ±1	10 ± 6
<0.11	1559 ±20	9220 ±120	868 ±43	5140 ±250	38 ±4	220 ±24
Total		23350 ±250		11790 ±290		280 ±26

Fuel mass lost during sampling = 64.1 g; or since 0.50/190 of the smoke was sampled, 0.169 g of fuel per sample.

Table 3. Run 15 - Flexible polyurethane foam.

Particle diameter (μm)	Total mass		Carbon mass		Black carbon mass	
	μg/sample	μg/g fuel	μg/sample	μg/g fuel	μg/sample	μg/g fuel
16-34	25 ±12	320 ±150	8 ±3	100 ± 40	1 ± 1	20 ± 10
5.8-16	22 ±12	280 ±150	-	-	2 ± 1	30 ± 10
2.9-5.8	-	-	18 ±3	230 ± 40	14 ± 1	180 ± 10
0.94-2.9	33 ±12	420 ±150	24 ±3	300 ± 40	22 ± 2	280 ± 30
0.74-0.94	-	-	13 ±3	170 ± 40	11 ± 1	140 ± 10
0.59-0.74	25 ±12	320 ±150	11 ±3	140 ± 40	9 ± 1	120 ± 10
0.42-0.59	-	-	12 ±3	150 ± 40	9 ± 1	120 ± 10
0.33-0.42	26 ±12	330 ±150	13 ±3	170 ± 40	13 ± 1	160 ± 10
0.20-0.33	24 ±12	310 ±150	9 ±3	110 ± 40	9 ± 1	110 ± 10
0.11-0.20	23 ±12	300 ±150	36 ±3	470 ± 40	31 ± 3	390 ± 40
<0.11	85 ±20	1090 ±260	176 ±9	2250 ±120	136 ±14	1750 ±180
Total		3370 ±480		4090 ±160		3300 ±190

Fuel mass lost during sampling = 29.6 g; or since 0.50/190 of the smoke was sampled, 0.0780 g of fuel per sample.

Table 4. Run 17 - Birch, solid wood.

Particle diameter (μm)	Total mass μg/sample	μg/g fuel	Carbon mass μg/sample	μg/g fuel	Black carbon mass μg/sample	μg/g fuel
16-34	45 ±12	83 ±22	-	-	-	-
5.8-16	45 ±12	83 ±22	-	-	-	-
2.9-5.8	65 ±12	119 ±22	6 ± 3	11 ± 6	-	-
0.94-2.9	92 ±12	169 ±22	31 ± 3	57 ± 6	-	-
0.74-0.94	75 ±12	138 ±22	11 ± 3	.20 ± 6	-	-
0.59-0.74	71 ±12	131 ±22	7 ± 3	13 ± 6	-	-
0.42-0.59	73 ±12	134 ±22	6 ± 3	12 ± 6	-	-
0.33-0.42	61 ±12	112 ±22	11 ± 3	21 ± 6	-	-
0.20-0.33	60 ±12	110 ±22	6 ± 3	11 ± 6	-	-
0.11-0.20	242 ±12	445 ±22	232 ±12	426 ±22	25 ±3	46 ± 6
<0.11	1129 ±20	2075 ±37	583 ±29	1072 ±53	59 ±6	108 ±11
Total		3479 ±79		1645 ±60		154 ±13

Fuel mass lost during sampling = 206.9 g; or since 0.50/190 of the smoke was sampled, 0.544 g of fuel per sample.

Table 5. Estimate of black carbon (Bl.C.) from fires, based on optical attenuation ($ATN = -100 \ln I/I_0$) of total filters and impactor afterfilters.

Fuel	Run no.	Fuel mass	ATN	Bl.C. $\mu g/cm^2$	Bl.C. $\mu g/sample$	Bl.C. $\mu g/g$ fuel	Total or afterfilter
Douglas fir plywood	2	39.0	178	7.8	75	731	Total
			59.7	2.6	25	239	After
Douglas fir solid wood	13	64.1	109	4.7	45	268	Total
			100	4.3	41	245	After
Flexible poly-urethane foam	15	29.6	262	12.0	116	1482	Total
			170	7.5	72	919	After
Birch solid wood	17	206.9	173	7.6	73	134	Total
			169	7.4	71	131	After

Table 6. Observations during individual tests.

Run 2 - Douglas fir plywood. The wood was ignited with a methane flame for 2 min prior to sampling. The wood burned with flaming for 4 min, following by 2 min of smoldering combustion before sampling was terminated.

Run 13 - Douglas fir solid wood. After ignition with a methane flame, we found it difficult to maintain flaming combustion. Sampling was carried out for 4 min, followed by reignition using the methane burner. Sampling was then resumed for another 6 min. The particles were brown in appearance with evidence of liquid nature.

Run 15 - Flexible polyurethane foam. The foam ignited easily with a match at the center of the top surface of the sample. Flames then moved out in a circular pattern, melting and burning the foam. Sampling was for 6 min, the time required to completely burn the fuel.

Run 17 - Birch solid wood. Ignition was with methane and was repeated twice as the flame died. Sampling was not conducted during ignition periods. Total sampling period was 9 min, exclusively while wood flames were present.
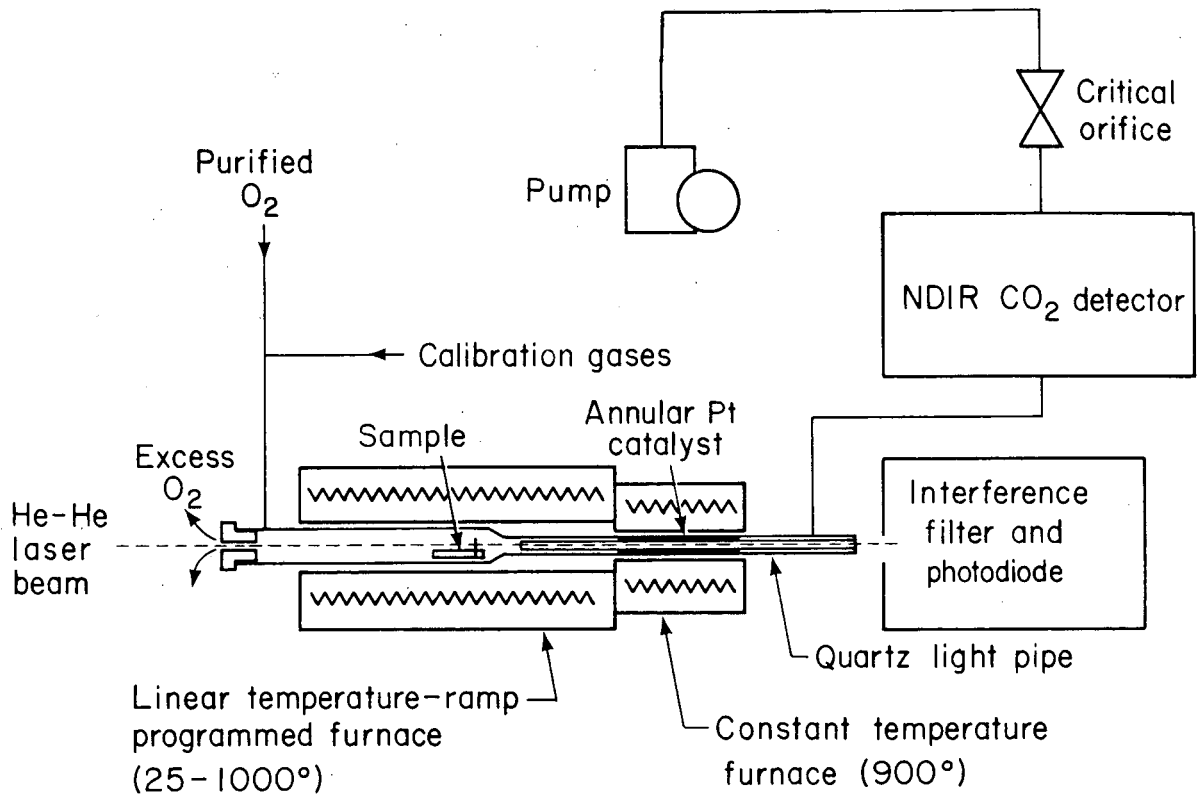
Figure 1.   Schematic diagram of CO_2 evolved gas analysis apparatus.
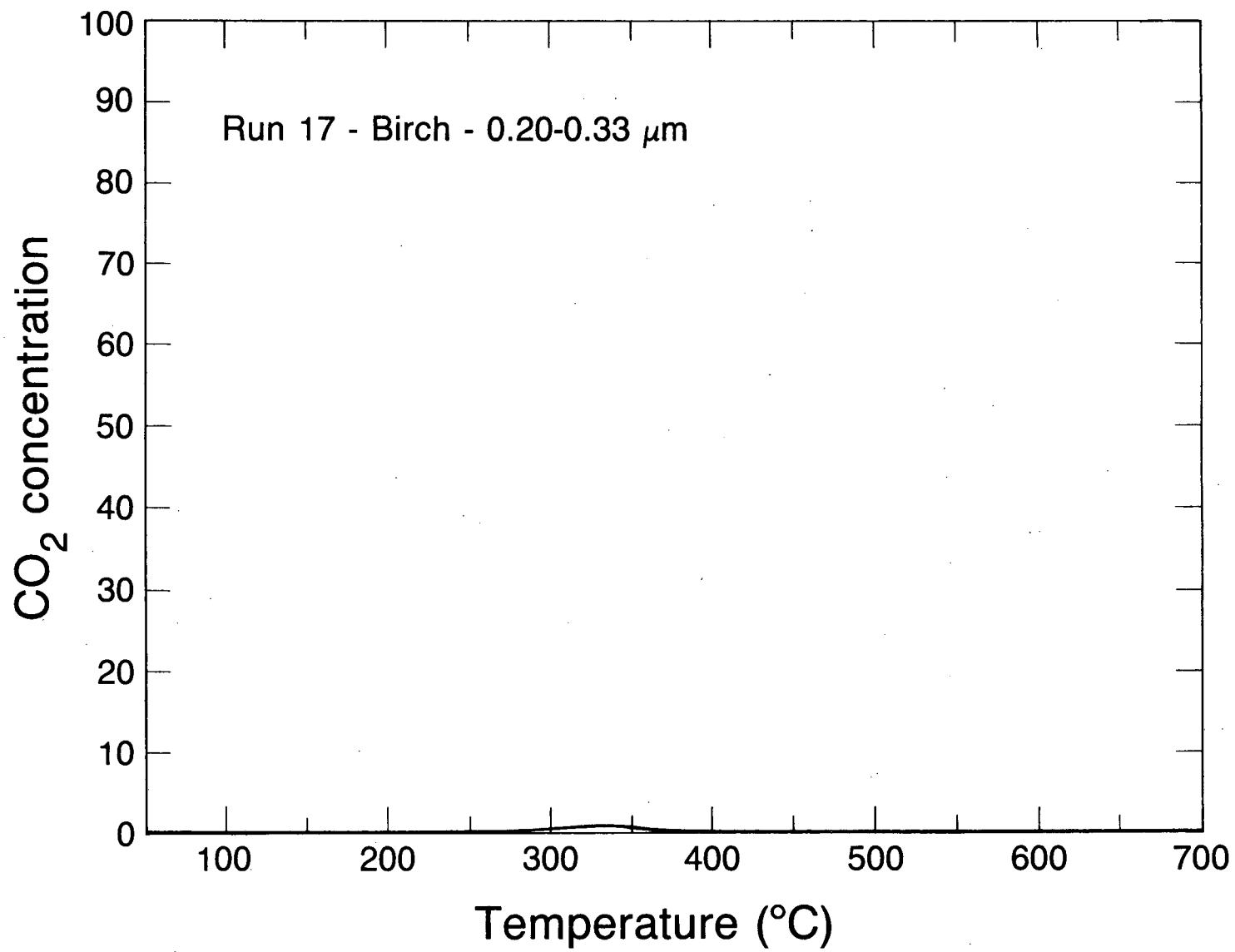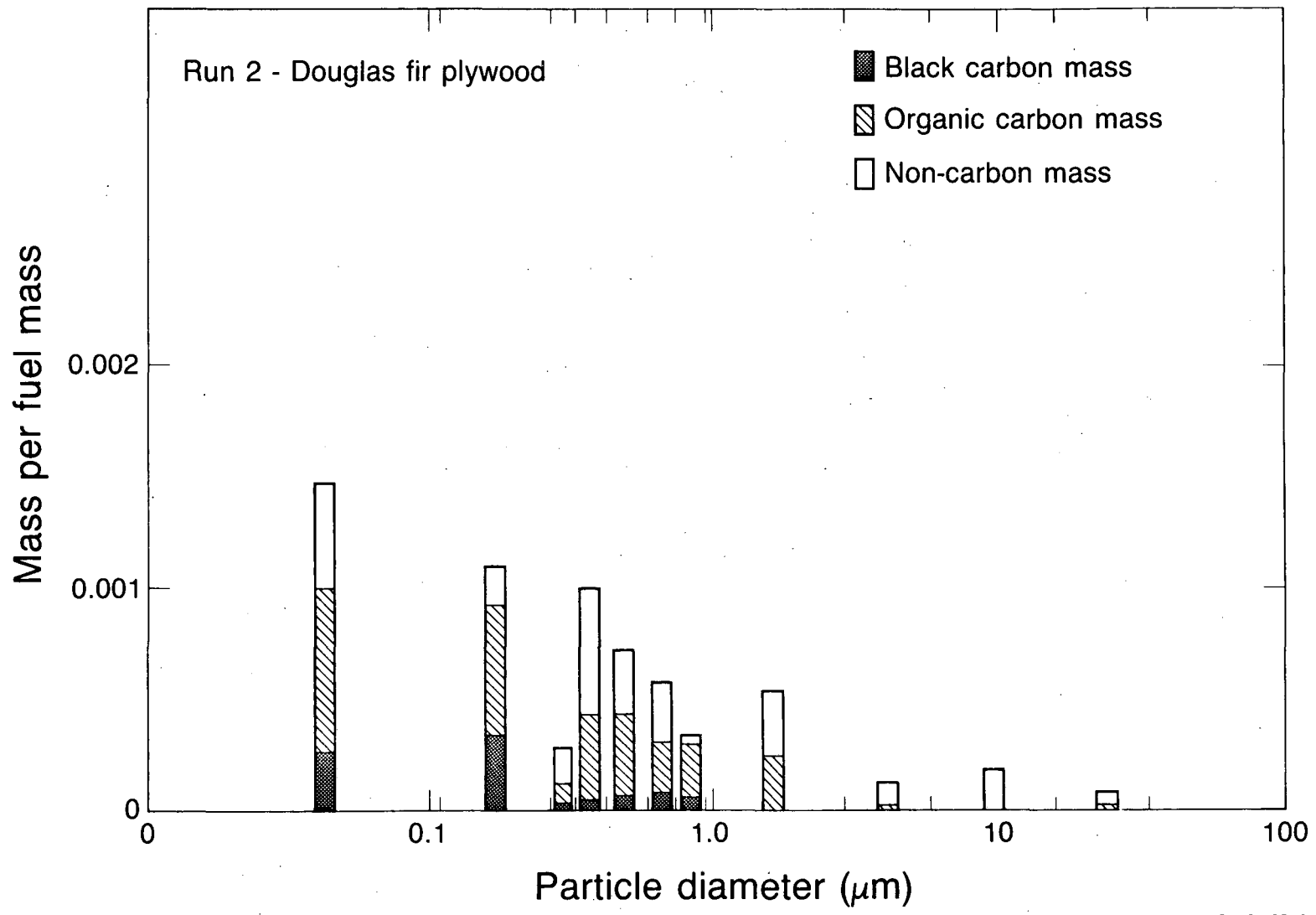
Run 15 - Polyurethane foam - <0.11 μm
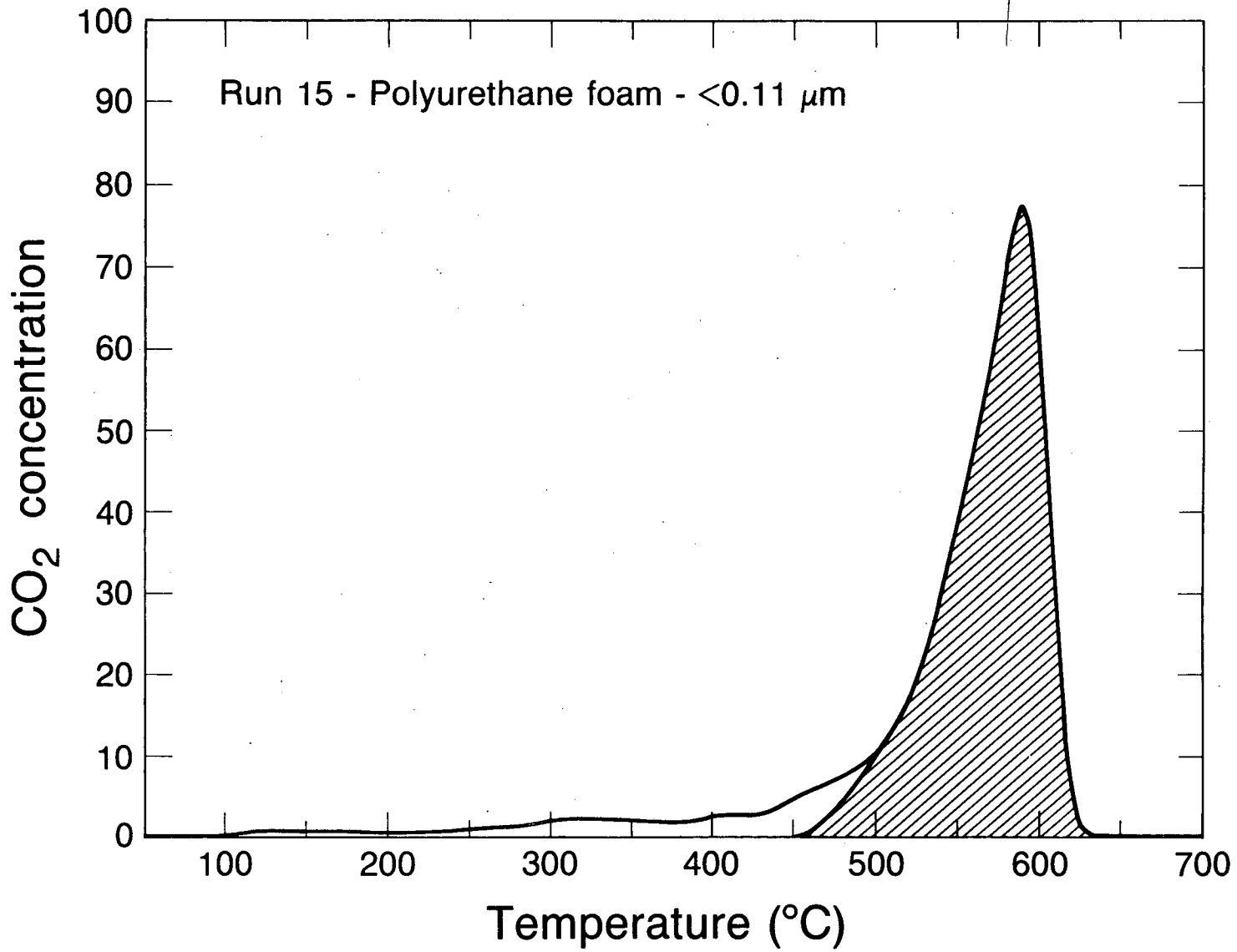
Figure 1.

XBL 8512-12813
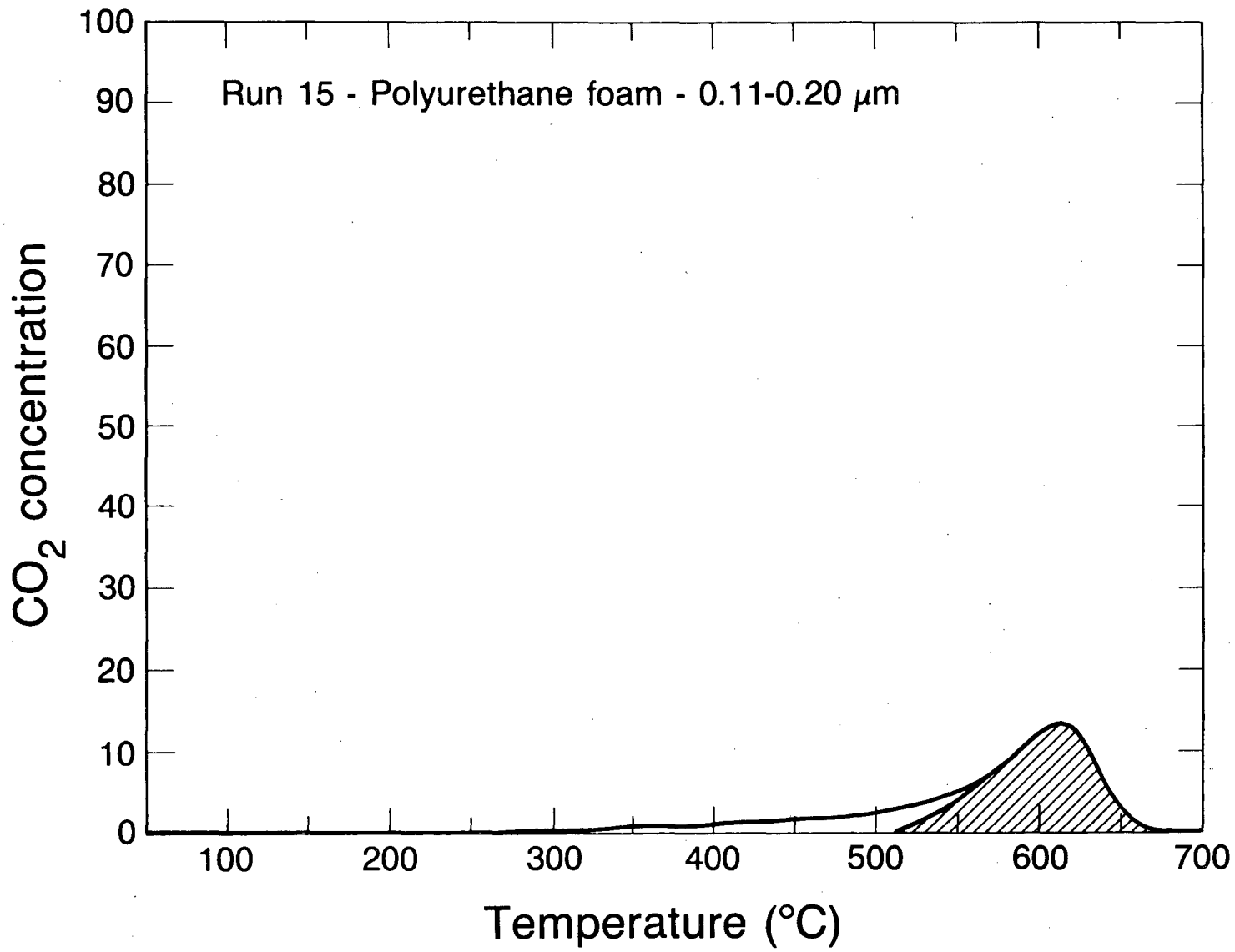
Figure 3.

XBL 8512-12814
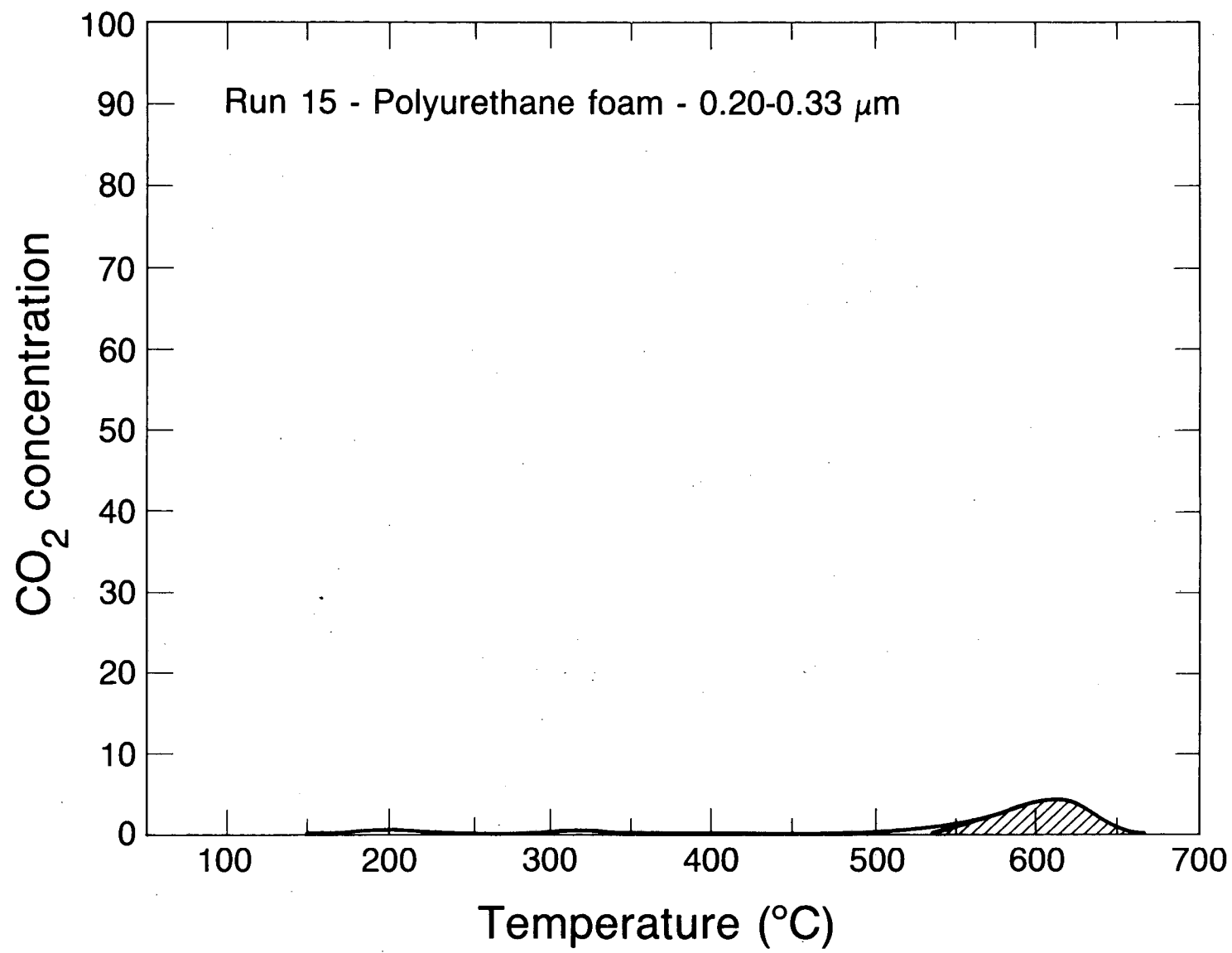
Figure 4.

XBL 8512-12815

Run 17 - Birch - <0.11 μm
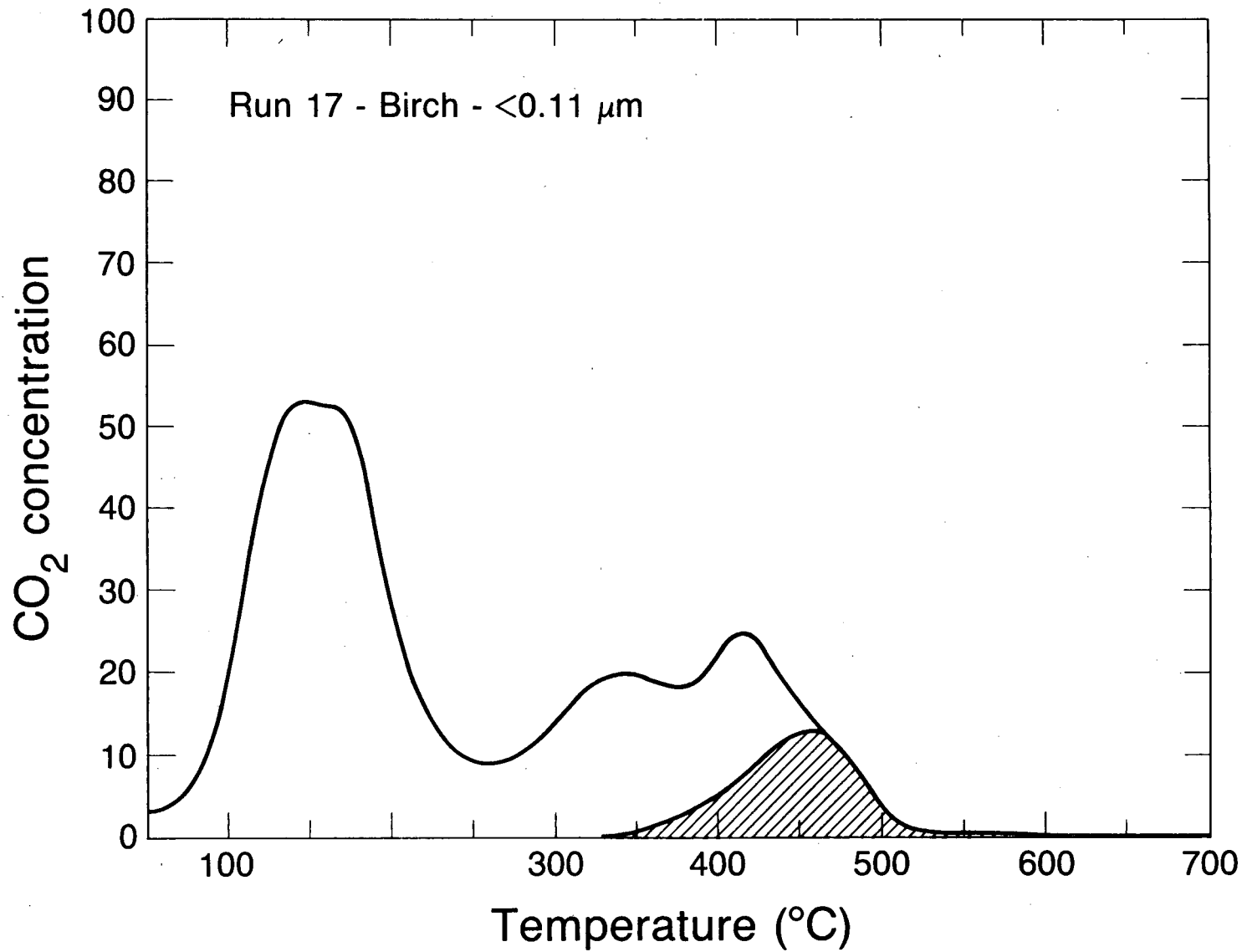
Figure 5.

XBL 8512-12816

19
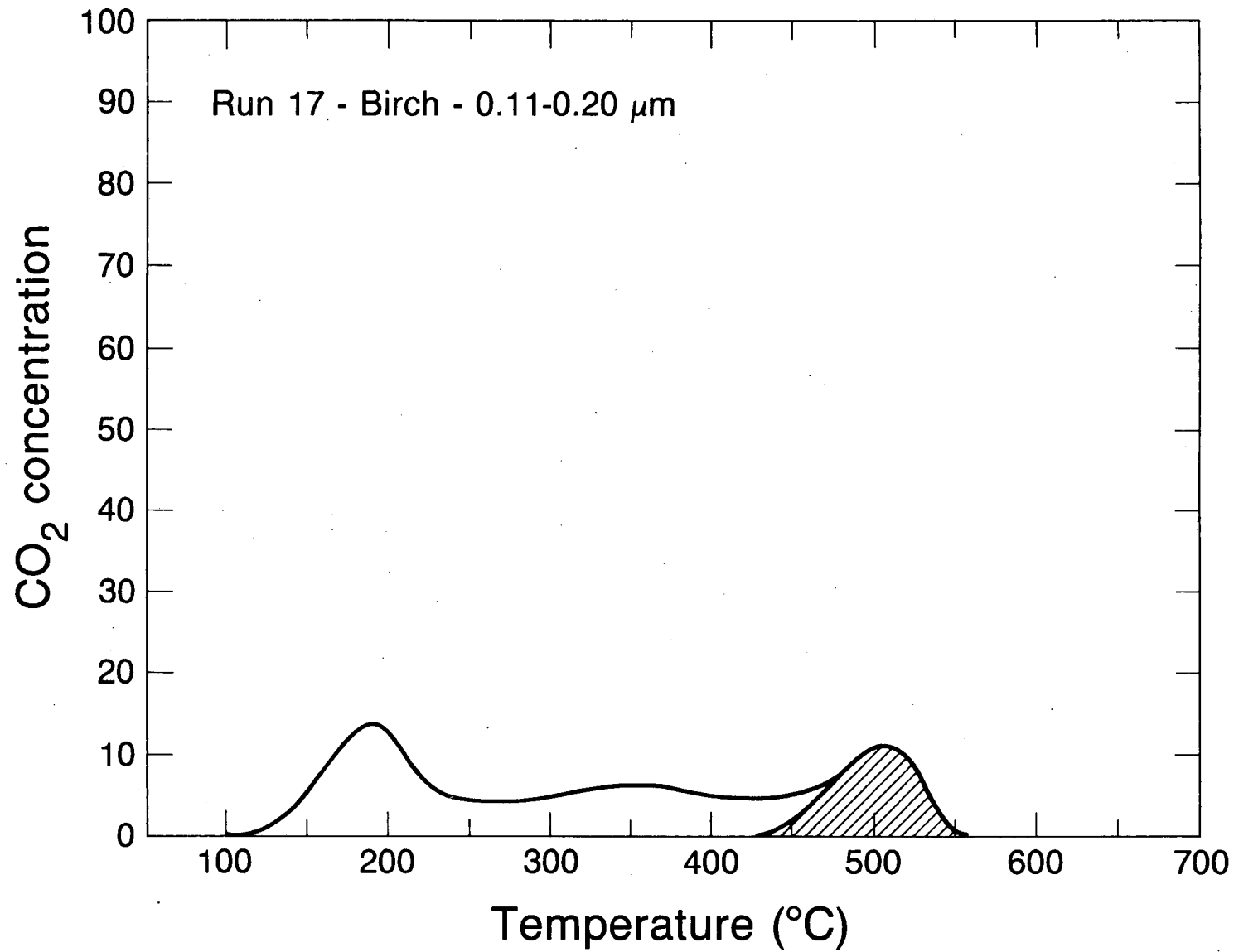
Figure 6.

XBL 8512-12817

Figure 7.

XBL 8512-12818

Figure 8.
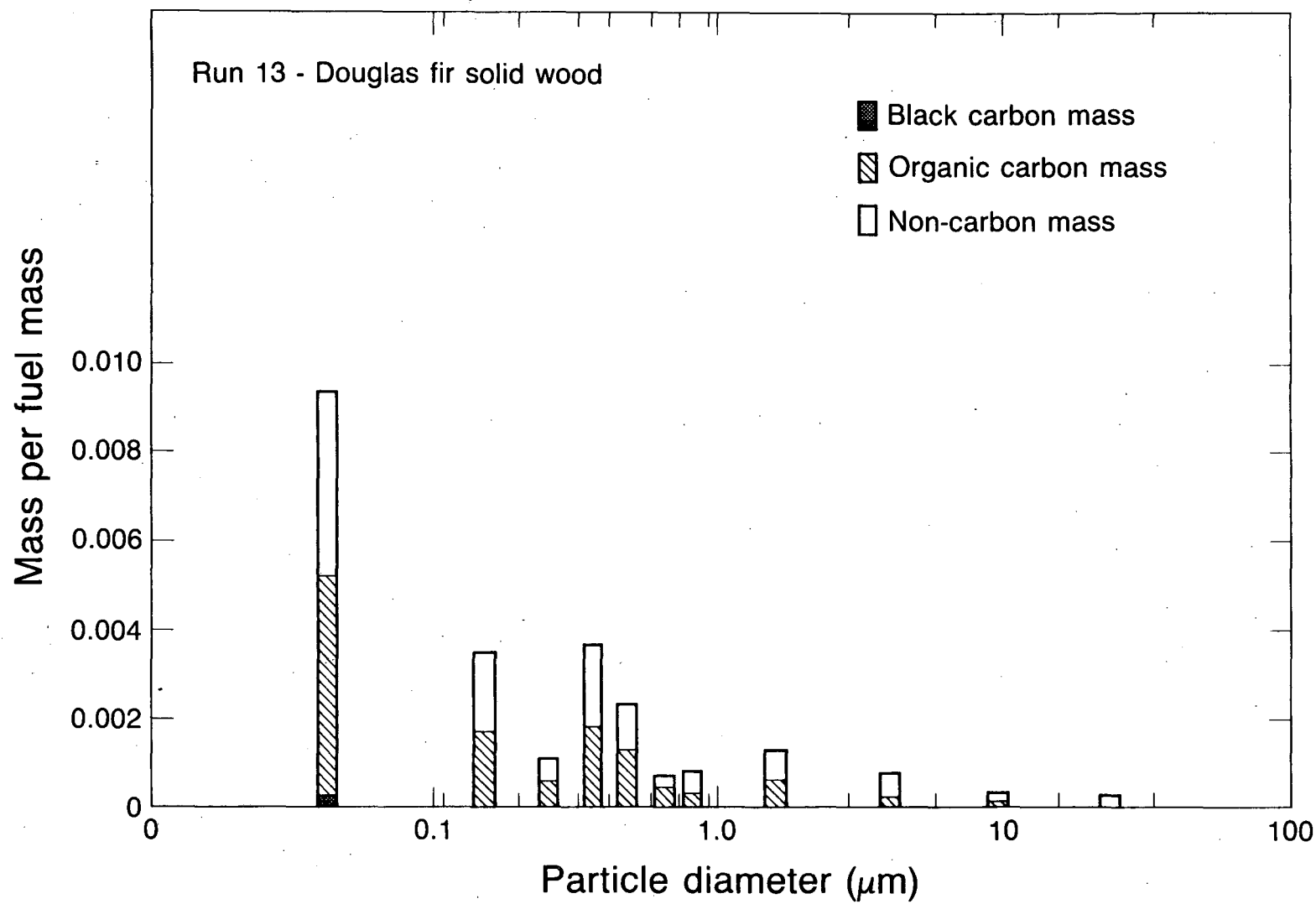
Figure 9.

XBL 8512-12820
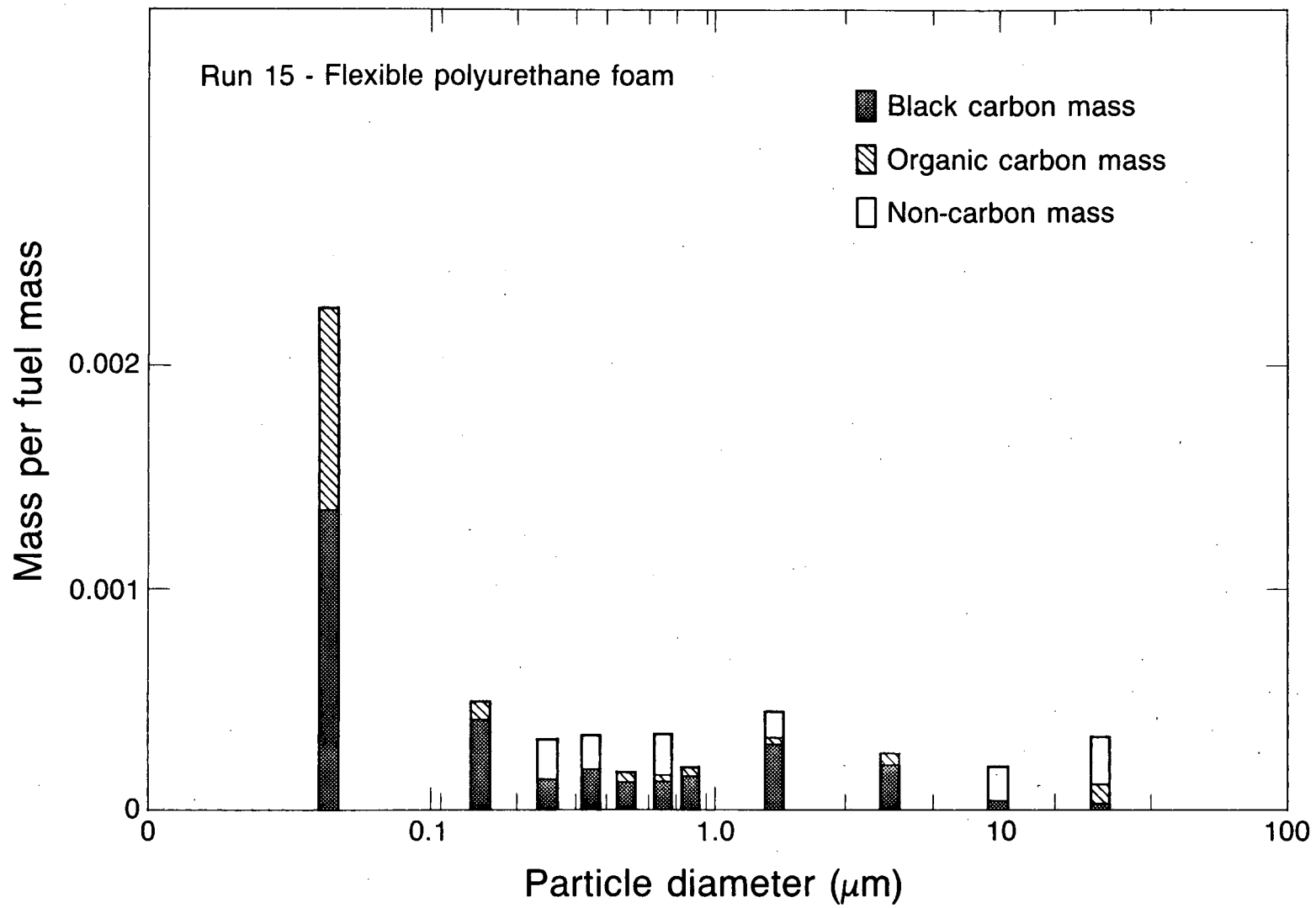
Figure 10.

XBL 8512-12821

Figure 11.

XBL 8512-12822