BORON CARBIDE 7506

B_4C MW: 55.26   CAS: 12069-32-8   RTECS: None

METHOD: 7506, Issue 2   **EVALUATION: PARTIAL**   **Issue 1: 15 May 1985**
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OSHA : no standard   **PROPERTIES:** solid; d 2.51 g/mL; MP 2350 °C
NIOSH: no standard
ACGIH: no standard

SYNONYMS: None

SAMPLING		MEASUREMENT	
SAMPLER:	CYCLONE + FILTER (10-mm cyclone, Higgins-Dewell (HD) + 5-µm PVC membrane)	**TECHNIQUE:**	X-RAY POWDER DIFFRACTION
		ANALYTE:	boron carbide
FLOW RATE:	HD cyclone: 2.2 L/min nylon cyclone: 1.7 L/min	**ASH:**	RF plasma asher
		SUSPEND:	in 2-propanol
VOL-MIN: -MAX:	100 L @ 1 mg/m^3 1000 L	**REDEPOSIT:**	0.45-µm Ag membrane filter
SHIPMENT:	routine	**XRD:**	Cu target X-ray tube Optimize for intensity; 1° receiving slit Graphite monochromator; scintillation detector Slow step scan, 0.02°/10 sec Integrated intensity with background subtraction
SAMPLE STABILITY:	stable		
FIELD BLANKS:	2 to 10 field blanks per set		
BULK SAMPLE:	required; area respirable or settled dust	**CALIBRATION:**	standard suspensions of B_4C in 2-propanol

ACCURACY		
RANGE STUDIED:	not studied	**RANGE:** 0.1 to 2 mg per sample
BIAS:	not determined	**ESTIMATED LOD:** 0.05 mg per sample
OVERALL PRECISION ($\hat{S}_{rT}$):	not determined	**PRECISION ($\hat{S}_r$):** 0.04 [1]
ACCURACY:	not determined	

APPLICABILITY: The working range is 0.2 to 4 mg/m^3 for a 500-L air sample. The method is specific for determining respirable boron carbide among other mine dusts.

INTERFERENCES: Titanium dioxide, silver, titanium diboride, niobium oxide, silver chloride interfere; also see APPENDIX A.

OTHER METHODS: This revises P&CAM 324 [1].

REAGENTS:

1. Boron carbide, ACS grade, <10-µm particle size.
    a. Wet-sieve ultrasonically with a 10-µm sieve to approximate respirable dust. Evaporate the alcohol. Dry the sieved material in an oven at 110 °C for 1 h, cool, and store in a desiccator.
2. 2-Propanol.
3. Desiccant.

EQUIPMENT:

1. Sampler:
    a. Filter: 37-mm diameter, 5.0-µm pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferrably, conductive) held together by tape or cellulose shrink band.
        NOTE: Test PVC filter for THF digestion (see Step 4).
    b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), or equivalent.
    c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Bulk sampler: PVC membrane filter, 37-mm, 5-µm pore size in two-piece filter cassette. Sample closed face at 4 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size. Filters commercially available (e.g., Poretics Corp., Millipore Corp.)
5. X-ray powder diffractometer equipped with copper target X-ray tube, graphite monochromator and scintillation detector.
6. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
7. Filtration apparatus and side-arm vacuum flask with 25- and 37-mm filter holders.
8. Sieve, 10-µm pore size, for wet sieving.
9. Analytical balance (0.01 mg).
10. Magnetic stirrer with thermally-insulated top.
11. Ultrasonic bath or probe.
12. Pipets, 2- to 20-mL.
13. Flask, volumetric, 1-L.
14. Desiccator.
15. Bottles, 1-L, with ground glass stoppers.
16. Drying oven.
17. Polyethylene wash bottle.
18. Beakers, borosilicate, 50-mL, and matching watchglasses.
19. Glue or tape for securing Ag filters to XRD sample holder.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with a nylon cyclone or 2.2 ± 5% with a HD cyclone for a total sample size of 100 to 1000 L. Do not exceed 2 mg dust loading on the filter.
    NOTE 1:   Do not allow the sampler assembly to be inverted at any time. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
    NOTE 2:   For determination of total boron carbide, sample on the PVC filter, without cyclone, at 1 to 4 L/min.
3. Take a bulk dust sample (e.g., 1 m ^{3} at 4 L/min).

SAMPLE PREPARATION:

4. Prepare the high-volume respirable dust or settled dust sample for qualitative analysis. Transfer to a filter and XRD sample holder by: (1) ashing and redepositing as described below for personal samples, (2) removing part of the dust from a thickly-coated sample and redepositing it, or (3) mounting all or part of the collection filter on the holder. The settled dust may be ground and/or wet sieved to best match the airborne dust exposure. Wet-sieving is done with a 10-µm sieve, 2-propanol, and an ultrasonic bath, followed by evaporation of excess alcohol, drying in an oven for 2 h, and overnight storage in a dessicator. Deposit the end product on a filter or pack in a conventional XRD powder holder and follow step 10.
    NOTE: For quantitative determination of percent boron carbide, weigh out, in triplicate, 2 mg of the respirable or sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with steps 6 and 7.
5. Place the filters in 50-mL beakers in the low temperature asher. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker.
6. Cover the beaker with a watchglass. Agitate in an ultrasonic bath for at least 3 min (until agglomerated particles are broken up). Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel. Control filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

8. Select six silver membrane filters randomly from the same box of filters used for depositing the samples. These will be used as media blanks to correct for sample self-absorption. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove and let dry. Determine the net normalized intensity for the silver peak, $\hat{I}^{\circ}_{Ag}$, for each media blank (step 11). Average the values for the six media blanks.
9. Prepare and analyze working standard filters.
    a. Weigh 10- and 100-mg portions of boron carbide to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L 2-propanol.
    b. Suspend the powder in 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer and add a stirring bar. Cool to room temperature before use.
    c. Mount a silver filter on the filtration apparatus. Place 2 to 4 mL 2-propanol on the filter. Turn off the stirrer and shake the suspension vigorously by hand. Immediately withdraw an aliquot from the center of the suspension. Do not adjust volume in the pipet by expelling

part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter, keeping the tip of the pipet just above the surface of the delivered suspension.

d. Rinse the pipet with several portions of 2-propanol, draining the rinses into the funnel.

e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Prepare working standard filters in triplicate by this technique at, e.g., 50, 100, 200, 500, 1000, and 2000 µg boron carbide.

f. Analyze by XRD (step 11). Use the same diffraction peaks and instrumental conditions as for samples. Designate the net and normalized XRD intensities for the working standard filters as I_x° (step 11.d) and $\hat{I}_x^\circ$ (step 11.e), respectively. Correct $\hat{I}_x^\circ$ for matrix absorption for standards containing >200 µg B_4C (steps 11.f and 12).

g. Prepare calibration graph ($\hat{I}_x^\circ$ vs. µg B_4C) using $1/\sigma^2$ weighted least squares.

h. Determine the slope, m (counts/µg), of the calibration graph. The intercept, b, of the line with the $\hat{I}_x^\circ$ axis should be zero ±5 µg.

MEASUREMENT:

10. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2-θ) of the settled dust bulk or high-volume respirable sample to determine the presence of boron carbide and any matrix interference (see APPENDIX). The expected diffraction peaks are:

	Peak (Degrees 2-θ)	
	Primary	Secondary
Boron carbide	37.80°	34.91°
Silver	38.12°	44.28°

11. Mount the filter (sample, standard or blank) in the X-ray diffractometer and:

a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N (approximately equal to the net count for the reference specimen peak). Use this value of N for all analyses.
NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently measured reference specimen intensity.

b. Measure the area of the most intense, interference-free diffraction peak of B_4C. Scan times must be long, e.g., 15 min.

c. Determine the position of the background for each sample. Measure the background on each side of the peak for one-half the time used for peak scanning. Add the counts from each side to obtain total background.

d. Calculate net intensity, I_x (peak count minus total background count).

e. Calculate the normalized intensity, $\hat{I}_x = I_x \cdot N/I_r$.

f. Determine the net normalized intensity, $\hat{I}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.

g. Scan each field blank over the same 2-θ range used for B_4C and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

12.   Calculate the concentration of boron carbide, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(T) - b}{m \cdot V} \text{ , mg/m}^3.$$

where: $\hat{I}_x$ = normalized intensity for sample peak
  b = intercept of calibration curve ($\hat{I}_x^\circ$ vs. W)
  m = initial slope of calibration curve, counts µg

  $f(T) = \dfrac{-R \ln T}{1 - T^R}$ = absorption correction factor (Table 1)

  $R = \sin(\theta_{Ag})/\sin(\theta_x)$
  $T = \hat{I}_{Ag}/(\text{average } \hat{I}_{Ag}^\circ)$ = transmittance of sample
  $\hat{I}_{Ag}$ = normalized silver peak intensity from sample
  average $\hat{I}_{Ag}^\circ$ = normalized silver peak intensity from media blanks (average of six values)

NOTE: For a more detailed discussion of the absorption correction procedure, see references [2] and [3].

EVALUATION OF METHOD:

The method was developed using the secondary B_4C peak because the primary B_4C peak interferred with the primary peak of AgCl, which is usually found on silver filters [1]. B_4C that was previously ground, sieved through a 10-µm sieve and dried, was used to prepare 30 working standards on 25-mm silver filters in the range 20 to 2000 µg per filter (10 levels, three at each level). The detection limit was 50 µg per filter. The limit of quantitation was 100 µg per filter. The calibration graph had a linear correlation coefficient of 0.9999 and a pooled relative standard deviation of 0.04 (n = 24). Recovery was 0.92 with s_r = 0.02 from five FWS-B (MSA Co.) filters spiked at the 600 µg level; the filters were ashed in a low temperature asher and were treated as described in SAMPLE PREPARATION.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 324, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[2] Leroux, J. and C. Powers. Direct X-Ray Diffraction Quantitative Analysis of Quartz in Industrial Dust Films Deposited on Silver Membrane Filters, Occup. Health Rev., 21, 26 (1970).
[3] Williams, D. D. Direct Quantitative Diffractometric Analysis, Anal. Chem., 31, 1841 (1959).

METHOD WRITTEN BY:

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APPENDIX:

INTERFERENCES

When using copper K α X-radiation, titanium dioxide (anatase) and the primary peak of silver interfere with the primary boron carbide peak; therefore, no measurements can be done with either the primary boron carbide or the silver peak. The secondary boron carbide peak is chosen as the analytical peak if no other interferences are present.

The secondary titanium diboride peak interferes to a small extent with the secondary boron carbide peak. The primary titanium diboride peak interferes with the secondary silver peak.

Niobium oxide interferes with the tertiary boron carbide peak.

Silver chloride, found as an impurity in the silver filter, may interfere with some low-intensity boron carbide peaks.

When peak overlaps are not severe, a smaller receiving slit or chromium X-radiation may be used; however, a new calibration graph will be necessary.

The presence of some elements in the sample (iron, in particular) can result in appreciable X-ray fluorescence, leading to high background intensity. This can be minimized by a diffracted beam monochromator.

The interfering effects of X-ray absorption by the sample result in attenuation of the diffracted beam and correction must be made (step 12 and Table 1).

Table 1. Matrix absorption correction factors, boron carbide/silver peak, degrees 2 θ.

Boron Carbide	34.91	23.54	22.11		34.91	23.54	21.11
Silver	44.28	44.28	44.28		44.28	44.28	44.28
T	f(T)	f(T)	f(T)	T	f(T)	f(T)	f(T)
1.00	1.000	1.000	1.000	0.74	1.2011	1.3038	1.3249
0.99	1.0063	1.0093	1.0099	0.73	1.2107	1.3187	1.3409
0.98	1.0127	1.0188	1.0200	0.72	1.2205	1.3340	1.3573
0.97	1.0193	1.0284	1.0302	0.71	1.2305	1.3495	1.3740
0.96	1.0259	1.0382	1.0407	0.70	1.2407	1.3654	1.3911
0.95	1.0326	1.0481	1.0513	0.69	1.2512	1.3816	1.4086
0.94	1.0394	1.0582	1.0620	0.68	1.2618	1.3982	1.4264
0.93	1.0463	1.0685	1.0730	0.67	1.2726	1.4152	1.4447
0.92	1.0533	1.0790	1.0842	0.66	1.2836	1.4325	1.4633
0.91	1.0604	1.0897	1.0955	0.65	1.2949	1.4502	1.4824
0.90	1.0676	1.1005	1.1071	0.64	1.3064	1.4683	1.5019
0.89	1.0750	1.1115	1.1189	0.63	1.3182	1.4868	1.5218
0.88	1.0825	1.1227	1.1309	0.62	1.3302	1.5058	1.5423
0.87	1.0900	1.1342	1.1431	0.61	1.3425	1.5252	1.5632
0.86	1.0977	1.1458	1.1555	0.60	1.3550	1.5450	1.5846
0.85	1.1056	1.1576	1.1682	0.59	1.3678	1.5654	1.6066
0.84	1.1135	1.1697	1.1811	0.58	1.3809	1.5862	1.6290
0.83	1.1216	1.1820	1.1943	0.57	1.3944	1.6076	1.6521
0.82	1.1298	1.1945	1.2077	0.56	1.4081	1.6295	1.6757
0.81	1.1382	1.2073	1.2213	0.55	1.4221	1.6519	1.7000
0.80	1.1467	1.2203	1.2353	0.54	1.4365	1.6750	1.7249
0.79	1.1554	1.2335	1.2495	0.53	1.4513	1.6986	1.7504
0.78	1.1642	1.2470	1.2640	0.52	1.4664	1.7229	1.7766
0.77	1.1732	1.2608	1.2787	0.51	1.4819	1.7478	1.8036
0.76	1.1823	1.2749	1.2938	0.50	1.4979	1.7734	1.8312
0.75	1.1916	1.2892	1.3092				

T = sample transmittance (step 12).
f(T) = sample correction factor (step 12).