

DIBORANE

6006



MW: 27.67

CAS: 19287-45-7

RTECS: HQ9275000

METHOD: 6006, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA : 0.1 ppm
 NIOSH: 0.1 ppm
 ACGIH: 0.1 ppm
 (1 ppm = 1.131 mg/m³ @ NTP)

PROPERTIES: gas; vapor density (air = 1) 0.96;
 BP -92.5 °C; MP -165.5 °C
 explosive range 0.8 to 98% v/v in air

SYNONYMS: boroethane, boron hydride

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + SOLID SORBENT TUBE (PTFE filter + oxidizer-impregnated charcoal, 100 mg/50 mg)	TECHNIQUE:	PLASMA EMISSION SPECTROMETRY
FLOW RATE:	0.5 to 1 L/min	ANALYTE:	boron
VOL-MIN:	60 L @ 0.1 ppm	DESORPTION:	10 mL 3% H ₂ O ₂ ; stand 30 min; ultrasonic bath 20 min
-MAX:	260 L	WAVELENGTH:	249.8 nm
SHIPMENT:	routine	ENTRANCE SLITS:	50 x 300 mm
SAMPLE STABILITY:	at least 7 days @ 25 °C [1]	CALIBRATION:	aliquots of 1% (v/v) diborane adsorbed on impregnated charcoal
FIELD BLANKS:	2 to 10 field blanks per set	RANGE:	7 to 30 µg diborane per sample [1]
ACCURACY		ESTIMATED LOD:	1 µg diborane per sample [1]
RANGE STUDIED:	0.06 to 0.25 mg/m ³ (120-L samples) [1]	PRECISION (\hat{S}_r):	0.063 @ 7 to 27 µg diborane per sample [1]
BIAS:	- 4.8%		
OVERALL PRECISION (\hat{S}_{rT}):	0.085 [1]		
ACCURACY:	± 21.5%		

APPLICABILITY: The working range is 0.05 to 0.22 ppm (0.06 to 0.25 mg/m³) for a 120-L air sample.

INTERFERENCES: The filter removes boron-containing particulates. Avoid borosilicate glassware during sample preparation to prevent boron contamination of samples. Higher boranes (e.g., tetraborane) interfere but are not likely to be encountered in most samples.

OTHER METHODS: This revises P&CAM 341 [2]. The measurement can also be done by inductively-coupled plasma atomic emission spectrometry (e.g., Method 7300).

REAGENTS:

1. Diborane, 1% (v/v), certified gas mixture.*
2. Hydrogen peroxide (H_2O_2), 3% w/v in deionized water.
3. Calibration stock solution, 1000 $\mu\text{g B/mL}$, commercially available or dissolve 0.572 g boric acid (H_3BO_3) in deionized water to make 100 mL solution. Store in a polyethylene bottle.
4. Argon, for DC plasma excitation.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. PTFE membrane filter, 13-mm diameter, 1- μm pore size (e.g., Millipore FALP), in a plastic cassette (Millipore SX00013 or equivalent).
 - b. Glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections (100 mg and 50 mg) of oxidizer-impregnated charcoal; separated and retained by silylated glass wool plugs.
2. Personal sampling pump, 0.5 to 1 L/min, with flexible connecting tubing.
3. Plasma emission spectrometer with a DC plasmaexcitation source.
4. Pipets, plastic, 10-mL, and 5- to 50- μL .
5. Volumetric flasks, plastic, 10-mL.
6. Bottles, screw-top, plastic, 60-mL.
7. Syringe, plastic, 10-mL, fitted with 0.5- μm PTFE filter.
8. Vials, plastic, 7-mL, screw-on septum caps.
9. Ultrasonic bath.
10. Gas-tight syringes, 0.5- and 5-mL, graduated.

SPECIAL PRECAUTIONS: Diborane is very toxic and flammable, having an Immediately Dangerous to Life or Health (IDLH) level of 40 ppm. It is a strong irritant with a repulsive, sweet odor [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the charcoal tubes immediately before sampling. Attach the filter cassette in front of the charcoal tube with a short piece of tubing. Attach the outlet of the charcoal tube to the personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 1 L/min for a total sample size of 60 to 260 L.
4. Separate the filter and the charcoal tube. Cap the charcoal tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Pipet 10.0 mL 3% H_2O_2 into a series of plastic bottles. Quickly add the front and back charcoal sections to separate bottles and screw on the caps. Discard the glass wool plugs.
6. Allow to stand 30 min and then place in an ultrasonic bath for 20 min.
7. Draw the sample through a 0.5- μm PTFE membrane filter with a syringe.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
 - a. Add known amounts of calibration stock solution to 3% H_2O_2 in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain boron concentrations in the range 0.1 to 4 $\mu\text{g B/mL}$.

- b. Analyze with samples and blanks (steps 11 and 12).
- c. Prepare calibration graph (response vs. μg boron).
9. Determine desorption efficiency (DE) at least once for each lot of impregnated charcoal in the range of interest. Prepare three tubes at each of five levels plus three media blanks.
 - a. Place 100 mg impregnated charcoal (e.g., unused front sorbent section) in a vial and screw on the septum cap.
 - b. Flush the gas-tight syringe with inert gas (e.g., N_2). Inject a known amount (0.1 to 5 mL) of diborane gas mixture with the syringe into the vial. Treat two parallel blanks in the same manner except that no diborane is added.
 - c. Allow the vials to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. μg boron recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set spectrometer to conditions on page 6006-1 and as specified by the manufacturer.
12. Analyze standards and samples.
NOTE: If response is above the range of the standards, dilute the sample solution with 3% H_2O_2 , reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of boron found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of diborane in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 1.28}{V}, \text{ mg/m}^3.$$

where: 1.28 = the stoichiometric conversion factor from boron to diborane.

EVALUATION OF METHOD:

The method was tested by analyzing 18 samples, prepared by spiking 100 mg of impregnated charcoal with 6.7, 13.4 or 26.8 mg of diborane gas representing the equivalent of 120-L air samples at 0.05, 0.1 and 0.2 ppm [2]. Desorption efficiency was determined to be 0.889, 0.964, and 0.994 at these three concentrations, respectively. After analysis, the precision at the three concentrations was 8.4, 4.0, and 3.8%, respectively. Test atmospheres at 0.05, 0.1, and 0.2 ppm were generated using diborane gas. The samples were collected at 1 L/min for 2 hours in charcoal tubes containing 100 mg front/50mg back of impregnated charcoal. Eighteen samples were collected, and were desorbed one day later. The backup sections of the samples at 0.2 ppm were analyzed also. Six additional generated samples at 0.1 ppm were stored and analyzed seven days later. The average recovery of the 18 samples was 95.2%, pooled $\bar{S}_r = 2.7\%$. No trace of diborane (boron) was found in the backup section.

The seven-day storage stability samples indicated an average recovery of $101.6 \pm 2.1\%$.

Breakthrough tests were conducted with a generated test atmosphere at 1.9 ppm with four impregnated charcoal tubes. The sample volume was 120 L. The average collection efficiency in the front sections was $99.8 \pm 0.3\%$. Breakthrough occurred in only two samples indicating 0.6 and 0.2% breakthrough. An additional breakthrough study was conducted with a generated test atmosphere containing 0.34 ppm diborane at a relative humidity of 60 to 70%. Two impregnated charcoal tubes were collected after

60 min, two after 120 min, and two after 235 min. No breakthrough was detected in any sample. Therefore, the capacity of the charcoal tube is at least 80 µg diborane.

A filter study was conducted with 12 samples collected simultaneously, six with a prefilter and six without the prefilter, at 0.1 ppm. The results indicated that the use of the PTFE filters does not affect the precision or accuracy of the method. Mixed cellulose ester membrane prefilters produced a loss of 7.5% in the collection efficiency and, therefore, are not recommended as prefilters.

REFERENCES:

- [1] Arthur D. Little, Inc., Backup Data Report for Diborane, prepared under NIOSH Contract No. 210-80-0099 (June 1, 1981).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 341, U.S. Department of Health and Human Services, Publ. (NIOSH) 82-100 (1981).
- [3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

METHOD REVISED BY:

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