DECABROMODIPHENYL OXIDE 2559

$C_{12}Br_{10}O$ MW: 959.12 CAS: 1163-19-5 RTECS: KN3525000

METHOD: 2559, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : no PEL
NIOSH: no REL
ACGIH: WEEL: 5.0 mg/m^3

PROPERTIES: solid, white powder; MP 300 °C; sp gr 3.0; decomposes @ ca. 425 °C

SYNONYMS: DBDPO; Pentabromophenyl ether; bis(pentabromophenyl)ether; decabromodiphenyl ether; decabromobiphenyl ether.

SAMPLING

SAMPLER: Filter (Quartz fiber filter, 37-mm)

FLOW RATE: 2.0 L/min

VOL-MIN: 48 L
-MAX: 960 L

SHIPMENT: Ship at ambient temperature.

SAMPLE STABILITY: At least 30 days @ room temp.

BLANKS: 2 to 10 field blanks per set.

ACCURACY

RANGE STUDIED: Generated atmospheres not studied.

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{rT}$): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Decabromodiphenyl oxide (DBDPO)

DESORPTION: 1.5 mL DMSO; place on a rotary shaker for minimum of 2 hours.

INJECTION VOLUME: 5 µL

MOBILE PHASE: 98% methanol/2% pH 7 buffer of KH_2PO_4 and Na_2HPO_4 @ 0.225 mL/min; ambient temperature.

COLUMN: C-18, 5 µm, 150 cm x 2.1 mm ID or equivalent .

DETECTOR: UV absorption @ 228 nm.

CALIBRATION: DBDPO dissolved in DMSO.

RANGE: 2 to 240 µg per sample.

ESTIMATED LOD: 1.0 µg per sample.

PRECISION ($\bar{S}_r$): 0.038 @ 2.6 to 240 µg per sample. [1]

APPLICABILITY: The working range is 0.002 to 5.0 mg/m^3. An appropriate range of calibration standards should be used to bracket the expected analyte concentration range. To prevent the need to switch detector sensitivity settings for field samples with higher levels of DBDPO, a calibration curve made from standards containing greater levels of DBDPO may be appropriate. This method was developed to analyze DBDPO in an air sample.

INTERFERENCES: None identified - however, compounds with a similar retention time may interfere. Positive identification may be confirmed by dual column chromatography using an appropriate alternative LC column. Identification can also be confirmed by mass spectrometry.

OTHER METHODS: None identified.

REAGENTS:

1. Methanol, HPLC grade.*
2. Dimethyl Sulfoxide (DMSO), HPLC grade.*
3. Decabromodiphenyl oxide, 98%. Sold as Pentabromophenyl ether (Sigma-Aldrich, Milwaukee, WI., or equivalent).*
4. Potassium dihydrogen phosphate (KH_2PO_4). (Sigma-Aldrich, Milwaukee, WI., or equivalent).
5. Disodium hydrogen phosphate (Na_2HPO_4). (Sigma-Aldrich, Milwaukee, WI., or equivalent).
6. Mobile phase buffer: 1.509 g KH_2PO_4 and 2.477 g Na_2HPO_4 in 1 L deionized water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: quartz fiber filter, 37-mm diameter, 0.45 mm thick (SKC, Eighty Four, PA, or equivalent), backed by a cellulose support pad 37-mm OD, in a two part, 37-mm cassette filter holder.
2. For calibration and QC samples, filter spacer rings are used instead of a support pad. Spacer Ring, 37 mm (SKC, Eighty Four, PA).
3. Personal sampling pump capable of operating for 8 hr at 2 L/min., with flexible connecting tube.
4. Labquake rotary shaker or equivalent.
5. Vials, Autosampler, glass with PTFE lined crimp or screw top cap.
6. Forceps.
7. Syringes, glass: 5-µL, 10-µL, 1-mL, other sizes as needed.
8. Liquid Chromatograph: Shimadzu LC-10ADvp pump, SIL-10ADvp auto injector, and SPD-10AVvp UV detector (or equivalent), Alltech Alltima C-18 5µ, 150 X 2.1 mm column (or equivalent).

SPECIAL PRECAUTIONS: Decabromodiphenyl Oxide is a cancer suspect agent and irritant. Methanol is a flammable liquid, toxic. DMSO is an irritant, wear protective clothing as it can penetrate the skin.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate of 1.0 to 2.0 L/min for a volume of 48 to 960 L.
3. After the sample is collected, place the plastic plugs in the tubing connector stubs on the sampling cassette.

SAMPLE PREPARATION:

4. Extract Filters:
   a. Remove the filter from the cassette with a pair of forceps, discard the support pad, fold the filter and transfer to an autosampler vial.
   b. Add 1.5 mL of DMSO and cap the vial with the appropriate top.
   c. Place the vial on the labquake rotary shaker (VWR Scientific, Batavia, IL). Rotate the samples for a minimum of 2 hours. Place samples in an ultrasonic bath for 30 minutes.
      NOTE: Decabromodiphenyl oxide is not a highly soluble compound. To insure complete solubility, both manual agitation and sonication are used on the samples to solubilize the decabromodiphenyl oxide.
5. Prepare the filter extract for analysis.
   a. Carefully remove the septum cap from the vial containing the extracted filter.
   b. Using a transfer pipette, remove as much liquid extract from the extraction vial as possible and transfer to an autosampler vial. Cap the vial with an appropriate septum cap.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six calibration standards to cover the concentration range of the samples. A typical liquid chromatogram of a DBDPO standard is shown in Figure 1.
   a. Prepare calibration standards by adding known amounts of the DBDPO standard solution or a secondary stock solution prepared from the standard solution to an autosampler vial containing 1.5 mL DMSO.
   b. Analyze with samples and blanks (steps 9 & 10).
   c. Prepare a calibration graph (peak area vs. µg DBDPO).
7. Determine the recovery (R) of the analyte from the sampling media using the quartz fiber filters with analyte spikes in the concentration range of the samples (see step 6). Prepare three filters at each of five levels plus two media blanks.
   a. Place a filter spacer ring in the bottom section of a two part 37-mm filter cassette. Place a 37-mm quartz fiber filter on top of the spacer ring (do not use a support pad).
   b. Inoculate the filter with a known amount of calibration stock solution with a microliter syringe, place the top section of the cassette in place and seal the filter in place by squeezing the two sections together.
   c. Place the plugs in the inlet and outlet tubing stubs and set the cassettes aside for a minimum of twelve hours.
   d. Prepare the filter samples (steps 4 & 5) and analyze with the calibration standards.
   e. Prepare a graph of R vs. µg DBDPO.
8. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and R graph are in control.

MEASUREMENT:

9. Set the liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2559-1. Inject sample with autosampler or by manual injection.
   NOTE: If peak area is above the linear range of the calibration standards, dilute the sample with DMSO, reanalyze, and apply the appropriate dilution factor in calculations. Or, prepare a calibration curve with standards of higher levels of DBDPO.
10. Measure peak area of DBDPO peak and determine µg per sample from calibration graph.

CALCULATIONS:

11. From the calibration graph, determine the mass, µg (corrected for R) for the sample (W), and average media blank (B).
12. Calculate concentration, C, of decabromodiphenyl oxide in the air volume sampled, V(L):

$$C = \frac{(W - B)}{V}, mg / m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

This method was not evaluated with laboratory generated air samples. All of the recovery and storage study determinations have been performed with laboratory spiked filters in the development of this method. Air was not pulled through the filters prior to analysis.

The LOD/LOQ values are 1.0 µg/sample and 3.3 µg/sample respectively, based on a liquid standard calibration curve.

Recovery of spiked quartz fiber filters ranged from 94.5% to 104.2% for analyte quantities of 2.63 to 25.1 µg/filter using liquid standards as the spiking solution.

A thirty day storage stability study of DBDPO spiked on quartz fiber filters indicates that the recovery of the analyte at a level of 5.01 µg/filter (N=12) is 103.0%. The samples were stored in a closed cardboard container at room temperature for the duration of the study.

REFERENCES:

[1] Jaycox LB, May LR [2001]. Backup data report for decabromodiphenyl oxide method development, Cincinnati, OH: National Institute for Occupational Safety and Health, DART/NIOSH (unpublished report).
[2] Riess M, van Eldik R [1998]. Identification of Brominated Flame Retardants in Polymeric Materials by Reversed-Phase Liquid Chromatography with Ultraviolet Detection. J Chromatography, *827* 65-71.

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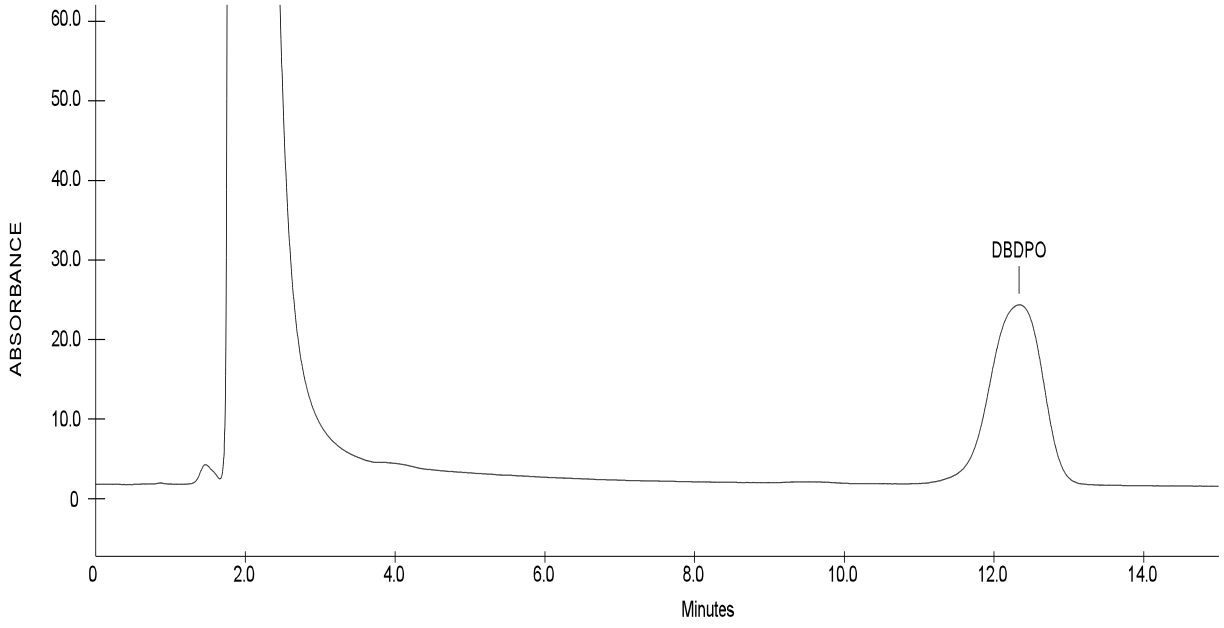

FIGURE 1: This chromatogram shows a standard of decabromodiphenyl oxide at 22.0 ug/sample. The major peak at approximately 12.2 minutes is DBDPO.