

# BENZOTHAZOLE IN ASPHALT FUME

2550

C<sub>7</sub>H<sub>5</sub>SN

MW: 135.19

CAS: 95-16-9

RTECS: DL0875000

METHOD: 2550, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 January 1998

OSHA: no PEL  
 NIOSH: no REL  
 ACGIH: no TLV

PROPERTIES: liquid; d 1.246 g/mL @ 20 °C; MP 2 °C; BP 231 °C; vp 4.5 kPa (34.0 mm Hg) @ 131 °C; vapor density 4.7 (air = 1)

SYNONYMS: Benzosulfonazole; 1-Thia-3-azaindene

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER + SORBENT TUBE (2-µm, 37-mm, PTFE + XAD-2, 100/50 mg)	<b>TECHNIQUE:</b>	GAS CHROMATOGRAPHY, SULFUR CHEMILUMINESCENCE DETECTOR
<b>FLOW RATE:</b>	1.0 to 2.0 L/min	<b>ANALYTE:</b>	benzothiazole
<b>VOL-MIN:</b>	480 L	<b>DESORPTION:</b>	4 mL hexane; stand 30 minutes
<b>-MAX:</b>	960 L	<b>INJECTION VOLUME:</b>	1 µL
<b>SHIPMENT:</b>	Ship samples with refrigerant packs	<b>TEMPERATURE-INJECTION:</b>	275 °C
<b>SAMPLE STABILITY:</b>	ca. 28 days @ 4 °C [1]	<b>-DETECTOR:</b>	1000 °C
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>-COLUMN:</b>	50 °C, 1.0 min; 15 °C/min to 225 °C, hold 15 min; 6 °C/min to 320 °C
<b>ACCURACY</b>		<b>CARRIER GAS:</b>	Helium @ 2.4 mL/min (splitless)
<b>RANGE STUDIED:</b>	not studied	<b>COLUMN:</b>	capillary, 30 m, 0.32-mm ID, 1.0-µm film, 100% dimethyl polysiloxane, Rtx-1® or equivalent
<b>BIAS:</b>	not determined	<b>CALIBRATION:</b>	solutions of benzothiazole in hexane
<b>OVERALL PRECISION (<math>\hat{S}_{rr}</math>):</b>	not determined	<b>RANGE:</b>	1.0 to 250 µg per sample
<b>ACCURACY:</b>	not determined	<b>ESTIMATED LOD:</b>	0.30 µg per sample (instrumental) [1]
		<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.5 @ 1.0 to 20 µg per sample

**APPLICABILITY:** The working range is 0.002 to 0.5 mg/m<sup>3</sup> for a 480-L air sample. This method was developed to determine benzothiazole in the presence of other sulfur compounds in asphalt fume samples (see Figure 1). This method may be used in conjunction with method 5800, Polycyclic Aromatic Compounds, Total [2]. An aliquot of the desorbed sample from method 5800 can be analyzed for benzothiazole by this method, since the sampler and desorbing solvent are the same.

**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 capillary column. Identification can also be confirmed by mass spectrometry.

**OTHER METHODS:** None identified.

**REAGENTS:**

1. Hexane,\* chromatographic grade.
2. Benzothiazole,\* reagent grade.
3. Benzothiazole primary stock solution, 10 mg/mL: Dissolve 1.0 g benzothiazole in 100 mL of hexane in a volumetric flask. (Correct for purity of standard.)
4. Benzothiazole secondary stock solution, 1 mg/mL: Dilute 1.0 mL of primary stock with hexane to 10 mL in a volumetric flask.

\* See SPECIAL PRECAUTIONS

**EQUIPMENT:**

1. Sampler
  - a. Prefilter: PTFE-laminate membrane filter, 2- $\mu$ m pore size, 37-mm, (Zefluor, Gelman Sciences, Ann Arbor, MI, or equivalent), backed by a gasket (37-mm OD, 32-mm ID) cut from a cellulose support pad or SKC #225-23, in cassette filter holder.  
NOTE: If sampling in bright sunlight, use opaque or foil-wrapped cassettes to prevent photodegradation.
  - b. Solid sorbent: glass tube, 100 mm, 10-mm OD, sealed ends with plastic caps, containing two sections of washed XAD-2 resin (front = 100 mg; back = 50 mg), separated and retained with glass wool plugs (Supelco ORBO-42 Large or equivalent), connected to filter with minimum length PVC tubing.
2. Personal sampling pump capable of operating for 8 h at 2 L/min., with flexible connecting tubing.
3. Gas Chromatograph, autosampler, nitrogen chemiluminescence detector (Antek Model 704E, or equivalent), integrator, and column (Restek Rtx-1®, or equivalent)(page 2550-1)
4. Vials, glass, PTFE-lined screw caps, 5-mL.
5. Vials, Autoinjector, glass with PTFE-lined crimp caps, 1.8-mL.
6. Forceps.
7. Syringes, 5-, 10- $\mu$ L, other sizes if needed.
8. Volumetric flasks, 10-mL, 100-mL.
9. Aluminum foil.
10. Refrigerant packs.
11. ORBO-43 sampling tubes (Supelco)

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**SPECIAL PRECAUTIONS:** Hexane is highly flammable. Benzothiazole has an irritating odor and is highly toxic by ingestion. Handle in a well ventilated hood and wear protective clothing.

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**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 total volume of 480 to 960 L.
3. Pack securely for shipment in refrigerant packs.
4. Store samples at 4°C upon receipt at the laboratory.

**SAMPLE PREPARATION:**

5. Remove samples from refrigerator and allow to equilibrate to ambient temperature. Prefilters may be analyzed for benzothiazole adsorbed on dust, or discarded.
6. If prefilters are to be analyzed, extract as follows:

- a. Remove the filters from cassettes with forceps and transfer to 5-mL, or larger, vials.
- b. Add 4 mL of hexane.
- c. Allow the samples to stand a minimum of 30 minutes with occasional agitation.
7. Extract solid sorbent.
  - a. Transfer front glass wool plug and front sorbent section to a 5-mL, or larger, sample vial.
  - b. Transfer the back sorbent section and remaining glass wool plugs to a separate 5-mL, or larger, sample vial.
  - c. Add 4 mL of hexane to each vial, cap, and agitate.
  - d. Let stand for a minimum of 30 minutes with occasional agitation.

#### CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six standards to cover the concentration range of the samples.
  - a. Add known amounts of the standard stock solution to 10-mL volumetric flasks and bring to volume with hexane.
  - b. Analyze with samples and blanks (steps 11 & 12).
  - c. Prepare calibration graph (peak area vs.  $\mu\text{g}$  benzothiazole).
9. Determine desorption efficiency (DE) in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.

NOTE: The sorbent bed of ORBO-42L tubes used for sampling is not always uniform in depth; therefore, ORBO-43 sampling tubes are recommended for determining DE (see EVALUATION OF METHOD).

  - a. Inject a known amount (1 to 20  $\mu\text{L}$ ) of calibration stock solution, or a serial dilution thereof, directly onto the front sorbent section with a microliter syringe.
  - b. Cap the tube and allow to stand overnight.
  - c. Desorb (step 7) and analyze together with calibration standards (steps 11 & 12).
  - d. Prepare a graph of DE vs.  $\mu\text{g}$  benzothiazole 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 gas chromatograph according to manufacturer's recommendations and to conditions given on page 2550-1. Inject sample manually using solvent flush technique or with autosampler.

NOTE: If peak height is above the linear range of the calibration standards, dilute the sample with hexane, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area of benzothiazole peak and determine  $\mu\text{g}$  per sample from calibration graph.

#### CALCULATIONS:

13. Determine the mass,  $\mu\text{g}$  (corrected for DE), of benzothiazole found in the sample tube 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 benzothiazole in the air volume sampled, V(L):

NOTE:  $\mu\text{g/L} \equiv \text{mg/m}^3$

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

NOTE:  $\mu\text{g/mL} \equiv \text{mg/m}^3$

#### EVALUATION OF METHOD

This method has been used to analyze field generated air samples from several NIOSH asphalt paving studies (Figure 1). It was not evaluated with laboratory generated air samples. All of the desorption efficiency, recovery and storage studies have been performed with laboratory spiked sorbent tubes.

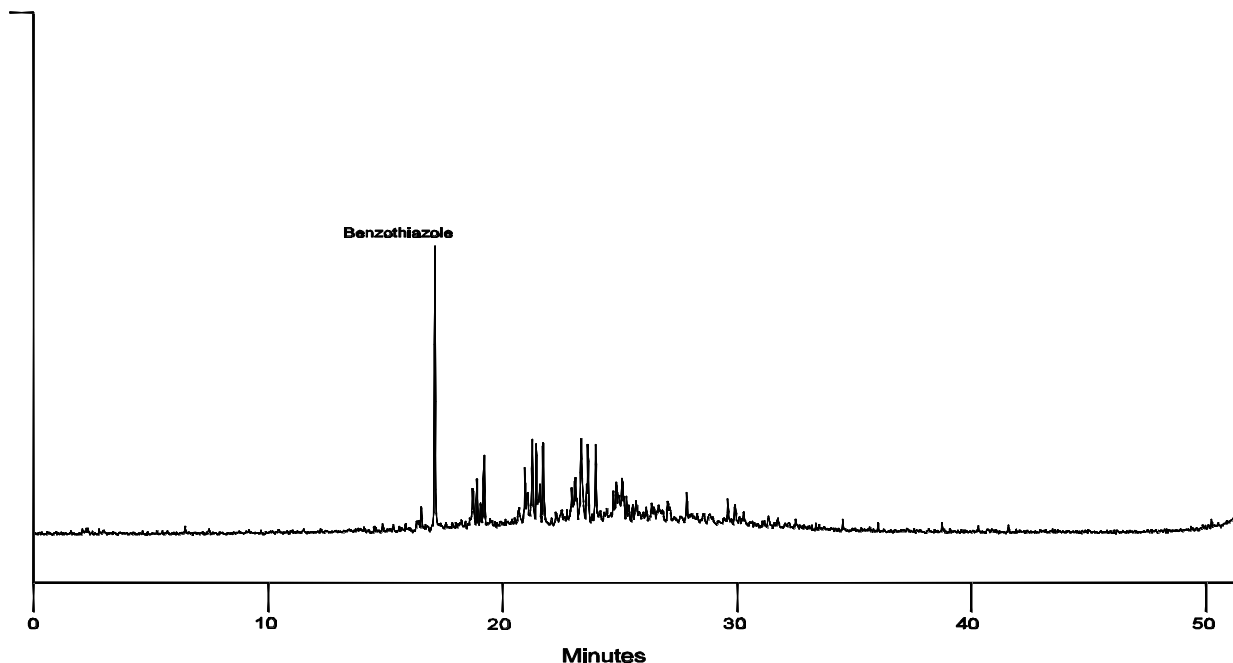
Sampling was done with ORBO-42 Large sampling tubes, because the 10-mm OD allowed for a reduced pressure drop, which enabled 8-h samples to be collected at 2 L/min. Benzothiazole in the vapor state is adsorbed on the washed XAD-2 of the ORBO-42 Large sampling tube. However, samples taken during field studies where high particulate matter was present have shown some benzothiazole on the Teflon® prefilters. This is most likely caused by the entrapment or adsorption of the benzothiazole on the particulate matter. Spiking studies of fresh Teflon filters have shown that benzothiazole is not retained by the filter. It is, therefore, suggested that in those sampling circumstances where particulate matter will be encountered during the sampling process that a Teflon pre-filter be used and analyzed in the same manner as the sampling tube media beds. The quantity of benzothiazole determined on the filter can then be added to the quantity found on the sampling tube to give a total benzothiazole mass for the sample.

Because of the larger diameter of the ORBO-42 Large sampling tube, the front sorbent bed is not always uniform in depth, thus making laboratory spiking of the sampling tubes difficult and recoveries variable. For this reason, ORBO-43 tubes, which contain the same amount of XAD-2 resin, but have a smaller tube diameter (8-mm OD) and a more uniform resin bed, were utilized to determine extraction efficiency, recovery, and storage stability of benzothiazole. Extraction efficiency of the benzothiazole from the ORBO-43 sorbent tubes is typically 89 to 96% (Figure 2). A thirty day storage study at 4°C for 20-µg samples showed a recovery of 89.1% based on day 1 data [1]. This falls slightly below the NIOSH stability criterion of  $\geq 90\%$  recovery.

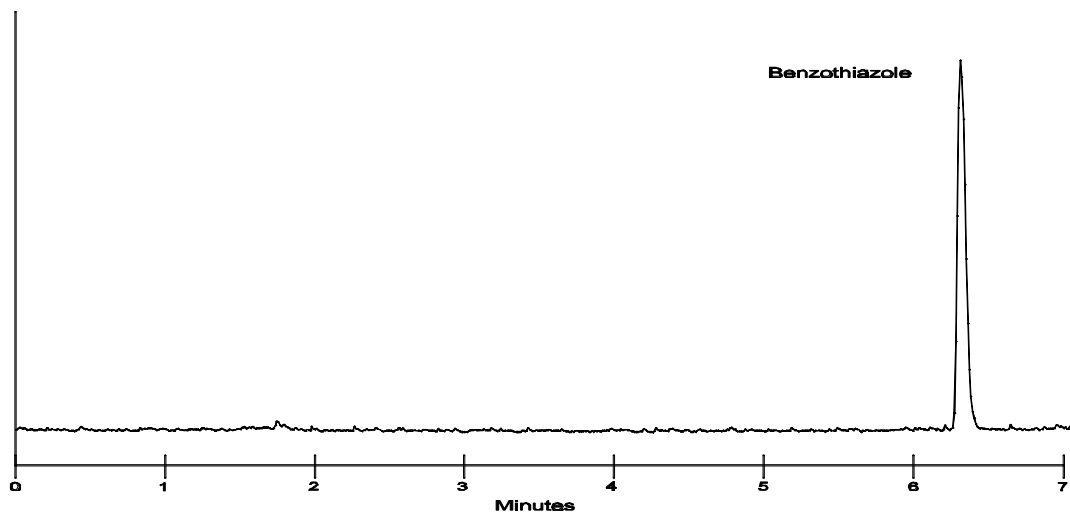
#### REFERENCES:

- [1] Jaycox LB [1997]. Backup Data Report for Method 2550, Benzothiazole in asphalt fume, (unpublished), NIOSH, DPSE.
- [2] NIOSH [1998]. Polycyclic aromatic compounds: Method 5800. In: Eller PM, Cassinelli ME. Eds. NIOSH Manual of Analytical Methods, 4<sup>th</sup> ed., 2<sup>nd</sup> Supplement. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-

**METHOD WRITTEN BY:** Larry B. Jaycox, Ph.D. NIOSH/DPSE



**FIGURE 1:** This is a chromatogram from the analysis of benzothiazole in an asphalt fume sample. The major peak at approximately 18 minutes is benzothiazole. In many cases, the sample matrix may not be this complex and the chromatographic conditions can be adjusted to suit the analysis needs.



**FIGURE 2:** The chromatogram shown here is a typical chromatogram from the analysis of a desorbed laboratory spiked ORBO-43 sampling tube. The chromatographic conditions have been altered to give a shorter retention time for the benzothiazole because there are no other interfering compounds present.