- **Part Number:** 1910
- **Part Title:** Occupational Safety and Health Standards
- **Subpart:** Z
- **Subpart Title:** Toxic and Hazardous Substances
- **Standard Number:** 1910.1051 App D
- **Title:** Sampling and Analytical Method for 1,3-Butadiene (Non-Mandatory)

OSHA Method No.: 56.
Matrix: Air.
Target concentration: 1 ppm (2.21 mg/m(3))
Procedure: Air samples are collected by drawing known volumes of air through sampling tubes containing charcoal adsorbent which has been coated with 4-tert-butylcatechol. The samples are desorbed with carbon disulfide and then analyzed by gas chromatography using a flame ionization detector.
Recommended sampling rate and air volume: 0.05 L/min and 3 L.
Detection limit of the overall procedure: 90 ppb (200 ug/m(3)) (based on 3 L air volume).
Reliable quantitation limit: 155 ppb (343 ug/m(3)) (based on 3 L air volume).
Standard error of estimate at the target concentration: 6.5%.
Special requirements: The sampling tubes must be coated with 4-tert-butylcatechol. Collected samples should be stored in a freezer.
Status of method: A sampling and analytical method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah 84165.

1. Background

This work was undertaken to develop a sampling and analytical procedure for BD at 1 ppm. The current method recommended by OSHA for collecting BD uses activated coconut shell charcoal as the sampling medium (Ref. 5.2). This method was found to be inadequate for use at low BD levels because of sample instability.
The stability of samples has been significantly improved through the use of a specially cleaned charcoal which is coated with 4-tert-butylcatechol (TBC). TBC is a polymerization inhibitor for BD (Ref. 5.3).

1.1.1 Toxic effects

Symptoms of human exposure to BD include irritation of the eyes, nose and throat. It can also cause coughing, drowsiness and fatigue. Dermatitis and frostbite can result from skin exposure to liquid BD. (Ref. 5.1)

NIOSH recommends that BD be handled in the workplace as a potential occupational carcinogen. This recommendation is based on two inhalation studies that resulted in cancers at multiple sites in rats and in mice. BD has also demonstrated mutagenic activity in the presence of a liver microsomal activating system. It has also been reported to have adverse reproductive effects. (Ref. 5.1)

1.1.2. Potential workplace exposure

About 90% of the annual production of BD is used to manufacture styrene-butadiene rubber and Polybutadiene rubber. Other uses include: Polychloroprene rubber, acrylonitrile butadiene-stryene resins, nylon intermediates, styrene-butadiene latexes, butadiene polymers, thermoplastic elastomers, nitrile resins, methyl methacrylate-butadiene styrene resins and chemical intermediates. (Ref. 5.1)

1.1.3. Physical properties (Ref. 5.1)

CAS No.: 106-99-0
Molecular weight: 54.1
Appearance: Colorless gas
Boiling point: -4.41 deg. C (760 mm Hg)
Freezing point: -108.9 deg. C
Vapor pressure: 2 atm @ 15.3 deg. C; 5 atm @ 47 deg. C
Explosive limits: 2 to 11.5% (by volume in air)
Odor threshold: 0.45 ppm
Structural formula: H(2)C:CHCH:CH(2)
Synonyms: BD; biethylene; bivinyl; butadiene; divinyl; buta-1,3-diene; alpha-gamma-butadiene; erythrene; NCI-C50602; pyrrolylene; vinylethylene.

1.2. Limit defining parameters

The analyte air concentrations listed throughout this method are based on an air volume of 3 L and a desorption volume of 1 mL. Air concentrations listed in ppm are referenced to 25 deg. C and 760 mm Hg.

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure was 304 pg per injection. This was the amount of BD which gave a response relative to the interferences present in a standard.

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure was 0.60 ug per sample (90 ppb or 200 ug/m(3)). This amount was determined graphically. It was the amount of analyte which, when spiked on the sampling device, would allow recovery approximately equal to the detection limit of the analytical procedure.

1.2.3. Reliable quantitation limit

The reliable quantitation limit was 1.03 ug per sample (155 ppb or 343 ug/m(3)). This was the smallest amount of analyte which could be quantitated within the limits of a recovery of at least 75% and a precision (+/- 1.96 SD) of +/- 25% or better.

1.2.4. Sensitivity(1)

_____

Footnote(1) The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operation parameters.

The sensitivity of the analytical procedure over a concentration range representing 0.6 to 2 times the target concentration, based on the recommended air volume, was 387 area units per ug/mL. This value was determined from the slope of the calibration curve. The sensitivity may vary with the particular instrument used in the analysis.

1.2.5. Recovery

The recovery of BD from samples used in storage tests remained above 77% when the samples were stored at ambient temperature and above 94% when the samples were stored at refrigerated temperature. These values were determined from regression lines which were calculated from the storage data. The recovery of the analyte from the collection device must be at least 75% following storage.

1.2.6. Precision (analytical method only)

The pooled coefficient of variation obtained from replicate determinations of analytical standards over the range of 0.6 to 2 times the target concentration was 0.011.

1.2.7. Precision (overall procedure)

The precision at the 95% confidence level for the refrigerated temperature storage test was +/- 12.7%. This value includes an additional +/- 5% for sampling error. The overall procedure must provide results at the target concentrations that are +/- 25% at the 95% confidence level.

1.2.8. Reproducibility

Samples collected from a controlled test atmosphere and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The average recovery was 97.2% and the standard deviation was 6.2%.

2. Sampling procedure

2.1. Apparatus

2.1.1. Samples are collected by use of a personal sampling pump that can be calibrated to within +/- 5% of the recommended 0.05 L/min sampling rate with the sampling tube in line.

2.1.2. Samples are collected with laboratory prepared sampling tubes. The sampling tube is constructed of silane-treated glass and is about 5-cm long. The ID is 4 mm and the OD is 6 mm. One end of the tube is tapered so that a glass wool end plug will hold the contents of the tube in place during sampling. The opening in the tapered end of the sampling tube is at least one-half the ID of the tube (2 mm). The other end of the sampling tube is open to its full 4-mm ID to facilitate packing of the tube. Both ends of the tube are fire-polished for safety. The tube is packed with 2 sections of

pretreated charcoal which has been coated with TBC. The tube is packed with a 50-mg backup section, located nearest the tapered end, and with a 100-mg sampling section of charcoal. The two sections of coated adsorbent are separated and retained with small plugs of silanized glass wool. Following packing, the sampling tubes are sealed with two 7/32 inch OD plastic end caps. Instructions for the pretreatment and coating of the charcoal are presented in Section 4.1 of this method.

2.2. Reagents

None required.

2.3. Technique

2.3.1. Properly label the sampling tube before sampling and then remove the plastic end caps.
2.3.2. Attach the sampling tube to the pump using a section of flexible plastic tubing such that the larger front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing ahead of the sampling tube. The sampling tube should be attached in the worker's breathing zone in a vertical manner such that it does not impede work performance.
2.3.3. After sampling for the appropriate time, remove the sampling tube from the pump and then seal the tube with plastic end caps. Wrap the tube lengthwise.
2.3.4. Include at least one blank for each sampling set. The blank should be handled in the same manner as the samples with the exception that air is not drawn through it.
2.3.5. List any potential interferences on the sample data sheet.
2.3.6. The samples require no special shipping precautions under normal conditions. The samples should be refrigerated if they are to be exposed to higher than normal ambient temperatures. If the samples are to be stored before they are shipped to the laboratory, they should be kept in a freezer. The samples should be placed in a freezer upon receipt at the laboratory.

2.4. Breakthrough

(Breakthrough was defined as the relative amount of analyte found on the backup section of the tube in relation to the total amount of analyte collected on the sampling tube. Five-percent breakthrough occurred after sampling a test atmosphere containing 2.0 ppm BD for 90 min at 0.05 L/min. At the end of this time 4.5 L of air had been sampled and 20.1 ug of the analyte was collected. The relative humidity of the sampled air was 80% at 23 deg. C.)
Breakthrough studies have shown that the recommended sampling procedure can be used at air concentrations higher than the target concentration. The sampling time, however, should be reduced to 45 min if both the expected BD level and the relative humidity of the sampled air are high.

2.5. Desorption efficiency

The average desorption efficiency for BD from TBC coated charcoal over the range from 0.6 to 2 times the target concentration was 96.4%. The efficiency was essentially constant over the range studied.

2.6. Recommended air volume and sampling rate

2.6.1. The recommended air volume is 3L.

2.6.2. The recommended sampling rate is 0.05 L/min for 1 hour.

2.7. Interferences

There are no known interferences to the sampling method.

2.8. Safety precautions

2.8.1. Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.
2.8.2. Follow all safety practices that apply to the work area being sampled.

3. Analytical procedure

3.1. Apparatus

3.1.1. A gas chromatograph (GC), equipped with a flame ionization detector (FID).(2)

_____
Footnote(2) A Hewlett-Packard Model 5840A GC was used for this evaluation. Injections were performed using a Hewlett-Packard Model 7671A automatic sampler.

3.1.2. A GC column capable of resolving the analytes from any interference.(3)

_____
Footnote(3) A 20-ft x 1/8-inch OD stainless steel GC column containing 20% FFAP on 80/100 mesh Chromabsorb W-AW-DMCS was used for this evaluation.

3.1.3. Vials, glass 2-mL with Teflon-lined caps.
3.1.4. Disposable Pasteur-type pipets, volumetric flasks, pipets and syringes for preparing samples and standards, making dilutions and performing injections.

3.2. Reagents

3.2.1. Carbon disulfide.(4)

_____
Footnote(4) Fisher Scientific Company A.C.S. Reagent Grade solvent was used in this evaluation.

The benzene contaminant that was present in the carbon disulfide was used as an internal standard (ISTD) in this evaluation.
3.2.2. Nitrogen, hydrogen and air, GC grade.
3.2.3. BD of known high purity.(5)

_____
Footnote(5) Matheson Gas Products, CP Grade 1,3-butadiene was used in this study.

3.3. Standard preparation

3.3.1. Prepare standards by diluting known volumes of BD gas with

carbon disulfide. This can be accomplished by injecting the appropriate volume of BD into the headspace above the 1-mL of carbon disulfide contained in sealed 2-mL vial. Shake the vial after the needle is removed from the septum.(6)

_____

Footnote(6) A standard containing 7.71 ug/mL (at ambient temperature and pressure) was prepared by diluting 4 uL of the gas with 1-mL of carbon disulfide.

3.3.2. The mass of BD gas used to prepare standards can be determined by use of the following equations:

$$MV=(760/BP)(273+t)/(273)(22.41)$$

Where:

MV = ambient molar volume
BP = ambient barometric pressure
T = ambient temperature
ug/uL = 54.09/MV
ug/standard = (ug/uL)(uL) BD used to prepare the standard

3.4. Sample preparation

3.4.1. Transfer the 100-mg section of the sampling tube to a 2-mL vial. Place the 50-mg section in a separate vial. If the glass wool plugs contain a significant amount of charcoal, place them with the appropriate sampling tube section.
3.4.2. Add 1-mL of carbon disulfide to each vial.
3.4.3. Seal the vials with Teflon-lined caps and then allow them to desorb for one hour. Shake the vials by hand vigorously several times during the desorption period.
3.4.4. If it is not possible to analyze the samples within 4 hours, separate the carbon disulfide from the charcoal, using a disposable Pasteur-type pipet, following the one hour. This separation will improve the stability of desorbed samples.
3.4.5. Save the used sampling tubes to be cleaned and repacked with fresh adsorbent.

3.5. Analysis

3.5.1. GC Conditions
Column temperature: 95 deg. C
Injector temperature: 180 deg. C
Detector temperature: 275 deg. C
Carrier gas flow rate: 30 mL/min
Injection volume: 0.80 uL
GC column: 20-ft x 1/8-in OD stainless steel GC column containing 20%
FFAP on 80/100 Chromabsorb W-AW-DMCS.

3.5.2. Chromatogram. See Section 4.2.
3.5.3. Use a suitable method, such as electronic or peak heights, to measure detector response.
3.5.4. Prepare a calibration curve using several standard solutions of different concentrations. Prepare the calibration curve daily. Program the integrator to report the results in ug/mL.
3.5.5. Bracket sample concentrations with standards.

3.6. Interferences (analytical)

3.6.1. Any compound with the same general retention time as the analyte and which also gives a detector response is a potential interference. Possible interferences should be reported by the industrial hygienist to the laboratory with submitted samples.
3.6.2. GC parameters (temperature, column, etc.) may be changed to circumvent interferences.
3.6.3. A useful means of structure designation is GC/MS. It is recommended that this procedure be used to confirm samples whenever possible.

3.7. Calculations

3.7.1. Results are obtained by use of calibration curves. Calibration curves are prepared by plotting detector response against concentration for each standard. The best line through the data points is determined by curve fitting.
3.7.2. The concentration, in ug/mL, for a particular sample is determined by comparing its detector response to the calibration curve. If any analyte is found on the backup section, this amount is added to the amount found on the front section. Blank corrections should be performed before adding the results together.
3.7.3. The BD air concentration can be expressed using the following equation:

$$mg/m(3)=(A)(B)/(C)(D)$$

Where:

A = ug/mL from Section 3.7.2
B = volume
C = L of air sampled
D = efficiency

3.7.4. The following equation can be used to convert results in mg/m(3) to ppm:

$$ppm=(mg/m(3))(24.46)/54.09$$

Where:

mg/m(3) = result from Section 3.7.3.
24.46 = molar volume of an ideal gas at 760 mm Hg and 25 deg. C.

3.8. Safety precautions (analytical)

3.8.1. Avoid skin contact and inhalation of all chemicals.
3.8.2. Restrict the use of all chemicals to a fume hood whenever possible.
3.8.3. Wear safety glasses and a lab coat in all laboratory areas.

4. Additional Information

4.1. A procedure to prepare specially cleaned charcoal coated with TBC

4.1.1. Apparatus.
4.1.1.1. Magnetic stirrer and stir bar.
4.1.1.2. Tube furnace capable of maintaining a temperature of 700 deg. C and equipped with a quartz tube that can hold 30 g of charcoal.(8)

_____

Footnote(8) A Lindberg Type 55035 Tube furnace was used in this evaluation.

4.1.1.3. A means to purge nitrogen gas through the charcoal inside the quartz tube.

4.1.1.4. Water bath capable of maintaining a temperature of 60 deg. C.

4.1.1.5. Miscellaneous laboratory equipment: One-liter vacuum flask, 1-L Erlenmeyer flask, 350-M1 Buchner funnel with a coarse fitted disc, 4-oz brown bottle, rubber stopper, Teflon tape etc.

4.1.2. Reagents

4.1.2.1. Phosphoric acid, 10% by weight, in water.(9)

_____

Footnote(9) Baker Analyzed" Reagent grade was diluted with water for use in this evaluation.

4.1.2.2. 4-tert-Butylcatechol (TBC).(10)

_____

Footnote(10) The Aldrich Chemical Company 99% grade was used in this evaluation.

4.1.2.3. Specially cleaned coconut shell charcoal, 20/40 mesh.(11)

_____

Footnote(11) Specially cleaned charcoal was obtained from Supelco, Inc. for use in this evaluation. The cleaning process used by Supelco is proprietary.

4.1.2.4. Nitrogen gas, GC grade.

4.1.3. Procedure.

Weigh 30g of charcoal into a 500-mL Erlenmeyer flask. Add about 250 mL of 10% phosphoric acid to the flask and then swirl the mixture. Stir the mixture for 1 hour using a magnetic stirrer. Filter the mixture using a fitted Buchner funnel. Wash the charcoal several times with 250-mL portions of deionized water to remove all traces of the acid. Transfer the washed charcoal to the tube furnace quartz tube. Place the quartz tube in the furnace and then connect the nitrogen gas purge to the tube. Fire the charcoal to 700 deg. C. Maintain that temperature for at least 1 hour. After the charcoal has cooled to room temperature, transfer it to a tared beaker. Determine the weight of the charcoal and then add an amount of TBC which is 10% of the charcoal, by weight.

CAUTION-TBC is toxic and should only be handled in a fume hood while wearing gloves.

Carefully mix the contents of the beaker and then transfer the mixture to a 4-oz bottle. Stopper the bottle with a clean rubber stopper which has been wrapped with Teflon tape. Clamp the bottle in a water bath so that the water level is above the charcoal level. Gently heat the bath to 60 deg. C and then maintain that temperature for 1 hour. Cool the charcoal to room temperature and then transfer the coated charcoal to a suitable container.

The coated charcoal is now ready to be packed into sampling tubes. The sampling tubes should be stored in a sealed container to prevent contamination. Sampling tubes should be stored in the dark at room temperature. The sampling tubes should be segregated by coated adsorbent lot number.

4.2 Chromatograms

The chromatograms were obtained using the recommended analytical method. The chart speed was set at 1 cm/min for the first three min and then at 0.2 cm/min for the time remaining in the analysis.

The peak which elutes just before BD is a reaction product between an impurity on the charcoal and TBC. This peak is always present, but it is easily resolved from the analyte. The peak which elutes immediately before benzene is an oxidation product of TBC.

5. References

5.1. "Current Intelligence Bulletin 41, 1,3-Butadiene", U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH.

5.2. "NIOSH Manual of Analytical Methods", 2nd ed; U.S. Dept. of Health Education and Welfare, National Institute for Occupational Safety and Health: Cincinnati, OH. 1977, Vol. 2, Method No. S91 DHEW (NIOSH) Publ. (US), No. 77-157-B.

5.3. Hawley, G.C., Ed. "The Condensed Chemical Dictionary", 8th ed.; Van Nostrand Rienhold Company: New York, 1971; 139.5.4. Chem. Eng. News (June 10, 1985), (63), 22-66.

[61 FR 56746, Nov. 4, 1996]

Next Standard (1910.1051 App E)

Regulations (Standards - 29 CFR) - Table of Contents