PROPARGYL ALCOHOL

Method no.:	97
Matrix:	Air
Target concentration:	1 ppm (2 mg/m^3) (skin)
Procedure:	Samples are collected by drawing air through sampling tubes containing petroleum-based charcoal which has been coated with hydrobromic acid. The samples are desorbed with toluene and analyzed by GC using an electron capture detector.
Recommended air volume and sampling rate:	6 L at 0.05 L/min
Reliable quantitation limit:	0.73 ppb (1.68 µg/m^3)
Standard error of estimate at the target concentration:	7.4%
Special requirements:	Store samples under refrigeration when they are not in transit.
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1. Background

1.1.1. History

Previous to this method, propargyl alcohol had been collected on coconut-shell charcoal, desorbed with various solvents, and analyzed by GC/FID (Ref. 5.1.). The desorbing solvents included carbon disulfide, carbon disulfide with dimethyl formamide (99:1), and methylene chloride with methyl alcohol (95:5). The desorption efficiencies obtained with these solvents were low and inconsistent (Ref. 5.2.). The collection of propargyl alcohol on Anasorb 747 and on silica gel was tested during the course of this work. Propargyl alcohol was efficiently collected but was not stable for either ambient or refrigerated temperature storage on Anasorb 747. It was fairly stable on silica gel, however, some storage migration was observed. Analytical problems made collection on silica gel unsatisfactory. The analytical problems were primarily associated with the use of water as the desorbing solvent.

Propargyl alcohol (2-propyn-1-ol) has three reactive sites: a primary hydroxyl group, a triple bond, and an acetylenic hydrogen (Ref. 5.3.). These reactive sites make the chemical an ideal candidate for derivatization. A derivative was quantitatively formed when propargyl alcohol was liquid spiked on petroleum-based charcoal which had been coated with HBr. The derivative was identified as 2,3-dibromo-2-propen-1-ol by GC/mass spectrometry. The reactive surface of the coated charcoal is apparently necessary for the derivatization reaction to proceed because the derivative was not formed when a dilute solution of HBr in dimethyl formamide was liquid spiked with propargyl alcohol.

The propargyl alcohol/HBr derivative has a double bond which makes the presence of *cis* and *trans* isomers possible. The analysis of air samples, collected from a controlled test atmosphere, revealed that both isomers were produced, but that the ratio of the isomers was greater than 99:1. The predominant isomer could be the *trans* isomer (with respect to the bromine atoms), because the *cis* isomer would be more difficult to form due to steric hinderance.

This method features air sample collection and derivatization of propargyl alcohol using commercially available sampling tubes containing petroleum-based charcoal which has been coated with HBr. The sampling tubes are the same as those used by OSHA to collect ethylene oxide. A stable propargyl alcohol/HBr derivative is formed which can be desorbed with toluene. The analytical method specifies analysis by GC using an electron capture detector. The derivative is commercially available for use as an analytical standard.

1.1.2. Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Propargyl alcohol is a primary skin irritant (but not a sensitizer), and a severe eye and mucous membrane irritant. It is toxic by ingestion, inhalation, and skin adsorption. The oral LD_{50} for rats is 70 mg/kg, 60 mg/kg for guinea pigs, and 50 mg/kg for mice. The 2-h LC_{50} for both mice and rats was reported to be 1000 mg/m^3 (850 ppm). The ACGIH TLV for propargyl alcohol was set at 1 ppm because of its structural and apparent toxicological similarity to allyl alcohol, which has a TLV of 2 ppm. (Ref. 5.4.)

1.1.3. Workplace exposure

Propargyl alcohol has been used as a chemical intermediate, a pharmaceutical intermediate, a corrosion inhibitor, a laboratory reagent, a solvent stabilizer, a soil fumigant, and to prevent hydrogen embrittlement of steel. The United States imported 1.85×10^8 g of propargyl alcohol in 1984. (Ref. 5.5.)

No estimate of U.S. production or of the number of workers potentially exposed to propargyl alcohol was found.

1.1.4. Physical properties and other descriptive information (Refs. 5.5. and 5.6. for propargyl alcohol)

chemical name:	propargyl alcohol
CAS no.:	107-19-7
molecular wt:	56.07
boiling point:	114-115°C
melting point:	-52 to -48°C
density:	0.9715 (d_4^{20})
vapor pressure:	11.6 mmHg at 20°C
vapor density:	1.93
description:	colorless to slightly straw-colored, moderately volatile liquid with a mild geranium-like odor
solubility:	soluble in water, benzene, chloroform, 1,2-dichloroethane, ethanol, ether, acetone, dioxane, and tetrahydrofuran; insoluble in aliphatic hydrocarbons
synonyms:	2-propyn-1-ol; 1-propyne-3-ol; 2-propynyl alcohol; ethynylcarbinol; 1-hydroxy-2-propyne; 2-propynol; 3-propynol; methanol, ethynyl; propiolic alcohol; propynyl alcohol; STCC 4907440; RCRA P102; OHS19730
structural formula:	$HC\equiv C-CH_2OH$

propargyl alcohol/HBr derivative (following data taken from Fluka's (vendor) catalog and reagent bottle label)

chemical name:	2,3-dibromo-2-propen-1-ol (*cis* and *trans*)
CAS no.:	7228-11-7
boiling point:	60-62°C at 0.1 mmHg
density:	2.216 (d_4^{20})
refractive index:	1.580 (n_D^{20})
molecular weight:	215.90
synonym:	2,3-dibromoallyl alcohol
structural formula:	$BrHC=CBr-CH_2OH$

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm and ppb are referenced to 25°C and 101.3 kPa (760 mmHg). The amounts presented are calculated as propargyl alcohol even though the derivative is the actual species analyzed.

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 1.8 fg per injection. This is the amount of analyte that will produce a major isomer peak with a height that is approximately 5 times the baseline noise. (Section 4.1.)

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 10.08 ng per sample. This is the amount of analyte spiked on the sampling device that, upon analysis, produces a peak similar in size to that of the detection limit of the analytical procedure. This detection limit corresponds to an air concentration of 0.73 ppb (1.68 µg/m^3). (Section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 10.08 ng per sample. This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. This reliable quantitation limit corresponds to an air concentration of 0.73 ppb (1.68 µg/m^3). (Section 4.3.)

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 analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4. Instrument response to the analyte

The instrument response over concentration ranges representing 0.5 to 2 times the target concentration was linear. (Section 4.4.)

1.2.5. Recovery

The recovery of propargyl alcohol from samples used in the 18-day ambient storage test remained above 80.3%. (Section 4.5., regression line of Figure 4.5.1.)

1.2.6. Precision (analytical procedure)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration is 0.011. (Section 4.6.)

1.2.7. Precision (overall procedure)

The precision at the 95% confidence level for the 18-day ambient temperature storage test is ±14.4%. (Section 4.7.) This includes an additional ±5% for sampling error.

1.2.8. Reproducibility

Six samples, prepared by liquid spiking, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 36 days of storage at about 5°C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.7. (Section 4.8.)

2. Sampling Procedure

2.1. Apparatus

2.1.1. A personal sampling pump that can be calibrated within ±5% of the recommended flow rate with the sampling device in line.

2.1.2. Samples are collected with 7-cm × 4-mm i.d. × 6-mm o.d. glass sampling tubes packed with 2 sections of petroleum-based charcoal that has been coated with HBr. The front section contains 100 mg and the back section 50 mg of coated charcoal. The 2 sections are held in place and retained with glass wool plugs. These are the same sampling tubes OSHA

uses to collect ethylene oxide samples. Sampling tubes were purchased from SKC, Inc. for this evaluation (catalog no. 226-38-03, lot 796).

2.2. Reagents

No reagents are required for sampling.

2.3. Technique

2.3.1. Break off both ends of the sampling tubes immediately before sampling. The holes in the broken ends of the sampling tubes should be approximately 1/2 the i.d. of the sampling tube. All tubes should be from the same lot.

2.3.2. Connect the sampling tube to the sampling pump with flexible tubing. Use a sampling tube holder with a protective tube shield to cover the sharp, jagged end of the sampling tube. Position the sampling tube so that sampled air passes through the 100-mg section first.

2.3.3. Sampled air should not pass through any hose or tubing before entering the sampling tube.

2.3.4. Attach the sampler vertically in the worker's breathing zone, with the 100-mg section pointing downward, and positioned so it does not impede work performance or safety.

2.3.5. Remove the sampling tube after sampling for the appropriate time and seal the sampler with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.6. Submit at least one blank with each set of samples. The blank should be handled the same as the other samples except no air is drawn through it.

2.3.7. Record the sample air volume (in liters of air) for each sample. Note any potential interferences.

2.3.8. Ship any bulk sample separate from air samples.

2.3.9. Submit air samples to the laboratory for analysis as soon as possible after sampling. Store the samples at reduced temperature if delay is unavoidable.

2.4. Sampler capacity

Several sampler capacity studies were performed using controlled test atmospheres and the recommended sampling tubes. The average propargyl alcohol concentration of the test atmospheres was 4.7 µg/L (2 ppm) at 73% relative humidity and 27°C. Samples were collected at 0.05 L/min for as long as 7.6 hours and no breakthrough from the front to the back section was observed in any of the test samples. The average propargyl alcohol recovery was 99% of theoretical, after correction for desorption efficiency.

An additional sampler capacity test was performed to determine if the relative humidity of the sampled air had an effect on sampler capacity. The propargyl alcohol concentration of the test atmosphere was 4.8 µg/L (2 ppm) at 19% relative humidity and 25°C. Samples were collected at 0.05 L/min for as long as 7.1 hours and, again, no breakthrough was observed. The average recovery of these samples was 105% of theoretical.

The recommended air volume (6 L at 0.05 L/min) is a significant reduction of the air volumes (more than 21 L) shown to be feasible by the capacity tests. The reduction was made as a precaution against the available HBr being entirely consumed at the head of the sampling tube and then propargyl alcohol being collected but not derivatized. This situation could cause low results, especially for stored samples. Storage tests confirmed this condition did not occur in samples collected for 2 h at 0.05 L/min (6-L samples). The analytical method can detect exceptionally low amounts of the propargyl alcohol/HBr derivative, therefore, a 2-h sampling time does not compromise the method in any way.

2.5. Desorption efficiency

2.5.1. The average desorption efficiency of propargyl alcohol from HBr-coated charcoal over the range of from 0.5 to 2 times the target concentration is 88.6%. (Section 4.9.1.)

2.5.2. Desorbed samples remain stable for at least 2 days. (Section 4.9.2.)

2.5.3. Desorption efficiencies should be confirmed periodically because differences may occur due to variations between sampling media lots, desorption solvent, and operator technique.

2.6. Recommended air volume and sampling rate

2.6.1. Sample 6 L of air at 0.05 L/min for TWA samples.

2.6.2. Sample 0.75 L of air at 0.05 L/min for short-term samples.

2.6.3. The air concentration corresponding to the reliable quantitation limit becomes larger when short-term samples are collected. For example, the reliable quantitation limit is 13.4 $\mu g/m^3$ (5.8 ppb) for a 0.75-L sample.

2.7. Interferences (sampling)

2.7.1. There are no known interferences with the collection of propargyl alcohol on HBr-coated charcoal. Any chemical that could deplete HBr from the sampling tube or prevent the derivatization reaction from occurring is a potential interference. The derivative itself, if present in the sampled air, would be an interference.

2.7.2. Suspected interferences should be reported to the laboratory when samples are submitted.

2.8. Safety precautions (sampling)

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 applicable to the work area.

2.8.3. Wear protective eyeware when breaking the ends of the glass sampling tubes.

3. Analytical Procedure

3.1. Apparatus

3.1.1. A GC equipped with an electron capture detector (ECD). A Hewlett-Packard 5890 GC, a 7673A automatic sampler, and an Ni-63 ECD were used in this evaluation.

3.1.2. A GC column capable of separating the HBr derivative of propargyl alcohol from the desorbing solvent and potential interferences. A Supelco 30-m × 0.32-mm i.d. PTE-5 (0.25-µm film thickness) capillary column was used in this evaluation.

3.1.3. An electronic integrator or other suitable means of measuring detector response. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4. Sample vials, 2- and 4-mL glass, with polytetrafluoroethylene-lined septum caps.

3.1.5. A mechanical tube rotator. A Fisher Roto-Rack was used in this evaluation.

3.2. Reagents

3.2.1. 2,3-Dibromo-2-propen-1-ol, practical grade or better. Fluka Chemical Corp. (Ronkonkoma, NY) Lot 51212-289 was used in this evaluation.

3.2.2. Toluene, reagent grade or better. b&j Brand, High Purity Solvent, Lot AY 377, was used in this evaluation.

3.2.3. Toluene/internal standard solution. The internal standard solution is prepared by adding an appropriate internal standard to toluene. *ortho*-Dichlorobenzene (*o*-DCB) (2 µL per 100 mL of toluene) was used as an internal standard for this method.

3.3. Standard preparation

3.3.1. Prepare stock standards by weighing 40-80 mg of 2,3-dibromo-2-propen-1-ol into 10-mL volumetric flasks and diluting to volume with toluene. Multiply this concentration by the decimal equivalent of the manufactures assay (typically 90-95%). The propargyl alcohol

equivalent of the derivative is obtained by multiplying the concentration of the derivative by the ratio of the molecular weights (56.07/215.90 = 0.2597).

3.3.2. Add 2.0 mL of toluene (without the internal standard) to each of several 4-mL glass vials. Seal the vials with polytetrafluoroethylene-lined septum caps. Prepare analytical standards by adding appropriate volumes of the stock standards to the 2.0-mL volumes of toluene. A standard equivalent to a 1 ppm air sample was prepared by adding 10 µL of a solution containing 1.41 mg/mL (propargyl alcohol equivalent) of 2,3-dibromo-2-propen-1-ol to 2.0 mL of toluene.

3.3.3. Prepare a sufficient number of analytical standards to generate a calibration curve. Analytical standard concentrations must bracket sample concentrations.

3.4. Sample preparation

3.4.1. Transfer the adsorbent sections of each sampling tube to separate 4-mL glass vials. Place the front and center glass-wool plugs in the same vial as the front section of coated adsorbent. The glass wool plugs are included in the desorption vial because they may contain derivatized propargyl alcohol. Discard the back glass wool plug and the empty sampling tube.

3.4.2. Add 2.0 mL of toluene (without the internal standard) to each vial.

3.4.3. Seal the vials with polytetrafluoroethylene-lined septum caps and rotate them at approximately 60 rotations/min on a mechanical tube rotator for 2 h.

3.5. Analysis

3.5.1. Dilute both standards and samples by adding 10 µL of each standard or sample to separate 2-mL glass vials containing 1.0 mL of the toluene/internal standard solution. This dilution was necessary to obtain a linear calibration curve. Further dilution of samples and standards may be necessary if non-linear calibration data is observed for the equipment in use. This dilution does not have to be included in the calculations if both standards and samples are diluted identically.

3.5.2. GC Conditions

temperatures (°C)
- injector: 250
- detector: 275
- column: 40, hold 1 min, program at 10°C/min to 220

gas flow rates (mL/min)
- column: 2.6 (H_2)
- split: 69.0 (H_2)
- septum purge: 3.0 (H_2)
- auxiliary: 53.0 (N_2)

miscellaneous
- detector: ECD (Ni-63)
- column: 30-m × 0.32-mm i.d. PTE-5 (df = 0.25 µm)
- injection size: 1 µL (28:1 split)

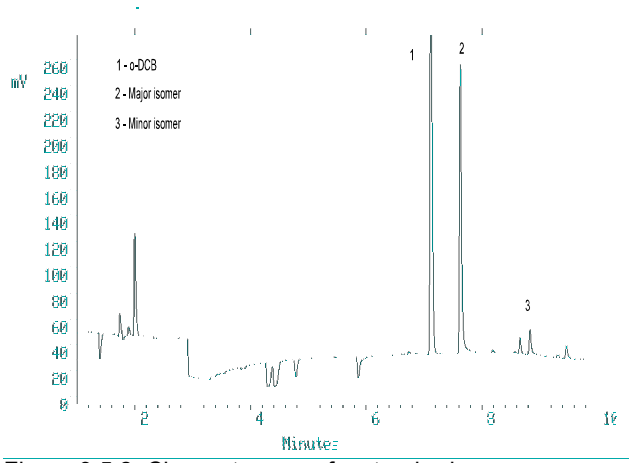

Figure 3.5.2. Chromatogram of a standard.

GC retention times (min)
o-DCB:

7.1

- major isomer: 7.6
- minor isomer: 8.8

The total GC run time was 19 min as a precaution to clear the column.

3.5.3. Commercial 2,3-dibromo-2-propen-1-ol (used for analytical standards) will usually contain both *cis* and *trans* isomers. It may be necessary to employ GC/mass spectrometry (or another suitable technique), using identical GC conditions as those used to analyze samples by GC/ECD, to identify which GC peaks correspond to the isomers. This is especially critical if a different GC column than the one specified in the method is used.

Determine the area percent ratio of the 2 isomers and use an internal standard method to calibrate the integrator. For example: the concentration of a standard is 14.0 µg/standard, the area of 1 isomer is 1078356, and the area of the other isomer is 97052. The percent ratio of the first isomer is 1078356/(1078356+ 97052) = 91.7%. Multiply the concentration by 0.917 (14.0 µg/standard × 0.917 = 12.8 µg/sample) and use an internal standard method to calibrate the integrator at 12.8 µg/sample for the major isomer and 1.2 µg/standard (14.0 - 12.8 = 1.2 µg/standard) for the minor isomer.

3.5.4. Add the integrator results for the 2 isomers of the standards together. Construct a calibration curve by plotting micrograms per standard versus summed integrator results for each standard.

3.5.5. Sum the integrator results for the samples. Analysis of air samples may reveal only the presence of the major isomer. The other isomer may not have been formed during sample collection.

3.6. Interferences (analytical)

3.6.1. Any compound that gives an ECD response and has a similar GC retention time as the analytes or the internal standard is a potential interference. Generally, chromatographic conditions can be altered to separate an interference.

3.6.2. Retention time on a single column is not proof of chemical identity. Confirmation of suspected identity should be performed by GC/mass spectrometry when necessary.

3.7. Calculations

The analyte amount per sample, micrograms of propargyl alcohol per sample, is obtained from the calibration curve. The back section of the sample is analyzed primarily to determine if there was any breakthrough from the front section during sampling. If a significant amount of analyte is found on the back section (e.g., greater than 25% of the amount found on the front section), this fact should be reported with sample results. If any analyte is found on the back section, it is added to the amount on the front section. The analyte amount is then corrected by subtracting the total amount found in the blank. The air concentration is obtained by using the following equations. The dilution specified in Section 3.5.1. does not have to be included in the calculations if it was performed on both standards and samples.

$$mg/m^3 = \frac{A}{B \times C}$$

where A = total micrograms of analyte per sample
B = liters of air sampled
C = desorption efficiency

$$ppm = \frac{24.46 \times mg/m^3}{MW}$$

where 24.46 = molar volume (liters) at 101.3 kPa (760 mmHg) and 25°C
MW = 56.07 for propargyl alcohol

3.8. Safety precautions (analytical)

3.8.1. Restrict the use of all chemicals to a fume hood.

3.8.2. Avoid skin contact and inhalation of all chemicals.

3.8.3. Wear safety glasses, gloves, and a lab coat at all times while working with chemicals.

4. Backup Data

4.1. Detection limit of the analytical procedure

The injection size recommended in the analytical procedure (1 µL, 28:1 split) was used in the determination of the detection limit of the analytical procedure. The detection limit was 1.8 fg on-column. It was determined by analyzing a dilute standard containing 10.08 ng/standard. This standard gave a major isomer peak (retention time 7.6 min) with a height about 5 times the height of the baseline noise. The peak for the minor isomer of 2,3-dibromo-2-propen-1-ol (retention time 8.8 min) was very small at this level.

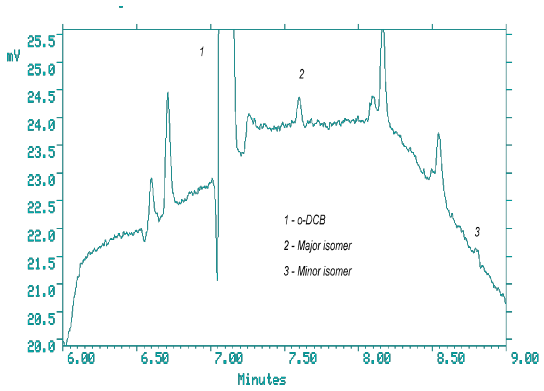

Figure 4.1. Detection limit of the analytical procedure.

4.2. Detection limit of the overall procedure

The detection limit of the overall procedure was determined by analyzing 100-mg portions of HBr-coated charcoal (including 2 glass wool plugs) spiked with 10.08 ng of 2,3-dibromo-2-propen-1-ol. This amount corresponds to an air concentration of 0.73 ppb (1.68 µg/m^3). The injection size listed in the analytical procedure (1 µL, 28:1 split) was used in the determination of the detection limit of the overall procedure.

Table 4.2.
Detection Limit of the
Overall Procedure

sample no.	ng spiked	ng recovered
1	10.08	8.36
2	10.08	9.13
3	10.08	8.81
4	10.08	10.08
5	10.08	8.22
6	10.08	11.04

4.3. Reliable quantitation limit

The reliable quantitation limit was determined by analyzing 100-mg portions of HBr-coated charcoal (including 2 glass wool plugs) spiked with 10.08 ng of 2,3-dibromo-2-propen-1-ol. This amount corresponds to an air concentration of 0.73 ppb (1.68 µg/m^3). Because the recovery of the analyte from the spiked samples was greater than 75% with a precision of ±25% or better, the detection limit of the overall procedure and reliable quantitation limit are the same.

Table 4.3.
Reliable Quantitation Limit
(Based on samples and data of Table 4.2.)

percent recovered	statistics
82.9	
90.6	mean = 92.0%
87.4	SD = 10.8%
100.0	Precision = (1.96)(±10.8%)
81.5	= ±21.2%
109.5	

4.4. Instrument response to the analyte

The instrument response to the isomers of 2,3-dibromo-2-propen-1-ol over the range of 0.5 to 2 times the target concentration was determined from multiple injections of analytical standards. The response was linear with a slope of 0.830.

Table 4.4.
Instrument Response

× target concn	0.5×	1.0×	2.0×
µg/standard	7.01	14.02	28.05
ISTD amts	7.47	13.82	25.23
	7.81	13.97	25.32
	7.58	13.97	25.31
	7.59	13.72	24.96
	7.50	13.74	24.99
	7.62	13.90	25.07
mean	7.60	13.85	25.15

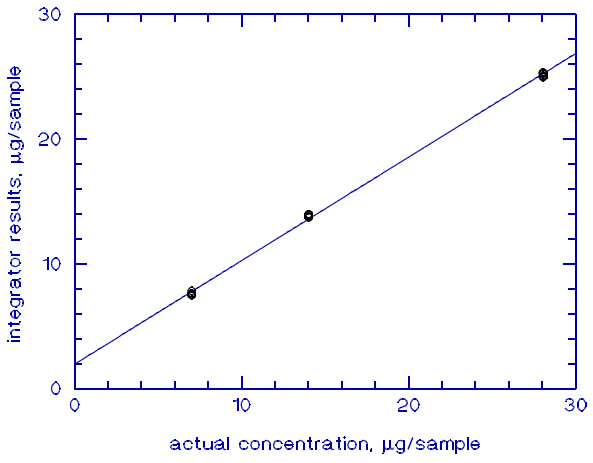

Figure 4.4. Calibration curve for 2,3-dibromo-2-propen-1-ol.

4.5. Storage data

Thirty-six samples were collected over 2 days (18 samples each day) from controlled test atmospheres containing an average of 1.0 ppm propargyl alcohol. Each sample was collected for 2 h at 0.05 L/min. The average relative humidity of the controlled test atmospheres was 75% at 27°C. Six samples (3 each day) were analyzed immediately after collection. Fifteen samples were stored in a refrigerator at about 5°C, and 15 different samples were stored in the dark at about 23°C. Every few days, 3 samples from each group were selected and analyzed. The recovery of propargyl alcohol from samples stored at ambient temperature remained above 80.3%.

Table 4.5.
Storage Test

days of amb. storage	% recovery (ambient)			days of ref. storage	% recovery (refrigerated)		
0	88.3	89.8	84.6	0	82.6	86.4	83.2
4	104.0	84.9	83.6	2	88.5	85.2	84.1
7	85.1	82.9	80.7	5	89.7	87.7	86.0
11	87.2	83.8	83.3	8	92.6	88.2	86.4
14	83.8	74.4	83.7	12	86.0	88.9	82.6
18	81.8	85.0	77.5	15	89.9	80.5	83.4

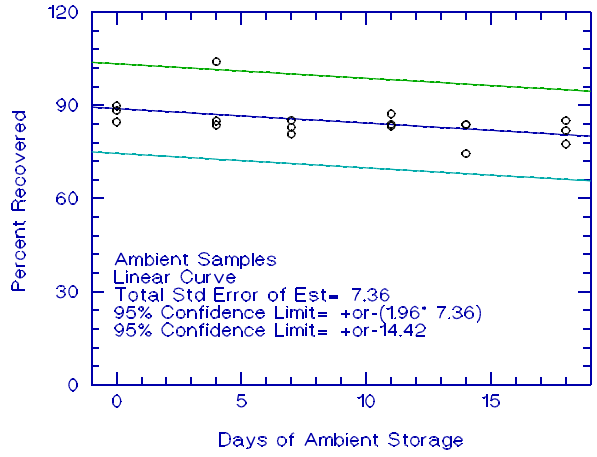

Figure 4.5.1. Ambient temperature storage test.

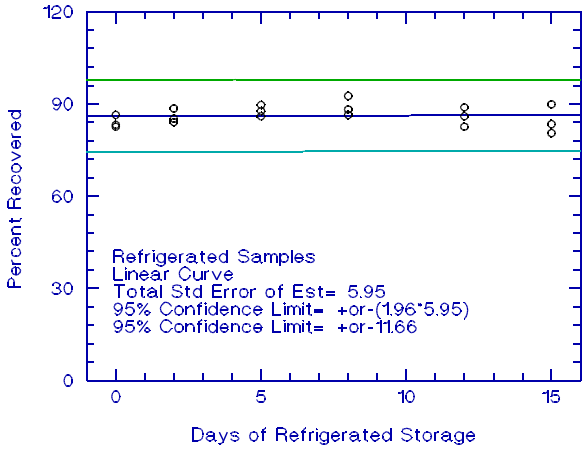

Figure 4.5.2. Refrigerated temperature storage test.

4.6. Precision (analytical method)

The precision of the analytical procedure is defined as the pooled coefficient of variation determined from replicate injections of analytical standards representing 0.5, 1, and 2 times the target concentration. The coefficients of variation are calculated from the data in Table 4.4. The pooled coefficient of variation is 0.011.

Table 4.6.
Precision of the Analytical Method
(Based on the Data of Table 4.4.)

× target concn	0.5×	1.0×	2.0×
µg/sample	7.01	14.02	28.05
SD[1]	0.1198	0.1106	0.1606
CV	0.0158	0.0080	0.0064

[1] in µg/sample

4.7. Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

where n = total number of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed percent recovery at a given time
Y_{est} = estimated percent recovery from the regression line at the same given time

An additional 5% for pump error is added to the SEE by the addition of variances. The precision at the 95% confidence level is obtained by multiplying the SEE (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression line in the storage graph as shown in Figure 4.5.1. The data for Figure 4.5.1. were used to determine the SEE of ±7.36% and the precision of the overall procedure of ±14.42%.

4.8. Reproducibility data

Six samples were prepared by liquid spiking sampling tubes with 2,3-dibromo-2-propen-1-ol. Six liters of humid air at 20°C and 76% RH were drawn through each sampler in order to subject the derivative to a humid environment. A draft copy of this method and the samples were submitted for analysis. The samples

Table 4.8.
Reproducibility Data

µg spiked	µg recovered	percent recovered	percent deviation
13.28	12.34	92.9	-7.1
13.28	12.70	95.6	-4.4
13.28	12.78	96.2	-3.8
13.28	12.73	95.9	-4.1
13.28	13.12	98.8	-1.2
13.28	12.70	96.6	-3.4

were analyzed after 36 days of storage at about 5°C. All of the sample results were within the precision of the overall procedure.

4.9. Desorption efficiency and stability of desorbed samples

4.9.1. Desorption efficiency

The desorption efficiency of 2,3-dibromo-2-propen-1-ol from HBr-coated charcoal was determined by liquid spiking 100-mg portions of coated charcoal (including 2 glass wool plugs) with 2,3-dibromo-2-propen-1-ol at 0.5, 1, and 2 times the target concentration. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average recovery was 88.6%.

Table 4.9.1.
Desorption Efficiency

× target concn µg/sample	0.5× 7.05	1.0× 15.1	2.0× 28.2
DE, %	88.2	88.5	90.4
	86.7	87.0	90.0
	89.8	87.9	90.2
	86.0	88.8	89.4
	87.4	90.0	89.5
	87.4	89.0	89.0
mean	87.6	88.5	89.8

Propargyl alcohol could probably be used to evaluate desorption efficiency because the derivatization reaction is quantitative. 2,3-Dibromo-2-propen-1-ol was used in this case because the intent was to determine the desorption of 2,3-dibromo-2-propen-1-ol from the sampling medium, not the combined total of the derivatization reaction efficiency and the desorption efficiency. Additionally, the derivative was used so that analytical standards could be prepared using the same reagent and technique used to prepare the test samples.

4.9.2. Stability of desorbed samples

The stability of desorbed samples was verified by reanalyzing the 1.0 times target concentration samples 2 days after the original analysis. The samples were resealed immediately after the original analysis and fresh standards were used in the reanalysis. Both the original desorbed (but not diluted) samples (4-mL vials) and the desorbed and diluted (2-mL vials) samples were reanalyzed. The average of the reanalysis of the desorbed but not diluted samples was 87.4% and for the desorbed and diluted samples, 87.9%.

Table 4.9.2.1.
Stability of Desorbed Samples

initial recovery (percent)	recovery after 2 days (percent)	percent change
88.5	87.3	-1.2
87.0	86.9	-0.1
87.9	88.3	+0.4
88.9	87.9	-1.0
90.0	86.6	-3.4
89.0	87.2	-1.8

Table 4.9.2.2.
Stability of Desorbed and Diluted Samples

initial recovery (percent)	recovery after 2 days (percent)	percent change
88.5	88.3	-0.2
87.0	86.2	-0.8
87.9	87.4	-0.5
88.8	88.6	-0.2
90.0	88.5	-1.5
89.0	88.4	-0.6

5. References

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