



Method number:	PV2140
Target concentration:	2 ppm (5 mg/m ³)
OSHA PEL:	2 ppm (5 mg/m ³) (Skin)
NIOSH REL	2 ppm (5 mg/m ³) (4 ppm STEL) (Skin)
ACGIH TLV:	0.5 ppm (skin)
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing coconut shell charcoal. Samples are extracted with 95:5 methylene chloride: methanol and analyzed by GC using a flame ionization detector (GC/FID).
Recommended sampling time and sampling rate:	200 min at 0.05 L/min (10 L)
Reliable quantitation limit:	0.07 mg/m ³
Special Requirement:	Samples should be refrigerated upon receipt at the laboratory.
Status of method:	Partially validated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History

This work was performed because the method that SLTC uses for allyl alcohol, NIOSH method 1402¹, does not have tests for the effects of humid air on sampler capacity, or for sample storage stability.

Results presented in this method show that samples extracted with 1 mL of 95:5 methylene chloride: methanol solution had good extraction efficiencies averaging 98.7%. The retention efficiency results showed no allyl alcohol on the back-up section of samples that had been spiked with 100 µg of allyl alcohol and then had 10 L of humid air drawn through them. The storage stability results showed 89.1% recovery for samples stored for up to 14 days at refrigerated temperature, and 83.9% at ambient temperature.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)²

Allyl alcohol is not classified as carcinogen or a suspect carcinogen by ACGIH. It may cause lung damage, skin irritation and irritation to eyes. The oral LD₅₀ is 64 mg/kg for rats.

1.1.3 Workplace exposure³

Allyl alcohol is primarily used in manufacturing of allyl compounds, war gases, resins and plasticizers. No information on exposure is available.

1.1.4 Physical properties and other descriptive information^{4,5}

CAS number:	107-18-6
IMIS ⁶ :	0130
molecular weight:	58.08
density:	0.854 g/mL (25 °C)
melting point:	-50 °C
boiling point:	96-97 °C
appearance:	colorless liquid
vapor pressure:	2.67kPa @20 °C
odor:	mustard like
molecular formula:	C ₃ H ₆ O
solubility:	miscible with water, alcohol, chloroform
synonyms:	2-propen-1-ol, 1-propenol-3, vinyl carbinol

¹ NIOSH Method 1402, .www.cdc.gov/niosh, (accessed October 2003).

² 2004 TLV and BEIs, Threshold Limit Values for Chemical Substance and Physical Agents, American Conference of Governmental Industrial Hygienists, (ACGIH): Cincinnati, OH, 2004.

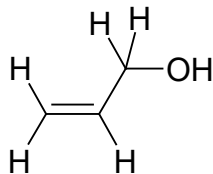
³ O'Neil, M., The Merck Index, 13th ed., Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 297.

⁴ 2004 TLV and BEIs, Threshold Limit Values for Chemical Substance and Physical Agents, American Conference of Governmental Industrial Hygienists, (ACGIH): Cincinnati, OH, 2004.

⁵ O'Neil, M., The Merck Index, 13th ed., Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 297.

⁶ OSHA Chemical Sampling Information, www.osha.gov, (accessed October 2003).

structural formula:



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"⁷. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 2.5 µg of allyl alcohol. This is the amount spiked on a sampler that would produce a peak at least 10 times the response for a sample blank. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and slope) for the calculation of the DLOP. The slope was 1910 and the SEE was 138.4. The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The DLOP and RQL were 0.22 µg and 0.72 µg, respectively. The recovery at the RQL was 89%.

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the author listed on the cover page of this method at (801)233-4900.

Table 1.2
Detection Limit of the Overall Procedure
for Allyl alcohol

mass per sample (µg)	area counts (µV-s)
0	0
0.25	999
0.50	1258
0.75	1579
1.00	2138
1.25	2482
1.50	3034
1.75	3596
2.00	4052
2.25	4520
2.50	5027

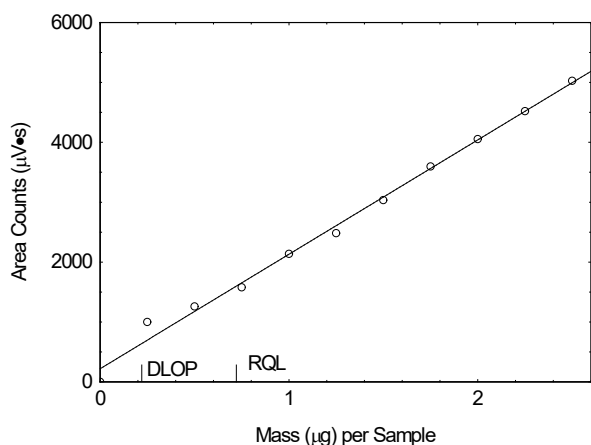


Figure 1.2.1 Plot of data to determine the DLOP/RQL for allyl alcohol ($y = 1910x + 220$)

⁷ Burreight, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis; OSHA Salt Lake Technical Center, U.S. Department of Labor, Salt Lake City, UT, 1999.

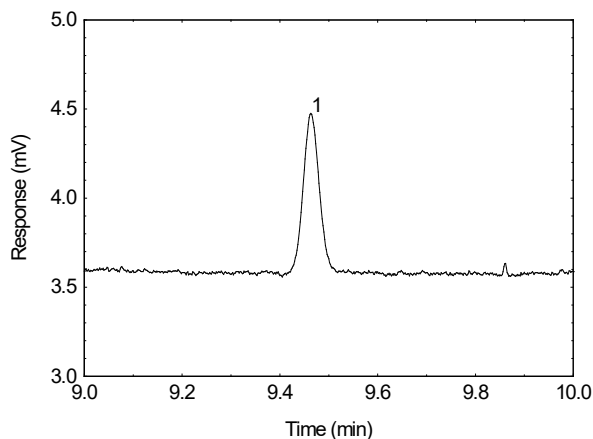


Figure 1.2.2 Chromatogram of allyl alcohol at the RQL level. [key:(1) allyl alcohol]

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

- 2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within $\pm 5\%$ of the recommended flow rate.
- 2.1.2 Samples are collected with 7-cm \times 4-mm i.d. \times 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of charcoal. The sections are held in place with foam plugs with a glass wool plug at the front. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-01 lot 2000).

2.2 Reagents

None required

2.3 Technique

- 2.3.1 Immediately before sampling break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking tube ends. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.
- 2.3.2 The smaller section of the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder, and tubing so they do not impede work performance or safety.

- 2.3.3 Draw air to be sampled directly into the inlet of the tube holder. The air being sampled is not to be passed through any hose or tubing before entering the sampling tube.
- 2.3.4 After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form as soon as possible.
- 2.3.5 Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.
- 2.3.6 Record sample air volumes (liters), sampling time (minutes), and sampling rate (L/min) for each sample, along with any potential interferences on the OSHA-91A form.
- 2.3.7 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

2.4 Extraction efficiency

The extraction efficiency was determined by spiking charcoal tubes (SKC, lot 2000) with allyl alcohol at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted for 30 minutes with shaking, and analyzed. The mean extraction efficiency over the studied range was 98.7%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto charcoal tubes which had 10 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them. The mean recovery for the wet samples was 97.8%.

Table 2.4
Extraction Efficiency (%) of Allyl Alcohol

<u>level</u>		<u>sample number</u>						
\times target concn	μ g per sample	1	2	3	4	5	6	mean
0.1	5.0	98.5	103.5	101.7	99.8	98.3	95.7	99.6
0.25	12.5	100.1	98.9	96.6	96.6	99.2	99.5	98.5
0.5	25	102.1	97.6	103.0	100.1	103.0	101.5	101.2
1.0	50	96.8	99.8	97.4	93.2	98.7	96.9	97.1
2.0	100	97.7	97.9	96.9	96.0	96.0	98.1	97.1
1.0 (wet)	50	97.8	98.8	97.3	96.8	97.6	98.2	97.8

2.5 Retention efficiency

Six charcoal tubes were spiked with 100 μ g of allyl alcohol, in the front section of the tubes, and allowed to equilibrate for 6 h. The tubes had 10 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) pulled through them at 0.05 L/min. The samples were extracted and analyzed. The mean retention recovery was 97.4%. There was no analyte found on the back-up section of any of the tubes.

Table 2.5
Retention Efficiency (%) of Allyl Alcohol

section	sample number						mean
	1	2	3	4	5	6	
front of spiked tube	96.1	95.5	97.5	97.9	100.9	95.9	97.4
rear of spiked tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	96.1	95.5	97.5	97.9	100.9	95.9	97.4

2.6 Sample storage

Fifteen charcoal tubes were each spiked with 50 µg of allyl alcohol. They were allowed to equilibrate for 6 h, then 10 L of air (absolute humidity of 15.9 mg/L of water about 80% relative humidity at 22.2 °C), were drawn through them. Three samples were analyzed immediately, and the rest were sealed. Six were stored at room temperature (23 °C), while the other six were stored at refrigerated temperature (4 °C). Three samples stored at room temperature and three samples stored at refrigerated temperature were analyzed after 7 days and the remaining six after 14 days. The amounts recovered indicate acceptable storage stability for the time period studied. Refrigerated samples show better recovery, therefore, it is advised to store samples at refrigerated temperature.

Table 2.6
Storage Test for Allyl Alcohol (% Recovery)

time (days)	ambient storage			refrigerated storage		
0	92.9	92.5	97.9			
7	85.7	87.2	87.0	88.1	90.2	88.2
14	81.0	83.9	86.7	90.1	88.9	88.3

2.7 Recommended air volume and sampling rate

Based on the data collected in this evaluation, 10 L air samples should be collected at a sampling rate of 0.05 L/min for 200 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of allyl alcohol.

2.8.2 Suspected interferences should be reported to the laboratory with submitted samples.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs.

3.1 Apparatus

3.1.1 A gas chromatograph equipped with an FID. An Agilent 6890 plus series Gas chromatograph equipped with a 7683 Automatic Sampler was used in this evaluation.

- 3.1.2 A GC column capable of separating allyl alcohol from the extraction solvent, internal standard, and any potential interference. A Phenomenex 60-m × 0.32-mm i.d. ZB-WAX (1.5- μ m df) capillary column was used in this evaluation.
- 3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium³² Data System was used in this evaluation.
- 3.1.4 Glass vials with poly (tetrafluoroethylene)-lined caps. Two-mL vials were used in this evaluation.
- 3.1.5 A dispenser capable of delivering 1.0 mL of extraction solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.
- 3.1.6 Volumetric flasks – 10-mL and other convenient sizes for preparing standards.
- 3.1.7 Calibrated 10- μ L or 20- μ L syringe for preparing standards.
- 3.1.8 A mechanical shaker. An Eberbach mechanical shaker was used in this evaluation.

3.2 Reagents

- 3.2.1 Allyl alcohol, reagent grade. Aldrich 99.5%, (lot 09427CS) was used in this evaluation.
- 3.2.2 Methanol, reagent grade. Fisher 99.8%, (lot 020390) was used in this evaluation.
- 3.2.3 Methylene chloride, HPLC grade. Fisher 99.7%, (lot 034459) was used in this evaluation.
- 3.2.4 2-Ethyl-1-hexanol, reagent grade, internal standard. Aldrich 99.7%, (lot 01319TR) was used in this evaluation.
- 3.2.5 The extraction solvent solution was methylene chloride: methanol (95:5) with 1.25 μ L/mL of 2-ethyl-1-hexanol as internal standard

3.3 Standard preparation

- 3.3.1 At least two separate stock standards should be prepared. Prepare a stock standard by injecting 3 μ L of allyl alcohol into a 10-mL volumetric flask containing the extraction solvent. Dilute this stock standard 1:5 to prepare a working standard equivalent to the PEL.
- 3.3.2 Bracket sample concentrations with standard concentrations. If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

3.4 Sample preparation

- 3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer the adsorbent sections to separate 2-mL vials. Discard the glass tube, urethane foam plug and glass wool plug.
- 3.4.2 Add 1.0 mL of extracting solvent to each vial.
- 3.4.3 Immediately seal the vials with poly(tetrafluoroethylene)-lined caps.

3.4.4 Shake the vials on a shaker for 30 minutes.

3.4 Analysis

3.5.1 Gas chromatographic conditions

GC conditions

column: initial 70 °C, hold 4 min, program temperature at 10 °C/min to 220 °C, hold 2 min

zone

temperatures: 250°C (injector)
250°C (detector)

run time: 21 min

column gas flow: 2.0 mL/min (hydrogen)

injection size: 1.0 µL (10:1 split)

column: Phenomenex -60-m × 0.32-mm i.d. capillary ZB-WAX with 1.5-µm df

retention times: 5.6, 6.0 min solvent
9.4 min (allyl alcohol)
15.2 min (2-ethyl -1-hexanol)

FID conditions

hydrogen flow: 30 mL/min

air flow: 400 mL/min

makeup flow: 25 mL/min (nitrogen)

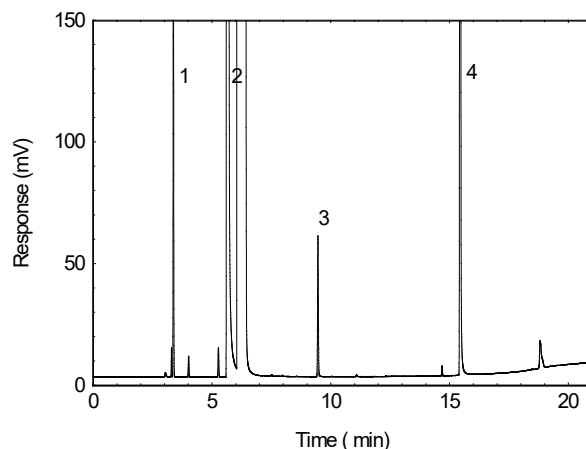


Figure 3.5.1 Chromatogram obtained at the target level with the recommended conditions. [key: (1) impurity; (2) solvent (3) allyl alcohol, and (4) 2-ethyl-1-hexanol]

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.5.3 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over the range of concentrations.

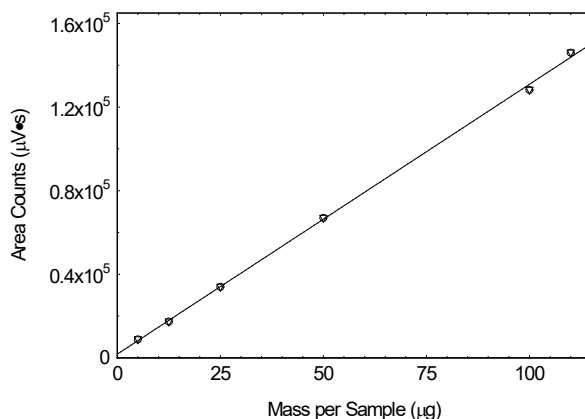


Figure 3.5.3. Calibration curve for allyl alcohol.
($y = 1291x + 1809$)

3.6 Interferences (analytical)

3.6.1 Any compound that produces a GC response and has a similar retention time as the analyte is a potential interference. If any potential interference were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak can be confirmed by GC-mass spectrometry. Figure 3.6.2 is a mass spectrum of allyl alcohol.

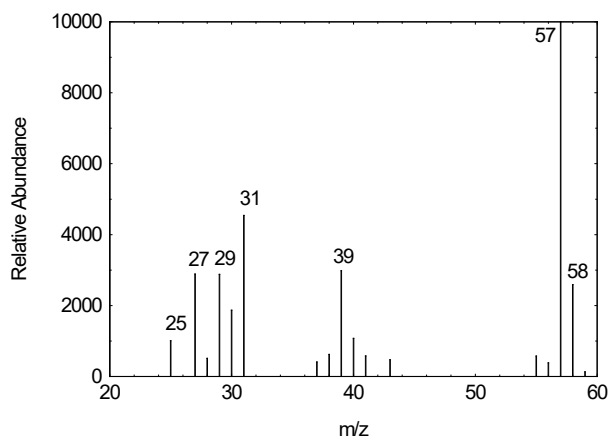


Figure 3.6.2 Mass spectrum of allyl alcohol

3.7 Calculations

The amount of analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight
 M is micrograms per sample
 V is liters of air sampled
 E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
 V_M is 24.46 (molar volume at NTP)
 C_M is concentration by weight
 M_r is molecular weight (58.08)

4. Recommendations for Further Study

Collection, reproducibility, and other detection limit studies need to be performed to make this a fully validated method.