Allyl Propyl Disulfide
Diallyl Disulfide
Dipropyl Disulfide

Method Number:	PV2086
Target concentration:	2 ppm (12 mg/m^3) allyl propyl disulfide OSHA TWA PEL
Procedure:	Samples are collected by drawing a known volume of air through a Chromosorb 106 tube. Samples are desorbed with trichloroethylene and analyzed by gas chromatography using a flame photometric detector (GC-FPD).
Air volume and sampling rate studied:	50 minutes at 0.2 Lpm (10 L)
Status of method:	Partially Validated Method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA laboratory recently received some samples collected in toluene impingers requesting allyl propyl disulfide. A solid sorbent collection method was wanted, so XAD-4, Tenax, and Chromosorb 106 tubes were investigated, and Chromosorb 106 tubes were found to have the best desorption efficiency. The retention and storage studies with Chromosorb 106 were also good.

1.1.2 Potential workplace exposure (Ref. 5.1)

Workers are exposed to allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide in onion and garlic processing plants.

1.1.3 Toxic effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Refs. 5.1- 5.7)

The OSHA PEL of 2 ppm for allyl propyl disulfide is based on study of worker exposure in an onion processing plant in 1946 by Feiner et al (Ref. 5.1). They took air samples in gasbags, oxidized the contents, and analyzed for total sulfur dioxide. They assumed the atmosphere sampled was all allyl propyl disulfide and calculated the amount allyl propyl disulfide present based on the amount of sulfur dioxide found. These amounts averaged 3.4 ppm. Since the workers at the plant had eye and skin problems from exposure, they recommended a PEL of 2 ppm. Grant recommends a PEL of 2-3 ppm for diallyl disulfide based on its presence in cut onion vapor (Ref. 5.2). Onions, when cut, form allyl propyl disulfide, diallyl disulfide, dipropyl disulfide, other disulfides, sulfides, trisulfides, thiosulfinates, sulfenic acids, mercaptans, sulfoxides, sulfates, and thial oxides (Ref. 5.3). All of these compounds form sulfur dioxide when oxidized and the assumption by Feiner et al that the compound measured was all allyl propyl disulfide, or in the cased of Grant allyl propyl disulfide and diallyl disulfide, may be erroneous. The concentration of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide changes with time after the onion is cut, with more found with time (Ref. 5.4). These concentrations are also dependant upon the variety of onion sampled. Some researchers found no allyl propyl disulfide in the vapor from some of the varieties of onion studied (Ref. 5.5). Block et al have suggested that the lachrimatory factor in onions is propanethial-S-oxide, which forms sulfuric acid immediately upon contact with water (Ref. 5.6). Burning of the throat and eyes was observed at the laboratory when trace levels of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide were released into the air by washing volumetrics in a dishwasher. The volumetrics had been allowed to dry before washing for five days (Ref. 5.7). This data suggest toxicity studies should be performed using the individual compounds mentioned and the PEL re-evaluated based on the new data.

1.1.4 Physical properties:

<u>Allyl propyl disulfide (Ref. 5.8)</u>

CAS:	2179-59-1
IMIS:	0150
RTECS:	J00350000; 32322
Compound:	$H_2C{=}CHCH_2S_2CH_2CH_2CH_3$
Molecular formula:	$C_6H_{12}S_2$
Synonyms:	Disulfide, allyl propyl

Molecular weight:	148.16
Density:	0.9289
Freezing point:	- 15 ºC
Odor:	onion odor
Color:	very pale yellow oil

Diallyl disulfide (Ref. 5.9)

CAS:	2179-57-9
IMIS:	D736
Compound:	$H_2C=CHCH_2S_2CH_2CH=CH_2$
Molecular formula:	$C_6H_{10}S_2$
Synonyms:	Allyl disulfide; Di-2-propenyldisulfide; 4,5-Dithia-1,7-octadiene
Molecular weight:	146.26
Density:	1.01
Boiling point:	79 ºC
Odor:	garlic odor
Color:	pale yellow oil

Dipropyl disulfide (Ref. 5.10)

CAS:	629-19-6
IMIS:	D626
Compound:	$H_3CCH_2CH_2S_2CH_2CH_2CH_3$
Molecular formula:	$C_6H_{14}S_2$
Synonyms:	Di-n-propyl disulfide; Propyl disulfide
Molecular weight:	150.31
Density:	0.9599
Boiling point:	193.5 ºC
Odor:	onion odor
Color:	pale yellow oil

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 1 µg for each of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide. This is the smallest amount that could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.02 ppm for each of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide. (All ppm amounts in this study are based on a 10-liter air volume.)

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

None known

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow.

2.1.2 Chromosorb 106 tubes containing 100-mg adsorbing section with 50-mg backup section, separated by urethane foam plug with silanized glass wool before the adsorbing section and urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., SKC tubes or equivalent.

2.2 Sampling technique

2.2.1 Open the ends of the Chromosorb 106 tube immediately before sampling.

2.2.2 Connect the Chromosorb 106 tube to the sampling pump with flexible tubing.

2.2.3 Place the tubes in a vertical position to minimize channeling, with the smaller section towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the Chromosorb 106 tube.

2.2.5 Seal the Chromosorb 106 tube with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except no air are drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate mailing container from other samples.

2.3 Desorption efficiency

2.3.1 Allyl propyl disulfide

Six tubes each were spiked at a loading of 64.25 µg (1.06 ppm), 120.8 µg (1.99 ppm), and 242.4 µg (4.00 ppm) of allyl propyl disulfide. They were allowed to equilibrate overnight at room temperature. They were then opened; each section placed into a separate 2-mL vial, desorbed with 1 mL of trichloroethylene for 30 minutes with occasional shaking, and analyzed by GC-FPD. The overall average desorption efficiency was 96.83%. (Table 2.3.1)

Table 2.3.1
Allyl Propyl Disulfide Desorption Efficiency

tube #	% recovery		
	64.25 µg	120.8 µg	242.4 µg
1	96.95	90.86	90.10
2	94.01	96.47	94.41
3	96.25	92.16	98.85
4	95.13	96.36	99.56
5	97.64	99.29	101.0
6	98.42	101.5	104.0
average	96.40	96.11	97.98

overall average = 96.83%
standard deviation = ±3.69

2.3.2 Diallyl disulfide

Six tubes each were spiked at each loading of 65.65 µg (1.10 ppm), 131.3 µg (2.19 ppm), and 262.6 µg (4.39 ppm) diallyl disulfide. They were allowed to equilibrate overnight at room temperature. They were then opened; each section placed into a separate 2-mL vial, desorbed with 1 mL of trichloroethylene for 30 minutes with occasional shaking, and analyzed by GC-FPD. (Table 2.3.2)

Table 2.3.2
Diallyl Propyl Disulfide Desorption Efficiency

tube #	% recovery		
	65.65 µg	131.3 µg	262.6 µg
1	89.50	101.4	100.8
2	86.44	101.2	91.52
3	84.79	96.48	99.49
4	88.09	103.5	98.50
5	84.56	102.6	102.2
6	85.54	102.8	107.0
average	86.49	101.3	99.93

2.3.3 Dipropyl disulfide

Six tubes each were spiked at each loading of 62.39 µg (1.01 ppm), 124.8 µg (2.03 ppm), and 249.6 µg (4.06 ppm) dipropyl disulfide. They were allowed to equilibrate overnight at room temperature. They were then opened; each section placed into a separate 2-mL vial, desorbed with 1 mL of trichloroethylene for 30 minutes with occasional shaking, and analyzed by GC-FPD. (Table 2.3.3)

Table 2.3.3
Dipropyl Disulfide Desorption Efficiency

tube #	% recovery		
	62.39 µg	124.8 µg	249.6 µg
1	85.24	95.72	97.18
2	79.73	97.54	101.3
3	80.72	97.30	102.1
4	81.81	94.66	101.1
5	85.45	95.72	101.9
6	80.52	92.97	104.9
average	82.25	95.65	101.4

2.4 Retention Efficiency

2.4.1 Allyl propyl disulfide

Since pure allyl propyl disulfide was expensive and difficult to obtain, the lab purchased only a small quantity. This was used up in the desorption studies. A mixture of allyl propyl disulfide, diallyl disulfide and dipropyl disulfide in a ratio of 42.75:10.91:46.34 respectively, was used for the retention and storage studies. Six tubes were liquid spiked with 124.8 µg (2.06 ppm) allyl propyl disulfide, allowed to equilibrate overnight, and had 10 liters humid air (80% RH) pulled through them at 0.1 Lpm. They were then opened, desorbed, and analyzed by GC-FPD. The retention efficiency averaged 98.95%. There was no allyl propyl disulfide found on the backup portions of the tubes. (Table 2.4.1)

Table 2.4.1
Allyl Propyl Disulfide Retention Efficiency

tube #	% recovered		
	'A'	'B'	total
1	99.17	0.0	99.17
2	97.32	0.0	97.32
3	99.80	0.0	99.80
4	104.9	0.0	104.9
5	95.78	0.0	95.78
6	96.70	0.0	96.70

average = 98.95%

2.4.2 Diallyl disulfide

Six tubes were liquid spiked with 131.3 µg (2.19 ppm) diallyl disulfide, allowed to equilibrate overnight, and had 10 liters humid air (80% RH) pulled through them at 0.1 Lpm. They were opened, desorbed, and analyzed by GC-FPD; the retention efficiency averaged 98.32%. There was no diallyl disulfide found on the backup portions of the tubes. (Table 2.4.2)

Table 2.4.2
Diallyl Disulfide Retention Efficiency

tube #	% recovered		
	'A'	'B'	total
1	94.59	0.0	94.59
2	100.4	0.0	100.4
3	101.6	0.0	101.6
4	97.29	0.0	97.29
5	95.56	0.0	95.56
6	100.5	0.0	100.5

average = 98.32%

2.4.3 Dipropyl disulfide

Six tubes were liquid spiked with 124.8 µg (2.03 ppm) dipropyl disulfide, allowed to equilibrate overnight, and had 10 liters humid air (80% RH) pulled through them at 0.1 Lpm. They were opened, desorbed, and analyzed by GC-FPD. The retention efficiency averaged 99.43%. There was no dipropyl disulfide found on the backup portions of the tubes. (Table 2.4.3)

Table 2.4.3
Dipropyl Disulfide Retention Efficiency

tube #	% recovered		
	'A'	'B'	total
1	98.32	0.0	98.32
2	98.01	0.0	98.01
3	101.8	0.0	101.8
4	105.7	0.0	105.7
5	95.59	0.0	95.59
6	97.15	0.0	97.15

average = 99.43%

2.5 Storage

2.5.1 Allyl propyl disulfide

Twelve tubes were each spiked with 124.8 µg (2.06 ppm) of allyl propyl disulfide. Six were stored at refrigerated temperature (0 ºC) and six at room (24 ºC) temperatures until opened and analyzed. The refrigerated temperature recoveries averaged 99.70% and the room temperature recoveries averaged 98.21% for allyl propyl disulfide for the 6-days stored. (Table 2.5.1)

Table 2.5.1
Allyl Propyl Disulfide Storage Study

day	% recovered	
	0 ºC	24 ºC
4	97.20	101.8
4	103.2	98.64
4	98.93	95.67
6	99.57	97.64
6	98.44	97.45
6	100.8	98.03
average	99.70	98.21

2.5.2 Diallyl disulfide

Twelve tubes were spiked with 131.3 µg (2.19 ppm) of diallyl disulfide. Six were stored at refrigerated temperature (0 ºC) and six at room (24 ºC) temperatures until opened and analyzed. The refrigerated temperature recoveries averaged 98.68% and the room temperature recoveries averaged 98.11% for diallyl disulfide for the 12 days stored. (Table 2.5.2)

Table 2.5.2
Diallyl Disulfide Storage Study

day	% recovered	
	0 ºC	24 ºC
7	93.83	97.19
7	90.18	93.79
7	98.98	96.09
12	102.9	98.10
12	103.7	103.5
12	102.5	100.0
average	98.68	98.11

2.5.3 Dipropyl disulfide

Twelve tubes were spiked with 124.8 µg (2.03 ppm) of dipropyl disulfide. Six were stored at refrigerated temperature (0 ºC) and six at room (24 ºC) temperatures until opened and analyzed. The refrigerated temperature recoveries averaged 99.01% and the room temperature recoveries averaged 97.28% for dipropyl disulfide for the 9 days stored. (Table 2.5.3)

Table 2.5.3
Dipropyl Disulfide Storage Study

day	% recovered	
	0 ºC	24 ºC
3	99.21	99.75
3	96.49	96.71
3	100.6	99.88
9	97.41	96.91
9	99.42	94.21
9	100.9	96.20
average	99.01	97.28

2.6 Air volume and sampling rate studied

2.6.1 The air volume studied was 10 liters.

2.6.2 The sampling rate studied was 0.2 liters per minute.

2.7 Interferences

Suspected interferences should be listed on sample data sheets.

2.8 Safety precautions

2.8.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.8.2 Safety glasses should be worn at all times in designated areas.

2.8.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame photometric detector with a sulfur filter.

3.1.2 GC column capable of separating the analyte from any interference. The column used in this study was a 10-ft. × 1/8-in stainless steel column packed with 20% SP2100 with 0.1% Carbowax 1500 on 80/100 Supelcoport. An alternate column is a 60-m x 0.32-mm i.d. (1.0 µm d_f DB-1) capillary column.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 1-µL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks, 5-mL, and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Allyl propyl disulfide

3.2.3 Diallyl disulfide, reagent grade

3.2.4 Dipropyl disulfide, reagent grade

3.2.5 Mixture of allyl propyl disulfide, diallyldisulfide, and dipropyl disulfide

3.2.6 Trichloroethylene, reagent grade

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2 Each section is desorbed with 1 mL of trichloroethylene.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide with trichloroethylene.

3.4.2 At least two separate stock standards should be made.

3.4.3 Dilutions of the stock standards are prepared to bracket the samples. For this study, the standards ranged from 1 to 300 µg/mL of each compound in the trichloroethylene.

3.5 Analysis

3.5.1 Gas chromatograph conditions for 10-ft. × 1/8-in stainless steel column packed with 20% SP2100 with 0.1% Carbowax 1500 on 80/100 Supelcoport.

Flow rates	**(mL/min)**	**Temperature**	**(ºC)**
Nitrogen:	24	Injector:	160
Hydrogen:	100	Detector:	200
Air:	60	Column:	130
Oxygen:	30		
Injection size:	1 µL		
Chromatogram:	(see Figure 1)		

3.5.2 Gas chromatograph conditions for 60-m x 0.32-mm i.d. (1.0 µm d_f DB-1) capillary column.

Flow rates	**(mL/min)**	**Temperature**	**(ºC)**
Nitrogen (makeup):	30	Injector:	240
Hydrogen (carrier):	2	Detector:	240
Air:	100	Column:	140
Hydrogen (detector):	75		
Injection size:	1 µL		
Chromatogram:	(see Figure 2)		

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

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 A calibration curve with area counts versus concentration was generated from the calibration standards.

3.7.2 The area counts for the samples are plotted on the calibration curve to obtain the concentration of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide in solution.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$mass\ of\ analyte,\ \mu g = \frac{(\mu g / mL)(desorption\ volume,\ mL)}{(desorption\ efficiency,\ decimal)}$$

$$moles\ of\ analyte = \frac{(mass\ of\ analyte,\ \mu g)(1\ g)}{(molecular\ weight)(10^6\ \mu g)}$$

$$volume\ of\ analyte = (moles\ of\ analyte)(molar\ volume)$$

$$ppm = \frac{(volume\ of\ analyte)(10^6)^*}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 10-liter air sample:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(L)(DE)(MW)}$$

Where:

µg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
10 L = Air volume, L
DE = Desorption efficiency, decimal

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all chemicals.

3.8.3 Wear safety glasses, gloves and a lab coat at all times in designated laboratory areas.

4 Recommendations for further study

The toxic effects of allyl propyl disulfide, diallyl disulfide, and dipropyl disulfide need to be further evaluated. The low levels which cause eye irritation at the OSHA laboratory suggest the PEL may need to be re-evaluated and toxicity studies be performed at lower levels. These studies should include diallyl disulfide and dipropyl disulfide besides the allyl propyl disulfide. Bolelens et al found allyl propyl disulfide appeared in the vapor only after 120 minutes had elapsed from the time the onions were cut (Ref. 5.4). This suggests the need to further explore the compounds in cut onion vapor. Block et al suggest propanethial-S-oxide as a lacrimatory agent formed in cut onion vapor (Ref. 5.6). This compound is highly unstable and reactive, forming sulfuric acid immediately upon contact with water. This compound should be studied for toxic effects and its relationship with the toxic effects of onion vapor.

Figure 1.

An analytical standard of 64.25 µg/mL allyl propyl disulfide, 65.65 µg/mL diallyl disulfide, and 62.39 µg/mL dipropyl disulfide in trichloroethylene, analyzed on a 10-ft. × 1/8-in stainless steel column packed with 20% SP2100 with 0.1% Carbowax 1500 on 80/100 Supelcoport. The retention times of the peaks are trichloroethylene 4.71 min, diallyl disulfide 13.49 min, allyl propyl disulfide 14.55 min, and dipropyl disulfide 15.70 min.

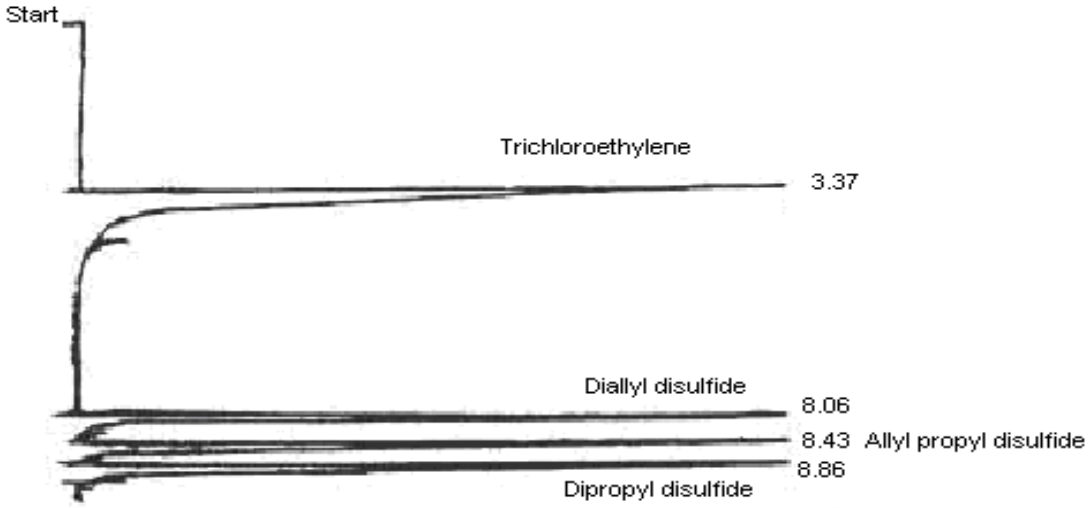

Figure 2.

An analytical standard of 64.25 µg/mL allyl propyl disulfide, 65.65 µg/mL diallyl disulfide, and 62.39 µg/mL dipropyl disulfide in trichloroethylene, analyzed on a 60-m x 0.32-mm i.d. (1.0 µm d_f DB-1) capillary column. The retention times of the peaks are trichloroethylene 3.37 min, diallyl disulfide 8.06 min, allyl propyl disulfide 8.43 min and dipropyl disulfide 8.86 min.

5 References

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