Method no:	PV2133
Target concentration:	1 mg/m^3 (AIHA Workplace Environmental Exposure Level (WEEL))
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing Chromosorb 106. Samples are extracted with 99:1 carbon disulfide: *N,N*-dimethylformamide and analyzed by GC using a flame ionization detector.
Recommended sampling time and sampling rate:	240 min at 0.2 L/min (48 L)
Reliable quantitation limit:	43 μg/m^3
Status of method:	Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

March 2004 Mary Eide

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1. General Discussion

1.1 Background

1.1.1 History

Air samples collected using Chromosorb 106 tubes were received at OSHA SLTC with requested analysis for 1,6-hexanediol diacrylate. This partially-validated work was performed because SLTC had no sampling and analytical method for 1,6-hexanediol diacrylate.

The result of a preliminary extraction efficiency study for 1,6-hexanediol diacrylate extracted from dry Chromosorb 106 with carbon disulfide was 99% recovery. The test was repeated with wet Chromosorb 106 and the recovery was initially the same, but then decreased to 85.2% when the samples were allowed to stand. The source of dry Chromosorb 106 was sampling tubes as received from SKC Inc. The source of wet Chromosorb 106 was dry Chromosorb 106 sampling tubes which had clean, humid air drawn through them. The extraction solvent was changed from pure carbon disulfide to 99:1 carbon disulfide: *N,N*-dimethylformamide and the wet Chromosorb 106 extraction efficiency test was repeated. The results of this test showed no decrease in recovery, therefore, the 99:1 carbon disulfide: *N,N*-dimethylformamide extraction solvent was selected for use in this work. The extraction efficiency was 98.9% using the 99:1 carbon disulfide: *N,N*-dimethylformamide extraction solvent.

1,6-Hexanediol diacrylate was found to be well retained on Chromosorb 106, with a retention efficiency recovery of 98.7% and the storage stability recovery of 97.3% on day 14 of ambient storage.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)[1,2]

1,6-Hexanediol diacrylate is a contact irritant severely affecting the skin, eyes, and respiratory system. It is moderately toxic by skin contact and may cause sensitization.

1.1.3 Workplace exposure[3]

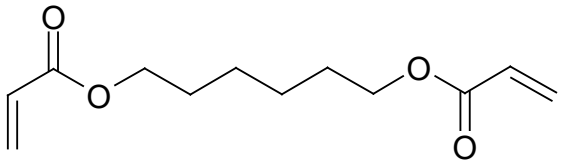
1,6-Hexanediol diacrylate is used as a cross-linking agent in UV curing, inks and coatings.

1.1.4 Physical properties and other descriptive information[4,5]

CAS number:	13048-33-4
synonyms:	acrylic acid hexamethylene ester; hexaneglycol diacrylate; Kayard HDDA; Photomer 4017; propenoic acid, 1,6-hexanediol ester; 2-propenoic acid, 1,6-hexanediyl ester; Setalux UV 2243; Viscoat 230
IMIS:[6]	H128
RTECS:	AT1430000

[1] Lewis, R., *Sax's Dangerous Properties of Industrial Materials,* Tenth ed., Vol. 3, John Wiley & Sons Inc., New York, 2000, p 1951.
[2] Material Safety Data Sheet: Hexanediol Diacrylate, Chemwatch, Victoria, Australia, (accessed 12/17/03).
[3] Lewis, R., *Sax's Dangerous Properties of Industrial Materials,* Tenth ed., Vol. 3, John Wiley & Sons Inc., New York, 2000, p 1951.
[4] Lewis, R., *Sax's Dangerous Properties of Industrial Materials,* Tenth ed., Vol. 3, John Wiley & Sons Inc., New York, 2000, p 1951.
[5] Material Safety Data Sheet: 1,6-Hexanediol Diacrylate, Aldrich Chemical Co., Milwaukee, WI, (accessed 10/3/03).
[6] OSHA Chemical sampling Information, http://www.osha.gov (accessed 12/17/03).

molecular weight:	226.3
density (g/mL):	1.01
melting point:	5 °C
boiling point:	107 °C
appearance:	clear liquid
flash point:	132 °C (270 °F) (Cleveland open cup)
odor:	mild ester-like
molecular formula:	$C_{12}H_{18}O_4$
solubility:	acetone, alcohol, benzene, and carbon tetrachloride
autoignition temperature:	235 °C (455 °F)
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 concentration, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 8.08 µg of 1,6-hexanediol diacrylate. 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 1007 and the SEE was 234. 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 0.70 µg and 2.32 µg, respectively. The recovery at the RQL was 98.2%.

[7] Burright, 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.

Table 1.2
Detection Limit of the Overall Procedure for
1,6-Hexanediol Diacrylate

mass per sample (µg)	area counts (µV-s)
0.00	0
0.81	721
1.62	1230
2.42	1863
3.23	2592
4.04	3586
4.85	4360
5.66	5341
6.46	6143
7.27	7105
8.08	8089

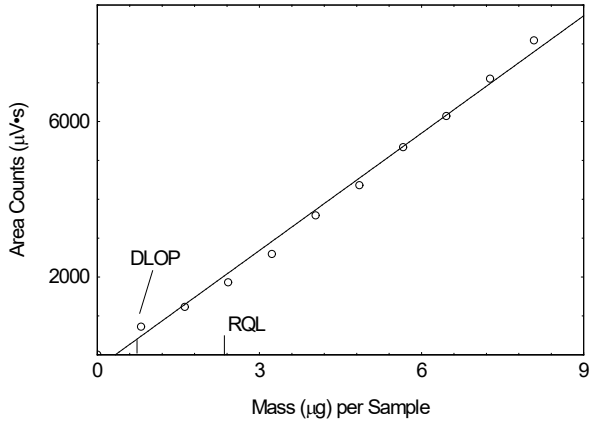


Figure 1.2.1 Plot of data to determine the DLOP/RQL for 1,6-hexanediol diacrylate.
(y = 1007x - 337)

Below is a chromatogram of 1,6-hexanediol diacrylate near the RQL. The recovery was 98.2% at this level.

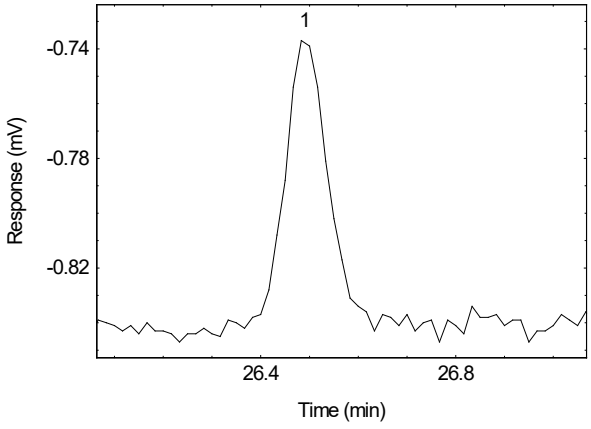


Figure 1.2.2 Chromatogram of 1,6-hexanediol diacrylate peak near the RQL.
(Key: (1) 1,6-hexanediol diacrylate)

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 ±5% of the recommended flow rate.

2.1.2 Samples are collected with 7-cm × 4-mm i.d. × 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of Chromosorb 106. The sections are held in place with foam plugs and with a glass wool plug at the front. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (Catalog no. 226-110, lot 2573).

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 the tube. 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 the 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 the front sections of Chromosorb 106 tubes with 1,6-hexanediol diacrylate at 0.1 to 2 times the target concentration, based on a 48-L air volume, for a loading of 4.85 to 97.0 µg/sample. These samples were stored overnight at ambient temperature and then extracted with 1 mL of extracting solvent on a shaker for 30 minutes, and analyzed by GC-FID. The mean extraction efficiency over the studied range was 98.9%. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto Chromosorb 106 tubes which had 48-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them immediately before spiking. The mean recovery for the wet samples was 98.7%.

Table 2.4
Extraction Efficiency (%) of 1,6-Hexanediol Diacrylate

Level		sample number						
× target concn	µg per sample	1	2	3	4	5	6	mean
0.1	4.85	98.7	99.3	97.9	97.6	99.0	99.1	98.6
0.5	24.3	99.8	99.9	99.4	98.7	99.9	99.7	99.6
1.0	48.5	98.9	99.0	98.3	98.0	98.5	98.2	98.5
1.5	72.7	99.0	97.9	98.7	98.3	98.7	98.9	98.6
2.0	97.0	98.7	99.2	99.0	98.9	99.1	99.2	99.0
1.0 (wet)	48.5	97.9	98.7	98.9	98.8	99.3	98.3	98.7

2.5 Retention efficiency

Six Chromosorb 106 tubes were spiked with 97.0 µg (2.02 mg/m^3) of 1,6-hexanediol diacrylate in the front sections, and allowed to equilibrate for 4 h. The tubes had 48-L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 ˚C) pulled through them at 0.2 L/min. The samples were extracted and analyzed. The mean recovery was 98.7%. There was no analyte found on the back-up section of any of the tubes.

Table 2.5
Retention Efficiency (%) of 1,6-Hexanediol Diacrylate

	sample number						
Section	1	2	3	4	5	6	mean
front of spiked tube	99.0	98.7	99.2	98.8	97.9	98.3	98.7
rear of spiked tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	99.0	98.7	99.2	98.8	97.9	98.3	98.7

2.6 Sample storage

Fifteen Chromosorb 106 tubes were each spiked with 48.5 µg (1.01 mg/m^3) of 1,6-hexanediol diacrylate. They were allowed to equilibrate for 6h, then 48 L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 23 °C), drawn through them. Three samples were analyzed immediately, and the rest were sealed. Six samples were stored at room temperature (23 °C), while the other six samples were stored at refrigerated temperature (4 °C). Three samples from each set of storage samples were analyzed after 7 days of storage and the remaining three from each set after 14 days. The amounts recovered indicate good storage stability for the time period studied.

Table 2.6
Storage Test for 1,6-Hexanediol Diacrylate

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.5	99.0	99.4			
7	98.1	98.6	97.8	98.8	99.1	98.2
14	96.9	98.0	97.0	98.2	98.9	97.8

2.7 Recommended air volume and sampling rate

Based on the data collected in this evaluation, 48-L air samples should be collected at a sampling rate of 0.2 L/min for 240 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of 1,6-hexanediol diacrylate.

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 detector. For this evaluation, an Agilent 6890 GC was used.

3.1.2 A GC column capable of separating 1,6-hexanediol diacrylate from the extraction solvent, internal standard, and any potential interferences. A 60-m × 0.32-mm i.d. capillary column coated with DB-1 with a 1.0-μm df (J&W Scientific, Folsom, CA) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium[32] Data System and an Agilent 3396 integrator were used in this evaluation.

3.1.4 Glass vials with poly(tetrafluoroethylene)-lined caps. For this evaluation 2-mL vials were used.

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-μL syringe for preparing standards.

3.1.8 A shaker or rotator to agitate samples during extraction. An Eberbach mechanical shaker was used in this evaluation.

3.2 Reagents

3.2.1 1,6-Hexanediol diacrylate, technical grade. Aldrich 80% (lot 16304HA) was used in this evaluation.

3.2.2 Carbon disulfide, Reagent grade. EM Science Omni-Solv® 99.99% (lot 43279343), was used in this evaluation.

3.2.3 *N,N*-Dimethylformamide, anhydrous. Aldrich 99.8% (lot 04643LA) was used in this evaluation.

3.2.4 *p*-Cymene, reagent grade. Aldrich 99% (lot 11703TR) was used in this evaluation.

3.2.5 The extraction solvent was a solution of 99:1 carbon disulfide: DMF with 0.25 µL/mL of *p*-cymene as internal standard.

3.3 Standard preparation

3.3.1 Prepare at least two stock analytical standards by injecting microliter quantities of 1,6-hexanediol diacrylate from a microliter syringe into volumetric flasks containing the extraction solvent. Working analytical standards are prepared by serial dilutions of the stock standard with the extraction solvent. A stock standard of 6 µL/10 mL (0.6 µL/mL) is equivalent to 485 µg/mL, based on the density and the purity of 80%. A 1:10 dilution of this stock standard is 48.5 µg/mL, which is equivalent to 1.01 mg/m^3 based on a 48-L air volume.

3.3.2 Bracket sample concentrations with standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, either analyze higher standards, or dilute the sample. Diluted samples should be prepared with the extracting solvent to obtain a concentration within the existing standard range. The range of standards used in this study was from 1 to 121 µg/mL. A check standard from a second source should be prepared to check the calibration.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer each adsorbent section to separate 2-mL vials. Discard the glass tube, urethane foam plug and glass wool plug.

3.4.2 Add 1.0 mL of extraction solvent to each vial using the same dispenser as used for preparation of standards.

3.4.3 Immediately seal the vials with poly(tetrafluoroethylene)-lined caps.

3.4.4 Agitate the vials on a shaker or rotator for 30 minutes.

3.5 Analysis

3.5.1 Gas chromatographic conditions

<u>GC conditions</u>

zone
temperatures: initial 50 °C, hold 1 min, ramp at 10 °C/min to 170 °C, hold 17 min

250 °C (injector)
250 °C (detector)
run time: 30 min
column gas flow: 3.2 mL/min (hydrogen)
injection size: 1.0 μL (10:1 split)
column: 60-m × 0.32-mm i.d. capillary DB-1 (df = 1 μm)
retention times: 4.0 min (CS_2); 7.0 min (DMF); 11.8 min (*p*-cymene); 26.5 min (1,6-hexanediol diacrylate)

FID conditions
hydrogen flow: 30 mL/min
air flow: 400 mL/min
makeup flow: 25 mL/min
(nitrogen)

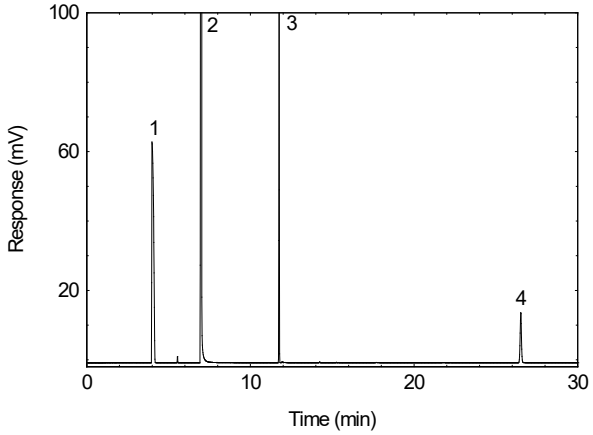


Figure 3.5.1 A chromatogram of 48.4 μg/mL 1,6-hexanediol diacrylate in 99:1 CS_2:DMF with 0.25 μl/mL *p*-cymene internal standard. (Key: (1) CS_2; (2) DMF; (3) *p*-cymene; (4) 1,6-hexanediol diacrylate)

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 ISTD-corrected response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over the range of concentrations.

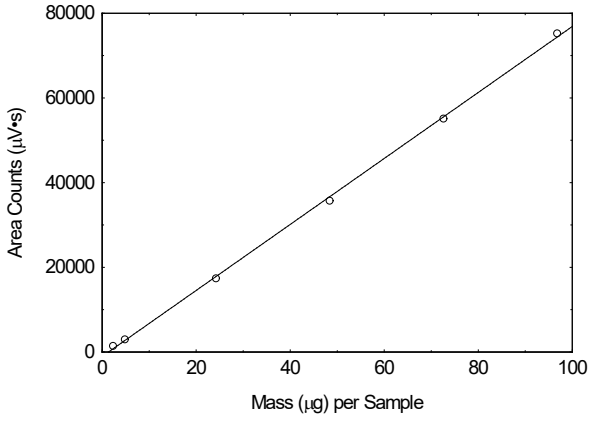


Figure 3.5.2 Calibration curve of 1,6-hexanediol diacrylate. (y = 779x - 1057)

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 interferences 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 may be confirmed by GC-mass spectrometry or by another analytical procedure. The mass spectrum in Figure 3.6.2 was from the NIST spectral library.

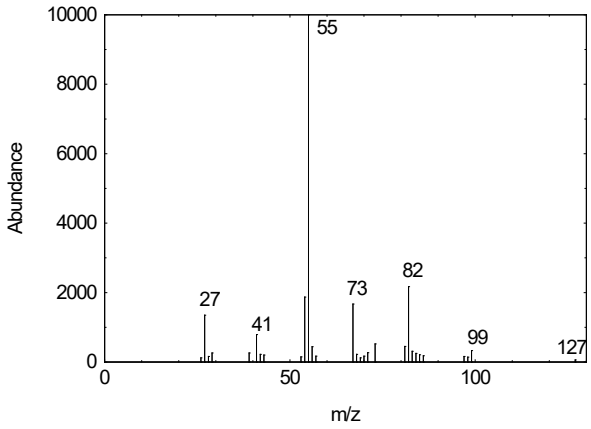


Figure 3.6.2 Mass spectrum of 1,6-hexanediol diacrylate.

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 formula.

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

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

4. Recommendations for Further Study

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