Tetrahydrofurfuryl Acrylate

Method no: PV2131

Target concentration: 1 mg/m^3

Procedure: Samples are collected by drawing a known volume of air through glass sampling tubes containing Chromosorb 106. Samples are extracted with a solution of 99:1 carbon disulfide: *N,N*-dimethylformamide and analyzed by GC using a flame ionization detector (GC/FID).

Recommended sampling time and sampling rate: 240 min at 0.2 L/min (48 L)

Reliable quantitation limit: 33 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.

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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 tetrahydrofurfuryl acrylate. This partially-validated work was performed because SLTC had no sampling and analytical method for tetrahydrofurfuryl acrylate.

The result of a preliminary extraction efficiency study for tetrahydrofurfuryl acrylate extracted from dry Chromosorb 106 with carbon disulfide was 98% recovery. The test was repeated with wet Chromosorb 106 and the recovery was initially the same, but then decreased to 85% 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 98.6% using the 99:1 carbon disulfide: *N,N*-dimethylformamide extraction solvent.

Tetrahydrofurfuryl acrylate was found to be well retained on Chromosorb 106, with a retention efficiency recovery of 99.1% and the storage stability recovery of 97.5% 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]

Tetrahydrofurfuryl acrylate is a contact irritant affecting the skin, eyes, and mucous membranes, and may cause sensitization through skin contact in certain individuals. If swallowed it causes irritation of the gastrointestinal tract, causing nausea, and vomiting.

1.1.3 Workplace exposure[2]

Tetrahydrofurfuryl acrylate is used as an intermediate in the manufacture of plasticizers and coating materials, and printing materials.

1.1.4 Physical properties and other descriptive information[3]

CAS number:	2399-48-6
synonyms:[4]	2-propenoic acid, (tetrahydro-2-furanyl)methyl ester; 2-propenoic acid, tetrahydrofurfuryl ester

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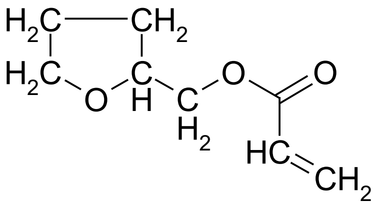
[1] Material Safety Data Sheet: Tetrahydrofurfuryl Acrylate, Chemwatch, Victoria, Australia, accessed 12/23/03.

[2] Howe-Grant, M., Kroschwitz, J., Ed, *Encyclopedia of Chemical Technology,* John Wiley & Sons, New York, 1998, Supplement, p 174.

[3] Material Safety Data Sheet: Tetrahydrofurfuryl Acrylate, Chemwatch, Victoria, Australia, accessed 12/23/03.

[4] Howard, P., Neal, M., Ed., *Dictionary of Chemical Names and Synonyms,* Lewis Publishers, Boca Raton FL, 1992, p I-705.

solubility:	insoluble in water, soluble in organic solvents
molecular weight:	156.18
density:	1.064 g/mL
boiling point:	87 ˚C
flash point:	110 ˚C (230 ˚F)(closed cup)
appearance:	clear liquid
molecular formula:	$C_8H_{12}O_3$
odor:	musty
IMIS:[5]	T420
structural formula:	



This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".[6] 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 equally descending increments of analyte, such that the highest sampler loading was 10.6 Φg of tetrahydrofurfuryl acrylate. 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 869 and the SEE was 137. 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 0.47 μg (10 $\mu g/m^3$) and 1.58 μg (33 $\mu g/m^3$) respectively. The recovery at the RQL level was 95.4%.

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[5] OSHA Chemical Sampling Information, www.osha.gov (accessed 12/17/03).

[6] 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 Tetrahydrofurfuryl acrylate

mass per sample (µg)	area counts (µV-s)
0.00	0
1.06	904
2.13	1797
3.19	2639
4.26	3482
5.32	4512
6.38	5453
7.45	6297
8.51	7249
9.58	8091
10.6	9478

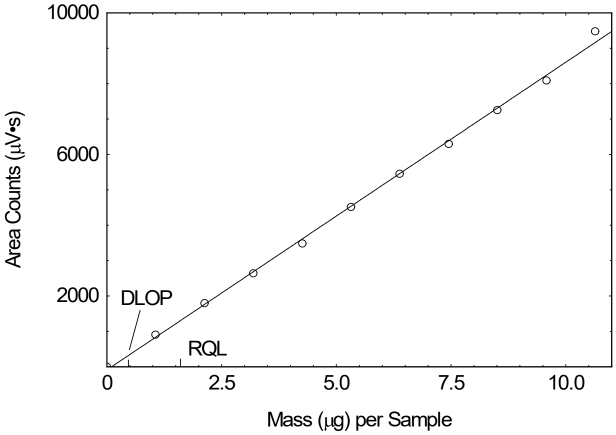

Figure 1.2.1 Plot of the data to determine the DLOP/RQL for tetrahydrofurfuryl acrylate. (y = 869x – 89.0)

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. The recovery at the RQL was 95.4%. Below is the chromatogram of the RQL level

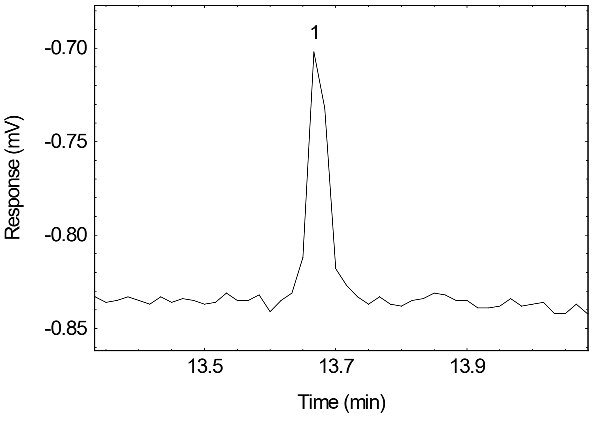

Figure 1.2.2. Chromatogram of the tetrahydrofurfuryl acrylate near the RQL. (Key: (1) tetrahydrofurfuryl acrylate)

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

Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

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 with a glass wool plug at the front. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalogue no. 226-110 lot 2573).

2.2 Reagents

None required.

2.3 Technique

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.

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.

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.

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.

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.

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.

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 Chromosorb 106 tubes with tetrahydrofurfuryl acrylate at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted with 1 mL of the extracting solvent for 30 minutes with shaking, and analyzed. The mean extraction efficiency over the studied range was 98.6%. The wet extraction efficiency was determined at 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 98.6%.

Table 2.4
Extraction Efficiency (%) of Tetrahydrofurfuryl Acrylate

level		sample number						
× target concn	µg per sample	1	2	3	4	5	6	mean
0.1	5.3	98.8	97.1	97.2	97.3	99.9	99.6	98.3
0.5	26.6	98.5	98.7	99.3	99.0	99.9	99.7	99.2
1.0	53.2	98.5	98.2	98.4	98.3	98.9	98.8	98.5
1.5	79.8	98.9	97.8	99.2	98.4	98.7	98.9	98.7
2.0	106	98.4	98.1	97.9	98.9	98.7	99.2	98.5
1.0(wet)	53.2	98.8	98.4	98.1	98.9	99.0	98.2	98.6

2.5 Retention efficiency

Six Chromosorb 106 tubes had their front sections spiked with 106 µg (2.21 mg/m^3) of tetrahydrofurfuryl acrylate and allowed to equilibrate for 6 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 99.1%. There was no analyte found on the back-up section of any of the tubes.

Table 2.5
Retention Efficiency (%) of Tetrahydrofurfuryl Acrylate

	sample number						
section	1	2	3	4	5	6	mean
front	99.4	100.2	98.7	99.3	99.3	98.3	99.1
rear	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	99.4	100.2	98.7	99.3	99.3	98.3	99.1

2.6 Sample storage

Fifteen Chromosorb 106 tubes were each spiked with 53 µg (1.1 mg/m^3) of tetrahydrofurfuryl acrylate and were allowed to equilibrate for 6 h, then 48-L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 ˚C), was drawn through them at 0.2 L/min. Three samples were analyzed immediately. The remaining samples were sealed and six were stored at room temperature (23 ˚C), while the other six were stored at refrigerated temperature (4 ˚C). On day 7 three samples from each group were analyzed, and the remaining three from each group was analyzed on day 14. The amounts recovered, indicate good storage stability for the time period studied, with an average recovery on day 14 of 97.5% for ambient storage and 98.1% for refrigerated storage.

Table 2.6
Storage Test for Tetrahydrofurfuryl Acrylate

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.1	98.3	98.5			
7	97.9	98.4	98.7	98.9	98.2	97.7
14	97.2	98.1	97.1	98.0	98.4	97.9

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)

There are no known compounds which will severely interfere with the collection of tetrahydrofurfuryl acrylate.

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 a FID detector. An Agilent 6890 Gas Chromatograph equipped with a FID and a 7683 Injector was used in this evaluation.

3.1.2 A GC column capable of separating tetrahydrofurfuryl acrylate from the extraction solvent, internal standard, and any potential interferences. A 60-m × 0.32-mm i.d. DB-1 (1.0-µm 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 Millennium^{32} Data System was 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 extracting 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 or 20-µL 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 Tetrahydrofurfuryl acrylate, Reagent grade. Aldrich 99% (lot 04106CO) was used in this evaluation.

3.2.2 Carbon disulfide, Reagent grade. Omni-Solv® 00.99% (lot 43279343) was used in this evaluation.

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

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

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

3.3 Standard preparation

3.3.1 Prepare working analytical standards by injecting microliter amounts of tetrahydrofurfuryl acrylate into volumetric flasks containing the extraction solvent. An analytical standard at a concentration of 106 µg/mL is equivalent to 2.2 mg/m^3 based on a 48-liter air volume.

3.3.2 Bracket sample concentrations with working standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, either analyze higher standards, or dilute the sample. The higher standards should be at least as high in concentration as the highest sample. Diluted samples should be prepared with extracting solvent to obtain a concentration within the existing standard range. Dilutions of stock standards are prepared using the extraction solvent for the concentration range of 1 to 213 µg/mL.

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 desorbing 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 Shake the vials on a shaker for 30 minutes.

3.5 Analysis

3.5.1 Gas chromatographic conditions

<u>GC conditions</u>	
temperatures:	
column:	initial 50 °C, hold 1 min, ramp at 10 °C/min to 170 °C, hold 7 min
injector:	250 °C
detector:	250 °C
run time:	20 min
column gas flow:	3.2 mL/min (hydrogen)
septum purge:	1.9 mL/min (hydrogen)
injection size:	1.0 µL (10:1 split)
column:	60-m × 0.32-mm i.d. capillary DB-1 (df = 1.0 µm)
retention times:	4.0 min carbon disulfide
	7.0 min DMF
	11.8 min *p*-cymene
	13.7 min tetrahydrofurfuryl acrylate
<u>FID conditions</u>	
hydrogen flow:	30 mL/min
air flow:	400 mL/min
makeup flow:	25 mL/min (nitrogen)

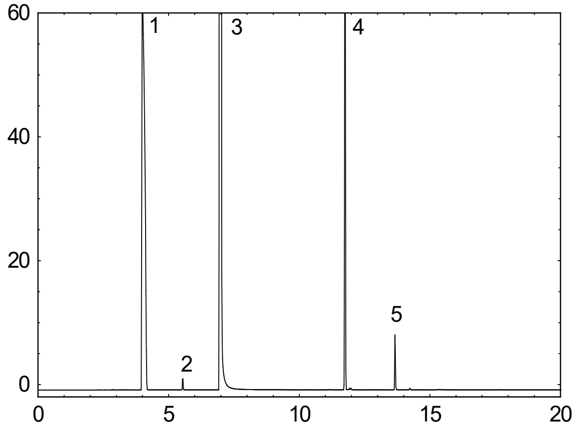

Figure3.5.1. A chromatogram of 53.0 µg/mL tetrahydrofurfuryl acrylate in 99:1 carbon disulfide: DMF with 0.25 µL/mL *p*-cymene internal standard. (Key: (1) carbon disulfide; (2) benzene contaminant in carbon disulfide; (3) DMF; (4) *p*-cymene; and (5) tetrahydrofurfuryl acrylate)

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

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

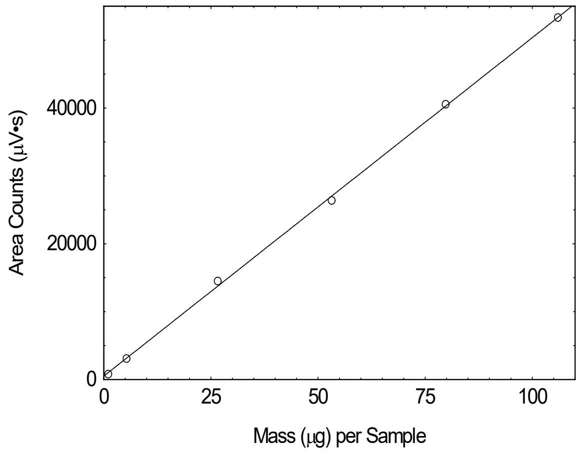

Figure 3.5.3 Calibration curve of tetrahydrofurfuryl acrylate. (y = 499x + 506)

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 mass spectrometry or by another analytical procedure. The mass spectrum in Figure 3.6 was from the analytical standard analyzed on an Agilent 6890 with a 5973 Mass Selective Detector.

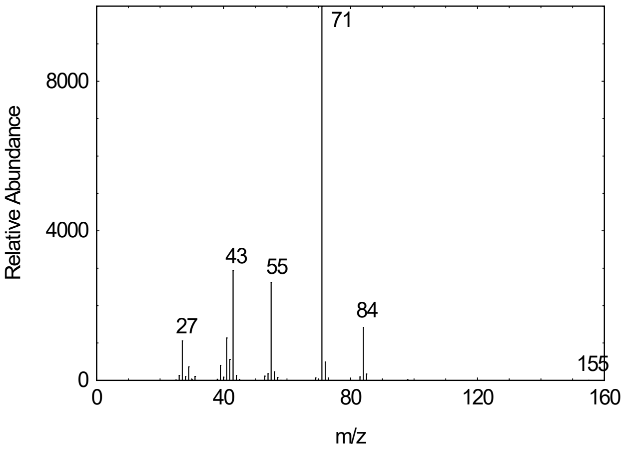

Figure 3.6.2 Mass spectrum of tetrahydrofurfuryl acrylate.

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.