

2-Hydroxypropyl Acrylate



Method no.: PV2078

Matrix: Air

Target concentration: 0.5 ppm (2.8 mg/m³) TWA (TLV)

Procedure: Samples are collected by drawing a known volume of air through glass sampling tubes containing coconut shell charcoal coated with 4-*tert*-butylcatechol. Samples are desorbed with 95/5 (v/v) methylene chloride/methanol and analyzed by gas chromatography (GC) using a flame ionization detector (FID).

Recommended air volume and sampling rate: 10 L at 0.10 L/min

Reliable quantitation limit: 0.045 ppm (0.240 mg/m³)

Status of method: Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

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Chemist: Wayne Potter

Organic Service Branch I
OSHA Salt Lake Technical Center
Salt Lake City, UT 84165-0200

1. General Discussion

1.1 Background

1.1.1 History

The validated OSHA Method 92 for ethyl acrylate and methyl acrylate uses coconut shell charcoal coated with 4-tert-butylcatechol (TBC) to collect samples which are desorbed with carbon disulfide. This collection procedure was tried with 2-hydroxypropyl acrylate (HPA) but a low desorption efficiency was observed. Other solvents such as carbon disulfide with 1% dimethyl formamide and toluene were explored with both TBC-coated charcoal and non-coated coconut shell charcoal but a low desorption efficiencies were also observed. Desorption with 95/5 (v/v) methylene chloride/methanol using coconut shell charcoal coated with 4-tert-butylcatechol gave 100.17% average recovery.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) (Ref. 5.1)

Acute toxicity studies indicate HPA to be more toxic than the corresponding ethyl derivative 2-hydroxyethyl acrylate (HEA). The rat oral LD₅₀ was 0.25-0.5 g/kg; the skin absorption LD₅₀ in rabbits about 0.25 mg/kg.

Direct contact caused severe eye burns and was corrosive to skin. Some sensitization was caused in guinea pigs. Inhalation at 650 ppm for 7 hours was not fatal to rats, however, industrial exposures for humans have been below 1 ppm. A 30-day inhalation study in rats, dogs, rabbits and mice (assumed to have been 7 hours a day, 6 days a week) indicated some irritation at the lowest level of 5 ppm.

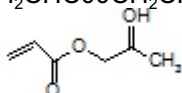
A 8 hour time-weighted average TLV of 0.5 ppm is recommended, based on irritant effects. As with HEA, the margin of safety is judged not to be unduly large. Inhalation of 2-hydroxypropyl acrylate irritates nose and throat and causes coughing. Lung injury may also occur. Ingestion causes irritation and burning of mouth and stomach. Vapors irritate the eyes. Contact with the liquid causes severe burns of eyes and skin. In animals, sensitization has been observed in exposed animals.

1.1.3 Workplace exposure (Ref. 5.1)

2-Hydroxypropyl acrylate is a monomer used in the manufacture of thermosetting resins for surface coatings.

1.1.4 Physical properties and other descriptive information (Ref. 5.1 and 5.2)

Synonyms: Propylene Glycol monoacrylate; Acrylic acid, 2-Hydroxypropyl ester; 2-Propenoic acid, 2-hydroxypropyl ester; 1,2-Propanediol, 1-acrylate
CAS number: 999-61-1
IMIS: H156
RTECS: AT1925000
Molecular weight: 130.14
Boiling point: 77°C @ (5 mmHg)
Odor: Faint unpleasant acrylate odor
Color: Clear colorless liquid
Density: 1.045 g/mL
Molecular formula: CH₂CHC(=O)OCH₂CH(OH)CH₃
Structural formula:



The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters of 10 liters and a desorption volume of 1 mL. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 0.72 µg per sample (0.014 ppm or 0.072 mg/m³). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank.

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient, and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

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

Y_{obs} = observed response
 Y_{est} = estimated response from regression curve
 n = total no. of data points
 k = 2 for a linear regression curve

At point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$

A = analytical sensitivity (slope)

therefore

$$DLOP = \frac{(Y_{DLOP} - Y_{BR})}{A}$$

Substituting $3(SEE) + Y_{BR}$ for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

Table 1.2.1
Detection Limit of the Overall Procedure

mass per sample (μg)	area counts ($\mu\text{V}\cdot\text{s}$)
0	0
0.732	0
1.463	229
1.76	236
2.05	321
2.34	323
2.63	350
2.93	381
3.51	454
4.096	544
4.68	705

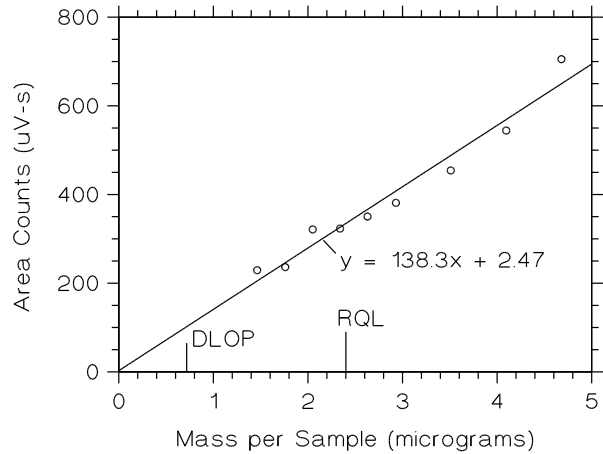


Figure 1.2.1. Plot of HPA data to determine the DLOP/RQL.

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DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with descending increments of analyte, such that the highest sampler loading was 4.68 $\mu\text{g}/\text{sample}$. This is the amount, when spiked on a sampler, would produce a peak approximately 10 times the background response for a sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 138.3 and 33.19 were obtained for A and SEE respectively. DLOP was calculated to be 0.72 $\mu\text{g}/\text{sample}$ (0.014 ppm, 0.072 mg/m^3).

- 1.2.2 The reliable quantitation limit (RQL) is 2.40 μg per sample (0.045 ppm or 0.240 mg/m^3). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

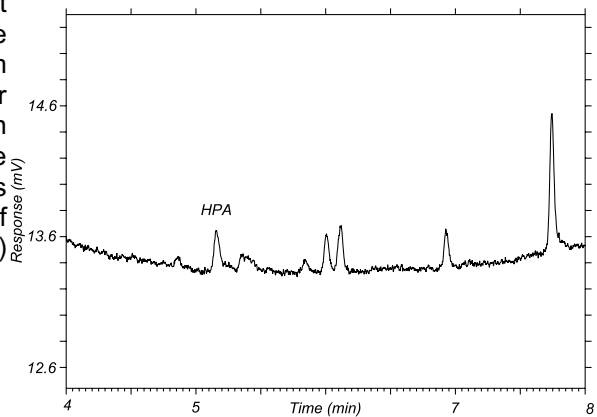


Figure 1.2.2. Chromatogram of the RQL.

2. Sampling Procedure

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 4-mm i.d. \times 6-mm o.d. \times 7.0 cm glass sampling tubes packed with two sections of coconut shell charcoal that has been coated with TBC, 10% by weight. The front section contains 110 mg and the back section contains 55 mg of TBC-coated coconut shell charcoal. The sections are held in place with glass wool plugs. For this evaluation, tubes were purchased from SKC, Inc. (catalog no. 226-73).

2.2 Technique

- 2.2.1 Immediately before sampling, break off the ends of the TBC-coated coconut shell charcoal tube. All tubes should be from the same lot.
- 2.2.2 Attach the sampling tube to the pump with flexible tubing. It is desirable to utilize sampling tube holders which have a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the reference, larger, section of the tube first.
- 2.2.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.
- 2.2.4 Attach the sampler vertically with the reference, larger, section pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.
- 2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.
- 2.2.6 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.
- 2.2.7 Record sample volumes (in liters of air) for each sample, along with any potential interferences.
- 2.2.8 Ship any bulk samples separate from the air samples.
- 2.2.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.3 Desorption efficiency

The desorption efficiencies (DE) of 2-hydroxypropyl acrylate were determined by liquid-spiking TBC-coated coconut shell charcoal tubes with 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average desorption efficiency over the studied range was 100.17%.

Table 2.3
Desorption Efficiency of 2-Hydroxypropyl Acrylate

Tube#	% Recovered			
	0.1× 2.9µg	0.5× 14.6µg	1.0× 29.3µg	2.0× 58.5µg
1	105.97	99.55	98.87	99.22
2	100.69	97.19	99.45	101.8
3	103.67	98.88	99.40	100.9
4	100.0	98.69	101.4	101.7
5	99.46	96.88	100.5	99.33
6	103.19	98.17	99.40	99.38
average	102.16	98.23	99.85	100.4
overall average	100.17			
SD	±2.05			

2.4 Retention efficiency

The TBC-coated coconut shell charcoal sampling tubes were spiked with 58.52 µg (1.0 ppm or 5.85 mg/m³), 2- hydroxypropyl acrylate, allowed to equilibrate 48 hours, and then had 10 L humid air (80% RH at 23°C) pulled through them at 0.1 Lpm. They were opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 92.72%. There was no 2-hydroxypropyl acrylate found on the backup portions of the tubes.

Table 2.4
Retention Efficiency of 2-Hydroxypropyl Acrylate

Tube #	A section recovery (%)	B section recovery (%)	total recovery (%)
1	90.62	0	90.62
2	92.13	0	92.13
3	93.35	0	93.35
4	95.46	0	95.46
5	90.58	0	90.58
6	94.20	0	94.20
		mean	92.72

2.5 Sample storage

The front sections of six TBC-coated coconut shell charcoal sampling tubes were each spiked with 29.3 µg (0.5 ppm) of 2-hydroxypropyl acrylate. Six more tubes had 10 liters of humid air (80% RH at 23°C) drawn through them before they were spiked with 29.3 µg (0.5 ppm) of 2-hydroxypropyl acrylate. They were sealed and stored at room temperature. Three dry samples and three humid air samples were analyzed after 7 days and the remaining three samples of each were analyzed after 14 days. The amounts recovered indicate good storage stability for the time period studied.

Table 2.5
Storage Test for 2-Hydroxypropyl Acrylate

Dry Air Samples		Humid Air Samples	
time (days)	recovery (%)	time (days)	recovery (%)
7	96.63	7	95.53
7	99.81	7	97.21
7	99.88	7	98.53
14	98.43	14	94.65
14	99.14	14	92.41
14	95.08	14	97.51
mean	98.16	mean	95.98

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 2.9, 14.6, 29.3, and 58.5 µg/mL 2-hydroxypropyl acrylate in the desorbing solution.

Table 2.6
2-Hydroxypropyl Acrylate Precision Study

injection #	2.9 µg/mL	14.6 µg/mL	29.3 µg/mL	58.5 µg/mL
1	444	2635	3769	9411
2	451	2627	3748	9318
3	450	2719	3669	9500
4	473	2700	3744	9517
5	481	2625	3793	9497
6	454	2689	3570	9408
mean	459	2666	3716	9442
SD	±14.7	41.6	82.5	76.8

2.7 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 10L air samples should be collected at a sampling rate of 0.10 L/min.

2.8 Interferences (sampling)

2.8.1 It is not known if any compounds will severely interfere with the collection of 2-hydroxypropyl acrylate on TBC-coated coconut shell charcoal tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of the TBC-coated coconut shell tubes to collect 2-hydroxypropyl acrylate.

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

2.9 Safety precautions (sampling)

2.9.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.9.2 All safety practices that apply to the work area being sampled should be followed.

2.9.3 Protective eye wear should be worn when breaking the ends of the glass sampling tubes.

3. Analytical Procedure

3.1 Apparatus

3.1.1 The instrument used in this study was a gas chromatograph, equipped with a flame ionization detector, specifically a Hewlett Packard model 5890.

3.1.2 A GC column capable of separating the analyte from any interferences. The column used in this study was a 45 meter DB-5, 0.32-mm i.d., 1.0 µm film thickness.

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

3.1.4 Two milliliter vials with Teflon™-lined caps.

3.1.5 A 10µL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. A 1-mL Repipette dispenser was used in this study.

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 2-Hydroxypropyl acrylate, Reagent grade

3.2.3 Methylene chloride, HPLC grade

3.2.4 Methanol, HPLC grade

3.2.5 *n*-Hexanol, Reagent grade

3.2.6 Desorbing solution; 95/5 (v/v) methylene chloride/methanol with 0.25 $\mu\text{L}/\text{mL}$ *n*-hexanol internal standard.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by diluting a known quantity of 2-hydroxypropyl acrylate with the desorbing solution.

3.3.2 A third analytical standard should be prepared at a high concentration to check the linearity of the detector response to the 2-hydroxypropyl acrylate. For this study two analytical standards were prepared at a concentration of 1 $\mu\text{L}/\text{mL}$ (29.26 $\mu\text{g}/\text{mL}$) and one at 4 $\mu\text{L}/\text{mL}$ (117.04 $\mu\text{g}/\text{mL}$) 2-hydroxypropyl acrylate in the desorbing solution of 95/5 (v/v) methylene chloride/methanol with 0.25 $\mu\text{L}/\text{mL}$ *n*-hexanol internal standard.

3.4 Sample preparation

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

3.4.2 Each section is desorbed with 1 mL of the desorbing solution of 95/5 (v/v) methylene chloride/methanol with 0.25 $\mu\text{L}/\text{mL}$ *n*-hexanol internal standard.

3.4.3 The vials are sealed immediately and allowed to desorb for 60 minutes with occasional shaking.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size: 1 μL

Flow rates (mL/min)

Nitrogen (make-up): 30

Hydrogen(carrier): 2

Hydrogen(detector): 60

Air: 450

Retention times (min)

Methanol: 1.45

Methylene chloride: 1.66

n-Hexanol: 3.44

HPA: 5.14

Temperatures ($^{\circ}\text{C}$)

Injector: 180

Detector: 220

Column: 100 $^{\circ}\text{C}$ for 5

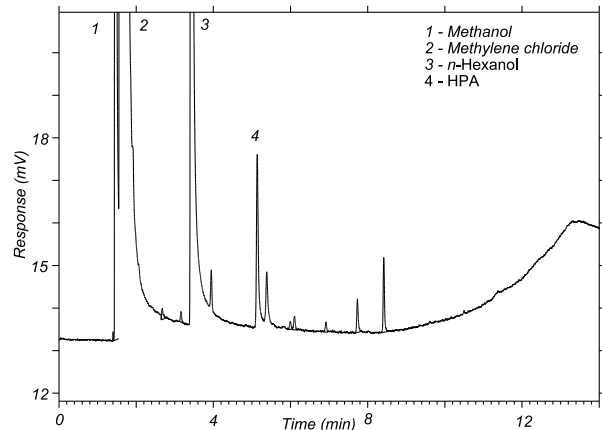


Figure 3.5.1 Chromatogram of the target concentration. 100 $^{\circ}\text{C}$ for 5 min then 10 $^{\circ}\text{C}/\text{min}$ to 180 $^{\circ}\text{C}$ for 2 min

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

3.6 Interferences (analytical)

3.6.1 Any compound that produces a 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 desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

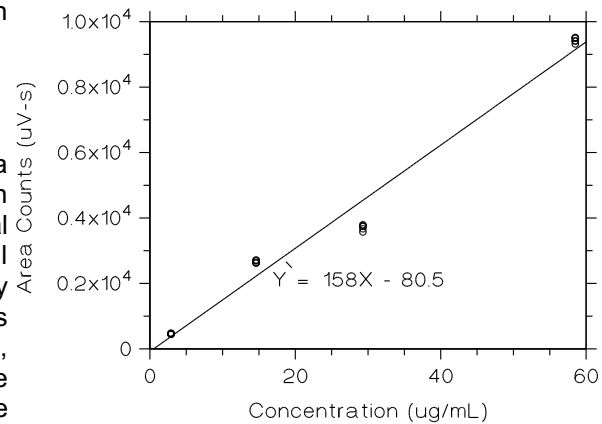


Figure 3.5.2 Calibration curve for HPA based on standards presented in 2.6.

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.

3.7 Calculations

3.7.1 The instrument was calibrated with a standard of 29.26 $\mu\text{g}/\text{mL}$ 2-hydroxypropyl acrylate in the desorbing solution. The linearity of the calibration was checked with standard of 117.04 $\mu\text{g}/\text{mL}$ 2-hydroxypropyl acrylate in the desorbing solution.

3.7.2 If the calibration is non-linear, two or more standards at different concentrations must be analyzed, bracketing the samples, so a calibration curve can be plotted and sample values obtained.

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

$$\text{mass of analyte in sample} = \frac{(\mu\text{g}/\text{mL})(\text{desorption volume})}{\text{desorption efficiency}}$$

$$\text{number of moles of analyte} = \frac{\text{mass of analyte in sample}}{\text{molecular weight}}$$

Volume the analyte will occupy at 25 °C and 760 mmHg is number of moles of analyte times the molar volume at 25 °C and 760 mmHg.

$$\text{ppm} = \frac{(\text{volume analyte occupies})(10^6)}{\text{air volume}}$$

3.7.4 The above equations can be consolidated to the following formula.

$$\text{ppm} = \frac{(\text{mg/mL})(\text{DV})(24.46)(10^6)(\text{g})(\text{mg})}{(10 \text{ L})(\text{DE})(\text{MW})(1000 \text{ mg})(1000 \text{ mg})}$$

µg/mL = concentration of analyte in sample or standard
 24.46 = molar volume (liters/mole) at 25 °C and 760 mmHg
 MW = molecular weight (g/mole)
 DV = desorption volume
 10 L = 10 liter air sample
 DE = desorption efficiency
 * All units must cancel.

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 Avoid skin contact and inhalation of all chemicals.

3.8.2 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

4. Recommendations for Further Study

Collection studies need to be performed.

5. References

5.1 "Documentation of the Threshold Limit Values and Biological Exposure Indices", Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p.320.

5.2 Sweet, D., "Registry of Toxic Effects of Chemical Substances", 1985-86 Edition, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 1, p. 247.