Method number:	PV2026
Target concentration:	5 ppm (38 mg/m^3) (Arbitrary). There is no OSHA Permissible exposure level (PEL) or ACGIH Threshold limit value (TLV) for 2-Ethylhexyl acrylate.
Procedure:	Samples are collected by drawing a known volume of air through a Coated CT (coconut shell charcoal coated with 4-tert-butylcatechol (TBC) tube. Samples are desorbed with 1 mL of carbon disulfide for 30 minutes with shaking on a rotator and analyzed by gas chromatography using a flame ionization detector.
Recommended air volume and sampling rate:	120 minutes at 0.1 L/min (12 L)
Reliable quantitation limit:	0.01 ppm (0.075 mg/m^3)
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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1 General Discussion

1.1 Background

1.1.1 History

OSHA method 92 uses TBC coated CT for ethyl acrylate and methyl acrylate, therefore it was decided to try TBC coated CT for 2-Ethylhexyl acrylate (EHA).

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) (Ref. 5.4)

Inhalation of EHA vapors can irritate the nose, throat, and lungs. Vapor concentrations of 25 ppm may not be tolerated for more than a few minutes. Higher concentration may cause drowsiness, dizziness, tiredness, headache, nausea, difficulty in breathing and convulsions. Vapors can be irritating to the eyes and cause tears. Liquid can cause severe burns of the eyes. Skin contact by pure liquid or concentrated solution of EHA can cause severe irritation and burns. There is no OSHA PEL, but toxic effects were identical to ethyl acrylate and methyl acrylate and the manufacturer also recommended a 5-ppm limit to the analyte. The 5-ppm target concentration is a recommendation only and does not reflect OSHA policy.

1.1.3 Workplace exposure (Ref. 5.2 and 5.3)

The monomer is mainly used for plastics, protective coatings, paper treatment and water based paints.

1.1.4 Physical properties and other descriptive information (Ref. 5.2 and 5.4)

CAS number:	103-11-7
IMIS:	1055
RTECS:	AT0855000; 4244
Synonyms:	2-Ethylhexyl-2-propeonate; octyl acrylate
Molecular weight:	184
Flash point:	82.2 °C
Boiling point:	213.5 °C
Freezing point:	- 90 °C
Odor:	acrid, musty
Color:	colorless
Density:	0.8865
Molecular formula:	$C_{11}H_{20}O_2$
Structural formula:	$CH_2CHCOOCH_2CH(C_2H_5)C_4H_9$

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. 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 0.31 µg per sample (0.025 mg/m^3). 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 standards 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:

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

Y_{obs} = observer response
Y_{est} = estimated response from regression curve
n = total number 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:

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

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

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

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 10 µg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the background response for the 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. DLOP was calculated to be 0.31 µg/sample (0.025 mg/m^3).

Table 1.2.1
Detection Limit of the Overall Procedure

mass/sample (µg)	area counts (µV-s)
0	0
1	1223
2	2408
3	3275
4	4398
5	5420
6	6488
7	7662
8	8644
9	9616
10	10717

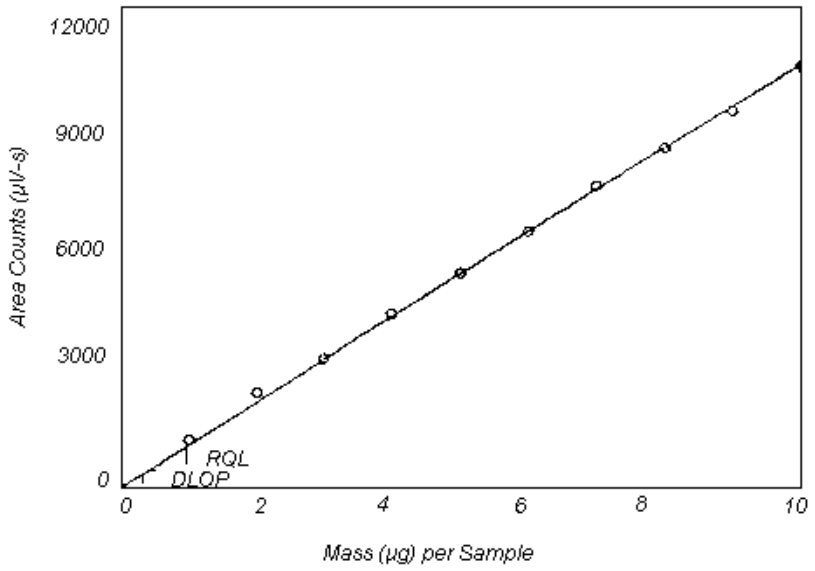

Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 0.9 µg per sample. 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

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

The RQL is the lowest loading at which 75% of the analyte can be recovered as determined from the regression line of the plotted data.

RQL = 0.9 µg per sample (0.075 mg/m^3)

The recovery at this concentration was 94%.

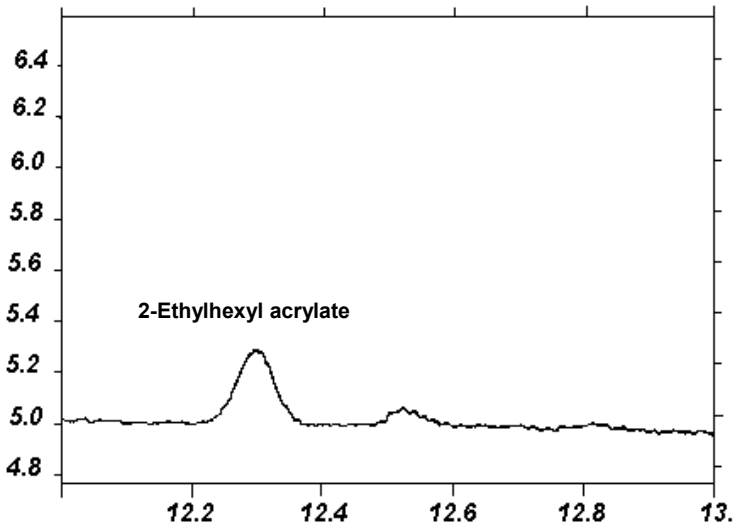

Figure 1.2.3 Chromatogram of the RQL.

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 ±5% of the recommended flow rate.

Samples are collected with 4 mm i.d. × 6 mm o.d. 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. The sections are held in place with glass wool plugs and are separated by a urethane foam plug. For this evaluation, commercially prepared sampling 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 sampling 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 front 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 front 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 interference.

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 efficiency of 2-Ethylhexyl acrylate was determined by liquid spiking the TBC coated charcoal tubes with the analytes at 0.1 to 2 times the target concentration. The loadings on the tubes were 46.1, 230.5, 461, and 922 mg of 2-Ethylhexyl acrylate. These samples were stored overnight at ambient temperature, then desorbed, and analyzed. The average desorption efficiency over the studied range was 100%.

Table 2.3
Desorption Efficiency of 2-Ethylhexyl acrylate

tube #	% recovery			
	0.1x µg	0.5x µg	1.x µg	2.0x µg
1	102.8	103.6	100.1	99.9
2	100.0	103.4	99.0	99.6
3	99.1	102.6	98.4	96.9
4	102.2	99.7	98.6	100.3
5	101.9	102.1	99.9	100.7
6	103.1	102.5	99.3	99.0
average	101.5	102.3	99.2	99.4

overall average = 100.0%
SD = ±1.7

2.4 Retention efficiency

Six sampling tubes were spiked with 922 µg (10 ppm) 2-Ethylhexyl acrylate, allowed to equilibrate for 24 hours at room temperature, and then had 12 L of humid air (80% RH at 22 °C) pulled through them at 0.1 Lpm. They were then opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 99.1%. There was no 2-Ethylhexyl acrylate found on the back sections of the tubes.

Table 2.4
Retention Efficiency of 2-Ethylhexyl acrylate

tube #	% recovered		
	front section	back section	total
1	99.3	0.0	99.3
2	98.1	0.0	98.1
3	100.1	0.0	100.1
4	99.2	0.0	99.2
5	97.7	0.0	97.7
6	100.1	0.0	100.1

average = 99.1%

2.5 Sample storage

The front sections of six sampling tubes were each spiked with 461 µg (5 ppm) of 2-Ethylhexyl acrylate. Six more tubes had 12 liters of humid air (80% RH at 22 °C) drawn through them before they were spiked with 461 µg (5 ppm) of 2-Ethylhexyl acrylate. They were sealed and stored at room temperature. Three of each type of samples was analyzed after 7 days and the remaining three samples of each type after 14 days. The amounts recovered indicate good storage stability for the time period studied and had an average recovery of 98.8%.

Table 2.5
Storage Test for 2-Ethylhexyl acrylate

time (days)	% recovered	
	humid	dry
7	98.2	99.4
7	99.6	101.3
7	100.9	98.2
14	97.5	97.7
14	96.0	97.9
14	99.6	98.2
average	98.6	98.9

2.6 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 12 L air samples should be collected at a sampling rate of 0.1 L/min.

2.7 Interferences (sampling)

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

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

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 Follow all safety practices that apply to the work area being sampled.

2.8.3 Wear eye protection 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 (FID), specifically a Hewlett-Packard model 5890.

3.1.2 A GC column capable of separating the analyte from any interference. The column used in this study was a 30-m x 0.32-mm i.d. x 4-mm o.d., SB-1 capillary.

3.1.3 An electronic integrator or some 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. A 1-ml dispenser was used in this study.

3.1.7 Volumetric flasks, 5 or 10-mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 GC grade Nitrogen, Hydrogen, and Air.

3.2.2 2-Ethylhexyl acrylate, Reagent grade

3.2.3 Carbon disulfide (CS_2) (desorbing solvent)

3.2.4 n-Hexyl benzene (internal standard)

3.2.5 Desorbing solution was 1 ml CS_2 with 0.25 µL/mL n-Hexyl benzene as internal standard.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by diluting a known quantity of 2-Ethylhexyl acrylate with the desorbing solution. The concentration of these stock standards was 1 µL/mL or 886.5 µg/mL.

3.3.2 A third standard at a higher concentration was prepared to check the linearity of the calibration. For this study, a 2 µL/mL (1773 µg/mL) standard of 2-Ethylhexyl acrylate in the desorbing solution was prepared.

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 carbon disulfide with 0.25 µL/mL n-Hexyl benzene internal standard.

3.4.3 The vials are sealed immediately and allowed to desorb for 30 minutes with constant shaking on rotator.

3.5 Analysis

3.5.1 Gas chromatography conditions.

Injection size:	1 µL
Flow rates	**(mL/min)**
Hydrogen (carrier):	1.5
Hydrogen (detector):	30
Air:	365
Temperatures	**(°C)**
Injector:	200
Detector:	240
Column:	150
Column:	30-m x 0.32-mm i.d. x 4-mm o.d., SB-1

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 are reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate the interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by GC-mass spectrometer or by another analytical procedure.

3.7 Calculations

3.7.1 The instrument was calibrated with a standard of 461 µg/mL 2-Ethylhexyl acrylate in the desorbing solution. The linearity of the calibration was checked with a standard of 1773 µg/mL (10 ppm).

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:

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

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

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

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

* All units must cancel.

$$ppm = \frac{(\mu g\ /\ mL)(DV)(24.46)}{(12\ L)(DE)(MW)}$$

Where:

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, mL
12 L = 12 liter air sample
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 (analytical)

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 from a dynamically generated test atmosphere.

5 References

5.1 Lewis, R., "Hawley's Condensed Chemical Dictionary," Twelfth Edition, Van Nostrand Reinhold Co. New York, 1993, p. 338.

5.2 Windholz, M., "The Merck Index," Eleventh Edition, Merck & Co., Rahway N.J., 1989, p. 427.

5.3 "Documentation of the Threshold Limit Values and Biological Exposure Indices," Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 161.

5.4 Occupation Health Services, Material Safety Data Sheets, New York, NY 10036.