

## Ethyl Methacrylate



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Method no.: PV2100

Matrix: Air

Target concentration: 100 ppm (467mg/m<sup>3</sup>)

Procedure: Samples are collected by drawing a known volume of air through a charcoal tube (100/50 mg, 20/40 mesh) lot 120. Samples are desorbed with carbon disulfide and analyzed by gas chromatography with a flame ionization detector (GC-FID).

Air volume and sampling rate studied: 10 liters at 0.2 L/min

Status of method: Stopgap 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 samples collected on charcoal tubes requesting analysis for ethyl methacrylate. A desorption study using carbon disulfide as the desorbing solvent showed a 92.8% recovery. The other analytes requested on the samples could not be desorbed with carbon disulfide. Other desorbing solvents tried were 1:99 dimethyl formamide: carbon disulfide (97.4% desorption efficiency) and 5:95 methanol: methylene chloride (98.5% desorption efficiency). The retention studies gave 100% recovery. The storage study for 14 days averaged 98.3% recovery.

#### 1.1.2 Toxic Effects (Ref. 5.1) (This section is for information purposes and should not be taken as the basis for OSHA policy.)

Ethyl methacrylate causes irritation to mucous membranes in high concentrations. Ethyl methacrylate in high concentrations is a teratogen.

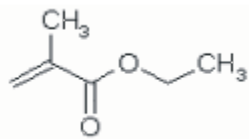
#### 1.1.3 Potential workplace exposure (Ref. 5.2)

Ethyl methacrylate is used in the manufacture of resins, polymers, fake nails, and contact lens.

#### 1.1.4 Physical properties: (Ref. 5.3)

Synonyms: Methacrylic acid, ethyl ester; ethyl 2-methylacrylate; ethyl 2-methyl-2-propenoate; Rhoplex AC-33; 2-propenoic acid, 2-methyl-ethyl ester.

Structure:



Molecular weight:	114.14
Density:	0.9135
Freezing point:	-75°C
Boiling point:	117°C
Odor:	acrylate odor
Color:	clear or light yellow liquid
Molecular formula:	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>
Flash point:	21°C (70°F)
CAS:	97-63-2
IMIS:	E115
RTECS:	47787 (OZ 4550000)

## 1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 1 µg ethyl methacrylate. This is the smallest amount that could be detected under normal operating conditions. 1.2.2 The overall detection limit is 0.02 ppm based on a 10 liter air volume. All ppm amounts in this study will be 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 Re-analysis 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 found.

## 2. Sampling procedure

### 2.1 Apparatus

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

2.1.2 Coconut shell charcoal tubes, lot 120, containing a 100 mg adsorbing section with a 50 mg backup section separated by a 2 mm portion of urethane foam, with a silane-treated glass wool plug before the adsorbing section and a 3 mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7 cm long, with a 6 mm O.D. and 4 mm I.D., SKC tubes or equivalent.

### 2.2 Sampling technique

2.2.1 The ends of the charcoal tube are opened immediately before sampling.

2.2.2 Connect the charcoal tube to the sampling pump with flexible tubing.

2.2.3 Tubes should be placed 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 charcoal tube.

2.2.5 Seal the charcoal tube with plastic caps immediately after sampling. Seal each sample lengthwise with OSHA Form-21 sealing tape.

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 that no air is drawn through it.

$$\text{CV (Coefficient of Variation)} = \frac{\text{standard deviation}}{\text{average}}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(\text{CV}1)^2 + A2(\text{CV}2)^2 + A3(\text{CV}3)^2 + A4(\text{CV}4)^2}{A1 + A2 + A3 + A4}}$$

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 the samples.

### 2.3 Desorption and/or Extraction efficiency

2.3.1 The desorption study of ethyl methacrylate with 1 mL carbon disulfide standard was performed by liquid spiking six charcoal tubes at each of the following levels; 0.4568 mg (9.79 ppm), 2.284 mg (48.9 ppm), and 4.568 mg (97.9 ppm). The tubes were allowed to equilibrate overnight at room temperature. They were opened, each section placed into separate 2 mL vials and desorbed with 1 mL carbon disulfide, for 30 minutes with occasional shaking. They were analyzed by GC-FID. The desorption efficiency was 92.8% (Table 2.3.1).

Table 2.3.1

Carbon Disulfide Desorption Study % Desorption			
Tube #	0.4568 mg	2.284 mg	4.568 mg
1	89.1	94.7	94.6
2	88.3	94.3	94.4
3	88.8	94.1	93.6
4	89.5	94.2	94.3
5	89.4	93.9	93.9
6	89.5	99.6	94.4
Average	89.1	95.1	94.1
Overall Average 92.8			
Standard Deviation ±2.98			

2.3.2 The desorption efficiency using 1:99 dimethyl formamide: carbon disulfide was performed by liquid spiking six tubes with ethyl methacrylate at the following levels (equivalent air concentrations) of 0.4568 mg (9.79 ppm), 2.284 mg (48.9 ppm), and 4.568 mg (97.9 ppm). The samples were stored overnight at room temperature. They were opened, each section placed into a separate 2 mL vial, desorbed with 1 mL desorbing solvent for 30 minutes with occasional shaking and analyzed by GC-FID. The desorption efficiency averaged 97.4% (Table 2.3.2).

Table 2.3.2

1:99 Dimethyl Formamide: Carbon Disulfide Desorption Study % Desorption			
Tube #	0.14568 mg	2.284 mg	4.568 mg
1	97.9	96.0	97.1
2	98.2	96.0	97.3
3	97.3	96.4	97.3
4	99.3	97.4	97.7
5	96.9	96.8	97.8
6	98.4	96.6	98.2
Average	98.0	96.5	97.6
Overall Average 97.4			
Standard Deviation $\pm 0.855$			

2.3.3 The desorption study using 5:95 methanol: methylene chloride was performed by liquid spiking six charcoal tubes with ethyl methacrylate at the following levels (equivalent air concentration), 0.4568 mg (9.79 ppm), 2.284 mg (48.9 ppm), 4.568 mg (97.9 ppm), and 9.135 mg (196 ppm). The tubes were allowed to equilibrate at room temperature overnight. They were opened, each section placed into a separate 2 mL vial, and desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking, and analyzed by GC-FID. The desorption efficiency averaged 98.5% (Table 2.3.3).

Table 2.3.3

5:95 Methanol: Methylene Chloride Desorption Study % Desorption				
Tube #	0.457 mg	2.28 mg	4.57 mg	9.14 mg
1	98.0	100	96.8	100
2	99.7	96.5	97.7	100
3	96.4	100	95.6	100
4	100	96.5	99.5	100
5	99.5	100	96.4	99.8
6	95.9	lost	95.3	100
Average	98.3	98.7	96.9	100
Overall Average 98.5				
Standard Deviation $\pm 1.79$				

#### 2.4 Retention efficiency

The retention efficiency was performed by spiking six tubes with 4.568 mg (97.9 ppm) ethyl methacrylate, and drawing 10 liters of humid air (94% RH) through them. They were opened, desorbed with 1 mL desorbing solution, and analyzed by GC-FID. The amounts in Table 2.4 are desorption corrected and the average recovery was 102%.

Table 2.4

Retention Efficiency			
1	104	ND	104
2	105	ND	105
3	101	ND	101
4	102	ND	102
5	101	ND	101
6	102	ND	102
		Average	102

## 2.5 Storage

Six charcoal tubes were spiked with 4.568 mg (97.9 ppm) and stored at room temperature. Three of these tubes were analyzed at 6 and 14 days after spiking. The amounts reported are desorption corrected. The average recovery was 99.7% (Table 2.5).

Table 2.5

Storage Study	
Days Stored	% Recovered
6	100
6	100
6	101
14	99.1
14	98.6
14	99.6
Average 99.7	

## 2.6 Precision

The precision was determined by six injections of standard at concentrations of 0.4568 mg/mL (9.79 ppm), 2.284 mg/mL (48.9 ppm), 4.568 mg/mL (97.9 ppm), and 9.135 mg/mL (196 ppm) (Table 2.6).

Table 2.6

Precision of the Analytical Procedure				
Injection Number	0.4568 mg/mL	2.284 mg/mL	4.568 mg/mL	9.135 mg/mL
1	498338	2444481	4974609	9745276
2	493750	2448606	4968818	9755312
3	492081	2479016	4940095	9774749
4	497300	2480853	4925562	9732824
5	498060	2476000	4980306	9718711
6	497177	2483968	4942801	9719335
Average	496118	2468821	4955365	9741035
Standard Deviation	±2574	±17497	±22849	±21887
CV	0.00519	0.00709	0.00461	0.00225
Pooled CV	0.00519			

A(1), A(2), A(3), A(4) = # of injections at each level  
 CV1, CV2, CV3, CV4 = Coefficients at each level

## 2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 10 liters.

2.7.2 The sampling rate studied was 0.2 liters per minute.

## 2.8 Interferences

Suspected interferences should be listed on sample data sheets.

## 2.9 Safety precautions

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

2.9.2 Safety glasses should be worn at all times.

2.9.3 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 ionization-detector.

3.1.2 GC column capable of separating the analyte and an internal standard from any interferences. The column used in this study was a 12 ft stainless steel column packed with 10% FFAP on 80/100 mesh Chrom WAW.

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

3.1.4 Two milliliter vials with Teflon-lined caps.

3.1.5 A 10- $\mu$ L syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. The Glenco 1 mL dispenser was used in this evaluation.

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 Ethyl Methacrylate, Reagent grade 3.2.3 Carbon Disulfide, Reagent grade

3.2.4 Internal Standard (p-Cymene) Reagent grade

3.2.5 Desorbing solution contains 1  $\mu\text{L}/\text{mL}$  p-cymene in carbon disulfide.

### 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 carbon disulfide with 1  $\mu\text{L}/\text{mL}$  p-cymene internal standard.

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 ethyl methacrylate with carbon disulfide containing 1  $\mu\text{L}/\text{mL}$  internal standard. A 1  $\mu\text{L}/\text{mL}$  standard of ethyl methacrylate in the desorbing solution contains 984.4  $\mu\text{g}/\text{mL}$  (21.09 ppm) corrected for the desorption efficiency of 92.8%.

3.4.2 At least two separate standards should be made.

3.4.3 A third standard at a higher concentration should be prepared to check the linearity of the analysis. This third standard is at 4  $\mu\text{L}/\text{mL}$ .

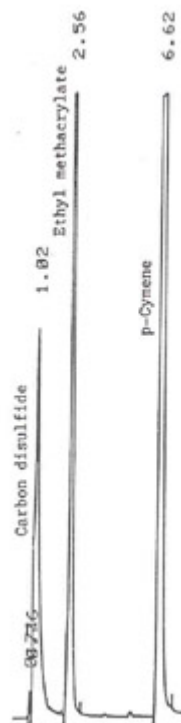
### 3.5 Analysis

#### 3.5.1 Chromatographic conditions

Flow Rates (mL/min)	Temperature ( $^{\circ}\text{C}$ )
Nitrogen (carrier): 29	Injector: 180
Hydrogen: 40	Detector: 220
Air: 240	Column: 80 $^{\circ}\text{C}$ , hold 4 min ramp at 10 $^{\circ}\text{C}/\text{min}$ to 140 $^{\circ}\text{C}$
Injection Size:	1 $\mu\text{L}$
Elution time:	2.56 min



Chromatogram:



3.5.2 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 or the internal standard used is an 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 The integrator is calibrated with two standards at the same concentration, and the linearity of the analysis is checked with the third standard.

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

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

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

$$\left( \text{number of moles of analyte} \right) \left( \text{molar volume at } 25^{\circ}\text{C \& 760mmHg} \right) = \text{volume the analyte will occupy at } 25^{\circ}\text{C \& 760 mmHg}$$

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

\* All units must cancel.

3.7.3 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 5-liter air sample:

$$\text{ppm} = \frac{(\mu\text{g/mL})(\text{DV})(24.46)(10^6)(\text{g})(\text{mg})}{(5 \text{ L})(\text{DE})(\text{MW})(1000 \text{ mg})(1000 \text{ mg})}$$

$\mu\text{g/mL}$	=	concentration of analyte in sample or standard
24.46	=	Molar volume (liters/mole) at $25^{\circ}\text{C}$ and 760 mmHg
MW	=	Molecular weight (g/mole)
DV	=	Desorption volume
5 L	=	5 liter air sample
DE	=	Desorption efficiency

3.7.4 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 solvents.

3.8.3 Wear safety glasses at all times.

## 4. Recommendations for further study:

Collection studies for ethyl methacrylate need to be performed.

## 5. References

- 5.1 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. 3A, p. 3060-101.
- 5.2 Hawley, G., "The Condensed Chemical Dictionary", Van Nostrand Reinhold Co. New York, N.Y. Tenth Edition, 1981, p. 440.
- 5.3 Weast, R.C., Grasselli, J.G., "Handbook of Data on Organic Compounds", CRC Press, Inc. Boca Raton, FL. 2nd Edition, 1985, page 3810.