ETHYL ACRYLATE
METHYL ACRYLATE

Method no.:	92
Matrix:	Air
Target concentration:	5 ppm (20 mg/m^3) for ethyl acrylate 10 ppm (35 mg/m^3) for methyl acrylate
Procedure:	Samples are collected by drawing air through glass sampling tubes containing coconut shell charcoal coated with 4-tert-butylcatechol. Samples are desorbed with carbon disulfide and analyzed by GC using a flame ionization detector.
Recommended air volume and sampling rate:	12 L at 0.05 L/min
Reliable quantitation limit:	20 ppb (80 µg/m^3) for ethyl acrylate 40 ppb (140 µg/m^3) for methyl acrylate
Standard error of estimate at the target concentration: (Section 4.7)	5.14% for ethyl acrylate 5.50% for methyl acrylate
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1 Background

1.1.1 History

The OSHA Salt Lake Technical Center has in the past used a modified form of NIOSH Methods 1450 and S-38 for the sampling and analysis of ethyl acrylate (EA) and methyl acrylate (MA) respectively. (Refs. 5.1 and 5.2) These methods specify collection on coconut shell charcoal, desorption with carbon disulfide (CS_2) and analysis by GC with a flame ionization detector (FID). The modification changed the desorption solvent to 95/5 methylene chloride/methanol. With these modified procedures, both EA and MA display an increase in their respective desorption efficiencies. However, the desorption efficiencies still remain a function of sampler loading. For example, the desorption efficiency for EA decreases from 99.8% to 84.9% as the amount on the sampler decreases from 1.7 to 0.08 times of target concentration, and for MA it decreases from 91.2% to 66.7% as the amount on the sampler decreases from 0.8 to 0.04 times of target concentration. To eliminate this deficiency, coconut shell charcoal coated with 4-tert-butylcatechol (TBC) was utilized for sampling. This material had been found to stabilize styrene at low sampler loading on the charcoal and eliminate the non-constant desorption efficiency. This same result was observed for EA and MA. An extended temperature program on the GC was used to remove the TBC from the chromatographic column after each injection and resulted in a 25 min run time.

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

Inhalation of EA vapors can irritate the nose, throat and lungs. Vapor concentrations of 25 ppm may not be tolerated for more than a few minutes. Higher concentrations 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 serious burns of the eyes. Skin contact by pure liquid or concentrated solutions of EA can cause severe irritation and burns. EA can cause marked local irritation of the mouth and digestive tract if ingested. Large doses can be fatal. (Ref. 5.3) In the Code of Federal Regulations, the final rule limits in Table Z-1-A specify a TWA of 5 ppm (20 mg/m^3) and a STEL of 25 ppm (100 mg/m^3). The table also lists a skin designation. (Ref. 5.4) International Agency for Research on Cancer (IARC) states there is sufficient evidence for the carcinogenicity of EA in experimental animals. No data on humans were available. (Ref. 5.5)

Inhalation of MA vapors can irritate the nose, throat and lungs. Irritation can occur at concentrations of 75 ppm. Higher concentrations may cause drowsiness, dizziness, tiredness, headache, nausea, difficulty in breathing and convulsions. Severe exposure can be fatal. Vapors can irritate the eyes and cause tears. Liquid can cause chemical burns of the eyes. Skin contact by liquid MA can cause severe irritation or burns. Vapors are irritating to the skin. Toxic amounts of MA can be absorbed through intact skin. MA can cause marked local irritation of the mouth and digestive system if ingested. Large doses can be fatal. (Ref. 5.3) In the Code of Federal Regulations, the final rule limits in Table Z-1-A specify a TWA of 10 ppm (35 mg/m^3) and lists a skin designation. (Ref. 5.4) IARC states there is inadequate evidence for the carcinogenicity of MA in experimental animals. No data on humans were available. (Ref. 5.6)

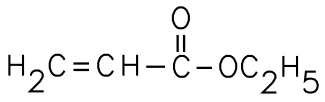
1.1.3 Workplace exposure

EA is used in the manufacture of acrylic emulsion polymers used in paints, surface coatings for textiles, paper and leather, adhesives and sealants; acrylic fibers; chemical intermediates; fragrance and flavoring agent. (Ref. 5.3) The U.S. International Trade Commission reported production of 131 million kilograms during 1983. (Ref. 5.5)

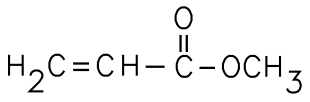
MA is used primarily as a co-monomer with acrylonitrile in the manufacture of acrylic and modacrylic fibers; in the manufacture of acrylic emulsion polymers used in paints, surface coatings for textiles, paper and leather, adhesives, sealants, and surfactants; and in the synthesis of vitamin B1. (Ref. 5.3) Fourteen million kilograms were produced during 1983. (Ref. 5.6)

1.1.4 Physical properties and other descriptive information (Ref. 5.3)

compound:	ethyl acrylate	methyl acrylate
CAS no.:	140-88-5	96-33-3
molecular weight:	100.12	86.09
melting point:	-75°C	-75°C
boiling point:	99°C	80°C
chemical formula:	$C_5H_8O_2$	$C_4H_6O_2$
vapor pressure (at 20°C):	4 kPa (30 mmHg)	9.2 kPa (69 mmHg)
density (at 20°C):	0.923 g/mL	0.957 g/mL
self-ignition temperature:	372°C	468°C
flash point (open cup):	10°C	-3°C
lower explosive limit:	1.4%	2.8%
upper explosive limit:	14%	25%
odor threshold:	0.5 ppb	14 ppb
solubility:	slightly soluble in water; soluble in alcohol and ether	moderately soluble in water; soluble in alcohol, ether, acetone and benzene
synonyms:	acrylic acid, ethyl ester; ethyl 2-propenoate; ethoxy carbonyl ethylene; 2-propenoic acid, ethyl ester	acrylic acid, methyl ester; methyl 2-propenoate; 2-propenoic acid, methyl ester



Ethyl Acrylate



Methyl Acrylate

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm and ppb are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limits of the analytical procedure are 0.077 and 0.135 ng per injection (1.0-L injection with a 12.5:1 split) for EA and MA respectively. These are the amounts of analyte that will produce peaks with heights that are approximately 5 times the baseline noise. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 0.961 and 1.682 µg per sample for EA and MA respectively. This is the amount of analyte spiked on the sampling device that, upon analysis, produces a peak similar in size to that of the respective detection limit of the analytical procedure. These detection limits correspond to air concentrations of 20 ppb (80 µg/m^3) and 40 ppb (140 µg/m^3) for EA and MA respectively. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limits are 0.961 and 1.682 µg per sample for EA and MA respectively. This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. These detection limits correspond to air concentrations of 20 ppb (80 µg/m^3) and 40 ppb (140 µg/m^3) for EA and MA respectively. (Section 4.3)

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4 Instrument response to the analyte

The instrument responses over concentration ranges representing 0.5 to 2 times the target concentration are linear. (Section 4.4)

1.2.5 Recovery

The recoveries of EA and MA from samples used in 16-day ambient storage tests remained above 96.9% and 96.7% respectively. (Section 4.5, regression lines of Figures 4.5.1.1 and 4.5.2.1)

1.2.6 Precision (analytical procedure)

The pooled coefficients of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentrations are 0.0046 and 0.0189 for EA and MA respectively. (Section 4.6)

1.2.7 Precision (overall procedure)

The precision at the 95% confidence level for the 16-day ambient temperature storage tests are ±10.1% and ±10.8% for EA and MA respectively. (Section 4.7) These each include an additional ±5% for sampling error.

1.2.8 Reproducibility

Six samples, liquid-spiked with EA and MA and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed for EA and MA after 11 days of storage at 12°C. No individual sample result for EA and MA deviated from its theoretical value by more than the precision reported in Section 1.2.7 (Section 4.8)

1.3 Advantages

1.3.1 The new adsorbent, TBC-coated coconut shell charcoal, provides constant desorption with CS_2 at low sampler loadings unlike the non-constant desorption of untreated coconut shell charcoal.

1.3.2 The sampler may be used for other analytes, i.e., styrene or vinyl benzene.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump that can be calibrated within ±5% of the recommended flow rate with the sampling device attached.

2.1.2 Samples are collected with 4-mm i.d. × 6-mm o.d. × 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 Reagents

No sampling reagents are required.

2.3 Technique

2.3.1 Immediately before sampling, break off the ends of the TBC-coated coconut shell charcoal tube. All tubes should be from the same lot.

2.3.2 Attach the sampling tube to the sampling 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 110-mg section first.

2.3.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.3.4 Attach the sampler vertically with the 110-mg section pointing downward, in the worker's breathing zone so it does not impede work performance or safety.

2.3.5 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.

2.3.6 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.

2.3.7 Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.3.8 Ship any bulk samples separate from the air samples.

2.3.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at reduced temperature.

2.4 Sampler capacity

2.4.1 The sampling capacity of the front section of a TBC-coated coconut shell charcoal sampling tube was tested by sampling from a dynamically generated test atmosphere of MA (70.5 mg/m^3 or 20.0 ppm). The samples were collected at 0.05 L/min and the relative humidity was 80%. A 5% breakthrough air volume was not attained after sampling for 6.5 h or 19.5 L, which is 63% greater than the recommended sample volume of 12 L.

2.4.2 The sampling capacity of the front section of a TBC-coated coconut shell charcoal sampling tube was tested by sampling from a dynamically generated test atmosphere of EA (40.9 mg/m^3 or 9.99 ppm). The samples were collected at 0.05 Lpm and the relative humidity was 80%. A 5% breakthrough air volume was not attained after sampling for 7 h or 21.0 L, which is 75% greater than the recommended sample volume of 12 L.

2.5 Desorption efficiency

2.5.1 The average desorption efficiencies from TBC-coated coconut shell charcoal adsorbent are 100.3% and 99.7% for EA and MA over the range of 0.5 to 2 times the target concentration. (Section 4.10.1)

2.5.2 Desorbed samples remain stable for at least 24 h. (Section 4.10.2)

2.6 Recommended air volume and sampling rate

2.6.1 For time-weighted average samples, the recommended air volume is 12 L collected at 0.05 L/min (4-h samples). An air volume, which is well within the capacity of the sampler, is recommended because of the potential sampling interferences caused by other substances collected during longer sampling times.

2.6.2 For short-term exposure limit samples, the recommended air volume is 0.75 L collected at 0.05 L/min (15-min samples).

2.6.3 When short-term exposure limit samples are required, the reliable quantitation limit becomes larger. For example, the reliable quantitation limits are 0.32 ppm (1.3 mg/m^3) and 0.64 ppm (2.3 mg/m^3) for EA and MA respectively when 0.75 L of air is collected.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of EA or MA on TBC-coated coconut shell charcoal. In general, the presence of other contaminant vapors in the air will reduce the capacity of TBC-coated coconut shell charcoal to collect EA or MA.

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

2.8 Safety precautions (sampling)

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

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

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

3. Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with a flame ionization detector (FID). A Hewlett-Packard 5890 Gas Chromatograph equipped with a 7673A Autosampler and an FID was used in this evaluation.

3.1.2 A GC column capable of separating EA, MA and the internal standard from the desorbing solvent and any potential interferences. A 60-m × 0.32-mm i.d. SPB-5 (1.0-µm film thickness) capillary column (Supelco, Inc.) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring detector response. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4 Two-milliliter vials with polytetrafluoroethylene-lined caps.

3.1.5 A dispenser capable of delivering 1.0 mL of desorbing solution is used to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

3.2 Reagents

3.2.1 Ethyl acrylate (EA). Practical Grade used in this evaluation was purchased from JT Baker Chemical Co. (Phillipsburg, NJ).

3.2.2 Methyl acrylate (MA). The MA used in this evaluation was purchased from JT Baker Chemical Co. (Phillipsburg, NJ).

3.2.3 Carbon disulfide, CS_2. Reagent grade or better should be used. The carbon disulfide used in this evaluation was purchased from EM Science (Gibbstown, NJ).

3.2.4 Desorbing solution. The desorbing solution is prepared by adding 250 µL of an appropriate internal standard to 1 L of CS_2. Benzene (reagent grade) was used in this evaluation and was purchased from EM Science (Gibbstown, NJ).

3.3 Standard preparation

3.3.1 Prepare concentrated stock standards of EA and MA in CS_2. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 2-mL vials containing 1 mL of desorbing solution delivered from the same dispenser used to desorb samples. For example, to prepare a target level standard, inject 10 µL of a stock solution containing 24 and 42 mg/mL of EA and MA respectively in CS_2 into 1 mL of desorbing solution.

3.3.2 Prepare a sufficient number of analytical standards to generate a calibration curve. Ensure that the amount of EA and MA found in the samples is bracketed by the range of the standards. Prepare additional standards if necessary.

3.4 Sample preparation

3.4.1 Remove the plastic caps from the sample tube and carefully transfer each section of the adsorbent to separate 2-mL vials. Discard the glass tube and glass wool plugs.

3.4.2 Add 1.0 mL of desorbing solution to each vial and immediately seal the vials with polytetrafluoroethylene-lined caps.

3.4.3 Shake the vials vigorously several times during the next 30 min.

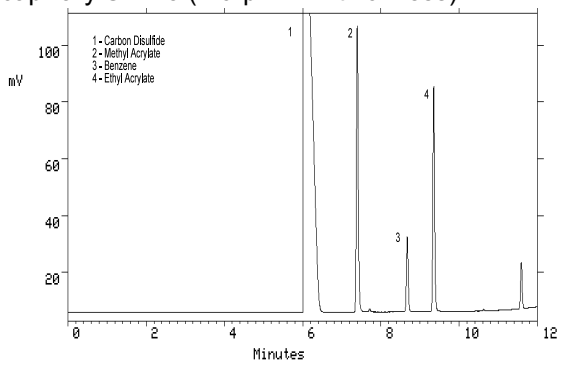
3.5 Analysis

3.5.1 Analytical conditions

GC conditions

initial
temperatures: 50°C (column)

250°C (injector)
300°C (detector)
temp program: increase temp at 5°C/min to 100°C, then increase temp at 25°C/min to 275°C, hold for 8 min.
run time: 25 min - this was used to elute the TBC from the column
column gas flow: 1.2 mL/min (hydrogen)
septum purge: 1.5 mL/min (hydrogen)
injection size: 1.0 µL (12.5:1 split)
column: 60 m × 0.32-mm i.d. capillary SPB-5 (1.0-µm film thickness)
retention times: 7.4 min (MA), 8.7 min (benzene), 9.4 min (EA)



FID conditions

hydrogen flow: 34 mL/min
air flow: 450 mL/min
nitrogen makeup flow: 33 mL/min

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

3.6 Interferences (analytical)

3.6.1 Any compound that produces an FID response and has a similar retention time as the analyte or internal standard 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.

3.6.2 Retention time on a single column is not considered proof of chemical identity. Analysis by an alternate GC column or confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

The amount of analyte per milliliter is obtained from the appropriate calibration curve in terms of micrograms per milliliter uncorrected for desorption efficiency. The back (55-mg) section is analyzed primarily to determine the extent of sample saturation during sampling. If any analyte is found on the back section, it is added to the amount on the front section. 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 formulae.

$$mg/m^3 = \frac{A \times B}{C \times D}$$

where:
A = micrograms of analyte per milliliter
B = desorption volume
C = liters of air sampled
D = desorption efficiency

$$ppm = \frac{24.46 \times mg/m^3}{MW}$$

where: 24.46 = molar volume (liters) at 101.3 kPa (760 mmHg and 25°C)
MW = 100.12 for EA
MW = 86.09 for MA

3.8 Safety precautions (analytical)

3.8.1 Restrict the use of all chemicals to a fume hood.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses, gloves and a lab coat at all times while working with chemicals.

4. Backup Data

4.1 Detection limit of the analytical procedure

The injection size recommended in the analytical procedure (1-µL, 12.5 split) was used to determine the detection limit of the analytical procedure. The detection limits of the analytical procedure are 0.077 and 0.135 ng on-column for EA and MA respectively. These were the amounts of analyte that gave a peak with a height about 5 times the height of the baseline noise. These detection limits were determined by analysis of a standard containing 0.961 µg/mL of EA and 1.682 µg/mL of MA.

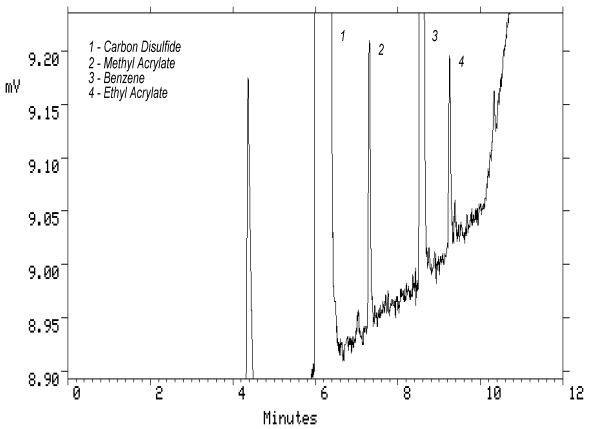


Figure 4.1. Detection limit of the analytical procedure.

4.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 0.961 µg per sample (20 ppb or 80 µg/m^3) for EA and 1.682 µg per sample (40 ppb or 140 µg/m^3) for MA. The injection size listed in the analytical procedure (1.0 µL, 12.5:1 split) was used in the determination of the detection limit of the overall procedure. Six vials containing 110 mg of TBC-coated coconut shell charcoal were liquid-spiked with 0.961 µg of EA and 1.682 µg of MA. The samples were stored at ambient temperature and were desorbed about 24 h after being spiked.

Table 4.2.1
Detection Limit of the
Overall Procedure for EA

sample no.	µg spiked	µg recovered
1	0.961	0.915
2	0.961	0.947
3	0.961	0.963
4	0.961	0.998
5	0.961	0.928
6	0.961	0.905

Table 4.2.2
Detection Limit of the
Overall Procedure for MA

sample no.	µg spiked	µg recovered
1	1.68	1.68
2	1.68	1.65
3	1.68	1.64
4	1.68	1.69
5	1.68	1.69
6	1.68	1.70

4.3 Reliable quantitation limit data

The reliable quantitation limits are 0.961 µg per sample (20 ppb or 80 µg/m^3) for EA and 1.682 µg per sample (40 ppb or 140 µg/m^3) for MA. The injection size listed in the analytical procedure (1.0 µL, 12.5:1 split) was used in the determination of the reliable quantitation limit. Six vials containing 110 mg of TBC-coated coconut shell charcoal were liquid-spiked with a CS_2 solution containing EA and MA. Because the recovery of the analytes from the spiked samples was greater than 75% and had a precision of ±25% or better, the detection limits of the overall procedure and reliable quantitation limit are the same.

Table 4.3.1
Reliable Quantitation Limit for EA
(Based on samples and data of Table 4.2.1)

percent recovered	statistics
95.2	
98.5	mean = 98.1
100.2	SD = 3.6
103.9	Precision = (1.96)(±3.6)
96.6	= ±7.1
94.2	

Table 4.3.2
Reliable Quantitation Limit for MA
(Based on samples and data of Table 4.2.2)

percent recovered	statistics
100.0	
98.2	mean = 99.7
97.6	SD = 1.5
100.6	Precision = (1.96)(±1.5)
100.6	= ±2.9
101.2	

4.4 Instrument response to the analyte

The instrument response to EA and MA over the range of 0.5 to 2 times the target concentration is linear with a slope of 904 and 744 (in ISTD-corrected area counts per microgram per milliliter) respectively. The precision of the response to the analytes was determined by multiple injections of standards. The data below is presented graphically in Figures 4.4.1 and 4.4.2.

Table 4.4.1
Instrument Response to EA

× target conc. µg/mL	0.5 × 120.1	1.0 × 240.2	2.0 × 480.5
area counts	114739	229235	439553
	115864	229263	438815
	114104	229393	442452
	114893	228508	442554
	115627	230194	444326
	114515	229596	443086
mean	114957	229365	441798

Table 4.4.2
Instrument Response to MA

× target conc. µg/mL	0.5 × 210.3	1.0 × 420.6	2.0 × 841.3
area counts	160525	319379	622744
	161938	307530	636503
	155385	307678	637850
	159164	319313	634148
	155422	308723	607192
	157746	321258	626962
mean	158363	313980	627566

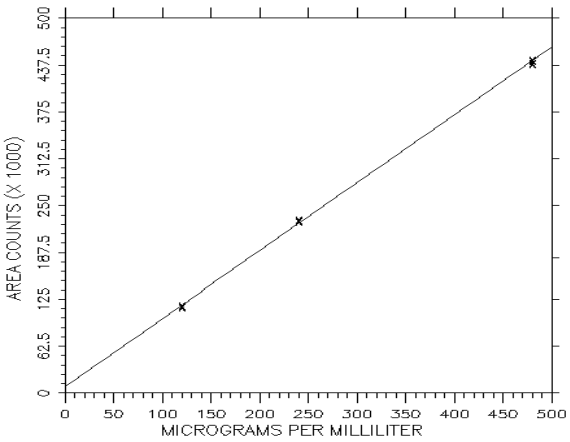


Figure 4.4.1 Calibration curve for ethyl acrylate.

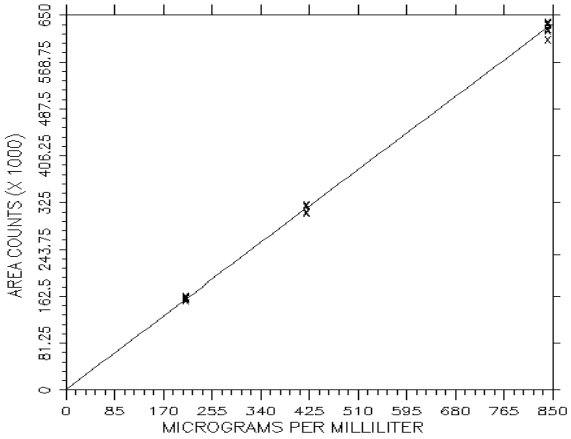


Figure 4.4.2 Calibration curve for methyl acrylate.

4.5 Storage data

Storage samples for EA and MA were prepared by injecting an aliquot of a CS_2 solution containing the analytes into the TBC-coated coconut shell charcoal. Humid air, 80% RH, was drawn through the tubes for 2 h at 0.05 L/min. Thirty-six storage samples were prepared. Six samples were analyzed immediately. Fifteen tubes were stored at reduced temperature (12°C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22°C). At 2-5 day intervals, three samples were selected from each of the two storage sets and analyzed. The results are listed below and shown graphically in Figures 4.5.1.1 - 4.5.2.2.

Table 4.5.1
Storage Test of EA

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	99.3	98.4	100.7	99.3	98.4	100.7
	100.2	99.1	98.7	100.2	99.1	98.7
5	97.3	96.8	96.4	100.5	98.2	98.6
7	98.5	100.2	100.7	100.0	99.6	100.6
12	98.1	97.9	97.1	100.0	100.8	100.4
14	97.5	98.6	96.5	100.3	99.0	100.3
16	97.2	95.4	96.4	98.7	100.8	100.4

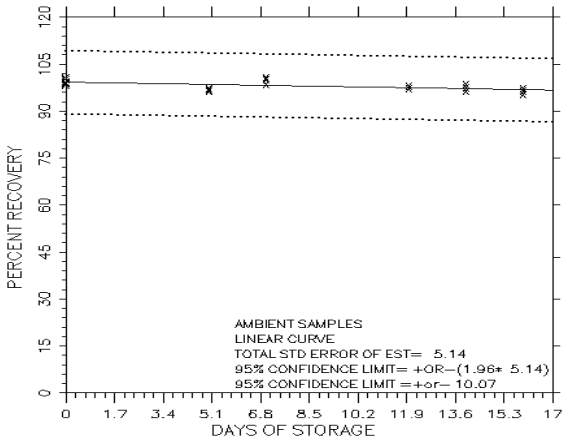


Figure 4.5.1.1 Ambient storage test for EA.

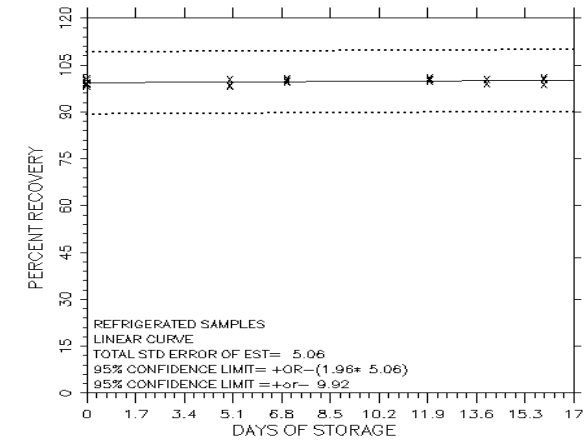


Figure 4.5.1.2 Refrigerated storage test for EA.

Table 4.5.2
Storage Test of MA

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	103.5	101.6	101.9	103.5	101.6	101.9
	99.5	102.4	101.8	99.5	102.4	101.8
5	99.6	100.5	95.8	99.3	99.4	101.8
7	100.0	95.8	93.8	95.9	100.9	95.8
12	100.8	98.8	100.2	100.6	103.6	105.5
14	95.6	96.6	99.1	98.9	99.6	97.5
16	96.5	94.5	98.8	99.3	99.5	99.1

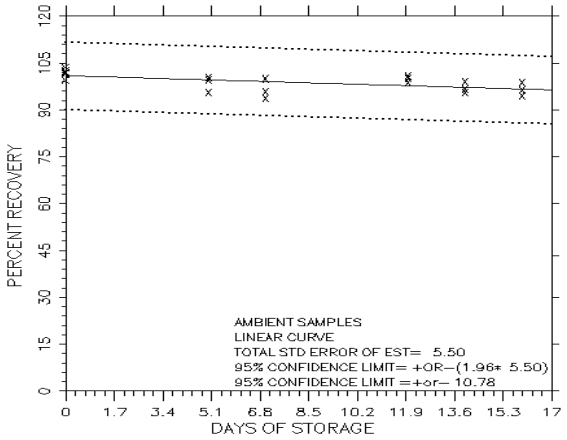


Figure 4.5.2.1 Ambient storage test for MA.

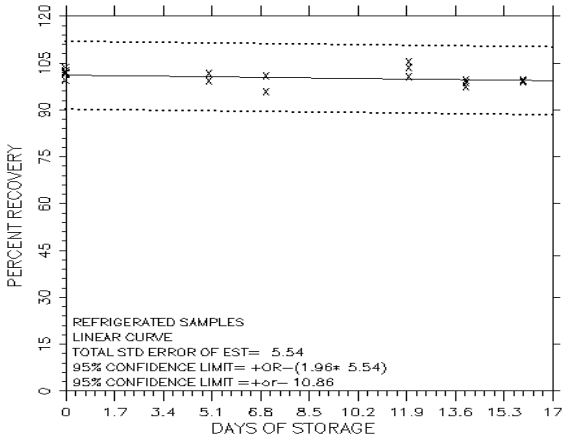


Figure 4.5.2.2 Refrigerated storage test for MA.

4.6 Precision (analytical method)

The precision of the analytical procedure is defined as the pooled coefficient of variation determined from replicate injections of EA and MA standards at 0.5, 1 and 2 times the target concentration. Based on the data of Tables 4.4.1 and 4.4.2, the coefficients of variation (CV) for the three levels and the pooled coefficient of variation (CV) were calculated and are listed below. The pooled coefficient of variations are 0.0046 and 0.0189 for EA and MA respectively.

Table 4.6.1
Precision of the Analytical Method for EA
(Based on the Data of Table 4.4.1)

× target conc. µg/mL	0.5 × 120.1	1.0 × 240.2	2.0 × 480.5
SD[1]	671	553	2148
CV	0.0058	0.0024	0.0049

1 - in area counts

Table 4.6.2
Precision of the Analytical Method for MA
(Based on the Data of Table 4.4.2)

× target conc. µg/mL	0.5 × 210.3	1.0 × 430.6	2.0 × 841.3
SD[1]	2684	6627	11558
CV	0.0169	0.0211	0.0184

1 - in area counts

4.7 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

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

where:

n = total number of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed percent recovery at a given time
Y_{est} = estimated percent recovery from the regression line at the same given time

An additional 5% for pump error is added to the SEE by the addition of variances. The precision at the 95% confidence level is obtained by multiplying the SEE (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression line in the storage graph as shown in Figure 4.5.1.1. The data for Figures 4.5.1.1 and 4.5.2.1 were used to determine the SEEs of ±5.14% and ±5.50% and the precision of the overall procedure of ±10.1% and ±10.8% for EA and MA respectively.

4.8 Reproducibility data

Six samples were prepared by injecting an aliquot of a CS_2 solution containing the analytes into the TBC-coated coconut shell charcoal. Humid air, 80% RH, was drawn through the tubes for 2 h at 0.05 L/min to add water to sampler matrix. The samples were given to a chemist unassociated with this study. The samples were analyzed after being stored for 11 days at 12°C. Sample results were corrected for desorption efficiencies. No sample result for EA or MA had a deviation greater than the precision of the overall procedure determined in Section 4.7, which are ±10.1% and ±10.8% respectively.

Table 4.8.1
Reproducibility Data for EA

µg spiked	µg recovered	percent recovered	percent deviation
240.2	216.8	90.3	-9.7
240.2	224.0	93.3	-6.7
240.2	223.6	93.1	-6.9
240.2	218.2	90.8	-9.2
240.2	218.5	91.0	-9.0
240.2	228.8	95.3	-4.7

Table 4.8.2
Reproducibility Data for MA

µg spiked	µg recovered	percent recovered	percent deviation
420.6	375.4	89.3	-10.7
420.6	395.5	94.0	-6.0
420.6	393.2	93.5	-6.5
420.6	379.6	90.3	-9.7
420.6	379.0	90.1	-9.9
420.6	406.1	96.6	-3.4

4.9 Sampler capacity

The sampling capacity of the front section of a TBC-coated coconut shell charcoal sampling tube was tested by sampling from a dynamically generated test atmosphere of MA (70.5 mg/m^3 or 20.0 ppm). The samples were collected at 0.05 L/min and the relative humidity was 80%. A complete TBC-coated coconut shell charcoal sampling tube was placed in-line with the test front section and changed at measured intervals. After sampling for 6.5 h or 19.5 L, the back tube (that had been used for only the last 30 min) contained 13.08 µg of MA, which was 1.02% of the upstream concentration. The prior sample had contained 0.54%, all other samples contained no MA. An extrapolation of this data was used to estimate the 5% breakthrough air volume, which resulted in an air volume of 24.0 L, well over the recommended air volume of 12 L.

Table 4.9
Breakthrough on the TBC-coated Charcoal Tube for MA

air volume (L)	sample time (min)	downstream (mg/m^3)	breakthrough (percent)
1.50	30	0.00	0.00
4.50	90	0.00	0.00
6.75	135	0.00	0.00
8.25	165	0.00	0.00
9.75	195	0.00	0.00
11.25	225	0.00	0.00
12.75	255	0.00	0.00
14.25	285	0.00	0.00
15.75	315	0.00	0.00
17.25	345	0.38	0.54
18.75	375	0.72	1.02

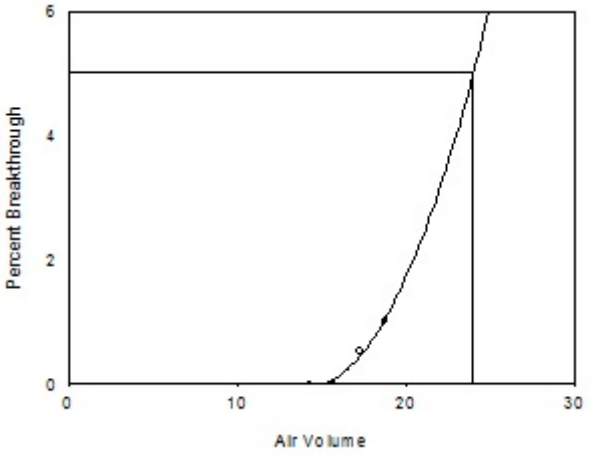


Figure 4.9. Estimated breakthrough air volume for methyl acrylate.

4.10 Desorption efficiency and stability of desorbed samples

4.10.1 Desorption efficiency

The desorption efficiencies (DE) of EA and MA were determined by liquid-spiking 110-mg portions of TBC-coated coconut shell charcoal with the analytes at 0.5 to 2 times the target concentrations. These samples were stored overnight at ambient temperature and then desorbed with desorbing solution and analyzed. The average desorption efficiency over the studied range was 100.3% and 99.7% for EA and MA respectively.

Table 4.10.1.1
Desorption Efficiency of EA

× target µg	0.5 × 120.1	1.0 × 240.2	2.0 × 480.5
DE, %	100.9	100.2	101.6
	99.3	100.3	101.7
	98.7	101.7	99.2
	99.9	100.3	99.4
	100.9	99.6	100.7
	98.9	101.0	101.2
mean	99.8	100.5	100.6

Table 4.10.1.2
Desorption Efficiency of MA

× target µg	0.5 × 210.3	1.0 × 420.6	2.0 × 841.3
DE, %	99.3	97.3	102.8
	105.8	95.8	103.7
	105.0	92.8	101.1
	100.4	97.7	100.4
	94.2	97.7	99.5
	105.7	99.5	96.4
mean	101.7	96.8	100.6

4.10.2 Stability of desorbed samples

The stability of desorbed samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. The original analysis was performed and the vials were not recapped after injection. The samples were reanalyzed with fresh standards. The average recovery of the reanalysis, compared to the average recovery of the original analysis, was 99.4% (-0.9% change) and 90.0% (-9.7% change) for EA and MA respectively.

Table 4.10.2.1
Stability of Desorbed Samples for EA

initial recovery (percent)	recovery after 24 h (percent)	percent change
101.0	100.8	-0.2
99.6	99.3	-0.3
100.3	99.9	-0.4
101.7	99.0	-2.7
100.3	99.4	-0.9
100.2	98.2	-2.0

Table 4.10.2.2
Stability of Desorbed Samples for MA

initial recovery (percent)	recovery after 24 h (percent)	percent change
99.5	86.8	-12.7
97.7	88.7	-9.0
97.7	94.6	-3.1
92.8	89.1	-3.7
95.8	92.3	-3.5
97.3	88.3	-9.0

5. References

5.1 "NIOSH Manual of Analytical Methods", 3rd ed.; U.S. Department of Health and Human Services, Center for Disease Control, National Institute of Occupational Safety and Health; Cincinnati, OH, 1984, Method 1450, DHHS (NIOSH) Publ. No. 84-100.

5.2 "NIOSH Manual of Analytical Methods", 3rd ed.; U.S. Department of Health and Human Services, Center for Disease Control, National Institute for Occupational Safety and Health; Cincinnati, OH, 1984, Method S-38, DHHS (NIOSH) Publ. No. 84-100.

5.3 Cheminfo Database on CCINFO CD-ROM disc 91-2, Canadian Centre for Occupational Health and Safety, Hamilton, Ontario.

5.4 "Code of Federal Regulations", Title 29, 1910.1000, Table Z-1-A. Limits for Air Contaminants, U.S. Government Printing Office, Washington, D.C., 1990.

5.5 International Agency for Research on Cancer, "IARC Monograph on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some Chemicals Used in Plastics and Elastomers", IARC, Lyon, France, 1986, Vol. 39, pp. 81-98.

5.6 International Agency for Research on Cancer, "IARC Monograph on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some Chemicals Used in Plastics and Elastomers", IARC, Lyon, France, 1986, Vol. 39, pp. 99-112.