Acrylic Acid
Methacrylic Acid

Method no.:	PV2005

Target concentration:
  Acrylic acid: 2 ppm (5.9 mg/m^3) (ACGIH TLV) (skin)
  Methacrylic acid: 20 ppm (70 mg/m^3) (ACGIH TLV)

Procedure: Samples are collected by drawing a known volume of air through two Anasorb 708 tubes connected in series. Samples are desorbed with 2 mL of methanol for 1 hour with shaking and analyzed by liquid chromatography using an ultraviolet detector at 210 nm (LC-UV).

Recommended air volume
and sampling rate: 240 minutes at 0.1 L/min (20 Liters)

Reliable quantitation limit:
  Acrylic acid: 0.00301 ppm (0.00888 mg/m^3)
  Methacrylic acid: 0.00475 ppm (0.0170 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

There is an OSHA validated method (28) for acrylic acid (Ref. 5.1) and a stopgap method for methacrylic acid (Ref. 5.2) which use two XAD-8 tubes connected in series for sampling in the sampling train. SKC is no longer making XAD-8 tubes, and state that Anasorb 708 tubes are the equivalent. The purpose of this study was to determine whether the Anasorb 708 tubes could be substituted for the XAD-8 tubes. The retention, storage, and desorption studies indicate that the Anasorb 708 tubes are a good substitution for the XAD-8 tubes.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) (Ref. 5.3 and Ref. 5.4)

Acrylic acid is an acute irritant to skin, eyes, and mucous membranes. Acrylic acid is readily adsorbed through the skin. Rats exposed to 300-ppm acrylic acid for 5 days/week for 4 weeks showed nose irritation, lethargy, and reduced weight gain. Mice exposed to 75-ppm acrylic acid 6 hours/day 5 days/week for 13 weeks showed slight degenerative lesions on the nasal mucous membranes. Methacrylic acid is a severe contact irritant, and direct contact can cause blindness and skin ulceration. Rats exposed to 300-ppm methacrylic acid for 20 days showed slight renal congestion. The TLVs of 2 ppm for acrylic acid and 20 ppm for methacrylic acid were established at these levels to prevent injury due to exposure to these compounds.

1.1.3 Workplace exposure (Ref. 5.3 and 5.4)

Acrylic acid and methacrylic acid are used as monomers for the manufacture of resins and polymers, and in organic syntheses. The U.S. production of acrylic acid and its esters is about 500,000 tons per year.

1.1.4 Physical properties and other descriptive information (Ref. 5.5 and 5.6)

Acrylic acid

|	
CAS number:	79-10-7
IMIS:	0117
Synonyms:	Acroleic acid; Ethylene carboxylic acid; Propene acid; Propenoic acid; Vinyl formic acid
RTECS:	AS4375000
DOT:	UN 2218 corrosive liquid
Molecular weight:	72.06
Flash point:	68 °C (155 °F) (oc)
Boiling point:	141 °C
Melting point:	14 °C
Odor:	acrid
Odor threshold:	1 ppm
Color:	colorless liquid
Autoignition Temperature:	238 °C (820 °F)
Density:	1.05204 (g/mL)
Molecular formula:	$C_3H_4O_2$

Structural formula:
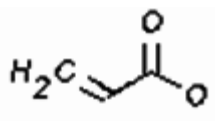
Methacrylic acid

CAS n.: 79-41-4
IMIS: M339
Synonyms: alpha-Methacrylic acid; 2-Methylenepropionic acid; 2-Methylpropenoic acid; 2-Methyl-2-propenoic acid
RTECS: OZ2975000
DOT: UN2531 corrosive liquid
Molecular weight: 86.09
Flash point: 76 °C (170 °F) (cc)
Boiling point: 163 °C
Melting point: 15 °C
Odor: acrid, like acetic acid
Color: colorless to pale yellow liquid
Autoignition temperature: 435 °C (815 °F)
Density: 1.0153254 (g/mL)
Molecular formula: $C_4H_6O_2$

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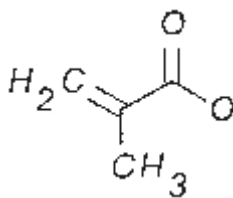
The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg)

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure for acrylic acid is 0.064 µg per sample (0.001 ppm or 0.00267 mg/m^3; and for methacrylic acid is 0.123 µg per sample (0.0015 ppm or 0.00513 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 is 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}).

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

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:

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

Y_{obs} = observed response
Y_{est} = estimated response for regression curve
n = total number of data points
k = 2 for 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

$$3(SEE) + Y_{BR} \text{ for } Y_{DLOP}$$

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 lowest sampler loading was 0.2 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. Values of 5157 and 109.9 were obtained for A and SEE respectively for acrylic acid. The DLOP for acrylic acid was calculated to be 0.064 µg/sample (0.001 ppm). Values of 2838 and 116 were obtained for A and SEE respectively for methacrylic acid. The DLOP for methacrylic acid was calculated to be 0.123 µg/sample (0.0015 ppm).

table 1.2.1.1
detection limit of the overall procedure
for acrylic acid

mass per sample (µg)	area counts (µV-s)
0.2	2048
0.4	2732
0.6	3824
0.8	4865
1.0	6039
1.2	6890
1.4	8103
1.6	9069
1.8	10113
2.0	11127

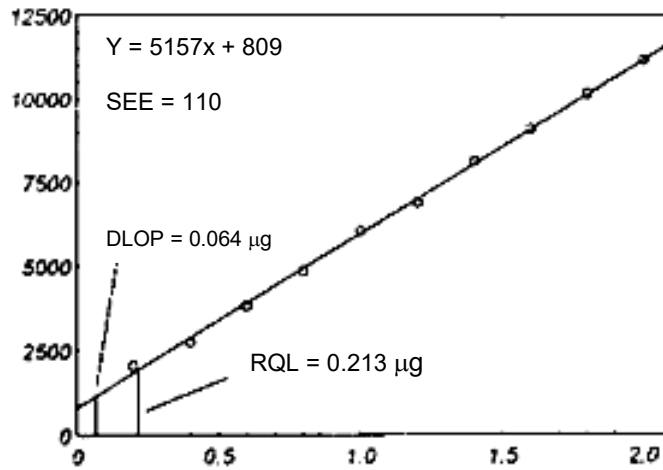Y = 5157x + 809

SEE = 110

DLOP = 0.064 µg

RQL = 0.213 µg

Figure 1.2.1.1. Plot of data to determine the DLOP/RQL for acrylic acid.

table 1.2.1.2
detection limit of the overall procedure
for methacrylic acid

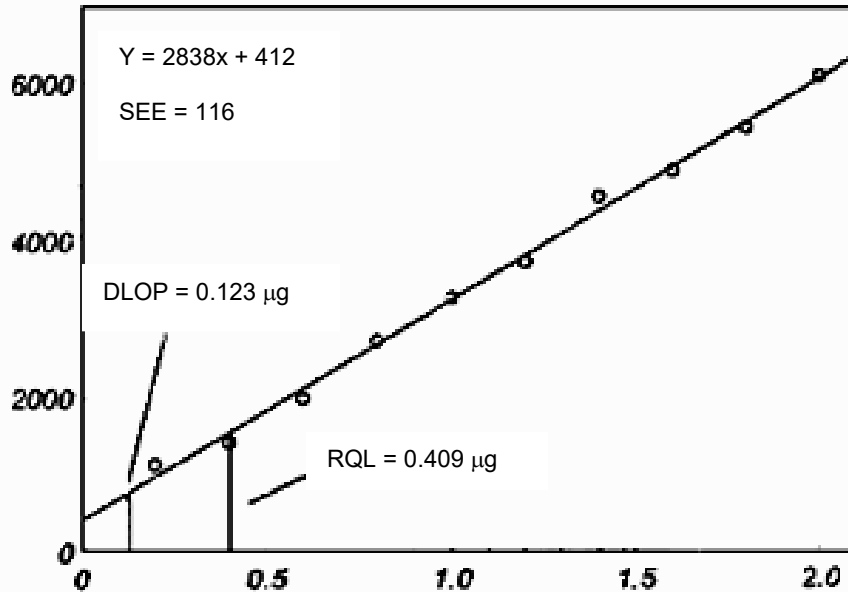| mass per sample (µg)	area counts (µV-s)
0.2	1138
0.4	1427
0.6	1985
0.8	2724
1.0	3278
1.2	3730
1.4	4569
1.6	4910
1.8	5455
2.0	6122

Figure 1.2.1.2. Plot of data to determine the DLOP/RQL for methacrylic acid.

1.2.2   Reliable quantitation limit (RQL)

The reliable quantitation limit is 0.213 μg per sample for acrylic acid (0.00301 ppm), and 0.409 μg per sample for methacrylic acid (0.00475 ppm). 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

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

Therefore

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

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

table 1.2.2.1
reliable quantitation limit for acrylic acid

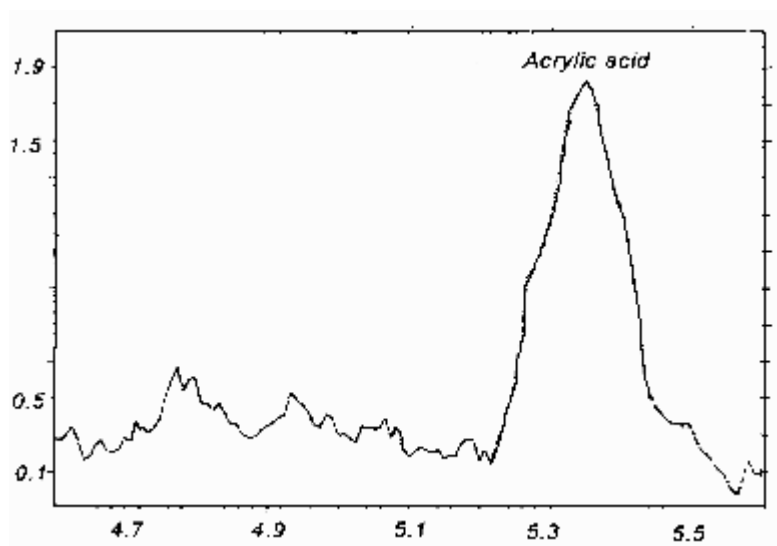| mass per sample (µg)	mass recovered (µg)	% recovered
0.2	0.197	98.5
0.4	0.388	97.0
0.6	0.592	98.7
0.8	0.780	97.5
1.0	0.941	94.1
1.2	1.189	99.1
1.4	1.387	99.1
1.6	1.582	98.9
1.8	1.753	97.4
2.0	1.934	96.7

Figure 1.2.2.1 a chromatogram of the RQL for acrylic acid.

table 1.2.2.2
reliable quantitation limit for methacrylic acid

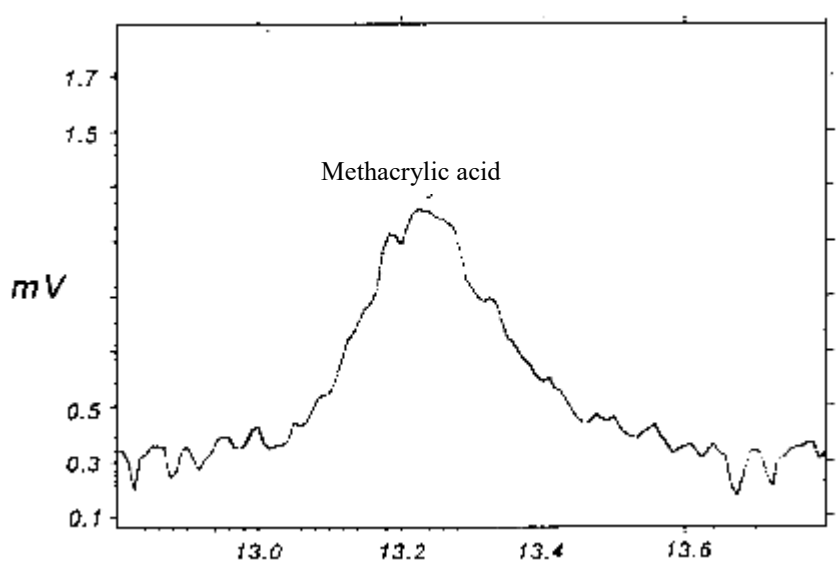| mass per sample (µg)	mass recovered (µg)	% recovered
0.2	.196	98.0
0.4	.396	99.0
0.6	.592	98.7
0.8	.772	96.5
1.0	.998	99.8
1.2	1.188	99.0
1.4	1.340	95.7
1.6	1.534	95.9
1.8	1.787	99.3
2.0	1.974	98.7

Figure 1.2.2.2 a chromatogram of the RQL for methacrylic acid.
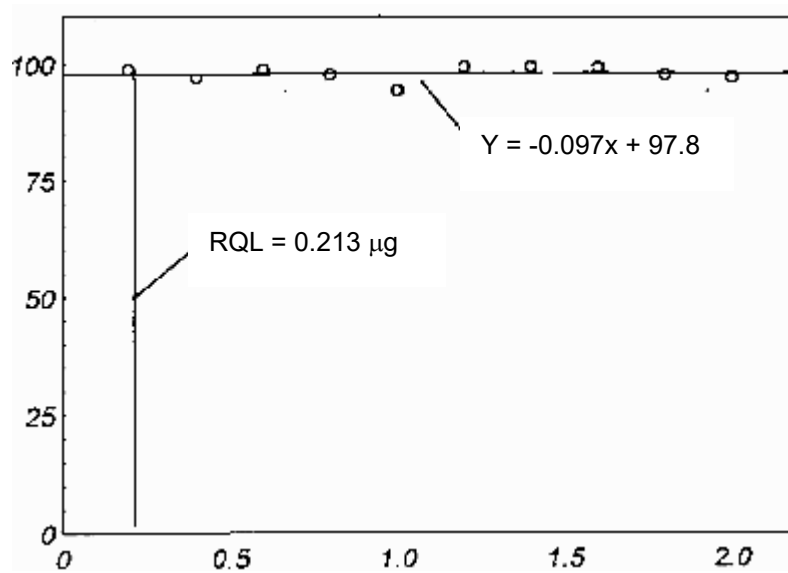
Figure 1.2.2.3 Plot of data to determine the RQL for acrylic acid.
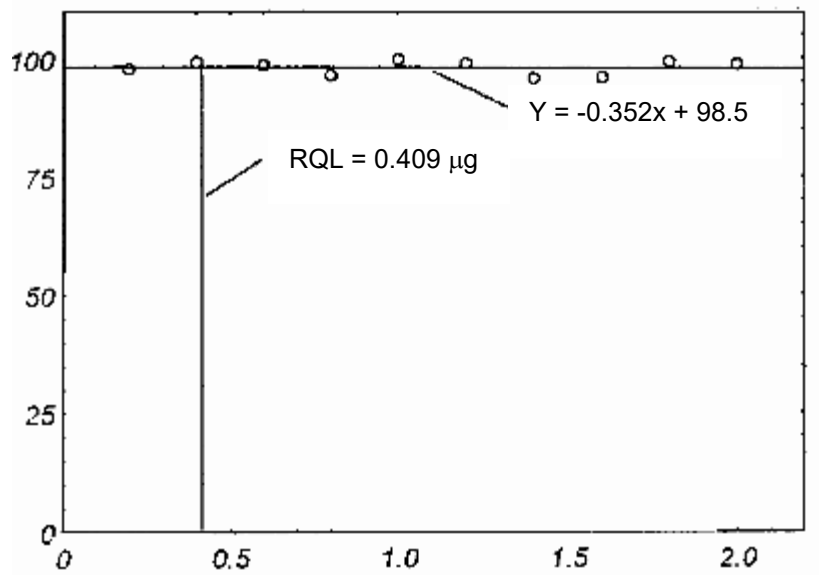
Y = -0.352x + 98.5

RQL = 0.409 μg

Figure 1.2.2.4 Plot of data to determine the RQL for methacrylic acid.

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.

2.1.2 Samples are collected with two 7-cm × 4-mm i.d. × 6-mm o.d. glass-sampling tubes packed with one section of 100 mg of Anasorb 708 in series. The section is held in place with glass wool plugs, in each tube. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (Fullerton, CA, catalog no. 226-30-8).

2.2 Technique

2.2.1 Immediately before sampling, break off the ends of the sampling tube. A sampling train is assembled by connecting two tubes in series, after the sealed end has been cut off. A small piece of flexible plastic tubing may be substituted for the cut red plastic end caps. The inside broken ends of the two Anasorb 708 tubes should be as close together as possible, after the sampling train is assembled. All tubes should be from the same lot.

2.2.2 Attach the sampling train 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.

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

2.2.4 Attach the sampling train vertically with the outer tube 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 train and seal each tube with intact plastic end caps. Wrap each tube separately 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 air 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

2.3.1   The desorption efficiencies of acrylic acid were determined by liquid spiking the Anasorb 708 tubes at loadings of 0.1 to 2 times the target concentration. The loadings on the tubes were 8, 40, 80, and 160 µg of acrylic acid. These samples were stored overnight at ambient temperature and then opened, placed into 4-mL vials, desorbed with 2 mL methanol for 1 hour on the shaker, and analyzed by LC-UV. The average desorption efficiency over the studied range was 98.7%.

table 2.3.1
% desorption efficiency of acrylic acid

tube #	0.1 x (8 µg)	0.5 x (40 µg)	1.0 x (80 µg)	2.0 x (160 µg)
1	98.0	98.6	98.1	99.7
2	98.4	98.5	98.2	99.5
3	99.9	98.6	98.5	99.0
4	98.8	99.2	98.2	99.2
5	97.0	98.6	99.0	98.8
6	98.5	98.0	99.2	99.0
average	98.4	98.6	98.5	99.2

overall average = 98.7%
standard deviation = ±0.629

2.3.2   The desorption efficiencies of methacrylic acid were determined by liquid spiking the Anasorb 708 tubes at loadings of 0.1 to 2 times the target concentration. The loadings on the tubes were 71, 355, 711, and 1420 µg of methacrylic acid. These samples were stored overnight at ambient temperature, then desorbed, and analyzed. The average desorption efficiency over the studied range was 98.6%.

table 2.3.2
% desorption efficiency of methacrylic acid

tube #	0.1 x (8 μg)	0.5 x (40 μg)	1.0 x (80 μg)	2.0 x (160 μg)
1	96.9	98.9	98.3	98.7
2	99.1	99.6	98.8	98.7
3	98.0	98.8	98.7	98.3
4	97.8	98.0	98.8	99.2
5	98.0	97.2	98.6	101
6	99.2	98.1	98.9	98.5
average	98.2	98.4	98.7	99.1

overall average = 98.6%
standard deviation = ±0.810

2.4 Retention efficiency

The sampling tubes were spiked at the 2 × PEL level, loadings of 160 μg acrylic acid and 1420 μg methacrylic acid, allowed to equilibrate 4 hours, and then had 24 L humid air (81% RH at 21 °C) pulled through them at 0.1 Lpm. They were opened, desorbed, and analyzed by LC-UV. The retention efficiency averaged 98.9% for acrylic acid and 99.7% for methacrylic acid. There was little or no acrylic and methacrylic acids found on the back sections of the tubes.

table 2.4.1
retention efficiency of acrylic acid

tube #	% recovered		
	front section	back section	% total
1	99.9	0.0	99.9
2	98.6	0.1	98.7
3	100	0.0	100
4	97.1	0.3	97.4
5	98.6	0.2	98.8
6	98.4	0.1	98.5

average = 98.9%

table 2.4.2
retention efficiency of
methacrylic acid

tube #	% recovered		
	front section	back section	% total
1	100	0.0	199
2	95.6	2.0	97.6
3	101	0.0	101
4	98.7	0.0	98.7
5	101	0.0	101
6	99.9	0.0	99.9

average = 99.7%

2.5   Sample storage

The front sections of twelve sampling tubes were each spiked with 80-μg acrylic acid and 711-μg methacrylic acid. Twelve more tubes were spiked at the same loadings and then had 24 liters of humid air (81% RH at 22 °C) drawn through them at 0.1 Lpm. Six samples from each group were stored at room temperature (24 °C) and the other six tubes stored at refrigerator freezer temperature (-4 °C). Three samples of each type were analyzed after 7 days and the remaining three samples of each type after 14 days. The amounts recovered, corrected for desorption efficiency, indicate good storage stability for the time period studied and had an average recovery of 99.3% for all acrylic acid conditions, and 99.4% for all methacrylic acid conditions.

table 2.5.1
storage test for acrylic acid

time (days)	% recovered			
	dry refrigerated	dry ambient	humid refrigerated	humid ambient
7	100	100	99.9	99.8
7	99.6	99.9	100	99.1
7	99.2	99.3	98.0	99.0
14	98.8	100	98.1	99.6
14	99.9	99.2	99.8	98.2
14	99.2	99.5	99.0	97.0
average	99.5	99.7	99.1	98.8

table 2.5.2
storage test for methacrylic acid

time (days)	% recovered			
	dry refrigerated	dry ambient	humid refrigerated	humid ambient
7	100	100	100	99.7
7	99.2	99.6	100	100
7	99.3	99.3	100	98.8
14	98.8	99.5	102	98.2
14	100	101	98.9	97.6
14	99.5	98.2	97.0	98.6
average	99.5	99.6	99.7	98.8

2.6   Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 24 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 acrylic and methacrylic acid on the sampling tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of the sampling tubes to collect acrylic and methacrylic acid.

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 liquid chromatograph equipped with an ultraviolet detector, specifically a Waters 600 E pump and system controller, Waters 717 autosampler, and Waters 490 E programmable multiwavelength detector.

    3.1.2   An LC column capable of separating the analyte from any interference. The column used in this study was a LC-8-DB column, 5µm film thickness, 25-cm long, 4.6-mm i.d.

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

    3.1.4   Four milliliter vials with PTFE-lined caps.

    3.1.5   A 100-µL syringe or other convenient size for sample injection.

    3.1.6   Pipettes for dispensing the desorbing solution.

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

  3.2 Reagents

    3.2.1   Acrylic acid, Reagent grade.

    3.2.2   Methacrylic acid, Reagent grade

    3.2.3   Methanol, HPLC grade

    3.2.4   Deionized water, the water used in this study was from a Millipore Milli-Q water purification system.

    3.2.5   Phosphoric acid, Reagent grade

    3.2.6   Acetonitrile, HPLC grade

    3.2.7   The mobile phase was 0.1:4:96 solution of phosphoric acid: acetonitrile: water.

  3.3   Standard preparation

    3.3.1   At least two separate stock standards are prepared by diluting a known quantity of acrylic and methacrylic acid with methanol. The concentration of these stock standards was 1050 µg/mL acrylic acid and 1015 µg/mL methacrylic acid.

    3.3.2   Dilutions of these stock standards were prepared to bracket the samples. The range of the standards used in this study was from 1.05 to 1050 µg/mL acrylic acid and 1.015 to 1015 µg/mL methacrylic acid.

3.4   Sample preparation

    3.4.1   Sample tubes are opened and the front and back section of each tube are placed in separate 4-mL vials.

    3.4.2   Each section is desorbed with 2 mL of methanol.

    3.4.3   The vials are sealed immediately and allowed to desorb for 1 hour with constant shaking.

3.5   Analysis

    3.5.1   Liquid chromatograph conditions.

Injection size: 10 µL
Column: LC-8-DB, 5µm, 25-cm, 4.6-mm i.d.
Mobile phase: 6% water/ 96% acetonitrile/0.1% phosphoric acid
Detector: Waters 490 E programmable multi wavelength detector at 210 nm.
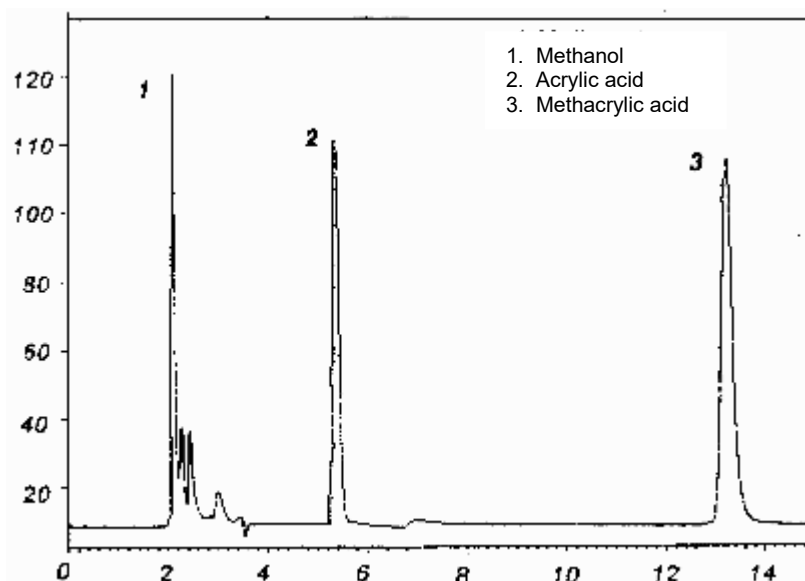
Figure 3.5 a chromatogram of an analytical standard of
105 µg/mL acrylic acid and 101.5 µg/mL methacrylic acid.

    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 interference is reported, it should be considered before samples are desorbed.   Generally, chromatographic conditions can be altered to separate 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.
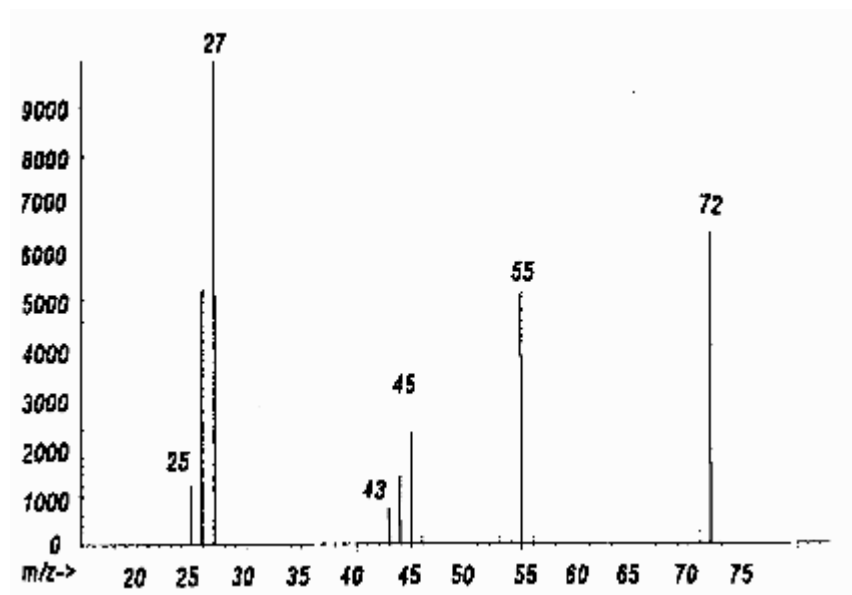
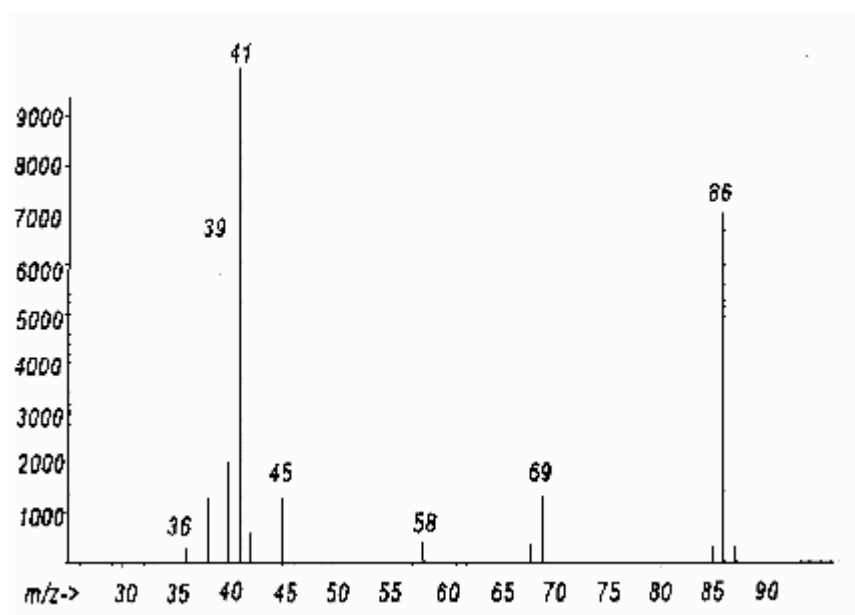Figure 3.6.2.1 a mass spectrum of acrylic acid.

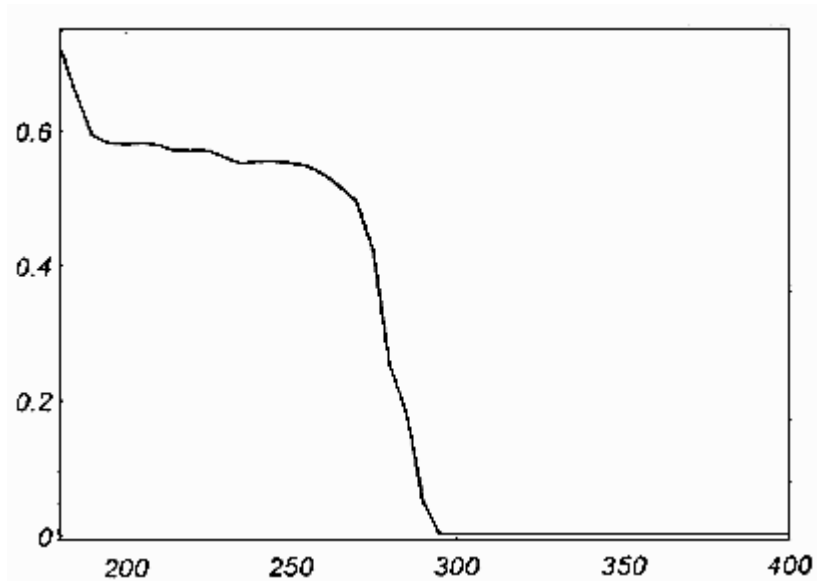Figure 3.6.2.2 a mass spectrum of methacrylic acid.
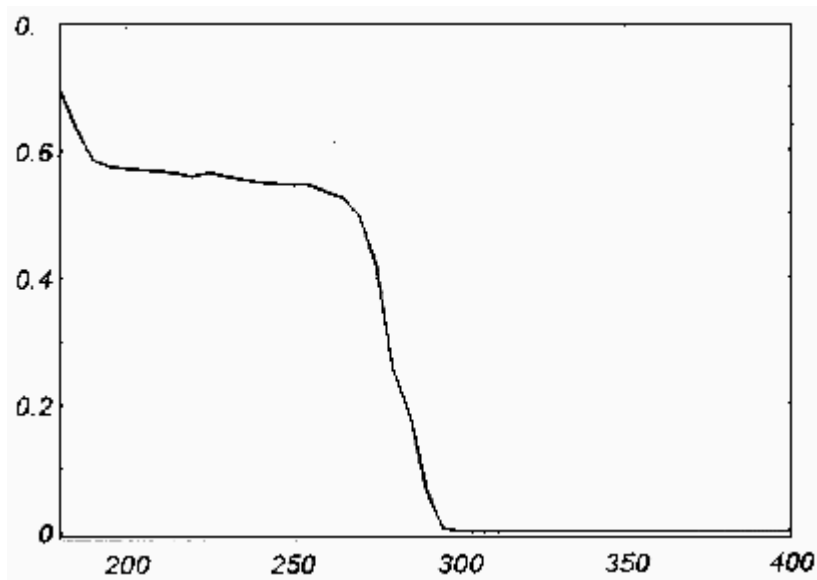
Figure 3.6.2.3 UV spectra of acrylic acid.

Figure 3.6.2.4 UV spectra of methacrylic acid.

3.7   Calculations

    3.7.1   The calibration curve was made from at least four standards at different concentrations
             bracketing the samples.

    3.7.2   The values for the air samples and blanks are obtained from the calibration curve.

    3.7.3   Values (µg) obtained for blanks are subtracted from air samples.

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

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

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

$$\text{volume of analyte} = (\text{moles of analyte})(24.46)$$

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

* All units must cancel.

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

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

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
20 L = Liters air sample collected
DE   = desorption efficiency, decimal

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 should be performed from a dynamically generated test atmosphere.

5   References

5.1   Cummins, K., Method 28, "Acrylic Acid," Organic Methods Evaluation Branch, OSHA Salt Lake Technical Center, 1981.

5.2   Eide, M., "Methacrylic Acid," Organic Service Branch I, OSHA Salt Lake Technical Center, 1988, OSHA SLTC in-house files.

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.14.1.

5.4   Documentation of the Threshold Limit Values and Biological Exposure Indices, Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p.362.

5.5   Budavari, S., The Merck Index, Twelfth Edition, Merck & Co., Inc., Whitehouse Station NJ, 1996, p. 23.

5.6   Budavari, S., The Merck Index, Twelfth Edition, Merck & Co., Inc., Whitehouse Station NJ, 1996, p. 1015.