Method number:	PV2293
Control number:	T-PV2293-01-9509-CH
Matrix:	Air
Target concentration:	10 ppm (30 mg/m^3) TWA PEL.
Procedure:	Samples are collected by drawing a known volume of air through a silica gel tube (520/260 mg). Samples are desorbed with 4 mL 50:50 acetone:water, and analyzed by gas chromatography (GC) with a flame ionization detector (FID).
Alternate analytical procedure:	Samples are desorbed with 1.5mM borate buffer in a bath of simmering water for 15 minutes, and analyzed by ion chromatography with a conductivity detector (See Appendix A).
Air volume and sampling rate studied:	18 liters at 0.2 Lpm (90 minutes)
Status of method:	Partially validated method. This method has been partially evaluated and is presented for information and trial use only.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA laboratory received samples collected on silica gel tubes requesting analysis for Propionic acid. A partially validated method for collection of Propionic acid on charcoal tubes showed low recoveries. An article (Ref. 5.1) discussed the collection of Propionic acid using silica gel tubes. There were two methods of analysis either the samples were desorbed with 50:50 acetone:water and titrated with sodium hydroxide, or desorbed with 1% aqueous Formic acid and analyzed by gas chromatography. The lowest concentration studied was 18.2 ppm based on an 18-liter air volume. The PEL for Propionic acid is 10 ppm, so further studies were needed. Desorption studies using the 50:50 acetone:water with analysis by GC-FID were performed at lower concentrations and found to give 99.9% desorption. The 50:50 acetone:water solvent was chosen for ease of analysis, and because acids tend to degrade capillary columns. Retention efficiency was evaluated in both humid and dry air conditions, using 18 liters and no breakthrough occurred.

1.1.2 Potential workplace exposure (Ref. 5.2)

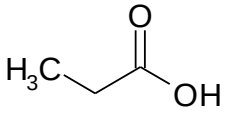
Propionic acid is used as a preservative and a mold inhibitor. It is also used as an esterifying agent, and in the production of cellulose propionate and other propionates. It is used in the manufacture of fruit flavors and perfume bases.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.3)

Propionic acid causes skin burns and redness in the eyes. The LD_{50} for skin exposure in rabbits was 500 mg/kg, and the oral exposure in rats was 4.3 g/kg. The TLV of 10 ppm was chosen due to the similarity of Propionic acid to Acetic acid.

1.1.4 Physical properties (Ref. 5.1)

CAS:	79-09-4
IMIS:	2168
Molecular formula:	$C_3H_6O_2$
Molecular weight:	74.08
Melting point:	- 21.5 °C
Boiling point:	141 °C
Density:	0.99336
Flash point:	58 °C (136 °F)
Synonyms:	Propanoic acid; methyl acetic acid; ethyl formic acid
Odor:	Pungent rancid odor
Color:	Clear liquid
Structure:	



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 2 ng, with a 1 µL injection volume. This is the smallest amount that could be detected under normal operating conditions.

1.2.2 The detection limit of the overall procedure is 2 µg/sample, or 0.04 ppm based on an 18-liter sample, 4 mL desorption volume, and 99.9% desorption efficiency. (All ppm amounts in this study are based on an 18 L 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 Reanalysis 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 GC column and parameters.

1.4 Disadvantages

None known

2 Sampling procedure

2.1 Apparatus

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

2.1.2 Silica gel tubes, lot 637, containing 520 mg adsorbing section with a 260 mg backup section separated by a 2-mm portion of urethane foam, with a silanized 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 11-cm x 8-mm o.d. and 6-mm i.d., SKC tubes or equivalent.

2.2 Sampling technique

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

2.2.2 Connect the silica gel 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 silica gel tube.

2.2.5 Seal the silica gel tube with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.

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.

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 container from the samples.

2.3 Desorption efficiency

Desorption study was performed by liquid spiking a solution of Propionic acid in water onto six silica gel tubes at each of three levels, 59.6 µg (1.09 ppm), 298 µg (5.46 ppm), and 596 µg (10.9 ppm). These tubes were stored overnight at room temperature. They were then opened, each section placed into a separate 4-mL vial, and desorbed with 2 mL 50:50 acetone:water. They were allowed to desorb for 60 minutes with constant shaking. The samples were analyzed by GC-FID. The overall desorption efficiency was 99.9% (Table 2.3).

Table 2.3
Propionic acid
Desorption Efficiency

tube #	% recovered		
	59.6 µg	298 µg	596 µg
1	98.2	99.8	99.7
2	102	98.9	102
3	100	98.1	98.9
4	100	103	99.9
5	101	97.1	101
6	100	99.4	100
average	100	99.4	100

Overall average = 99.9%
Standard deviation = ±1.48

2.4 Retention efficiency

2.4.1 Five hundred ninety-six micrograms (10.9 ppm) Propionic acid was spiked onto eight silica gel tubes which were allowed to equilibrate at room temperature for four hours. Four of the tubes had 18 liters of humid air (91% RH) drawn through them. The other four tubes had 18 liters of dry air (16% RH) drawn through them. All were desorbed with 50:50 acetone:water and analyzed by GC-FID. There was no Propionic acid found on the backup portion of the silica gel tube (Table 2.4.1).

Table 2.4.1
Propionic acid
Retention Efficiency
(18 Liters)

tube #	% recovered		total
	'A'	'B'	
dry 1	101	0.0	101
dry 2	98.8	0.0	98.8
dry 3	97.0	0.0	97.0
dry 4	95.8	0.0	95.8
humid 1	99.2	0.0	99.2
humid 2	102	0.0	102
humid 3	96.8	0.0	96.8
humid 4	99.8	0.0	99.8

average = 98.8%

2.4.2 A loading of 2480 µg (45.47 ppm) Propionic acid was spiked onto eight silica gel tubes, which were allowed to equilibrate at room temperature for four hours. One tube had 30 liters, and three of the tubes had 20 liters of humid air (89% RH) drawn through them.

The other four tubes had 20 liters of dry air (18% RH) drawn through them. They were desorbed with 50:50 acetone:water and analyzed by GC-FID. There was no Propionic acid found on the backup portion of the silica gel tubes with low humidity, but high humidity showed Propionic acid on the backup portions of some of the tubes. At 30 liters, breakthrough was beginning to occur (Table 2.4.2).

Table 2.4.2
Propionic acid
Retention Efficiency
(20 & 30 Liters)

tube #	air volume	% recovered		total
		'A'	'B'	
dry 1	20	98.6	0.0	98.6
dry 2	20	102	0.0	102
dry 3	20	101	0.0	101
dry 4	20	95.3	0.0	95.3
humid 1	30	76.1	22.3	98.4
humid 2	20	93.3	6.7	100
humid 3	20	98.1	0.0	98.1
humid 4	20	98.4	1.5	99.9

average = 99.2%

2.5 Storage study

Six tubes were spiked with 596 µg (10.9 ppm) Propionic acid. These tubes were stored at room temperature. On days 7 and 14, three of the tubes were analyzed. There was an average recovery of 100% for the 14 days stored (Table 2.5).

Table 2.5
Propionic acid
Storage Study

days stored	% recovered
7	101
7	102
7	98.0
14	95.8
14	101
14	102
average	100%

2.6 Precision study

The precision was calculated using the area counts from six injections of each standard at concentrations of 14.9, 74.5, 149, and 298 µg/mL Propionic acid in 50:50 acetone:water. The pooled coefficient of variation was 0.0180. (Table 2.6)

Table 2.6
Propionic acid
Precision Study

injection number	µg/mL			
	14.9	74.5	149	298
1	822	4433	7820	14638
2	792	4407	7856	14659
3	793	4250	7915	14791
4	835	4230	7949	14567
5	791	4238	7872	14584
6	836	4233	7985	14671
average	812	4299	7900	14652
standard deviation –	±21.9	±94.7	±61.6	±79.7
CV -	0.0270	0.0220	0.00780	0.00544

pooled CV = 0.0180

where:

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

$$Pooled\ CV = \sqrt{\frac{A1\left(CV1\right)^2 + A2\left(CV2\right)^2 + A3\left(CV3\right)^2 + A4\left(CV4\right)^2}{A1 + A2 + A3 + A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 18 liters.

2.7.2 The sampling rate studied was 0.2 liter 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 (GC) equipped with a flame ionization detector (FID); a Hewlett Packard 5890 GC was used in this study.

3.1.2 GC column capable of separating the analyte from any interferences. A 60-m x 0.32-mm i.d. (with 0.5 µm d_f DB-Wax) capillary column was used in this study.

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

3.1.4 Four milliliter or larger vials with PTFE-lined caps for sample desorption.

3.1.5 Two milliliter vials with PTFE-lined caps for sample analysis.

3.1.6 A 1.0 uL syringe or other convenient size for sample injection.

3.1.7 Pipettes for dispensing the desorbing solution and sample preparation.

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

3.2 Reagents

3.2.1 Nitrogen, hydrogen, and air, Purified GC grade.

3.2.2 Propionic acid, Reagent grade

3.2.3 Deionized water, HPLC grade

3.2.4 Acetone, Reagent grade

3.2.5 Desorbing solution is a 50:50 mixture of Acetone and Deionized water.

3.3 Sample preparation

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

3.3.2 Each section is desorbed with 2 mL of the 50:50 acetone:water solution..

3.3.3 The vials are sealed immediately and allowed to desorb for 60 minutes with constant shaking.

3.3.4 One milliliter of sample is removed from the silica gel and placed in a 2-mL vial for GC analysis.

3.4 Standard preparation

3.4.1 Stock standards are prepared by diluting a known quantity of Propionic acid with the desorbing solution.

3.4.2 Several working range standards covering the range of the samples were made, from 1 to 1192 µg/mL. The Propionic acid peak tailed slightly, and was nonlinear at the low end of the standard curve. Lower standards were made by dilutions of the stock standards

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Flow rates	**(mL/min)**	**Temperature**	**(^{0}C)**
Nitrogen (makeup):	30	Injector:	200
Hydrogen (carrier):	1.5	Detector:	200
Hydrogen (detector):	60	Column:	150
Air:	450		

Injection size: 1 µL
Elution time: 8.242 min
Chromatogram: (See Figure 1)

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

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

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

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

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

* All units must cancel.

3.7.2 The above formulas can be condensed to the following formula. To calculate the ppm of analyte in the sample based on an 18-liter air sample, and a 2 mL desorbing solution:

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

Where:

µg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, 2 mL
L = Air volume, 18 L
DE = Desorption efficiency, decimal

3.7.3 This calculation is done for each section of the sampling tube and then 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.

3.8.4 Gloves should be worn at all times.

3.8.5 Lab coat or apron should be worn when working with chemicals.

4 Recommendations for further study

Collection efficiencies need to be done for Propionic acid. Finish validating method.

5 References

5.1 Gilland, J.C., Johnson, G.T., and McGee, W.A., Am. Ind. Hyg. Assoc. J., 1981, vol. 42, p 630-32.

5.2 Windholz, M., "The Merck Index", Tenth Edition, Merck & Co., Rahway N.J., 1983, p.1127.

5.3 "Documentation of the Threshold Limit Values and Biological Exposure Indices", Fifth Edition, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1986, p 498.

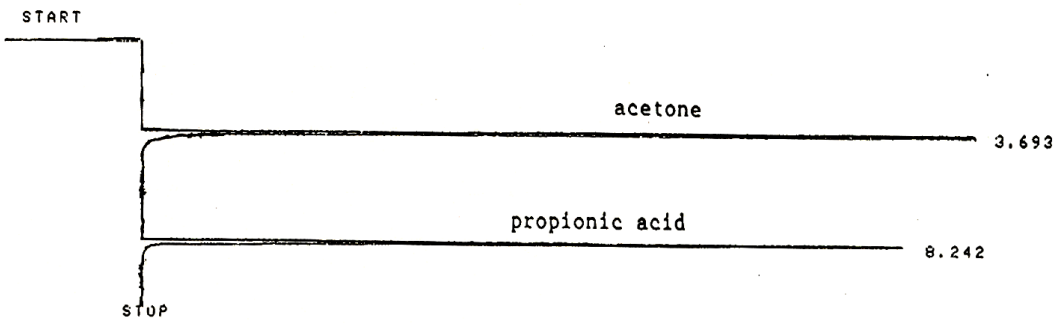


Figure 1 An analytical standard of 74.5 µg/mL Propionic acid in 50:50 acetone:water.

Appendix A
Ion Chromatography Analysis

A1 Desorption study

The desorption study was performed by spiking six silica gel tubes at each concentration of 59.6, 298, 596, and 1192 µg Propionic acid. These tubes were allowed to equilibrate overnight at room temperature. They were opened, each section placed into a 20-mL scintillation vial, 5 mL of 1.5mM Borate buffer was added, the vials were capped, and placed in a bath of simmering water to desorb for 15 minutes. (The Borate buffer was prepared by placing 0.625 grams of $Na_2B_4O_7$•10 H_2O in 1 liter of deionized water.) The samples were allowed to cool to room temperature, and analyzed by Ion chromatography with a Conductivity detector. The desorption efficiency averaged 99.4%.

Table A1
Propionic acid
Desorption Efficiency

tube #	% recovered			
	59.6 µg	298 µg	596 µg	1192 µg
1	99.8	100	101	99.3
2	101	98.3	98.2	100
3	98.4	99.3	99.8	99.6
4	98.4	99.2	101	101
5	97.6	101	98.9	97.7
6	98.0	99.5	98.9	100
average	98.9	99.6	99.6	99.6

overall average = 99.4%

A2 Analytical conditions

Type of instrument:	Dionex Ion chromatograph with a Conductivity detector.
Injection volume:	50 µL
Analytical column:	IonPac AS4A-SC
Eluent:	2.0 mL/min 1.5mM Borate buffer
Retention time:	2.83 min
Note:	Acetic acid (the acetate ion) and Propionic acid (the propionate ion) do not separate on this column.
Chromatogram:	See Figure A1.

A3 Sample preparation

A3.1 Samples were opened and each section placed into a separate, labeled, 20-mL scintillation vial.

A3.2 Each section was desorbed with 5 mL of 1.5mM Borate buffer. (The Borate buffer was prepared by placing 0.625 grams of $Na_2B_4O_7$•10 H_2O in 1 liter of deionized water.)

A3.3 The vials were capped, and placed in a bath of simmering water to desorb for 15 minutes. The samples were allowed to cool to room temperature.

A3.4 An aliquot was removed from the scintillation vial and placed into another, 0.5-mL vial, for analysis.

A4 Standard preparation

A4.1 Standards may be prepared in the Borate buffer using either Propionic acid or a soluble salt of Propionic acid. For this study, Propionic acid was used. A stock solution of 6 µL/25 mL Propionic acid in the Borate buffer corresponds to 238.4 µg/mL. When preparing standards, allow a few minutes for the disassociation of the Propionic acid into ions before analysis. A range of standards was prepared, from 1 to 238.4 µg/mL, to check the linearity of the analysis.

A4.2 When standards are prepared from sodium propionate, the amount of Propionic acid is calculated from the ratio of the molecular weights of sodium propionate and Propionic acid. A standard of 0.1297 g sodium propionate in 1.0-liter borate buffer corresponds to 100 µg/mL Propionic acid.

A5 Calculations

The ppm amount of Propionic acid found in the samples is calculated from the amount (µg/mL), of Propionic acid from the plot of the standards, and the air volume given, using the following formula:

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

Where:

µg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (74.08 g/mole)
DV = Desorption volume, 5 mL
L = Air volume, 18 L
DE = Desorption efficiency, 0.994 decimal

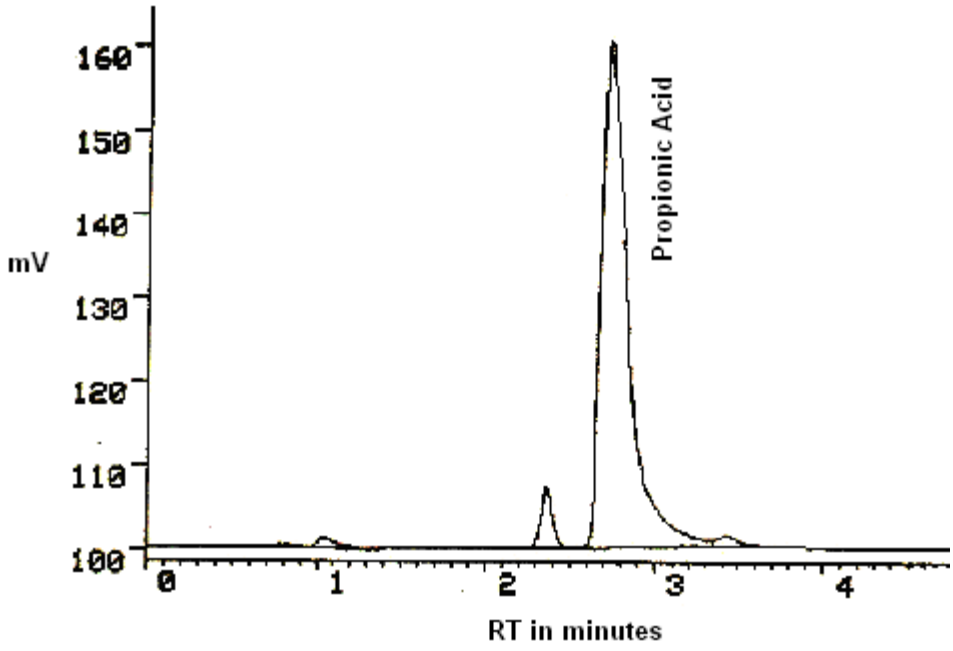


Figure A.I Chromatogram of the target concentration.