Method number:	PV2041
Target Concentration:	100-ppm (246 mg /m^3) OSHA permissible exposures limit (PEL).
Procedure:	Samples are collected by drawing known volumes of air through Anasorb 747 sampling tube (6-mm i.d. glass tube, the front section contains 400 mg and the back 200 mg of sorbent). Samples are desorbed with a 90:10 (v/v) methyl alcohol/dimethylformamide solution and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended air volume and sampling rate:	60 minutes at 0.05 L/min (3 L)
Detection limit of the overall procedure	1.16 ppm (2.84 mg/m^3) (based on the recommended air volume and the analytical detection limit)
Special requirements:	After sampling, ship the samples cold to the laboratory and analyzed immediately.
Status of method:	Partially evaluated method. This method has been partially evaluated and is presented for information and trial use only.

April 1992 (final)

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken to develop a sampling and analytical procedure for methyl formate at the OSHA PEL 100 ppm (Ref. 5.1).

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

Inhalation of vapor produces nasal and conjunctiva irritation, retching, narcosis, and death from pulmonary effects (Ref. 5.2, 5.3, and 5.4).

1.1.3 Potential workplace exposure

Methyl formate has been employed as a fumigant and larvacide, as well as a solvent for cellulose acetate and in organic synthesis. (Ref. 5.2, 5.3, and 5.4) No data is available on the extent of work place exposure.

1.1.4 Physical properties (Ref. 5.2, 5.3, and 5.4)

CAS number:	107-31-3
IMIS number:	1770
Molecular weight:	60.05
Molecular formula:	$C_2H_4O_2$
Density:	0.987 at 20 °C
Boiling point:	31.5 °C at 101.3 kPa (760 mmHg)
Solubility:	soluble in about 3.3 parts water, miscible with alcohol and ether
Chemical name:	methyl formate
Synonyms:	methyl methanoate; formic acid methyl ester
Appearance:	colorless liquid with an agreeable odor
Structure:	$HCOOCH_3$

1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 2.7:1 split ratio, is 3.16 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

2 Sampling Procedure

2.1 Apparatus

2.1.1 A sample is collected by using a personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line.

2.1.2 A sample is collected with 6-mm i.d. × 8-mm o.d. glass sampling tube packed with two sections of Anasorb 747 separated by a 2-mm portion of urethane foam. The sampling section contains 400 mg and the back section contains 200 mg of Anasorb 747. The sorbent is held in place with a glass wool plug at the front and a foam plug at the end of the sorbent bed. The sampling tubes are commercially available from SKC.

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

2.3.1 Immediately before sampling, break off the ends of the sampling tube. All tubes should be from the same lot.

2.3.2 Attach the sampling tube to the sampling pump with flexible tubing. Position the tube so that sampled air first passes through the 400-mg section.

2.3.3 Attach the tube vertically in the employee's breathing zone in such a manner that it does not impede work performance.

2.3.4 After sampling for the appropriate time, remove the sample tube and seal it with plastic caps.

2.3.5 Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.6 Record the air volume for each sample and list any possible interference.

2.3.7 Submit at least one blank for each set of samples. Handle the blank in the same manner as the samples, except no air is drawn through it.

2.3.8 Ship the samples cold after sampling to the laboratory and analyzed immediately.

2.3.9 Submit bulk samples for analysis in a separate container. Do not ship bulk samples with air samples.

2.4 Desorption efficiency

Twelve vials, each containing 400-mg portion of Anasorb 747, were divided into four groups of three vials each. Vials of the first and the second groups were liquid spiked with 1.2 and 3.8 µL of 10% methyl formate in methyl alcohol, respectively. Vials of the other two groups were liquid spiked with 1.6 and 3.2 µL of 50% methyl formate in methyl alcohol, respectively. These amounts represent 0.15×, 0.5×, 1.0×, and 2.0× the target concentration. The vials were stored overnight in a refrigerator (0 °C), desorbed with 3.0 mL of the desorbing solution, and analyzed as in Section 3. The average desorption efficiency was 95.7%. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

sample #	µg spiked	µg found	% recovered
1	115	115	100
2	115	112	97.4
3	115	115	100
average of 0.15x PEL = 99.1%			
4	366	343	93.7
5	366	343	93.7
6	366	347	94.8
average of 0.5x PEL = 94.0%			
7	770	717	93.1
8	770	729	94.7
9	770	742	96.4
average of 1.0x PEL = 94.7%			
10	1540	1327	92.7
11	1540	1474	95.7
12	1540	1494	97.0
13	blank	0	0
average of 2.0x PEL = 95.1%			

2.5 Retention efficiency

Four Anasorb 747 tubes were each liquid spiked with 1.6 µL (1× PEL) of 50% methyl formate in methyl alcohol. These were allowed to equilibrate for 2 hours and then 3 L of humid air (~80% relative humidity) were drawn through each tube at 0.05 L/min. The tubes were then desorbed with 3.0 mL of desorbing solution, and then analyzed as in Section 3. The results are listed in Table 2.5.

Table 2.5
Retention Efficiency

sample #	µg spiked	µg found	% recovered
1	770	711	92.3
2	770	724	94.0
3	770	770	100
4	770	748	97.1
average = 95.9%			

2.6 Sample storage

Nine Anasorb 747 tubes were each liquid spiked with 1.6 µL (1× PEL) of 50% methyl formate in methyl alcohol. These were allowed to equilibrate for 2 hours and then 3 L of humid air (~80% relative humidity) were drawn through each tube at 0.05 L/min. The nine tubes were divided into three groups of three tubes each. The first group was stored in a drawer at ambient temperature, the second group was stored in a refrigerator (0 °C) and the third group was stored in a freezer (-5 °C). After seven days, they were extracted and analyzed as in Section 3. No analytes were observed in backup section. The results are given in Tables 2.6.1, 2.6.2, and 2.6.3.

Table 2.6.1
Ambient Storage

days stored	µg spiked	µg found	% recovered
7	770	95	12.3
7	770	143	18.6
7	770	91	11.8

average = 14.2%

Table 2.6.2
Refrigerator Storage

days stored	µg spiked	µg found	% recovered
7	770	615	79.9
7	770	640	83.1
7	770	633	82.2

average = 81.7%

Table 2.6.3
Freezer Storage

days stored	µg spiked	µg found	% recovered
7	770	623	80.9
7	770	642	83.4
7	770	649	84.3

average = 82.9%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 3 L.

2.7.2 The recommended flow rate is 0.05 L/min.

2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of methyl formate. Any suspected interferences should be reported to the laboratory with submitted samples.

2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

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

3. Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with an 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 methyl formate from any interference. A 60-m × 0.32-mm i.d. (1.0 µm d_f STABILWAX) capillary column was used in this evaluation.

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

3.1.4 Volumetric flasks, pipettes, and syringes for preparing standards, making dilutions and performing injections.

3.1.5 Vials, 2-mL and 4-mL with PTFE-lined caps.

3.1.6 Mechanical shaker.

3.2 Reagents

3.2.1 Methyl formate. Methyl formate, 97.5+% purity, was obtained from Eastman Chemical Company.

3.2.2 Methyl alcohol. The methyl alcohol used in this evaluation was purchased from Fisher Scientific.

3.2.3 Dimethylformamide (DMF). The DMF was purchased from Burdick and Jackson.

3.2.4 Desorbing solution, 90/10 (v/v) methyl alcohol and DMF.

3.3 Standard preparation

Prepare standards at concentrations of 1 µL, 2 µL and 4 µL of methyl formate per milliliter of desorbing solution. Standards must be used the day they are prepared.

3.4 Sample preparation

3.4.1 Transfer the 400-mg section of the sampling tube to a 4-mL vial. Place the 200-mg backup section in a separate 4-mL vial.

3.4.2 Add 3.0 mL of desorbing solution to each vial and seal with a PTFE-lined cap.

3.4.3 Shake the vials on a mechanical shaker for an hour.

3.5 Analysis

3.5.1 Instrument conditions

Column:	60-m × 0.32-mm i.d., (1.0 µm d_f STABILWAX)
Temperature	**(ºC)**
Injector temperature:	150 °C
Detector temperature:	200 °C
Column temperature:	50 °C (initial temp)

Temperature program: hold initial temp. 5 min, increase temperature at 10 °C/min to 190 °C, hold final temperature 2 min

Gas flow rates:	**(mL/min)**
Column (hydrogen)	2.0
Septum purge (hydrogen)	7.5

Detector Gas	**(mL/min)**
FID (hydrogen)	32
FID (nitrogen)	34
FID (air)	400

Injection volume: 1 µL
Split ratio: 2.7:1
Retention times: 5.4 min (methyl formate)
8.7 min (methyl alcohol)
18.9 min (DMF)

3.5.2 Chromatogram (Figure 1.)

3.5.3 Measure detector response using a suitable method such as electronic integration.

3.6 Interferences (analytical)

3.6.1 Any collected compound which produces an FID response and has a similar retention time as methyl formate is a potential interference.

3.6.2 GC conditions may generally be varied to circumvent interferences.

3.6.3 Retention time on a single column is not proof of chemical identity. Analysis by an alternate GC column, high performance liquid chromatography (HPLC) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 An external standard (ESTD) calibration method is used. A calibration curve is constructed by plotting the standard concentration (µg/mL) of methyl formate vs detector response.

3.7.2 Bracket the samples with freshly prepared analytical standards over a range of concentrations.

3.7.3 Determine the µg/mL of methyl formate in both sections of each sample and blank from the calibration curve. If methyl formate is found on the backup section, it is added to the amount found on the front section. Blank corrections should be performed before adding the results together.

3.7.4 Determine the air concentration by using the following formula.

$$mg/m^3 = \frac{(\mu g/mL,\ blank\ corrected)(desorption\ volume,\ mL)}{(air\ volume,\ L)(desorption\ efficiency,\ decimal)}$$

$$ppm = \frac{(mg/m^3)(24.46)}{(60.05)}$$

Where:

24.46 = molar volume (liters/mole) at 25 °C and 101.3 kPa (760 mmHg)
60.05 = molecular weight (g/mole) methyl formate

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to methyl formate.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses in laboratory.

4 Recommendation for Further Study

This method should be fully validated. Another sampling media should be sought that would hold methyl formate during sample storage.

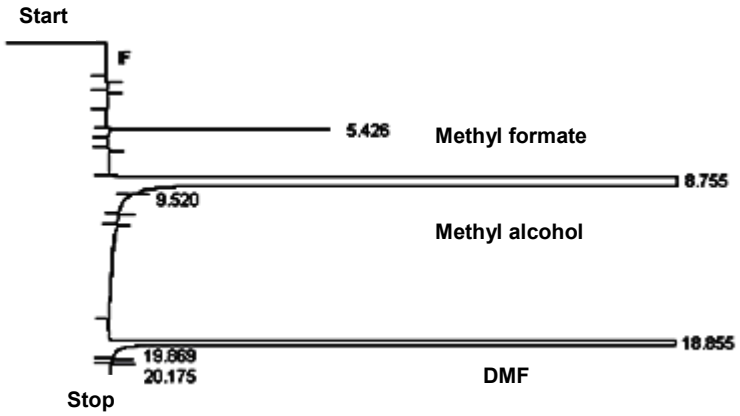

Figure 1. Chromatogram of methyl formate at 1.0× target level.

5 References

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

5.2 Documentation of the Threshold Limit Values and Biological Exposure Indices, American Conference of Governmental Industrial Hygienist INC., 5th ed., 1986; p 397.

5.3 Sitting, M., Handbook of Toxic and Hazardous Chemicals, Noyes Publications, Park Ridge, N.J., 1981; p 453.

5.4 Windholz, M., Budavari, S., Blumetti, RF., and Otterbein, E., The Merck Index, 10th ed., Merck & CO., Inc., Rahway, N.J., 1983; p 870.