Analyte:	Methyl Formate	Method No.:	S291
Matrix:	Air	Range:	108-542 mg/cu m
OSHA Standard:	100 ppm (250 mg/cu m)	Precision ($\overline{CV}_T$):	0.065
Procedure:	Adsorption on Carbosieve B, desorption with ethyl acetate, GC/FID	Validation Date:	2/17/78

1. Synopsis

A known volume of air is drawn through two glass tubes connected in series containing Carbosieve B to trap methyl formate vapors.

Methyl formate is desorbed from the Carbosieve B with ethyl acetate, and the sample is analyzed by gas chromatography using a flame ionization detector.

2. Working Range, Sensitivity, and Detection Limit

This method was validated over the range of 108-542 mg/cu m at an atmospheric temperature of 22°C and atmospheric pressure of 769 mm Hg, using a 3-liter sample. This maximum sample size is based on the capacity of the Carbosieve B to collect vapors of methyl formate in air at high relative humidity. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

The upper limit of the range of the method depends on the adsorptive capacity of the Carbosieve B. This capacity may vary with the concentrations of methyl formate and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of Carbosieve B) reaches 5% of the concentration in the test gas mixture. Breakthrough occurred after sampling for 115.5 minutes at an average sampling rate of 0.047 liter/minute and relative humidity of 85% and temperature of 22°C. The breakthrough test was conducted at a concentration of 530 mg/cu m.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Any compound that has the same retention time as methyl formate at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 108-542 mg/cu m was 0.065. This value corresponds to a 16 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations obtained at 0.5, 1, and 2 times the OSHA environmental limit were 6.3% higher than the dynamically generated test concentrations (n = 18). The desorption efficiency was determined to be 0.940 for a collector loading of 0.390 mg. In storage stability studies, the mean of samples analyzed after 7 days were within 5% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of methyl formate found on the backup Carbosieve B tube exceeds 25% of that found on the front tube, the probability of sample loss exists.

The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one set of tubes only.

6. Apparatus

Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate. Each personal sampling pump must be calibrated with a representative

front and backup Carbosieve B tube in the line to minimize errors associated with uncertainties in the volume sampled.

6.2 Carbosieve B Tubes. Glass tube with both ends unsealed, 7-cm long with a 6-mm O.D. and a 4-mm I.D., containing 80/100 mesh Carbosieve B*. The tube contains 100 mg of Carbosieve B. A plug of silylated glass wool is placed at the ends of the tube. Two tubes connected in series with a short piece of polyvinyl chloride tubing are used for sampling. The pressure drop across the tubes must be less than 1 inch of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the empty glass tubes should be rinsed with acetone and dried to eliminate the problem of Carbosieve B adhering to the walls of the glass tubes. The tubes are capped with plastic caps at each end.

6.3 Gas chromatograph equipped with a flame ionization detector and a temperature programmer.

Column (4-ft long x 1/8-in O.D. stainless steel) packed with 50/80 mesh Porapak Q.

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

Microliter Syringes: 10-microliter.

Pipets: 10-mL and other convenient sizes for preparing standards.

Volumetric Flasks: Convenient sizes for preparing standard solutions.

Serum Bottles: 5-mL glass bottles with 20-mm O.D. mouth.
Septa: 20-mm rubber septa with Teflon lining.
Aluminum tear-away seals to fit serum bottles.

6.10 Hand crimper for sealing septa to serum bottles.

6.11 Stopwatch.

6.12 Manometer.

7. Reagents

Whenever possible, all reagents used must be ACS reagent grade or better.

7.1 Acetone.

7.2 Methyl formate.

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* Carbosieve B is a high purity carbon manufactured by Supelco, Inc., and is used as a gas chromatographic column packing material.

Ethyl acetate.

Methyl formate stock standard solution. Prepare a stock standard solution containing 195 mg/mL methyl formate in ethyl acetate. To prepare the standard, add approximately 30 mL of ethyl acetate to a 50-mL flask. Deliver 10 mL of methyl formate under the surface of the solvent, then bring the volume to 50 mL. It is recommended that this standard be made to this total volume, because a smaller volume may lead to low and less accurate results because of the high volatility of methyl formate.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

Air, filtered, compressed.

8. Procedure

Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, remove the caps from the ends of the Carbosieve B tubes. All tubes must be packed with Carbosieve B from the same manufacturer's lot.

8.2.2 Two tubes connected in series are used for sample collection. The tubes are connected with a short piece of polyvinyl chloride tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The tube nearest the sampling pump is the backup tube.

8.2.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Carbosieve B.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the front Carbosieve B tube.

8.2.5 A sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter/minute. Do not sample at a flow rate less than 0.01 liter/minute. Record sampling time, flow rate, and type of sampling pump used.

8.2.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.2.7 The Carbosieve B tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of

tubes should be marked to identify the front Carbosieve B tube with the corresponding backup Carbosieve B tube.

8.2.8 With each batch or partial batch of ten samples, submit one set of tubes (two Carbosieve B tubes) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. Label these tubes as the blanks.

8.2.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Carbosieve B tubes. A minimum of 18 extra Carbosieve B tubes should be provided for desorption efficiency determinations.

8.3 Analysis of Samples

8.3.1 Desorption of Methyl Formate. Pipet 2.0 mL of ethyl acetate into a 5-mL serum bottle. Remove the plastic caps from both ends of the front Carbosieve B tube and transfer the entire contents of the tube to the serum bottle. This is accomplished by pushing the contents out of the tube with a clean glass rod. Firm tapping of the tube may be necessary to effect the complete transfer of the Carbosieve B. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. The backup Carbosieve B tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.

8.3.2 Shake the sample vigorously. Desorption is complete in 15 minutes. Analyses should be completed within one day after the methyl formate is desorbed.

8.3.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 mL/min (60 psig) nitrogen carrier gas flow
65 mL/min (24 psig) hydrogen gas flow to detector
500 mL/min (50 psig) air flow to detector
150°C injector manifold temperature
250°C detector manifold temperature
65°C column temperature

8.3.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and

plunger. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into considration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9-2.0 microliters in the barrel of the syringe. After injection, the column temperature is held at 65°C for 7 minutes to elute the methyl formate. The ethyl acetate solvent is then removed from the column by temperature programming to 200°C at a rate of 60°C/minute and holding for 5 minutes. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. It is not advisable to use an automatic sample injector because of possible plugging of the syringe needle with Carbosieve B.

A retention time of approximately 6 minutes is to be expected for methyl formate under the above conditions and using the column recommended in Section 6.4.

8.3.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.4 Determination of Desorption Efficiency

8.4.1 The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Carbosieve B to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Carbosieve B.

8.4.2 Carbosieve B sample tubes, prepared as described in Section 6.2, are used to determine desorption efficiency. The Carbosieve B must be from the same batch as that used in obtaining the samples. A known amount of an ethyl acetate solution of methyl formate containing 195 mg/mL (Section 7.4) is injected directly into the Carbosieve B with a microliter syringe, and the tube is capped with plastic caps. The amount injected is equivalent to that present in a 3-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the Carbosieve B, because the amounts to be added would be too small to measure accurately and evaporation losses could occur because of the high vapor pressure of methyl formate.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the methyl formate onto the Carbosieve B. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

8.4.3 To prepare standards at each level, add approximately 70 mL of ethyl acetate to each of three 100-mL volumetric flasks. Deliver 100, 200, and 400 microliters of the 195 micrograms/liter stock solution to each flask under the surface of the solvent, then bring the volume to 100-mL.

Note: Dilutions with large volumes are necessary to prepare standards accurately. Significant errors may be introduced in using small volumes because of the volatility of methyl formate.

8.4.4 The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)-Blank (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of methyl formate collected on the Carbosieve B. Plot the desorption efficiency versus weight of methyl formate found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/2.0 mL versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

From the stock standard solution of methyl formate in ethyl acetate (Section 7.4), appropriate aliquots are withdrawn and dilutions are made in ethyl acetate. Prepare at least 5 working standards to cover the range of 0.075-2.3 mg/2 mL. This range is based on a 3-liter sample.

Analyze the standards as described in Section 8.3.

Prepare a standard calibration curve by plotting concentration of methyl formate in mg/2 mL versus peak area.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/2.0 mL ethyl acetate and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front sample tube

mg blank = mg found in front blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.4.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of methyl formate in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liters/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of methyl formate
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11.2 Backup Data Report for Methyl Formate, prepared under NIOSH Contract No. 210-76-0123.