Analyte:	Methyl Acetylene	Method No.:	S84
Matrix:	Air	Range:	520-1880 ppm
OSHA Standard:	1000 ppm (1600 mg/cu m)	Precision ($\overline{CV}_T$):	0.049
Procedure:	Collection in gas sampling bag, GC with flame ionization detection	Validation Date:	1/20/78

1. Synopsis

1.1 An air sample is pumped into a gas sampling bag with a personal sampling pump.

The methyl acetylene content of the samples is determined by gas chromatography.

Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 520-1880 ppm at an atmospheric temperature of 21°C and atmospheric pressure of 763 mm Hg using a 3-liter sample volume.

The limit of detection is estimated at less than 10 ng methyl acetylene. Using a 2.0-mL gas sampling loop, this corresponds to a level of approximately 2.5 ppm.

3. Interferences

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

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as 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 520-1880 ppm was 0.049. This value corresponds to a standard deviation of 49 ppm at the OSHA standard

*Propyne

level. Statistical information can be found in Reference 11.1. Details of the test procedure can be found in Reference 11.2.

4.2 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 0.5X, 1X, and 2X the OSHA environmental limit averaged 8.3% lower than the dynamically generated test concentrations (n=18). This difference does not represent a bias in the method, but rather a random variation from the experimentally determined "true" concentration. The analytical method recovery was determined to be 0.977 for a collector loading of 500 ppm. In storage stability studies, the mean of samples analyzed after 7 days were within 8.2% 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

5.1 The sampling device is portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The samples in bags are analyzed by means of a quick instrumental method.

One disadvantage of the method is that the gas sampling bag is rather bulky and may be punctured during sampling and shipping.

5.3 It is difficult to ship the samples by air.

6. Apparatus

Personal Sampling Pump. A personal sampling pump capable of filling a gas sampling bag at approximately 0.05 liter/minute is required. Each personal pump should be calibrated to within ±5% to minimize errors associated with uncertainties in the sample volume collected. Although sample volume is not used to determine sample concentration, the pump should be calibrated to make certain that the collected sample represents a time-weighted average concentration and to avoid over filling of the bags; i.e., a maximum sampling time can be determined based on the flow rate and sample volume which is less than 80% of the volume of the bag.

The personal sampling pump must be equipped with an in/out valve. To ensure a leak-free apparatus, adjust the pump so that it delivers at the proper flow rate, and attach the pump outlet to a water manometer with a short piece of flexible tubing. Turn the pump on and observe the water level difference; it should push at least 30 cm of water. If it does not, the pump is incapable of filling the sampling bag and cannot be used.

6.2 Gas Sampling Bag. Five-liter capacity, five-layer sampling bags manufactured by Calibrated Instruments, Inc. (731 Saw Mill River Road, Ardsley, New York 10502) were found to be satisfactory for sample collection and storage for at least 7 days. The bag is fitted with a metal valve and hose bib. The valves used in validation studies

were found to leak when in the open position. It may be necessary to wrap the valve stem connection with Teflon tape to ensure a leak-free connection. For the preparation of calibration standards in the laboratory, Saran or Tedlar bags could be used.

Gas chromatograph, equipped with a flame ionization detector, 2-mL gas sampling loop, and a temperature programmer.

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

6.5 Area integrator. An electronic integrator or some other suitable method for measuring peak areas.

Gas-tight syringes. Convenient sizes for preparing standards.

6.7 Regulator for compressed air which is capable of metering gas at approximately 1 liter/minute. The regulator should be equipped with a septum-tee for standards preparation.

6.8 Water manometer.

Thermometer.

7. Reagents

reagents used must be ACS reagent grade or better.

7.1 Methyl acetylene.

7.2 Helium, purified.

Hydrogen, purified.

Air, filtered, compressed.

8. Procedure

Cleaning of Sampling Bags and Checking for Leaks. The bags are cleaned by opening the valve and bleeding out the air sample. The use of a vacuum pump is recommended although this procedure can be carried out by manually flattening the bags. The bags are then flushed with air and evacuated. This procedure is repeated at least twice.

Bags should be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Observe for any discernable leaks and any volume changes or slackening of the bag, especially along seams and in the valve stem, for at least a one-hour period.

Collection and Shipping of Samples

8.2.1 Immediately before sampling, attach a small piece of Teflon tubing to the hose bib of the five-layer gas sampling bag. Rubber tubing should not be used.

8.2.2 Unscrew the valve fitting and attach the tubing to the outlet of the sampling pump. Make sure that all connections are tight and leak-free. The bag valve must be fully opened during sampling.

8.2.3 Air being sampled will pass through the pump and tubing before entering the sampling bag, since a "push" type pump is required. No tubing is attached to the inlet of the pump.

8.2.4 A sample size of 3-4 liters is recommended. Sample at a flow rate of 0.05 liter/minute or less, but not less than 0.01 liter/minute. The flow rate should be known with an accuracy of at least ±5%.

8.2.5 Set the flow rate as accurately as possible using the manufacturer's directions. Although the volume of sample collected is not used in determining the concentration, it is necessary to keep the volume to 80% or less of the bag's capacity. Observe the bag frequently to ensure that it is filling properly.

8.2.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation. Also record sampling time, flow rate, and type of sampling pump used.

8.2.7 The gas sampling bag should be labeled appropriately and sealed tightly.

8.2.8 Gas sampling bags should be packed loosely and padded before they are shipped to minimize the danger of their being punctured during shipping. Do not ship the bags by air, unless they are stored in a pressurized cabin.

8.2.9 With each batch or partial batch of ten samples, submit one bag from the same lot of bags used for sample collection. This bag must be subjected to exactly the same handling as the samples except that no air is pumped into it. This bag should be labeled as the blank. Before analysis, 3-4 liters of air is metered into the bag using a calibrated source of air equipped with a septum-tee.

8.3 Analysis of Samples

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

30 mL/min (25 psig) helium carrier gas flow
ambient injector temperature
150°C detector temperature
column temperature, program from 50-150°C as described below.

8.3.2 GC Analysis. Attach the gas sampling bag to the sample loop of the gas chromatograph with a short piece of flexible tubing. Open the valve of the bag and fill the loop by using a vacuum pump or manually applying pressure to the sample bag. Allow the loop to attain atmospheric pressure, and inject the sample. Begin temperature programming after the methyl acetylene peak elutes. Temperature program at the maximum rate. The initial temperature should be 50°C and the final temperature should be 150°C. This is necessary to elute contaminants in the sample. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. A retention time of approximately 3 minutes is to be expected using the above conditions.

8.3.3 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and the results are read from a standard curve as discussed in Section 9.

9. Calibration and Standardization

A series of standards, varying in concentration over the range of 100-3000 ppm 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 ppm versus peak area.

Completely evacuate and flush several times with air a 5-liter gas sampling bag, preferably with the aid of a vacuum pump. Using a calibrated source of air equipped with a septum-tee, meter 3-4 liters of air into the bag. Inject appropriate aliquots of methyl acetylene via a gas tight syringe through the septum. Knead the bag to ensure adequate mixing. Prepare at least 5 working standards to cover the range of 100-3000 ppm.

The concentration of the bag in ppm equals the volume of methyl acetylene in mL divided by the amount of air in L.

$$\text{ppm} = \frac{\text{volume of methyl acetylene (mL)}}{\text{volume of air (L)}} \times 10^3$$

10. Calculations

10.1 Read the concentration in ppm, corresponding to each peak area from the standard curve.

10.2 A correction for the blank must be made for each sample.

ppm = ppm sample - ppm blank

where:

ppm sample = ppm found in sample bag

ppm blank = ppm found in blank bag

10.3 Another method of expressing concentration is mg/cu m.

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

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight, 40.06 g/mole
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 Acetylene, prepared under NIOSH Contract No. 210-76-0123.