Methyl Acetylene-Propadiene Mixture*

Analyte:	Methyl Acetylene-Propadiene Mixture	Method No.:	S85
Matrix:	Air	Range:	480-1990 ppm
OSHA Standard:	1000 ppm (1800 mg/cu m)	Precision ($\overline{CV}_T$):	0.048
Procedure:	Collection in gas sampling bag, flame ionization detection	Validation Date:	4/13/79

1. Synopsis

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

The MAPP content of the sample is determined as total hydrocarbon by flame ionization detection.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was validated over the range of 480-1990 ppm at an atmospheric temperature of 20°C and atmospheric pressure of 760 mm Hg using a 3-liter sample volume.

2.2 Under the instrumental conditions used in the validation study, a 0.5-mL injection of a 500 ppm MAPP standard resulted in a peak whose height was 70% of full scale on a 1-millivolt recorder. The amplifier of the gas chromatograph was set on range 10 and attenuation 4, and the recorder at attenuation 8.

2.3 The limit of detection is estimated at less than 10 ng MAPP. Using a 0.5-mL gas sampling loop, this corresponds to a level of approximately 11 ppm.

3. Interferences

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

* MAPP

The sample is analyzed for total hydrocarbon content, and any substance which produces a response using the flame ionization detector will be an interference.

4. Precision and Accuracy

The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 480-1990 ppm was 0.048. This value corresponds to a 48 ppm standard deviation at the OSHA standard. 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 averaged 8.2% lower than the dynamically generated test concentrations (n = 18). Storage stability studies on samples collected from a test atmosphere at a concentration of 998 ppm indicated that collected samples are stable for at least 7 days. The mean of samples analyzed after 7 days were within 3.3% 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 portable and involves no liquids. 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 or shipping. It is difficult to ship the samples by air.

The analytical method is specific only for total hydrocarbon content, and it is subject to interferences.

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%. 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 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 fitted with an outlet port so it is capable of filling a bag. 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 be capable of pumping against a pressure of at least 30 cm of water. If it does not, the pump is incapable of filling the sampling bag and cannot be used.

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. This 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 is necessary to wrap the valve stem connection with Teflon tape or Parafilm to ensure a leak-free connection. For the preparation of calibration standards in the laboratory, Saran or Tedlar bags could be used.

Before sampling each bag should be analyzed as a "blank" just prior to use to ensure that no contamination is present.

6.3 Gas chromatograph, equipped with a flame ionization detector and 0.5-mL gas sampling loop.

Tubing (20 ft long x 1/8-in I.D. stainless steel) equipped with proper column fittings. No column packing is used in the method.

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

Gas-tight Syringes. Convenient sizes for preparing standards.

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

Water Manometer.

Thermometer.

7. Reagents

7.1 MAPP, technical product.

Helium, purified.

Hydrogen, prepurified.

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. Prior to use, background hydrocarbon content should be determined by the analytical method. If it is unacceptably high, the bags should be flushed again.

Bags should be checked for leaks by filling the bag with air until taut, sealing and applying gentle pressure to the bag. Check 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 $\pm$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.

8.3 Analysis of Samples

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

25 mL/min hydrogen to detector
25 mL/min helium carrier gas flow
100 mL/min air to detector
125°C detector temperature
injector port and column at ambient conditions.

Note: The gas chromatograph is being used as a total hydrocarbon analyzer since the column is not packed.

8.3.2 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. One peak will elute in approximately one minute. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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. Peak heights may also be used for quantitation.

9 Calibration and Standardization

It is recommended that the MAPP used as a standard be taken from a cylinder that is no more than 50% depleted. This is to assure the relative composition of the components in the mixture, since studies (Reference 3) have shown that the fraction of less volatile components may be abnormally high when 80% or more of the cylinder is depleted.

A series of standards, varying in concentration over the range of 0-3000 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 a known

amount of air into the bag. Inject appropriate aliquots of MAPP 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 0-3000 ppm.

The concentration of the bag in ppm equals the volume of MAPP in milliliters divided by the amount of air in liters x 10^3

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

Prepare a standard curve by plotting concentration in ppm vs peak area, after correction for the blank.

10. Calculations

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

10.2 It is not recommended that the concentration of MAPP be expressed in mg/cu m, because MAPP is a mixture and has no specific molecular weight.

11. References

11.1 Documentation of the 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-Propadiene Mixture, prepared under NIOSH Contract No. 210-76-0123.

11.3 Huston, Robert F., Cyril A. Barrios, and Robert A. Holleman, "Weathering and Stability of Methyl Acetylene-Propadiene-Hydrocarbon Mixtures," Journal of Chemical and Engineering Data, 15(1), (1970), 168.