
Analyte:	Morpholine	Method No.:	S150
Matrix:	Air	Range:	28.5-108.4 mg/cu m
OSHA Standard:	20 ppm (70 mg/cu m) - skin	Precision (\overline{CV}_T):	0.057
Procedure:	Adsorption on silica gel, desorption with 0.05 M sulfuric acid, GC	Validation Date:	7/4/75

1. Principle of the Method (Reference 11.1)

- 1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.

The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 0.05 M sulfuric acid.

An aliquot of the desorbed sample is transferred to another small stoppered sample container and made alkaline with 1.2 M sodium hydroxide.

An aliquot of the alkaline solution is injected into a gas chromatograph.

- 1.5 The area of the resulting peak is determined and compared with areas obtained for standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 28.5-108.4 mg/cu m at an atmospheric temperature and pressure of 23°C and 763 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 7-210 mg/cu m. The method is capable of measuring much 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 is dependent on the adsorptive capacity of the silica gel tube. This capacity varies with the concentrations of the analyte and other substances in

the air. The first section of the silica gel tube was found to hold at least 6.0 mg of analyte when a test atmosphere containing 135 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. At that time the concentration of morpholine in the effluent was less than 5% of the influent. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

Silica gel has a high affinity for water, so organic vapors may not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.

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

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 proof of chemical identity.

If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (\overline{CV}_T) for the total analytical and sampling method in the range of 28.5-108.4 mg/cu m was 0.057. This value corresponds to a 4.0 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collection medium. Thus, no correction for collection efficiency was necessary, and it was assumed that no significant bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which a desorption efficiency correction was made. Thus \overline{CV}_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions.
- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

Furthermore, 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 tube only.

6. Apparatus

A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. Reference 11.4.

- 6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

Gas chromatograph equipped with a flame ionization detector.

Column (4-ft long by 1/4-in stainless steel) packed with 80/100 mesh Chromosorb 103. A 3-in Ascarite "precolumn" is inserted at the inlet end of the column and is separated from the Chromosorb 103 column packing by a plug of glass wool. The Ascarite "precolumn" should be checked periodically for salt buildup. The column should be baked out at 200°C at the end of each day, and the Ascarite "precolumn" should be changed at least once a month. (Reference 11.2)

The GC inlet should have a removable glass liner that can be cleaned.

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

Two-milliliter sample containers with glass stoppers or Teflon-lined caps.

Microliter syringes: 10-microliter, and other convenient sizes for making standards

Pipets: 1.0-ml delivery pipets.

6.10 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Sulfuric acid, 0.05 M.

Sodium Hydroxide, 1.2 M.

Morpholine, reagent grade

n-Hexane, reagent grade.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

Purified nitrogen.

pH paper - Hydrion.

8. Procedure

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

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

- 8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the silica gel tube.
- 8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least + 5%.
- 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.
- 8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 With each batch of ten samples, submit one tube from the same lot of tubes which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.
- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of 0.05 M sulfuric acid is pipetted into each sample container. The sample is desorbed for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. Transfer a 0.5-ml aliquot of the desorbed sample to a new vial, and add 50 microliters of 1.2 M sodium hydroxide to make the solution alkaline. Mix the solution well. The pH of the resulting solution should

be greater than 10 as indicated with pH paper. This solution should be analyzed immediately to avoid loss of the volatile analyte which is present as a free base.

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

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 250°C injector temperature
5. 280°C manifold temperature (detector)
6. 200°C column temperature

The glass inlet liner should be removed from the gas chromatograph and cleaned with water and acetone rinses at the end of each day. Reinsert the glass inlet into the injection port, and let it bake out overnight.

8.4.4 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 distillation 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. Three 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 5-microliter aliquot is withdrawn, taking into consideration 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 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of silica gel is used.
- 8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm. A known amount of hexane solution of morpholine containing 350 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X OSHA standard levels) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. 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 8.4.

Two or three standards are prepared by injecting the same volume of compound into a solution prepared from 1.0 ml of 0.05 M sulfuric acid and 100 microliters of 1.2 M sodium hydroxide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

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

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml 0.05 M sulfuric acid basified with 100 microliters of 1.2 M sodium hydroxide, because samples are desorbed in this amount of eluent. The density of the analyte is used to calculate mgs from microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, are 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/1.0 ml versus peak area. Note: Since no internal standard is used in the 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.

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/1.0 ml 0.05 M sulfuric acid basified with 100 microliters of 1.2 M sodium hydroxide 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:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front section. 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 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

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 (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 Evan E. Campbell, Gerry O. Wood, and Robert G. Anderson, "Development of Air Sampling Techniques, Los Alamos Scientific Laboratory Progress Reports LA-5634-PR (June 1974), LA-5973-PR (July 1975), LA-6057-PR (September 1975).
- 11.2 C. E. Andre and A. R. Mosier, "Precolumn Inlet System for the Gas Chromatographic Analysis of Trace Quantities of Short-Chain Aliphatic Amines," *Analytical Chemistry* 45, 1971 - 1973 (1973).
- 11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.
- 11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.