Analyte:	Ethylamine	Method No.:	S144
Matrix:	Air	Range:	7.41-31.8 mg/cu m
OSHA Standard:	10 ppm (18 mg/cu m)	Precision ($\overline{CV}_T$):	0.113
Procedure:	Adsorption on silica gel, desorption with aqueous sulfuric acid	Validation Date:	7/4/75

1. Principle of the Method (Reference 11.1)

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

1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 0.1 M sulfuric acid in an ultrasonic generator.

1.3 An aliquot of the desorbed sample is made alkaline with 0.25 M sodium hydroxide, and an aliquot of the alkaline solution is injected into a gas chromatograph.

The area of the resulting peak is determined and compared with areas obtained from standards.

2. Range and Sensitivity

This method was validated over the range of 7.41-31.8 mg/cu m at an atmospheric temperature and pressure of 25°C and 741 mm Hg, using a 30-liter sample. Under the conditions of sample size (30 liters) the probable range of this method is 1.8-54 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. 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 1.5 mg of the analyte when a test atmosphere of

31.8 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 240 minutes. Breakthrough did not occur at this time, i.e., no analyte was found in the backup section of the tube. (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

3.1 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.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study 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.

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

4. Precision and Accuracy

The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 7.41-31.8 mg/cu m was 0.113. This value corresponds to a standard deviation of 2.03 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result in Section 10.5.

5. Advantages and Disadvantages of the Method

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 compounds suspected to be present in the same sample by simply changing gas chromatographic conditions.

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.

5.3 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 accurately (±5%) at the recommended flow rate (Reference No. 11.3)

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and 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 150 mg of silica gel, the backup section 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 1 inch of mercury at a flow rate of 1 liter per minute.

Gas chromatograph equipped with a flame ionization detector

6.4 Column (6-ft x 1/4-in glass) packed with 4% Carbowax 20M, plus 0.8% KOH on Carbopack B.

The GC inlet should have a removable glass liner.

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

Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

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

Pipets: 0.5 and 1.0-ml delivery type.

6.10 Ultrasonic bath capable of continuous operation for at least 3 hours.

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

7. Reagents

Eluent: 0.1 M sulfuric acid.

Aqueous sodium hydroxide, 0.25 M.

Purified nitrogen.

Prepurified hydrogen

Filtered compressed air.

Hydrion pH paper.

Aqueous ethylamine (33% by wt.), Matheson, Coleman and Bell.

8. Procedure

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

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.

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 backup 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 maximum sample size of 30 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 $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

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 Blank. 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 for 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.

8.4 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 or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Pipette 1.0 ml of 0.1 M sulfuric acid into each sample container. Stopper it securely and place it in an ultrasonic bath for three hours. Let the silica gel settle and pipette 0.5 ml of the supernatant solution into a second 2-ml glass sample container. Add 0.5 ml of 0.25 M sodium hydroxide solution and mix the resulting solution thoroughly. The pH of the resulting solution should be greater than 11 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. 30 ml/min (80 psig) nitrogen carrier gas flow.

2. 30 ml/min (50 psig) hydrogen gas flow to detector.

3. 300 ml/min (50 psig) air flow to detector.

4. 170°C injector temperature

5. 210°C manifold temperature (detector).

6. 100°C column temperature.

The glass inlet liner should be removed from the GC 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. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case five-microliter injections are recommended.

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 Determination of Desorption Efficiency

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 that 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 (150 mg) is measured into a 2.0-ml sample container. 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. A known amount of an aqueous solution containing 135 mg/ml of ethylamine is injected directly into the silica gel with a 10-microliter syringe, and the container is capped. The amount injected is equivalent to that present in a 30-liter sample at the selected level.

At least six tubes at each of the three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the silica gel. These six 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 0.1 M sulfuric acid and 1.0 ml 0.25 M sodium hydroxide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

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

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

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus the 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 0.1 M sulfuric acid basified with 1 ml 0.25 M sodium hydroxide. A series of standards, varying in concentration over the range of interest, 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/ml versus peak area.

Note: Standard solutions should 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 weights, 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 0.1 M sulfuric acid basified with 1 ml 0.25 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.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte 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.

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

10.6 Another method of expressing concentration is ppm.

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

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 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.