Analyte:	Isopropylamine	Method No.: S147
Matrix:	Air	Range: 8.9-21.5 mg/cu m
OSHA Standard:	5 ppm (12 mg/cu m)	Precision ($\overline{CV}_T$): 0.067
Procedure:	Bubbler collection in dilute sulfuric acid, GC analysis of the collected samples after basification with sodium hydroxide	Validation Date: 7/4/75

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a midget bubbler containing 10 ml of 0.05 M sulfuric acid to trap the organic vapors present.

   1.2 The resulting solution is made alkaline with 4 M sodium hydroxide.

   1.3 An aliquot of sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with the areas for standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 8.9-21.5 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 1-35 mg/cu m.

3. Interferences

   3.1 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.

3.2 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 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 8.9-21.5 mg/cu m was 0.067. This value corresponds to a 0.8 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 11.2.

4.2 A collection efficiency of 1.00 was determined for the collection medium. Thus, no correction for collection efficiency is necessary, and it is assumed that no significant bias is introduced in the sample collection step. There is no apparent bias in the analytical method. 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 samples collected in bubblers are analyzed by means of a quick, instrumental method.

5.2 A major disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the adsorbing solution during sampling may occur which will result in loss of the sample.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:

6.1.1 A glass midget bubbler containing the collection medium (Section 7.2).

6.1.2 A pump suitable for sampling at least 1 liter per minute for 100 minutes. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Gas chromatograph equipped with a hydrogen flame ionization detector.

6.3 Column (6-ft long X 1/4-in O.D. glass) packed with 4% Carbowax 20 M and 0.8% KOH on Carbopak B. A 3-in Ascarite "precolumn" is inserted at the inlet end of the column and is separated from the column packing with 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 should be changed at least once a month. (Reference 11.1)

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

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

6.6 Microliter syringes: 10-microliter, and other convenient sizes for making standards and injecting samples into the GC.

6.7 Volumetric flasks: convenient sizes for making solutions.

6.8 Pipets: 10-ml or other convenient sizes.

7. Reagents

7.1 Isopropylamine, reagent grade.

7.2 Collection medium, 0.05 M sulfuric acid.

7.3 Sodium hydroxide, 4 M (160 g of sodium hydroxide in distilled water, diluted to a final volume of 1 liter).

7.4 Purified nitrogen.

7.5 Purified hydrogen.

7.6 Filtered compressed air.

7.7 Hydrion pH paper.

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 Sampling Pumps. Each pump should be calibrated by using an integrating volume meter (Section 6.1.3) or other means.

8.3 Collection and Shipping of Samples.

8.3.1 Pour 10 ml of the collection medium (Section 7.2) into each midget bubbler, and mark the liquid level.

8.3.2 Connect the midget bubbler with a 5-cm glass splashover tube (6-mm I.D. and 8-mm O.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

8.3.3 Turn the pump on to begin sample collection. Care should be taken to measure the flow rate, the time and/or the volume as accurately as possible. Record the atmospheric pressure and temperature. If the pressure reading is not available, record the elevation. The sample should be taken at a flow rate of 1 liter per minute or less. A sample size of 100 liters is recommended.

8.3.4 After sampling, the bubbler stem may be removed and cleaned. If necessary, bring the volume of each sample to the 10-ml mark with 0.05 M sulfuric acid. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1 ml of 0.05 M sulfuric acid, adding the wash to the bubbler. The bubblers are sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the bubblers should be tightly sealed to prevent leakage during shipping.

8.3.5 Care should be taken to minimize spillage or loss by evaporation.

8.3.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special bubbler shipping cases designed by NIOSH should be used to ship the samples.

8.3.7 With each batch of ten samples, submit one bubbler from the same lot of bubblers 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.

8.4 Analysis of Samples

8.4.1 The sample in each bubbler is analyzed separately.

8.4.2 Add 1 ml of 4 M sodium hydroxide to the sample and mix the solution thoroughly. The pH of the resulting solution should be greater than 10 as indicated with pH paper. The total volume of the solution should be 12 ml and 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. 205°C injector temperature
5. 270°C manifold temperature (detector)
6. 110°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.

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

8.5 Standard Solutions

8.5.1 Procedure for preparing standard solutions. Standards at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are prepared by introducing a known amount of isopropylamine in water (300 mg/ml) into 11 ml of 0.05 M sulfuric acid in a bubbler. The amount introduced is equivalent to that present in a 100-liter air sample. The standards are made alkaline with 1.0 ml of 4 M sodium hydroxide. The solution should be checked with pH paper to make sure that its pH is greater than 10. A parallel blank is prepared in the same manner, except that no analyte is added. The standards and blank are analyzed in exactly the same manner as the samples in Section 8.4.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/sample. 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 mg/sample 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/sample 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 sample bubbler

mg blank = mg found in blank bubbler

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.4 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 Di Corcia, Antonio and Roberto Samperi, "Gas Chromatographic Determination at the Parts-per-Million Level of Aliphatic Amines in Aqueous Solution," Anal. Chem., 46, No. 8, July 1974, 977-981.

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.