DIETHYLCARBAMOYL CHLORIDE

Measurements Research Branch

Analytical Method

Analyte:	Diethylcarbamoyl chloride	Method No.:	P&CAM 317
Matrix:	Air	Range:	8-240 mg/m^3 for a 5-L sample
Procedure:	Adsorption on Porapak P, desorption with ethyl acetate, GC analysis via FID	Precision:	0.077
Date Issued:	1/6/80		
Date Revised:		Classification:	E (Proposed)

1. Synopsis

A known amount of air is drawn through a sorbent tube containing Porapak P to trap the analyte present. The Porapak P is transferred to a small stoppered sample container and the analyte is desorbed with ethyl acetate. An aliquot of the resulting solution is injected into a gas chromatograph equipped with a flame ionization detector. The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

The method was evaluated over the range 8-240 mg/m^3 at a temperature and pressure of 20°C and 756 torr using 5-L samples. This corresponds to the collection of 40-1250 µg of analyte.

The upper limit of the method is dependent upon the capacity of the Porapak P to retain the analyte. No breakthrough was observed when 2.5 mg of the analyte in humid air was evaporated from a U-tube onto a 100 mg bed of the sorbent. In this experiment, 12 L of air were pulled through the sorbent bed at 0.2 L/min.

3. Interferences

3.1 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.

3.2 The analyte reacts readily with amines and alcohols. In experiments in which the analyte was trapped with an amine co-contaminant, diethylamine and aniline proved to have no effect on sample stability, while benzylamine appeared to cause a decrease in the recovery which was significantly dependent on temperature and quantity of amine. In addition, the sampling medium has a negligible capacity for diethylamine, a potential co-contaminant. Since the reactive nature and concentration of co-contaminants may be unknown, it is advisable to refrigerate the samples immediately after collection. Analysis should be completed as soon as possible after collection.

4. Precision and Accuracy

4.1 The relative standard deviation for the total sampling and analytical method in the range 8-240 mg/m^3 was 7.7%. At the lower end of the analytical range, this corresponds to 0.62 mg/m^3.

4.2 Five-liter samples from bag standards containing 8 mg/m^3 diethylcarbamoyl chloride in dry air were collected on Porapak P and exposed to humid air (relative humidity > 70%) for one hour. The analyte was quantitatively recovered from these samples after storage for 28 days.

5. Advantages and Disadvantages

5.1 This method was developed for monitoring personal exposures. However, it has not been field tested.

5.2 Due to the hydrophobic nature of the Porapak P, water vapor is not efficiently trapped on the sorbent. Therefore, the capacity of the sampling tube should be unaffected by high relative humidity. The volume of air that can be sampled by the Porapak P is, therefore, high (at least 12 L). However, when the amount of DECC found on the backup section of the sampling tube exceeds 10% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the sampling train. This variation will affect the flow and cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of sampling at 0.2 L/min. The pump should be calibrated with a representative Porapak P tube in line.

6.2 Porapak P* tube. Glass tube, 7.0-cm long, 6-mm outside diameter, and 4-mm inside diameter containing 100-mg front and 50-mg backup sections of 50/80 mesh pre-extracted Porapak P. The sorbent beds are separated by a 2-mm portion of urethane foam and contained at the ends by silanized glass wool plugs. Prior to use, the sorbent is extracted with acetone in a Sohxlet apparatus for two hours, allowed to air-dry, and then placed in the drying tube of the apparatus shown in Figure 1. This apparatus is connected to the carrier gas inlet port of a GC oven and exhausted into the detector. Several grams of the sorbent are dried at 120 °C under helium flowing at 20 mL/min for several hours. The sorbent is allowed to cool in a clean dessiccator. Care should be taken to avoid excessive agitation of the Porapak P during handling. A static charge can be induced in the material and is not readily dissipated. This will cause the individual particles to agglomerate, making the material difficult to handle while packing the collection tubes. The tubes should be washed with acetone and thoroughly dried prior to packing with Porapak P. This prevents the sorbent from adhering to the tube walls. Cap the sorbent tubes with plastic caps prior to use.

6.3 Gas chromatograph equipped with a flame ionization detector. This must be an instrument with a 10-cm or shorter glass or glass-lined transfer line from the column to the detector. Silanize the transfer line prior to use.

6.4 GC column, 2-m long x 4-mm inside diameter silanized glass, packed with 3% Dexsil-300 on 80/100 Supelcoport.

6.5 Electronic integrator or some other suitable method of determining peak areas.

6.6 Vials, 2-mL, with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes, 10-µL and other convenient sizes, for preparing standards.

6.8 Pipets, delivery type, 10-mL and other convenient sizes.

*Porapak P is a styrene-divinylbenzene porous polymer manufactured by Waters Associates.

6.9 Volumetric flasks, 10-mL and other convenient sizes, for preparing standard solutions.

6.10 Stopwatch.

6.11 Manometer.

6.12 Sohlet extractor.

6.13 Parafilm.

6.14 Glass tubes, 7-cm x 4-mm i.d., flame sealed at one end, used for desorption experiments.

6.15 Distillation apparatus.

7. Reagents

7.1 Acetone, chromatoquality.

7.2 Diethylcarbamoyl chloride. The technical grade material must be purified by distillation at 182 °C prior to use. It is stored over 10A molecular sieves and should be protected from light and heat.

7.3 Ethyl acetate, distilled in glass.

7.4 Helium, purified.

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

8. Procedure

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

8.2 Collection and Shipping of Samples.

8.2.1 Immediately before sampling, remove the caps from the ends of the tube. All tubes must be packed with Porapak P from the same manufacturer's lot.

8.2.2 Connect the Porapak P tube to the sampling pump with a piece of flexible plastic tubing. The samller section of the Porapak P tube is used as a backup and should be positioned nearer the sampling pump.

8.2.3 The tube should be placed in a vertical position during sampling to minimize channeling through the Porapak P.

8.2.4 Air being sampled should not pass through any hose or tubing before entering the Porapak P tube.

8.2.5 The sampling volume will depend upon the concentration of the analyte in air. At least 12 L of air can be sampled. Record the collection time and the flow.

8.2.6 Record the temperature, pressure and relative humidity of the atmosphere being sampled. If the pressure reading is not available, record the elevation.

8.2.7 Seal the Porapak P tube with plastic caps immediately after sampling. Rubber caps should not be used.

8.2.8 With each batch of ten samples, submit at least one blank tube made from the same lot of Porapak P as used for sample collection. This tube should be subjected to exactly the same handling as the samples (break, seal, transport) except that no air is drawn through it.

8.2.9 Capped tubes must be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.2.10 Any samples of bulk material should be submitted to the laboratory in glass containers with a Teflon lined cap. These samples should not be transported in the same container as the Porapak P tubes.

8.2.11 Refrigerate the Porapak P tubes as soon after sampling as possible.

8.3 Analysis of Samples.

8.3.1 Preparation of Samples. Remove the plastic cap from the inlet end of the Porapak P tube. Remove the glass wool plug and transfer the first (longer) section of sorbent to a 2-mL stoppered vial. Remove the separating section of urethane foam and transfer the backup section of Porapak P to another stoppered vial. It may be necessary to tap the tube sharply to affect complete transfer of the Porapak P. Analyze the two sections separately.

8.3.2 Desorption of Samples. Pipette 1.0 mL of ethyl acetate into each sample container. Shake the sample a few times during the desorption period. Allow the samples to desorb for at least one hour. If preliminary analysis

indicates that 10 μg or less of the analyte has been collected on the tube(s), the samples should be desorbed in a sonic bath for an additional hour. Analyses should be completed the same day that the samples are desorbed.

8.3.3 GC Conditions.

	Flow Rates (mL/min)		Temperatures (°C)
Helium	20	Injector	150
Hydrogen	40	Detector	150
Air	400	Column	60

The analyte has a retention time of approximately 9 minutes under these conditions using the column recommended in Section 6.4. The ethyl acetate will elute from the column before the analyte.

8.3.4 Injection. Inject a 5-μL aliquot into the gas chromatograph using the solvent-flush technique. It may not be advisable to use an automatic sample injector because of possible plugging of the syringe needle with Porapak P particles.

8.3.5 Measure the area of the sample peak by an electronic integrator or some other suitable form of area measurement.

8.4 Determination of Desorption Efficiency.

8.4.1 The desorption efficiency of diethylcarbamoyl chloride may vary from one laboratory to another and, also, from one batch of Porapak P to another. Thus, it is necessary to determine the desorption efficiency for each batch of Porapak P used.

8.4.2 One hundred milligrams of Porapak P is measured into a 7-cm x 4-mm i.d. glass tube, flame sealed at one end. This Porapak P must be from the same batch as that used in obtaining the samples. The open end is capped with parafilm. A known amount of an ethyl acetate solution containing 1-10 μg/μL of DECC is injected directly into the Porapak P bed with a microliter syringe and the tube is capped with more parafilm. The amount injected is equivalent to that present in an air sample at a selected level.

Six tubes at each of three levels covering the range of interest are prepared in this manner and allowed to stand

overnight to assure complete adsorption of the DECC onto the Porapak P. 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 as described in Section 8.4.

Standards are prepared by injecting the same volume of DECC solutions into a 1.0-mL of ethyl acetate with the same syringe as used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D) equals the average weight of DECC in µg recovered from the tube (Q_r) divided by the weight in µg added to the tube (Q_a).

$$D = \frac{Q_r}{Q_a}$$

If D varies significantly with sample weight, plot D vs. Q_r and use the curve to correct for adsorption losses in Section 10.4.

9. Calibration and Standardization

9.1 Prepare a stock standard solution containing 10 µg/µL of DECC in ethyl acetate.

9.2 From the stock solution, prepare at least five standards to cover the range 10-100 µg in 1.0-mL of ethyl acetate.

9.3 Analyze the standards with the samples.

9.4 Prepare a calibration curve by plotting concentration of DECC in µg/1.0 mL versus peak area.

10. Calculations

10.1 Read the weight in µg corresponding to each peak area from the standard curve.

10.2 No blank is expected. If the blank is significant, determine its source and eliminate or correct for it.

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

10.4 If the desorption efficiency (D) is significantly different from 1.0 (Section 8.4.2), divide the total weight (W) by the desorption efficiency to obtain the corrected weight in µg (Wc).

$$W_c = \frac{W}{D}$$

10.5 The concentration (C) of DECC in the air sampled can be expressed in μg/L.

$$C = \frac{W_c}{V}$$

where V is the volume of air sampled in liters. This number is numerically equal to the concentration of DECC in mg/m^3.

10.6 C may be converted to the concentration in ppm (C') by use of the following formula:

$$C' = C \times \frac{24.45}{M} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:
- P = the pressure of air sampled in torr
- T = the temperature of air sampled in °C
- 24.45 = the molar volume of an ideal gas in liters
- M = molecular weight (g/mole) of diethylcarbamoyl chloride (135 g/mole)
- 760 = standard pressure in torr
- 298 = standard temperature in °K

11. References

11.1 R. A. Glaser. Unpublished report. Development of a Quantitative Sampling and Analytical Method for Diethylcarbamoyl Chloride. Report of Research performed during Fiscal Years 1978 and 1979.

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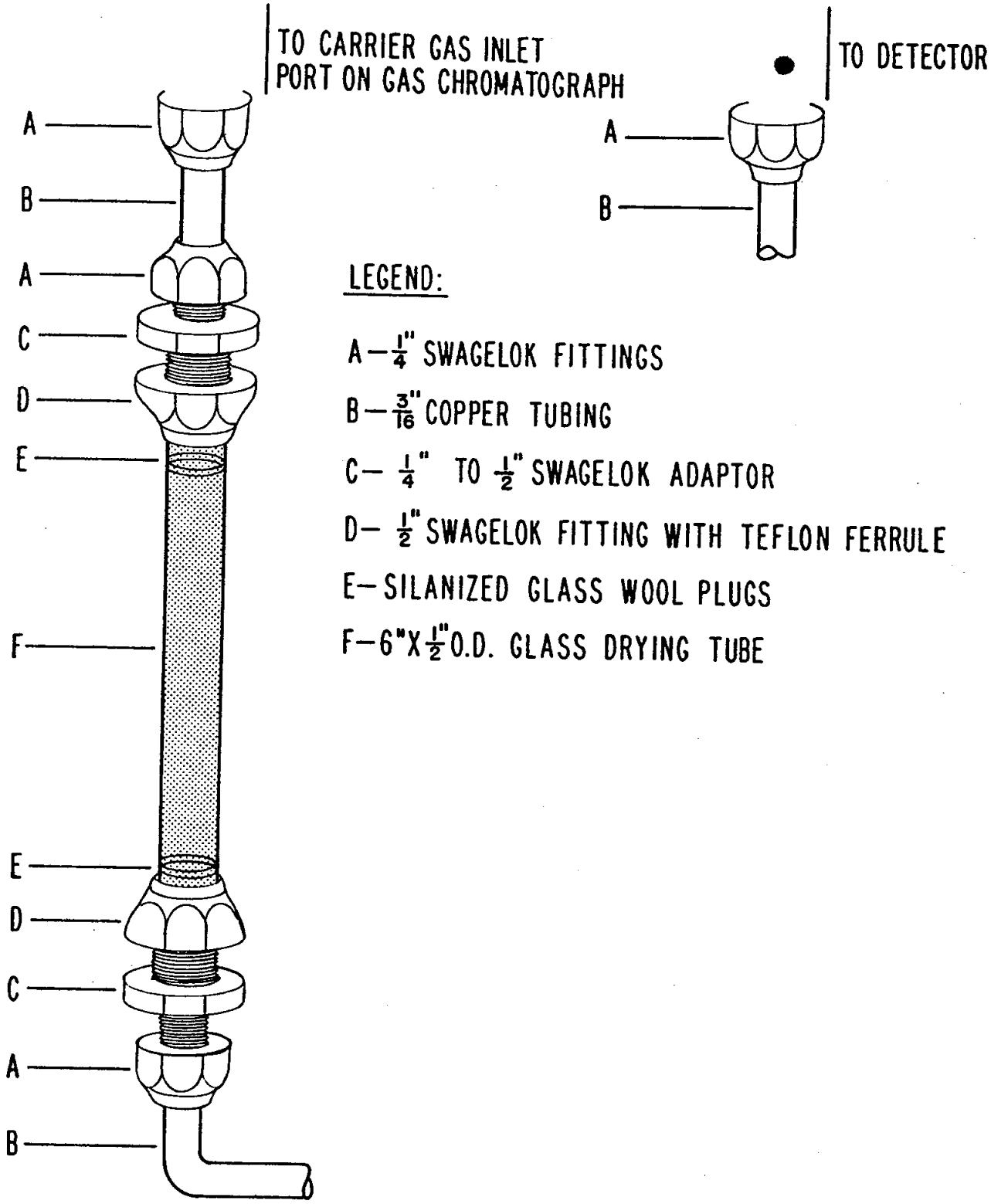
TO CARRIER GAS INLET
PORT ON GAS CHROMATOGRAPH
TO DETECTOR
A
B
A
C
D
E
F
E
D
C
A
B
A
B
LEGEND:
A—1/4" SWAGELOK FITTINGS
B—3/16" COPPER TUBING
C— 1/4" TO 1/2" SWAGELOK ADAPTOR
D— 1/2" SWAGELOK FITTING WITH TEFLON FERRULE
E—SILANIZED GLASS WOOL PLUGS
F—6"X1/2"O.D. GLASS DRYING TUBE

Figure 1.