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## CHROMOSORB 103 AS AN ADSORBENT FOR SAMPLING OF AMINES IN AIR

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### SUMMARY

Chromosorb 103 was investigated as an adsorbent for the sampling of amines in air. A model system was used in which N-methylmorpholine was sampled from a test atmosphere (concentration 0.25–7 mg/m<sup>3</sup>). The amine was thermally desorbed and analysed by gas chromatography. This method was compared with sampling by absorption in 0.05 M sulphuric acid. No significant difference was obtained between the two methods, indicating a 100% recovery. Amine concentrations in air could be determined with a relative standard deviation of less than 3%. The presence of moisture in the air was shown to have no influence on the recovery or reproducibility. The breakthrough volume (for a concentration of 0.65 mg/m<sup>3</sup> in air with 70% humidity) is approximately 100 l per gram of adsorbent. Adsorption tubes could be stored for at least 16 days before analysis without significant losses. A practical test demonstrated the applicability of the method.

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### INTRODUCTION

Volatile amines occur frequently in the industrial environment. An important example is the polyurethane industry, where isocyanates are also used, which have been regarded as being responsible for the occurrence of asthma and other respiratory problems. It has recently been proposed that amines, often occurring in much higher concentrations than isocyanates, also cause these ailments<sup>1</sup>. In the study cited, the predominant amine was N-methylmorpholine, which is used as a catalyst in the polymerization process.

Sampling of amines in air is routinely performed by means of absorption in an acidic solution for subsequent gas chromatographic (GC) analysis<sup>2,3</sup>. Another method is adsorption on silica followed by liquid extraction<sup>4</sup>, as recommended by NIOSH.

These sampling methods produce a solution, a relatively small aliquot of which is analysed. On the other hand, when using adsorption on a porous polymer followed by thermal desorption directly into a gas chromatograph, all of the collected air sample is used for one analysis. This may be regarded as a disadvantage, as it excludes the possibility of multiple analyses. However, this method inherently offers much higher sensitivity, making it possible either to reach a lower detection limit or to

reduce the sampling time. This permits the monitoring of rapid variations in concentration. Thermal desorption has not been widely used for amines, although some studies have been published<sup>5-7</sup>.

In principle, the adsorbent should be chosen so that the adsorption process is reversible. If thermal desorption is to be used, it is disadvantageous to rely on specific forces for the adsorption such as acid-base interactions. Rather, weak non-specific adsorption and a high surface area of the adsorbent are to be preferred. These criteria are the same as those imposed on a GC packing.

A porous polymer especially intended for analysis of amines by gas chromatography is Chromosorb 103<sup>8</sup>. The retention volumes obtained when using this material are relatively large<sup>9</sup>, so it is a logical choice as an air sampling adsorbent. Some data on breakthrough volumes for the most volatile amines can be found in the literature<sup>10</sup>.

In this paper we report an evaluation of the properties of Chromosorb 103 as an adsorbent for sampling N-methylmorpholine in ambient air. We have chosen this system as a model for the industrial environmental sampling of amines.

## EXPERIMENTAL

Adsorption tubes were made from glass tubing, 10 cm × 6 mm O.D. × 4 mm I.D. They were provided with restriction joints to facilitate the connection and disconnection to 3 mm PTFE tubing (Fig. 1). The tubes were packed with approximately 0.2 g of Chromosorb 103 (60-80 mesh) (Johns-Manville, New York, NY, U.S.A.), placed near one end of the tube. The tubes were conditioned for about 1 h with a flow of nitrogen (30-60 ml/min) at 200°C.

Gas mixtures were prepared according to the method of Vejrosta and Novák<sup>11</sup>, in which a gas stream is directed through a saturator containing the compound of interest coated on a GC support. This produces a saturated gas mixture, which is diluted in two steps to the desired concentration. A separate gas stream saturated with water can be introduced to adjust the humidity to a desired value.

Environmental sampling was simulated by taking samples from the outflow of the gas mixer. We used a constant-flow air sampling pump (Model P 4000, DuPont, Wilmington, DE, U.S.A.), which was operated at a flow-rate of 80-90 ml/min.

The desorption apparatus is shown in Fig. 2. By means of a valve the carrier gas can be directed in two ways. In the open (desorption) position, carrier gas from A (30 ml/min) flows through the adsorption tube. To avoid losses and unswept volumes at the ordinary carrier gas inlet, a small stream, B (10 ml/min), is connected. In the closed position both A and B enter the column at the ordinary inlet. In this

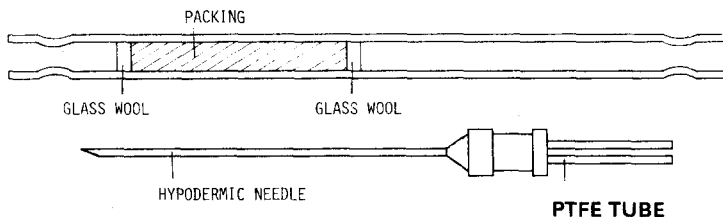


Fig. 1. Adsorption tube and injection needle.

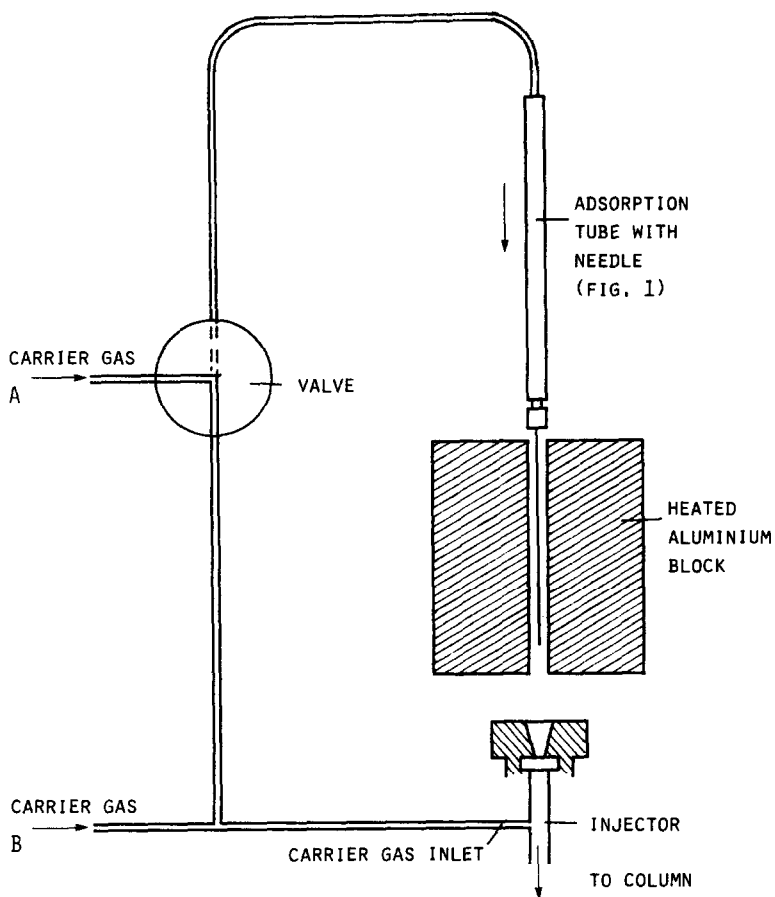


Fig. 2. Apparatus for thermal desorption.

position the equipment functions as an ordinary gas chromatograph and calibration solutions can be injected through the septum in the usual manner.

The adsorption tube is fitted with a hypodermic needle (Record type) (Fig. 1) prior to the desorption procedure, connected to the carrier gas and inserted through a thermostated aluminium block ( $200^{\circ}\text{C}$ ). The valve is then turned and the sample is desorbed and swept on to the column. After a chromatogram has been obtained, the tube can be removed and re-used without reconditioning.

Independent control measurements of the gas concentration of the amine were obtained by sampling the gas stream by absorption in  $0.05\text{ M}$  sulphuric acid using a glass impinger and the pump mentioned above. Sample solutions obtained in this way and calibration solutions, also in  $0.05\text{ M}$  sulphuric acid, were adjusted to  $\text{pH} \approx 12$  with saturated sodium hydroxide. The injector was impregnated with sodium hydroxide<sup>3</sup>.

### Chromatography

The chromatography system consisted of a Varian 3700 gas chromatograph

(Varian, Palo Alto, CA, U.S.A.) equipped with a thermionic specific detector, a Model 3390A integrator (Hewlett-Packard, Avondale, PA, U.S.A.) and a glass column (1 m × 3 mm I.D.) packed with 10% Pennwalt 223 + 4% potassium hydroxide on Gas-Chrom R (80–100 mesh) (Alltech, Arlington Heights, IL, U.S.A.). This type of column has been shown to be satisfactory for amine analysis<sup>2,9</sup>.

### Chemicals

N-Methylmorpholine (99% purity) was obtained from Fluka (Buchs, Switzerland). Calibration solutions for the thermal desorption were prepared in analytical-reagent grade *n*-hexane (Merck, Darmstadt, F.R.G.).

## RESULTS AND DISCUSSION

### Recovery and reproducibility

Various concentrations of N-methylmorpholine in nitrogen, dry air and moist air (50% relative humidity) were analysed (typically five times), using the thermal desorption method, and compared with analyses by absorption in solution. The results are shown in Table I, together with standard deviations, *s*. The variation in the analyses of the standard solutions is included in the calculation of *s*.

No significant difference was obtained between the two methods, which indicates that the collection efficiency and the recovery are near 100%, independent of the type of gas.

The reproducibility of the thermal desorption method was slightly better than that of the reference method. This is due to the fact that analysis of an alkaline salt solution is more difficult to perform than that of an organic solution.

### Desorption times and peak shapes

Sample introduction by thermal desorption results in a different chromatogram than normal injection by syringe (see Fig. 3). Our observations can be summarized as follows:

(1) Retention times differ substantially, typically by 60 sec. This is the time needed to heat the glass tube and the adsorbent to the temperature where the de-

TABLE I  
COMPARISON OF TWO SAMPLING METHODS FOR N-METHYLMORPHOLINE IN AIR  
Values in parentheses are relative standard deviations (%).

Concentration in air (mg/m <sup>3</sup> )		Ratio	Notes
Thermal desorption	Liquid absorption		
3.83 (2.2)	3.45 (2.4)	1.11 (3.3)	Nitrogen
4.64 (1.7)	4.59 (4.6)	1.01 (4.9)	Dry air
0.250 (1.6)	0.230 (5.8)	1.09 (6.0)	Dry air
2.58 (2.1)	2.70 (2.9)	0.96 (3.6)	Moist air (50%)

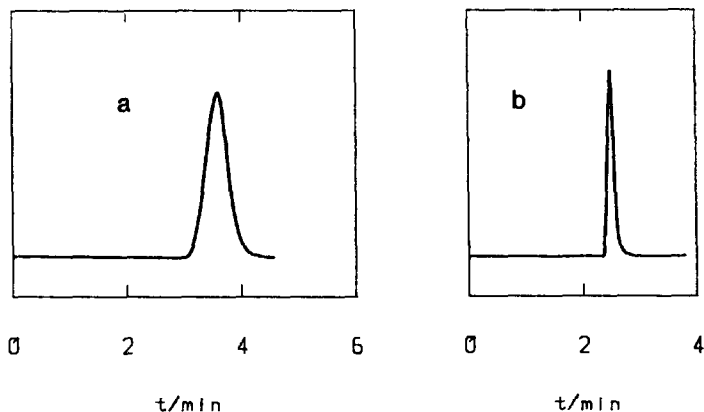


Fig. 3. Chromatograms of N-methylmorpholine. Column temperature, 80°C. (a) Thermal desorption (3.1  $\mu\text{g}$ ), attenuation 16 $\times$ ; (b) syringe injection of calibration solution (4.6  $\mu\text{g}$  in 2  $\mu\text{l}$  of *n*-hexane), attenuation 64 $\times$ .

sorption rate becomes significant. Similar observations have been made by other workers<sup>12</sup>.

(2) The peak is wider after thermal desorption. The increase in peak width can be calculated as follows: the variance resulting from the chromatographic process alone is obtained from normal injections. This can be subtracted from the variance obtained using thermal desorption, giving the variance increase due to the desorption. Expressed as standard deviation, we find a value of approximately 10 sec. This peak broadening reflects the fact that an instantaneous desorption is impossible owing to the slow heating discussed above.

#### Breakthrough volumes

Breakthrough volumes were determined by sampling a gas mixture of constant concentration for different lengths of time (*i.e.*, different volumes). The results from the desorption were plotted against the sampling volume. Breakthrough occurs when this plot deviates from linearity.

Fig. 4 shows such a plot for a relatively low concentration in moist air. The curve indicates a breakthrough volume of approximately 20 l, corresponding to a specific breakthrough volume of 100 l/g.

Fig. 5 shows the plot from a similar experiment made with a relatively high concentration sampled from dry air. In this instance the deviation arises from the limited linear range of the detector. The breakthrough volume is, however, at least 5 l, and probably larger.

In both instances the capacity is large enough for practical sampling. Moisture in the air does not seem to have an adverse effect on the capacity.

#### Storage stability

N-Methylmorpholine (0.3 mg/m<sup>3</sup>) was sampled from moist air and stored for different lengths of time before analysis. After 16 days no significant decrease in the amount desorbed could be detected.

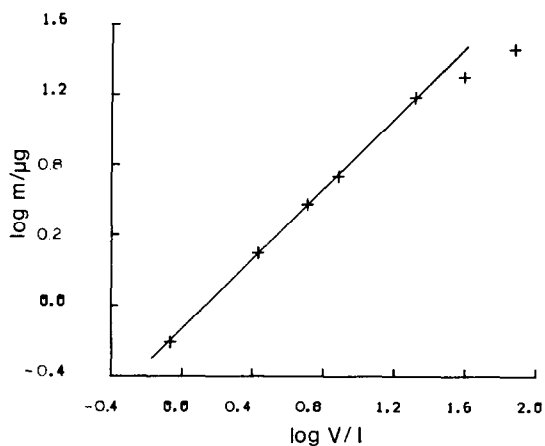


Fig. 4. Amount desorbed,  $m$ , as a function of sample volume,  $V$ . Gas concentration,  $0.65 \text{ mg/m}^3$  in moist air (70% humidity).

#### Practical test

A small amount ( $100 \mu\text{l}$ ) of N-methylmorpholine was released in a small room (*ca.*  $25 \text{ m}^3$ ), simulating an industrial situation where spillage has occurred. To follow the course of the change in concentration, 13 samples of air were taken with adsorption tubes, each tube representing a 3-min interval. A reference sample was taken in parallel by adsorption in acid for 40 min, which should give the concentration average over the total time period.

Fig. 6 shows the concentration changes thus recorded. The concentration rapidly reaches a maximum and then decreases slowly as the amine is removed from the room by ventilation. The mean value of all 13 measurements agrees reasonably well with the single reference measurement.

The chromatographic advantages of the adsorption tube method were obvious in this experiment. The peaks are larger because the entire sample from 3-min sam-

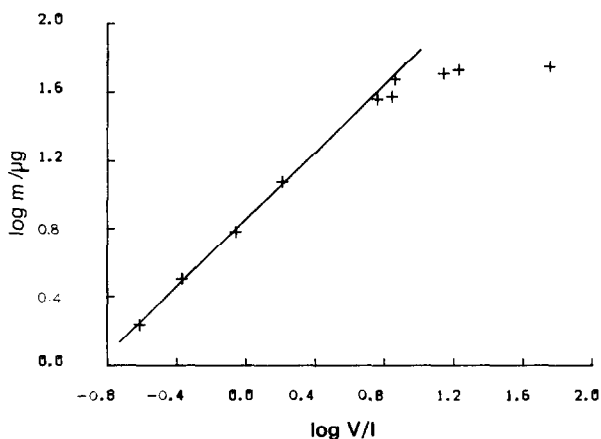


Fig. 5. Amount desorbed,  $m$ , as a function of sample volume,  $V$ . Gas concentration,  $7.4 \text{ mg/m}^3$  in dry air.

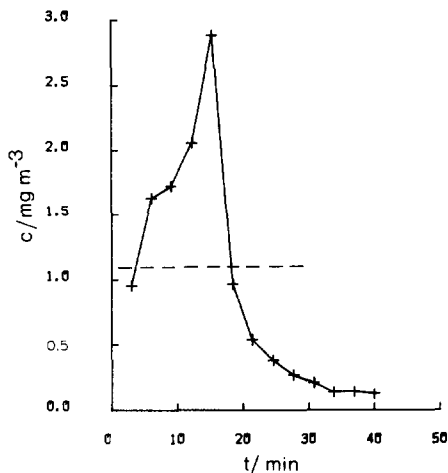


Fig. 6. Results from the practical test. Concentration in air,  $c$ , as a function of time,  $t$ . Each point represents a 3-min sampling period. The broken line represents the 40-min liquid absorption sampling.

pling is analysed. With the liquid absorption method, only a small aliquot (typically 1/3000) is analysed. This is only partially offset by the use of higher flow-rates and longer sampling times. Further, owing to the absence of a solvent, the chromatograms from the adsorption tube method are cleaner.

Hence the 3-minute sampling time was entirely satisfactory even for the low concentrations encountered at the end of the experimental period, whereas it is not practicable to use such short sampling times with the liquid absorption method. The experiment illustrates that it is possible to monitor rapid concentration changes with the adsorption tube method.

#### ACKNOWLEDGEMENTS

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