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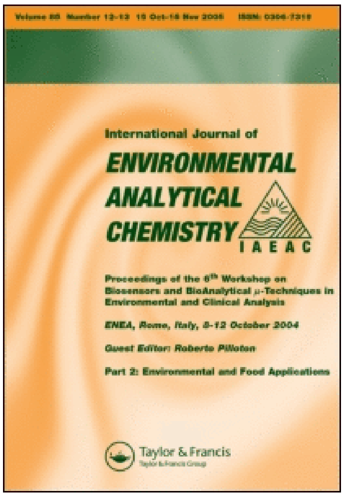

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STANDARD GAS MIXTURE PRODUCTION BASED ON THE DIFFUSION METHOD*

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The vapour diffusion behaviour through glass capillary tubes was studied aiming at the production of a standard composition gas mixture. The diffusion rates were quantified by means of gravimetric measurements, taking into account the various problems inherent in the glass material weighing.

Some parameters of the well-known diffusion equation were rechecked because of a lack of studies in this field. The carrier gas flow was found to play a fundamental role, although it is not ordinarily considered. The array's geometrical significance was also demonstrated. Some general procedural suggestions concerning the development of gas mixture systems are proposed.

KEY WORDS: Standard gas mixture, gas diffusion equation, carrier gas flow, standard benzene atmosphere, diffusion cell.

INTRODUCTION

Atmospheric analytical data can be used for a better ecosystem understanding, to recognise the environmental impacts as well as for monitoring purposes. In all such situations, one of the fundamental problems is the accuracy of the data to be obtained. Undoubtedly, the best procedure to evaluate the accuracy of an analytical method is to apply it to a standard sample in which the desired element or compound concentration is known with the highest confidence level. Thus, the standard sample should be as similar as possible to the composition and concentration of the real sample (matrix). Moreover, the standard sample should be stable, reproducible and easily manipulated. Because of these facts and the environmental problem relevance, systematic studies on the preparation of standard samples began in the sixties.[1-8]

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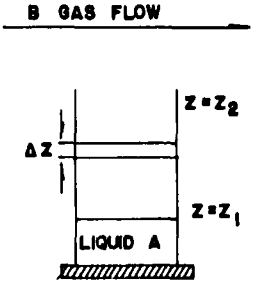

Figure 1 The vapour molecules *A*, originating from liquid vaporisation diffuse in the stagnant molecules of gas *B*, inside the diffusion tube. At the top of the tube, they are carried along by the *B* gas flow.

STANDARD GAS MIXTURE—DIFFUSION METHOD

When high volumes of a standard gas mixture are needed or adsorption problems are critical, it is essential that the mixture is obtained continuously through a contaminant source in the stationary state and in a dilution gas flow. Knowledge of the contaminant dilution gas rate is also required. Thus, the fundamental problem for the dynamic gas mixture production is the appropriate choice of the generation source.

As the preparation of a standard gas mixture from volatile liquids was a problem, it was decided to use the diffusion method to solve it. The gas diffusion phenomenon is represented by the empirical rate diffusion equation:[8]

$$R = 2.21 \times 10^6 \frac{DMPA}{TL} \log\left(\frac{P}{P-p}\right) \tag{1}$$

where: R = diffusion rate; D = diffusion coefficient; M = molecular mass of the vapour; P = pressure in the diffusion cell; p = partial pressure of the diffusing vapour at temperature T, T = absolute temperature of diffusion tube; A = cross-sectional area of the diffusion tube; and L = diffusion path length.

Study of some variables comprised in Eq. (1) should help to solve the problem at hand.

Eq. (1) was evaluated by considering a system in which the diffusion tube is immersed in a flux of molecules of gas B (Figure 1). Inside the tube, the vapour molecules originating from the vaporisation of liquid A, diffuse in the stagnant molecules of gas B and, at the top of the tube, are carried along by the B gas flow.[9]

The non-ideal behaviour of Eq. (1) has already been verified;[5,10,11] therefore, it can not be applied directly to predict the diffusion rate of real systems.

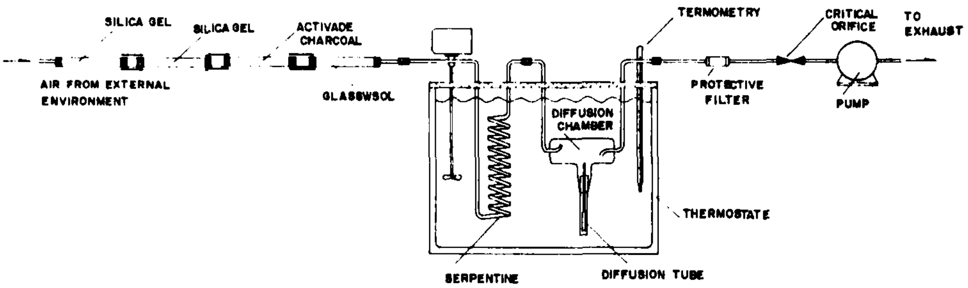

Figure 2 The basic system for the production of a gas mixture.

EXPERIMENTAL

Apparatus

The basic system for the production of a gas mixture is shown in Figure 2. Two diffusion tubes were used in the investigation (Figure 3). The diffusion rates were obtained through the determination of mass differences of the tubes. The accuracy accepted was ±0.01 mg, taking into account all the requirements necessary to obtain it.

The pumped air after passing through clearing cartridges reaches the diffusion chamber where an appropriate diffusion tube containing the solvent was installed. Thermostating was within 0.5 °C for the diffusion chamber. The air flow was controlled by a properly designed critical orifice. The metal coil used in the thermostat provided equilibration of the air flow before it reached the diffusion chamber. The solvents used were of analytical grade quality.

RESULTS AND DISCUSSION

Temperature-change Effects on the Diffusion Rate

The diffusion rates of benzene at different temperatures were determined by using two diffusion tubes (geometrically different) and a carrier air flow of $163\,\mathrm{ml\,m}^{-1}$ (Table 1).

By using the equation:

$$D_r = \frac{V_E - V_T}{V_T} \times 100 \tag{2}$$

where: D_r = relative deviation of experimental diffusion related to the theoretical diffusion rate: V_E = experimental diffusion rate; and V_T = theoretical diffusion rate calculated from Eq. (1), it was possible to calculate the differences in the experimental rates at various temperatures (Table 2).

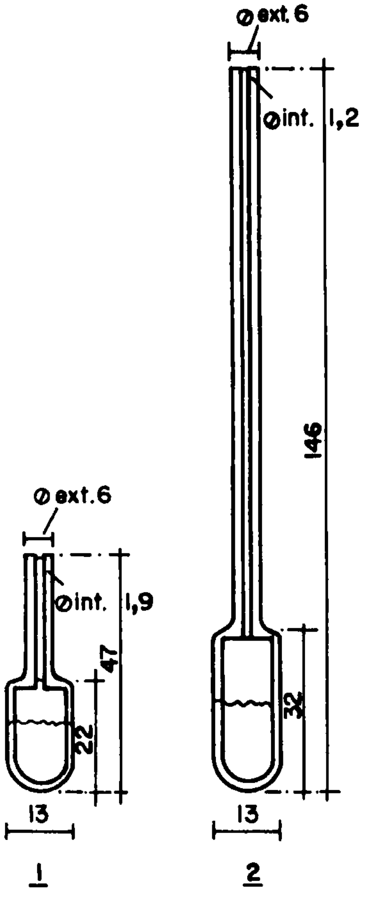

Figure 3 Two diffusion tubes 1 and 2 used in this study.

Table 1 Diffusion rate of benzene at a carrier gas flow of 163 ml min^{-1}

Temp ($\pm 0.5\,°C$)	*Diffusion tube 1* ($A = 2.8 \times 10^{-2}\ cm^2$; $L = 2.5\ cm$)	*Diffusion tube 2* ($A = 1.1 \times 10^{-2}\ cm^2$; $L = 11.4 cm$)
	Diffusion rate ($\mu g\ min^{-1}$)	*Diffusion rate* ($\mu g\ min^{-1}$)
30.5	37.6 ± 0.4	4.0 ± 0.1
34.0	45.7 ± 0.1	5.0 ± 0.1
38.0	56.7 ± 0.4	6.6 ± 0.3
42.6	71.9 ± 0.1	8.6 ± 0.3
46.7	88.9 ± 0.9	10.3 ± 0.4

Table 2 Relative deviation, D_r, at various temperatures

Temperature (±0.5 °C)	*Theoretical diffusion rate (μg min^{-1})*	*Experimental diffusion rate (μg min^{-1})*	*Relative deviation D_r (%)*
Diffusion tube 1			
30.5	38.5	37.5	−2.3
34.0	45.2	45.7	1.1
38.0	55.0	56.7	3.1
42.6	70.1	71.9	2.6
46.7	83.1	88.9	7.0
Diffusion tube 2			
30.5	3.7	4.0	8.3
34.0	4.4	5.0	14.0
38.0	5.3	6.6	23.0
42.6	6.8	8.6	26.0
46.7	8.1	10.3	27.0

These data show that when the temperature increases, the relative deviation of the experimental diffusion rate in relation to the theoretical diffusion rate increase compared with Eq. (1). This fact is more distinct when tube 2 is used.

Effect of Carrier Gas Flow Change on Diffusion Rate

Although the theoretical value of the diffusion rate as calculated from Eq. (1) is independent of the carrier gas flow, the literature recommends that flows higher than 1 l min^{-1} should be avoided.[2] Taking this fact into account, it was decided to investigate the effect of the gas flow on the diffusion rate. Experiments were run with tubes 1 and 2 at $t = 34.5 \pm 0.5$ °C with different carrier gas flows. The results are presented in Figure 4.

The data show an exponential increase in the diffusion rate as the carrier gas flow increase. That is, there is a carrier gas flow range that affects the diffusion rate very little, but there also are regions where small variations of the carrier gas flow produce large changes in diffusion rates. In other words, in the system used the carrier gas flow seems to be a limiting factor.

Carbon tetrachloride was selected to verify the observed phenomenon, because —compared with benzene—its molecular mass is roughly twice as high and its vapour pressure is also higher; besides, carbon tetrachloride is a dangerous environmental contaminant. The results are presented in Figure 5.

To compare the diffusion rate dependence of both solvents on the carrier gas flow, the experimental relative differences were calculated using Eq. (2). Figure 6 shows these results, which allow several conclusions. The tube geometry plays an important role: in tube 2 the diffusion rate is larger than in tube 1. For tube 1, at 34.5 ± 0.5 °C, there is an ideal flow for each substance when the relative deviation (D_r) is zero. Thus, under these conditions, the diffusion rate can be predicted by

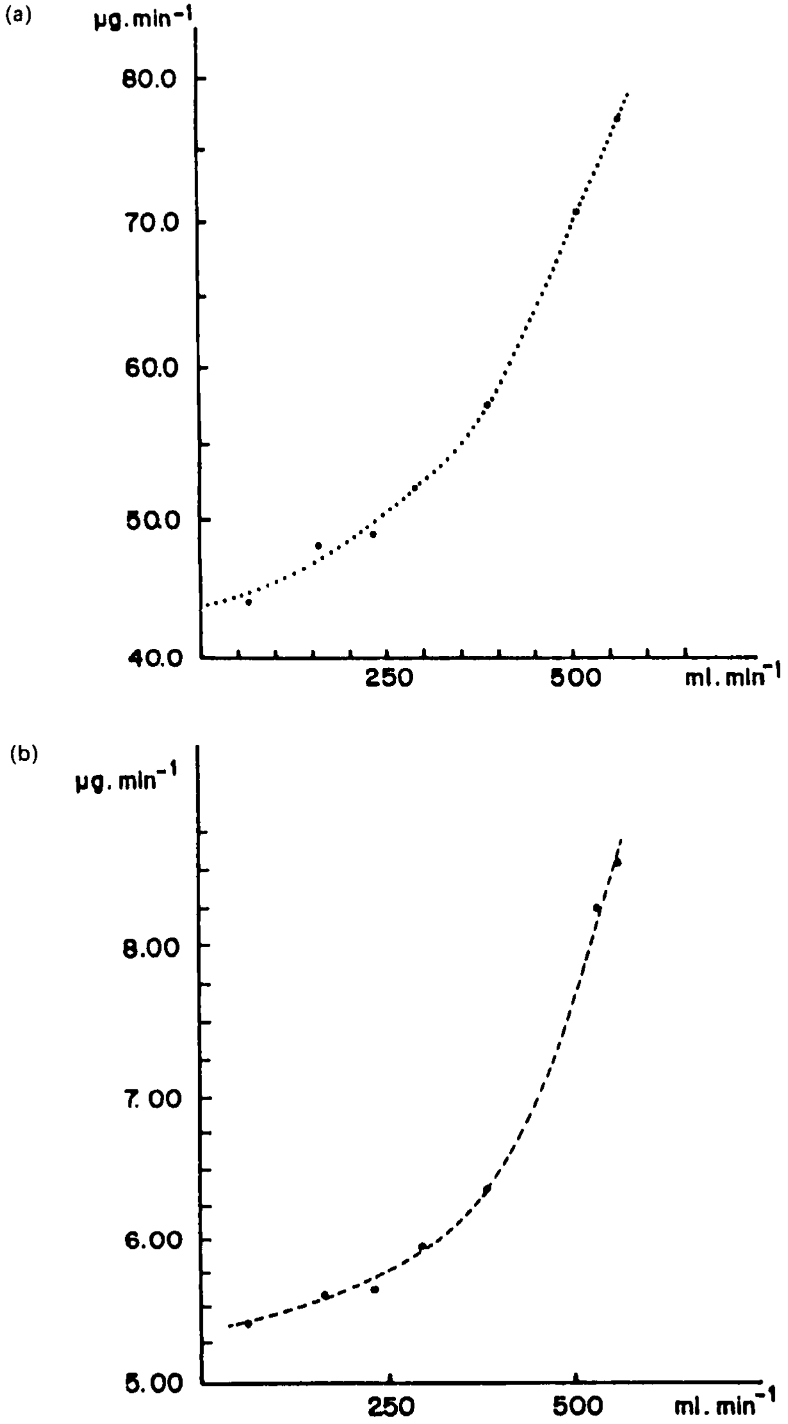

Figure 4 Effect of carrier gas flow change on the diffusion rate of benzene: (a) Diffusion tube 1; (b) Diffusion tube 2.

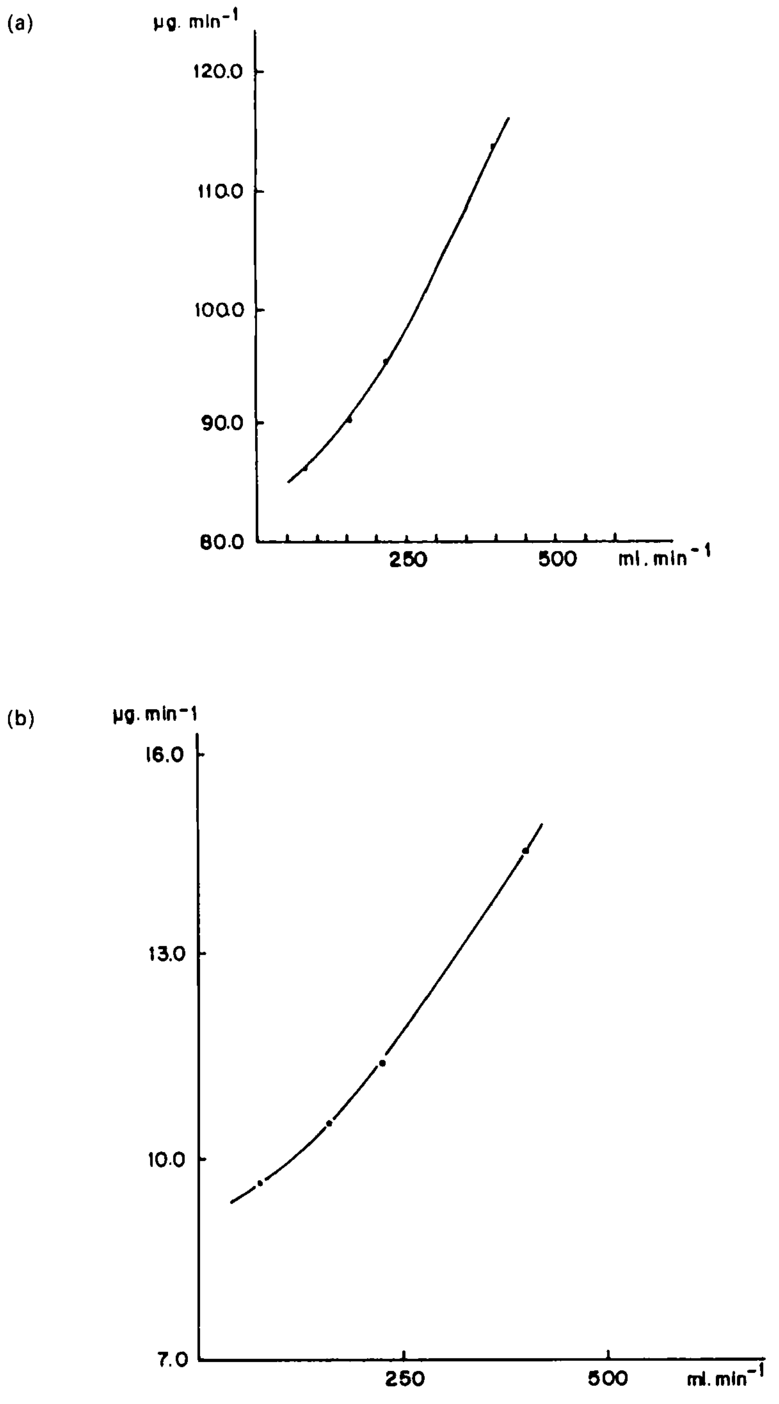

Figure 5 Effect of carrier gas flow change on the diffusion rate of carbon tetrachloride: (a) Diffusion tube 1; (b) Diffusion tube 2.

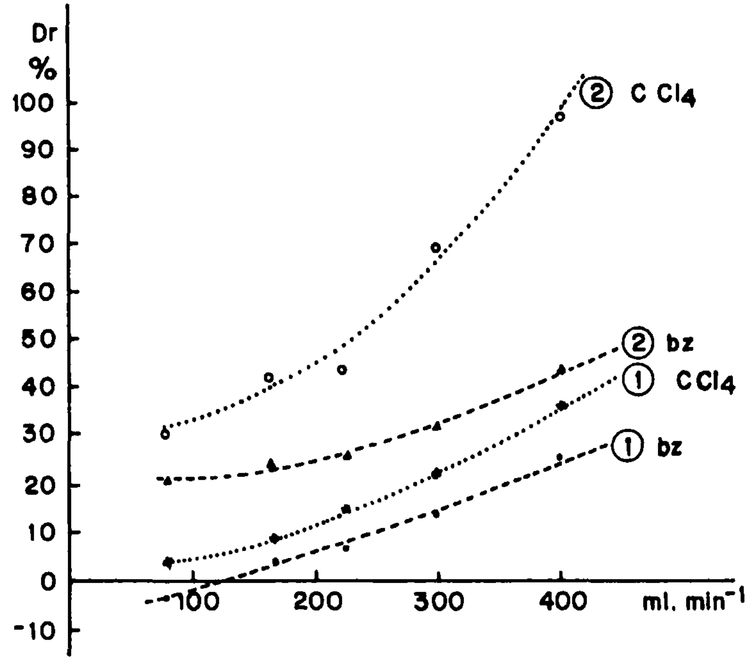

Figure 6 Comparison of the diffusion rate dependence of benzene and carbon tetrachloride on the carrier gas flow: (a) Tube 1; (b) Tube 2.

Eq. (*1*). For tube 2 there is a range in the beginning of the curve, where the relative deviation (D_r) is slightly dependent on the gas flow. The influence of the vapour pressure of the solvent on the diffusion rate is remarkable: the higher the vapour pressures are, the higher the diffusion rate differences. One should avoid working with high carrier gas flow, where small flow variations will produce significant changes in the diffusion rate. Finally, the carrier gas flow and the diffusion temperature should be compatible with the vapour pressure of the substance used.

The Position of the Diffusion Tube in the Diffusion Chamber

Because the results obtained until now show that the diffusion tube geometry affects the diffusion rate, it was decided to study the influence of the tube position in the diffusion chamber. Tube 2 was chosen because of its versatility regarding the different positions in which it can be inserted in the chamber.

Three positions have been selected, as displayed in Figure 7. Benzene was used and various carrier gas flows were selected to perform this experiment.

From the results shown in Table 3, one can infer that there is little dependence of the diffusion rate on positive heights in the chamber. When the height is negative, the diffusion rate becomes smaller than that calculated from Eq. (1).

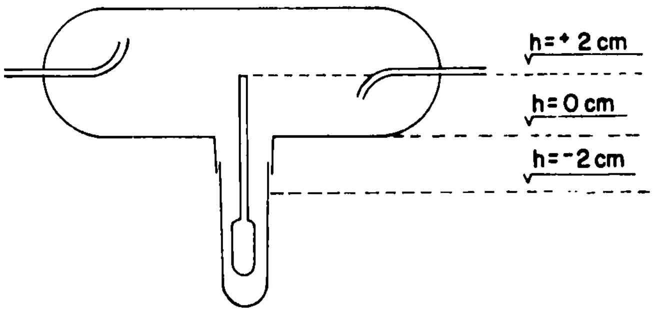

Figure 7 The diffusion tube position in the diffusion chamber.

Table 3 Dependence of the diffusion rate on heights in the chamber.[a]

Height (cm)	*Diffusion rate (a) (μg min⁻¹)*	*Relative deviation Dr (%)*	*Diffusion rate (b) (μg min⁻¹)*	*Relative deviation Dr (%)*
+2	45.8	−0.2	49.9	8.6
0	45.5	−0.8	49.4	7.6
−2	44.4	−3.3	47.7	−3.7

[a] Temperature: 34.8 ± 0.5 °C. Vapour source: benzene.
(a) Flow 83 ml min⁻¹; (b) Flow 217 ml min⁻¹

Probably the vapour molecules that reach the top are not instantaneously taken up by the carrier gas.

Diffusion Chamber with Carrier Gas Flow Parallel to the Diffusion Tube

From the evaluation of the above results one can conclude that the system produces a gas flow with standard composition within a confidence level, which basically depends on the possibility of keeping under control all the factors that affect the diffusion rate. In the present system the main factor is the carrier gas flow.

Therefore, a new system was built, where the turbulence produced by the carrier flow should be diminished. The first chamber was replaced by another one, with the carrier gas flowing parallel to the diffusion tube (Figure 8). The glass wool on the bottom, apart from sustaining the tube, reduces the carrier gas turbulence.

Preliminary results are shown in Figure 9; they compare the diffusion rate in the two systems. The second system seems to be advantageous, since it is easier to assemble, higher carrier gas flows can be used with both tubes, and solvents with higher vapour pressure can also be used, because probably the turbulence phenomenon decreases. However, when low carrier gas flows are used, the experimental diffusion rate is smaller than the predicted one. With these flows, the carrier gas probably cannot carry along all vapour molecules that reach the top of

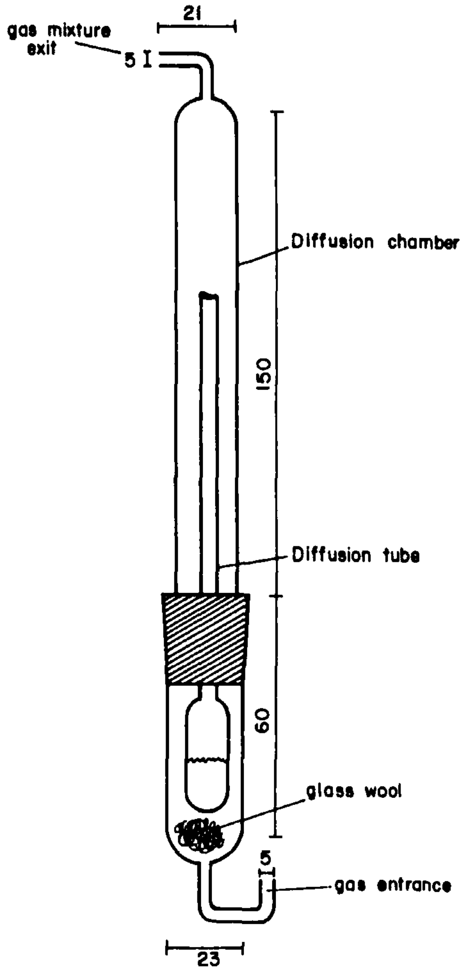

Figure 8 Diffusion chamber with carrier gas flow parallel to the diffusion tube.

the tube. Another possible drawback for this system is that the gas mixture may not be totally homogeneous at the diffusion chamber end. This fact may probably be circumvented by coupling a new mixing chamber to the system.

CONCLUSIONS

The experimental results, when compared with the calculated values from Eq. (1) (for the same vapour), show that the geometry of the diffusion tube and diffusion chamber are variables that affect the diffusion rate deviation directly. Equation (1) can only be applied under a very restricted set of conditions, which can only be defined by taking into account the experimental evaluation for each vapour. The diffusion rate is dependent on the carrier gas flow, although Eq. (1) does not

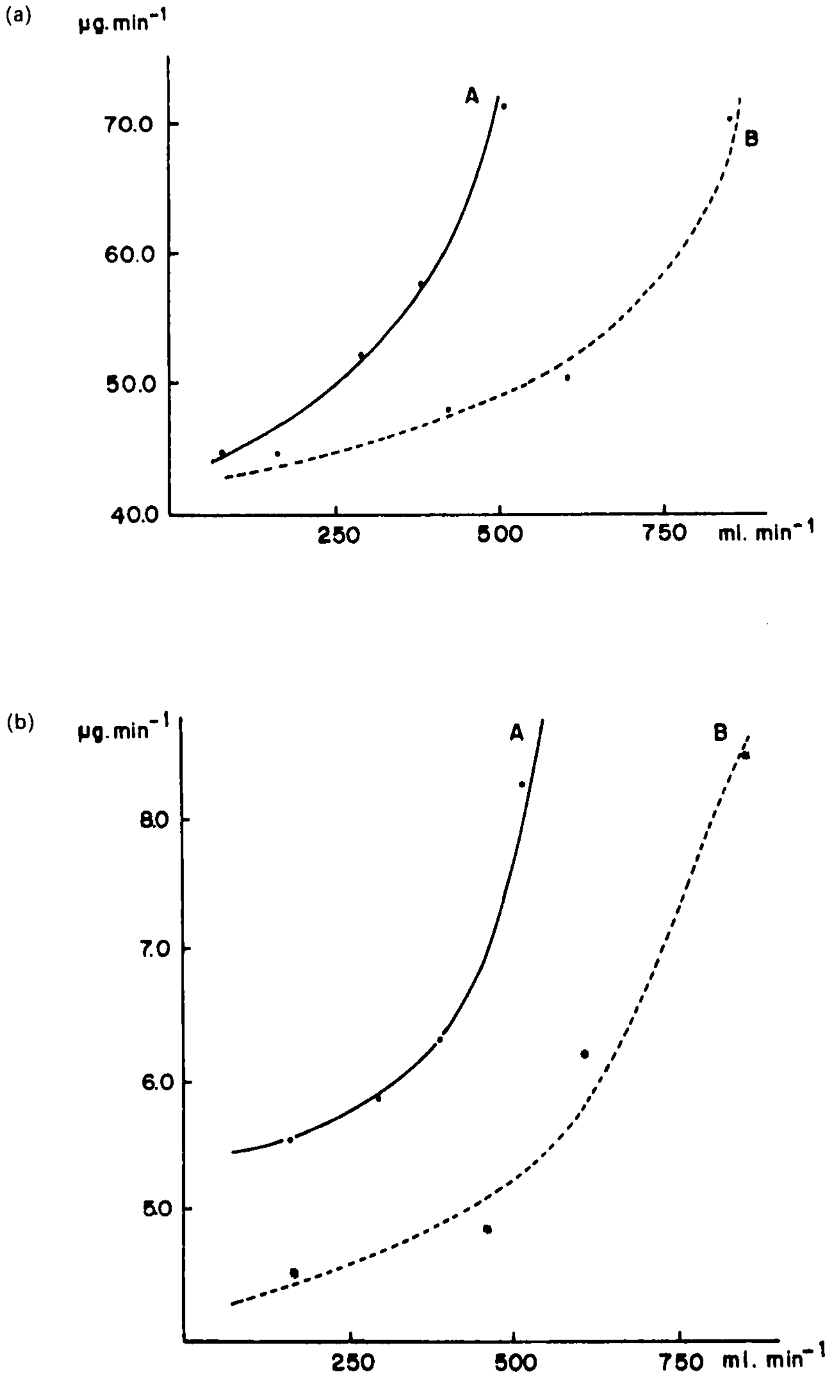

Figure 9 Comparison of diffusion rates. A = diffusion chamber with gas flow perpendicular to the diffusion tube. B = diffusion chamber with gas flow parallel to the diffusion. (a) Diffusion tube 1; (b) Diffusion tube 2.

include it. The temperature and carrier gas flow should be chosen considering the solvent vapour pressure.

In the diffusion chamber with the carrier gas flow perpendicular to the diffusion tube, one must keep the tube end always at the same height as the carrier gas flow.

On the basis of the model of Lee and Wilke[11] one may conclude that the relative deviation (D_r) at high carrier gas flows is due to gas turbulence generated at the diffusion tube end. However, to explain deviations when the diffusion temperature rises or solvents with high vapour pressure are used, one should consider that the vapour flow also contributes to an increase of the turbulence at the tube end.

A final remark should be made: the relative deviations presented in this paper are valid for the diffusion tubes and chambers discussed here only.

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