THE GAS-CHROMATOGRAPHIC SEPARATION OF MIXTURES OF HYDRAZINE, METHYLHYDRAZINE AND 1,1-DIMETHYLHYDRAZINE

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Mixtures of hydrazine and some of its alkyl derivatives, which have recently become important in many fields, were studied with the aid of gas chromatography, a technique used by the present authors in earlier investigations on aliphatic amines[1].

Apart from the resolution of the mixtures, it was possible to carry out a rapid quantitative determination of the individual components under discussion and to avoid the numerous causes of interference which are usually encountered in other methods[2-13].

MATERIALS

1,1-Dimethylhydrazine (Eastman Kodak Co.) was used after a preliminary gas-chromatographic check had shown the presence of negligible quantities of impurities. The methylhydrazine was supplied by K. and K. Laboratories, Plainview, New York.

The following adsorbent systems were examined in order to determine the best experimental conditions:

(a) Carbowax 400 on Celite C 22;

(b) Carbowax 400 on Celite C 22, subsequently treated with KOH (7 % by weight with respect to the solid support);

(c) Carbowax 400 on Celite C 22, previously rendered alkaline with KOH (7 % by weight with respect to the solid support);

(d) Carbowax 1500 on Celite C 22;

(e) Carbowax 1500 on Celite C 22, subsequently rendered alkaline as under (b);

(f) Carbowax 1500 on Chromosorb W.

The gas-chromatographic determinations were carried out with the aid of a Fractovap type B instrument (C. Erba, Milan). The samples were introduced into the vaporisation chamber by means of an Agla microsyringe (Burroughs Wellcome Co., London) with a capacity of 0.5 ml. The flow-rate of the carrier gas was measured with a soap-bubble flow meter.

EXPERIMENTAL

Polyethylene glycols of various degrees of polymerisation were chosen as the stationary phase, owing to their high polarity. Alkalisation of the entire adsorbent system after permeation with the stationary phase had been tried with good results

in the work mentioned above[1]. This alkalisation differs from that used by HARDY AND POLLARD[14] on the support alone before permeation with the stationary phase.

Adsorbent system (b) clearly proved to be best for the present work. Carbowax 1500 on Chromosorb W was extremely sensitive and gave peaks even for extremely low concentrations. However, although the peak for hydrazine, whether hydrated or anhydrous, was very similar to that obtained with system (b), the peaks corresponding to the two methyl derivatives were less symmetrical and did not show a satisfactory separation. Lastly, Carbowax 1500 on Celite C 22, whilst having the same short-comings as Carbowax 1500 on Chromosorb W as regards the methyl derivatives, did not even exhibit the same sensitivity for hydrazine as system (f).

Concluding that Carbowax 400 on Celite C 22, after alkalisation, was the best system for the present work, a series of tests were carried out at different temperatures to calculate the retention volumes and to determine the optimum temperature for the gas-chromatographic determination of the components of the mixtures in question. The tests were carried out using a column 2 m long, at a helium flow rate of 109 ml/min, and at the following temperatures: 85°, 90°, 100°, 105° and 110°.

The retention volumes of hydrazine, methylhydrazine and 1,1-dimethyl-hydrazine, calculated for different temperatures, are listed in Table I. A plot of the

TABLE I

RETENTION VOLUMES (V_r) AS A FUNCTION OF $1/T$

$1/T^*$	$(CH_3)_2N\text{-}NH_2$	$CH_3\text{-}NH\text{-}NH_2$	$N_2H_4 \cdot H_2O$
$2.790 \cdot 10^{-3}$	1035	2905	—
$2.755 \cdot 10^{-3}$	891	2450	—
$2.717 \cdot 10^{-3}$	747	2043.4	5346
$2.681 \cdot 10^{-3}$	650.5	1730	4288
$2.645 \cdot 10^{-3}$	540	1423.4	3440
$2.610 \cdot 10^{-3}$	440.5	1230	2864

* Temperature in degrees absolute.

experimental values of the retention volumes on a semi-logarithmic scale, against the reciprocal of the absolute temperature, gives linear graphs, as shown in Fig. 1.

Some authors[15] have found, by thermodynamic methods, that the graphs for gas–liquid systems are linear when the partial molar heat of vaporisation of the compound in question is constant within the temperature range investigated.

It can be seen from Fig. 1 that the considerable differences in the retention volumes of the three hydrazines makes their qualitative separation possible in the temperature range under consideration. The V_r values of hydrazine fall off more steeply with increasing temperature than do those of methylhydrazine and especially those of 1,1-dimethylhydrazine. This may be explained by assuming that hydrazine and the polyethylene glycol of the stationary phase interact to form hydrogen bonds, and that this interaction decreases with increasing temperature.

On the other hand, the formation of hydrogen bonds between the alkyl hydra-zines (especially 1,1-dimethylhydrazine) and the stationary phase is less likely or, at any rate, less frequent. It must also be borne in mind that hydrazine has a greater dipole moment than the methyl derivatives in question (see Table II), so that a
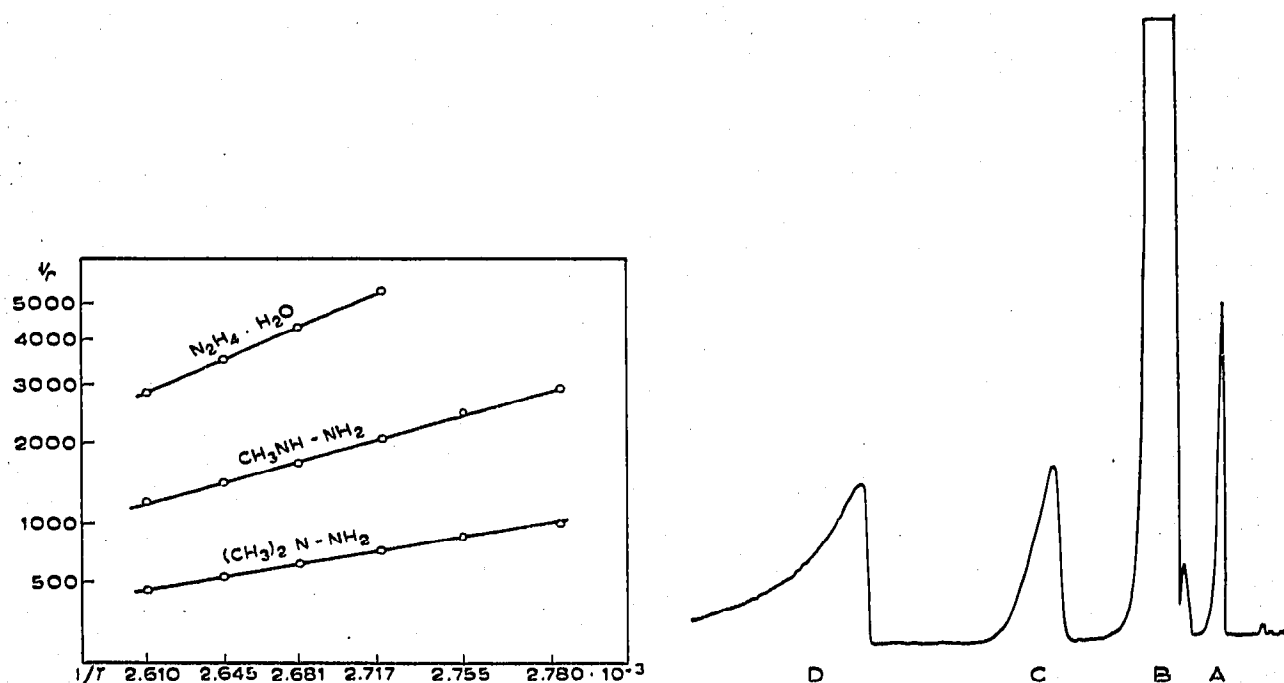
Fig. 1. The variation of the retention volumes with the reciprocal of the absolute temperature.

Fig. 2. Gas-chromatographic separation. A = $(CH_3)_2N-NH_2$; B = CH_3-CH_2-OH; C = $CH_3-NH-NH_2$; D = $N_2H_4 \cdot H_2O$. Experimental conditions: Support: Celite C 22 (30–60 mesh); stationary phase: Carbowax 400 (25 %) + 7 % of KOH; carrier gas: helium; column temperature: 130° ± 0.2°; inlet pressure: 0.7 kg/cm²; flow rate: 204 ml/min; current of bridge circuit: 24.5 mA; chart speed: 1.25 cm/min; length of column: 2 m; internal diameter of column: 0.6 cm. Retention time: dimethylhydrazine: 1 min 59 sec; methylhydrazine: 6 min 36 sec; hydrazine: 11 min 42 sec.

stronger association takes place between the dipoles of hydrazine and the strongly polar polyethylene glycol. This association decreases with increasing temperature. This effect is more noticeable with hydrazine because it is initially more highly associated than the alkyl hydrazines. This behaviour results in a steeper gradient of the top graph in Fig. 1 in comparison with the other two, or more precisely, in a decrease in the gradient with decreasing polarity of the compound.

The analytical separation of mixtures of hydrazine hydrate, methylhydrazine and dimethylhydrazine has been achieved under the conditions described, in strict agreement with the retention volume graphs in Fig. 1. Fig. 2 shows a chromatogram

TABLE II

Compound	Dipole moment	B.p. (°C)	V_r (at 100°)
$(CH_3)_2N-NH_2$	1.35[a]	62.2	650.5
CH_3NH-NH_2	1.68 ± 0.14[b]	87.5	1730
$N_2H_4 \cdot H_2O$	1.83 – 1.85[c]	118.5	4288

[a] Measured in n-heptane at 25° [16].
[b] Measured in benzene at 15° [17].
[c] Measured in benzene at 18° [18].

of the three components in question. The excellent resolution of the peaks achieved under the given experimental conditions can clearly be seen.

The calibration curve of each individual component of the mixtures was plotted and used to find experimental conditions which would permit a good separation, together with symmetrical peaks, and the maximum possible sensitivity at low concentrations. The first calibration curve studied was that of 1,1-dimethylhydrazine, when it was found necessary to dilute the compounds as far as possible with a solvent in order to record the curve at very low concentrations. A solvent was chosen which was completely miscible with the samples, and whose retention time did not interfere with the analysis.

Hydrazines are completely soluble in alcohols but less soluble in other solvents examined, such as n-heptane, ether, chloroform and dioxane. n-Propanol was therefore chosen as the solvent. A mixture of three hydrazines in this alcohol was chromatographed and the following sequence of peaks was obtained: 1,1-dimethylhydrazine (b.p. 62.2°), n-propanol (b.p. 97°), methylhydrazine (b.p. 87.5°) and hydrazine hydrate (b.p. 118.5°). The analysis was carried out at a temperature of 90° and a flow rate of 109 ml/min, the other experimental conditions being as reported for Fig. 2. The fact that an impurity in the propanol gave a peak which was partly superimposed on that of the 1,1-dimethylhydrazine made planimetry difficult. The peaks were therefore suitably resolved and the areas of the triangles obtained were measured geometrically.

1,1-Dimethylhydrazine was used in 2 % and 0.4 % solutions. The absolute detection limit of the analytical method for dimethylhydrazine was $1.95 \cdot 10^{-7}$ moles with the detector used. At higher dilutions, the method is of purely qualitative value, since the areas of the peaks are no longer reproducible and are also difficult to measure.

The same experimental conditions were used in the study of methylhydrazine. This compound gave an excessively high retention time, and above all, gave an asymmetric and flattened peak which would make planimetry difficult. By suitable variation of temperature and flow rate, it was found that at 115° and 204 ml/min a more regular and easily measurable methylhydrazine peak was obtained. A 2 % (by volume) solution in propanol was used, since the use of more dilute samples resulted in the superposition of the solvent peak on that of the methylhydrazine. An irreversible adsorption of methylhydrazine on the stationary phase was observed, and in the first determinations this gave rise to a poor reproducibility of the areas of the peaks. Constant, and hence reliable, values were obtained only when saturation had been achieved, *i.e.* after the third or fourth run. The density of methylhydrazine, determined at 20°, was found to be 0.884.

The calibration curve of methylhydrazine was recorded under conditions specified in Fig. 2, except that the temperature and the flow rate were 115° and 204 ml/min, respectively. A temperature of 130° and a flow rate of 500 ml/min were used in the determination of the calibration curve of hydrazine hydrate. The other experimental conditions remained unaltered. A more concentrated (10 %) alcoholic solution was used, since it was found that hydrazine was also subject to strong irreversible adsorption on the stationary phase, which interfered with its determination at very high dilutions.

The limiting concentrations for quantitative determinations were as follows: $2.5 \cdot 10^{-6}$ moles for hydrazine, $1.95 \cdot 10^{-7}$ moles for 1,1-dimethylhydrazine, and $0.46 \cdot 10^{-7}$ moles for methylhydrazine.

CONCLUSIONS

Examination of the results reported shows that 1,1-dimethylhydrazine has the highest thermal conductivity, which is followed by that of methylhydrazine, whilst the thermal conductivity of hydrazine is much lower. Consequently, in order to obtain peaks of the same surface area, e.g. 2 cm², the following quantities have to be used: $1.95 \cdot 10^{-7}$ moles of 1,1-dimethylhydrazine, $2.2 \cdot 10^{-7}$ moles of methylhydrazine, and $1.03 \cdot 10^{-5}$ moles of hydrazine, under the conditions specified above.

The gas-chromatographic determination of water in mixtures of hydrazines was not undertaken, since this problem, which has already been subjected to gas-chromatographic investigation by other authors[16,20], may be solved indirectly by the same technique as was described above. In fact, the water peak is well resolved in relation to those of the hydrazine peaks, although it is unsuitable for direct planimetric or geometric measurement, owing to its extremely flat and asymmetric shape. However, the water can be calculated by difference. It is quite probable that the concentrations of all the components in the mixtures discussed can be determined by one single measurement using a programmed gas-chromatographic instrument.

SUMMARY

The experimental conditions used for the separation of mixtures of hydrazine, methylhydrazine and 1,1-dimethylhydrazine are described. The limits of sensitivity found with the apparatus used in the quantitative determination of these products are given.

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