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LIGAND-EXCHANGE GAS CHROMATOGRAPHY OF DIALKYL SULPHIDES

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SUMMARY

The separation and retention behaviour of dialkyl sulphides in ligand-exchange gas chromatography have been studied using a copper(II) stearate stationary phase and an ammonia-containing mobile phase. Short retention times and sharp peaks were obtained when ammonia was introduced into the mobile phase. On a solid copper(II) stearate column a linear relationship was found between the capacity factors and the reciprocal of the ammonia concentration, and some equilibrium constants have been calculated. At higher temperatures, copper(II) stearate behaved as a liquid crystalline stationary phase. A good separation of sulphides was achieved by appropriate adjustment of the ammonia concentration and the column temperature. Factors affecting the retention and sample selectivity are discussed.

INTRODUCTION

Among the variety of separation methods, ligand-exchange chromatography (LEC) is one of the most powerful techniques for resolving complex-forming substances. Since its introduction in the early 1960s¹, much work has been done on the separation of isomers or homologues of amines^{2,3}, phenols⁴, amino acids⁵⁻¹⁰ and other organic ligands containing nitrogen or oxygen atoms. LEC is now a very common technique in high-performance liquid chromatography, and some commercial packings for optical resolution are available, *e.g.*, Chiralpak WH/WM (JASCO, Tokyo, Japan). Since many types of samples or stationary phases can be selected and modification of the mobile phase is easy and effective, liquid chromatographic systems were generally used in the cases cited above. There are still some limitations, however, in operating an LEC system using a liquid mobile phase. Detection is sometimes difficult if a UV-visible detector is used. Reversed-phase solvents can easily elute the stationary phase metal ions leading to column deterioration. The addition of metal ions to the mobile phase, often used to avoid this column instability, contaminates the sample and may complicate the retention mechanisms. Taking into account these disadvantages, ligand-exchange gas chromatography (LEGC) is expected to have greater potential for the study of volatile samples.

Organic sulphides are now of importance in synthetic and biological chemistry, but are still insufficiently characterized chromatographically. Recently we reported a study on the LEC of dialkyl sulphides using a non-polar liquid mobile phase and metal immobilized on silica gels. The technique was found to be applicable to the separation and characterization of sulphides¹¹. In this paper we describe a theoretical treatment of an LEGC system and the separation of dialkyl sulphides. The chromatographic data obtained by this technique as well as those obtained by ligand-exchange liquid chromatography (LELC) are considered to provide valuable information on organic sulphur compounds.

In a previous paper we reported an LEGC separation of aliphatic amines, using metal stearates as the stationary phase and ammonia and water vapour as the mobile phase ligands¹². The use of stearates led to a high column efficiency owing to their hydrophobic surfaces and mesophase character in an appropriate temperature range. Since copper(II) salts gave the best results for the separation of amines and Cu^{2+} was suitable as the central ion of sulphide-containing complexes, as indicated in the LEC study using a liquid mobile phase¹¹, copper(II) stearate was chosen as the stationary phase in this study. In order to obtain a high column stability in the temperature region of the mesophase where the column is highly efficient and to simplify the discussion of the retention mechanism, only ammonia was employed as the mobile phase ligand, since the presence of water in the mobile phase was found to be less effective and to lower the column stability.

EXPERIMENTAL

Gas chromatography

A Hitachi gas chromatograph Model 023 (Hitachi Seisakusho Co., Tokyo, Japan) equipped with a hydrogen flame ionization detector and an on-column sample injector was used. The flow-rate was 20 ml/min and the column temperature was varied in the range of 70–120°C. The column inlet pressure was 1.05–1.20 kg/cm².

Samples and chemicals

All chemicals were of the highest grade available. Seventeen sulphides were purchased from various suppliers and used without further purification, and the other twenty-seven sulphides were prepared in our laboratory according to the usual methods. All sulphides were diluted to 2% (v/v) in hexane or nonane and 1 μl of each solution was injected.

Column

Copper(II) stearate (Wako, Osaka, Japan) was recrystallized twice from chloroform and coated (5%, w/w) on Chromosorb G AW DMCS (80–100 mesh) (Johns-Manville, Denver, CO, U.S.A.) by vacuum evaporation. The material was resieved and packed in a 3 m \times 4 mm I.D. glass spiral column. The column was conditioned for 5 h before measurements.

Mobile phases

Nitrogen containing 3, 5, 7 and 10% (v/v) ammonia, at 35°C under pressures of 120, 85, 60 and 40 kg/cm², respectively (Taiyo Sanso, Kanagawa, Japan), was

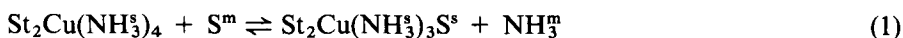
used as the mobile phase. Pure nitrogen was used as the reference. The molar concentrations of ammonia in the mobile phase were measured titrimetrically to be 1.90, 3.09, 4.24 and 6.19 mmol/l for 3, 5, 7 and 10% ammonia, respectively.

RESULTS AND DISCUSSION

Effect of ammonia on retention

The presence of ammonia in the mobile phase drastically reduced the retention of samples when solid copper(II) stearate was used as the stationary phase. Fig. 1 shows the effect of ammonia at 70°C, and similar results were obtained in the range of 70–100°C. Since the retention data obtained on a liquid crystalline copper(II) stearate column indicated a complicated mechanism, as described later, the following discussion is based on the data obtained on a solid copper(II) stearate column.

As discussed previously, the effect of the mobile phase ligand on retention is expressed as follows¹²



$$\beta = \frac{[\text{St}_2\text{Cu}(\text{NH}_3)_3\text{S}^m][\text{NH}_3^m]}{[\text{St}_2\text{Cu}(\text{NH}_3)_4][\text{S}^m]} \quad (2)$$

$$k' = \frac{[\text{St}_2\text{Cu}(\text{NH}_3)_3\text{S}^m]}{[\text{S}^m]} \cdot \Psi = \frac{\beta C_{\text{Cu}}}{[\text{NH}_3^m]} \cdot \Psi \quad (3)$$

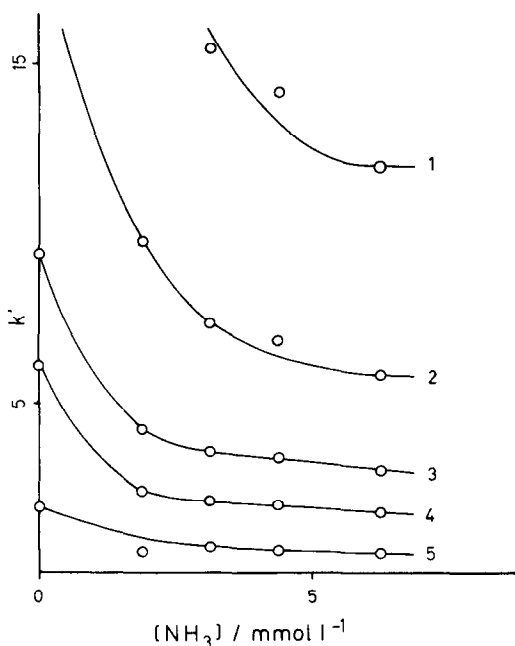


Fig. 1. Effect of ammonia in the mobile phase on retention. Column temperature: 70°C. Flow-rate: 20 ml/min. Samples: 1 = di-*n*-butyl sulphide; 2 = diisobutyl sulphide; 3 = pentamethylene sulphide; 4 = tetrahydrothiophene; 5 = diethyl sulphide.

where St , S , β , k' and Ψ are stearate ion, the sample solute, the formation constant, the capacity factor of the solute and the phase ratio of the column, respectively, and the superscripts m and s indicate that the molecule exists in the mobile phase and in the stationary phase, respectively. The value of $[St_2Cu(NH_3)_4]$ can be replaced by constant, C_{Cu} , since it is much greater than the total concentration of the sample solute. Eqn. 3 is based on the assumption that the sample is retained mainly by ligand-exchange reaction. It shows that k' is proportional to the reciprocal of the concentration of ammonia and should approach zero as $1/[NH_3]$ tends to zero.

Plots of the k' values of some sulphides *versus* $1/[NH_3]$ are shown in Fig. 2. Table I lists the formation constant, β , of some symmetrical sulphides calculated from eqn. 3 using the slopes of the plots. Though a linear relationship is observed, each line has a positive intercept, which means that another retention mechanism is involved. It is very probable that this effect is due to the hydrophobic interaction between the alkyl chain of a sample sulphide and the stearate moiety of the stationary phase. The capacity factor, k' , can then be written as follows

$$k' = k_{LE} + k_{AD} \quad (4)$$

or

$$k' = \frac{\beta C_{Cu}}{[NH_3]^m} \cdot \Psi + k_{AD} \quad (5)$$

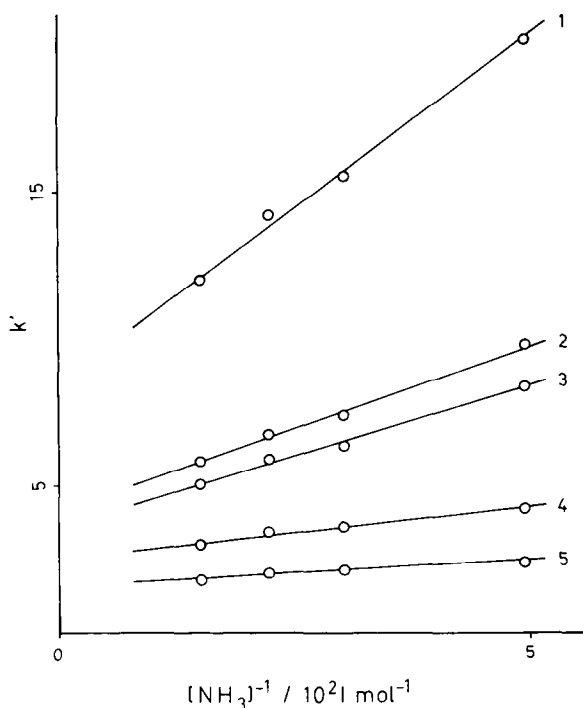


Fig. 2. Plot of k' versus $[NH_3]^{-1}$. Column temperature: 70°C. Flow-rate: 20 ml/min. Samples: 1 = di-*n*-butyl sulphide; 2 = diisobutyl sulphide; 3 = di-*sec.*-butyl sulphide; 4 = pentamethylene sulphide; 5 = tetrahydrothiophene.

TABLE I

COMPLEX-FORMATION CONSTANTS OF SOME SYMMETRICAL SULPHIDES AT VARIOUS COLUMN TEMPERATURES

Sample	β^*				$K(l/mol)^{**}$			
	70°C	80°C	90°C	100°C	70°C	80°C	90°C	100°C
Diethyl sulphide	0.46	0.33	0.18	0.13	12.5	7.5	4.4	3.6
Dipropyl sulphide	4.12	2.14	1.04	0.59	57.4	28.4	17.3	13.4
Dibutyl sulphide	15.84	8.09	3.74	1.54	667	160	86.6	53.1
Tetrahydrothiophene	1.31	0.79	0.61	0.31	40.9	22.8	13.4	9.5
Pentamethylene sulphide	2.28	1.53	0.92	0.52	61.6	33.5	20.1	14.8

* Parameters Ψ and C_{Cu} used for calculating β values are given in ref. 12.

** K values were calculated using $X_{Cu} = 2.19$ mmol. The value of V_0 was obtained from the column dead time using methane as the test solute.

where k_{LE} and k_{AD} are the contributions of ligand exchange and hydrophobic interaction, respectively, to the capacity factor. The value of k_{AD} is obtained directly from Fig. 2 by extrapolation.

The β values in Table I are somewhat smaller than those of aliphatic amines obtained in a similar LEGC system¹², indicating the relatively weak gas-phase basicities of dialkyl sulphides compared with those of amines. The weak basicity or complex-forming ability of sulphides explains the fact that even pure nitrogen as carrier gas was able to elute the samples as shown in Fig. 1. Assuming that k_{AD} is not affected by the change in concentration of ammonia in the mobile phase, its value can be used for interpreting the results obtained when pure nitrogen is used as the mobile phase. The retention of a sample in this case can be represented by



$$K = \frac{[\text{St}_2\text{Cu-S}]}{[\text{S}^m][\text{St}_2\text{Cu}]} \quad (7)$$

where $\text{St}_2\text{Cu-S}$ and St-S indicate the sample retained by complex formation on the Cu^{2+} and by hydrophobic interaction with the stearate moiety, respectively, and K is the equilibrium constant for the former mechanism. The following equations can be derived

$$k' = k_{CF} + k_{AD} \quad (8)$$

$$\begin{aligned}
 k' - k_{AD} &= k_{CF} = K'_D \Psi \\
 &= \frac{[\text{St}_2\text{Cu-S}]V^s}{[\text{S}^m]V^m} \\
 &= \frac{K[\text{St}_2\text{Cu}]V^s}{V^m} = \frac{K X_{\text{Cu}}}{V_0} \quad (9)
 \end{aligned}$$

$$K = k_{CF} V_0 / X_{\text{Cu}} \quad (10)$$

where k_{CF} , K'_D , X_{Cu} and V_0 are the contribution of complex formation to the capacity factor, the distribution coefficient of the retention by complex formation, the number of moles of the total Cu^{2+} in the stationary phase and the retention volume of a non-retained solute, respectively. In the present case, since the solid copper(II) stearate deposited on the surface of the support forms a bulky uneven layer, all the molecules of copper(II) can be considered to participate in the complex formation. Calculated values of K are also listed in Table I.

Effect of ammonia on peak shape

The presence of ammonia in the mobile phase was found also to be effective for improving the peak shape. The plate numbers for tetrahydrothiophene at 0, 3, 5, 7 and 10% ammonia at 90°C were 186, 1668, 2019, 2030 and 2253, respectively. A similar trend was observed on a solid copper(II) stearate column for all the other samples. Pure nitrogen as carrier gas gave broad and severely tailed peaks irrespective of the sample size, which indicates that the reaction expressed by eqn. 7 is not so rapid as that expressed by eqn. 2 and/or the adsorption isotherm is non-linear. Evidently a pure nitrogen mobile phase system is not suitable for the separation of these samples. A very high concentration of ammonia, however, reduced the retention times of all samples so much that poor sample selectivity resulted, though the peaks were still sharp and symmetrical.

Effect of column temperature on retention

In the temperature range where copper(II) stearate is a solid, the retention of samples was reduced and the peak shape was improved with increasing column temperature. However, short retention times caused poor sample selectivity for early eluting samples.

It is known that copper(II) stearate behaves as a liquid crystal in the temperature range of 115–120°C¹³. The effects of column temperature on retention when pure nitrogen and ammonia-containing nitrogen were used as the mobile phase are shown in Fig. 3a and b, respectively. Similar temperature dependences were observed in each mobile phase system, indicating that another retention mechanism such as partition of samples into the liquid crystal structure must be taken into account in addition to ligand-exchange reaction. Although the presence of ammonia in the mobile phase was found also to affect the retention and peak shape in this temperature region, linearity between k' and $1/[\text{NH}_3]$ was not established. This suggests that ammonia is responsible not only for the ligand-exchange reaction but also for the partition of samples between the mobile phase and the liquid crystalline stationary

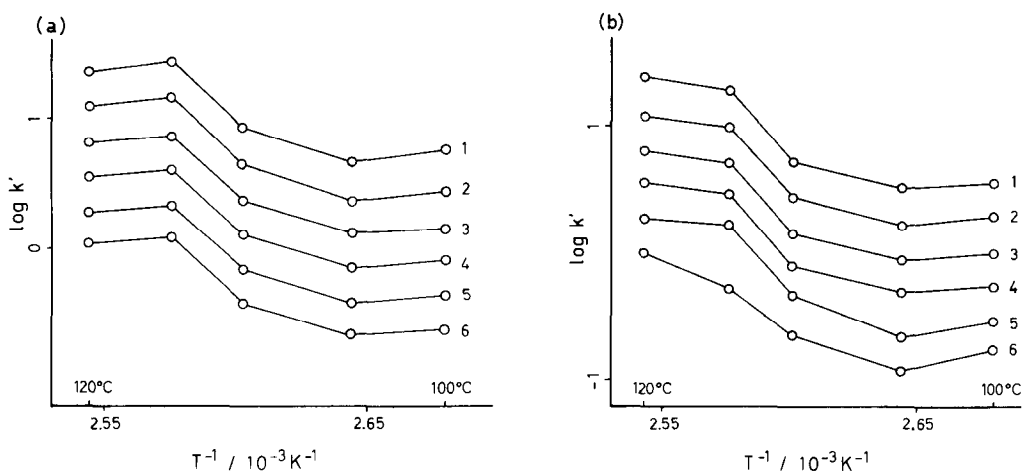


Fig. 3. Effect of column temperature on retention. Mobile phases: a, pure nitrogen; b, nitrogen containing 10% ammonia. Flow-rate: 20 ml/min. Samples: 1 = di-*n*-butyl sulphide; 2 = diisobutyl sulphide; 3 = di-*n*-propyl sulphide; 4 = ethyl *n*-propyl sulphide; 5 = diethyl sulphide; 6 = ethyl methyl sulphide.

phase. The liquid crystalline stationary phase also gave sharp and symmetrical peaks, indicating that the partition isotherm is linear and the partition process is rapid enough compared with the ligand exchange.

Separation of sulphides

As discussed above, both the concentration of ammonia and the column temperature are important factors for the separation of sulphides. Since the liquid crystalline stationary phase showed a high efficiency and appropriate retention times for highly volatile samples such as C_2 – C_4 sulphides, a good separation was obtained under these conditions as shown in Fig. 4. The longer retention of tetrahydrothiophene than those of diethyl sulphide or other C_4 sulphides indicates that the retention is affected by the steric environment around the sulphur atoms of the sulphides.

The liquid crystalline stationary phase was found also to be efficient for the separation of other sulphides. Fig. 5 shows a chromatogram of some C_5 sulphides. Cyclic sulphides such as pentamethylene sulphide or 2-methyltetrahydrothiophene also showed longer retention times than acyclic C_5 sulphides, as in the case of C_4 sulphides.

The solid copper(II) stearate stationary phase gave good separations of C_6 , C_7 or C_8 sulphides, as shown in Figs. 6, 7 and 8, respectively. These samples were strongly retained on a liquid crystalline stationary phase and were not eluted from the column in a reasonable analysis time, though a good selectivity was expected. On the other hand, the column operated at a temperature slightly lower than that of the phase transition showed appropriate retention times without greatly reducing the sample selectivity.

Sample selectivity

As described above, the ligand-exchange equilibrium is important in determining the retention, and the basicity of the sulphur atom of a sulphide, which is a

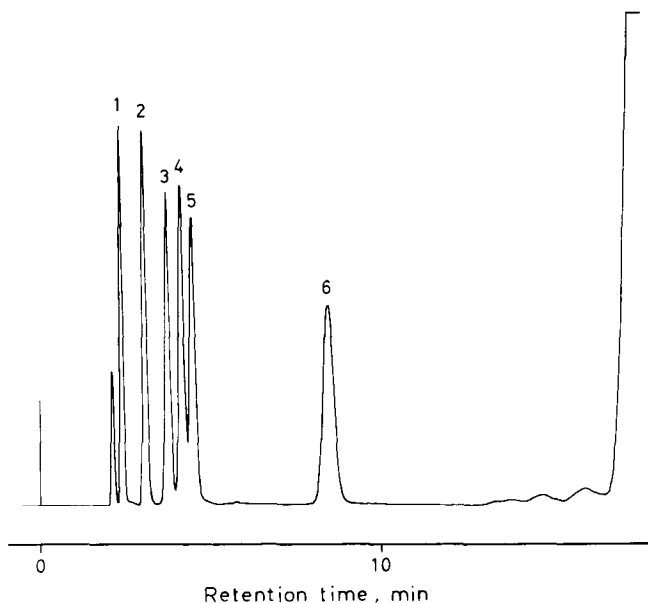


Fig. 4. Separation of C_2 - C_4 sulphides. Column temperature: 115°C . Mobile phase: nitrogen containing 7% ammonia. Flow-rate: 20 ml/min. Peaks: 1 = dimethyl sulphide; 2 = ethyl methyl sulphide; 3 = diethyl sulphide; 4 = methyl isopropyl sulphide; 5 = methyl *n*-propyl sulphide; 6 = tetrahydrothiophene.

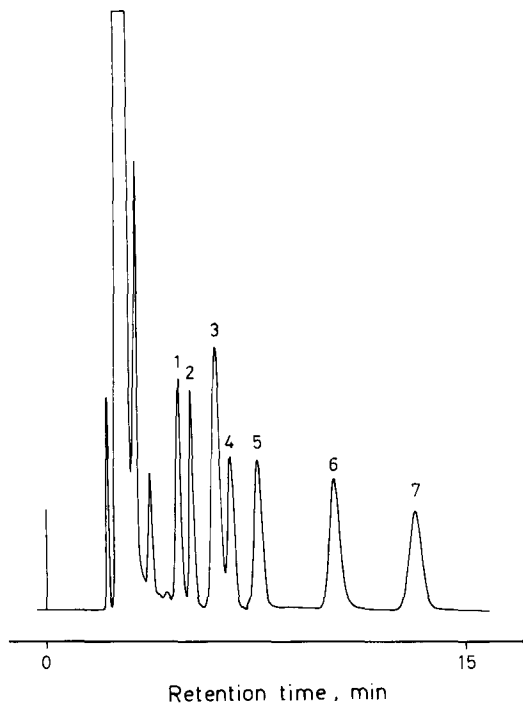


Fig. 5. Separation of C_5 sulphides. Conditions as in Fig. 4. Peaks: 1 = methyl *tert.*-butyl sulphide; 2 = methyl isobutyl sulphide and methyl *sec.*-butyl sulphide; 3 = ethyl isopropyl sulphide; 4 = ethyl *n*-propyl sulphide; 5 = methyl *n*-butyl sulphide; 6 = 2-methyltetrahydrothiophene; 7 = pentamethylene sulphide.

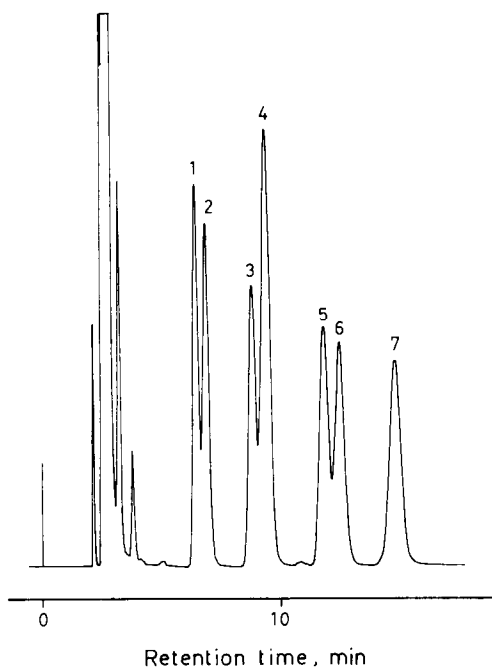


Fig. 6. Separation of C_6 sulphides. Column temperature: 110°C . Mobile phase: nitrogen containing 3% ammonia. Flow-rate: 20 ml/min. Peaks: 1 = diisopropyl sulphide; 2 = ethyl *tert.*-butyl sulphide; 3 = *n*-propyl isopropyl sulphide; 4 = ethyl isobutyl sulphide and ethyl *sec.*-butyl sulphide; 5 = di-*n*-propyl sulphide; 6 = ethyl *n*-butyl sulphide; 7 = *n*-amyl methyl sulphide.

measure of the ability to undergo copper(II)-sulphur coordination, is thought to be responsible for the elution order. However, since the basicities of dialkyl sulphides are not much different from one another in an aqueous phase¹⁴, there should be other factors that affect the elution order.

Based on the chromatograms obtained, the factors responsible for the retention order are considered to be as follows.

(1) *Steric hindrance around the sulphur atom.* Branching of the alkyl group inhibits the copper(II)-sulphur coordination and causes weak retention. The retention time becomes shorter as the alkyl group becomes bulkier and/or the branching is nearer to the sulphur atom. On the other hand, the sulphur atom of a di-*n*-alkyl or a cyclic sulphide is less hindered, and so such sulphides show longer retention times. The order of elution of butyl alkyl sulphide isomers demonstrates this effect; the *tert.*-butyl isomer is eluted first and the *n*-butyl isomer last. The longer retention times of cyclic sulphides such as tetrahydrothiophene, pentamethylene sulphide or 2-methyltetrahydrothiophene than those of the other sulphides having the same carbon number can be explained similarly.

(2) *The position of the sulphur atom.* For sulphides having the same carbon number and which possess two *n*-alkyl groups, that which has the longest alkyl chain is most strongly retained. For example, di-*n*-propyl sulphide, ethyl *n*-butyl sulphide and methyl *n*-amyl sulphide are eluted in this order as shown in Fig. 6. Since the

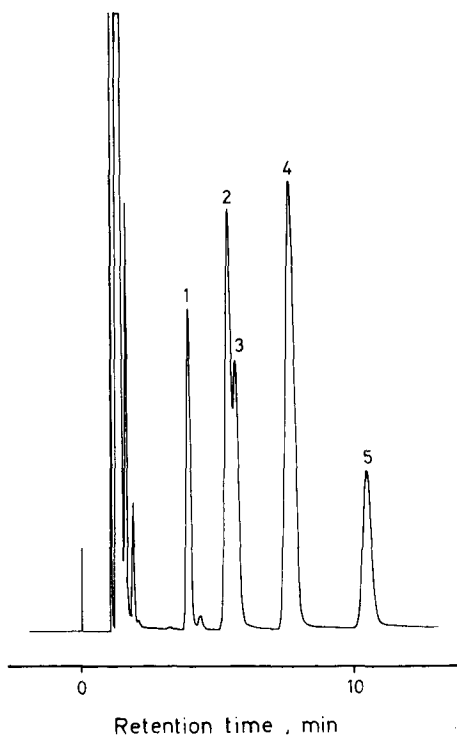


Fig. 7. Separation of butyl propyl sulphides. Conditions as in Fig. 6. Peaks: 1 = *tert.*-butyl isopropyl sulphide; 2 = *tert.*-butyl *n*-propyl sulphide and *sec.*-butyl isopropyl sulphide; 3 = isobutyl isopropyl sulphide; 4 = isobutyl *n*-propyl sulphide, *sec.*-butyl *n*-propyl sulphide and *n*-butyl isopropyl sulphide; 5 = *n*-butyl *n*-propyl sulphide.

basicities of the sulphur atoms of these three sulphides are expected to be almost the same, the differences in retention should be due to the differences in hydrophobic interaction between the larger alkyl chain of the sample and the stearate moiety in the stationary phase.

(3) *Vapour pressure of samples.* Since the retention of a sample molecule is based on its gas–solid distribution, the difference in the vapour pressures of samples at a given column temperature is an important factor in determining the elution order. Thus the volatility or the molecular weight of a sample is responsible for retention. The elution order of homologous series such as di-*n*-alkyl sulphides was the same as the order of their carbon numbers.

Since the factor 1 is based on the nature of the sample, its contribution to the elution order in an LEGC system is expected to be the same as in an LELC system when the same metal ion species is used as the stationary phase. On the contrary, the other two factors are characteristic of this LEGC system; the effectiveness of factor 2 is limited to the cases when metal stearates or other similar stationary phases having a hydrocarbon part are used as the stationary phase, while factor 3 is valid for any type of LEGC system. Considering these advantageous factors, the copper(II) stearate–ammonia system is expected also to be effective for the separation or char-

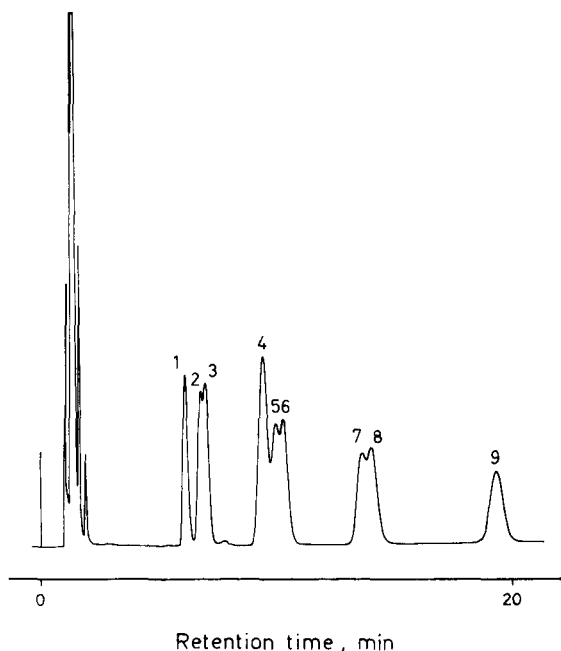


Fig. 8. Separation of dibutyl sulphides. Conditions as in Fig. 6. Peaks: 1 = di-*tert.*-butyl sulphide; 2 = *sec.*-butyl *tert.*-butyl sulphide; 3 = isobutyl *tert.*-butyl sulphide; 4 = di-*sec.*-butyl sulphide and *n*-butyl *tert.*-butyl sulphide; 5 = isobutyl *sec.*-butyl sulphide; 6 = diisobutyl sulphide; 7 = *n*-butyl *sec.*-butyl sulphide; 8 = *n*-butyl isobutyl sulphide; 9 = di-*n*-butyl sulphide.

acterization of other organic sulphur compounds. The application of this technique to the separation of aromatic sulphides will be reported in the following paper.

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