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LIGAND-EXCHANGE GAS CHROMATOGRAPHIC SEPARATION OF AROMATIC SULPHIDES

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SUMMARY

A column packed with copper(II) stearate coated on a diatomaceous support gave a good separation of aryl alkyl sulphide homologues under mild conditions. Good selectivity was also obtained on a column packed with copper(II)-modified Porasil E or F; the use of the latter as a packing material in a capillary column was particularly effective for the separation of positional isomers. Ammonia was effective as a mobile phase ligand, resulting in sharp peaks and suitable retention times. The length and the degree of branching of the alkyl chain of a sample as well as the position of substituents in the benzene ring were found to affect the elution order. The preparation and the use of a Porasil packed column is briefly described.

INTRODUCTION

Ligand-exchange chromatography (LEC) is now commonly employed, and has been adopted for the separation of amines, phenols, amino acids and recently organic sulphur compounds[1–10]. Although liquid chromatographic (LC) systems are commonly utilized in LEC, ligand-exchange gas chromatography (LEGC) is expected also to be suitable for the separation of volatile samples. In the course of our investigations on LEC, LEGC has been found to be applicable to the separation of aliphatic and aromatic amines and dialkyl sulfides[11–14]. The purpose of this study is to demonstrate the advantage of LEGC by applying it to the separation of some aromatic sulphides, which has not been achieved by ligand-exchange or common LC techniques.

There are some limitations on the selection of the mobile phase ligand in an LEGC system; in particular, volatility and interference with detection must be taken into account. In the present study, ammonia, which had given satisfactory results in the separation of dialkyl sulphides, was employed.

The choice of the ligand species in the stationary phase is also an important factor. Since metal stearates, despite their low stability at high temperatures, were efficient and selective in the previous studies, the corresponding copper(II) salt which gave the best results for amines and dialkyl sulphides was mainly used with the

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manganese(II) salt as the reference. In view of the relatively low volatility of the sample sulphides, some chemically bonded silica gels were also prepared as thermally stable stationary phases, which could be useful as capillary column packings in further applications.

The use of chemically bonded supports is established in LC systems, but little has been reported on the use of such materials in GC systems. Since diatomaceous supports or conventional porous silica gels as the starting material for surface modification gave unsatisfactory results such as severe peak tailing or irreversible adsorption, silica gels of low surface activity were employed, *i.e.*, Porasil E or F, GC grade silica gels of the smallest surface area commercially available. Although many types of bonded silica gels for LC are known, diaminosilylation of silica was exclusively used for the synthesis of LEGC bonded phases. It results in one of the simplest structures for immobilizing metal ions by coordination, and affords basic information on the retention characteristics of such phases.

With the expectation that a comparison of the retention data obtained on LEGC columns with those obtained on columns containing conventional liquid phases would give some information on the sample selectivity of LEGC systems, two liquid phases were used as the reference: silicon OV-101 as a typical non-polar liquid phase and polyethylene glycol 20M (PEG 20M) as a polar one.

A large number of reports have been published on the preparation or application of capillary columns in GC, of which open-tubular coated or cross-liked columns are the most popular[15]. It is apparent, however, that the retention on an LEGC column is based on a gas–solid distribution process, and the presence of a liquid or a pseudo-liquid in the stationary phase is unsuitable for the study of capillary LEGC systems. Furthermore, open-tubular columns generally do not offer a sufficient sample capacity for gas–solid distribution systems. One way to combine both the high efficiency of capillary columns and the high selectivity of LEGC is to employ packed capillary columns, for which thermally stable packing materials are essential. The preparation and some applications of a Porasil-packed capillary column are first described in this paper. The introduction of such columns will give valuable information on LEC and capillary column technology.

EXPERIMENTAL

Gas chromatography

Two GC systems were used: an Hitachi Model 023 (Hitachi Seisakusho, Tokyo, Japan) equipped with a hydrogen flame ionization detector, for packed columns (except for Porasil-packed columns), and a Shimadzu Model GC8APF (Shimadzu, Kyoto, Japan) equipped with a dual flame ionization detection system for Porasil-packed and capillary columns. The flow-rate and column inlet pressure for packed columns were 20 ml/min and 0.95–1.20 kg/cm^2, respectively. The column temperature was varied in the range of 100–180°C.

Ammonia-equilibrated nitrogen (3, 5, 7 and 10%; Taiyo Sanso, Kanagawa, Japan) and pure nitrogen were used as the mobile phase.

Samples and chemicals

All chemicals were of the highest grade available, purchased from various sup-

pliers. Copper(II) stearate (Wako Pure Chemical, Osaka, Japan) was recrystallized from chloroform, and manganese(II) stearate (Nakarai Chemicals, Kyoto, Japan) from benzene. N-(3-Trimethoxysilylpropyl)ethylenediamine and hexamethyldisilazane were distilled prior to use. All solvents were dried according to the usual methods.

All sample sulphides except thioanisole were prepared in our laboratory according to known methods, and were purified by distillation. Thioanisole was used as received. The samples were diluted in hexane (1%, v/v) and 1 μl of each solution was injected.

Column preparation

Copper(II) stearate, 5% (w/w), was coated on Chromosorb G AW DMCS (80–100 mesh) (Johns-Manville, Denver, CO, U.S.A.) by vacuum evaporation. The packing material was resieved and packed in a 3 m × 4 mm I.D. glass column. Columns of manganese(II) stearate, silicon OV-101 (Nishio Industry, Tokyo, Japan) and PEG 20M (Gasukuro Kogyo, Tokyo, Japan) were prepared similarly. A column of PEG 20M coated with 3% (w/w) potassium hydroxide was also prepared (PEG 20M/KOH).

Gas chromatography grade Porasil, type E or F (Waters Assoc., Milford, MA, U.S.A.), was sieved to 80–100 mesh and dried *in vacuo* at 120°C for 6 h before use. For the preparation of packed columns, Porasil was modified in batch processes. An amount of 10 g of Porasil was added to 100 ml of a solution of 5% (w/w) N-(3-trimethoxysilylpropyl)ethylenediamine in toluene, and the mixture was refluxed for 12 h. The aminated Porasil was filtered off, washed with toluene and dried *in vacuo*. End-capping was carried out by treating the aminated silica with 100 ml of a solution of 5% (w/w) hexamethyldisilazane in toluene under reflux for 6 h. The modified Porasil was filtered off, washed with toluene and then methanol and air-dried (N2-Porasil E/F). Copper(II) was loaded on N2-Porasils by rinsing the latter with a 0.01 *M* methanolic solution of copper(II) nitrate. The N2-Porasils and copper(II)-modified Porasils (Cu-Porasil E/F) were dried *in vacuo*, resieved to 80–100 mesh and packed in 1.5 m × 2.6 mm I.D. columns.

A Porasil-packed capillary column was prepared in the following manner. Dried Porasil (Type F, unmodified) was packed in a Pyrex glass tube (7 mm O.D., 2.5 mm I.D.), and the tubing was drawn to a ratio of 100:1 in length (0.7 mm O.D., 0.25 mm I.D.) on a Shimadzu Model GDM-1B glass-drawing apparatus. A 20-m portion of the coiled material was cut off and dried *in vacuo* in a desiccator at room temperature. After filling the column with degassed toluene, diaminosilylation of Porasil was performed by passing a large excess of a degassed solution of N-(3-trimethoxysilylpropyl)ethylenediamine in toluene through the column which was placed in a water-bath at 75°C. A nitrogen pressure of 15 kg/cm^2 had to be applied to the solution at the inlet of the column so that the reaction products were eluted from the other end of the column. A similar process was employed for washing the column with toluene or methanol, end-capping with a solution of hexamethyldisilazane in toluene or loading of copper(II) with a solution of copper(II) nitrate in methanol. After washing with methanol, the column was dried in a stream of nitrogen and then *in vacuo*.

RESULTS AND DISCUSSION

Retention on a copper(II) stearate column

The sample sulphides were strongly retained on the copper(II) stearate column and were not eluted when pure nitrogen was used as the mobile phase. However the use of ammonia-containing nitrogen as carrier gave suitable retention times. As discussed previously[13,14], the presence of ammonia in the mobile phase as a competitive ligand strongly affects the sample retention. The effect of ammonia on the capacity factor, k', when solid copper(II) stearate was used as the stationary phase is illustrated in Fig. 1. The slopes of the linear plots correspond to the contributions of ligand exchange to the sample retention, and the intercepts to those of the hydrophobic interactions between the alkyl or aryl group of the sample and the stearate moiety of the stationary phase. From these results, the contribution of ligand exchange to the sample retention is considered to be relatively small compared with that for amines[13] or dialkyl sulphides[14]. This means that the complex-forming abilities or gas-phase basicities of the sulphur atoms of the sulphides are rather low, although the application of the LEGC technique to the separation of such sulphides still gave good results.

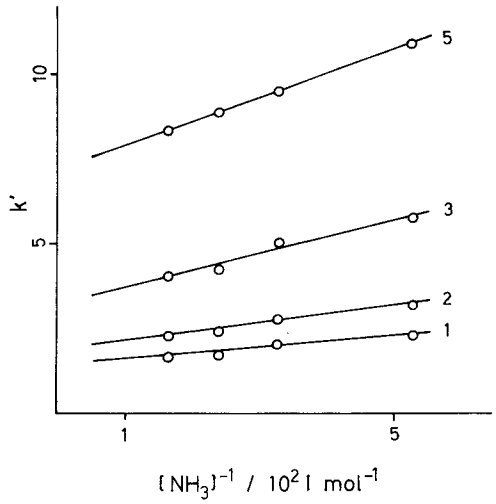

Fig. 1. Effect of ammonia in the mobile phase on retention. Column: copper(II) stearate, 5% (w/w) on Chromosorb G AW DMCS (80–100 mesh), 3 m × 4 mm I.D.; temperature, 100°C. Mobile phase: nitrogen-containing ammonia; flow-rate, 20 ml/min. For sample numbers see Table I.

The copper(II) stearate column acted as a liquid crystalline stationary phase in the temperature range of 115–120°C as shown in Fig. 2. Although it showed a high efficiency, the retention times were much longer than those obtained on a solid copper(II) stearate column, with no improvement in sample selectivity, making impractical its use in this temperature region for the separation of samples.

The separation of homologous series such as phenyl alkyl sulphides or benzyl alkyl sulphides was successfully achieved on a solid copper(II) stearate column as shown in Fig. 3.

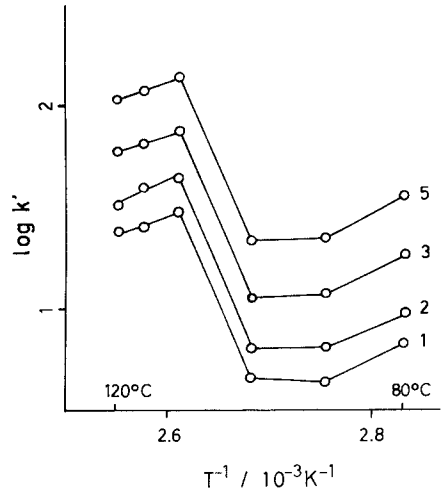

Fig. 2. Effect of column temperature on retention. Mobile phase: nitrogen containing 10% ammonia; flow-rate, 20 ml/min. Other details as in Fig. 1.

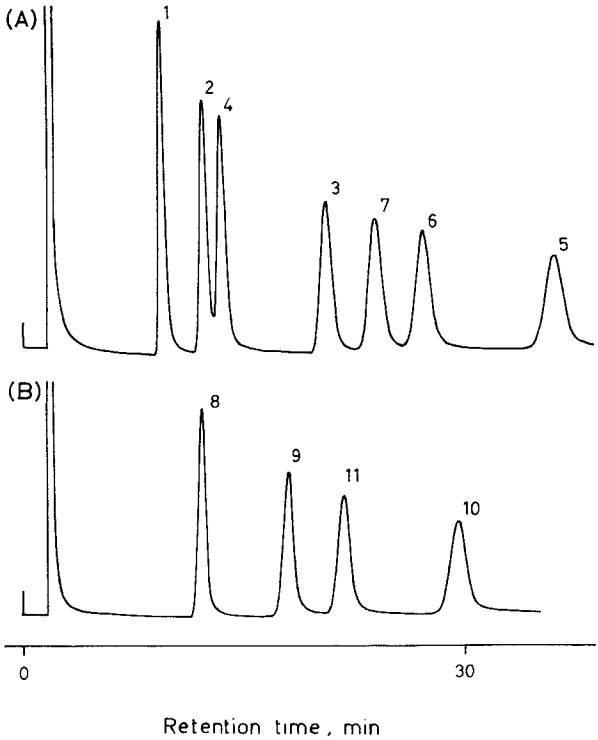

Fig. 3. Separation of phenyl alkyl sulphides (a) and benzyl alkyl sulphides (b). Column as in Fig. 1. Mobile phase: nitrogen containing 7% ammonia; flow-rate,. 20 ml/min. For peak identification see Table

TABLE I

CAPACITY FACTORS OF ARYL ALKYL SULPHIDES ON VARIOUS STATIONARY PHASES

Column dimensions: 1.5 m × 2.6 mm I.D. for Cu-Porasil, 3 m × 4 mm I.D. for the others.

No.	*Sample*	*Copper(II) stearate*	*Manganese(II) stearate*	*Cu-Porasil E*	*Cu-Porasil F*	*Silicon OV-101*	*PEG 20M/ KOH*
		Temperature (°C)					
		80	*100*	*150*	*150*	*150*	*180*
		Ammonia (%)					
		5	*10*	*10*	*10*	*0*	*0*
1	Phenyl methyl sulphide	6.92	8.18	23.22	6.46	8.86	9.60
2	Phenyl ethyl sulphide	9.86	11.05	37.14	10.20	10.07	10.38
3	Phenyl *n*-propyl sulphide	18.78	19.30	68.92	18.58	18.14	13.68
4	Phenyl isopropyl sulphide	11.33	12.53	52.37	14.06	13.69	9.65
5	Phenyl *n*-butyl sulphide	37.99	35.13	136.86	35.71	28.66	19.00
6	Phenyl isobutyl sulphide	26.76	26.28	109.30	29.09	23.52	15.16
7	Phenyl *sec.*-butyl sulphide	22.94	23.20	90.84	27.03	21.93	13.52
8	Benzyl methyl sulphide	11.00	10.80	53.90	13.11	13.07	12.79
9	Benzyl ethyl sulphide	18.43	16.63	100.04	23.20	18.59	15.55
10	Benzyl *n*-propyl sulphide	34.14	28.20	184.75	41.43	27.97	20.35
11	Benzyl isopropyl sulphide	23.90	20.80	152.42	34.26	22.72	16.27
12	*o*-Tolyl methyl sulphide	13.77	12.95	39.27	10.60	14.10	12.90
13	*o*-Tolyl ethyl sulphide	19.66	17.05	62.51	16.52	18.28	13.47
14	*o*-Tolyl *n*-propyl sulphide	36.01	26.50	116.37	30.26	27.79	17.81
15	*o*-Tolyl isopropyl sulphide	20.61	18.38	84.42	22.03	22.79	12.33
16	*m*-Tolyl methyl sulphide	13.89	13.05	47.40	12.57	14.17	13.55
17	*m*-Tolyl ethyl sulphide	19.52	17.40	77.79	19.80	18.72	14.20
18	*m*-Tolyl *n*-propyl sulphide	37.30	30.33	144.97	36.49	27.09	18.95
19	*m*-Tolyl isopropyl sulphide	22.16	19.28	106.78	26.74	21.86	13.00
20	*p*-Tolyl methyl sulphide	14.26	13.15	50.67	12.97	14.17	13.08
21	*p*-Tolyl ethyl sulphide	20.47	17.88	84.04	20.86	18.72	14.12
22	*p*-Tolyl *n*-propyl sulphide	39.23	31.40	158.34	38.60	29.07	19.08
23	*p*-Tolyl isopropyl sulphide	23.83	20.55	119.82	29.09	21.86	13.49

Sample selectivity

Some retention values obtained on packed columns of copper(II) or manganese(II) stearate, copper(II)-modified Porasil E or F, silicon OV-101 and PEG 20M/KOH are listed in Table I. The GC conditions were adjusted so that similar k' values were obtained on each column, except for the Cu-Porasil E column. The latter gave relatively long retention times, and the selection of conditions was rather difficult. Columns packed with N2-Porasil E or F, not modified with copper(II), did not show significant retention of samples. A PEG 20M column containing no potassium hydroxide gave severely tailed peaks at long retention times and did not have enough efficiency. Retention data pertaining to these three columns are therefore not reported.

As for the retention of the samples on columns of metal stearates, the manganese(II) salt gave a narrow range of k' and relatively broad peaks compared with those obtained on copper(II) salts, indicating the superiority of the latter. The chromatograms of phenyl alkyl and benzyl alkyl sulphide mixtures on a solid manganese(II) stearate column resemble those in Fig. 3a and b, respectively, but the separation was not improved.

The two liquid phases showed different selectivities, seen most clearly with homologous pairs of ethyl and isopropyl aryl sulphides. Although the data in Table I indicate that the selectivity of silicon OV-101 for each homologous series is slightly better than that of PEG 20M/KOH, broad and tailed peaks led to insufficient separations. In addition, both columns showed a poor selectivity for isomers such as tolyl alkyl sulphides, especially for *m*- and *p*-isomers.

From the data in Table I, it can be concluded that the sample selectivity of LEGC stationary phases is comparable to that of silicon OV-101 if the contribution of ligand exchange is excluded. This is probably due to the relatively hydrophobic nature of these LEGC packing materials, in good agreement with the finding that columns packed with aminated Porasils which were not end-capped gave tailed peaks or irreversible adsorption of samples even in the absence of copper(II) ion. This fact also implies the importance of end-capping of aminated Porasils.

Table II compares the selectivities of two LEGC stationary phases and silicon OV-101 liquid phase, indicating that there are three factors which are responsible for determining the retention order of homologues or isomers.

(1) *The carbon number of the alkyl group.* The basicity of the sulphur atom of a sulphide, which is a measure of the complex-forming ability of the sulphide, is expected to increase as the alkyl group becomes larger. Probably the order of elution of the ethyl and isopropyl aryl sulphides is due to this effect. The same is also valid for the *n*-alkyl aryl sulphide homologous series; the separation factors obtained on both the LEGC stationary phases are greater than those on OV-101 liquid phase.

(2) *Branching of the alkyl group.* Branching of the alkyl chain causes steric hindrance to coordination, as demonstrated by the larger difference in separation factors between propyl or butyl aryl sulphides obtained on LEGC columns than on liquid phases.

(3) *Vapour pressure of samples.* The vapour pressures or boiling points of homologous series are of importance in determining their elution order. Although the difference in carbon numbers is expected to result in the differences in basicity as noted in (1), the effect of vapour pressure should additionally be taken into account.

TABLE II

SEPARATION FACTORS FOR HOMOLOGUES AND ISOMERS

Values were calculated from the data listed in Table I.

*Solute pair**		*Copper(II) stearate*	*Cu-Porasil E*	*Silicon OV-101*
1	2	1.425	1.599	1.137
2	3	1.905	1.856	1.801
3	5	2.023	1.986	1.580
8	9	1.675	1.856	1.422
9	10	1.852	1.847	1.505
12	13	1.428	1.592	1.296
13	14	1.832	1.862	1.520
16	17	1.405	1.631	1.321
17	18	1.911	1.743	1.553
20	21	1.435	1.659	1.321
21	22	1.916	1.884	1.553
4	3	1.658	1.316	1.325
6	5	1.420	1.252	1.129
7	6	1.167	1.203	1.073
11	10	1.428	1.212	1.231
15	14	1.747	1.378	1.219
19	18	1.683	1.358	1.330
23	22	1.646	1.321	1.330

* For sample numbers, see Table I; for each pair, the sample having smaller retention time is given first.

Copper(II)-modified Porasil columns showed a good selectivity for positional isomers, though a higher column temperature was needed to improve peak shapes than in the case of copper(II) or manganese(II) stearate columns. Chromatograms of tolyl alkyl sulphides on a Cu-Porasil E packed column are shown in Fig. 4, where the differences in retention of the positional isomers is apparent. A column of Cu-Porasil F showed similar results but all retentions were smaller than those obtained on the Cu-Porasil E column under the same conditions. This indicates the difference in the nature of the surfaces of the two bonded phases. The selectivities for tolyl alkyl sulphides on some stationary phases are summarized in Table III, where the large separation factors indicate the advantage of the Cu-Porasil phase.

Separation of isomers

As described above, copper(II)-modified Porasils were expected to give a good separation of tolyl alkyl sulphide isomers. Since the use of small bore packed columns, so-called micro-packed columns, was unsuccessful, capillary columns packed with Porasil were employed. Only Type F was used as the packing material, because the Cu-Porasil E packed column gave extremely long retention times, which should be avoided when using capillary columns. Satisfactory separations of isomers of tolyl alkyl sulphides were obtained on a Porasil F packed capillary column. A typical chromatogram is shown in Fig. 5.

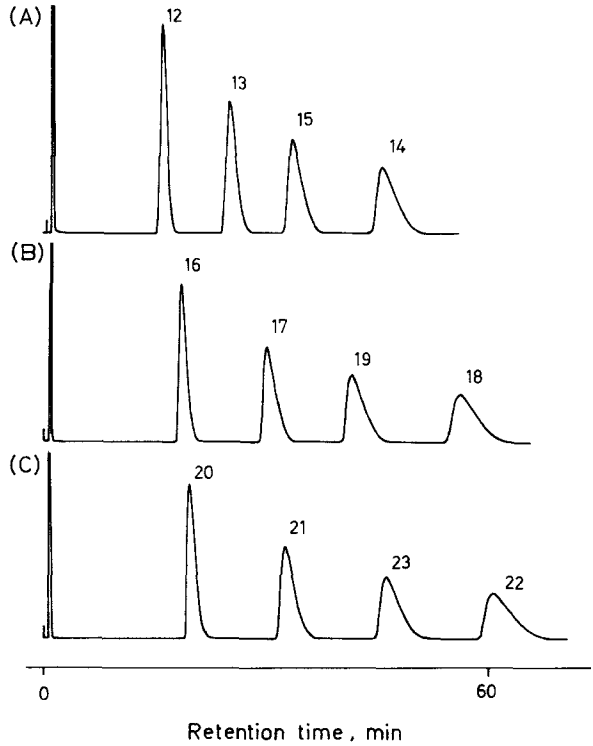

Fig. 4. Separation of *o*-tolyl alkyl sulphides (a), *m*-tolyl alkyl sulphides (b) and *p*-tolyl alkyl sulphides (c). Column: Cu-Porasil E 1.5 m × 2.6 mm I.D.; temperature, 150°C. Mobile phase: nitrogen containing 10% ammonia; flow-rate, 20 ml/min. For peak identification see Table I.

TABLE III

SEPARATION FACTORS OF TOLYL ALKYL SULPHIDE ISOMERS

Details as in Table II.

Solute pair	*Copper(II) stearate*	*Cu-Porasil E*	*Silicon OV-101*	*PEG 20M/ KOH*
12 16	1.009	1.207	1.005	1.050
16 20	1.027	1.069	1.000	1.034*
13 17	1.007*	1.224	1.024	1.054
17 21	1.049	1.080	1.000	1.006*
14 18	1.036	1.246	1.046	1.064
18 22	1.052	1.092	1.000	1.007
15 19	1.075	1.265	1.042*	1.054
19 23	1.075	1.122	1.000	1.038

* The elution order was reversed in this case.

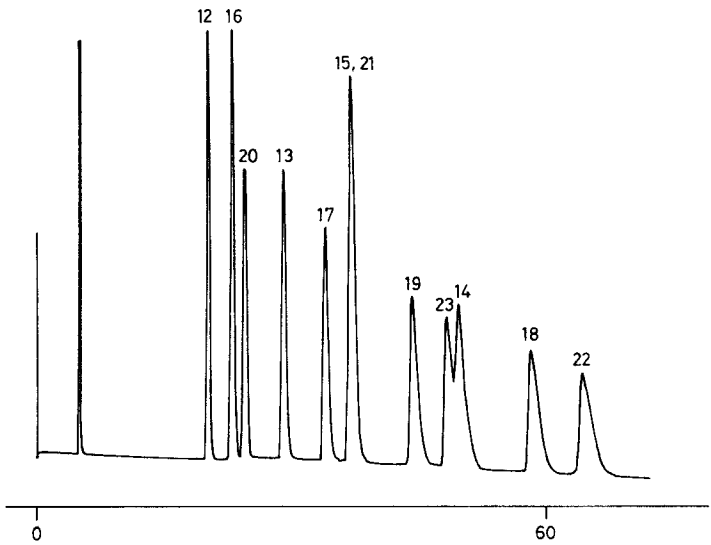

Fig. 5. Separation of positional isomers of tolyl alkyl sulphides. Column: Cu-Porasil F capillary, 20 m × 0.25 mm I.D.; temperature 160°C. Mobile phase: nitrogen containing 7% ammonia; linear velocity, 6.7 cm/s. For peak identification see Table I.

The elution order of the positional isomers was *o*- < *m*- < *p*- in all cases. Since the two liquid phases showed only poor selectivity and the non-copper(II)-modified N2-Porasil phases showed much shorter retention times than those obtained on Cu-Porasil, the good selectivity for positional isomers obtained in this study may be regarded as an advantage of LEGC on a Cu-Porasil packed capillary column. The methyl substituent of the tolyl groups is considered to determine the retention order in two ways.

(a) *Steric hindrance around the sulphur atom.* The effect of the methyl substituent is much greater in the case of *o*-isomers than in the cases of *m*- or *p*-isomers, essentially as in the case of branching of the alkyl group.

(b) *Basicity of the sulphur atom.* The difference in the boiling points of *m*- and *p*-tolyl alkyl sulphide isomers is so small that the OV-101 column was unable to distinguish between these two solutes. The results obtained on the PEG 20M/KOH column are a reflection of the small difference in their polarities, the elution order being the reverse of that observed on the other stationary phases. Since it is very unlikely that substitution at the *m*-position results in much more steric hindrance to the sulphur atom than that occurring at the *p*-position, the longer retention time of the *p*-isomer may be attributed to the difference in the basicity of the sulphur atom between the *m*- and *p*-isomers.

The use of a Porasil F packed capillary column is expected to be effective not only for the separation of aryl alkyl sulphides but also for other complex-forming substances. Further investigations on the characterization and application of the LEGC technique using this type of column are now in progress.

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