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Application of dithiocarbamate resin-metal complexes as stationary phases in gas chromatography

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ABSTRACT

A chelating resin with dithiocarbamate functional groups to which silica gel was used as a matrix and silanes were used with diamino functional groups as a spacer was synthesized. The structure and the conversion of functional groups of the resin were confirmed by IR spectra and elemental analysis. The influence of pH on the adsorption of the resin for metal ions was also examined. The resin under optimum pH conditions formed a 1:1 metal complex with copper ion. The affinity of metal ions toward the synthesized resin decreased in the order Hg(II) > Cu(II) > Cd(II) > Zn(II). The resin exhibited efficient complexation of transition metal cations. The cadmium, copper and zinc complexes were investigated for application as stationary phase for the gas chromatographic analysis of dialkyl sulphides. The material was packed in a 2.1 m × 3.2 mm I.D. spiral glass column. Factors affecting the retention and sample selectivity were also studied. A shorter retention time and sharp peaks were obtained when ammonia was introduced into the mobile phase. At an oven temperature of 100°C, a flow-rate of 60 ml min^{-1} and use of a flame ionization detector, the analysis of dialkyl sulphides showed that the copper resin complex as the stationary phase gave the best results. The stationary phase was also used for the separation of dialkyl sulphide from a hydrocarbon mixture.

INTRODUCTION

Dithiocarbamates and their derivatives are valuable reagents for the separation and photometric determination of heavy metals. Previous literature on their analytical applications is extensive [1]. The immobilization of such groups, either on a polymer or on a silica matrix, can convert them into useful metal-chelating sorbents. These can be used for the selective removal of heavy metal ions from aqueous solutions [2] and, in particular, for ligand-exchange chromatography (LEC). LEC is a process in which complex-forming compounds are separated through the formation and breaking up of labile coordinate bonds to a central metal atom, coupled with partitioning between a mobile and a stationary phase. It separates ligands by causing them to change places around metal ions. The exchange can occur in either the stationary or the mobile phase.

LEC is one of the most powerful techniques among the variety of commonly used separation methods for resolving complex-forming substances. Much work has been done previously since its introduction in the early 1960s on the separation of isomers or homologues of amines, phenols, amino acids and other organic ligands containing nitrogen or oxygen atoms [3]. Some limitations in operating an LEC system through use of a liquid mobile phase exist, even though many types of samples or stationary phase can be selected and modification of the mobile phase is easy and effective. Additionally, detection is sometimes difficult if a UV-visible detector is being used. A stronger complexing group, dithiocarbamates, was introduced in this work into silica as the LEC sorbent, as a result of taking into account these disadvantages. So far, only a few workers have used the potential of dithiocarbamate resins as LEC sorbents [4,5]. The mobile

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phase they used was, however, a liquid phase. Although the main principle of LEC is valid both for liquid chromatography in all its versions and for gas chromatography, the latter technique often cannot employ the same coordination systems. In liquid chromatography, solvent molecules or specially added components of the mobile phase actively compete with the solute species for vacant positions in the coordination sphere of the complexing metal ion. A real ligand exchange thus proceeds in the moving chromatographic zone of each solute. In contrast, nitrogen, helium or the other inert gases used in gas chromatography as mobile phases are not able to displace ligands from their sorption complexes. Only extremely labile complexes that easily dissociate at moderate temperatures can therefore be employed in gas chromatographic systems [6].

The complexing behaviour and the stability of the synthesized resin were studied in this investigation. The feasibility of using metal-loaded sorbents as stationary phases for the separation of dialkyl sulphides with a gaseous mobile phase, namely ligand-exchange gas chromatography, was also investigated.

EXPERIMENTAL

Apparatus

Infrared spectra of the synthesized resin and its metal complexes in KBr were recorded in the range 4000–200 cm-' on an IR spectrophotometer (Perkin-Elmer 983). The electron paramagnetic resonance (EPR) spectra of the metal-resin complexes in the solid state were recorded at room temperature on an EPR spectrophotometer (Bruker ESP 300).

A gas chromatograph (Shimadzu Model GC-9A) equipped with a hydrogen flame ionization detector and integrator (Shimadzu Chromatopac C-R2AX) was used. Pure nitrogen and nitrogen containing 5 and 10% (v/v) of ammonia were used as carrier gases at flow-rates in the range 20-90 $\mathrm{mL\,min^{-1}}$. The column temperature varied in the range 70–100°C.

Chemicals

Most chemicals were of analytical-reagent grade from Merck (Darmstadt, Germany). Dialkyl sulphides were supplied by Aldrich (Milwaukee, WI, USA).

Synthesis of sorbents

Silica gel (50 mesh) was ground, sieved and refluxed in 2-propanol for 2 h, then washed successively with water and acetone. A solution of N-[3-(trimethoxy silyl)propyl]ethylenediamine (5 ml) in toluene (100 ml) was added to this purified silica (4 g); after reaction at 75°C with acetic acid as catalyst for 3 h, the resulting modified silica was washed successively with 2-propanol, water and acetone and then dried overnight under vacuum at 60°C. A solution of carbon disulphide (10 ml) and potassium *tert.*-butoxide (6 g) in toluene (300 ml) was added to the above product. The mixture was stirred for 6 h at 60°C. The product was called S-DTC.

Preparation of metal-loaded sorbents

A 3-g amount of the synthesized resin was suspended in 0.1 *M* Cd(II), Cu(II), Hg(II) or Zn(II) solution (90 ml). Acetic acid-sodium acetate buffer (1 *M*, pH 5) (10 ml) was added and each mixture was mechanically shaken for 4 h. The metal-loaded phases were collected on glass filters and washed with pure water (> 16 MΩ, 100 ml) and dried for 2 h in a vacuum oven.

Analytical application

Gas chromatography was carried out on 2.1 m × 3.2 mm I.D. spiral glass columns which were packed under ultrasonic conditions with the synthesized resin metal complexes. The columns were conditioned for 5 h before measurements were taken.

RESULTS AND DISCUSSION

Characterization

The composition and structures of the synthesized resin were characterized after each step of the synthesis by elemental analysis and IR spectrometry. The functionality of ethylenediamine to the silica gel was 1.55 $\mathrm{mmol\,g^{-1}}$ and that of dithiocarbamate to the above product was 1.41 mmol g-i. The elemental analysis data are given in Table I.

The $\mathrm{p}K_\mathrm{a}$ values of the synthesized resin were determined by potentiometric titration and calculated by a modification of Bjerrum's method. The $\mathrm{p}K_\mathrm{a}$ values were 7.0 and 9.4 (Table II). By comparison with the $\mathrm{p}K_\mathrm{a}$ values of some protonated amine [7] and dithiocarbamate compounds [8], the former

TABLE I

ELEMENTAL ANALYSIS DATA OF CHELATING RESINS WITH SILICA GEL AS MATRIX

Resin	C		H (%)	N		S		EN group (mm01 g $^{-1}$)	DTC group (mmol g $^{-1}$)
	%	mmol g $^{-1}$		%	mmol g $^{-1}$	%	mmol g $^{-1}$		
S-EN	10.35	9.03	2.31	4.35	3.10	–	–	1.55	_
S-DTC	13.41	11.17	3.30	4.46	3.18	9.03	2.82	1.59	1.41

valve can be concluded possibly to be the dissociation constant of the NH_2^+ group and the latter the dissociation constant of the $-NCS_2H$ group of S-DTC resin. The results are reasonable as the steric hindrance is larger in the resin, even though the pK_a values for the resin are higher than those for the monomeric compounds.

The adsorption capacities of the resin for Cd(II), Cu(II), Hg(II) and Zn(II) were measured at various pH values and the results are shown in Fig. 1. At the optimum pH, the adsorption capacities of S-DTC for Cd(II), Cu(II), Hg(II) and Zn(II) were 0.63, 1.12, 3.06 and 0.43 mmol g $^{-1}$, respectively. The resin presumably formed a 1:1 metal complex with copper ion and water molecules might be ligands for the unsaturated coordination site of the copper ion. The affinity of metal ions toward the synthesized resin decreased in the order Hg(II) > Cu(II) > Cd(II) > Zn(II) on the basis of the sorptive capacity. This order was coincident with that for the analogous complexes of the monomeric dithiocarbamate in aqueous solution [8]. Hence the fixation of the dithiocarbamate group on the silica surface does not lead to substantial changes in the complexing properties of its functional groups. The relatively high uptake of mercury by the resin might be attributed to the additional complexing power of the two nitrogen atoms of the spacer. The capacity of the resin for each metal ion nearly approached saturation in the medium in the pH range 4-5, ex-

TABLE II

pK_a VALUES OF SOME PROTONATED AMINE AND DITHIOCARBAMATE COMPOUNDS

Species	pK_a	Species	pK_a
NH,+	9.24”	Me_2NCS_2H	3.66[b]
n-$BuNH_3$ +	10.60[a]	Et_2NCS_2H	4.04[b]
$Me_2NH_2^+$	10.77”	n-Pr_2NCS_2H	4.79[b]
$^+NH_3CH_2CH_2NH_3^+$ pK_1	6.95”	n-Bu_2NCS_2H	5.19[b]
	pK_2 9.93”		
NH_2^+ of S-DTC	9.4	$-NCS_2H$ of S-DTC	7.0

[a] Ref. 7.

[b] Ref. 8.

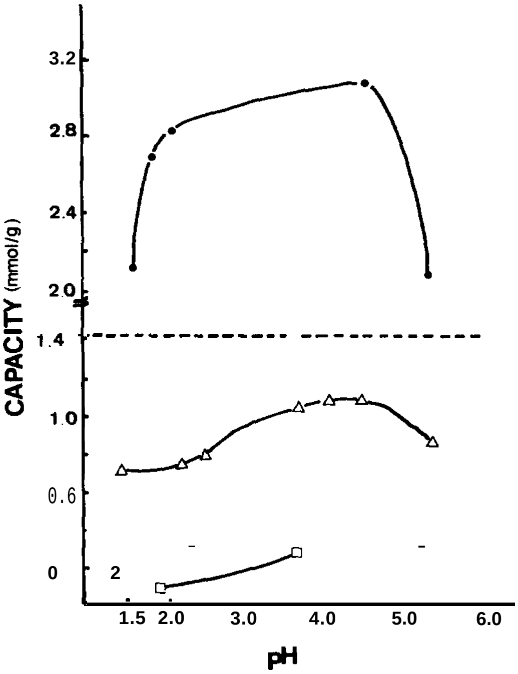
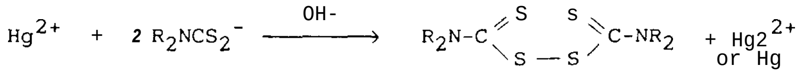


Fig. 1. Metal capacity as a function of pH for S-DTC resin. ● = Hg(II); △ = Cu(II); A = Cd(II); □ = Zn(II). Dashed line: functionality of S-DTC.

TABLE III

PRINCIPAL IR ABSORPTION BANDS (cm^{-1}) OF THE SYNTHESIZED RESIN AND ITS METAL COMPLEXES

Material	ν(OH)	ν(NH)	ν(CH)	δ(NH)	$\nu(N\text{-}CS_2) + \delta(CH_2)$	ν[(C)CN]	$\nu(CNC + CS_2)$
S-DTC	3433		2937	1618	1467	1096	959
Cu-S DTC	3447	3425		1639	1510	1109	
Hg-S-DTC	3446	3415		1629	1511	1095	



cept that for mercury, which approached saturation in the medium in the pH range 2-5. The metal ion capacity at pH > 5 obviously decreases, and the yellow colour of the resin turns greyish black. These effects might be due to the reducing power of the resin, undergoing the following reaction as reported by Dwyer and Mellor [9] for the reaction of Et_2DTC and Cu(II) at pH > 5 shown above. All the phenomena stated above appeared to occur with the metal ions tested. However, the potential difference of the oxidation-reduction pair is not as large for Cu(II), Cd(II) and Zn(II) as that for Hg (II).

Peak positions and assignments of the IR spectra are given in Table III. Coordination of dithiocarbamate causes $\nu(N\text{–}CS_2)$ to move towards higher wavenumbers and the $\nu(CNC + CS_2)$ peak intensity decreases. This is evidence for the coordination of the dithiocarbamate groups of the resin for each metal ion.

TABLE IV

PARAMETERS OF THE EPR SPECTRA OF Cu-S-DTC COMPLEXES AT VARIOUS pH VALUES

Condition	g Values			
pH 1.5	–	2.167	2.080	–
pH 2.8	2.335	2.144	2.077	–
pH 4.5	2.335	–	2.061	–
pH 5.3	2.335	–	2.031	2.012
Start at pH 1.5 then complexation with Cu(II) at pH 4.5	2.335	–	2.031	–

All the EPR spectra of the copper-loaded S-DTC resin complexes in Table IV were measured at room temperature. In the EPR spectra the g value decreased with increasing pH of the solution. The g value at a higher pH of the solution was coincident with that for the monomeric Cu–diethyldithiocarbamate complex (2.035) [10]. The value at a lower pH of the solution approached that of the Cu–polyiminoethylenedithiocarbamate complex (2.089) [11]. The result is rational, even though the latter was a one-dimensional polymer and the resin studied here was a three-dimensional polymer. At pH < 3, one additional very broad signal results with an average g value of 2.14. This must be caused by a weak Cu-Cu interaction resulting in the disappearance of the hyperfine structure. At pH > 2.5, $g_{\parallel}$ components with an average value of 2.335 and an $A_{\parallel}$ value of 107 could be found in their EPR spectra. This indicated the presence of Cu-O coordination [12]. The oxygen came from a water molecule. The results indicated that the presence of an unsaturated coordination of copper in the resin complexes was suitable for application in LEC.

The basic principle of LEC is that a metal ion is fixed on a solid support via a chelating ligand. The interaction occurring between a transition metal and the solute occurs with the formation of coordination bonds inside the coordination sphere of the complex-forming ion, provided that the coordination sphere of this ion is unsaturated. This applies even though various mechanisms could also be responsible for the interaction between the solute to be determined and LEC sorbents, such as ion exchange and hydrophobicity, in addition to ligand exchange. The specific coordination properties are

TABLE V

RESULTS OF DETERMINING THE STABILITY CONSTANTS OF COPPER-RESIN COMPLEXES (25°C)

Parameter	Value
pK_a (EN)	9.4
pK_a (DTC)	7.0
pH for complexation	5.5
pH for decomplexation	3.5
Log K_f	10.8

expected to play the most important role. As the complexation properties and complex equilibria can be characterized by the formation constant, for the calculation of the stability constants of the copper-resin complexes the following equation was used [13]:

$$\log K_{MR} = \log B'_j - nD_{pH}$$

where B'_j is the apparent cumulative protonation constant of the ligand, n is the number of protons bound to the ligand and D_{pH} is the pH for decomplexation. The protonation constant of the synthesized resin and the D_{pH} values of the copper-resin complex were investigated and are given in Table V. The stability constant of the copper-resin complex can then be calculated (Table V).

Analytical application of the synthesized resin in ligand-exchange chromatography

Thermal stability was studied with regard to the practical use of S-DTC metal complexes as stationary phases in gas chromatography. Thermogravimetric analysis (TGA) (Fig. 2) showed that S-DTC-Cu was very stable below 150°C. Mass loss occurred above 160°C, *i.e.*, at 164.15, 313.73 and 388.51°C, corresponding to N–CS_2 and Si-C bond cleavage and loss of surface silanol groups of silica gel, respectively [14]. The S-DTC-Cu phase was also found to be very stable for longer than 25 days with continuous heating at 90°C. These properties suggested the suitability of the resin for use as a stationary phase in gas chromatography for the separation of volatile compounds.

In LEC, a change in the concentration of ligands

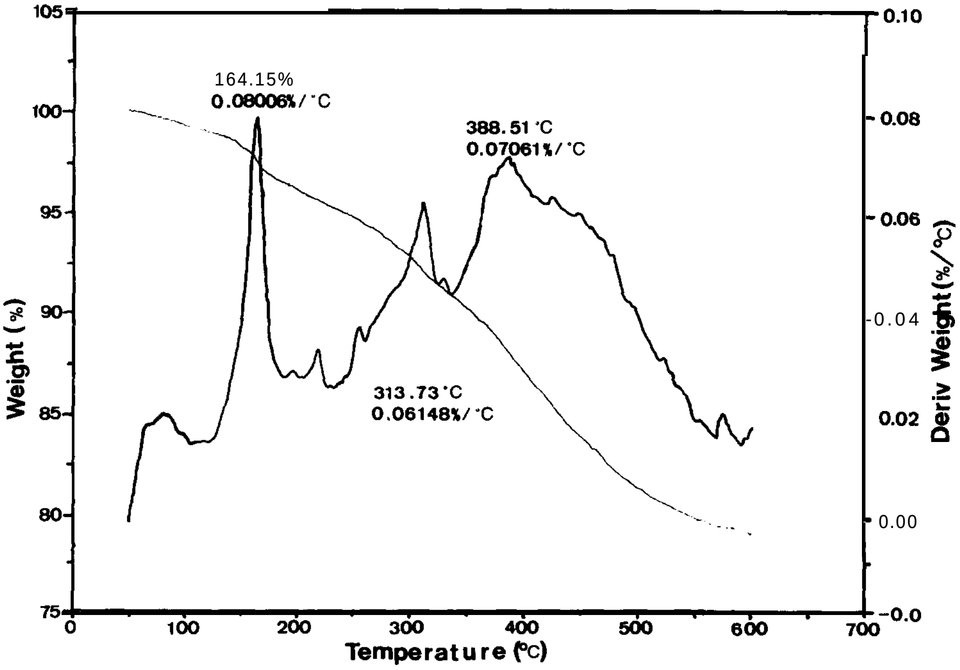


Fig. 2. TGA of S-DTC–Cu(II) complex.

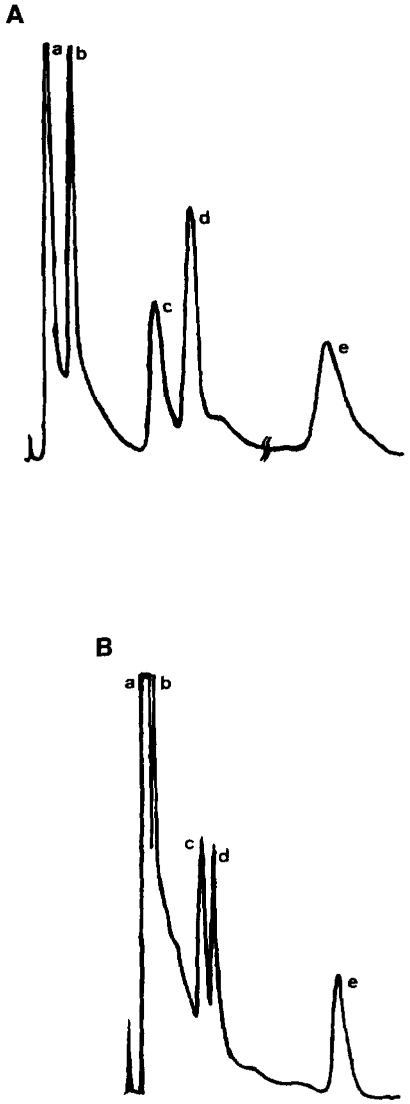


Fig. 3. Separation of mixtures. Stationary phase, S-DTC–Cu(II) complex; carrier gas, (A) nitrogen and (B) 10% (v/v) NH,-N,; flow-rate, 60 ml min^{-1}; oven temperature, 100°C; injection temperature, 155°C; sample, 2 μl, 1% in CS,. (A) Peaks: a = CS_2 (t_R = 2.2 min); b = dimethyl sulphide (t_R = 13.0 min); c = allyl methyl sulphide (t_R = 49.4 min); d = diethyl sulphide (t_R = 64.4 min); e = diisopropyl sulphide (t_R = 186.3 min). (B) Peaks: a = CS, (t_R = 2.2 min); b = dimethyl sulphide (t_R = 8.8 min); c = ally1 methyl sulphide (t_R = 28.9 min); d = diethyl sulphide (t_R = 33.4 min); e = diisopropyl sulphide (t_R = 86.0 min).

in the mobile phase had a pronounced effect on the retention of sample components. The presence of ammonia in the mobile phase drastically reduced the retention of samples. The concentration of ammonia tested was 5% and 10% (v/v) in nitrogen. The presence of ammonia in the mobile phase was found to affect not only the retention but also the peak shape (Fig. 3). A 10% concentration of ammonia in nitrogen was chosen as the mobile phase. The effects of flow-rate and column temperature on retention when 10% ammonia in nitrogen was used as the mobile phase are shown in Figs. 4 and 5. The theoretical plate numbers in the separation of dialkyl sulphides using S-DTC-Cu as the stationary phase under various conditions are shown in Tables VI and VII.

The concentration of ammonia, flow-rate and the column temperature are important factors for the separation of sulphides, as discussed above. The factors responsible for the retention order are con-

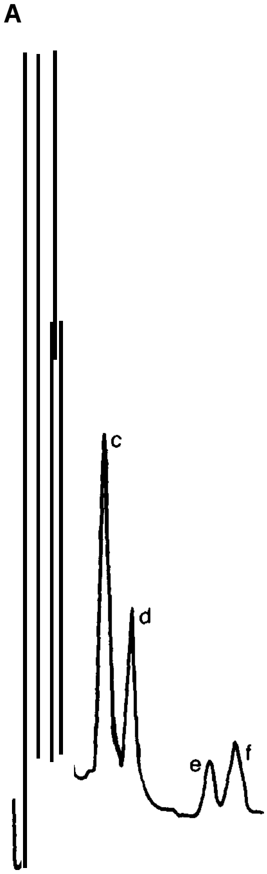


Fig. 4

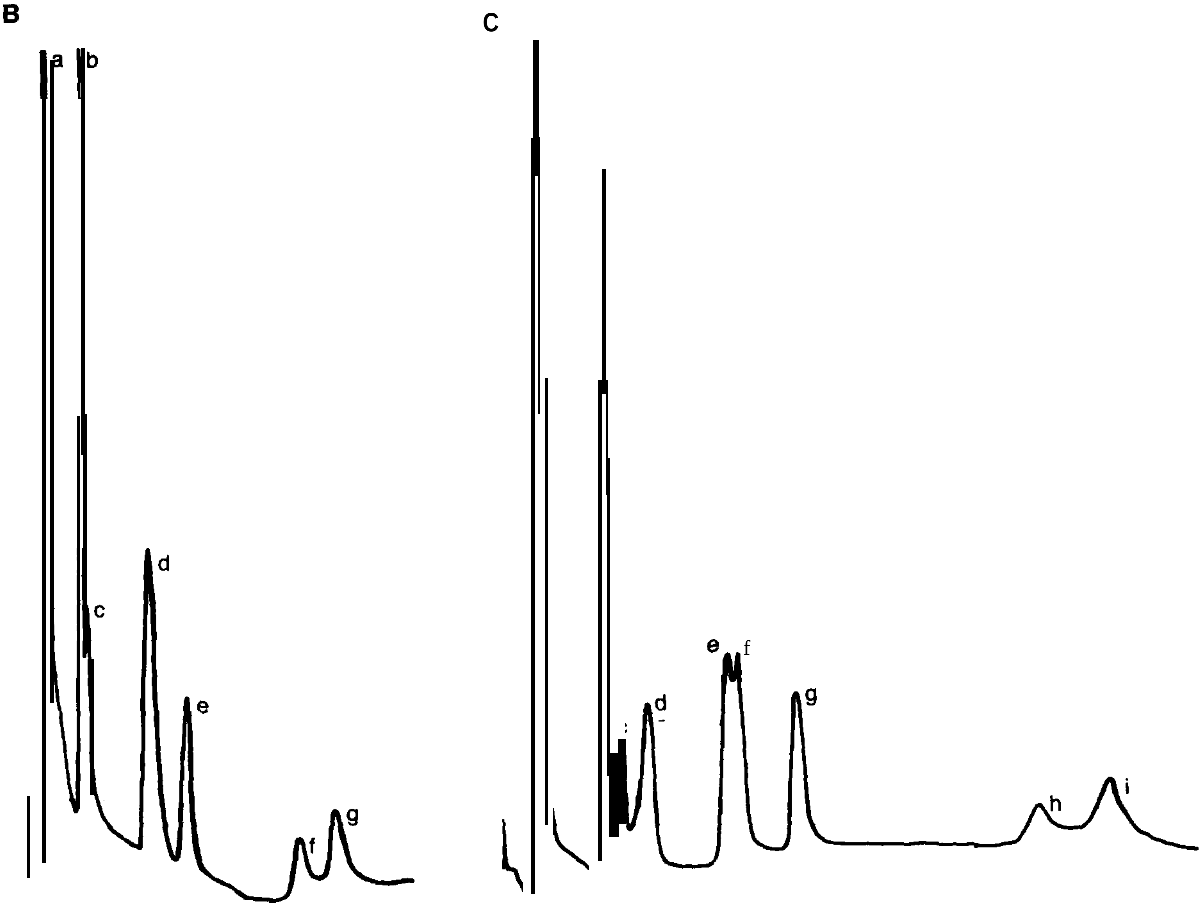


Fig. 4. Separation of hydrocarbons and dialkyl sulphides. Stationary phase, S-DTC–Cu(II) complex; carrier gas, 10% (v/v) NH,-N,; flow-rate, (A) 30, (B) 60 and (C) 90 ml min^{-1}; oven temperature, 100°C; injection temperature, 155°C; samples, 2 μl, 1% in CS,. (A) Peaks: a = CS, (t_R = 3.0 min); b = cyclohexane and n-hexane (t_R = 8.5 min); c = dimethyl sulphide (t_R = 9.3 min); d = n-heptane and benzene (t_R = 19.1 min); e = iso-octane (t_R = 24.7 min); f = allyl methyl sulphide (t_R = 41.4 min); g = diethyl sulphide (t_R = 47.0 min). (B) Peaks: a = CS, (t_R = 3.9 min); b = cyclohexane and n-hexane (t_R = 11.2 min); c = dimethyl sulphide (t_R = 12.7 min); d = n-heptane and benzene (t_R = 26.0 min); e = iso-octane (t_R = 33.3 min); f = allyl methyl sulphide (t_R = 57.0 min); g = diethyl sulphide (t_R = 64.6 min). (C) Peaks: a = CS, (t_R = 6.6 min); b = cyclohexane (t_R = 21.3 min); c = n-hexane (t_R = 25.3 min); d = dimethyl sulphide (t_R = 38.6 min); e = n-heptane (t_R = 47.2 min); f = benzene (t_R = 49.3 min); g = iso-octane (t_R = 62.2 min); h = allyl methyl sulphide (t_R = 105.9 min); i = diethyl sulphide (t_R = 121.0 min).

TABLE VI

THEORETICAL PLATE NUMBERS OF DIALKYL SULPHIDES USING S-DTC–Cu(II) AS STATIONARY PHASE AT AN OVEN TEMPERATURE OF 100°C AND A FLOW-RATE OF 60 ml min^{-1} WITH DIFFERENT CARRIER GASES

Carrier gas	Dimethyl sulphide	Diethyl sulphide	Allyl methyl sulphide
10% NH,-N,	2344	763	233
Nitrogen	108	694	195

TABLE VII

THEORETICAL PLATE NUMBERS OF DIALKYL SULPHIDES USING S-DTC–Cu(II) AS STATIONARY PHASE WITH 10% NH,-N, AS CARRIER GAS AT DIFFERENT OVEN TEMPERATURES AND FLOW-RATES

Oven temperature (“C)	Flow-rate (ml/min)								
	90	60	30	90	60	30	90	60	30
	Dimethyl sulphide			Diethyl sulphide			Ally1 methyl sulphide		
100	670	2344	1826	667	763	1913	168	233	438
85	190	268	1293	501	948	2154	462	518	411
70	774	676	417	1413	1362	1368	1095	924	1246

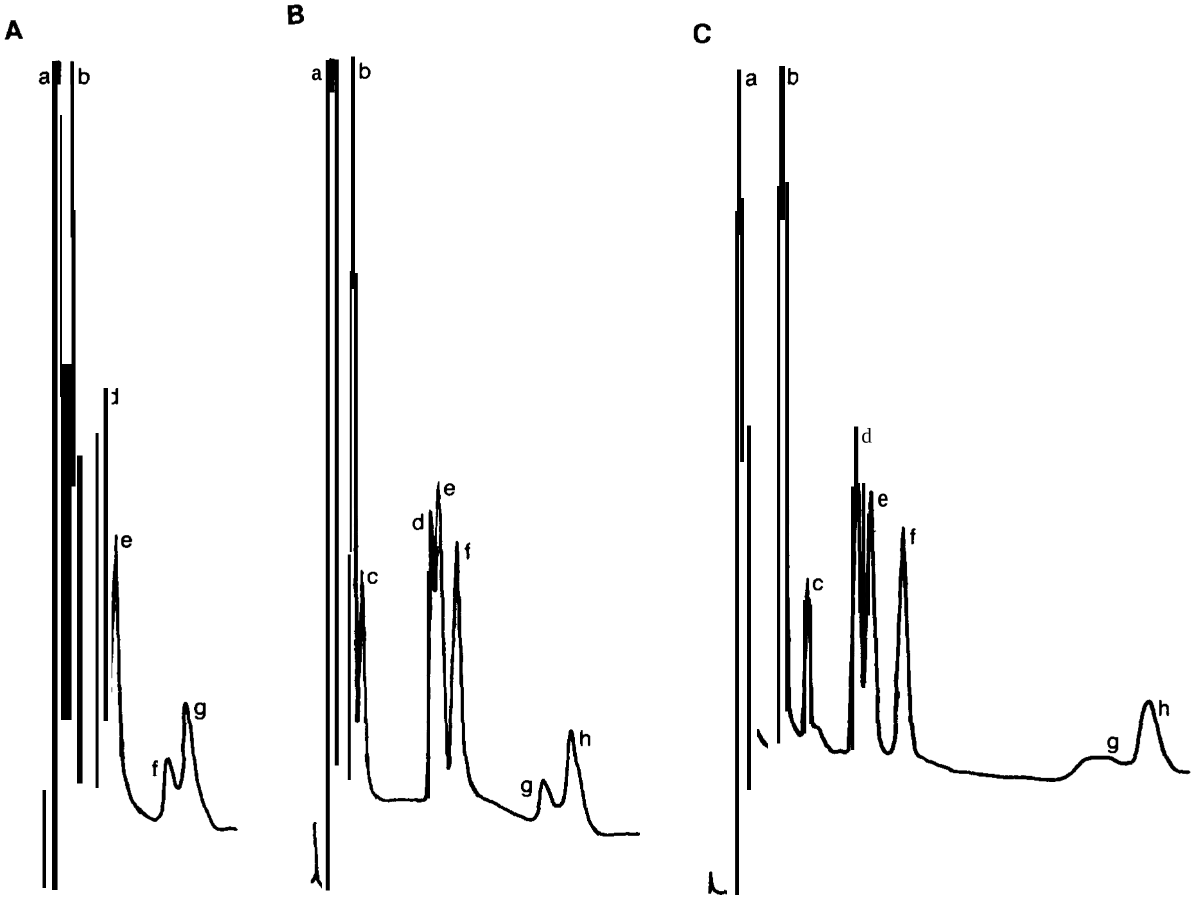


Fig. 5. Separation of hydrocarbons and dialkyl sulphides. Stationary phase, S-DTC–Cu(II) complex; carrier gas, 10% (v/v) NH,-N,; flow-rate, (A) 30, (B) 60 and (C) 90 ml min^{-1}; oven temperature, 85°C; injection temperature, 155°C; sample, 2 μl, 1% in CS,. (A) Peaks: a = CS, (t_R = 2.2 min); b = cyclohexane and n-hexane (t_R = 5.6 min); c = dimethyl sulphide (t_R = 6.9 min); d = n-heptane and benzene (t_R = 12.3 min); e = iso-octane (t_R = 15.0 min); f = ally1 methyl sulphide (t_R = 26.8 min); g = diethyl sulphide (t_R = 30.7 min). (B) Peaks: a = CS, (t_R = 3.0 min); b = cyclohexane and n-hexane (t_R = 8.02 min); c = dimethyl sulphide (t_R = 9.1 min); d = n-heptane (t_R = 16.4 min); e = benzene (t_R = 17.8 min); f = iso-octane (t_R = 21.6 min); g = ally1 methyl sulphide (t_R = 39.8 min); h = diethyl sulphide (t_R = 46.2 min). (C) Peaks: a = CS, (t_R = 5.5 min); b = cyclohexane and n-hexane (t_R = 15.0 min); c = dimethyl sulphide (t_R = 20.2 min); d = n-heptane (t_R = 30.6 min); e = benzene (t_R = 33.5 min); f = iso-octane (t_R = 40.5 min); g = ally1 methyl sulphide (t_R = 81.1 min); h = diethyl sulphide (t_R = 92.8 min).

sidered, on the basis of the chromatograms, to be as follows. In LEC, the ligand-exchange equilibrium and the basicity of the sulphur atom of a sulphide are thought to be responsible for the elution order. Other factors should exist that affect the elution order, as the basicities of dialkyl sulphides are not very different from one another. Branching of the alkyl group inhibits the copper-sulphur coordination and causes weak retention. Di-sec.-butyl sulphide (retention time > 180 min) and di-tert.-butyl sulphide (retention time > 130 min), for example, were eluted in this order (not shown in Fig. 6). For sulphides having the same carbon number and which possess two alkyl groups, that which has the longest alkyl chain was most strongly retained. Diethyl sulphide and methyl allyl sulphide, for example, were eluted in this order (Fig. 4). The difference in the vapour pressure of samples at a given column temperature was an important factor in determining the elution order, because the retention of a sample molecule was based on its gas-solid distribution. The boiling point of dimethyl sulphide is the lowest among the sulphides studied, hence in most separations dimethyl sulphide was eluted first.

The determination of dialkyl sulphides by the proposed ligand-exchange GC method was also studied (Fig. 6). The calibration graphs are shown in Fig. 7. As these compounds were highly volatile and difficult to handle accurately, the correlation coefficients were lower than expected, with values of 0.9983 (dimethyl sulphide), 0.9963 (allyl methyl sulphide), 0.9857 (diethyl sulphide) and 0.9970 (diisopropyl sulphide), based on the average of three measurements of the sample mixture.

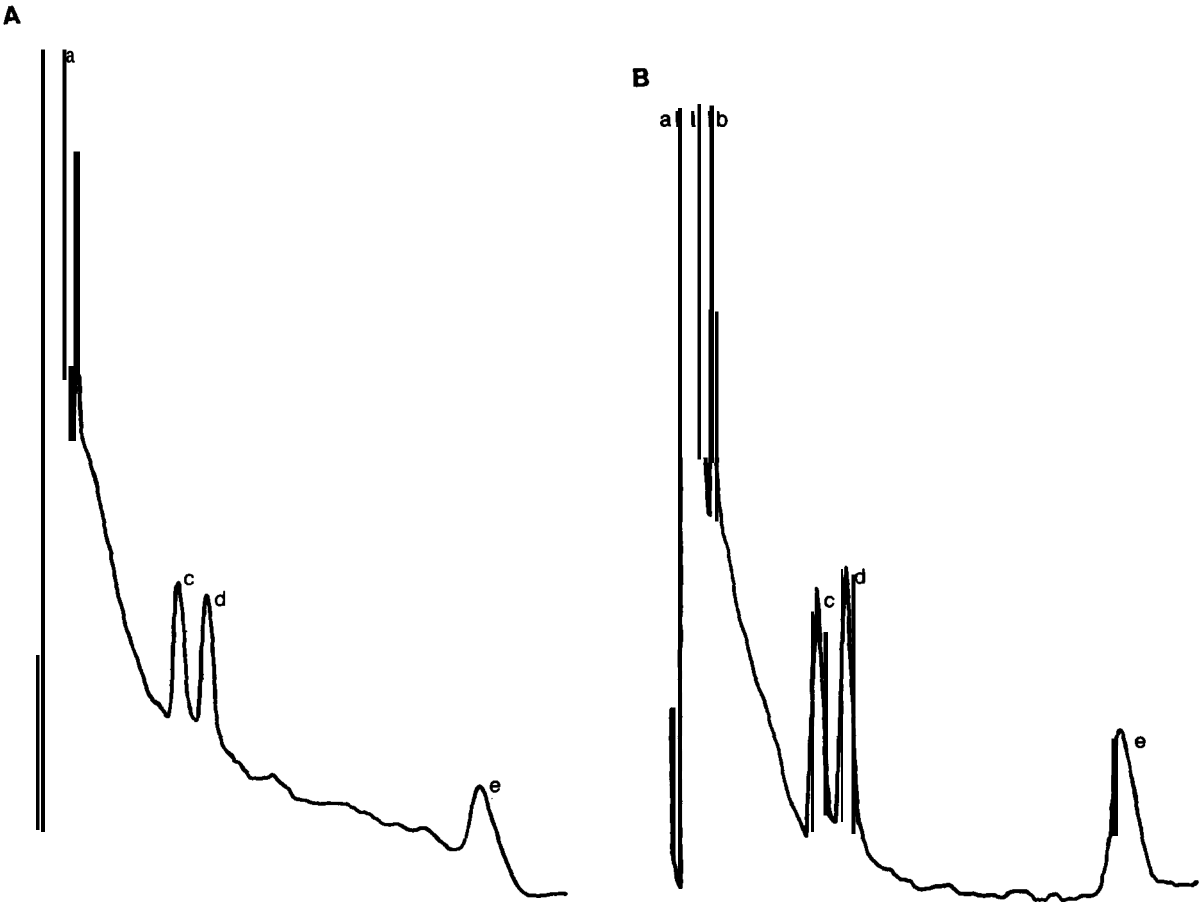


Fig. 6.

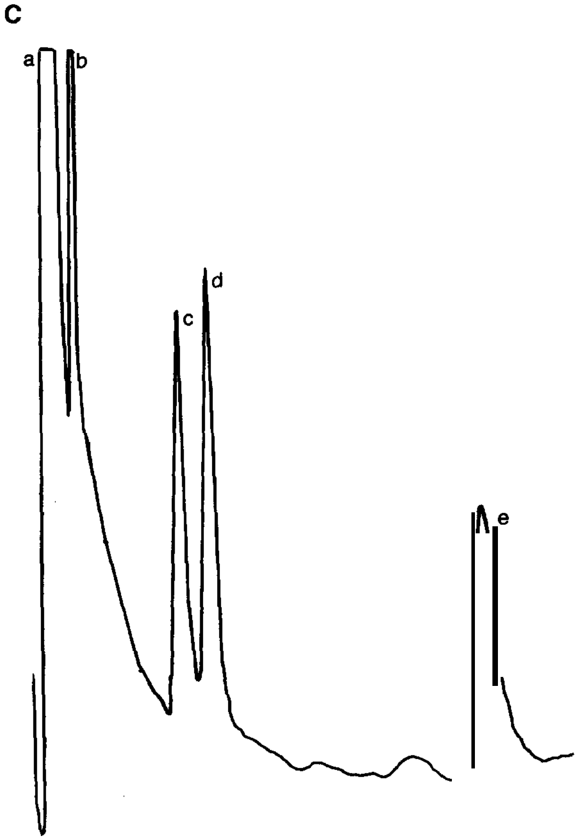


Fig. 6. Separation of mixtures. Stationary phase, S-DTC–Cu(II) complex; carrier gas, 10% (v/v) NH_3-N_2; flow-rate, 60 ml min^{-1}; oven temperature, 100°C; injection temperature, 155°C. (A) Peaks: a = CS_2 (t_R = 2.4 min); b = dimethyl sulphide (t_R = 9.3 min, 1.06 μg); c = allyl methyl sulphide (t_R = 32.3 min, 1.59 μg); d = diethyl sulphide (t_R = 38.7 min, 1.17 μg); e = diisopropyl sulphide (t_R = 110.5 min, 1.35 μg). (B) Peaks: a = CS_2 (t_R = 2.4 min); b = dimethyl sulphide (t_R = 9.3 min, 1.99 μg); c = allyl methyl sulphide (t_R = 32.6 min, 2.63 μg); d = diethyl sulphide (t_R = 39.3 min, 2.67 μg); e = diisopropyl sulphide (t_R = 112.6 min, 2.71 μg). (C) Peaks: a = CS_2 (t_R = 2.4 min); b = dimethyl sulphide (t_R = 9.3 min, 4.78 μg); c = allyl methyl sulphide (t_R = 32.8 min, 5.45 μg); d = diethyl sulphide (t_R = 39.6 min. 5.10 μg); e = diisopropyl sulphide (t_R = 111.6 mm, 5.40 μg).

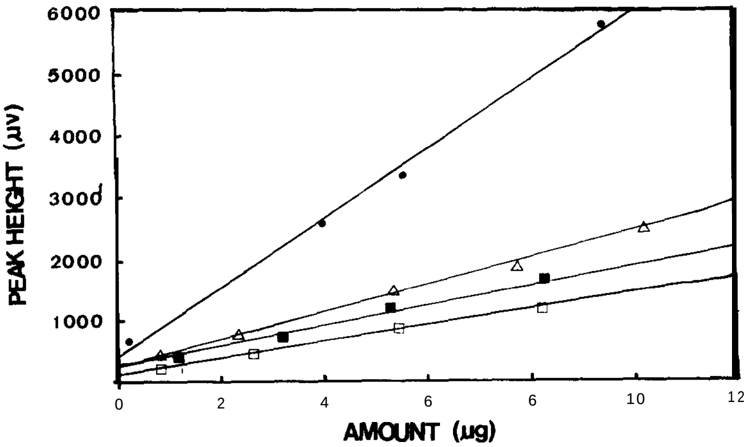


Fig. 7. Determination of dialkyl sulphides by ligand-exchange GC. Oven temperature, 100°C; carrier gas, 10% (v/v) NH_3-N_2; flow-rate, 60 ml min^{-1}; injection temperature, 155°C. ● = dimethyl sulphide (r = 0.9983); △ = allyl methyl sulphide (*r* = 0.9963); ■ = diethyl sulphide ([illegible] 0.9857); □ = diisopropyl sulphide (*r* = 0.9970).

CONCLUSIONS

The synthesized dithiocarbamate resin has been demonstrated to have a high affinity for the metal ions studied. The thermal stability of the resin-metal complexes made them very suitable for use as stationary phases for the ligand-exchange GC for the separation of dialkyl sulphides. The results showed that the elution order of samples was dependent on the surface structure of the matrices, the central metal ion, the complex-forming ability of the sample and the steric hindrance to complex formation.

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