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INVESTIGATION OF WHISKER-WALLED OPEN TUBULAR COLUMNS COATED WITH MANGANESE(II) CHLORIDE AND COBALT(II) CHLORIDE

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SUMMARY

Whisker-walled open tubular columns were coated with either manganese(II) chloride or cobalt(II) chloride These inorganic salt coated columns were employed to study the interaction of these sorbents with aromatic hydrocarbons that possessed varying π-electron density and alkyl substitution Halogenated aromatic hydrocarbons eluted according to boiling point. whereas the retention of alkyl-substituted benzenes increased with alkyl chain length and the degree of substitution The open tubular columns provided increased performance compared to packed columns containing these inorganic salts The dynamic procedure was considered a practical method for coating the whisker-walled columns The effects of column dimensions, adsorbent concentration and sample capacity were studied

INTRODUCTION

Early reports of gas–solid chromatography with open tubular glass capillary columns described techniques that involved severe leaching of the surface to obtain the adsorptive silica layer[1–3]. Subsequent studies reported on the development of porous-layer open tubular (PLOT) columns where silica[4–6], alumina[7 8] and graphitized carbon black[9–12] were layered on the inner wall of metal or glass columns. More recent interest has been generated in preparing columns containing metal compounds. Micropacked capillaries containing alkaline earth metal di-*n*-hexylphosphinates were studied by Nawrocki *et al.*[13] and an ammonium-hydroxide-roughened open tubular column coated with rubidium chloride[14] has been investigated for the separation of polynuclear aromatic hydrocarbons. Since two inorganic salts,

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manganese(II) chloride and cobalt(II) chloride, were studied in packed columns by one of us[15], the application of these salts to open tubular columns was of interest. We report here on the preparation of whisker-walled open tubular columns coated with these salts and their influence upon the separation of various groups of substituted aromatic hydrocarbons

EXPERIMENTAL

Apparatus

A Hewlett-Packard Model 5750 gas chromatograph was modified for glass capillary gas chromatography (GC). A glass-lined stainless steel split injection system (Model GISS-4A, Scientific Glass Engineering, Austin, TX, U S A) was installed in the injection port from an F&M Model 810 gas chromatograph Glass-lined stainless steel tubing (GLT) (1/16 in. O.D. × 0.3 mm I D.) was employed with heat-shrink Teflon for connection of the capillary columns to the splitter and flame detector Helium was used as the make-up gas and entered the detector combined with the hydrogen gas. Divert and metering valves were installed to allow for separate measurement and control of the hydrogen and helium flow-rates The end of the GLT entering the detector was positioned past the hydrogen and make-up gas entrance inside the detector to maintain sample integrity.

The conditions for each analysis are presented with the appropriate chromatogram in the figures The flow-rates of air, hydrogen and helium make-up gas were maintained for all of the analyses at 360, 40 and 66 ml/min. respectively. The linear velocities were calculated from the leading edge of the solvent front which was identical to that of a natural gas injection

Pyrex 7740 glass tubing, 10 mm O D × 2.5 mm I D and 8 mm O D. × 4 mm I D , were drawn (Model GDM-1 glass drawing machine, Shimadzu Scientific Instruments, Columbia, MD, U S A.) to capillary tubing 1 mm O.D × 0 25 mm I D and 1 mm O.D. × 0 5 mm I D., respectively, having a 10-cm coil diameter. The glass capillary tubing was subjected to a whisker-growth technique[16,17] using 2-chloro-1,1,2-trifluoroethyl methyl ether at concentrations suggested by Sandra and Verzele[18]

Reagents

Manganese(II) chloride tetrahydrate and cobalt(II) chloride hexahydrate, both 99.999 % gold label, were purchased from Aldrich, Milwaukee, WI, U S A ; absolute ethanol (U.S Industrial Chemical Co , New York, NY, U.S A.); nitrogen, helium and hydrogen, each 99 999%, and air zero gas (Liquid Carbonic through West Point Supply, West Point, PA, U S A).

Preparation of columns

Hydrated inorganic salts, $MnCl_2$ and $CoCl_2$, contained in 1/4-in O D glass tubes were dehydrated under dry nitrogen flow in a gas chromatograph. The chromatograph oven was programmed at 5°C/min from 25 to 125°C for $MnCl_2$ and 200°C for $CoCl_2$ After 1 h of conditioning, the dehydrated salts were secured in the 1/4-in. O.D. tubes under dry nitrogen using Teflon®-coated septums and stored at room temperature

For static coating, the whisker-walled glass capillary tubing was filled with degassed absolute ethanol and allowed to set overnight to properly wet the surface Typically, a 2% (w/v) coating solution of the dehydrated inorganic salt was prepared in absolute ethanol and degassed The ethanol in the capillary column was pulled back slightly from one end, then the degassed coating solution was drawn into the column with approximately 20% excess using vacuum A seal was made by drawing glue into one end The column, which was secured on a plastic cylinder in a close-packed vertical position, was placed in a 28°C double water bath and attached to vacuum The vacuum was increased until the ethanol started to evaporate The vacuum was held constant while the water-bath temperature was gradually increased to maintain an even coating rate. Seven days were necessary to coat a 30-m column Immediately after coating, the column was installed in the chromatograph under helium flow and thoroughly dried at 60°C overnight

If the initial water-bath temperature was set too high (ca 55°C), the coating of inorganic salt tended to remain suspended on top of the whiskers, as seen in the scanning electron micrograph in Fig 1a The scanning electron micrograph in Fig 1b illustrates the coating obtained under proper conditions

Owing to the prohibitively long time needed to coat longer columns (ca 50 m), the dynamic coating method was employed As in the static procedure, the column was filled with degassed absolute ethanol and allowed to set overnight The ethanol was removed and the column conditioned in the gas chromatograph with helium flow while temperature programming from 40 to 100°C at 2°/min with a 1 h hold at 100°C A buffer capillary was attached to the column and a degassed solution of the de-hydrated inorganic salt in absolute ethanol was drawn into the column from the opposite end to fill 10–15% of the column volume Pressure-controlled dry-nitrogen flow was regulated to transport the solution through the column at a constant velocity of 0 5–2 cm/sec. After coating, the column was detached from the buffer capil-
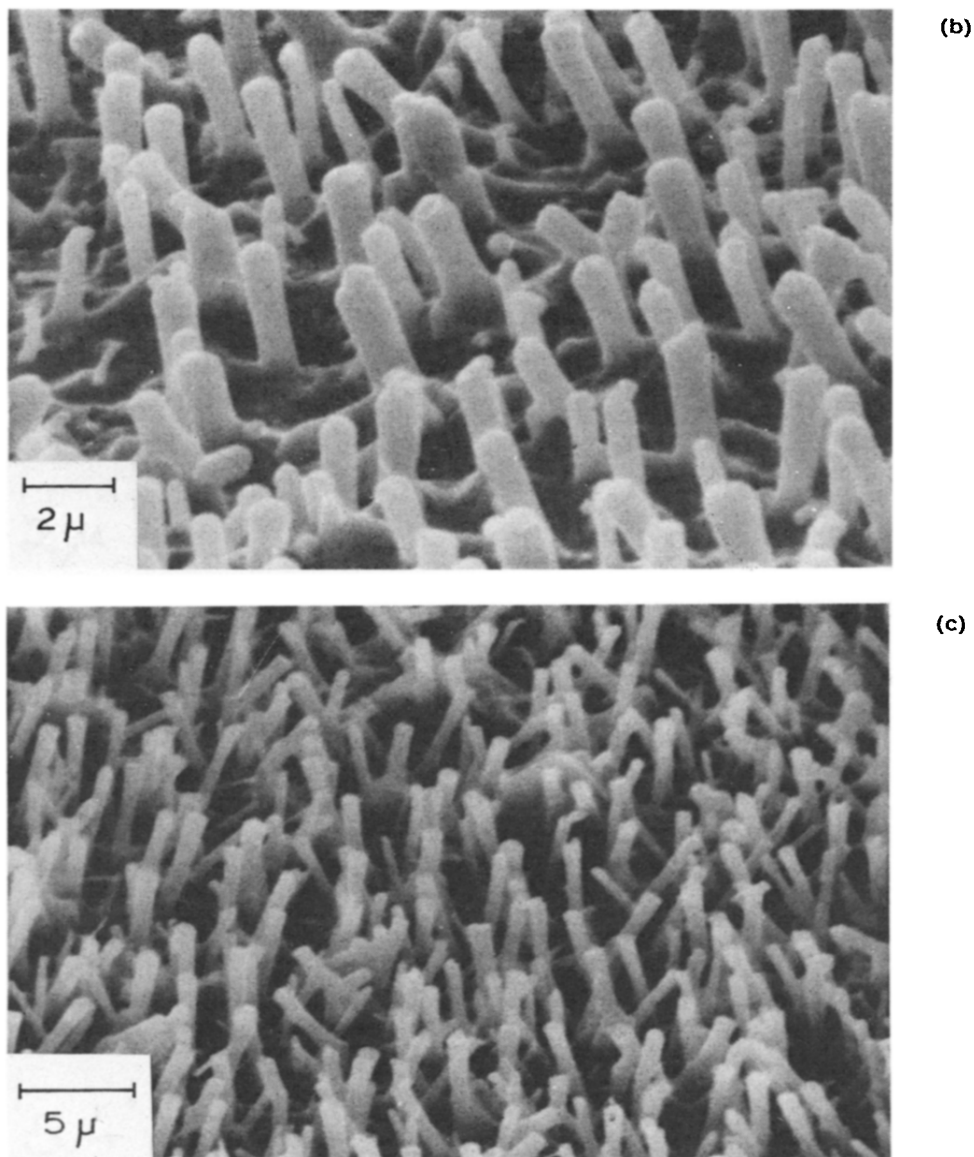

(a)

5 μ

Fig. 1

(b)

(c)

Fig. 1 Scanning electron micrographs of whisker-glass capillary column surfaces a, static coated with a sheet of $MnCl_2$; b, properly static coated with $MnCl_2$; c, dynamic coated with $MnCl_2$

lary and nitrogen supply and connected to the injection port in the instrument. With 10 p.s.i. helium pressure, the column was allowed to thoroughly dry at 60°C overnight. A typical scanning electron micrograph of a whisker-walled glass capillary column containing 0 5 mg/m of $MnCl_2$ following dynamic coating is presented in Fig 1c Results from X-ray microanalysis of whisker-walled glass capillaries dynamically coated with $MnCl_2$ and $CoCl_2$ substantiated the successful coating of the columns

TABLE I

SUMMARY OF THE PARAMETERS EMPLOYED FOR PREPARING THE INORGANIC-SALT-COATED COLUMNS

Inorganic salt coated	Length (m)	Diameter (mm)	mg m coated	Coating method	Coating solution concentration (% w/v)	Coating velocity (cm sec)	Coating pressure (p.s.i.)
MnCl$_2$	28	0 25	1	static	2	—	—
MnCl$_2$	45	0 25	1	dynamic	25	0 26	14
MnCl$_2$	45	0 25	0 5	dynamic	12 5	1 5–1 75	8–9
MnCl$_2$	45	0 25	0 25	dynamic	6 25	0 7–1	5
CoCl$_2$	58	0 25	0 9	dynamic	25	1 5–2	22
CoCl$_2$	56	0 25	0 5	dynamic	12 5	1	14
CoCl$_2$	51	0 25	0 2	dynamic	6 25	0 5	6

The parameters employed for preparing the columns by the static and dynamic procedures are summarized in Table I

Column conditioning

A helium carrier gas pressure of 10 p s i was utilized with the columns connected only to the injection port of the gas chromatograph The oven temperature was programmed at 1 /min from 40 to 220°C for CoCl$_2$ and from 40 to 245°C for MnCl$_2$ and maintained at these temperatures at least overnight or as long as 24 h

RESULTS

McGonigle and Grob[15], using MnCl$_2$ and CoCl$_2$ in packed columns, demonstrated that these salts exhibited different adsorptive specificity in the separation of several substituted aromatic hydrocarbons Retention of these components was shown to increase with the increased π-electron density of the adsorbate In the present investigation, open tubular columns were employed to provide increased resolution for a further study of this phenomenon

The retention characteristics of 35 different compounds were studied on the MnCl$_2$ and CoCl$_2$ open tubular columns The results and pertinent chromatographic conditions are listed in Tables II and III and shown more explicitly in the graphical plots in Figs 2 and 3, respectively.

In Figs 2 and 3, the increasing *n*-alkyl-substituted benzenes are on one curve while a series of *n*-alkanes of similar boiling point containing no π-electron density exhibit a curve at less retention Halogen-substituted benzenes are known to deactivate the aromatic system through a withdrawal of the π-electron density Several compounds of this type produce a retention–boiling point relationship which is similar to the *n*-alkane series The retention effect shown by the halogenated compounds is more pronounced on the MnCl$_2$-coated column Bromo-, chloro- and iodobenzene lay on a curve which is close to that of the *n*-alkanes However, their curve tends to differ slightly, with iodobenzene experiencing less retention than an *n*-alkane of similar boiling point, particularly on MnCl$_2$ It is known that the ability for π-electron feedback into the aromatic system is reduced as the size of the halogen

TABLE II

ADJUSTED RETENTION DATA ACQUIRED ON $MnCl_2$

Column- 45 m × 0 25 mm I.D. $MnCl_2$ (1 mg/m) whisker-walled glass capillary. Helium carrier gas at 25 p.s.i. split ratio = 100/1, attenuation = 4 × 1, linear velocity = 21 5 cm/sec Temperatures detector, 265°C; injector, 250°C; column, 100–250°C programmed at 6°/min.

Order of elution	Compound	B.p (°C)	t'_R (min)
1	n-Octane	125–126	0 62
2	Benzene	80 1	0 84
3	Chlorobenzene	132	1 06
4	Bromobenzene	155–156	1 84
5	m-Dichlorobenzene	172	1.88
6	p-Dichlorobenzene	174	2.58
7	o-Chlorotoluene	159	2.74
8	o-Dichlorobenzene	179	2.76
9	Toluene	110 6	2.92
10	m-Chlorotoluene	162	3 00
11	n-Decane	174 1	3 30
12	Iodobenzene	189	3 62
13	p-Chlorotoluene	162	3 80
14	Ethylbenzene	136	5.12
15	Isopropylbenzene	152–153	6 32
16	o-Xylene	144	7 22
17	p-Xylene	138	7 24
18	m-Xylene	139	7 36
19	sec.-Butylbenzene	173	8 12
20	n-Propylbenzene	159 2	8 30
21	tert -Butylbenzene	168	8 36
22	n-Dodecane	216 3	8 90
23	Isobutylbenzene	173	9 10
24	n-Butylbenzene	183	10 60
25	1,3,5-Trimethylbenzene	164.7	10 96
26	o-Diethylbenzene	183 5	11 26
27	m-Diethylbenzene	181–182	11 76
28	1,2,4-Trimethylbenzene	169 5	12.08
29	1-Isopropyl-3-methylbenzene	177	12 20
30	p-Diethylbenzene	182–183	13 16
31	n-Amylbenzene	205 3	13.96
32	Methoxybenzene	153 8	14 14
33	n-Tetradecane	253 5	14 96
34	n-Hexylbenzene	226	16.70
35	n-Heptylbenzene	233	19.30

increases. This trend was clearly observed in these results. On $CoCl_2$ columns the dichlorobenzenes exhibited retention characteristics similar to the n-alkanes, whereas on $MnCl_2$ a less retentive affect from the increased withdrawal of π-electron density was noticed. The reduced retention of the dichlorobenzenes with respect to the n-alkanes of similar boiling point demonstrates the effect of bulk geometry on the retention of the n-alkanes. In contrast to the other halogenated compounds, the chlorotoluenes were retained to a greater extent than n-alkanes of similar boiling point. The additional electron-donating capacity from the methyl group provided

TABLE III

ADJUSTED RETENTION DATA ACQUIRED ON CoCl$_2$

Column 58 m × 0 25 mm I D CoCl$_2$ (0 9 mg/m) whisker-walled glass capillary Helium carrier gas at 24 p s i Split ratio = 100/1, attenuation = 4 × 1, linear velocity = 13 5 cm/sec Temperatures detector, 265°C, injector, 250°C, column, 160–290°C programmed at 6°/min

Order of elution	Compound	B p (°C)	t_R (min)
1	Benzene	80 1	0 30
2	n-Octane	125–126	0 36
3	Chlorobenzene	132	0 60
4	Toluene	110 6	0 86
5	Bromobenzene	155–156	1 06
6	o-Chlorotoluene	159	1 32
7	m-Dichlorobenzene	172	1 34
8	Ethylbenzene	136	1 48
9	m-Chlorotoluene	162	1 52
10	n-Decane	174 1	1 56
11	p-Dichlorobenzene	174	1 64
12	o-Dichlorobenzene	179	1 78
13	p-Chlorotoluene	162	1 84
14	Isopropylbenzene	152–153	1 96
15	Iodobenzene	189	2.22
16	n-Propylbenzene	159 2	2 58
17	tert -Butylbenzene	168	2 60
18	p-Xylene	138	2 70
19	m-Xylene	139	2 74
20	sec -Butylbenzene	173	2 74
21	o-Xylene	144	2 92
22	Isobutylbenzene	173	3 36
23	n-Butylbenzene	183	4 38
24	n-Dodecane	216 3	5 34
25	1-Isopropyl-4-methylbenzene	177	5 40
26	o-Diethylbenzene	183 5	6 00
27	m-Diethylbenzene	181–182	6 08
28	p-Diethylbenzene	182–183	6 38
29	1,3,5-Trimethylbenzene	164 7	6 74
30	n-Amylbenzene	205 3	6 78
31	1,2,4-Trimethylbenzene	169 5	8 24
32	n-Hexylbenzene	226	9 50
33	Methoxybenzene	153 8	9 54
34	n-Tetradecane	253 5	11 60
35	n-Heptylbenzene	233	12 65

more π-electron density to the aromatic system which accounted for this change. As a group, the retention increased $p > m > o$ which demonstrated the bulk geometry effect.

Alkyl substitution on benzene is known to provide electron donation into the aromatic system In Figs 2 and 3 the retention–boiling point relationships for the alkyl-substituted benzenes were clearly defined and demonstrated greater column retention in the order: trisubstituted, disubstituted, monosubstituted. This observation was more pronounced with CoCl$_2$. Although o- and p-xylene have different
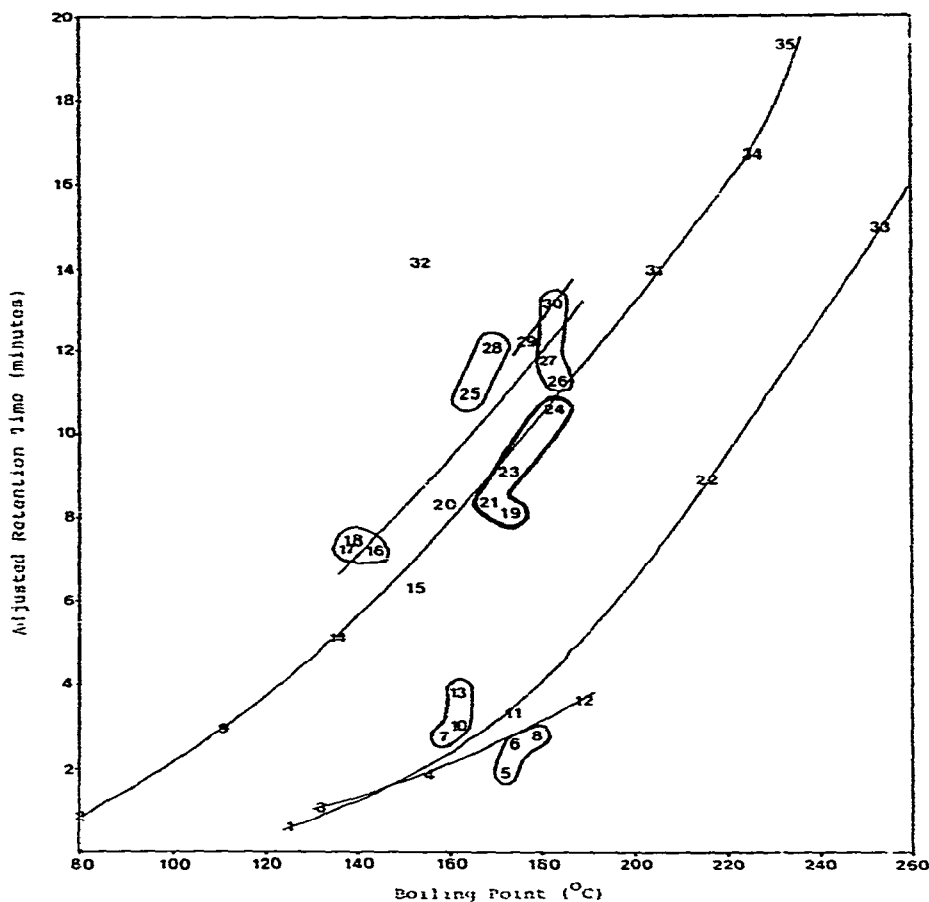
Fig. 2. Plot of adjusted retention data *versus* boiling point for MnCl$_2$ Numbers correspond to compounds listed in Table II. The numbers encircled represent groups of similarly substituted compounds

boiling points, their elution from the MnCl$_2$ column was very similar. In addition, the elution order did not correspond to increasing boiling point. However, the interactions on CoCl$_2$ proceeded according to boiling point ($p < m < o$) as expected. The retention of the diethylbenzenes differed on both salts; whereas the three diethylbenzenes were all grouped together on the CoCl$_2$ dialkyl-substituted curve, their interaction with MnCl$_2$ produced a decreasing retention in the order of $p > m > o$ with o-diethyl benzene near the *n*-alkyl substituted curve and *p*-diethylbenzene near the trisubstituted curve. Although this geometric effect with the diethylbenzenes was not encountered on CoCl$_2$, an effect was observed for the butylbenzenes which was not prominent on MnCl$_2$ In this case, isobutylbenzene and *n*-butylbenzene lay on the *n*-alkyl-substituted benzene curve, whereas *sec.*- and *tert.*-butylbenzene exhibit shorter retention on the CoCl$_2$ surface. These data suggest that branching on the α-carbon of the *n*-alkyl chain provides less interaction with the adsorbent surface than branching further from the aromatic system.

Finally, methoxybenzene occupied a retention–boiling point position above
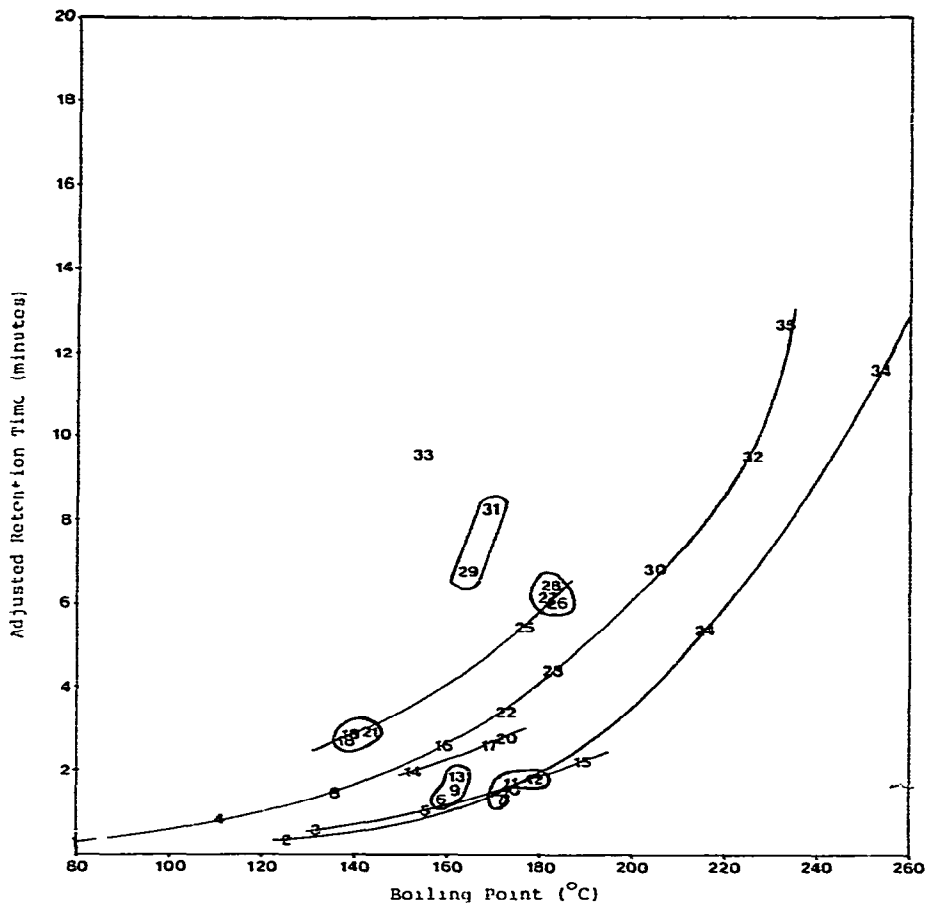
Fig. 3 Plot of adjusted retention data *versus* boiling point for CoCl₂ Numbers correspond to compounds listed in Table III The numbers encircled represent groups of similarly substituted compounds

the trimethyl-substituted benzenes for both salts, as predicted by the increased reso-
nance donation of the methoxy group

A mixture of fourteen substituted aromatic hydrocarbons, similar to those
investigated on packed columns by McGonigle and Grob[15], was studied on several
MnCl₂ and CoCl₂ whisker-walled open tubular columns A chromatogram of this
mixture on a column coated 0.9 mg/m with CoCl₂ is presented in Fig 4. Chromato-
grams of these compounds on two MnCl₂ columns coated 1 mg/m are present in Figs
5 and 6 The increase in resolution and reduction of tailing observed in these chroma-
tograms in contrast to that observed by McGonigle and Grob[15] provides an excellent
example of the performance offered by open tubular columns in gas–solid chromato-
graphy.

The amount of inorganic salt in the capillary column was varied to determine
the effects upon the retention of the same adsorbates. The linear velocity and column
length were held constant for each column to evaluate properly the influence of
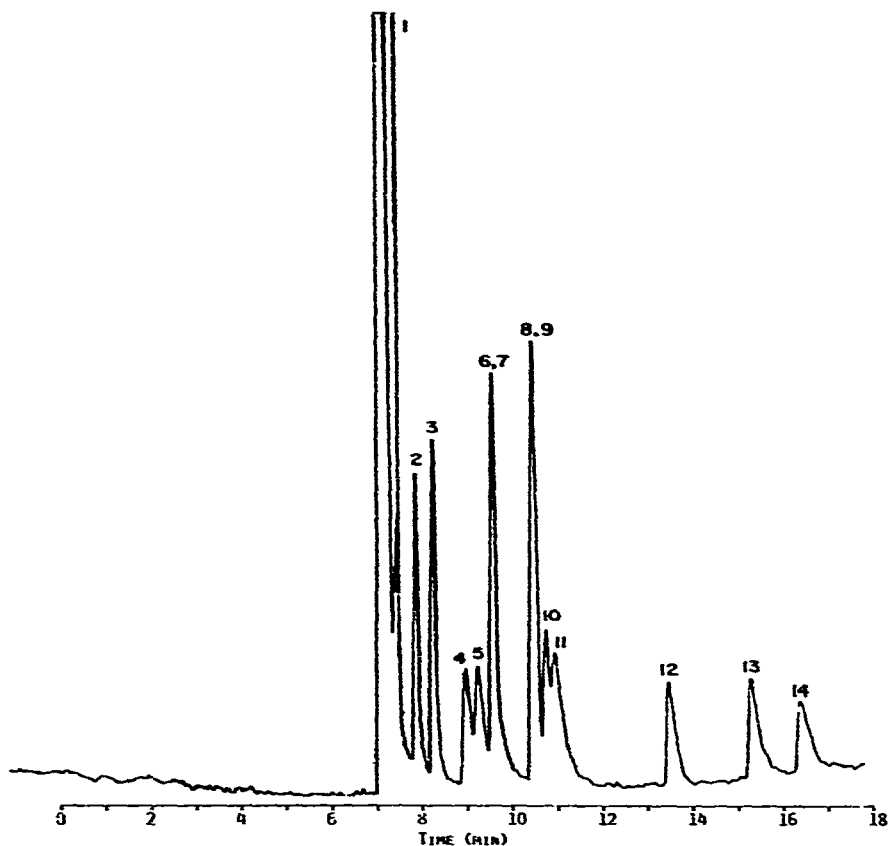varying concentrations of these inorganic salts. As illustrated in Table IV, changing

Fig. 4 Chromatogram of a fourteen-compound aromatic hydrocarbon mixture on a 58 m × 0 25 mm I D CoCl$_2$ whisker-glass capillary column coated 0 9 mg/m Linear velocity, 13 8 cm/sec, helium carrier gas at 25 p.s.i.; temperatures detector 265°C, injector 250°C, column 160–250°C, programmed at 6°C/min, split ratio, 100 1; attenuation, 4 × 1, sample, 2 μl of 0 07% of each compound in methylene chloride. Peaks. 1 = benzene, 2 = chlorobenzene, 3 = toluene; 4 = o-chlorotoluene, 5 = m-chlorotoluene, 6 = p-chloro-toluene; 7 = isopropylbenzene, 8 = tert-butylbenzene, 9 = m-xylene, 10 = p-xylene, 11 = o-xylene, 12 = 1-isopropyl-4-methylbenzene, 13 = 1,3,5-trimethylbenzene, 14 = 1,2,4-trimethylbenzene

the concentration of CoCl$_2$ from 0.9 to 0.5 mg/m reduced the adjusted retention time of the adsorbates by half. However, a minimal change was observed when the concentration was decreased from 0.5 to 0 2 mg/m. The retention order remained essentially the same on the three columns except for tert.-butylbenzene and isopropylbenzene. Their retention increased with respect to the other components as the amount of solid phase decreased. As the amount of CoCl$_2$ decreased, m- and p-xylene eluted closer to each other and finally merged into one peak on the 0.2-mg/m-coated column Similar decreases in retention of the fourteen compounds were observed on MnCl$_2$ when the concentration was reduced (Table V). Unlike the CoCl$_2$ column, the retention order varied in an unpredictable fashion The shift in the retention order of the xylenes changed with respect to isopropylbenzene and tert.-butylbenzene whose retention order appeared unaffected. Although the elution order of the last three components
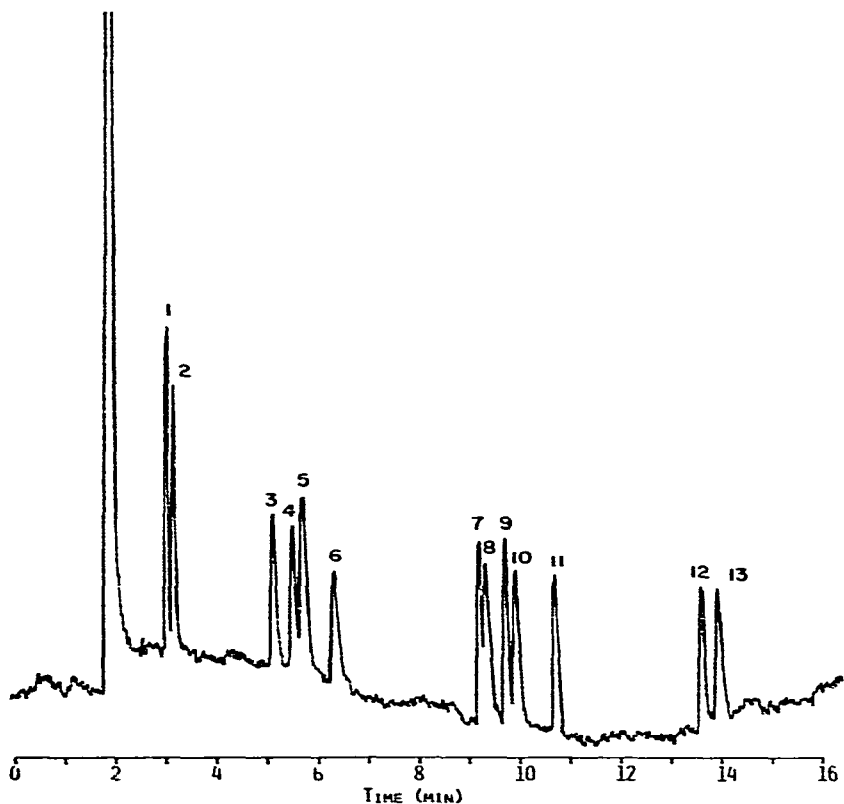
Fig 5 Chromatogram of a thirteen-compound aromatic hydrocarbon mixture on a 25 m × 0 25 mm I D MnCl₂ whisker-glass capillary column coated 1 mg/m Linear velocity 27 5 cm/sec, helium carrier gas at 25 p s i , temperatures detector 265°C, injector 250°C, column 100–200°C, programmed at 6°C/min split ratio, 140 1; attenuation, 2 × 1; sample, 0 3 μl of 0 1 % of each compound in methylene chloride Peaks 1 = benzene, 2 = chlorobenzene, 3 = *o*-chlorotoluene, 4 = *m*-chlorotoluene, 5 = toluene, 6 = *p*-chlorotoluene, 7 = isopropylbenzene, 8 = *m*-xylene, 9 = *o*-xylene, 10 = *p*-xylene, 11 = *tert* -butylbenzene, 12 = 1-isopropyl-4-methylbenzene, 13 = 1 2 4-trimethylbenzene

remained the same, a shift in the relative retention of 1-isopropyl-4-methylbenzene was noticed as the concentration of the inorganic salt was decreased.

The fourteen compounds used in this study were injected into a bare 60 m × 0 25 mm I.D. whisker-walled open tubular column, under similar conditions, to determine if the silica glass surface influenced the retention order. All of the compounds eluted essentially unretained, as they all eluted with the solvent front. This was confirmed by headspace analysis of each compound individually

Fig. 7 presents a separation of eight alkylbenzenes which was undertaken to study the influence of double-bond conjugation with the aromatic system. Styrene (b.p. = 145°C) eluted prior to ethylbenzene (b.p. = 136°C) Apparently, conjugation with the aromatic system does not produce the anticipated longer retention from additional π-electrons. The spatial geometry of the molecule appears to effect its retentive characteristics more than the contribution of additional π-electrons to the aromatic system. Allylbenzene, containing an unconjugated side chain, and *trans-β-*
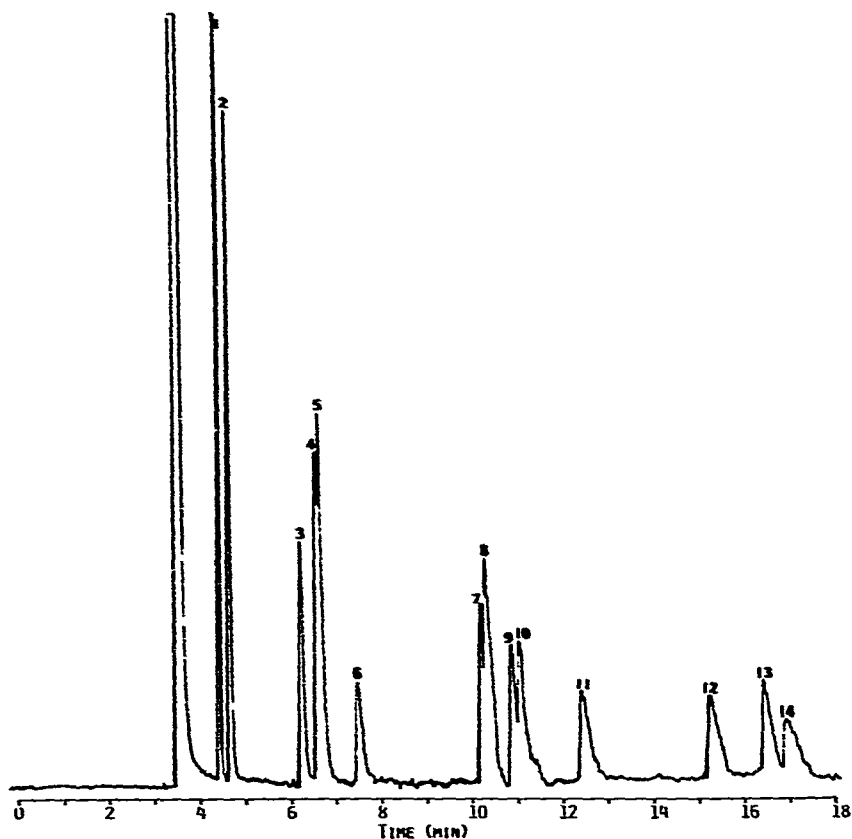
Fig. 6. Chromatogram of a fourteen-compound aromatic hydrocarbon mixture on a 45 m × 0 25 mm I D $MnCl_2$ whisker-glass capillary column coated 1 mg/m Linear velocity, 21 8 cm/sec, helium carrier gas at 25 p s.i ; temperatures detector 265°C, injector 250°C, column 100–210°C, programmed at 6°C/min; split ratio, 100:1; attenuation, 4 × 1; sample, 1.0 µl of 0 07% of each compound in methylene chloride Peaks· 1 = benzene; 2 = chlorobenzene; 3 = o-chlorotoluene; 4 = m-chlorotoluene; 5 = toluene; 6 = p-chloro-toluene; 7 = isopropylbenzene; 8 = m-xylene; 9 = o-xylene; 10 = p-xylene; 11 = tert.-butylbenzene, 12 = 1 3,5-trimethylbenzene, 13 = 1-isopropyl-4-methyl-benzene; 14 = 1,2,4-trimethylbenzene.

methylstyrene, of similar substitution except for the conjugated double bond po-sition, both elute according to boiling point with respect to n-propylbenzene. There-fore, no marked interaction was observed with a longer alkyl function conjugated to the benzene system. Styrene and trans-β-methylstyrene did not elute from the $CoCl_2$ column. Consequently, the effects of this type of conjugation were not studied with this salt The effect of conjugation in the ring was investigated with cyclohexane, cyclohexene, 1,3- and 1,4-cyclohexadiene and benzene. The chromatograms from headspace sampling of a mixture of these compounds is found in Figs. 8 and 9 for $MnCl_2$ and $CoCl_2$, respectively. An increase in the π-electron density (cyclohexane < cyclohexene < cyclohexadiene < benzene) resulted in an increase in the retention of these compounds on $MnCl_2$ regardless of boiling point. The conjugated 1,3-cyclo-hexadiene eluted earlier than the 1,4-cyclohexadiene demonstrating that the isolated unconjugated π-electrons were adsorbed more strongly than the delocalized con-

TABLE IV

COMPARISON OF ADJUSTED RETENTION DATA FOR FOURTEEN AROMATIC HYDRO-
CARBONS ANALYZED ON WHISKER-WALL OPEN TUBULAR COLUMNS COATED WITH
VARYING CONCENTRATIONS OF CoCl$_2$

Linear velocity 13 8 cm/sec Carrier gas helium Temperatures detector, 265°C, injector, 250°C, column,
160–250°C programmed at 6°/min Split ratio 100/1 Attenuation 4 × 1

Compound	Adjusted retention time t_R (min)		
	0 9 mg/m*	0.5 mg/m**	0 2 mg/m***
Benzene	0 40	0 20	0
Chlorobenzene	0 84	0 32	0 24
Toluene	1 22	0 50	0 36
o-Chlorotoluene	1 98	0 70	0 56
m-Chlorotoluene	2 24	0 80	0 64
p-Chlorotoluene	2.54	0 88	0 74
Isopropylbenzene	2 54	1 14	0 90
tert -Butylbenzene	3 42	1 50	1 24
m-Xylene	3 42	1 32	1 0
p-Xylene	3 74	1 42	1 04
o-Xylene	3 94	1 54	1 16
1-Isopropyl-4-methylbenzene	6 46	3 14	2 42
1 3,5-Trimethylbenzene	8 28	3 30	2 84
1,2,4-Trimethylbenzene	9 40	3 94	3 62

  * Column 58 m × 0 25 mm I D
 ** Column 56 m × 0 25 mm I D
*** Column 51 m × 0 25 mm I D

TABLE V

COMPARISON OF ADJUSTED RETENTION DATA FOR FOURTEEN AROMATIC HYDRO-
CARBONS ANALYZED ON WHISKER-WALL OPEN TUBULAR COLUMNS COATED WITH
VARYING CONCENTRATIONS OF MnCl$_2$

Column dimensions 45 m × 0 25 mm I D Linear velocity 21 8 cm/sec Carrier gas helium. Temperatures
detector, 265°C, injector, 250°C, column, 100°–210°C programmed at 6°/min Split ratio 100/1 Attenu-
ation 4 × 1

| Compound	Adjusted retention time t_R (min)		
	1 mg/m	0.5 mg/m	0 2 mg/m
Benzene	0 94	0 30	0 36
Chlorobenzene	1 18	0 40	0 32
o-Chlorotoluene	2.74	1 10	0 92
m-Chlorotoluene	3 10	1 28	1 08
Toluene	3 16	1 24	1 14
p-Chlorotoluene	4 00	1 56	1 30
Isopropylbenzene	6 72	3 30	3 04
m-Xylene	6 82	3 46	3 66
o-Xylene	7 40	3 88	3 46
p-Xylene	7.56	3.96	3 66
tert -Butylbenzene	8 94	4 78	4 42
1,3,5-Trimethylbenzene	11 80	7 48	7 38
1-Isopropyl-4-methylbenzene	12.96	8 18	7 58
1,2,4-Trimethylbenzene	13 48	8 30	7 98
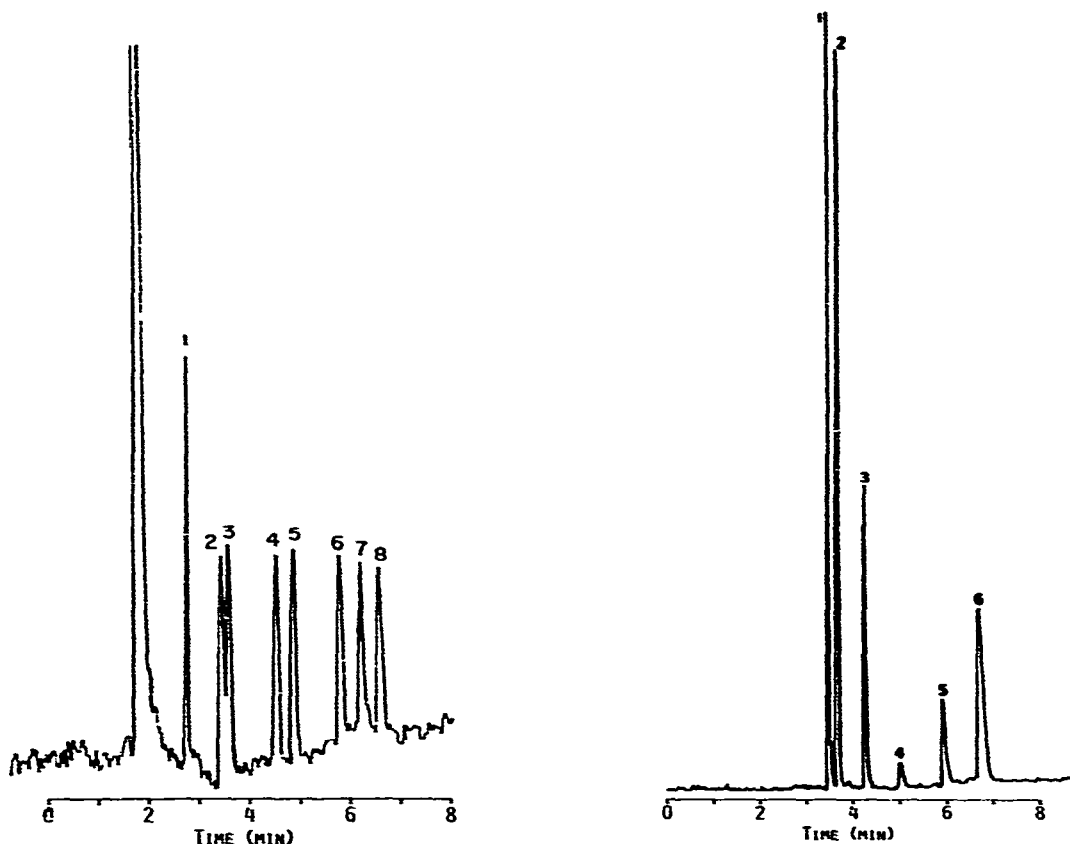
Fig. 7. Chromatogram of compounds selected to study the effect of $MnCl_2$ on conjugation with the benzene system. Column, linear velocity and carrier gas as in Fig. 5, temperatures. detector 235°C, injector 250°C, column 100–200°C, programmed at 10°C/min; split ratio, 130 1; attenuation, 2 × 1; sample, 0.5 μl of 0 1 % of each compound in methylene chloride. Peaks. 1 = toluene, 2 = styrene, 3 = ethylbenzene; 4 = allylbenzene; 5 = propylbenzene; 6 = isobutylbenzene, 7 = trans-β-methylstyrene; 8 = n-butylbenzene.

Fig. 8 Chromatogram of compounds selected to study the effect of $MnCl_2$ on conjugation in the six-membered ring. Column and carrier gas as in Fig. 6, linear velocity, 22.1 cm/sec, temperatures; detector 225°C, injector 230°C, column 45°C (2-min hold)–70°C, programmed at 6°C/min; split ratio, 100 1, attenuation, 4 × 1; 20-μl headspace sample. Peaks: 1 = cyclohexane; 2 = hexane; 3 = cyclohexene, 4 = 1,3-cyclohexadiene; 5 = 1,4-cyclohexadiene; 6 = benzene.

jugated system. A similar retention order is obtained on $CoCl_2$ except that 1,4-cyclohexadiene (b.p. = 85.6°C) eluted just after benzene (b p. = 80.1°C). The difference in selectivity of this salt may result from the difference in boiling points or from the difference in conjugation of the sorbate molecules. In contrast to $MnCl_2$, the retention of 1,4-cyclohexadiene containing the two unconjugated double bonds on $CoCl_2$ was greater than the retention of benzene containing the three conjugated double bonds. In Fig. 3 the n-alkylbenzene curve was closer to the n-alkane curve for $CoCl_2$ than in Fig. 2 for $MnCl_2$. This may indicate that the contribution of π-electron density to the separation is more pronounced with $MnCl_2$ than with $CoCl_2$. Figs. 8 and 9 show hexane to be eluted in a similar retention position. Although the boiling point of hexane (68°C) is much less than cyclohexane (81°C) the greater confor-

mational spatial geometry of hexane allows it to interact with more of the adsorbent surface and experience longer retention. The chromatograms of ten alkyl-substituted benzenes on $MnCl_2$ and $CoCl_2$ are presented in Figs. 10 and 11, respectively. On $CoCl_2$ the retention was in the order of mono-, di- and tri-substitution. On $MnCl_2$, however, the retention order was somewhat scattered with regard to alkyl substitution. The retention order of the butylbenzenes was similar to that observed on graphitized carbon black according to Kiselev and Yashin[19]. The explanation of this elution sequence is based upon the size of the side-chain links were n-butylbenzene is largest and tert.-butylbenzene is smallest. As discussed earlier, the larger side chain provides more direct contact with the adsorbent surface and was retained longer
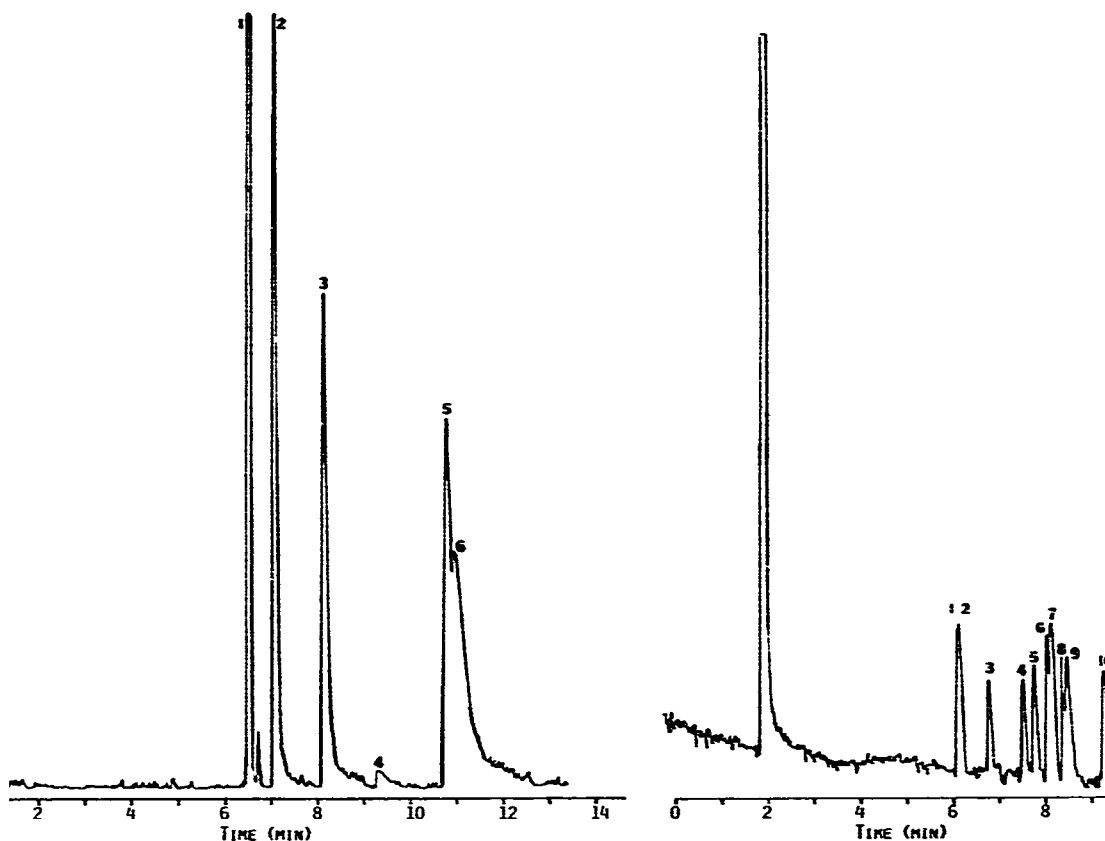

Fig. 9 Chromatogram of compounds selected to study the effect of $CoCl_2$ on conjugation in the six-membered ring Column as in Fig. 4, linear velocity, 15 1 cm/sec, helium carrier gas at 24 p s i , temperatures detector 225°C, injector 230°C column 60–73°C, programmed at 1°C/min, split ratio, 100 1, attenuation, 4 × 1, 35-μl headspace sample. Peaks 1 = cyclohexane, 2 = n-hexane, 3 = cyclohexene, 4 = 1,3-cyclohexadiene; 5 = benzene, 6 = 1,4-cyclohexadiene

Fig 10 Chromatogram of ten aromatic hydrocarbons Column and carrier gas as in Fig 5, linear velocity, 25 9 cm/sec; temperatures detector 265°C, injector 250°C, column 120–200°C, programmed at 8°C/min, split ratio, 140 1, attenuation, 4 × 1; sample, 0 4 μl of 0 1 % of each compound in methylene chloride Peaks 1 = sec-butylbenzene, 2 = tert.-butylbenzene, 3 = isobutylbenzene, 4 = n-butylbenzene, 5 = 1,3,5-trimethylbenzene, 6 = o-diethylbenzene, 7 = m-diethylbenzene, 8 = 1,2,4-trimethylbenzene, 9 = 1-isopropyl-4-methylbenzene, 10 = p-diethylbenzene

Isobutylbenzene, which has the dimethyl substitution and the β-carbon of the side chain, appears to the adsorbent as a larger group than that of sec.-butylbenzene and, therefore, was retained longer.
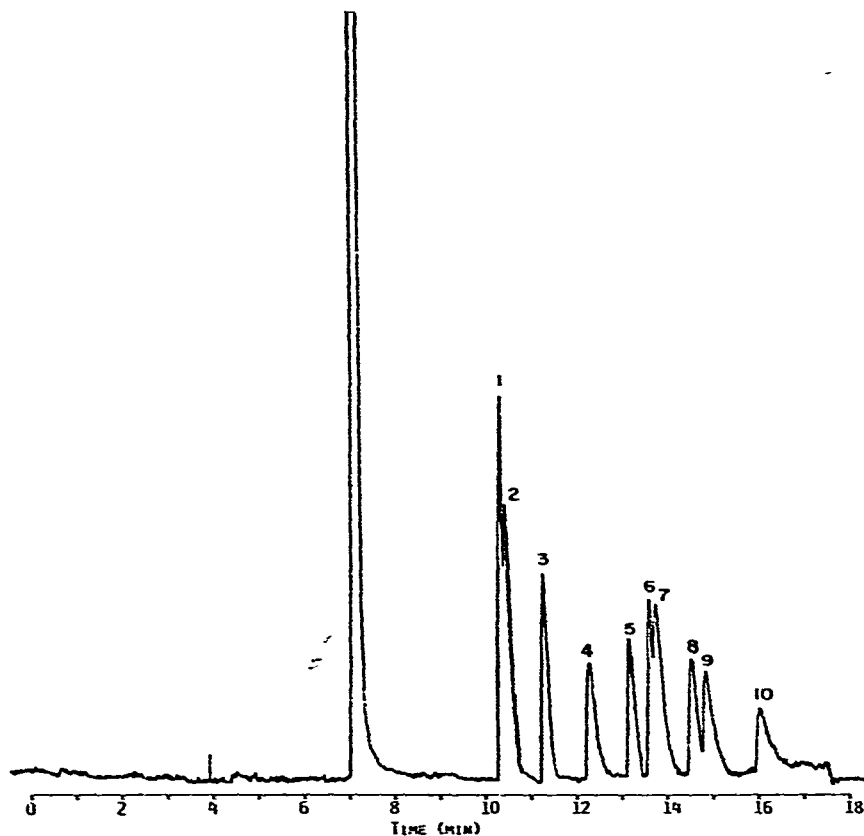

Fig. 11 Chromatogram of ten aromatic hydrocarbons Column, linear velocity, carrier gas and temperatures as in Fig. 4; split ratio, 112:1, attenuation, 4 × 1; sample, 1 μl of 0 14% of each compound in methylene chloride. Peaks: 1 = tert.-butylbenzene, 2 = sec -butylbenzene; 3 = isobutylbenzene; 4 = n-butylbenzene, 5 = 1-isopropyl-4-methylbenzene; 6 = o-diethylbenzene; 7 = m-diethylbenzene, 8 = p-diethylbenzene; 9 = 1 3 5-trimethylbenzene; 10 = 1,2,4-trimethylbenzene.

The sample capacity of both the $MnCl_2$ and $CoCl_2$ columns is rather limited. The amount of each component analyzed on the 28-m $MnCl_2$ column in Fig. 5 was ca. 2 ng compared to ca. 7 ng on the 45-m column in Fig 6 where the peaks exhibited more tailing. If larger amounts of sample were injected, this phenomenon increased.

Columns of 0.5 mm I.D. were prepared with 2 mg/m and 5 mg/m coatings of $MnCl_2$, which correspond to 2 × and 5 × the amount contained in the 0.25 mm I.D. columns, respectively. These columns did not provide sufficient retention of the aromatic hydrocarbons. Also, in preliminary work, 0.25 mm I.D. columns much less than 30 m in length did not provide adequate resolution of the compounds studied.

DISCUSSION

The difficulties of coating a glass open tubular column with inorganic salts is synonymous with coating polar liquid stationary phases Many techniques have been employed to roughen glass capillary columns The growth of silica whiskers, however, produces increased surface area which allows for increased adsorbent exposure to the adsorbates as well as a sufficiently roughened surface to stabilize the adsorbent Static coating of the salts was a lengthy, laborious procedure with blockage occurring at coating-solution concentrations greater than 5% The dynamic procedure provided a more practical approach for coating the inorganic salts A 25% w/v coating solution was considered the maximum for proper deposition of the salts A similar result was observed by Ober *et al* [14] in coating rubidium chloride The retention order of the fourteen-compound aromatic hydrocarbon mixture obtained on the whisker-walled columns containing $MnCl_2$ and $CoCl_2$ was similar to that obtained on conventional packed columns by McGonigle and Grob[15]. The major differences were the increased resolution and reduced peak tailing exhibited by the open tubular columns As a consequence of the increased resolution with these columns it was possible to examine the influence of π-electron density and substitution on several aromatic hydrocarbons The halogenated aromatic hydrocarbon series chloro-, bromo-, and iodobenzene; *m*-, *p*- and *o*-dichlorobenzene, and *o*-, *m*- and *p*-chlorotoluene eluted according to increasing boiling points on both salt coated columns. In contrast, the elution of the positional isomers of the xylenes and the diethylbenzenes was affected more by geometric considerations than boiling point. With both salts, the diethylbenzenes eluted in the sequence *ortho, meta, para* indicating that the increased physical bulk of the molecule produces longer retention. The xylenes eluted in an unpredictable manner on $MnCl_2$, whereas on $CoCl_2$ they were retained according to boiling point Therefore, the geometrical interaction is not evident with less than a two-carbon alkyl substitution. The elution order of geometrical isomers containing a butyl side chain demonstrated an increased retention with a corresponding increase in side chain length on both salts regardless of boiling point

A compound containing a double bond in conjugation with an aromatic system eluted earlier than the corresponding alkyl benzene of similar boiling point on $MnCl_2$ The effect of conjugation in the six-membered ring also indicated that compounds containing isolated double bonds (1,4-cyclohexadiene) are retained to a greater extent than those containing an equivalent number of conjugated double bonds (1,3-cyclohexadiene) Although this study demonstrated that increased retention accompanied increasing π-electron density, 1,4-cyclohexadiene was retained longer on $CoCl_2$ than benzene. Data obtained by Nawrocki *et al* [13] in analyzing cyclohexane, cyclohexene, 1,3- and 1,4-cyclohexadiene and benzene on alkaline earth metal di-*n*-hexylphosphinate micropacked capillary columns provided a retention order similar to that obtained with the whisker-wall-coated $CoCl_2$ columns

The columns containing the same concentration of $MnCl_2$ prepared by either the static or dynamic method provided similar retention data. Varying the concentration of the salt coated on the whisker-walled columns of similar dimension provided evidence that the surface of $MnCl_2$ and $CoCl_2$ was porous, since an increase in salt concentration resulted in a corresponding increase in retention of the adsorbates. Columns of 0 5 mm I D. were not adequate; therefore, use of smaller I D columns

was necessary. The optimum length of the columns appeared to be 25–30 m since longer columns did not offer increased efficiency. The sample capacity of these salt-coated columns is lower than that of liquid-phase-coated open tubular columns.

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