rations[7] of SF_4 from SOF_2, COF_2 from CO_2, and SOF_4 from SO_2F_2. In all cases the alkali metal salt forms an adduct with the more highly fluorinated parent compound and not with its hydrolysis product, thus permitting a simple purification of the parent oxyfluoride.

Use of an alkali metal fluoride column in GSC is limited by two common impurities, H_2O and HF. Because of the deliquescent nature of the metal fluorides care must be taken to minimize the adsorption of atmospheric water vapor during the preparation and packing of the column. Adsorption of moisture by the fluoride results in a marked decrease in the surface area and consequently in the number of active acceptor sites.

Hydrogen fluoride also readily interacts with the alkali metal fluorides to form the very stable bifluorides, MHF_2.

Regeneration of an HF contaminated column has not been generally successful. As some HF cannot generally be avoided in the majority of samples containing nonmetallic oxyfluorides, the only recourse is a periodic column replacement.

Although, as we have noted, there are some difficulties involved in the use of alkali metal fluoride columns in GSC, the novel separation which can be achieved warrants their consideration in any attempt to separate nonmetallic oxyfluoride derivatives.

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CHROM. 4736

Nickel complexes as adsorbents in gas–solid chromatography

The first attempt at modifying stationary phases of gas chromatographic columns with an inorganic electrolyte was by BRADFORD[1] and consisted of silver nitrate dispersed in glycol. Since this time, a number of papers concerned with using inorganic salts and salt-modified stationary phases has appeared[2-5]. PHILLIPS *et al.*[6] reported on the use of N-dodecyl salicylaldimines of Ni, Pd, Pt, and Cu and the methyl-*n*-octyl glyoximes of Ni, Pd, and Pt as stationary phases. They found that retardation

factors for paraffins and olefins were indicative of interactions between the metal complexes and aromatic hydrocarbons. The interaction between primary and secondary amines with the salicylaldimine complexes increased in the order Pt, Pd, Ni, while the order of interaction is reversed in the glyoxime complexes. n-Nonyl-β-diketone complexes of Be, Al, Ni, and Zn were used as liquid phases by CARTONI et al.[7]. Relative retention volumes of various compounds on metal complex columns versus the relative retention volume on a squalane column yielded straight lines passing through the origin. The values of alcohols on the metal complex columns increased from tertiary to primary alcohols. PECSOK AND VARY[8] employed transition metal-phthalocyanine complexes in silicon oil as the stationary phase, and attributed variations in retention volume to interactions between the measured compound and the metal ion. More recently, ILIE[9] reported on the use of transition metals with 1,10-phenanthroline and 2,2'-bipyridine as stationary phases. It was noted both by PECSOK AND VARY[8] and ILIE[9] that the interaction of oxygen-containing compounds on these complexes decreased in the order Fe > Ni > Co > Zn > Cu.

No one has compared the environment surrounding any one transition metal ion. The glyoximes and salicylaldimines offer an ideal case as the substituted groups on either ligand can be easily varied.

In this study we have prepared several sets of complexes utilizing nickel as the transition metal ion, and show the dependence of retention volume of various organic liquids upon the environment surrounding it.

Experimental

Materials. Columns using bis(dimethylglyoximato)nickel(II), bis(1,2-cyclo-hexanedionedioximato)nickel(II), bis(salicylaldimino)nickel(II), and nickel perchlorate as stationary phases were prepared, and are referred to as Ni-DMG, Ni-CHD, Ni-SAL, and $Ni(ClO_4)_2$, respectively. After the columns were prepared the per cent composition was determined by dissolving the complex and found to be of the following composition: Ni-DMG, 4.5%, 8.2%, and 26.8%; Ni-CHD, 12.7% and 27.7%; Ni-SAL, 3.8%, 12.6%, and 25.7%. The nickel perchlorate column was 26.0%. A column using only the solid support was used as a reference. The solid support, used as received, was Gas-Chrom P, 100–120 mesh, acid/base washed, and was obtained from Applied Science Laboratories.

All other chemicals were of reagent grade quality and were used as received. The chemicals used for investigation gave only one peak when chromatographed and were assumed pure enough for use.

Apparatus. A Perkin-Elmer Model 154 gas chromatograph fractometer modified with a thermostatically controlled oven (± 2.0°) and a thermister detector was used with a Leeds and Northrup Speedomax H recorder for retention volume measurements. All measurements were made isothermally at 50°, 85°, and 125°. Thermogravimetric data were obtained on a Dupont 950 thermogravimetric analyzer using a nitrogen atmosphere and a heating rate of 20°/min.

Copper tubing, 6 ft. × 1.4 in. O.D., was filled with the dried packing material. Uniform distribution was achieved by vibration of the column.

Results and discussion

Thermogravimetric analysis on the solid packing materials showed absolute

TABLE I

NET RETENTION VOLUME (ml) ON NICKEL COLUMNS AT 50°a

Compound	26.8% Ni-DMG	27.7% Ni-CHD	25.7% Ni-SAL	26.0% Ni(ClO₄)₂	Gas-Chrom P
Hydrocarbons					
1-Pentene	6.7	8.1	2.0	0.6	0.3
n-Pentane	7.7	7.0	1.9	0.4	—
Allyl chloride	7.5	10.7	2.6	1.4	0.8
n-Hexane	13.4	17.7	4.1	1.2	0.7
Cyclopentane	9.5	13.2	3.2	0.8	0.5
Allyl bromide	13.7	26.0	6.2	2.7	1.9
Cyclohexane	23.2	33.5	6.9	1.4	0.8
Cyclohexene	27.2	40.6	8.4	2.7	1.9
2-Bromobutane	28.6	45.1	10.1	4.3	2.7
n-Heptane	32.1	45.7	9.4	3.0	1.7
n-Bromobutane	37.8	64.7	14.6	6.0	3.9
Benzene	24.0	40.9	9.0	2.9	2.4
Toluene	60.2	106	22.8	9.3	4.3
n-Butylbenzene	N.P.	N.P.	279	129	55.8
Chlorobenzene	115.8	239	51.5	13.2	7.2
m- and *p*-xylene	140	262	58.2	25.2	11.1
o-Xylene	169	325	72.0	30.0	13.2
Bromobenzene	239	538	120	28.9	13.7
Mesitylene	334	683	132	68.4	26.5
p-Cymene	499	N.P.	215	105	40.3
Benzyl chloride	477	N.P.	259	119	443
Aldehydes					
Propionaldehyde	5.4	9.0	3.4	4.7	11.1
Isobutyraldehyde	8.9	12.6	3.9	3.7	6.0
Butyraldehyde	12.4	19.2	5.6	6.8	7.5
n-Valeraldehyde	20.9	49.6	17.0	21.0	17.8
n-Heptaldehyde	167	293	91.1	N.P.	101
2-Ethylhexanal	254	464	113	N.P.	199
Benzaldehyde	321	N.P.	256	N.P.	55.1
Salicylaldehyde	N.P.	N.P.	N.P.	—	—
Esters					
Methyl acetate	7.1	9.4	3.2	5.4	5.3
Cyclohexanone	161	383	116	80.4	102
2,6-Dimethyl-4-heptanone	312	525	127	79.8	174
2-Octanone	375	712	211	84.7	196
Ethers					
Ethyl ether	5.4	6.4	1.1	1.7	2.4
Tetrahydrofuran	17.4	24.5	9.0	7.2	9.6
Dioxane	32.1	57.0	17.6	7.8	22.6
Di-*n*-butyl ether	144	224	48.2	18.5	88.9
Anisole	211	454	111	—	33.2
Alcohols					
Methanol	4.8	16.6	27.1	23.9	3.6
Ethanol	6.2	18.3	22.2	29.9	14.5
tert.-Butanol	11.8	14.9	5.8	N.P.	31.8
Isopropanol	7.5	16.2	11.6	70.5	18.1
n-Propanol	14.9	42.5	39.6	61.8	37.8
Isobutanol	25.0	58.0	39.3	70.5	73.0
n-Butanol	37.4	102	93.9	N.P.	84.9
2-Pentanol	43.7	96.3	49.8	N.P.	—
Isopentanol	69.0	179	N.P.	N.P.	—
n-Pentanol	95.5	280	N.P.	N.P.	203
n-Hexanol	234	567	N.P.	N.P.	207

TABLE I (continued)

Amines					
tert.-Butylamine	16.2	13.4	5.2	9.9	14.9
Diethylamine	17.4	N.P.	0.7	N.P.	8.2
n-Butylamine	51.8	87.3	N.P.	N.P.	42.1
Triethylamine	28.2	44.8	14.9	N.P.	47.5
Pyridine	90.2	254	N.P.	N.P.	63.0
Aniline	N.P.	N.P.	N.P.	N.P.	74.2
N,N-Dimethylaniline	N.P.	N.P.	488	103	128
Acids					
Acetic	N.P.	531	N.P.	N.P.	N.P.

[a] In the case of slight peak asymmetry retention times were measured to peak maxima. N.P. = no peak.

thermal stability of all supports to 220° in a nitrogen atmosphere. Significant decomposition of the nickel complexes occurred only above 250°. At 150°, a temperature exceeding that of any of the chromatographic studies, column packings showed a weight loss of less than 0.1 % upon an extended heating period of 100 h.

Net retention volumes for seventy-four compounds on five of the columns at 50° are presented in Table I. The members within each class of compounds have been arranged in order according to boiling point. With few exceptions, it is noted that retention volumes increase in this same order.

Retention volumes for a compound, measured at the same temperature, were observed to pass through a minimum as the per cent nickel complex on the solid support increased. The retention volumes for a given compound on the same column decreased as the temperature was increased, but the relative order of elution of a class of compounds remained unchanged. In Fig. 1, linear plots for homologous series of alcohols, aldehydes, aliphatic hydrocarbons, and aromatic hydrocarbons are presented. In one case, the first member in the series shows anomalous behavior in being retained in the column for an abnormally long time. This is attributed to the relatively high dipole moment of the small molecule, and its relative ease of polarizability.

Pronounced tailing was observed for compounds on the column packed with uncoated Gas-Chrom P. Peaks obtained on the nickel perchlorate column were less well defined than peaks obtained for the same compounds on the columns made using the nickel complexes as stationary phases. Only aliphatic and aromatic hydrocarbons were eluted from this column at 50°.

For the columns containing nickel complexes as the solid phase peak symmetry was improved by increasing the per cent complex on the solid support (Fig. 2). Comparing retention volumes obtained at the same temperature on columns made from the same complex, varying only in per cent loading, it was noticed that the retention volumes passed through a minimum and increased as the per cent stationary phase increased. This may be explained by attributing the retention volumes on the 4.5% Ni-DMG and the 3.8% Ni-SAL columns to a solid support incompletely covered by the complex and the adsorbates being influenced by the solid support. On the 8.2% Ni-DMG and 12.6% Ni-SAL columns, there may be a thin layer of complex that neutralized the active sites on the solid support, allowing a minimum of interaction with an adsorbate. On columns with higher per cent complex coatings, there may be
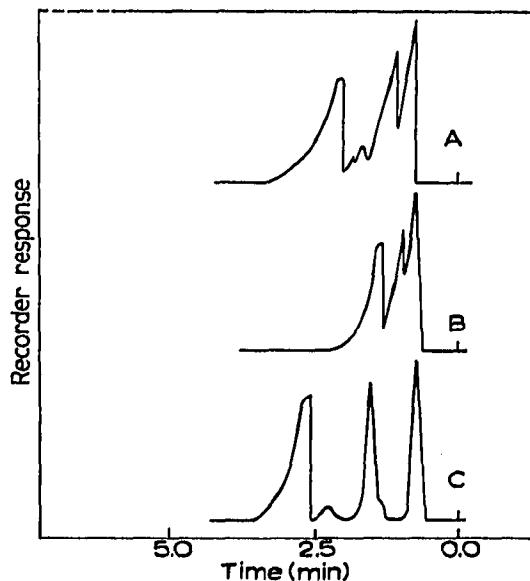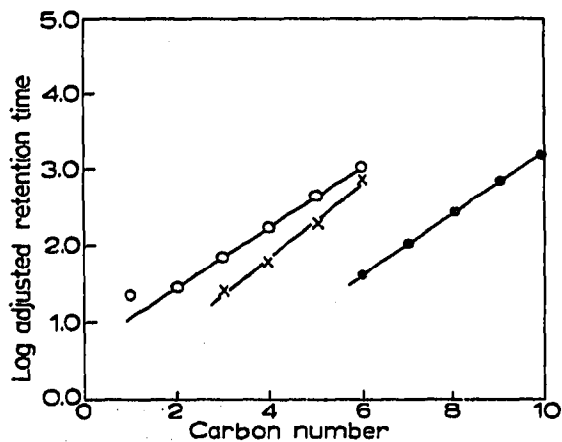
Fig. 1. Logarithm of adjusted retention time for homologous series *versus* carbon number on the 26.8% Ni-DMG column at 50°. ○, Alcohols; ×, aldehydes; ●, aromatics.

Fig. 2. Separation of pentane, hexane, and heptane on Ni-DMG columns. (A) 4.5%; (B) 8.2%; (C) 26.8%.

an excess of complex that completely eliminates active sites on the solid support and allows a maximum of interaction of the adsorbent with the adsorbate.

Satisfactory separation of C_3–C_7 aldehydes was observed using the 26.8% Ni-DMG column; however, a mixture of alcohols was incompletely resolved. Acetic acid was eluted from this column as a symmetrical peak but was not eluted at all from the Ni-SAL column.
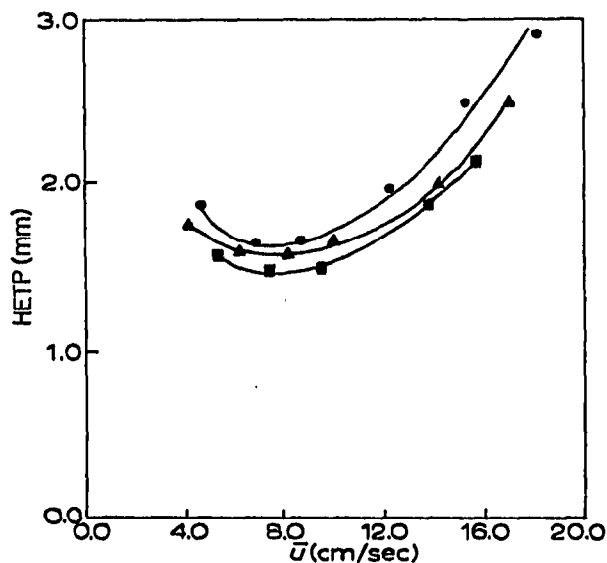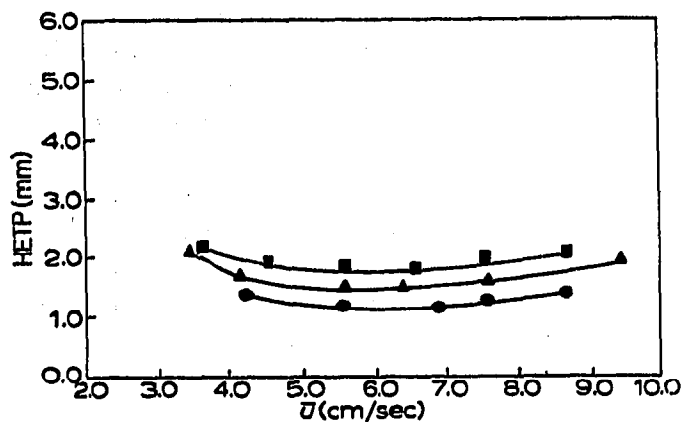

Fig. 3. Comparison of HETP curves for *n*-hexane at 50° (●), 85° (▲), and 125° (■) on the 26.8% Ni-DMG column.

Fig. 4. Comparison of HETP curves for *n*-hexane at 50° (●), 85° (▲), and 125° (■) on 3.8% Ni-SAL column.

The elution of amines from columns constructed of Ni-CHD and Ni-SAL resulted in asymmetrical peaks. Symmetry of these peaks was improved considerably by preconditioning the columns with three to five injections before data were collected. Amine peaks with the best symmetry were obtained using the 26.8% Ni-DMG column.

The number of theoretical plates obtained on the columns varied from 450 to 1600, and a minimum HETP value of 0.98 mm was observed on the 27.7% Ni-CHD column at 50°. For the Ni-DMG columns, plate height increased as column temperatures increased (Fig. 3), but for Ni-SAL a decrease was noted (Fig. 4). Typical Van Deemter data were obtained on the Ni-CHD column. Optimum flow rates were found to be between 6.0 and 8.5 cm/sec.

Benzene and n-hexane were used to study the effect of increasing sample size on retention volume (Fig. 5). In all cases, the sample size varied from 0.05 to 5.0 μl. For
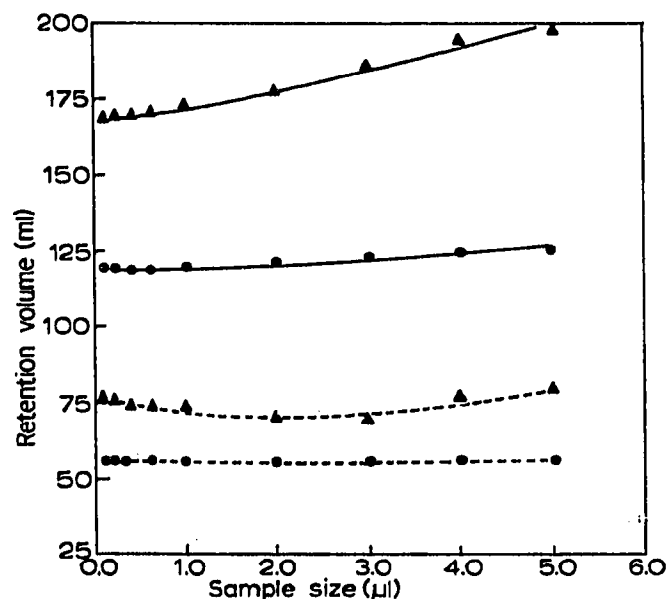

Fig. 5. Retention volume *versus* sample size (μl) at 50° on 26.8% Ni-DMG (▲—▲, benzene; ●—●, n-hexane) and 25.7% Ni-SAL (▲— — —▲, benzene, ●— — —●, n-hexane).

the ten columns studied, the average change of retention volume over the range of sample size examined was only 2–4%. The decrease in retention volume indicates a heterogeneous surface and strongly suggests that adsorption isotherms are concave toward the pressure axis.

Heats of adsorption for a few of the compounds studied on the complexes used as stationary phases were calculated in the usual manner[10] and are presented in Table II. Results are shown for the most symmetrical peaks with retention times being measured at the peak maximum. Comparing the data in Table II for the three columns of interest, 26.8% Ni-DMG, 27.7% Ni-CHD, and 25.7% Ni-SAL, shows that ΔH values are not as large on the Ni-DMG column as the Ni-CHD column, and almost identical to those obtained on the Ni-SAL column. The order of decreasing heats of adsorption, and an indication of increased interaction between adsorbents and adsorbates is Ni-DMG = Ni-SAL < Ni-CHD. This is also the order of increased tailing of compounds on the metal complex columns. The heats of adsorption may be used,

TABLE II

HEATS OF ADSORPTION (kcal/mole)

Columns: (A) 26.8% Ni-DMG;
(B) 27.7% Ni-CHD;
(C) 25.7% Ni-SAL

Compound	Column		
	A	B	C
n-Pentane	−5.7	−5.8	−5.5
n-Hexane	−5.8	−6.3	−5.1
n-Heptane	−7.0	−7.0	−7.2
Diethyl ether	−5.7	−6.0	−3.5
Dibutyl ether	−8.5	−8.9	−8.6
Dioxane	−6.5	−7.1	−6.6
THF	−6.1	−6.3	−6.1
Benzene	−6.3	−6.5	−5.0
p-Xylene	−8.1	−7.5	−6.2
Mesitylene	−9.1	−8.3	−5.9
Bromobenzene	−8.5	−8.9	−6.1

therefore, to explain partially the difference in the amounts of tailing on the three sets of columns studied.

In conclusion, we can say that it is possible to make a chromatographic packing of a slightly soluble complex on a solid support. This type of column has shown selective retention for various classes of organic compounds and can be used for separations of mixtures. Of the metal complexes used as stationary phases, tailing increased in the order: Ni-DMG < Ni-SAL < Ni-CHD. Tailing of the liquids decreased as per cent stationary phase increased, and was found to follow the order: aliphatic hydrocarbons < ethers < esters < ketones < aldehydes < alcohols = amines.

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