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APPLICATIONS OF FUSED-SILICA WALL-COATED OPEN-TUBULAR COLUMNS

II. NON-FLUORINATED SCHIFF BASE CHELATES

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SUMMARY

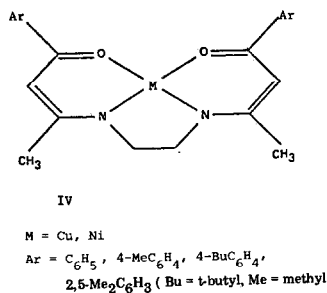
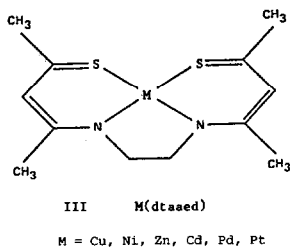
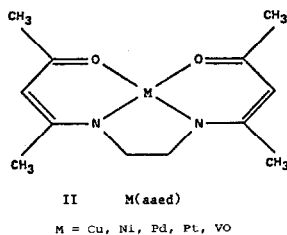
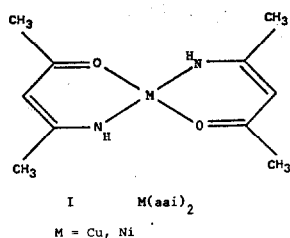
The gas chromatography on fused-silica capillary columns are reported for seventeen transition metal complexes of non-fluorinated Schiff base ligands, including aminothione ligands. Data presented include chromatograms showing various group separations, column activity effects, detection limits, specific retention volumes, rate constants for the chelate decompositions and enthalpies for the solution processes in the bonded stationary phases. The fused-silica columns were found to be generally superior to packed columns, particularly with regard to peak symmetry and resolution. However, activity effects were still evident, with distinct contributions from reversible adsorption, irreversible adsorption and catalysis being observed. The reactive nature of some of the chelates, notably the aminothione chelates and palladium and platinum chelates, seems to preclude their utilization for analytical purposes.

INTRODUCTION

The development of fused-silica wall-coated open-tubular (WCOT) columns has been one of the most significant advances in gas chromatography (GC) of the past ten years^{1,2}. Advantages of these columns include ease of handling, high efficiency, rapid analyses and an intrinsic inertness which can be enhanced by a variety of deactivation procedures³⁻⁸. Inertness, which is the distinctive feature of these columns, has greatly facilitated the trace determination of many polar⁹⁻¹⁵, sensitive^{16,17} or low volatility compounds^{18,19}, as well as complex mixtures which invariably contain such compounds²⁰⁻²⁶.

Many compounds and procedures are currently being reassessed for GC with

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fused-silica columns. One class of compounds which has consistently proved difficult to gas chromatograph due to reactivity and instability is metal chelates²⁷⁻²⁹. Frequently these compounds give abnormal peak shapes, poor separations, tailing and irreversible adsorption. Much of the data available at present, however, are on packed columns. Recent studies with fused-silica columns have been encouraging^{19,30-34} though even here undesirable GC behaviour has already been observed^{33,34}. In a continuation of our recent studies of Schiff base chelates³⁴ we are extending our attention to the non-fluorinated types, I-IV. On packed columns many of these elute unsatisfactorily due to lability³⁵ (I, M = Cu), thermal or catalytic instability³⁶ (II, M = Pd or Pt; III) or low volatility³⁷ (IV). This paper examines, from the analytical viewpoint, the GC of these compounds on five commercial phase-bonded fused-silica columns. Specific retention volumes, kinetic data and thermodynamic data are also reported and discussed in terms of chelate or stationary phase properties.

EXPERIMENTAL

Syntheses

Chelates I-III were prepared from the corresponding ligands; 4-aminopent-3-en-2-one [HaaI], 2,2'-(ethane-1,2-diyl)diimino)bis(pent-2-en-4-one) [H₂aaed] and 2,2'-(ethane-1,2-diyl)diimino)bis(pent-2-en-4-thione) [H₂dttaed] as previously reported^{35,36}. Data are also given for the nickel complex of 2,2'-(methylene-1,2-diyl)diimino)bis(pent-2-en-4-one) [H₂aapd]. The aryl substituted chelates IV were synthesized by procedures similar to those used for II³⁷ and are characterized below. Symbols for transitions observed in differential thermal analysis (DTA) are defined under *Thermal analyses*.

1,1'-Diphenyl-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-one) [H_2baed]. m.p. 179–180°C. Found: C, 75.6; H, 6.8; N, 7.7. Calc. for $C_{22}H_{24}N_2O_2$: C, 75.9; H, 6.9; N, 8.0%. DTA: F, 181°C; D, 316°C.

[1,1'-Diphenyl-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-onato)]copper(II). m.p. 273°C d. Found: C, 63.6; H, 5.4; N, 6.8. Calc. for $C_{22}H_{22}CuN_2O_2$: C, 64.0; H, 5.4; N, 6.8%. DTA: F, 274°C; D, 331°C; D, 349°C.

[1,1'-Diphenyl-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-onato)]nickel(II). m.p. 290–291°C. Found: C, 65.2; H, 5.5; N, 6.9. Calc. for $C_{22}H_{22}NiO_2$: C, 65.2; H, 5.4; N, 6.9%. DTA: F, 292°C; V, 414°C.

1,1'-Bis(2',5'-dimethylphenyl)-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-one) [$H_2,5(CH_3)_2baed$]. m.p. 119°C. Found: C, 77.3; H, 7.6; N, 6.7. $C_{26}H_{32}N_2O_2$ requires C, 77.2; H, 7.9; N, 6.9%. DTA: F, 119°C; D, V, 352°C.

[1,1'-Bis(2',5'-dimethylphenyl)-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-onato)]copper(II). m.p. 160°C. Found: C, 67.1; H, 6.6; N, 5.9. $C_{26}H_{30}CuN_2O_2$ requires C, 66.7; H, 6.4; N, 6.0%. DTA: F, 162°C; D, 248°C; D, 361°C.

1,1'-Bis(4'-methylphenyl)-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-one) [H_2pCH_3baed]. m.p. 178–179°C. Found: C, 77.0; H, 7.5; N, 7.3. $C_{24}H_{28}N_2O_2$ requires C, 76.6; H, 7.4; N, 7.4%. DTA: F, 183°C; D, 338°C.

[1,1'-Bis(4'-methylphenyl)-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-onato)]copper(II). m.p. 261°C. Found: C, 65.5; H, 5.9; N, 6.3. $C_{24}H_{26}CuN_2O_2$ requires C, 65.5; H, 5.9; N, 6.4%. DTA: F, 262°C; D, 345°C; D, 358°C.

1,1'-Bis(4'-tert.-butylphenyl)-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-one) [$H_2p^tBubaed$]. m.p. 225–227°C. Found: C, 77.8; H, 8.8; N, 6.0. $C_{30}H_{40}N_2O_2$ requires C, 78.3; H, 8.7; N, 6.1%. DTA: F, 227°C; D, 299°C.

[1,1'-Bis(4'-tert.-butylphenyl)-3,3'-(ethane-1,2-diyldiimino)bis(but-2-en-1-onato)]copper(II). Found: C, 66.0; H, 7.2; N, 5.0. $C_{30}H_{38}CuN_2O_2$ requires C, 68.9; H, 7.3; N, 5.4%. DTA: F, 260°C; D, 338°C; D, 353°C.

Methods

Thermal analyses. The thermal data were collected on a combined thermogravimetric (TG)-differential thermal analysis (DTA) instrument as previously reported³⁸. DTA data are presented as temperatures measured at peak maxima for the various transitions, identified as fusion (F), decomposition (D), and volatilization (V), as appropriate.

Gas chromatography. A Pye-Unicam Series 304 GC equipped with an SGE Unijector, a flame ionization detector and a Pye-Unicam PU4850 video chromatography control centre was used. Fused-silica WCOT columns are identified as (1) 26 m × 0.33 mm I.D. Chrompack CP Sil 5CB; 0.11 μm film thickness; (2) 25 m × 0.32 mm I.D. Phase Sep OV-1, 0.20 μm film thickness; (3) 25 m × 0.22 mm I.D. SGE BP-1, 0.25 μm film thickness; (4) 25 m × 0.22 mm I.D. Quadrex Methyl Silicone, 0.25 μm film thickness; and (5) 25 m × 0.22 mm I.D. SGE BP-10, 0.25 μm film thickness. All columns contained bonded cross-linked phases.

Column activity. Columns were conditioned, prior to use, at 280°C for 3 h using hydrogen as carrier gas. For assessing column activity, the carrier gas flow was adjusted to give a methane peak at 36 s with the splitter set to 50 ml min⁻¹. Column, injection port and detector temperatures were 90, 240 and 280°C, respectively. A series of injections of the activity mix, consisting of octanal; octan-1-ol;

2,6-dimethylphenol; *n*-undecane, methyl octanoate; 2,6-dimethylaniline; naphthalene; *n*-dodecane; *n*-tridecane; and methyl decanoate, were made and the capacity factor (k') and number of effective theoretical plates (N_{eff}) calculated for each solute. The relative response (peak area or height of solute relative to the peak area or height of *n*-dodecane) was also calculated, as were the Trennzahl (TZ) for *n*-undecane-*n*-dodecane and *n*-dodecane-*n*-tridecane and the acid:base ratio (peak area of 2,6-DMP: peak area of 2,6-DMA). Finally, the column temperature was programmed from 40°C to 120°C at 3.5°C min⁻¹ and the relative response, TZ and acid:base ratio again calculated.

Specific retention volume, V_g . V_g (ml carrier gas/g stationary phase) was calculated from the equation

$$V_g = j[F_c(t_R - t_M)/m_L] 273/T$$

where j = compressibility factor according to James and Martin³⁹; F_c = flow-rate, corrected to column temperature; t_R = retention time (min); t_M = "column" dead-time, determined⁴⁰ by injection of a series of alkanes; m_L = mass of stationary phase (g); T = column temperature (K). The compressibility factor, j , was calculated from the measured inlet pressure (P_i) and the outlet pressure (P_o assumed to be 1 atmosphere) as follows:

$$j = \frac{3 (P_i/P_o)^2 - 1}{2 (P_i/P_o)^3 - 1}$$

Carrier gas flow-rate (F_a) was measured at ambient temperature (T_a) and pressure (P_a) with a bubble flow meter connected directly to the end of the column. F_c was obtained using Charles Law

$$F_c = F_a(T_c/T_a)[1 - (P_w/P_a)]$$

where the latter term corrects for the vapour pressure of water in the bubble flow meter.

The mass of stationary phase was estimated from the known column dimensions using

$$V_L = \Pi d_c d_f L$$

where d_c = column diameter; d_f = film thickness; L = column length, to calculate the volume of stationary phase. Hence, m_L was obtained from the known density and estimated volume.

Although values for V_g were reproducible to $\pm 4\%$, accuracies were limited by estimates of the mass of liquid phase. The procedure used for this estimation was considered more accurate for bonded phase columns than an alternative procedure⁴¹. Data were not corrected for virial effects (non-ideality of gas phase, solubility of gas phase in the liquid phase and compressibility of stationary liquid phase). These effects should be insignificant for the low column inlet pressures (<2.5 atm.) used.

Trennzahl and capacity factor. The Trennzahl, TZ was calculated from

$$TZ = \frac{t_{R(z+1)} - t_{R(z)}}{W_{h(z)} + W_{h(z+1)}} - 1$$

and the capacity factor, k' , from

$$k' = (t_R - t_M)/t_M = t'_R/t_M$$

Heat of solution. The heat of solution, ΔH_s , was obtained from

$$\Delta H_s = -RS_v$$

where S_v is the slope⁴² of a plot of $\ln V_g$ against $1/T$.

*Catalytic activity*⁴³. A test mixture containing a derivative of either H₂aaed or H₂dtaaed and a suitable inert reference substance (*n*-C₂₂H₄₆ or *n*-C₂₆H₅₄, respectively) was injected at three different carrier gas flow-rates at constant temperature (190°C or 220°C). The first-order rate constants for the decomposition, k , were measured from the change in relative peak area, A , according to

$$k = \frac{\ln(A_1/A_2)}{t'_{R2} - t'_{R1}}$$

and the half-life, $t_{1/2} = \ln 2/k$.

RESULTS AND DISCUSSION

Comparison of columns

Before exposing the new columns to chelate vapours, comparisons were made of their separation efficiency and activities according to the Grob standardized tests⁴⁴⁻⁴⁶. The results of this comparison are summarized in Figs. 1 and 2 and Tables I and II.

Differences in efficiencies of columns are represented by the separation number (Trennzahl, TZ) and the number of effective theoretical plates (N_{eff}). Notwithstanding criticisms of both parameters as indicators of separation efficiency^{45,47}, greatest efficiency is attributed to column 3 (from Table II and Fig. 1) followed, in order, by columns 4, 2 and 1. Generally, the columns with the lowest phase ratio (columns 3 and 4) generated more effective theoretical plates per metre than the higher phase ratio columns. The increase in TZ observed for temperature programmed runs (Table II) can be attributed to the temperature optimization associated with temperature programming⁴⁴⁻⁴⁶. Significantly, separation efficiency was unaffected following the injection of chelates onto the columns.

With regard to the activity of the columns toward metal chelates it is relevant to point out that fused-silica columns often have a demonstrable degree of activity, even after deactivation. Extra-column effects and use can also enhance the real or apparent activity of the columns³⁴. Column activities are due to reversible adsorption, irreversible adsorption or catalysis. All three effects give rise to reduced peak

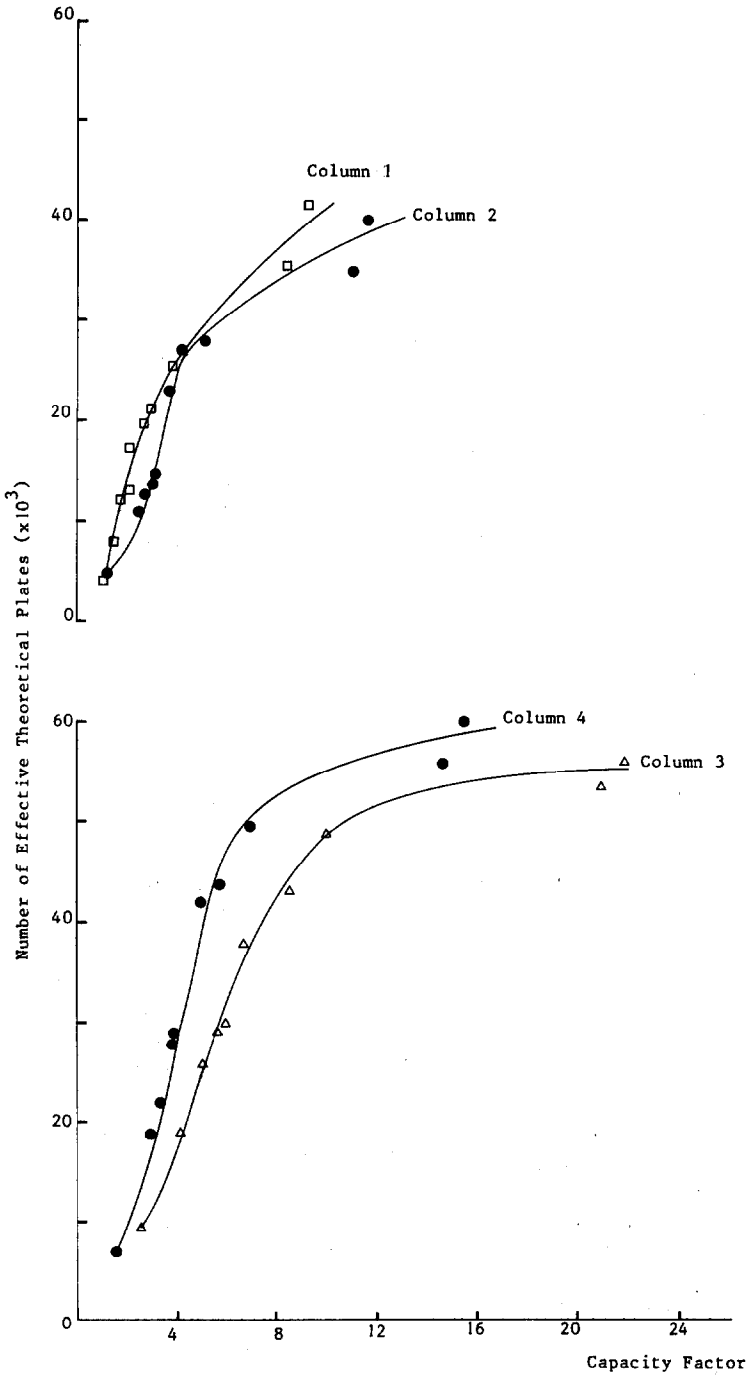


Fig. 1. Number of effective theoretical plates *versus* the partition ratio for the components of the activity mix. Conditions are as described for Table I.

TABLE I
CAPACITY FACTOR FOR THE COMPONENTS OF THE ACTIVITY MIXTURE AT 90°C
Other conditions as in Experimental.

Compound	Partition ratio			
	Column 1	Column 2	Column 4	Column 3
Octanal	0.9	1.3	1.6	2.5
Octan-1-ol	1.5	2.1	2.8	4.1
2,6-Dimethylphenol	1.8	2.5	3.4	5.0
<i>n</i> -Undecane	2.1	2.9	3.8	5.6
Methyl octanoate	2.2	3.0	4.0	5.8
2,6-Dimethylaniline	2.6	3.7	4.8	7.1
Naphthalene	3.0	4.2	5.6	8.4
<i>n</i> -Dodecane	3.8	5.2	6.9	10.0
<i>n</i> -Tridecane	8.4	11.0	14.5	20.8
Methyl decanoate	8.9	11.6	15.3	21.8

heights for susceptible solutes. Reversible adsorption is distinguishable in that it gives rise to tailing or broadened peaks, often with increased retention, but with correct peak areas⁴⁴. Irreversible adsorption and catalysis, which are less easily distinguishable, lead to reduced peak area due to the permanent loss of solute^{44,48}.

Data comparing activities for columns 1-4 are given in Fig. 2. Based on relative peak areas for constituents of the activity mixture, no significant differences in column activities were found. This was not the case with chelates as will be shown shortly. The data showed no temperature or concentration dependence for the ranges 70-130°C and 1 µg-1 ng of solute, respectively, indicating good deactivation of the commercial columns. Comparisons of peak height utilizing temperature programme runs revealed variations from column to column but no clear differences (Fig. 2c). This indicates the occurrence of reversible adsorption. It is noteworthy that the measured activity represents residual activity and extra-column effects since the columns were already commercially deactivated.

Two further observations were made in this preliminary study. The first was

TABLE II
TRENZAHL FOR *n*-UNDECANE-*n*-DODECANE AND *n*-DODECANE-*n*-TRIDECANE

Conditions: isothermal conditions (as described for Table I) and temperature programmed conditions (40°C, hold for 2 min followed by heating at 2.5°C/min to 120°C). In each case, data for the isothermal run is listed first.

Column	Internal diameter (mm)	Phase thickness (µm)	Phase ratio	Trenzahl C ₁₁ /C ₁₂	Trenzahl C ₁₂ /C ₁₃
1	0.33	0.11	750	17.7; 25.0	24.6; 38.4
2	0.32	0.20	400	21.5; 32.6	33.1; 40.1
3	0.22	0.25	220	33.0; 45.4	44.0; 59.5
4	0.22	0.25	220	33.6; 34.8	39.2; 42.4

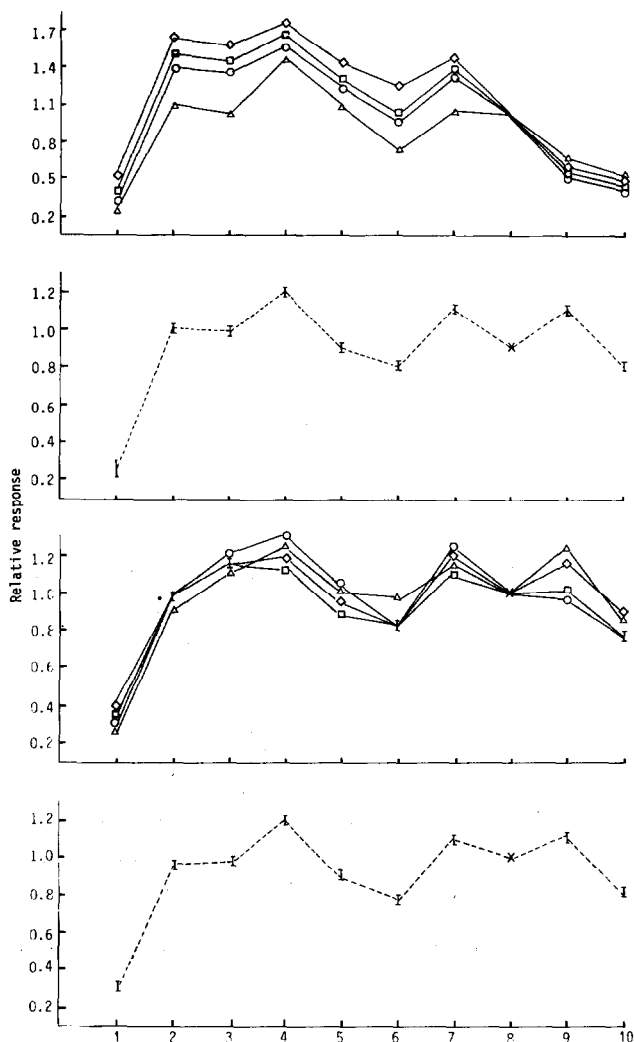


Fig. 2. Detector response for components of the activity mixture relative to *n*-dodecane using isothermal (a and b) and temperature programmed conditions (c and d) and based on peak height (a and c) or peak area (b and d). Columns are identified as Chrompack (◇), Phase Sep (□), SGE (△), or Quadrex (○). Conditions as in Table II. Compounds: 1 = octanal; 2 = octanol; 3 = 2,6-dimethylphenol; 4 = undecane; 5 = methyl octanoate; 6 = 2,6-dimethylaniline; 7 = naphthalene; 8 = dodecane; 9 = tridecane; 10 = methyl decanoate.

that the activity mixture deteriorated on standing (24 h). In particular, the peak area for the octanal peak decreased rapidly as the activity mixture developed a straw colour. This problem may be avoided by keeping the mixture deaerated, cold and away from light. The second observation was the column activity sometimes increased significantly following overnight conditioning. This appeared to be due to dust or other material condensing at the column ends and was overcome by removing a section of column (about 2 cm) from the end.

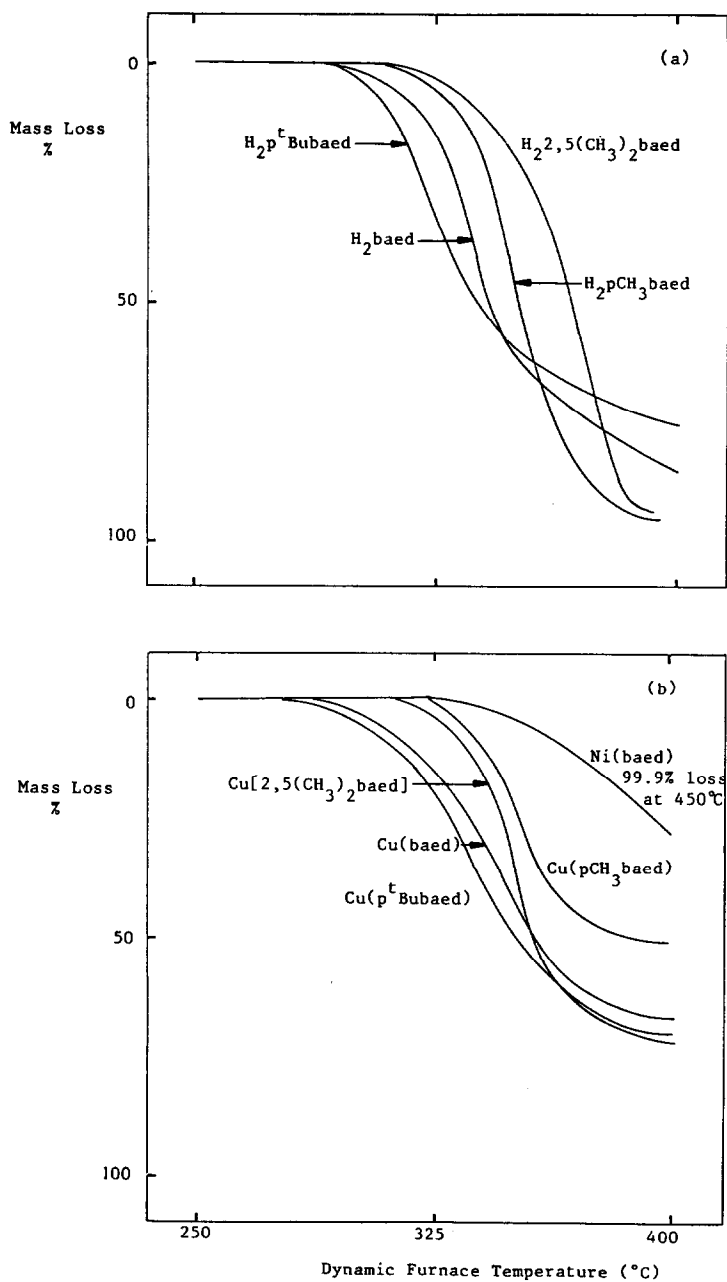


Fig. 3. Thermogravimetric curves for (a) aryl β-ketoenamines and (b) some Cu(II) and Ni(II) chelates.

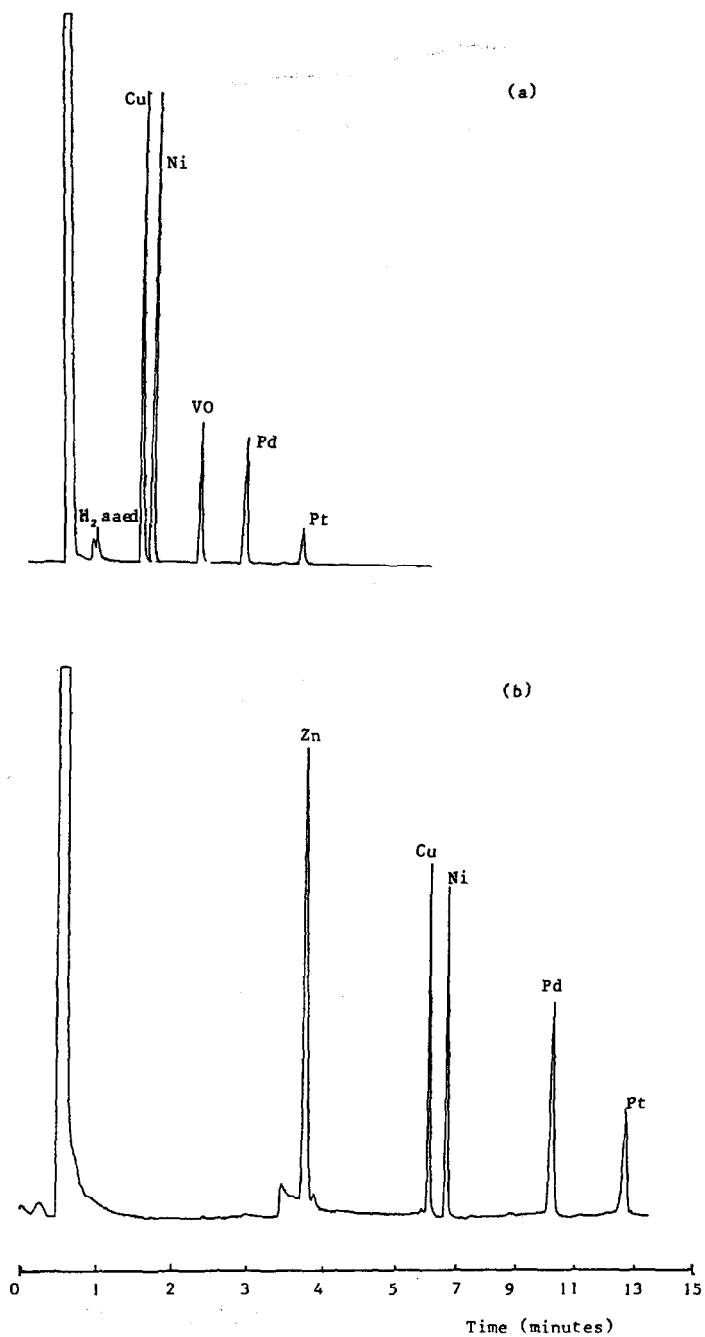


Fig. 4. Chromatograms of the derivatives of (a) H₂aaed and (b) H₂dtaaed on column 4 at 250°C (hydrogen carrier gas, 82.5 cm s⁻¹). Injection port and detector temperatures were 260 and 280°C, respectively.

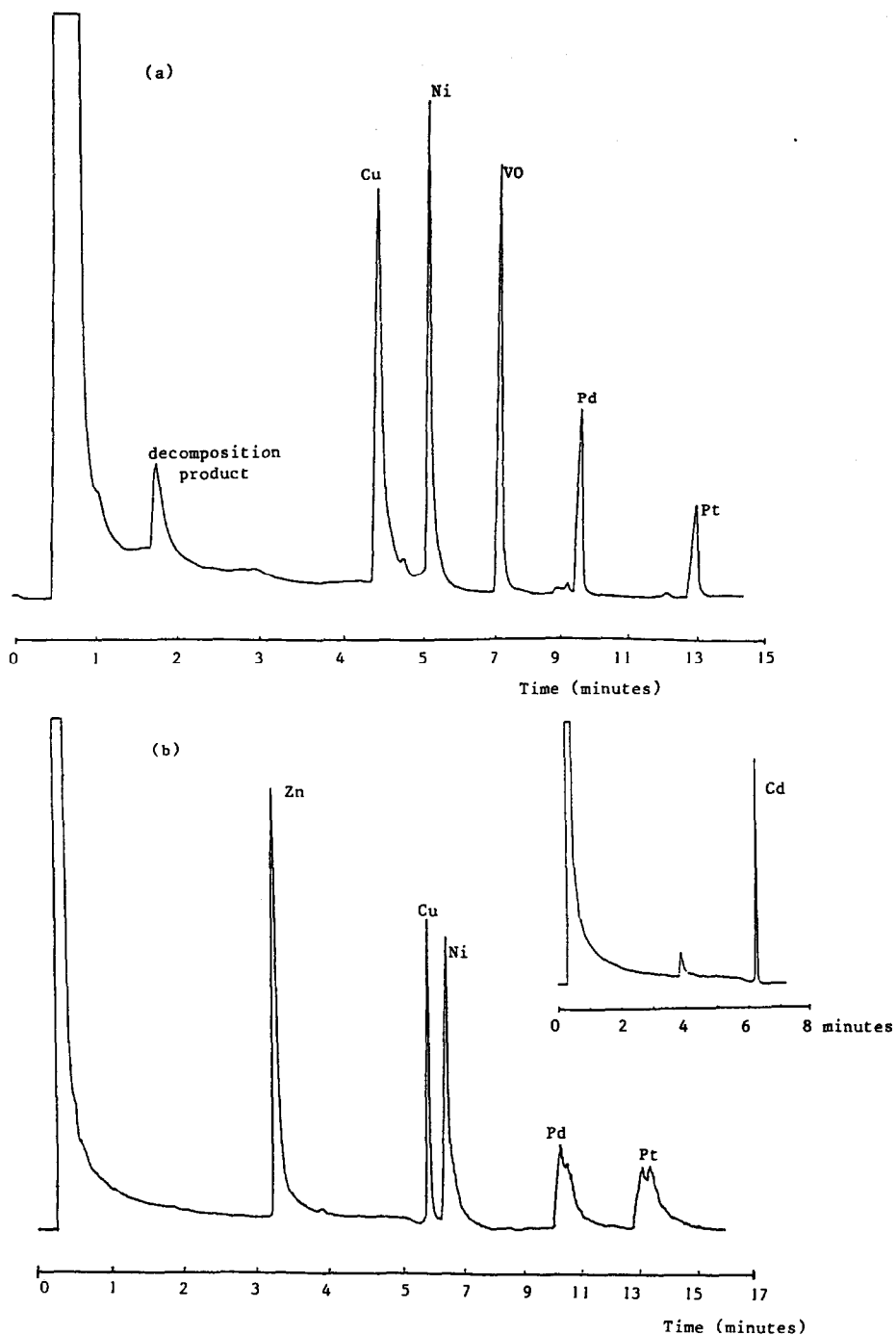


Fig. 5. Chromatograms of the derivatives of (a) H_2aaed and (b) $H_2dtaaed$ on column 3 at 220° (hydrogen carrier gas, 82.5 cm s^{-1}), and $245^\circ C$ (133 cm s^{-1}), respectively. Injection port and detector temperatures were 260 and $280^\circ C$. In (b), Cd(dtaaed) is shown separately, because of coelution.

TABLE III
ADJUSTED RETENTION TIMES FOR THE CHELATES

Injection port and detector temperature were 260 and 280°C, respectively. Column 1, temperature 190°C, carrier gas velocity 160 cm s⁻¹; column 3, 220°C, 83 cm s⁻¹; column 4, 250°C, 83 cm s⁻¹; column 5, 240°C, 76 cm s⁻¹.

Compound	Adjusted retention time (min)			
	Column 1	Column 3	Column 4	Column 5
Zn(dtaaed)	4.88	11.9	3.18	Not eluted
Cu(dtaaed)	10.23	23.5	5.25	Not eluted
Cd(dtaaed)	Not eluted	23.9	Not eluted	Not eluted
Ni(dtaaed)	12.03	26.8	5.90	Not eluted
Pd(dtaaed)	2.50*	11.5**	9.33	Not eluted
Pt(dtaaed)	3.07*	13.5**	11.57	Not eluted
Cu(aaed)	1.40	3.95	1.17	6.52
Ni(aaed)	1.73	4.67	1.22	8.45
VO(aaed)	2.63	6.83	1.70	17.3
Pd(aaed)	3.53	9.32	2.30	20.2
Pt(aaed)	5.24	12.8	3.05	21.3
Cu(aai) ₂	0.2	0.5	0.3	0.3
Ni(aai) ₂	0.3	1.31	0.4	0.5
Ni(aapd)	1.32	3.77	1.12	6.14

* Column temperature, 240°C.

** Column temperature, 260°C.

Stability and GC of chelates

The stability and volatility of chelates I–III have been reported previously^{33,34}. All appear sufficiently stable for GC with the possible exception of Zn(dtaaed), Cd(dtaaed) and Cu(dtaaed) which decompose at relatively low temperatures (200–240°C). Relative volatilities established for each group were:

TABLE IV

DETECTION LIMITS (FID) FOR THE DERIVATIVES OF H₂dtaaed AND H₂aaed ON COLUMN 1 AT 220 AND 240°C, RESPECTIVELY

Split ratio 1:20.

Compound	Detection limit (ng)
Zn(dtaaed)	60
Cu(dtaaed)	80
Cd(dtaaed)	Not eluted
Ni(dtaaed)	10
Pd(dtaaed)	80
Pt(dtaaed)	160
Cu(aaed)	25
Ni(aaed)	21
VO(aaed)	30
Pd(aaed)	80

Haai chelates: Cu(II) > Ni(II)

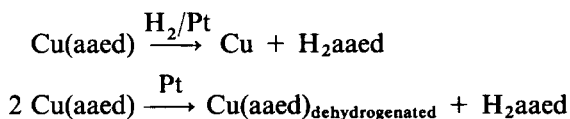
H₂aaed chelates: Cu(II) > Ni(II) > VO(IV) > Pd(II) > Pt(II)

H₂dtaaed chelates: Zn(II) > Cd(II) > Cu(II) > Ni(II) > Pd(II) > Pt(II)

Generally, for a given ion, volatility decreases appreciably in proceeding from I to II to III.

TG data for the aryl substituted ligands and their copper(II) and nickel(II) complexes IV are summarized in Fig. 3. These compounds are relatively stable but of low volatility and with the singular exception of Ni(baed) (III, M = Ni, Ar = phenyl), decompose extensively during volatilization at 300–400°C. From Fig. 3 it is also seen that substituents in the aromatic ring give no significant enhancement in either volatility or stability and therefore provide no advantage for GC.

Chromatograms showing the complete separation of II and III group chelates are given in Figs. 4 and 5. Generally, elution orders paralleled volatilities (Table III) while flame ionization detection limits (Table IV) (taking into account the split ratio for the fused silica column) were comparable to those on packed columns³⁶. As expected, peak symmetry and resolution were an immediate improvement to those achieved on packed columns. A particular improvement was observed for the relatively labile Cu(aai)₂ which eluted as a sharp symmetrical peak with considerably less baseline elevation than observed on packed columns. However, the reactive nature of the aminothione chelates III previously observed on packed columns³⁶ was still evident. For Cd(dtaaed) a sharp peak of small area was obtained on column 3 but no peaks (probably due to complete decomposition) were observed on any other columns. None of the aminothione chelates could be eluted from the moderately polar column 5. Strangely, it was the thermally more stable Pd(II) and Pt(II) complexes* of this group which decomposed to the greatest extent suggesting a catalytic induced decomposition for these chelates (vide infra). Similar problems were encountered in the corresponding H₂aaed chelates of these ions. Here, not only did Pd(aaed) and Pt(aaed) decompose but they sensitized the decomposition of the copper(II) complex, apparently to H₂aaed (see Figs. 4a and 5a). Suggested reactions, with the possible involvement of the hydrogen carrier gas are:



Such reactions are most likely to occur at the injection port.

Not surprisingly, the aryl-substituted derivatives IV proved difficult to chromatograph and we could not obtain identifiable peaks for these compounds at 200–280°C on columns 1–4. We are currently investigating the use of short columns for these complexes.

Chelates and column activity

Measurements of the time, temperature and concentration dependence of the losses of injected solutes have been used⁴³ to distinguish reversible adsorption (physi-

* TG data show³⁶ that these complexes are stable above 360°C.

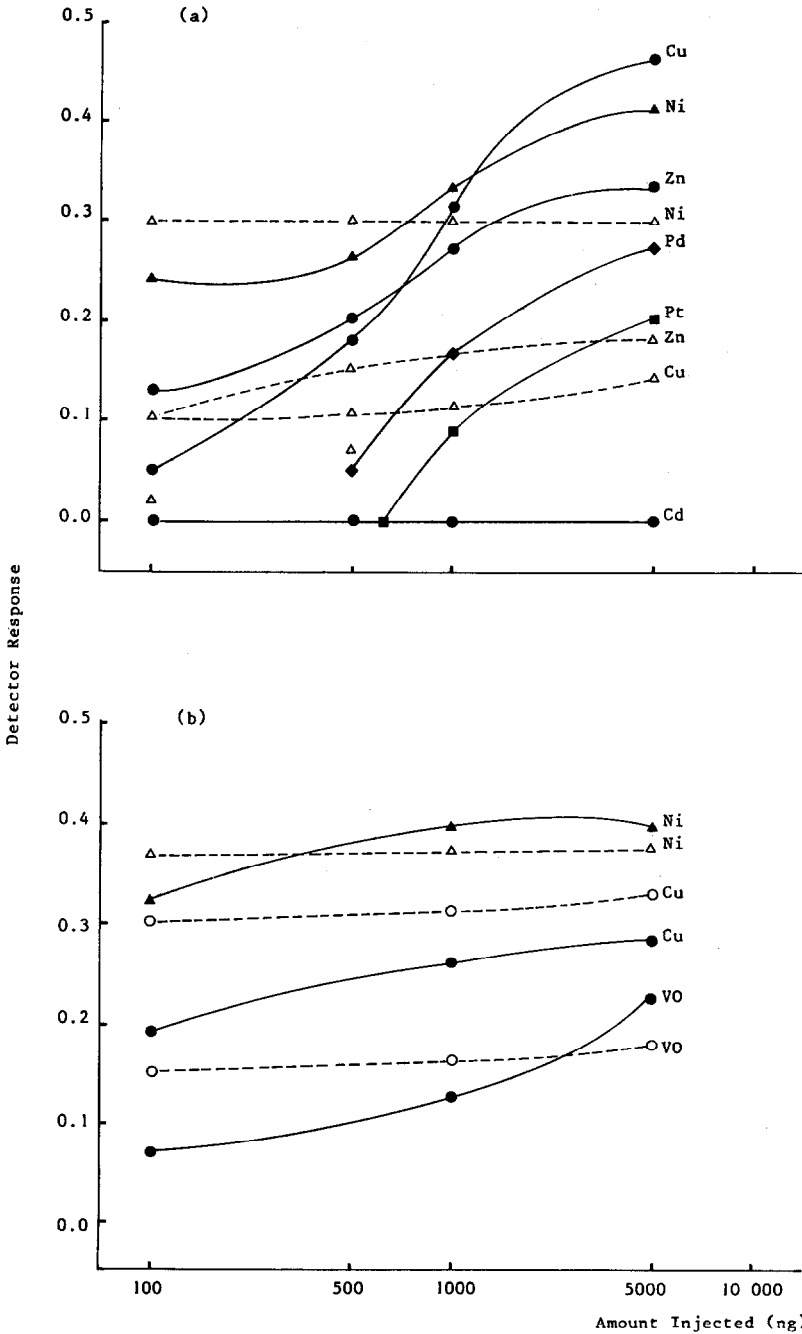


Fig. 6. Detector response (peak area) for derivatives of (a) H₂dtaaed and (b) H₂aaed relative to equal concentrations of *n*-C₂₈H₅₈ and *n*-C₂₂H₄₆, respectively on column 1 (closed symbols) or column 3 (open symbols) at 220 or 240°C, respectively. Other conditions are as described in Table III. Split ratio 1:5.

TABLE V

FIRST-ORDER DECOMPOSITION RATE CONSTANTS AND HALF-LIVES FOR SELECTED CHELATES ON COLUMN 1

<i>Compound</i>	<i>Decomposition rate constant (s^{-1})</i>	<i>Half-life (min)</i>
Zn(dtaaed)	$16.7 \cdot 10^{-3}$	0.72
Cu(dtaaed)	$3.8 \cdot 10^{-3}$	3.1
Ni(dtaaed)	$0.39 \cdot 10^{-3}$	29.6
Pd(dtaaed)	$\approx 10^{-1}$ – 10^{-2}	*
Pt(dtaaed)	$\approx 10^{-1}$ – 10^{-2}	*
Cu(aaed)	10^{-5}	large
Ni(aaed)	10^{-5}	large
VO(aaed)	10^{-5}	large

* Data were not reproducible for these chelates.

cal adsorption), irreversible adsorption (chemisorption) with non-zero activation energy and catalytic activity in GC columns. Our measurements on fused-silica columns implicated all three mechanisms in the loss of chelate solutes with variations from column to column. Thus, Cu(aaed), Ni(aaed) and VO(aaed) exhibit a concentration-dependent loss on column 1 (Fig. 6) characteristic of irreversible adsorption whereas on column 3, these effects were absent.

Catalytic activity appears to regulate the behaviour of aminothione chelates III on the fused-silica columns. This was evident from the time-dependent, concentration-independent nature of solute losses on column 3 (Fig. 6 and Table V). On column 1 the same chelates showed both time- and concentration-dependent losses indicating separate irreversible adsorption and catalytic effects. Time- and concentration-dependent losses were observed for all four Pd(II) and Pt(II) derivatives on

TABLE VI

SPECIFIC RETENTION VOLUMES FOR SELECTED CHELATES ON COLUMNS 1, 3, 4 AND 5 AT 192°C

Experimental conditions were as described for Fig. 8.

<i>Compound</i>	<i>Specific retention volume ($ml\ g^{-1}$)</i>			
	<i>Column 1</i>	<i>Column 3</i>	<i>Column 4</i>	<i>Column 5</i>
Cu(aai) ₂	392	399	*	*
Ni(aai) ₂	498	491	*	*
Cu(aaed)	2059	2101	1572	7708
Ni(aaed)	2592	2618	1772	9897
Ni(aapd)	1882	1845	1313	7406
Zn(dtaaed)	6768	7044	4722	*
Cu(dtaaed)	14186	14913	9701	*
Ni(dtaaed)	16815	15994	11384	*

* Not examined.

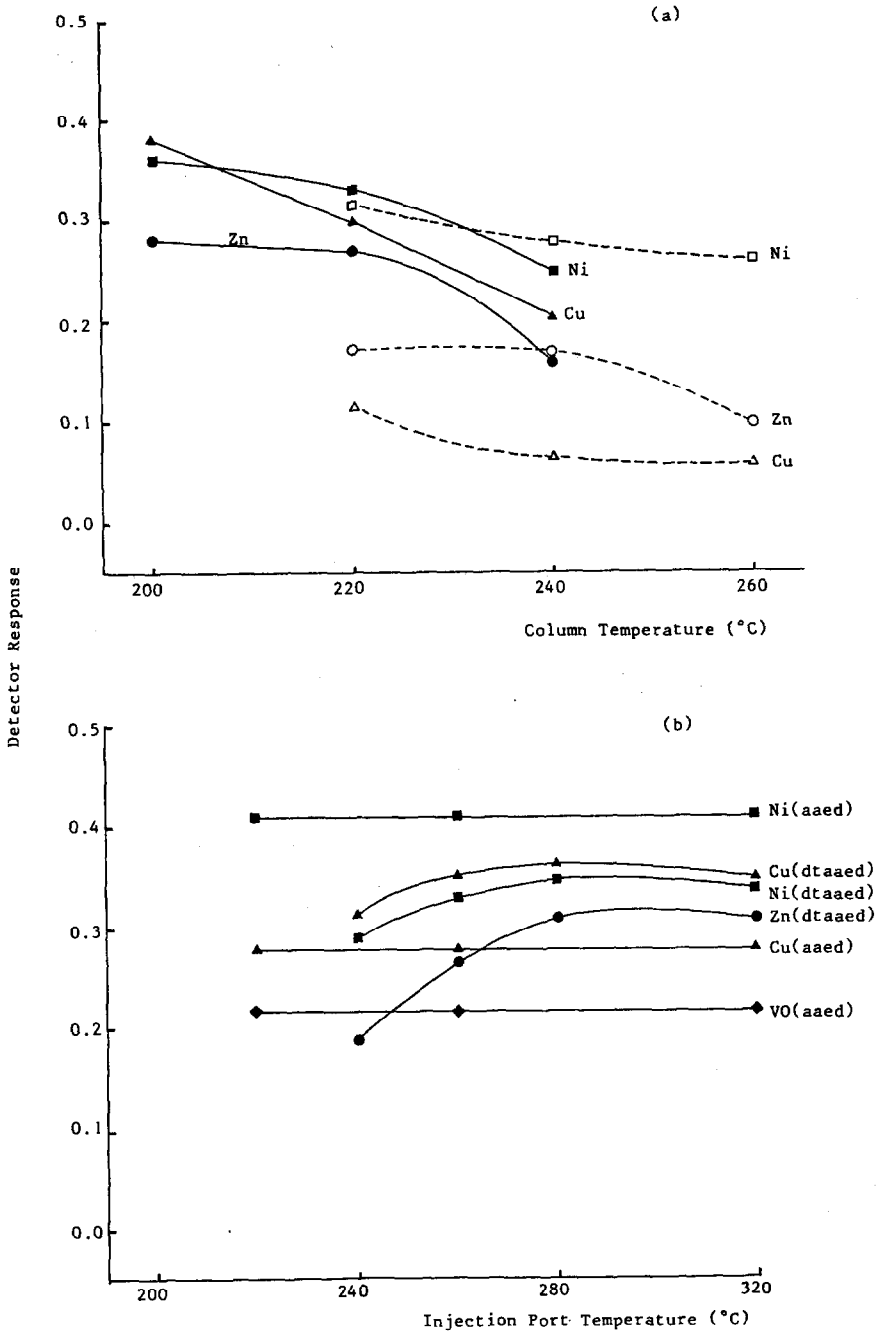


Fig. 7. Relative response for (a) derivatives of H₂dtaaed on columns 1 (closed symbols) and 3 (open symbols) versus column temperature and (b) derivatives of H₂dtaaed and H₂aaed on column 1 versus injection port temperature. In (a) flow-rate was varied to maintain a constant adjusted retention time. Other conditions as in Fig. 6.

TABLE VII

HEATS OF SOLUTION (kJ mole^{-1}) FOR SELECTED COMPOUNDS ON COLUMNS 1, 3, 4 AND 5

Compound	Heat of solution (kJ mole^{-1})			
	Column 1	Column 3	Column 4	Column 5
$n\text{-C}_{20}\text{H}_{42}$	-62.8	*	*	*
$n\text{-C}_{22}\text{H}_{46}$	-73.5	*	*	*
$n\text{-C}_{24}\text{H}_{50}$	-80.2	*	*	*
$\text{Cu}(\text{aai})_2$	-60.7	*	*	*
$\text{Ni}(\text{aai})_2$	-60.2	*	*	*
$\text{Cu}(\text{aaed})$	-68.6	-72.3	-66.0	-75.9
$\text{Ni}(\text{aaed})$	-70.2	-74.5	-64.3	-78.2
$\text{Ni}(\text{aapd})$	-69.4	-71.5	-62.6	-75.1
$\text{Zn}(\text{dtaaed})$	-74.8	-77.9	-69.3	*
$\text{Cu}(\text{dtaaed})$	-79.4	-81.8	-74.0	*
$\text{Ni}(\text{dtaaed})$	-79.8	-77.7	-75.8	*

* Not examined.

columns 1-4. In fact, data for these chclates were irreproducible and depended on the amount and type of complexes previously injected into the column. These complexes therefore appear very sensitive to catalytic decomposition, possibly from products of their own decomposition (most likely metallic palladium and platinum). The occurrence of thermal-catalytic decomposition for the chelates is supported by the reduction in response with increase in column temperature (Fig. 7a). Note from Fig. 7b, however, how the injector temperature affects results for the aminothione chelates. Here, it appears that the latter are strongly adsorbed or discriminated against in the injector below 280°C . Although data presented here cannot distinguish between catalytic and thermal decomposition, catalytic decomposition is likely for $\text{Pt}(\text{dtaaed})$ and $\text{Pd}(\text{dtaaed})$ as they are thermally stable above 360°C but decompose well below this temperature on the columns.

Specific retention volumes and heats of solution

The specific retention volume, V_g , is an important GC parameter since it relates directly to the chemical properties of the solute and stationary phase. We have therefore calculated V_g and the heat of solution, ΔH_s , for a variety of chelates on columns 1-5 to examine differences in the characteristics of (i) the chelates and (ii) the bonded phases.

Data presented in Table VI for selected chelates show that differences in retention (Table III) for various chelates on columns 1 and 3 are simply due to differences in the phase ratio rather than a fundamental difference in the retention mechanism. On the other hand, the lower values of V_g on column 4 suggest this phase is less polar than the previous two, even though they are all polydimethylsiloxane columns. The high values for V_g on column 5 are consistent with a more polar column.

The enthalpy change for the process: solute (ideal vapour; T K; 1 atm) \rightarrow solute (solution; T K; infinite dilution in solvent) which is the heat of solution, was evaluated⁴² from the temperature dependence of V_g in the equation

$$-\Delta H^0 = R[\text{dln } V_g/\text{d}(1/T)]$$

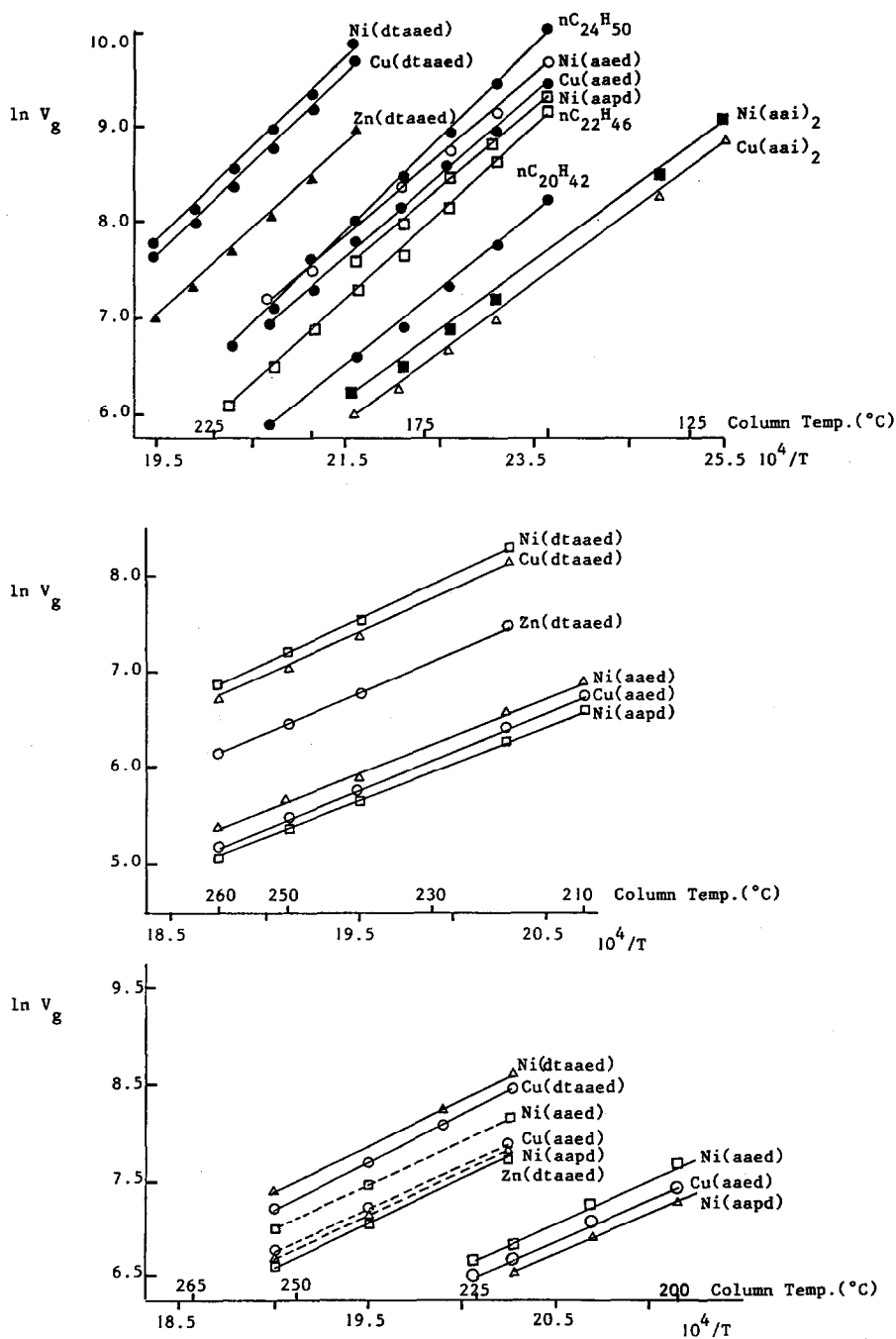


Fig. 8. Plot of $\ln V_g$ against $10^4/T$ for selected chelates on (a) column 1; (b) column 4; and (c) columns 3 (solid curves) and 5 (broken curves). Injection port and detector temperatures were 260 and 265°C, respectively.

using a linear least squares fit of $\ln V_g$ versus $10^4/T$ (Fig. 8). Although the heats of solution (Table VII) do not differ greatly between the various chelates* there is a significant decrease in ΔH_s for chelates I, II and III paralleling the order of increasing polarity**. Generally, ΔH_s also decreases in going to a more polar phase (column 5). The presence of a methyl substituent at the bridging carbon as in H₂aapd shows no change in ΔH_s relative to the derivatives of the unsubstituted H₂aaed. Finally, for each chelate type, no significant difference in ΔH_s between the copper(II) and nickel(II) members was found, as expected for structurally similar compounds of similar polarity.

CONCLUSION

Fused-silica columns provide improved peak symmetry and resolution of Schiff base chelates but cannot compensate for extremely labile or reactive complexes. Measurable activities, which vary from column to column, or the same column with usage and time, means that columns should be regularly tested with the chelates to be chromatographed. Finally, some means of reducing the enhanced activity of columns contaminated with catalytically active metal or metal oxide deposits would be desirable.

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* Using a mean value of 72.2 kJ mole⁻¹, the variation is $\pm 16\%$.

** Dipole moments measured for Ni(aai)₂, Ni(aaed) and Ni(dtaaed) in benzene at 25°C were 0, 4.5 and 6.1 Debye, respectively⁴⁹.

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