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

I. SCHIFF BASE CHELATES

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SUMMARY

The gas chromatographic behaviour of tetradentate Schiff base chelates of Cu(II), Ni(II), Pd(II) and VO(IV) on fused-silica wall-coated open-tubular columns have been examined and compared to results obtained on packed columns. The fused-silica columns, expectedly, produced significant improvements in peak shape, resolution and detection limits. For example, fluorinated chelates of Cu(II) and Ni(II) which have previously not been resolved on packed columns were completely separated on the capillary columns. Nonetheless, limitations due to the reactivity and stability of the chelates remained. Residual activity in the column and activity created by chelates previously introduced onto the column were also evident. These effects were minimized by careful selection of ligand, column and column conditions.

INTRODUCTION

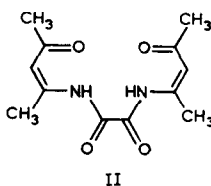
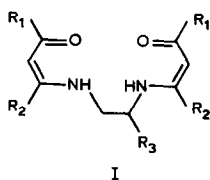
Despite adequate volatility and thermal stability many metal chelates have had restricted applications in analytical gas chromatography (GC)^{1,2}. This is due mainly to the adverse on-column behaviour exhibited by many of these compounds and due, in turn, to their chemical reactivity. To a lesser extent, the reactivity of the GC column itself may also contribute to this problem. Attempts to improve column behaviour have focused mainly on varying the ligand or ligand substituents to enhance chelate volatility and stability. Thus, while fluorinated β -diketones³⁻⁵ are suitable for the kinetically inert Cr(III), Rh(III) and Co(III) ions, β -ketoenamines⁶⁻⁹ have proved more suitable for Cu(II), Ni(II) and VO(IV). On the other hand, soft class B ions^{10,11} such as Pt(II), Pd(II) and Pb(II) have been more amenable to GC with

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sulphur donor ligands such as the dialkyldithiocarbamates¹² or monothio- β -diketonates¹³. The utilization of tetradentate⁸ or hexadentate ligands¹⁴ to enhance stability by the "chelate effect" has also been effective in improving GC behaviour.

Attempts to reduce column reactivity have in the past employed borosilicate glass columns^{2,3}, deactivated diatomaceous supports and on-column silanization¹⁵. More recently, highly deactivated fused-silica wall-coated open-tubular (WCOT) columns have been applied to the GC of dialkyldithiocarbamates¹² and variously substituted β -diketonates¹⁶. The much improved behaviour on these columns was reflected in lower detection limits and the reduction of peak and baseline abnormalities. Nonetheless, even these columns possess a residual activity¹⁶⁻²² which may be greatly enhanced by introduction of chelates onto the column. It is therefore important in critical applications to assess column activity as well as separation efficiency¹².

In this paper we examine the GC of Cu(II), Ni(II), Pd(II) and VO(IV) chelates of the tetradentate Schiff bases (I) and the Cu(II) and Ni(II) chelates of the tetraketo ligand (II) on fused-silica WCOT columns. Optimum conditions which could be utilized in future analytical applications are identified. In addition, the effects on the activity and separation efficiency following the introduction of chelates onto the columns are assessed.



Ligand	R ₁	R ₂	R ₃
H ₂ aaed	CH ₃	CH ₃	H
H ₂ tfaed	CF ₃	CH ₃	H
H ₂ tpmed	t-butyl	CF ₃	H
H ₂ tfapd	CF ₃	CH ₃	CH ₃

EXPERIMENTAL

Chelates

Ligands and chelates were synthesised as previously described²³⁻²⁵. Each chelate was prepared initially in dichloromethane (or acetone) as a 0.1% (w/v) solution and diluted with dichloromethane as required.

Instrumentation and columns

Most of the work was performed on a Pye Unicam Model 304 gas chromatograph equipped with a Scientific Glass Engineering (SGE) Unijector injection system, flame ionization detector and Pye Unicam PU4810 computing integrator. Where cold on-column injection was required a PU4900 gas chromatograph was utilized. Fused-silica WCOT columns (25 m × 0.22 mm I.D. except where otherwise stated) with coated phases (OV-101, OV-17, Carbowax 20M) or bonded phases (BP-1, BP-10, BP-20) were supplied by SGE. Carrier gas was high-purity hydrogen. Packed col-

umns, consisting of borosilicate glass coils (0.9 m \times 4 mm I.D.) packed with 3% loading of stationary phase on either Chromosorb W or Chromosorb 750, were silylated and conditioned before use, as previously described²⁶. The nitrogen carrier gas flow was 40 ml min⁻¹. Column, injection port and detector temperatures were 200°C, 210°C and 210°C, respectively.

Determination of activity of fused-silica WCOT columns

Prior to use, columns were conditioned at maximum allowable operating temperatures (as specified in the supplier's catalogue) for 10 h with nitrogen carrier gas. The activity and efficiency of the conditioned columns were then determined with SGE test mixtures containing octan-2-one; octan-1-ol; 2,6-dimethylphenol (2,6-dmp); 2,4-dimethylaniline (2,4-dma); naphthalene and various alkanes. For this purpose, partition ratios (k'), separation number (S) and the number of effective theoretical plates for 2,6-dmp and 2,4-dma were calculated for each column using 1 μ l of diluted (1:10) SGE test mixture. Response data (peak height and area) relative to *n*-dodecane or *n*-hexadecane were also determined for the various components of the mixtures.

RESULTS AND DISCUSSION

Column performance and activity were measured before and after the introduction of chelates onto the WCOT columns. For this purpose we preferred to use split rather than splitless injection to avoid the complicating effect of introducing relatively large quantities of solvent directly onto the column. With split injection, however, discrimination effects were apparent for early eluting solutes (partition ratio, $k' < 1.5$). An alkane with a k' value in the range 2–6 was therefore chosen as reference peak. As shown in Fig. 1 this eliminates the volume dependence of relative response data.

The separating efficiency of the columns, expressed as the number of effective theoretical plates and the separation number of 2,6-dmp and 2,4-dma (Table I), was unaffected by injection of chelates onto the columns. Similarly, partition ratios for organic test solutes and chelates remained unaltered. On the other hand, the results reveal interesting changes in activity of the various columns following the injection of 2–10 μ g chelates. Thus, the activities of the OV-17 and BP-10 columns were unaltered whereas those of OV-101 and BP-1 columns increased following chelate injection. This is seen in Fig. 2 as a change in the relative response for the various test solutes. Reduction in the relative peak height (shown for OV-101) can be attributed to reversible adsorption of the test compounds by Lewis acid sites (octanone), metal adsorptive sites (naphthalene) and hydrogen bonding sites (octanol) in the column. All columns gave an acid:base ratio (peak area 2,6-dmp:peak area 2,4-dma) less than 1.0 indicating selective retention of acidic components due to an excess of basic sites in the column. However, in the case of OV-101, the reduction in relative peak area observed for octanone is evidently due to irreversible adsorption on Lewis acid sites. Surprisingly, the relative peak area of test solutes other than octanone increased following introduction of chelates into the OV-101 and BP-1 columns. The data suggest selective retention of the reference compound, *n*-dodecane or, more probably, saturation of existing sites by the chelates leading to an enhanced relative response for the test solutes. The active sites giving rise to these phenomena appeared to be

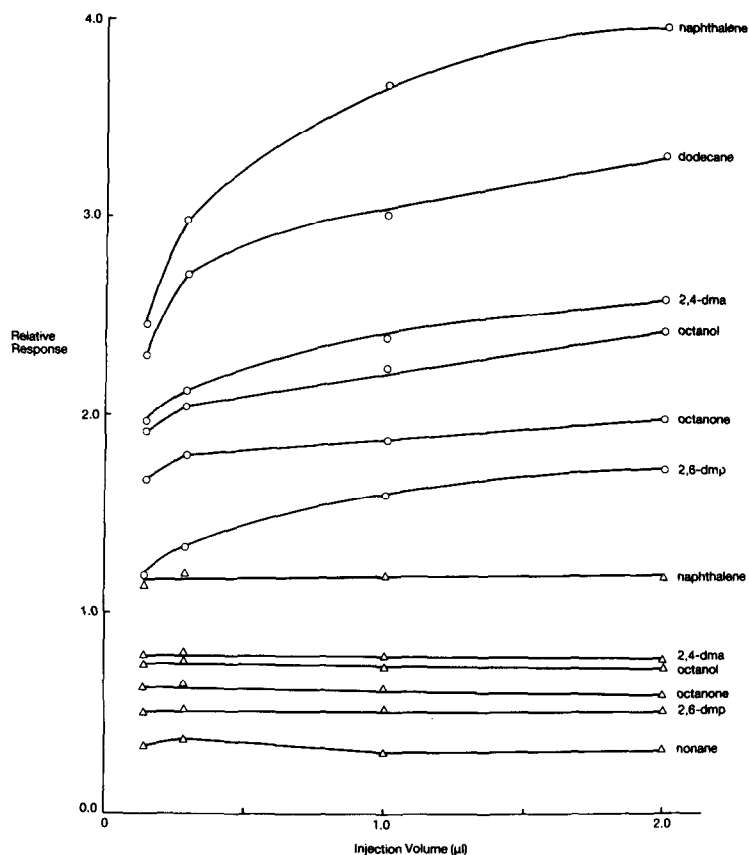


Fig. 1. Response (peak area) of organic test compounds relative to *n*-nonane (○—○) or *n*-dodecane (△—△) for different injection volumes on an OV-101 column.

localized at either end of the column since removal of 5 cm of column from both ends restored relative responses to those of new columns. Finally, the activities of the polar Carbowax 20M and BP-20 columns were increased by the injection of chelates. For these columns the original activities could not be restored by removal of end-ports. This appears to be a general phenomenon^{1,2,14} due to dissociation or strong retention of chelates in the polar stationary phase. It is possible, however, that reversibility can be obtained with long conditioning times, or following treatment with ligand.

Relevant data on packed columns are presented before examining the GC of the chelates on fused-silica WCOT columns.

Packed columns

The copper(II) and nickel(II) chelates of H_2aaed and H_2tfaed were studied on packed columns with SE-30, OV-3, OV-17, OV-25, OV-210 and Dexsil-300 stationary phases. The results, obtained at temperatures of 200°C, are represented in Figs. 3 and 4. For convenience, chromatograms of the oxovanadium(IV) chelates are presented here, also. In proceeding from SE-30 to the more polar stationary phases

TABLE I

PERFORMANCE PARAMETERS (N_{eff} AND S) FOR THE WCOT COLUMNS AT VARIOUS CARRIER GAS FLOW-RATES

Injection port and detector temperatures were 280 and 300°C, respectively.

Column	Column temperature (°C)	Carrier gas velocity (cm s ⁻¹)	Compound*	Partition ratio, k'	N_{eff}	S
OV-101	115	42	a	3.0	45 182	8.8
			b	3.7		
OV-17	115	42	a	3.2	52 469	7.1
			b	3.8		
Carbowax 20M	145	42	b	4.1	28 514	4.0
			a	4.6		
BP-1	115	50	a	2.0	35 456	7.1
			b	2.5		
BP-10	115	50	a	6.1	60 086	8.1
			b	7.2		
BP-20	155	42	b	7.3	63 469	4.5
			a	7.9		

* a = 2,6-dmp; b = 2,4-dma.

OV-3, OV-17 and OV-25 retention times increased significantly. For example, the retention times of Cu(aaed) on SE-30, OV-3, OV-17 and OV-25 were 7, 15, 32 and 48 min, respectively. Retention of the corresponding nickel chelates was correspondingly longer. Similar trends in retention times were observed for the H₂tfaed derivatives.

The relative retention of Cu(tfaed) and Ni(tfaed) gradually reversed in proceeding to more polar stationary phases. On OV-25, for which complete separation of the chelates was obtained, the less volatile Ni(tfaed) eluted prior to the corresponding copper(II) chelate. This interesting reversal, due to stationary phase selectivity, observed also on OV-210, probably arises from the higher polarity of Cu(tfaed) compared to Ni(tfaed). For the least polar stationary phases, SE-30 and Dexsil-300, the retention of Ni(tfaed) was slightly greater than that of Cu(tfaed) due to the lower volatility of the former⁸, but on more polar stationary phases dipole forces may prevail in determination of retention, resulting in longer retention times for the more polar copper chelate.

The most suitable stationary phases for separating the H₂aaed and H₂tfaed derivatives were OV-3 and OV-25, respectively. Using these phases flame ionization detection (FID) detection limits for the copper and nickel chelates were in the 100–140 ng range.

Fused-silica WCOT columns

Effects from the injection system and carrier gas. Split, Grob splitless and cold on-column injection were investigated for use with fused-silica WCOT columns. A

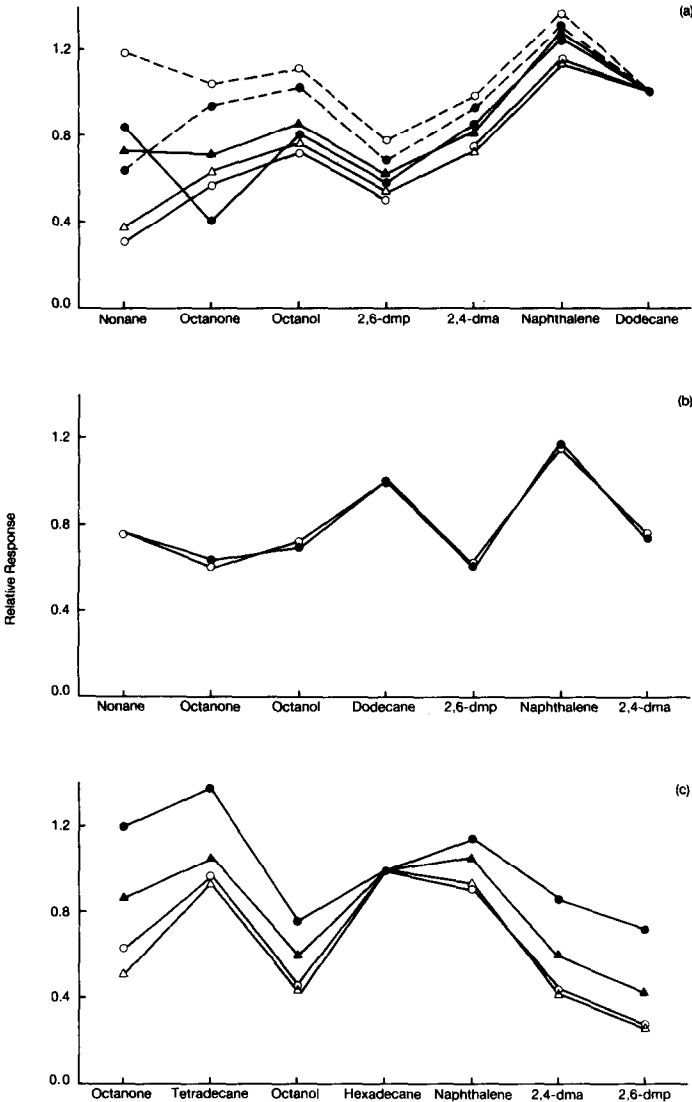


Fig. 2. Response of organic test compounds relative to *n*-dodecane (a and b) or *n*-hexadecane (c) using peak height (broken curve) and area (solid curve). Data are shown for (a) OV-101 (O—O) and BP-1 (Δ — Δ); (b) OV-17 and BP-10; and (c) Carbowax 20M (Δ — Δ) and BP-20 (O—O) for an unused column (open symbol) and for the same column following the introduction of chelates (closed symbol).

problem common to the split and Grob splitless modes was the accumulation of septum and graphite ferrule fragments within the injection port. Any resulting increase in activity is potentially more severe than with packed columns because of the reduced injection quantities. However, if the increased activity is restricted to reversible adsorption the problem will not be apparent with Grob splitless injection due to the reconcentrating effect at the head of the column.

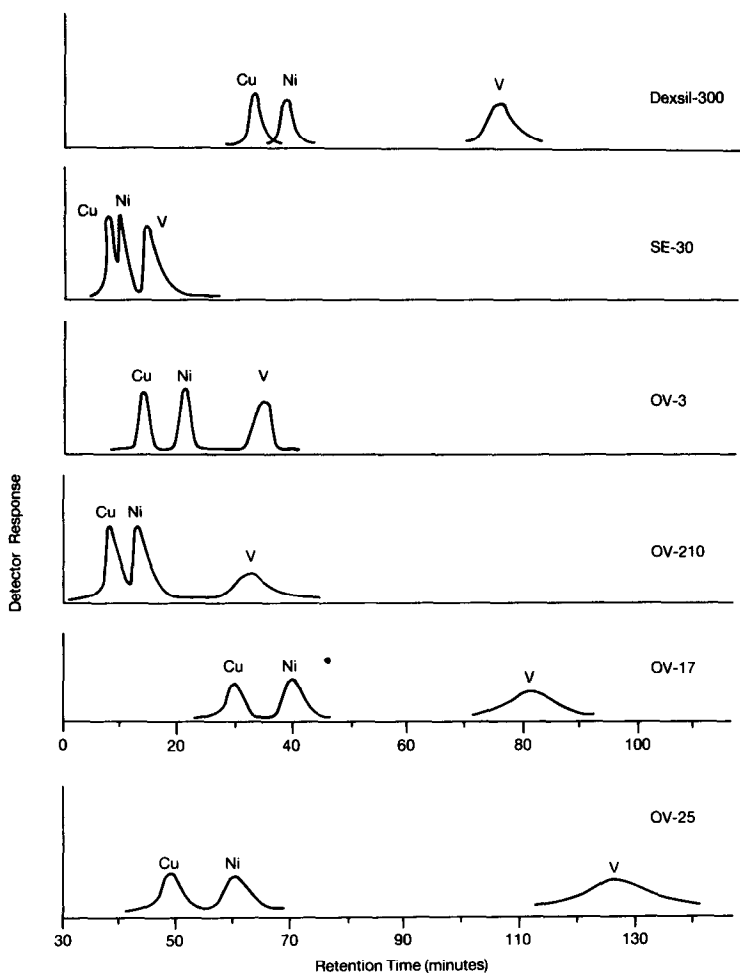


Fig. 3. Chromatograms (schematic) showing the separation of the copper(II), nickel(II) and oxovanadium(IV) derivatives ($2 \mu\text{g}$ each) of H_2aaed on packed columns. Conditions are described in the Experimental section.

Precision determined for the split and on-column injection modes, expressed as the relative standard deviation of peak areas for repeated injections, were 12% and 2%, respectively. With split injection, occasional blockage of the splitter valve required constant attention to avoid changes in the split ratio. Of the three injection modes, Grob splitless injection produced the least satisfactory chromatograms as shown in Fig. 5. Two explanations can be advanced to account for the additional peaks consistently observed with this injection mode. Firstly, although the injection port is nominally all-glass, rapid expansion of the sample upon flash-vapourization is likely to carry chelate outside the glass-lined tubing into contact with reactive, heated metal surfaces. Alternatively, chelate decomposition may occur as a result of protracted residence at the base of the injection port and following condensation of

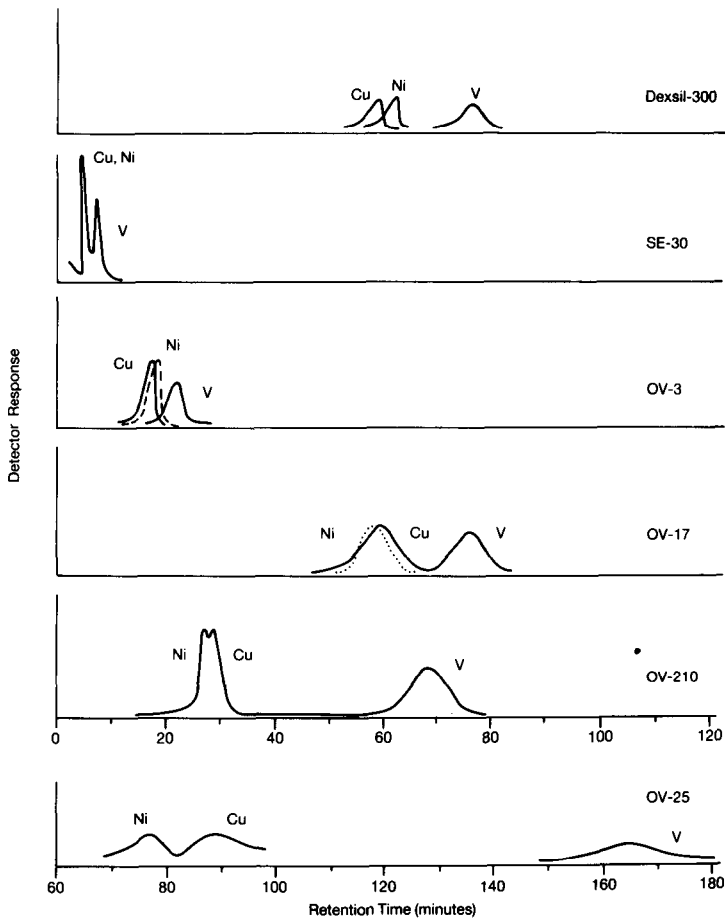


Fig. 4. Chromatograms (schematic) for the H₂faed derivatives on packed columns. Conditions are described in the Experimental section.

chelates at the head of the column. Whichever mechanism is operative the data suggest the unsuitability of Grob splitless injection for such compounds.

Van Deemter plots for Cu(tpmed) with hydrogen and nitrogen carrier gases (Fig. 6) established optimal linear gas velocities of 35 and 11 cm s⁻¹, respectively, corresponding to flow-rates close to 0.8 and 0.3 ml min⁻¹, respectively. From the Golay eqn.²⁷

$$H = \frac{2D_G}{u} + \frac{1 + 6k' + 11(k')^2}{24(1 + k')^2} \cdot \frac{r^2}{D_G} u + C_L u$$

the optimum linear gas velocity (\bar{u}_{opt}), corresponding to the minimum height equivalent of a theoretical plate, may be expressed as

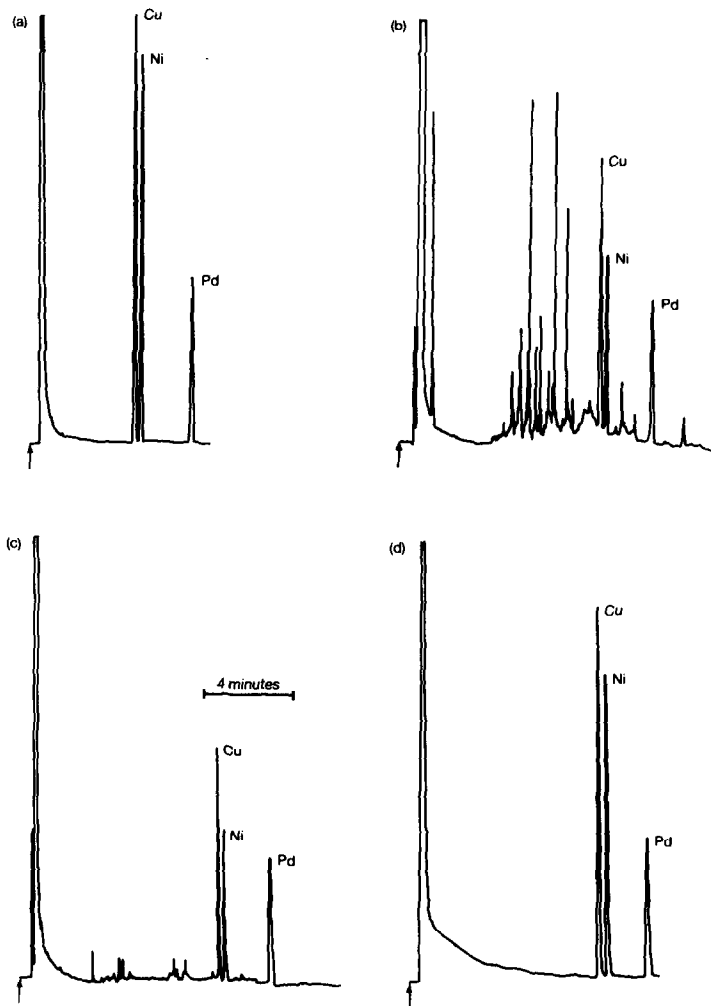


Fig. 5. Chromatograms of the H_2tpmed derivatives on BP-1 using (a) split injection, (b) and (c) Grob splitless injection and (d) cold on-column injection. Column temperatures were 190°C in (a) and 50°C, 2 min hold, heated at 25°C/min to 205°C in (b), (c) and (d) with injection port temperatures of 295, 280, 220 and 350°C, respectively. Detector temperature and hydrogen carrier gas flow were constant at 295°C and 2.0 ml min⁻¹ (measured at 100°C), respectively.

$$\bar{u}_{opt} = \left[\frac{2D_G}{\frac{1 + 6k' + 11(k')^2}{24(1 + k')^2} \cdot \frac{r^2}{D_G} + C_L} \right]^{\frac{1}{2}}$$

and, if C_L is assumed to be negligibly small (a reasonable assumption for WCOT columns) then

$$\bar{u}_{opt} = 4 \frac{D_G}{r} \left[\frac{3(1 + k')^2}{1 + 6k' + 11(k')^2} \right]^{\frac{1}{2}}$$

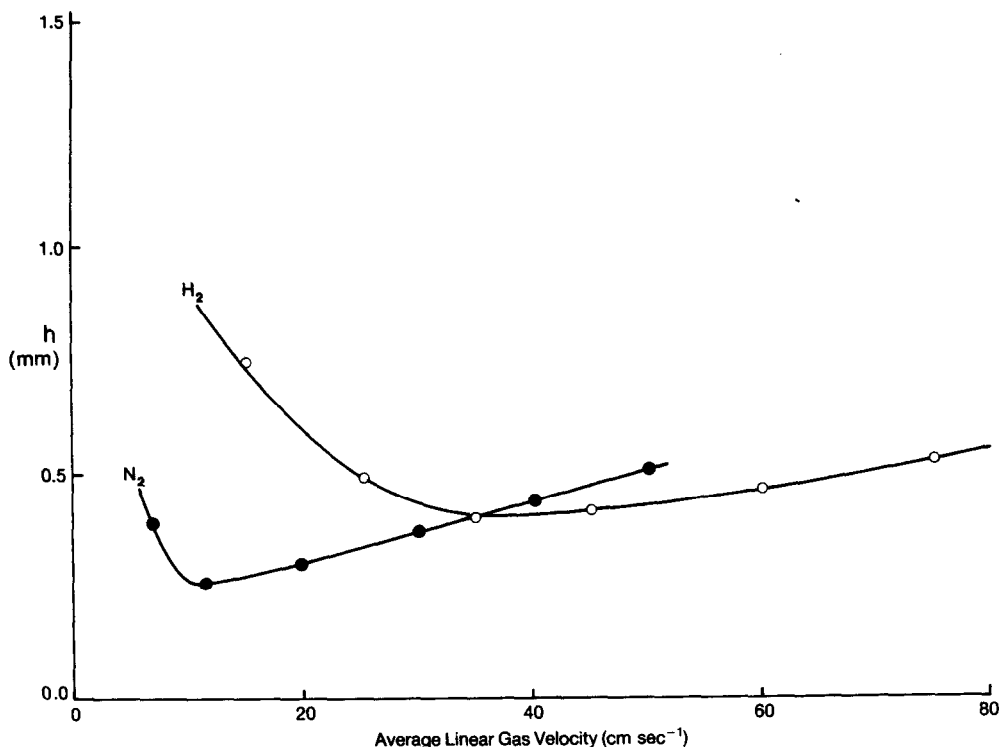


Fig. 6. Van Deemter plots for Cu(tpmed) on BP-1 at 190°C with hydrogen and nitrogen as carrier gas.

which correctly predicts a smaller \bar{u}_{opt} for the higher density nitrogen (low gaseous diffusion coefficient, D_G). In practical terms, this means that to achieve the smallest possible H , the analysis time will become excessively long. On the other hand, hydrogen can be used at flow-rates considerably above \bar{u}_{opt} (for example, 160 cm s^{-1} or $\approx 4 \text{ ml min}^{-1}$) without too adverse an effect on column efficiency. More importantly, as shown in Fig. 7, this enabled the use of lower column temperatures with a consequent reduction in deleterious column interactions. Moreover, detection limits (Table II) are approximately an order of magnitude lower for hydrogen as carrier gas than for nitrogen. This contrasts with the situation¹⁶ for β -diketonates on fused-silica WCOT columns.

Effects of the stationary phase. Separation of the Cu(II), Ni(II) and Pd(II) chelates of the four Schiff bases was examined on various fused-silica WCOT columns. Derivatives of H₂tpmed were readily separated (in contrast to packed columns) and eluted as sharp peaks at 180–210°C on both non-polar and highly polar (Carbowax 20M) columns. Best results were obtained on the bonded, non-polar BP-1 column (Fig. 8). Chelates of H₂aaed, H₂tfaed and H₂tfapd similarly eluted from the OV-101, BP-1 and BP-10 columns as sharp peaks, albeit with some decomposition, evident mainly from baseline elevations in the chromatograms. Whereas derivatives of H₂aaed and H₂tfaed were completely separated on the non-polar columns, resolution of the Cu(II) and Ni(II) derivatives of H₂tfapd required the moderately polar

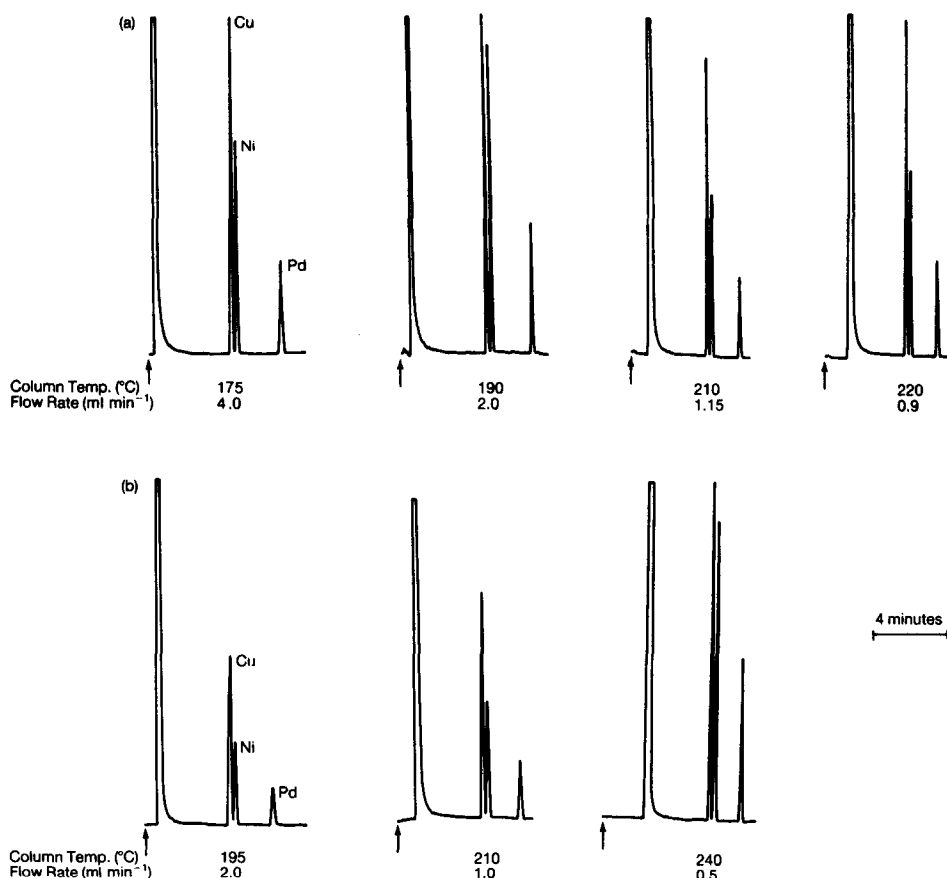


Fig. 7. Chromatograms showing the separation of the copper, nickel and palladium derivatives of H_2tpmed (0.5, 0.3 and 0.5 $mg\ ml^{-1}$, respectively) on BP-1 using (a) hydrogen and (b) nitrogen carrier gas. Split ratio 25:1. Injection port and detector temperatures were 260 and 290°C, respectively.

TABLE II

DETECTION LIMITS (FID) FOR DERIVATIVES OF H_2tpmed , H_2aaed , H_2tfaed and H_2tfapd ON BP-1 USING COLUMN TEMPERATURES OF 215, 245, 245 AND 245°C, RESPECTIVELY

Hydrogen carrier gas flow-rate was 1.5 $ml\ min^{-1}$. With nitrogen as carrier gas, column temperatures were 20°C higher and the flow-rate was 0.8 $ml\ min^{-1}$. Injection port and detector temperatures were 270°C and 285°C, respectively. ND = Not determined.

Metal	Detection limit (ng)					
	H_2tpmed		H_2aaed	H_2tfaed		H_2tfapd
	H_2	N_2	H_2	H_2	N_2	H_2
Cu(II)	0.4	2.0	25	0.8	40	11
Ni(II)	0.2	1.6	21	0.6	10	5
Pd(II)	0.9	8	80	4	65	20
VO(IV)	ND	ND	ND	2	60	ND

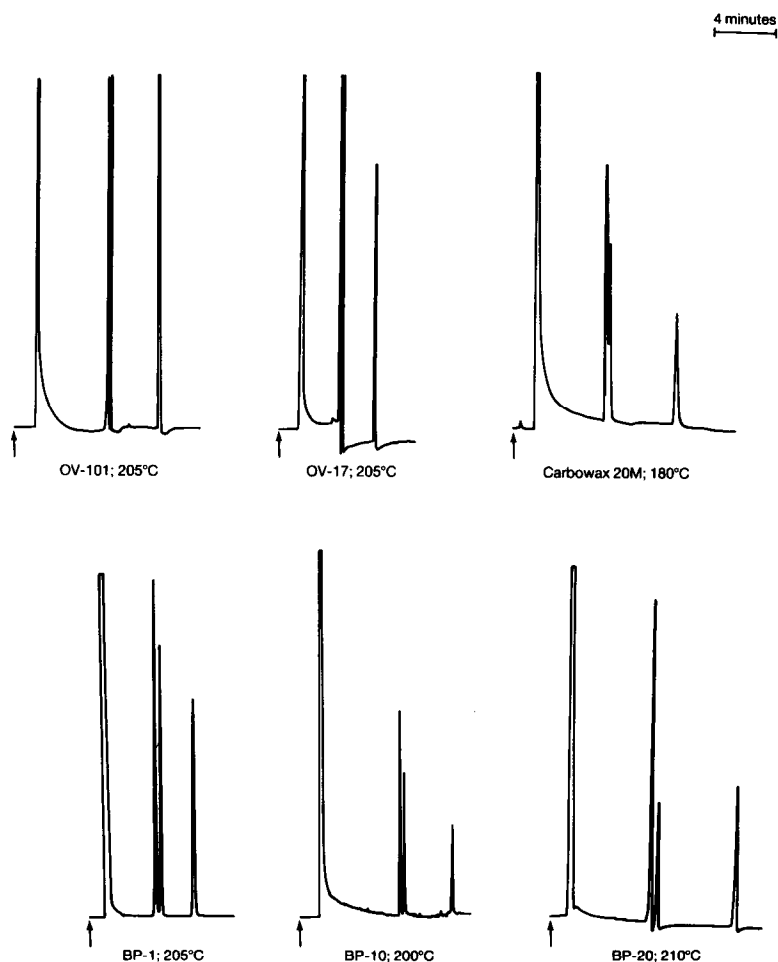


Fig. 8. Chromatograms showing the separation of the copper, nickel and palladium derivatives of H_2tpmed on several fused-silica columns at the specified column temperatures. Other conditions as in Fig. 7 except for hydrogen carrier gas flow of 1.0 ml min^{-1} . The same elution sequence was observed for all six columns.

BP-10 column (Fig. 9). Chelates of these three ligands, could not be eluted from polar OV-17, Carbowax 20M and BP-20 columns below 260°C . Generally, for a given non-polar column, greatest resolution of the Cu(II) and Ni(II) chelates was achieved as the H_2aaed derivatives, consistent with their greater volatility differences. Separation of the Cu(II) and Ni(II) derivatives of the fluorinated ligands which is not satisfactory with packed columns was readily achieved with the fused-silica WCOT columns.

A serious problem encountered in the GC of the Schiff base chelates was column deterioration. This was observed as an increased tendency toward degradation of the chelate peaks following repeated injection of chelates (approximately 100 injections of $1 \mu\text{l}$ corresponding to a total chelate load of $20 \mu\text{g}$). The most pronounced

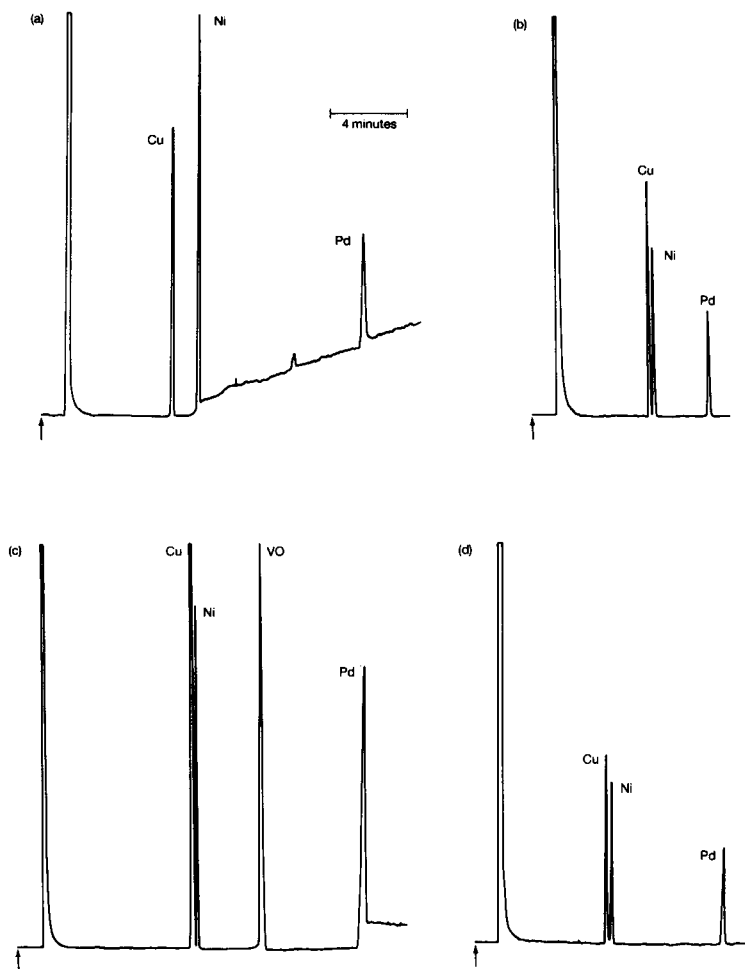


Fig. 9. Chromatograms showing the separation of the derivatives of (a) H_2aaed , (b) H_2tpmed , (c) H_2tfaed and (d) H_2tfapd on BP-10 at 270, 205, 270 and 270°C, respectively. Carrier gas flow was 0.8 ml min^{-1} with a split ratio of 100:1. Injection port and detector temperature, 295°C. Other conditions as in Fig. 7.

effects were observed for the Pd(II) chelates and H_2aaed and H_2tfapd derivatives. This can be interpreted in terms of chelate decomposition to the metallic element or oxide which may then catalyse decomposition of chelates subsequently injected into the column. Indeed, metal catalysed dehydrogenation reactions of Schiff base chelates have been demonstrated²⁸.

Response curves for the chelates (Fig. 10) demonstrate the advantages of considering both relative height and relative area in generating such data. Thus, adsorption and catalysis were apparently absent at the 5-ng level (*i.e.* 0.2 ng on-column after allowance is made for the split ratio) for Ni(tfaed) and the H_2tpmed derivatives whereas irreversible adsorption was apparent for Cu(tfaed) and Pd(tfaed).

Column efficiencies for the metal chelates and organic solutes were comparable

TABLE III
RETENTION DATA FOR THE CHELATES ON WCOT COLUMNS USING 1.3 ml min^{-1} HYDROGEN CARRIER GAS FLOW (EXCEPT FOR BP-10,
 0.8 ml min^{-1})

Separation number S , is given for the copper and nickel chelate and N_{eff} for the copper chelate.

Chelate	Column																	
	OV-101			OV-17			Carbowax 20M			BP-1			BP-10			BP-20		
	t_R (min)	N_{eff}	S	t_R (min)	N_{eff}	S	t_R (min)	N_{eff}	S	t_R (min)	N_{eff}	S	t_R (min)	N_{eff}	S	t_R (min)	N_{eff}	S
Cu(aaed)	2.7	47 518	4.5	*			*			3.0	49 860	6.5	6.1	61 085	6.7	*		
Ni(aaed)	3.0									3.5			7.3					
Pd(aaed)	5.0									6.7			16.2					
Column temp. (°C)		270						245						270				
Cu(tpmed)	5.2	65 077	4.3	2.9	29 146	3.0	4.8	18 160	1.5	2.3	42 417	2.8	5.2	60 097	3.9	5.1	45 622	2.7
Ni(tpmed)	5.5			3.1			5.2			2.5			5.5			5.4		
Pd(tpmed)	7.7			5.3			9.4			3.5			8.6			9.0		
Column temp. (°C)		205			205			180						215		205		210
Cu(tfapd)	2.4	29 329	0.1	*			*			3.2	42 621	0.1	6.1	62 498	3.4	*		
Ni(tfapd)	2.4									3.2			6.4					
Pd(tfapd)	3.4									4.2			12.6					
Column temp. (°C)		270									245			270				
Cu(tfaed)	2.9	23 210	1.2	*			*			2.9	40 829	1.4	8.3	65 416	2.3	*		
Ni(tfaed)	3.0									3.0			8.6					
Pd(tfaed)	5.3									5.2			17.7					
VO(tfaed)	3.3									3.2			12.1					
Column temp. (°C)		250									245			270				

* Not eluted below 260°C.

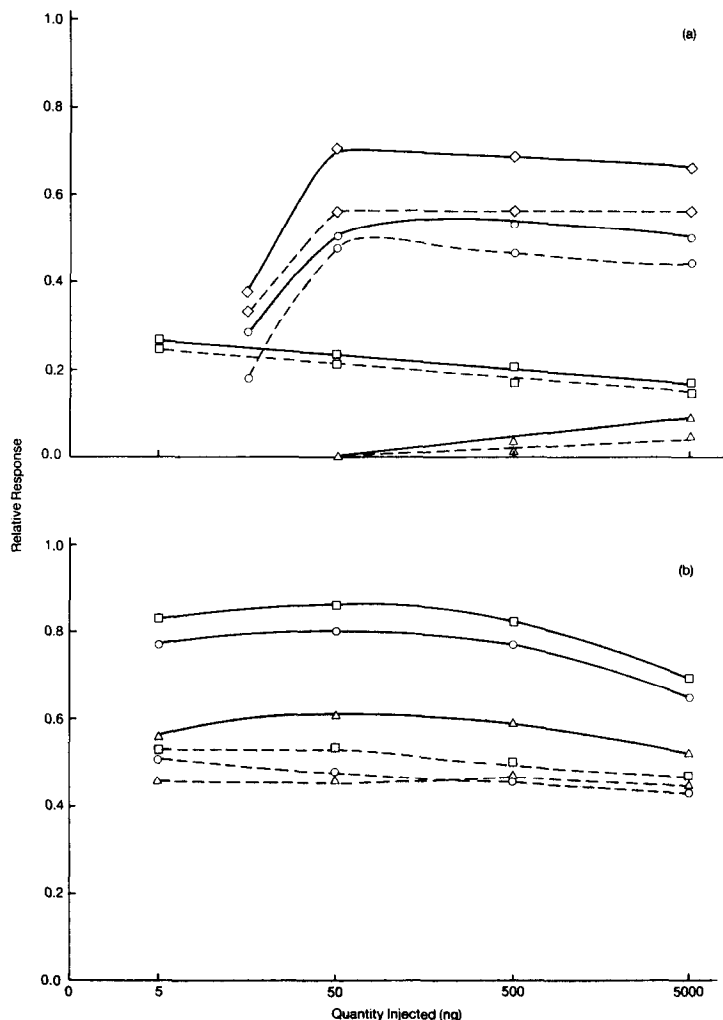


Fig. 10. Response curves for the chelates of (a) H_2tfaed and (b) H_2tpmd plotted as detector response (solid curve, peak height; broken curve, peak area) relative to an equal concentration of $n-C_{26}H_{54}$ (a) or $n-C_{22}H_{46}$ (b). Chelates are identified as copper(II), $\circ-\circ$; nickel(II), $\square-\square$; palladium(II), $\triangle-\triangle$; oxovanadium(IV), $\diamond-\diamond$. Column was BP-1 using the same conditions as for Table III.

as seen by comparing values of N_{eff} for the chelates (Table III) with values for 2,6-dmp and 2,4-dma (Table I). The use of shorter WCOT columns (Fig. 11) sacrificed some resolution [e.g. $Cu(tfapd)$ and $Ni(tfapd)$ are not resolved] yet, had the advantage of reduced retention times and column temperatures with a decrease in deleterious column interactions. However, the advantage of lower column temperatures was partially offset by the need to use lower carrier gas flow-rates than were possible with the longer columns. Nevertheless, elution temperatures for a 6.3-m column were typically 20–30°C lower than for a corresponding 25-m column. Indeed, the use of polar phases may be feasible with short columns.

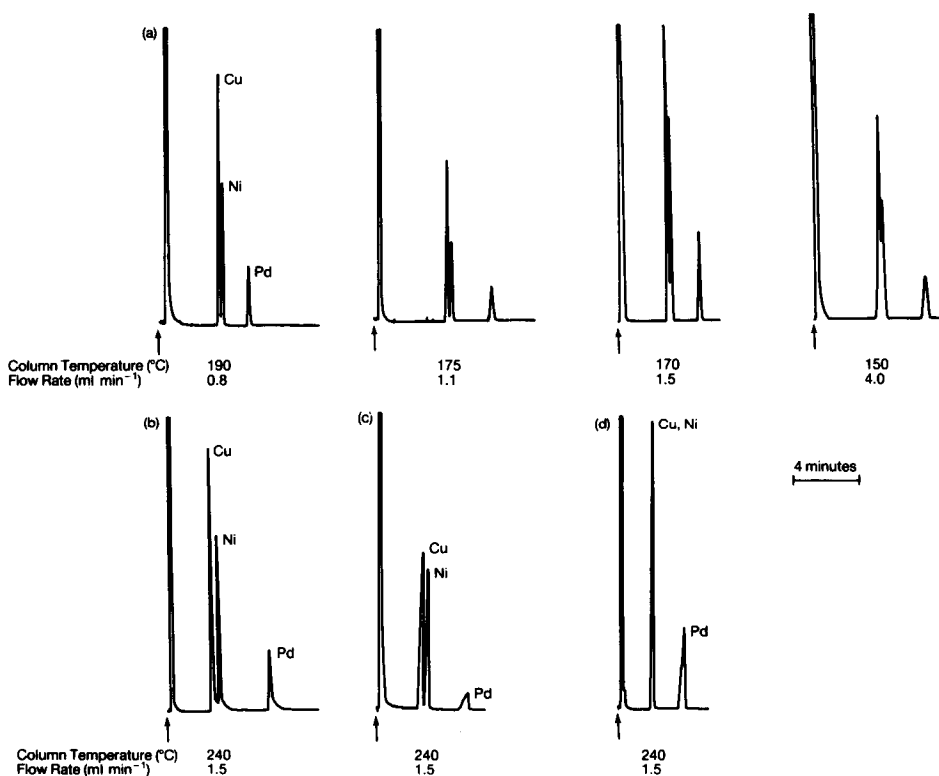


Fig. 11. Chromatograms showing the separation of the derivatives of (a) H₂tpmed at various column temperatures and carrier gas flow-rates, (b) H₂aaed, (c) H₂tfaed and (d) H₂tfapd on a short (6.3 m × 0.22 mm I.D.) OV-101 column.

Other Schiff base chelates. Some Schiff base chelates are particularly difficult to elute satisfactorily from packed columns. These include derivatives of bidentate ligands²⁹, oxovanadium(IV) complexes²⁶ (see Figs. 3 and 4) and polar derivatives of tetraketo ligands (II)²⁸. All show considerably improved behaviour on fused-silica WCOT columns. Thus, although the Ni(II) derivative of II elutes from deactivated packed columns with considerable tailing, while the copper chelate cannot be eluted at all²⁸, both elute with ideal peak shapes on a non-polar BP-1 column (Fig. 12). Oxovanadium(IV) chelates show similar marked improvement on these columns (Fig. 9). In both cases, however, column and injection port temperatures were critical as decomposition became apparent much above 200°C. It is noteworthy that VO(tfapd) gave two distinct peaks. This observation, which represents the first chromatographic separation of oxovanadium diastereoisomers, will be the subject of another report.

CONCLUSIONS

Fused-silica WCOT columns offer greatly improved GC performance over packed columns for all types of volatile Schiff base chelates. This is revealed in sharper, more symmetrical peaks, enhanced resolution and lower detection limits.

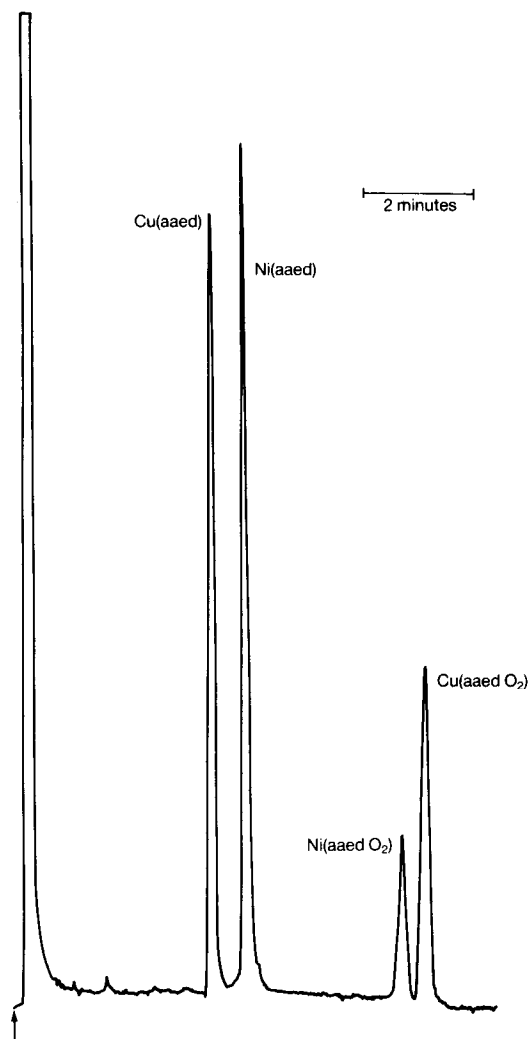


Fig. 12. Chromatograms showing the elution of the copper and nickel derivatives of H_2aaed and II [denoted as $Cu(aaedO_2)$ and $Ni(aaedO_2)$] on BP-1 at $195^\circ C$ with a hydrogen carrier gas flow of 2.0 ml min^{-1} . Injection port and detector temperatures: 245 and $265^\circ C$, respectively.

Such columns therefore seem more suitable for analytical applications than packed columns. Methods for overcoming remaining problems include careful selection of ligand, the use of short, non-polar columns, split injection systems and hydrogen as carrier gas.

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