Journal of Chromatography, 176 (1979) 305–318

CHROM. 11,911

RETENTION OF FLUORINATED TRANSITION-METAL β-DIKETONATES IN GAS CHROMATOGRAPHIC COLUMNS

SERGIO DILLI

Department of Analytical Chemistry, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

and

EMILIOS PATSALIDES

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600 (Australia)

(Received April 13th, 1979)

SUMMARY

Retention of the Al(III), V(III), Cr(III), Fe(III), Mn(III), Co(III) and Cu(II) derivatives of the β-diketones, 1,1,1-trifluoropentane-2,4-dione, 1,1,1,5,5,5-hexafluoropentane-2,4-dione, 1,1,1-trifluoro-5-methylhexane-2,4-dione, 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione, 1,1,1,2,2-pentafluoro-6,6-dimethylheptane-3,5-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione in chromatographic columns with various supports has been studied. Chemical effects due to the nature of the support, ligand and the metal ion probably contribute to the observed magnitude of the retention. Irreversibility of the phenomenon is interpreted as arising from dissociation in the stationary phase and retention therein or to reaction at active sites on the support. Several mechanisms for these reactions are proposed.

INTRODUCTION

There is now ample evidence[1–3] that many chelates (involving different metals and ligand systems) exhibit the volatility and thermal stability necessary for gas chromatography (GC). Yet, due to the *hetero-molecular* interactions which can occur when these compounds are introduced into a chromatographic column (in contrast to the essentially *homo-molecular* environment prevailing during the evaluation of thermal properties), numerous problems become apparent. Inevitably, the result has been a delay in the application of the GC of metal chelates to a wider range of analyses.

For the most widely studied class of chelates, the β-diketonates, many have been shown to be too reactive for chromatographic analysis. Even in solution reactions unfavourable to chromatographic separation are known to occur. For example, derivatives of lanthanide ions, including those of ligands with sterically hindering substituents, associate[4] in solution forming binuclear and trinuclear clusters. Another peculiarity of β-diketonate reactivity, which has been demonstrated by GC[5], is their participation in "scrambling" reactions[5–8] in solution. Furthermore, among the ab-

normalities reported[9–11] for β-diketonates as evidence of their on-column reactions have been "adsorption" and displacement effects, extraneous peaks and shoulders, unusual peak shapes and elevated baselines. Additional on-column reactions are the "olation" reaction occurring with monohydrates of various lanthanide acetylacetonates[12], and reaction of the β-diketonates of the alkali and alkaline-earth metals[13–15] leading to the formation of heteronuclear species. On-column redox transformations[5,16] have also been observed with the β-diketonates of both vanadium(III) and oxovanadium(IV), and may even occur with chelates of other transition metal ions such as cobalt, iron and manganese.

From these observations, it is possible to envisage two different phenomena occurring inside the packed GC column. In the first, which ultimately sets the chromatographic limits of detection, the mainly *physical* effect includes true adsorption and perhaps, displacement effects displayed by the support. Since weak forces are generally involved, this process is reversible and provides a plausible explanation of the regular deactivation of columns of the type reported in the earlier and successful[17–20] gas chromatographic studies of the less reactive β-diketonates. Those which do not show obvious reactivity, such as the trifluoroacetylacetonates of Al(III)[17,18], Ga(III)[18], In(III)[18] and Rh(III)[19], or the still more favourable derivatives of Be(II)[20] and Cr (III)[21] which have been determined at sub-nanogram levels, probably fall into this category. The second group of phenomena includes the diverse reactions of a *chemical* nature such as those dealing with the chelates *per se*, or their reactivity towards a stationary phase or, indeed, impurities therein or in the support. Into this group would be placed those instances of marked retention* in the column irrespective of the chemical reaction involved. In fact, many of these reactions are not well understood and some, at least, may be no more than the predictable consequence of reactions, at elevated temperatures, of impurities present within the column or introduced with the chelates (especially traces of water, oxygen or solvents[22]). An example is the retention of the stable chromium(III) chelate of trifluoroacetylacetone in columns containing diatomite supports, and this has been attributed[23] to surface silanol (–Si–OH) groups. As is shown later, improvements in column performance achieved with silylated supports are enhanced by further on-column silylation before use. In other reactions, column performance may be expected to deteriorate under the influence of chelates capable of functioning as Lewis acids in the chemical degradation[22] of polysiloxane stationary phases, and there is evidence[24] for this when dealing with fluorinated alkyl and the more volatile of the fluorinated aryl β-diketonates.

Within this context, this paper presents data illustrating several features of the two effects, originating from the chelates of various transition metal ions and column support materials, upon the column behaviour of a group of β-diketonates. Inasmuch as the chemical effect leads to irreversible chemical reactions in the column, we refer to this retention of chelates as *absorption* in preference to, and by way of distinction from, adsorption. The chelates used for the study comprise the aluminium(III),vanadium(III), chromium(III), iron(III), manganese(III), cobalt(III) and copper(II) complexes of 1,1,1-trifluoropentane-2,4-dione (HTfa), 1,1,1,5,5,5-hexafluoropentane-2,4-dione (HHfa), 1,1,1-trifluoro-5-methylhexane-2,4-dione (HTbm), 1,1,1-trifluoro-5,5-

* Retention, here, is not to be confused with the partitioning process occurring in the GC column.

dimethylhexane-3,5-dione (HTpm), 1,1,1,2,2-pentafluoro-6,6-dimethylheptane-3,5-dione (HPpm) and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (HHpm).

EXPERIMENTAL

Gas chromatography

A Hewlett-Packard F & M Model 5750B gas chromatograph, equipped with flame ionization detectors, was used for this work. Carrier gas was filtered, high-purity, dry nitrogen at a flow-rate of 35 ml/min.

Columns were borosilicate glass coils (3 ft. × 1/4 in. O.D.), prepared for packing by washing (with water and detergent followed by distilled water, distilled methanol and chloroform) then dried in an oven. Supports were commercially available materials (80–100 mesh, acid-washed diatomites, and all DMCS-treated). Diatomite supports (Chromosorb W, G and 750) were coated with a 3% nominal loading of SE-30 by the solvent-evaporation technique. The glass microbeads were similarly coated with a 0.2% loading of the same stationary phase. Columns were plugged with silanized glass wool and conditioned at 200–220° for 12 h before further on-column silylation (4 × 50 μl) with both hexamethyldisilazane (HMDS) and N,O-bis(trimethylsilyl)trifluoroacetamide, then conditioned for another 12 h before use. For the data of Figs. 1 and 3, one of each pair of columns was silylated with HMDS only (4 × 50 μl), 2 h before use. Direct on-column injection reduced contact between the chelate vapours and hot metal surfaces to the 2–3 cm between the end of the column and the detector tip.

Chelates

All chelates were prepared and purified by methods described elsewhere[3,25]. Solutions were prepared by dissolving 5.0 mg of chelate and 1.0 mg of the internal standard in the solvent and diluting to volume (10.0 ml). The internal standards were *n*-decane for the chelates of HHfa, and *n*-octadecane for all other derivatives.

Column loading curves

As a measure of the interaction of the chelate with, and its retention in, the column, *loading curves* were obtained by plotting response ratios against the total amount of chelate injected onto the column. Response ratios are the ratios of chelate peak areas (determined by triangulation) to internal standard peak areas. Each curve was obtained by injecting 1.0 μl of the solution onto the column every 30 min (for a total of 7–10 injections).

For the chromium(III) chelates, only the first peak due to the *trans*-isomer was measured.

RESULTS AND DISCUSSION

Two features of the results presented here are noteworthy. Firstly, the use of relatively small amounts of chelates (<20 μg) has highlighted, in contrast with earlier work[9,26,27], the importance of on-column silylation in the deactivation of column packings. Secondly, the chromatographic behaviour reflects the chemical properties of individual chelates (dependent on the ionic species and ligand structure). This

behaviour deteriorated in the order chromium, aluminium, vanadium(III), cobalt (III), copper(II), iron(III) and manganese(III).

Effect of on-column silylation

The effect of on-column silylation is demonstrated in such systems as are represented by Figs. 1–3. These data draw attention to the inadequacy of the common practice of filling GC columns with coated, silylated diatomites because of the ephemeral nature of deactivation prior to the actual coating and packing steps. Fig. 1 shows, for $V(Tfa)_3$ examined on two identical columns, that more is involved in producing a deactivated column (including the packing material, glass wall and end-plugs) than the mere silylation of the packed column. Thus, on the untreated column (see Fig. 1a), no peak was observed for the first five injections due to complete retention of the chelate. At the sixth injection, an attenuated, tailing peak emerged, and from the ninth or tenth injection the peak was reproducible. On the silylated column (see Fig. 1b), the peak shape was symmetrical for the first injection, however, this deteriorated rapidly so that by the eighth or ninth injection of the chelate, a peak characterized by fronting and marked tailing was obtained, but was reproducible thereafter. As shown in Fig. 2 for another similar column, the elevated baseline is more clearly indicative of an on-column reaction.

In the case of $V(Hpm)_3$, its behaviour on two freshly packed columns (pre-

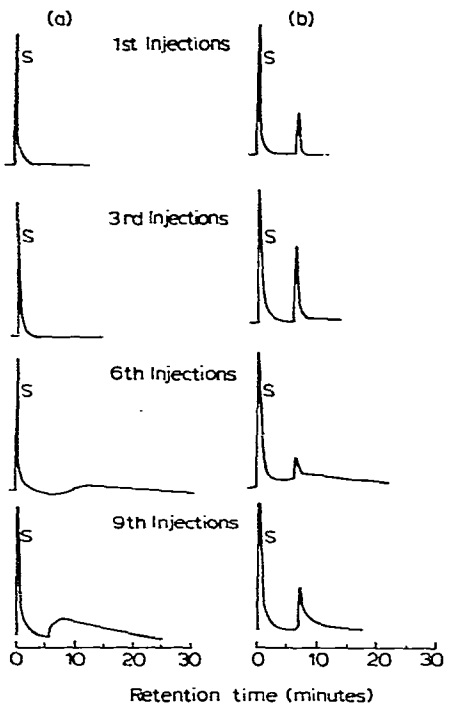


Fig. 1. Chromatograms for consecutive injections (20 μg each) of $V(Tfa)_3$ on coated Chromosorb W before (a) and after (b) on-column silylation. Freshly packed columns were used for each series. Column temperature 120° (injector block and detector, 140°). Solvent (S) was benzene.

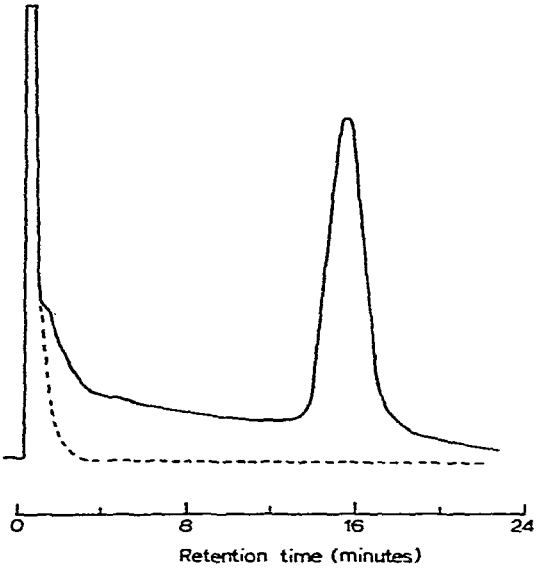


Fig. 2. Chromatogram for 20 μg $V(Tfa)_3$ on coated Chromsorb W without on-column silylation. Solvent (benzene) is shown, under the same conditions, as a broken line. Column temperature 120° (injector block and detector, 150°).

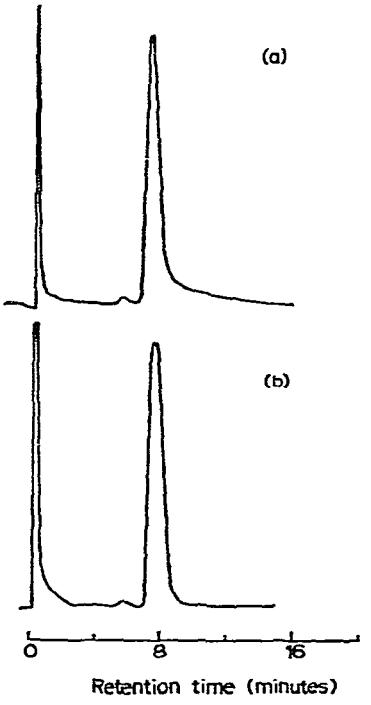


Fig. 3. Chromatogram for 20 μg $V(Hpm)_3$ on coated Chromosorb W before (a) and after (b) on-column silylation. Column temperature 140° (injector block and detector, 160°). Solvent was dichloromethane.

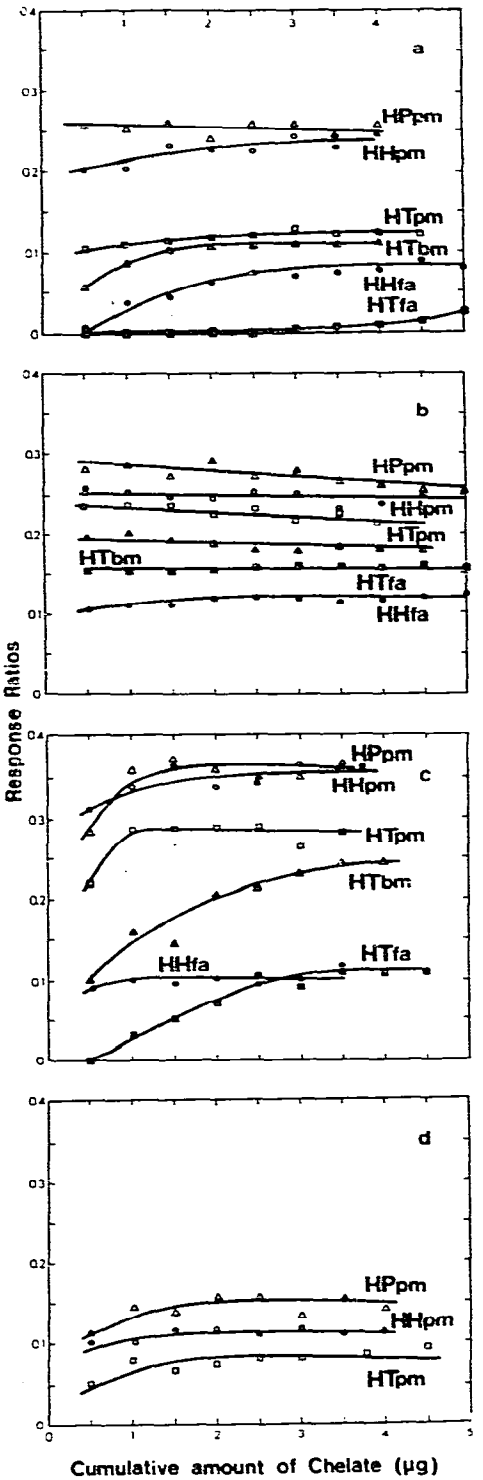


Fig. 4. Retention of vanadium(III) derivatives on different, coated supports after on-column silylation. Supports: (a) Chromosorb W; (b) Chromosorb 750; (c) glass microbeads and (d) Chromosorb G. Each plot was obtained with a fresh column.

pared from the same batch of coated support) was different again to that of $V(Tfa)_3$. In the absence of on-column deactivation (see Fig. 3a), a tailing peak was obtained but this was reproducible for at least ten injections. With the silylated column, a completely symmetrical peak resulted from the first injection and was also reproducible for at least ten injections. Significantly, no evidence of column loading was seen for the compound in either case. However, by way of contrast, $Cr(Tfa)_3$ eluted without tailing or loading effects on both silylated and untreated columns. For this exceptional compound, results similar to those obtained with $V(Tfa)_3$ have been observed[23] only on a *totally* unsilylated and uncoated diatomite support.

Retention by various chromatographic supports

The elution behaviour of vanadium(III) chelates of HTfa, HTbm, HTpm, HPpm and HHpm was compared on the supports Chromosorb W, 750, G and glass micro-beads. Response ratios of these chelates on each of the supports are shown in Fig. 4. Of the various derivatives, $V(Tfa)_3$ demonstrated the greatest tendency toward column loading, being particularly evident with Chromosorb W and glass micro-beads as supports. In fact, with the possible exception of $V(Ppm)_3$, all chelates showed some degree of loading on these two supports. However, this chelate has been eluted and detected at nanogram levels with the electron-capture detector without evidence[16] of adverse behaviour and forms the basis of an analytical procedure[5] for traces of vanadium. On Chromosorb 750, no column loading was observed for the chelates and only on this support was slow oxidation seen (over *ca.* 5 h) as a gradual decrease of chelate peak heights and, hence, a lower response ratio. On Chromosorb G, although there was little evidence of column loading with the three chelates examined, the response ratio was considerably reduced in each instance when compared with Chromosorb 750 but particularly so for $V(Ppm)_3$ when compared with the other three supports. The reason for this, as suggested in Fig. 5, is that decomposition, possibly catalytically induced at the support surface, occurs even on silylated Chromosorb G. Similar chromatograms were observed for $V(Tpm)_3$ and $V(Hpm)_3$ but are not reproduced here.

As an example of the difficulty in recognizing reversible and irreversible processes in column behaviour, the reversible and reproducible nature of the column loading, typical of some compounds, is shown in Fig. 6 for $V(Hfa)_3$ on the support Chromosorb W. Here, the same column was conditioned overnight (16 h at 200–220°) after saturation of the active sites, on four successive days. A similar behaviour was observed with $V(Tfa)_3$ when partial revival of column loading, in an apparently saturated column, occurred after only 2–3 h conditioning.

Possible retention mechanisms

Consistent with previous observations[9,23], the improvement produced by on-column silylation suggests that the silanol groups are largely responsible for the tailing and absorption of metal chelates seen on unsilylated columns.

There are two mechanisms which may account for the adverse effects caused by silanol groups. In the first of these, where more stable chelates such as the chromium(III)-β-diketonates are involved, *hydrogen-bonding* of a silanol group with an oxygen of the chelate ring may occur. In the second case, it is possible that an irreversible *ion-exchange*[28] or *ion-binding* reaction occurs with the less stable β-diketonates

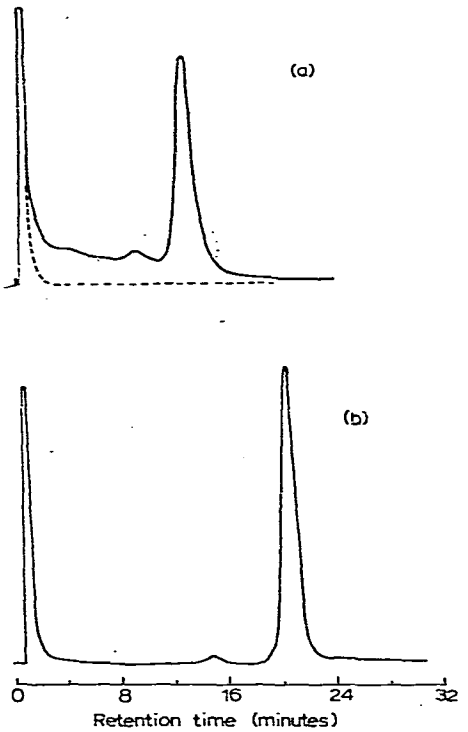


Fig. 5. Chromatograms for 0.5 μg V(Ppm)$_3$ on coated columns with Chromosorb G (a) and Chromosorb 750 (b) supports after on-column silylation. Column temperature 140° (injector block and detector, 150°). Solvent (hexane) is shown in (a) as a broken line.

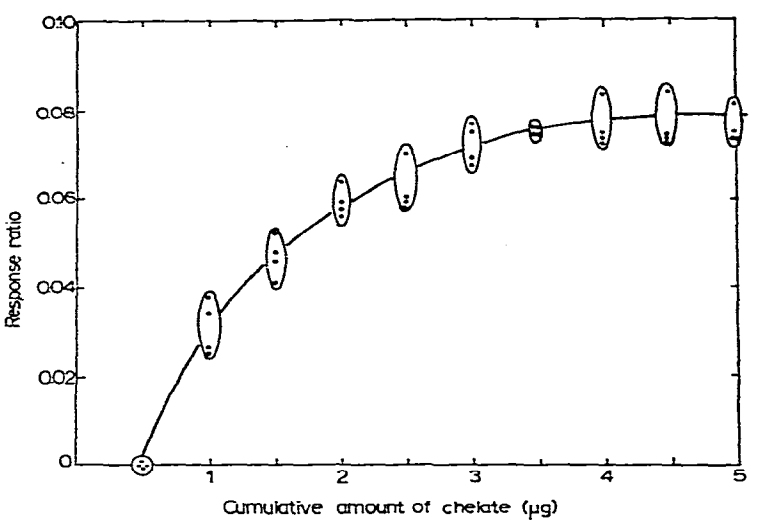


Fig. 6. Curves showing the reproducibility of the column loading behaviour of V(Hfa)$_3$ on a coated Chromosorb W column after on-column silylation. The data were obtained on four successive days following overnight (16 h) conditioning of the column at 200°. Column temperature 40° (injection block and detector, 100°). For each run, a fresh solution of the chelate, in dichloromethane, was used (0.5 μg per injection).

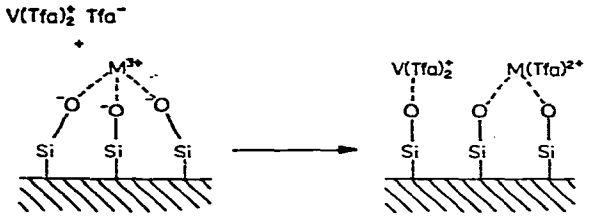
such as those of V(III), Fe(III) and Mn(III). This process is based on the fact that these chelates have a substantially ionic character in their metal–oxygen bonds. Consequently, in the liquid stationary phase, particularly if this is polar, a finite equilibrium of the type shown in eqn. 1 can exist for the labile chelates:

$$M(\beta\text{-diketonate})_3 \rightleftharpoons M(\beta\text{-diketonate})_2^+ + (\beta\text{-diketone})^- \quad (1)$$

A combination of circumstances where silanol groups are exposed to labile chelates may, then, by means of an ion-exchange process presented in Scheme 1 explain the absorption of the metal-containing species on the support surface or in the stationary phase. Accordingly, thermal decomposition suggested in the chromatogram of Fig. 2 for $V(Tfa)_3$ on an ordinary silylated column can be interpreted as an on-column reaction involving absorption of $V(Tfa)_2^+$ and liberation of the free ligand, HTfa. This interpretation is compatible with the elevated baseline and the observation[10,11] that free ligand in the carrier gas stream results in considerable improvement of the peak shape obtained for several chelates of HTfa. Improvement may be due largely to the maintenance of the equilibrium favouring the volatile undissociated chelate.

Scheme 1.

Consideration of Figs. 2 and 6 implies that the reversible and irreversible column processes can occur simultaneously and that active sites other than silanol groups may be present on the surfaces of diatomite and glass micro-bead supports. Indeed Ottenstein[29–31] has drawn attenuation to at least two types of surface activity found in diatomite supports, namely, silanol groups and the lesser-characterized Lewis-acid sites associated with transition metal ions. The composition of acid-washed commercial diatomites suggests that such sites may be linked with calcium, magnesium and, particularly, with iron or aluminium (M^{3+}) if these are in silicate structures unaffected by acid-washing. Extending this concept, fracture of the friable diatomite particles after treatment with acid merely re-exposes additional sites so that a variety of cations may then produce a range in the activity of these sites, in turn capable of some selectivity, and perhaps reversibility, in reactions with the eluting chelate molecules. A possible mechanism whereby such sites may result in irreversible retention of the chelate is depicted in Scheme 2, again using $V(Tfa)_3$ as the example.



Scheme 2.

Retention of individual chelates

For the purpose of comparing the influence of the metal ion as well as the structure of the ligand on column retention, a series of β-diketonates of aluminium (III), chromium(III), cobalt(III), manganese(III) and copper(II) were examined on the supports Chromosorb W and 750. There are three notable features of the results which are shown in Figs. 7–10. The first emphasizes the importance of the metal ion and appears as wide differences in the behaviour of the various chelates. Another concerns the role of the ligand structure, and the third demonstrates the consistently superior performance of Chromosorb 750 in chelate gas chromatography for reasons which are obscure but probably due to a combination of higher surface purity, lower surface area and friability. Referring to Figs. 7 and 8, the chelates of chromium and aluminium elute from both columns without evidence of column loading from the 0.5-μg level. Predictably, the chromium chelates, as yard-sticks for this type of study)

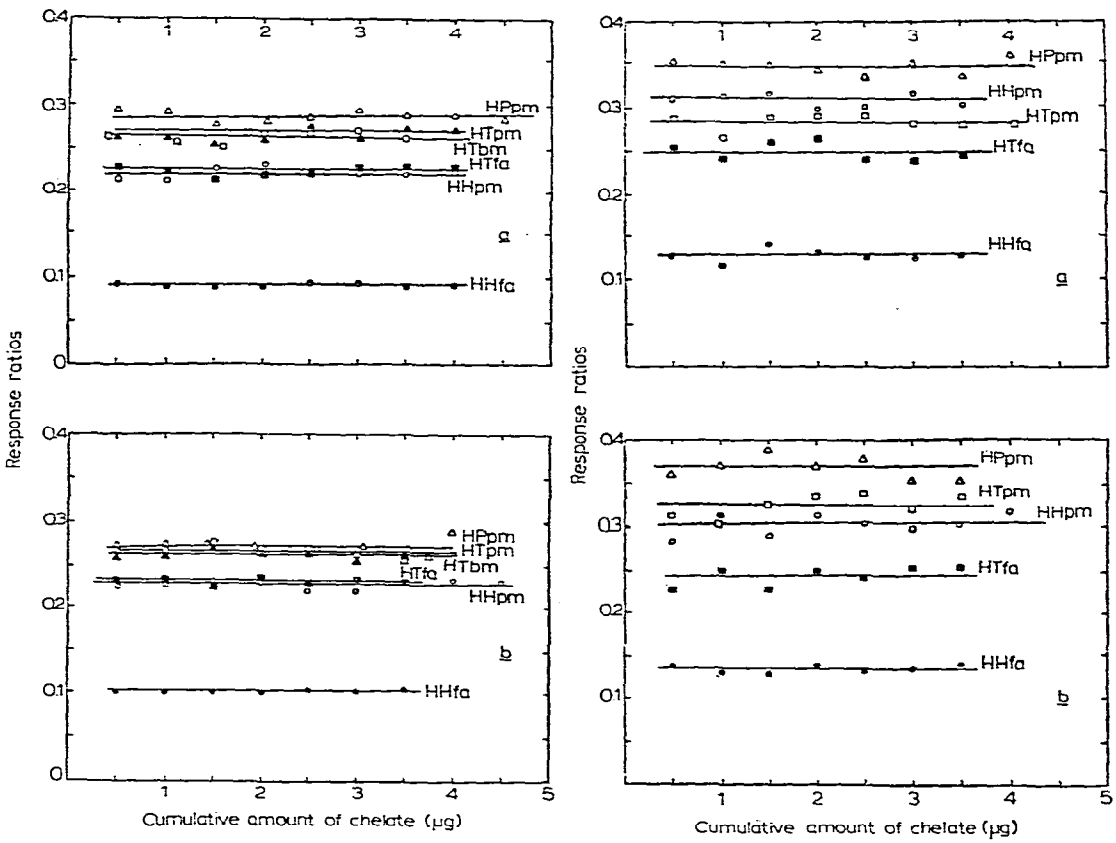


Fig. 7. Column loading for chromium(III) derivatives on coated columns of Chromosorb W (a) and Chromosorb 750 (b) after on-column silylation. Column temperature 130° (except for chelates of HHfa, 40°); injector block and detector temperatures 150°. Fresh columns were employed for each compound (0.5 μg per injection of benzene solutions).

Fig. 8. Column loading with aluminium(III) derivatives on coated columns of Chromosorb W (a) and Chromosorb 750 (b) after on-column silylation. Other conditions are as for Fig. 7.

show relatively little scatter of the plots* especially on Chromosorb 750, and little dependence on ligand structure. For the aluminium chelates, there is less dependence on the actual support although there is a reversal of the positions occupied by Al $(Hpm)_3$ and $Al(Tpm)_3$. These results are consistent with the early, successful developments of analytical methods for the two elements.

In contrast, the behaviour of the cobalt chelates (see Fig. 9) was even more dependent on the substituents in the β-diketone, and the support, than the vanadium chelates (see Fig. 4). Here, $Co(Hfa)_3$, $Co(Tfa)_3$, $Co(Tbm)_3$ and $Co(Tpm)_3$ were completely retained on the Chromosorb W columns at the 0.5 μg level. $Co(Ppm)_3$ and $Co(Hpm)_3$ were partially eluted on the same support but column loading and low response were evident. On Chromosorb 750 columns, higher response ratios were obtained but the column loading persisted. Even with this support, $Co(Tfa)_3$ was nearly totally retained while $Co(Hfa)_3$ remained completely absorbed. Clearly, these results indicate the need to select carefully both support and ligand in an analytical

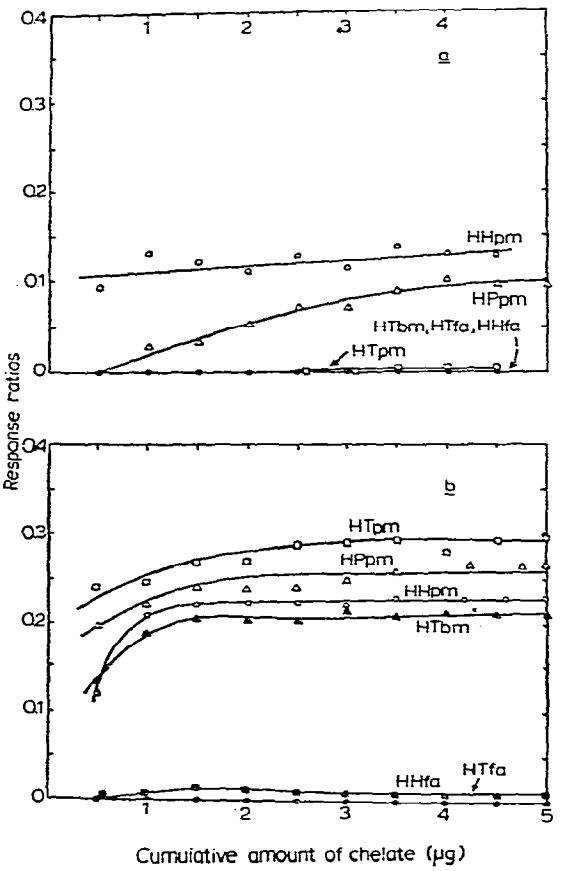


Fig. 9. Column loading with cobalt(III) derivatives on coated columns of Chromosorb W (a) and Chromosorb 750 (b) after on-column silylation. Other conditions are as for Fig. 7.

* Because of the experimental procedure, no significance can be attached to the lower response ratios for the Cr(III) chelates in comparison with those for the Al(III) chelates.

procedure for determining cobalt. Understandably, HHpm has been used[32] for this purpose with success.

Among the copper chelates (see Fig. 10), little improvement in behaviour can be seen. On Chromosorb W, $Cu(Hfa)_2 \cdot 2H_2O$, $Cu(Tfa)_2$, $Cu(Tbm)_2$ and $Cu(Tpm)_2$ were totally absorbed over the loading range (*ca.* 0.5–4.0 μg). As for the corresponding cobalt chelates, $Cu(Ppm)_2$ and $Cu(Hpm)_2$ eluted with reduced response and evidence of loading. In addition, and unlike the derivatives of the trivalent ions, considerable tailing was observed for the copper chelates on Chromosorb W. On Chromosorb 750, peak shapes and response ratios were improved but loading persisted and $Cu(Hfa)_2 \cdot 2H_2O$ was totally absorbed from the 0.5 μg level. Similar work[27] with labelled $Cu(Tfa)_2$, although not directly comparable with these findings, has established the irreversible retention of portion of the chelate within the packed column.

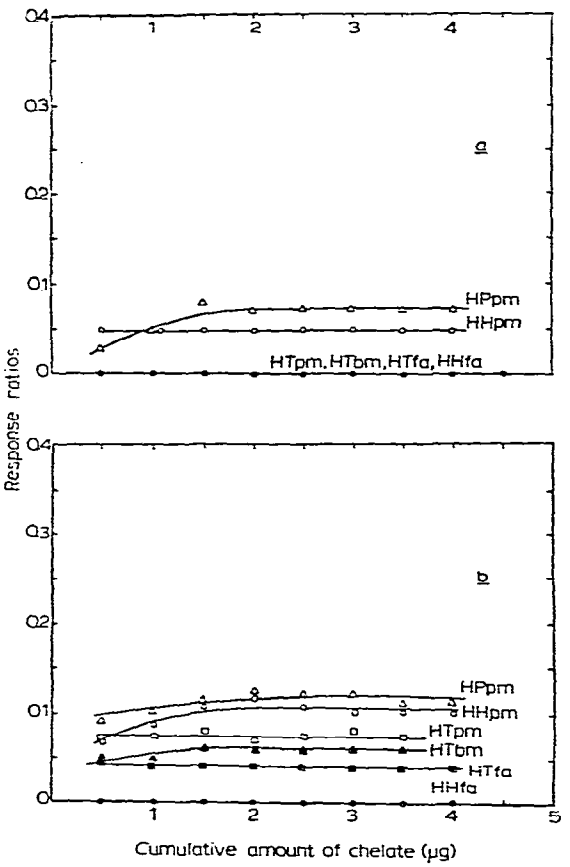


Fig. 10. Column loading with copper(II) derivatives on coated columns of Chromosorb W (a) and Chromosorb 750 (b) after on-column silylation. Other conditions are as for Fig. 7.

The results for the iron(III) and manganese(III) chelates resembled the majority of the copper chelates insofar as the four chelates examined were totally absorbed, from the 0.5-μg level, on Chromosorb W. An indication of the abnormal peak shapes and the extent of peak broadening on Chromosorb 750 is given in Fig. 11. Since all

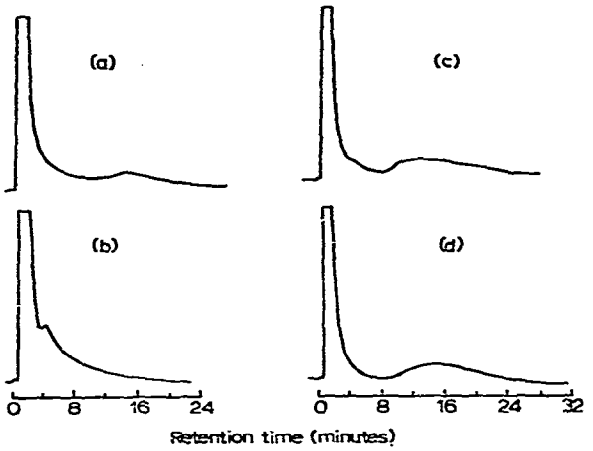
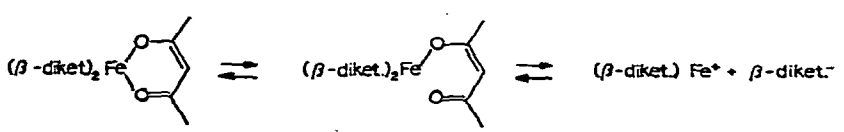


Fig. 11. Chromatograms showing the unfavourable elution of iron(III) and manganese(III) derivatives on Chromosorb 750 after on-column silylation. Column temperatures 140° (except for the derivative of HHfa, 50°); injection block and detector, 150°. Solvent in each case was dichloromethane. Samples: (a) 10 μg $Fe(Hfa)_3$; (b) 0.5 μg $Fe(Tfa)_3$; (c) 0.5 μg $Fe(Hpm)_3$ and (d) 5 μg $Mn(Hpm)_3$.

of the chelates [except $Mn(Tfa)_3$] are thermally stable at the column temperatures employed[5], the known poor behaviour[33,34] of iron β-diketonates may indicate dissociation in the stationary phase, as represented by eqn. 1. With evidence[35] that iron (III) β-diketonates dissociate even at room temperature (see Scheme 3), peak broadening may be due to a retention mechanism additional to those described for more stable β-diketonates[23,26,36] involving interconversion of the involatile species II or III to the volatile I. Thus, the observed effects may be a manifestation of retention of species such as II or III in either the support surface, the stationary phase, or both, with slow elution occurring as re-conversion to I takes place. On this basis, the elution behaviour of the β-diketonates can be expected to improve with the introduction of free ligand into the carrier gas stream. Furthermore, although supports of greater surface inertness may be required for trace analyses, substantial improvement in elution behaviour is not to be expected if peak broadening arises principally from dissociation of the chelate in the stationary phase. To this end, chelates of greater stability are necessary. Finally, of course, practical issues may direct future work to the use of detectors insensitive to ligands in carrier gas streams, and the introduction of synthetic supports to overcome the unsatisfactory and uncontrollable performance of materials presently available.



Scheme 3. I II III

Although limited to results for seven elements, the chromatographic behaviour of the chelates indicates that the metal ions exert the dominant role among the trivalent species, with an improvement when bulky substituents are present in the ligand. For divalent copper, ligand structure is more important because of its in-

fluence on the Lewis acidity of the complex. This is probably greater in the chelates of HHfa than in those of HTpm, HPpm and HHpm where, despite extended fluorination of the chain, fluorination is confined to a single substituent in the β-diketone.

ACKNOWLEDGEMENT

Financial support of this work by the Australian Atomic Energy Commission is gratefully acknowledged.

REFERENCES

1 K. J. Eisentraut and R. E. Sievers, *J. Inorg. Nucl. Chem.*, 29 (1967) 1931.
2 K. C. Joshi and V. N. Patnak, *Coord. Chem. Rev.*, 22 (1977) 37.
3 S. Dilli and E. Patsalides, *Aust. J. Chem.*, 29 (1976) 2369.
4 A. H. Bruder, S. R. Tanny, H. A. Rockefeller and C. S. Springer, *Inorg. Chem.*, 13 (1974) 880.
5 S. Dilli and E. Patsalides, unpublished results.
6 T. J. Pinnavaia and S. O. Nweke, *Inorg. Chem.*, 8 (1969) 639.
7 T. J. Pinnavaia, J. M. Sebeson and D. A. Case, *Inorg. Chem.*, 8 (1969) 644.
8 D. R. Eaton and K. L. Chua, *Can. J. Chem.*, 49 (1971) 56.
9 P. C. Uden and C. R. Jenkins, *Talanta*, 16 (1969) 893.
10 T. Fujinaga and S. Murai, *Anal. Chim. Acta*, 71 (1974) 141.
11 T. Fujinaga, T. Kuwamoto and S. Murai, *Talanta*, 18 (1971) 429.
12 N. K. Khalmurzaev, I. A. Muraveva, L. I. Martynenko and V. I. Spitsyn, *Zh. Neorg. Khim. (Eng. Ed.)*, 21 (1976) 894.
13 C. G. MacDonald and J. S. Shannon, *Aust. J. Chem.*, 19 (1966) 1545.
14 R. Belcher, A. W. L. Dudeney and W. I. Stephen, *J. Inorg. Nucl. Chem.*, 31 (1969) 625.
15 J. E. Schwarberg, R. E. Sievers and R. W. Moshier, *Anal. Chem.*, 42 (1970) 1828.
16 S. Dilli and E. Patsalides, *Aust. J. Chem.*, 29 (1976) 2381.
17 C. Genty, C. Houin, P. Malherbe and R. Schott, *Anal. Chem.*, 43 (1971) 235.
18 G. P. Morie and T. R. Sweet, *Anal. Chem.*, 37 (1965) 1552.
19 W. D. Ross, R. E. Sievers and G. Wheeler, *Anal. Chem.*, 37 (1965) 598.
20 J. K. Foreman, T. A. Gough and E. A. Walker, *Analyst (London)*, 95 (1970) 797.
21 J. Savory, H. T. Glenn and J. A. Ahlstrom, *J. Chromatogr. Sci.*, 10 (1972) 247.
22 F. G. A. Stone and W. A. G. Graham (Editors), *Inorganic Polymers*, Academic Press, New York, 1962, pp. 222 and 253–256.
23 H. Veening and J. F. K. Huber, *J. Gas Chromatogr.*, 6 (1968) 326.
24 S. Dilli and K. Robards, unpublished results.
25 E. Patsalides, *Ph. D. Thesis*, University of New South Wales, Kensington, 1977.
26 C. A. Burgett and J. S. Fritz, *J. Chromatogr.*, 77 (1973) 265.
27 D. N. Sokolov, A. V. Davydov, S. Yu. Prokofyev, S. S. Travnikov, E. V. Fedoseev and B. F. Myasoedov, *J. Chromatogr.*, 155 (1978) 241.
28 L. F. Druding and G. B. Kauffman, *Coord. Chem. Rev.*, 3 (1968) 409.
29 D. M. Ottenstein, *J. Gas Chromatogr.*, 1 (1963) 11.
30 D. M. Ottenstein, *J. Gas Chromatogr.*, 6 (1968) 134.
31 D. M. Ottenstein, *J. Chromatogr. Sci.*, 11 (1973) 136.
32 W. D. Ross, W. G. Scribner and R. E. Sievers, *Gas Chromatography, Proc. 8th Int. Symp. Gas Chromatography, Dublin, 1970*, Elsevier, Amsterdam, 1970, p. 369.
33 R. E. Sievers, J. M. Connelly and W. D. Ross, *J. Gas Chromatogr.*, 5 (1967) 241.
34 G. P. Morie and T. R. Sweet, *Anal. Chim. Acta*, 34 (1966) 314.
35 B. B. Tomazic and J. W. O'Laughlin, *Anal. Chem.*, 45 (1973) 1519.
36 R. Fontaine, C. Pommier, C. Eon and G. Guiochon, *J. Chromatogr.*, 104 (1975) 1.