

CHROM. 17 534

## IMPROVED ELUTION OF METAL $\beta$ -DIKETONATES ON FUSED-SILICA WALL-COATED OPEN-TUBULAR COLUMNS

SERGIO DILLI

*Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington 2033 (Australia)*

and

SALLY MILLER and KEVIN ROBARDS\*

*School of Applied Science, Riverina College of Advanced Education, P.O. Box 588, Wagga Wagga 2650 (Australia)*

(Received January 8th, 1985)

---

### SUMMARY

The behaviour of several  $\beta$ -diketonates on fused-silica wall-coated open-tubular columns is presented and, although elution abnormalities persist, albeit at the nanogram level, performance is improved considerably relative to packed columns. The importance of the ligand structure, injection system and stationary phase is demonstrated. However, the nature of the coordinated metal ion remains the dominant factor in determining on-column behaviour and, in particular, column retention. Mechanisms leading to column retention are discussed.

---

### INTRODUCTION

The gas chromatography (GC) of  $\beta$ -diketonates has been examined extensively on packed columns<sup>1-5</sup>, and numerous elution problems have been identified. In earlier work these problems were manifest<sup>6</sup> at the milligram level whereas improvements in column construction (glass *versus* metal) and use of more inert solid supports have witnessed<sup>4,5</sup> a reduction in this level to microgram amounts. Thus, using inert silanized supports and glass columns, it has been possible<sup>3,5</sup> to examine a range of metal ion derivatives at the microgram level. However, difficulties arising from diverse on-column reactions are still apparent, and the solid support has been established<sup>5</sup> as an important factor. Elimination of the solid support, as in a wall-coated open-tubular (WCOT) column, is a logical extension of earlier work and yet, despite the simplification afforded by it, there are few publications in this area<sup>7-11</sup>. Indeed, capillary column GC studies involving the versatile  $\beta$ -diketones are restricted to the trifluoroacetylacetonates<sup>7,8</sup>. Although retention phenomena have been reported<sup>9</sup> for metal and glass capillary columns, some success has been achieved<sup>7</sup> with short, highly inert fused-silica columns.

In this paper, the behaviour of several  $\beta$ -diketonates on fused-silica WCOT columns is presented. Because of the established importance<sup>3,5</sup> of the ligand system,

aryl, alkyl and fluoroalkyl  $\beta$ -diketonates, including those of copper(II), aluminium(III), cobalt(III), chromium(III), iron(III), manganese(III), vanadium(III) and oxovanadium(IV), were investigated. Although considerable improvement is achieved relative to the performance on packed columns, elution abnormalities persist, albeit at the nanogram level.

## EXPERIMENTAL

### *Syntheses*

All chelates were prepared and purified by methods described elsewhere<sup>3,12</sup>. Solutions were prepared by dissolving the chelate in hexane, toluene or acetone. Ligands used in this work were 4,4,4-trifluoro-1-(pentafluorophenyl)butane-1,3-dione (HF<sub>5</sub>bta), 4,4,4-trifluoro-1-(2'-trifluoromethylphenyl)butane-1,3-dione (HoCF<sub>3</sub>bta), 4,4,4-trifluoro-1-(2',4'-difluorophenyl)butane-1,3-dione (H<sub>2</sub>,4F<sub>2</sub>bta), 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (Hhpm), and 2,2,6,6-tetramethylheptane-3,5-dione (Hdpm).

### *Gas chromatography*

A Pye Unicam Model PU4500 gas chromatograph, equipped with a flame ionization detector, was used for this work. The carrier gas was filtered, high purity, dry nitrogen at a flow-rate of 1.5 ml min<sup>-1</sup> for splitless injection or 1.0 ml min<sup>-1</sup> for split injection (split ratio 1:40). Detector and injection port temperatures were maintained 40°C above that of the column, together with a make-up gas flow-rate of 40 ml min<sup>-1</sup>.

Columns were fused-silica WCOT (0.2 mm I.D.) obtained from Scientific Glass Engineering and were 3 m long, unless stated otherwise.

## RESULTS AND DISCUSSION

The reduction in level at which elution abnormalities appear is the most noteworthy change in moving from packed to WCOT columns. Thus, using packed columns, column loading, baseline elevation, spurious peaks and tailing are typical<sup>3-5</sup> for microgram amounts whereas, on WCOT columns, these abnormalities arise only at sub-microgram levels.

### *Retention by various liquid phases*

Fig. 1 suggests, because of the extremes of stationary phase polarities, that successful elution can be achieved only on relatively non-polar phases such as OV-101 and SE-30, with severe tailing occurring on the more polar Carbowax 20M and FFAP. It was observed that column loading also increased with the polarity of the stationary phase, implying a non-equilibrium association of the chelate with the liquid phase. Thus, for example, on OV-101, Cr(F<sub>5</sub>bta)<sub>3</sub> eluted without evidence of retention at the 20-ng level but this amount was totally retained on Carbowax 20M. Retention persisted on this phase even with 0.4  $\mu$ g of chelate. In contrast, initial total retention and/or decomposition of the copper(II) derivative occurred at the 50-ng level even on OV-101 followed, however, by a gradual improvement in peak shape and detector response until both became reproducible after injection of 500-ng of chelate onto the column.

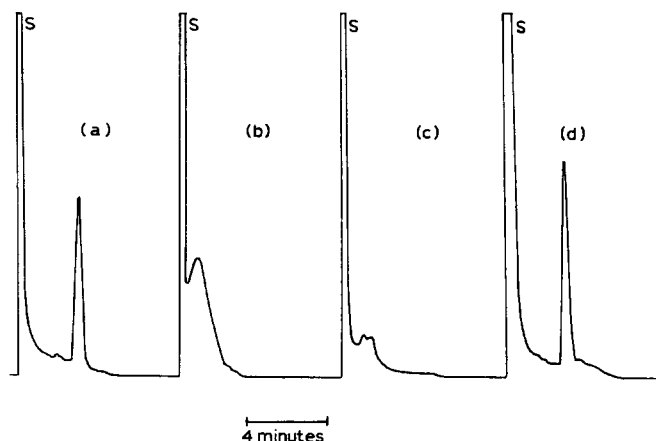


Fig. 1. Chromatograms of the elution of  $\text{Cr}(\text{F}_5\text{bta})_3$  ( $0.4 \mu\text{g}$ ) on (a) OV-101, (b) Carbowax 20M, (c) FFAP and (d) SE-30. Column temperatures are 155, 175, 145 and  $165^\circ\text{C}$ , respectively. Solvent (S) was hexane.

This represents a significant reduction in column loading relative to packed columns, where  $\text{Cu}(\text{F}_5\text{bta})_2$  is totally retained at sub-microgram levels<sup>3</sup>. Furthermore, the absence of a loading effect for  $\text{Cu}(\text{F}_5\text{bta})_2$  at the 50-ng level for an OV-101 column previously used for  $\text{Cr}(\text{F}_5\text{bta})_3$  appears to be the result of the saturation of reactive sites within the column by the chromium derivative.

#### *Injection system*

Split and splitless injection modes were compared for OV-101 and  $\text{Cr}(\text{F}_5\text{bta})_3$ , and, as shown in Fig. 2, poorer precision is associated with the split mode. In this mode, the injection port temperature is critical<sup>7</sup> (see Fig. 3), requiring a compromise between the need for rapid sample vaporization and the thermal stability of the sample.

In the case of  $\text{Al}(\text{F}_5\text{bta})_3$ , at an injection port temperature of  $165^\circ\text{C}$  thermal decomposition was evident from the accumulation of a black glossy residue in the glass-wool packing of the injection port. Although precision was improved and the rate of residue buildup decreased when an empty injection port was used, split injection remained inferior to the splitless mode. However, here again, residues increased in the glass-lined injection port. This accumulation was accompanied by a deterioration in chelate performance, requiring regular cleaning of the injection port (typically after a total injection of  $5 \mu\text{g}$  of chelate) to restore performance to its original level.

#### *Elution behaviour of aryl derivatives*

For the purpose of comparing the influence of the ligand structure as well as the metal ion on elution behaviour, a series of  $\beta$ -diketonates was examined on OV-101 and SE-30. Despite there being little difference between the behaviour on the two phases, the performance on OV-101 (see Fig. 4) is marginally superior. There are two notable features of the data. Firstly, the importance of the metal ion and ligand structure is emphasized by the wide variation in the behaviour of the different che-

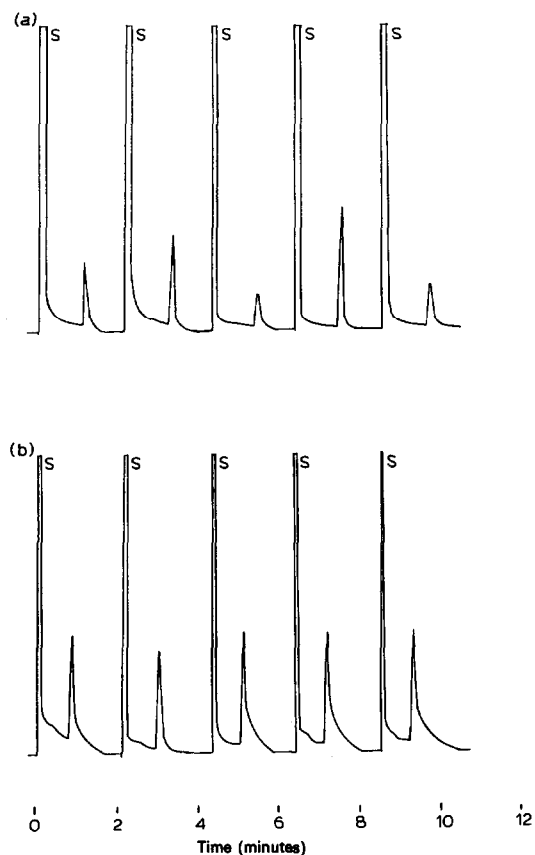


Fig. 2. Chromatograms showing the precision for injections with (a) split and (b) splitless (5 m column) modes. Column temperature and amount of chelate injected are (a) 145°C and 400 ng, and (b) 175°C and 30 ng. Solvent (S) was hexane.

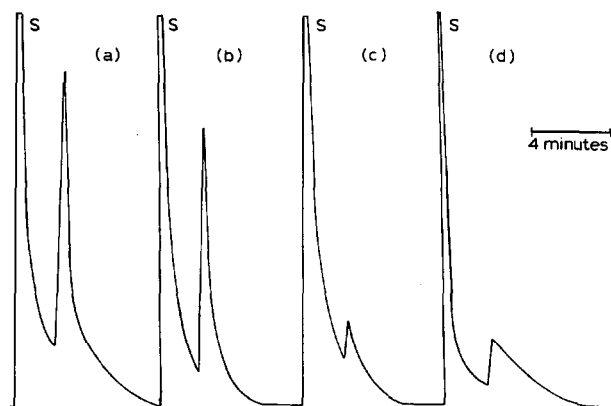


Fig. 3. Chromatograms showing the elution of  $\text{Al}(\text{F}_3\text{bta})_3$  (0.4  $\mu\text{g}$ ) at 132°C on OV-101 using split injection and injection port temperatures of (a) 170°C, (b) 160°C, (c) 140°C and (d) 133°C.

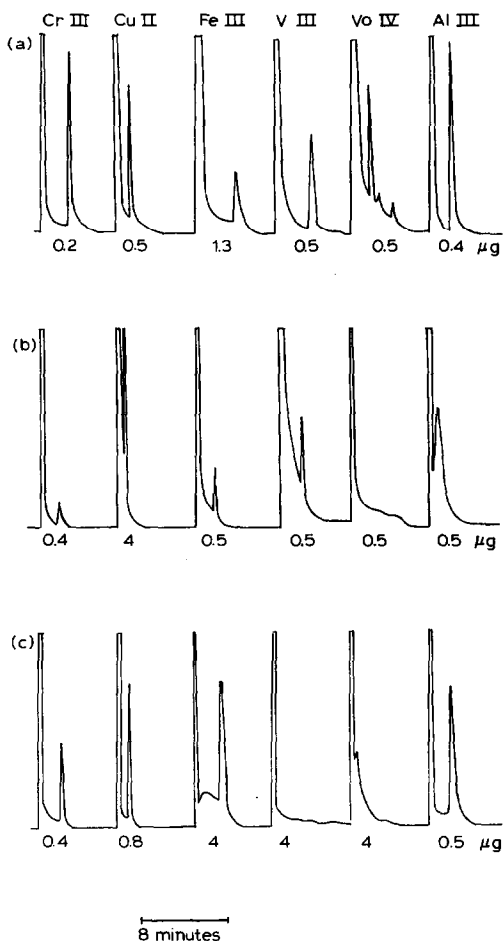


Fig. 4. Chromatograms showing the sequential elution of chelates derived from (a)  $\text{HF}_5\text{bta}$ , (b)  $\text{HoCF}_3\text{bta}$  and (c)  $\text{H}_2,4\text{F}_2\text{bta}$  using splitless injection and OV-101. Column temperatures are 155, 185 and 175°C, respectively.

lates. Of the three aryl ligands,  $\text{HF}_5\text{bta}$  is generally the more satisfactory yet, irrespective of ligand structure, performance deteriorated in the order  $\text{Cr(III)} > \text{Al(III)} > \text{Cu(II)} > \text{V(III)} > \text{Fe(III)} > \text{VO(IV)}$ . This trend again indicates the overriding importance of the metal ion in determining elution behaviour. Secondly, on-column redox transformations remain a problem with vanadium chelates although an important distinction arises with  $\text{V(F}_5\text{bta)}_3$ , which is partially oxidized to the oxovanadium(IV) derivative, in contrast to the situation on packed columns<sup>13-15</sup>. However, representative chromatograms (Fig. 5) are consistent with the oxidative instability of vanadium(III) chelates<sup>13,16,17</sup>.

Serial injection of free ligand onto a previously used column resulted in the elution of chelates [of copper(II) and iron(III)] with retention times dependent on the ligand injected (Fig. 6) rather than on the chelate previously injected. Since the in-

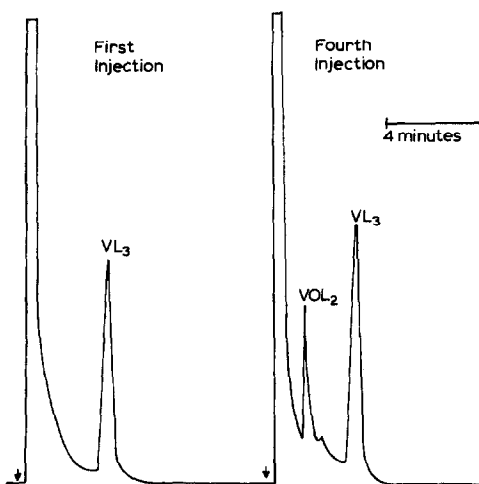


Fig. 5. Chromatograms illustrating the on-column transformation of  $V(F_5bta)_3$  to  $VO(F_5bta)_2$  on OV-101 at  $155^\circ C$ . Chromatograms are shown for the first and fourth injections ( $0.5 \mu g$  of chelate) onto a previously unused column.

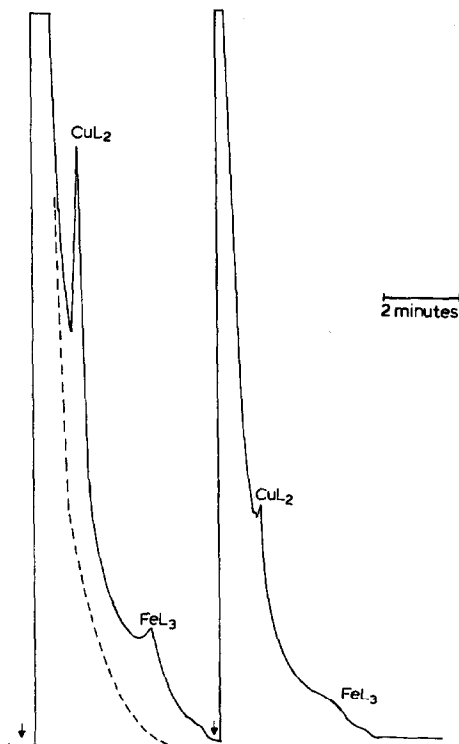


Fig. 6. Chromatograms obtained after the injection of  $H_2,4F_2bta$  (HL) onto a previously used column with a clean injection port. Chromatogram of the free ligand injected onto a previously unused column, under the same conditions, is shown as a broken line.

jection port was cleaned prior to injection of ligand, the results imply elution of previously retained metal ion residues from the column.

### Elution behaviour of fluoroalkyl derivatives

The elution of alkyl and fluorinated alkyl chelates on packed columns is superior to the performance of fluorinated aryl  $\beta$ -diketonates<sup>3,5</sup>, and this is also the case on WCOT columns (Figs. 4 and 7). Although the order of elution of the Hhpm derivatives  $\text{Al(III)} < \text{Cu(II)} < \text{Cr(III)}_{\text{trans}} < \text{Co(III)}_{\text{trans}} \approx \text{Cr(III)}_{\text{cis}} < \text{Fe(III)} < \text{Co(III)}_{\text{cis}} \approx \text{Sc(III)} \approx \text{Mn(III)}$  varies from volatility trends<sup>12</sup>, a parallel with the elution sequence<sup>12</sup> on packed columns is apparent. Fig. 8 presents chromatograms of mixtures of these chelates on a packed and a WCOT column and shows a substantial improvement in the separation on the WCOT column. The chemical properties (notably, thermal, oxidative and kinetic stability) of the individual chelates are reflected in their chromatographic behaviour, which deteriorated in the order chromium, aluminium, cobalt(III), copper(II), iron(III), scandium(III) and manganese(III). With the exception of manganese(III), which undergoes on-column decomposition, the chelates eluted as sharp symmetrical peaks at the 50-ng level. On the other hand, at the 1- $\mu\text{g}$  level,  $\text{Mn(hpm)}_3$  eluted as a symmetrical peak with on-column decomposition still apparent, as evidenced by the peak preceding the main chelate peak (Fig. 9). However, the relative area of the pre-peak was greatly reduced, suggesting that the extent of on-column decomposition was limited by the availability of an on-column reactant. Moreover, on subsequent injection of  $\text{Sc(hpm)}_3$ , severe tailing of the scandium peak was observed whereas, following conditioning for 2 h,  $\text{Sc(hpm)}_3$  eluted as a sharp symmetrical peak (as seen in Fig. 7).

From these results, we conclude that the elution of the Hhpm derivatives is vastly improved on capillary columns. Indeed, on packed columns the iron(III) and manganese(III) derivatives are totally retained<sup>5</sup> at the 0.5- $\mu\text{g}$  and 5- $\mu\text{g}$  level, respec-

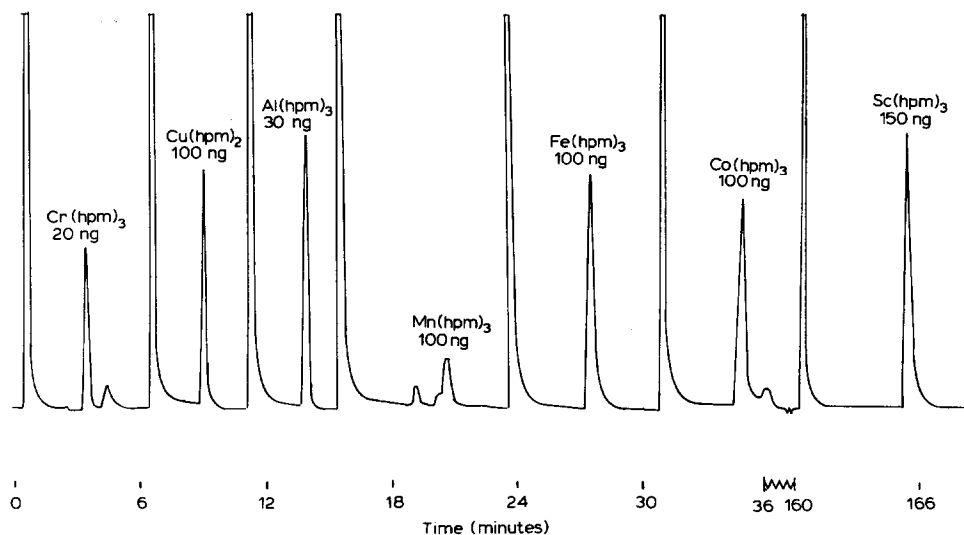


Fig. 7. Chromatograms showing the elution of Hhpm derivatives on OV-101 at 115°C (column length 4.5 m).

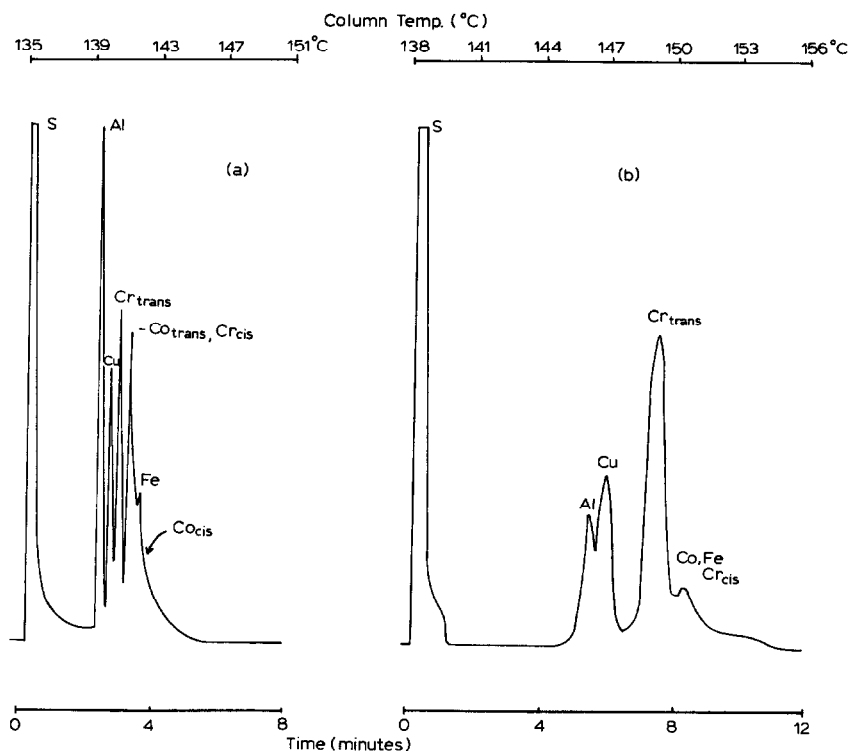


Fig. 8. Chromatograms showing the elution of a mixture of the Hhpm derivatives of Al(III), Cu(II), Cr(III), Co(III) and Fe(III) on (a) WCOT OV-101 column (10 m  $\times$  0.2 mm I.D.; nitrogen carrier gas at 1 ml min<sup>-1</sup>; 50 ng of each chelate) and (b) packed column (3% SE-30 on Chromosorb 750; on-column silylated; 1 m  $\times$  4 mm I.D.; nitrogen carrier gas at 35 ml min<sup>-1</sup>, 5  $\mu$ g of each chelate). Solvent (S) was acetone.

tively, whereas these chelates are satisfactorily eluted from WCOT columns at much lower levels (Figs. 7 and 9). For example, approximate detection limits using nitrogen as carrier gas for the Hhpm derivatives (expressed as nanograms of chelate) are: chromium(III), 1; aluminium(III), 1; cobalt(III), 6; copper(II), 10; iron(III), 13; scandium(III), 20; manganese(III), 50. The performance of the chelates and, more specifically, the detection limits, deteriorate when hydrogen is used as carrier gas, evidently owing to the greater reactivity of the hydrogen atmosphere.

#### *Elution behaviour of alkyl derivatives*

Ligands containing bulky alkyl substituents have demonstrable advantages<sup>1</sup> for the GC of metal ions, and of these ligands 2,2,6,6-tetramethylheptane-3,5-dione (Hdpm) is noteworthy. Although the iron(III) derivative of this ligand eluted as a symmetrical peak at the 1- $\mu$ g level from packed columns (0.5 m; coated and on-column silylated Chromosorb 750), retention was evident. For example, on SE-30 this corresponds to 25  $\mu$ g of chelate. Closer examination of the injection port-end of the column revealed a red band, which failed to move on conditioning of the column but which shifted 2 cm on injection of free ligand (4  $\mu$ l). Mass spectral examination of the column packing also showed the presence of Hdpm in the packing taken from



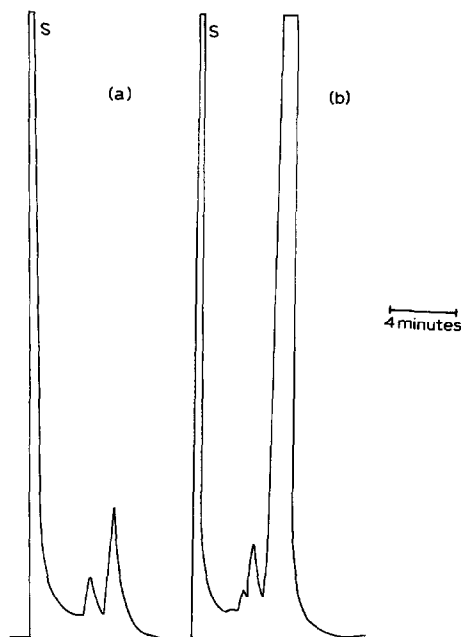


Fig. 9. Chromatograms typical of the elution of  $\text{Mn}(\text{hpm})_3$  at the (a) 100 ng and (b) 1  $\mu\text{g}$  level. Conditions as for Fig. 7.

the site of the red band, whereas other regions contained neither free ligand nor any metal-derived species. These findings not only support a dissociative ion-exchange mechanism for chelate retention but also suggest that the  $-\text{SiO}-\text{ML}_2$  bond<sup>5</sup> is sufficiently strong to favour further loss, within the mass spectrometer, of HL rather than  $\text{ML}_2^+$ . In marked contrast, on an OV-101 fused-silica WCOT column,  $\text{Fe}(\text{dpm})_3$  elutes as a sharp symmetrical peak with no loading effect at the 50-ng level.

#### Column chemistry

As stated elsewhere<sup>3,5</sup>, the breakdown of a sample component during GC analysis does not necessarily implicate the column. Indeed, the observation of residue in the injection port, as noted above, provides direct evidence of the thermal degradation of the chelates in this region. Since sample injection<sup>18</sup> remains the most critical aspect of capillary column GC, this situation is accentuated<sup>7</sup> further when dealing with high boiling solutes such as metal chelates, and only cold on-column injection, which excludes such problems, may present a solution to this difficulty. Even in the event of on-column decomposition, this chemical reaction may be primarily spontaneous (as has been shown<sup>19</sup> for triglycerides) and due to the chemical reactivity of the chelates *per se*.

Abnormalities specifically requiring the intervention of the column are considered to arise from two different mechanisms. In the first, adsorption involves a reversible, physical interaction of the chelate and column components. This mechanism is envisaged then as leading to displacement phenomena prevalent<sup>3</sup> on packed columns. There was no evidence of chelate displacement in the present study, con-

sistent with the low adsorptive characteristics<sup>20</sup> of fused-silica columns. However, such interpretations are complicated by the operating conditions, which can affect the nature of chromatographic results. For example, highly adsorptive columns can produce satisfactory results<sup>21</sup> if a sufficiently elevated column temperature is used.

The second group of phenomena, which are largely chemical in nature and arise from irreversible chemical reactions of the chelate and column, have been termed abstraction<sup>22</sup> (referring to organic solutes) and, more specifically, absorption<sup>5</sup> processes. Included in this group are the reactions of the chelates with the stationary phase and, in particular, with any surface silanol groups. This may involve hydrogen bonding between the chelate and the silanol group and/or an irreversible ion-exchange reaction<sup>5</sup>. Furthermore, a bulk liquid phase interaction involving partially dissociated chelate is feasible<sup>5</sup>, as demonstrated in a thermoanalytical study of the reaction between  $\text{Fe}(\text{hpm})_3$  and SE-30. Thus, whereas  $\text{Fe}(\text{hpm})_3$  volatilized between 150 and 250°C, in admixture (equimass basis) the mass loss occurred<sup>16</sup> between 185 and 370°C. A mass spectral examination of the condensate also confirmed the presence of  $\text{Fe}(\text{hpm})_3$  but no species derived from the siloxane structure. Clearly, these data indicate extensive interaction of the chelate and liquid phase, and this is likely to be enhanced in a GC column owing to the less favourable concentration ratio and the protracted residence times therein. It may be noted that liquid phases are not totally inert, since thermal<sup>23</sup> and oxidative<sup>24,25</sup> degradation have been reported and are likely to be enhanced by the introduction of a chemically reactive species such as a metal chelate.

Other phenomena included in this second group are column-wall effects due to reaction of chelate with surface silanols and Lewis acid sites associated with the presence of transition metal ions. Indeed, the improved performance of the chelates in this study may partly reflect the reduced incidence<sup>22</sup> of these sites on fused silica. The reactions of chelates with impurities introduced into the column, with the sample, the carrier gas or the liquid phase, are also included here. Again, the chemical degradation of polysiloxane liquid phases induced by chelates capable of functioning as Lewis acids<sup>25,26</sup> has been noted<sup>3</sup> in relation to packed columns. To this end, higher purity carrier gases and the development of non-siloxane type liquid phases (for use with fused-silica WCOT columns) appear to be necessary. Finally, reactions initiated by an electron-transfer process, either with or without the intervention of the liquid phase, are mainly responsible for the on-column behaviour of the vanadium and manganese chelates, and may even occur with chelates of other transition metal ions such as iron and cobalt.

Of course, as these problems are overcome, a new set of limitations will become important. One of these will probably be sample contact with the syringe needle<sup>3</sup> or, related to this, contact of the sample with the metal of the detector jet, a factor already established<sup>27</sup> as a source of loss of organic solutes. In conclusion, although the detection limits attainable by capillary column GC appear to be an adequate incentive, attention to all aspects of the chromatographic system, including the design of more stable chelates, remains a necessity before the full potential of the use of GC in trace metal analysis can be realized.

## REFERENCES

- 1 P. C. Uden and D. E. Henderson, *Analyst (London)*, 102 (1977) 889.
- 2 P. M. Patni and S. P. Pande, *Chemical Era*, (1982) 1.
- 3 S. Dilli and K. Robards, *J. Chromatogr.*, 322 (1985) 1, 23.
- 4 D. N. Sokolov, A. V. Davydov, S. Yu. Prokofyev, S. S. Travnikov, E. V. Fedoseev and B. F. Myasoedov, *J. Chromatogr.*, 155 (1978) 241.
- 5 S. Dilli and E. Patsalides, *J. Chromatogr.*, 176 (1979) 305.
- 6 P. C. Uden and C. R. Jenkins, *Talanta*, 16 (1969) 893.
- 7 L. Sucre and W. Jennings, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 452.
- 8 P. C. Uden, D. E. Henderson, F. P. DiSanzo, R. J. Lloyd and T. Tetu, *J. Chromatogr.*, 196 (1980) 403.
- 9 G. Hartmetz, R. Neeb and J. Borneff, *Naturwissenschaften*, 68 (1981) 477.
- 10 M. L. Riekkola, *Mikrochim. Acta*, 1 (1982) 327.
- 11 M. L. Riekkola, *Finn. Chem. Lett.*, 7 (1980) 83.
- 12 E. Patsalides, *PhD. Thesis*, University of New South Wales, 1977.
- 13 S. Dilli and E. Patsalides, *Anal. Chim. Acta*, 128 (1981) 101.
- 14 S. Dilli and E. Patsalides, *Aust. J. Chem.*, 29 (1976) 2381.
- 15 D. N. Sokolov and G. N. Nesterenko, *Zh. Anal. Khim.*, 30 (1975) 2377.
- 16 S. Dilli and K. Robards, unpublished data.
- 17 B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, 8 (1969) 498.
- 18 S. P. Cram, T. H. Risby, L. R. Field and Wei-Lu Yu, *Anal. Chem.*, 52 (1980) 324R.
- 19 K. Grob, Jr., *J. Chromatogr.*, 205 (1981) 289.
- 20 K. Grob, Jr., *J. Chromatogr.*, 208 (1981) 217.
- 21 K. Grob Jr., G. Grob and K. Grob, *J. Chromatogr.*, 156 (1978) 1.
- 22 W. G. Jennings, *Comparisons of Fused Silica and Other Glass Columns in Gas Chromatography*, Dr. Alfred Hüthig Verlag, Heidelberg, 1981, pp. 33 and 11–20.
- 23 Yu. A. Aleksandrova, T. S. Nikitina and A. N. Pravednikov, *Vysokomol. Soedin., Ser. A*, 10 (1968) 1078.
- 24 M. B. Evans, *J. Chromatogr.*, 160 (1978) 277.
- 25 A. E. Coleman, *J. Chromatogr. Sci.*, 11 (1973) 198.
- 26 F. G. A. Stone and W. A. G. Graham (Editors), *Inorganic Polymers*, Academic Press, New York, 1962, pp. 222 and 253–256.
- 27 R. R. Freeman, in L. Keith (Editor), *Advances in the Identification and Analysis of Organic Pollutants in Water*, Ann Arbor Science, Ann Arbor, MI, 1981.