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## CAPILLARY GAS CHROMATOGRAPHY OF METAL-PORPHYRIN COMPLEXES

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### SUMMARY

The first reported (conventional) gas chromatographic results for transition metal porphyrin complexes are presented. They may be the first metal complexes containing a closed macrocyclic ring to be gas chromatographed. Kovats retention indices are in the range of 5200-5600, necessitating the use of short capillary columns. For Aetioporphyrin I, complete separation of Cu, Ni, VO, Co, Pd and Pt complexes is possible, but with octaethylporphyrin the nickel and vanadyl complexes are incompletely resolved.

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### INTRODUCTION

Some years ago, Corwin and co-workers<sup>1-3</sup> described the hyperpressure gas chromatographic (GC) technique for analysis of a range of metallo- and free-base porphyrins. Whilst the chromatographic behaviour (efficiency and resolution) of solutes subjected to this technique was not particularly good, the fact that porphyrins could be supercritically chromatographed was significant since they were previously believed to be not suited to GC analysis. Even in the light of Corwin's work, such compounds were still considered "non-chromatographable" using conventional GC apparatus (the hyperpressure or supercritical technique relies upon a "solvent" carrier gas operated at high pressure, thereby increasing a solute's solubility in the mobile gas phase). This unsuitability of the porphyrins and metalloporphyrins was attributed to their low vapour pressure, the constraints placed upon the then conventional GC technique being insurmountable. This was predominantly due to adsorption upon the solid support within the packed columns employed. Since these early reports, however, no re-evaluation of the GC of free and metalloporphyrins has appeared in spite of recent advances in GC technology. Not surprisingly, therefore, White *et al.*<sup>4</sup> placed little importance on the supercritical technique as holding value for further studies.

An alternative approach to porphyrin GC is that initiated by Boylan and Calvin<sup>5</sup>, involving the preparation of volatile bis(trimethylsiloxy)silicon(IV) derivatives of alkyl porphyrins. These compounds were gas chromatographed using conventional packed column procedures; however, their behaviour was believed to be

somewhat unfavourable until their analysis on flexible fused-silica capillary columns was realised<sup>6</sup>. It is reasonable, therefore, that if the facile determination of silicon derivatives has been made possible with highly deactivated flexible silica columns, then other metalloporphyrins, including those studied by Corwin, should be likewise reinvestigated. Further, it was felt that since many metalloporphyrins possess quantifiable vapour pressure and can be readily sublimed at temperatures of around 200°C under diffusion-pump vacuum, the only limitation to their GC analysis would be the temperature at which these analyses should be carried out.

Abundant precedence for the chromatography of metal chelates exists in the literature, and some reviews<sup>7,8</sup> illustrate the extent to which this area of analysis has been expanded. Recently studied chelates include the dithiocarbamates<sup>9</sup> and dithiophosphates<sup>10</sup>, though tetradentate ligands, with chelation through nitrogen and oxygen or sulphur, have received considerable attention<sup>7</sup>. The latter are not, however, closed ring systems of the type represented by porphyrins. In this paper we describe the successful gas chromatographic analysis of a range of metalloporphyrins.

## EXPERIMENTAL

### Gas chromatography

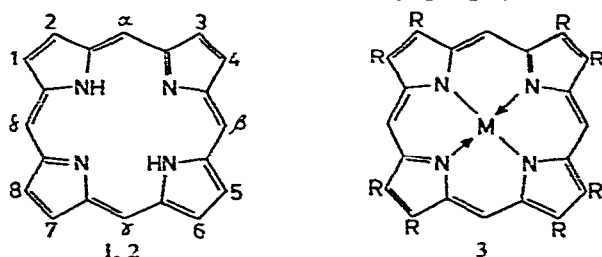
The gas chromatograph employed in this work was a Carlo Erba FTV 4160 instrument incorporating Grob-type split/splitless and on-column injectors. Flame ionisation detection was used. The same instrument was interfaced with an AEI MS30 magnetic-sector mass spectrometer to confirm that chelates were chromatographed unchanged.

A Hewlett-Packard 6 m × 0.3 mm I.D. flexible fused-silica capillary column, OV-1 coated and siloxane deactivated, was used for the results presented; however, satisfactory chelate elution was also obtained on a Chrompack CP Sil 5 coated glass column (10 m × 0.3 mm I.D., on-column injection).

Usual chromatographic conditions were: detector and injector (latter for when split/splitless mode used) at 315°C, on-column injection (with secondary cooling) and oven at 60°C. Hydrogen carrier at 0.2 kg cm<sup>-2</sup> inlet pressure producing an average carrier flow velocity of *ca.* 100 cm sec<sup>-1</sup> was usually used, with temperature programming for splitless and on-column injection modes of either heating from 60°C to 300°C at 7°C min<sup>-1</sup>, or heating from 60°C to 240°C (in approximately 3 min) followed by programming to 300°C at 7°C min<sup>-1</sup>.

### Metalloporphyrin preparations

Free-base porphyrins, 1,3,5,7-tetramethyl-, 2,4,6,8-tetraethyl porphyrin (Actio<sup>1</sup>, 1) and 1,2,3,4,5,6,7,8-octaethyl porphyrin (OEP, 2) were obtained from Dr. J.



- 1 Actio<sup>1</sup>; 1 = 3 = 5 = 7 = CH<sub>3</sub>; 2 = 4 = 6 = 8 = C<sub>2</sub>H<sub>5</sub>;  $\alpha$ - $\delta$  = H
- 2 OEP; 1-8 = C<sub>2</sub>H<sub>5</sub>;  $\alpha$ - $\delta$  = H
- 3 M(II) porphyrin

G. Erdman and Porphyrin Products (Logan, UT, U.S.A.), respectively. They were used as starting materials for preparation of the various metal(II), vanadyl and titanyl porphyrins listed in Table I. Structure 3 represents that of a typical metal(II) porphyrin; vanadyl and titanyl possess an axial oxide ligand with the M=O bond perpendicular to the plane defined by the four nitrogen atoms. Standard methods were used for the bulk of the preparations<sup>11,12</sup>. The procedure of Fournari *et al.*<sup>13</sup> was used to prepare the titanyl derivative.

TABLE I

GAS CHROMATOGRAPHIC RETENTION DATA FOR METALLOPORPHYRINS, COLUMN AND CONDITIONS AS GIVEN IN THE EXPERIMENTAL SECTION

ND = Not determined.

Metal	Actio <sup>1</sup> derivative		OEP derivative	
	Relative retention*	Kovats index**	Relative retention*	Kovats index**
Zn(II)	3.4	5220	6.5	5350
Cu(II)	3.6	5240	7.3	5390
Ni(II)	4.8	5290	8.4	5410
V(IV)***	5.7	5320	8.6	5420
Co(II)	6.8	5380	11.2	5490
Pd(II)	10.4	5470	17.0	ND
Ti(IV)***	13.2	5530	—	—
Pt(II)	15.8	5600	—	—

\* Given as minutes to peak maximum after elution of *n*-pentacosane (C<sub>50</sub>). *n*-C<sub>50</sub> elutes at ca. 6 min after reaching 300°C—the isothermal hold region at top of temperature programme—under the conditions employed.

\*\* These values are calculated by interpolation within two *n*-alkane standards—*n*-pentacosane and *n*-hexacosane, and are approximate. They are quoted to nearest 10 index units.

\*\*\* V(IV) as vanadyl, V=O and Ti(IV) as titanyl, Ti=O.

## RESULTS AND DISCUSSION

The range of metalloporphyrins successfully chromatographed is presented in Table I, along with relative retentions, given as elution time after *n*-pentacosane (*n*-C<sub>50</sub>), and approximate Kovats indices. All of these compounds elute at the top of the temperature programme (conditions as in Experimental) after isothermal conditions (300°C) have been established. Under the standard conditions employed to obtain these results, the hydrocarbon reference appears at 6 min after onset of isothermal.

A chromatographic trace of a mixture of metalloporphyrins is given in Fig. 1. Initial success for these chelates was obtained on a 2-m length of the Hewlett-Packard OV-1 capillary column. Poor separations and broad peaks were obtained on this short column (with the chelates eluting at similar times after *n*-C<sub>50</sub> as given in Table I, at an isothermal hold temperature of 270°C). A 6-m length of the same material was utilised to give better separations and greater overall efficiency, whilst only requiring a moderate increase in temperature to 300°C, with results as illustrated in Fig. 1.

At the maximum temperature employed (300°C), a marked increase in the

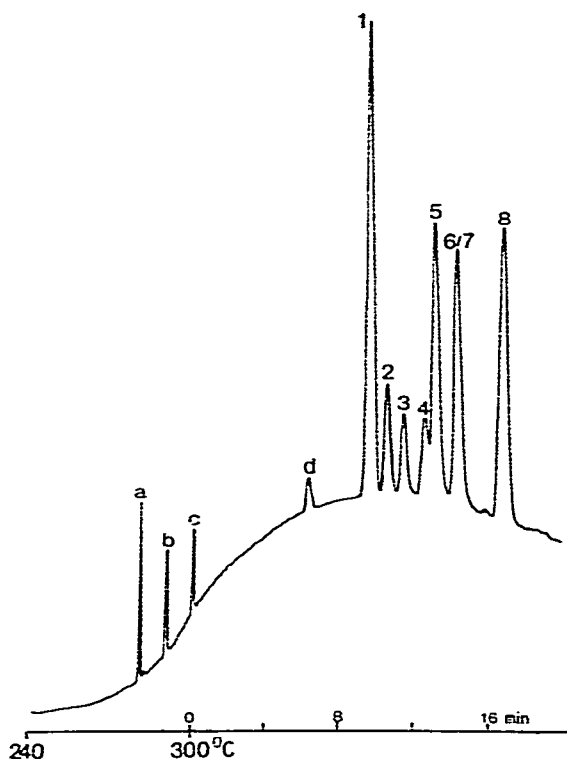


Fig. 1. Capillary gas chromatogram of a mixture of *n*-alkanes and metalloporphyrins. Flexible silica column (6 m  $\times$  0.3 mm I.D.), operated under conditions given in the Experimental section, with isothermal hold at 300°C. Peaks: a = *n*-tetracosane (*n*-C<sub>40</sub>); b = *n*-dotetracosane (*n*-C<sub>42</sub>); c = *n*-tetratetracosane (*n*-C<sub>44</sub>); d = *n*-pentacosane (*n*-C<sub>50</sub>); 1 = Cu Aetio; 2 = Ni Aetio; 3 = VO Aetio; 4 = Co Aetio; 5 = Cu OEP; 6 = Ni OEP; 7 = VO OEP; 8 = Co OEP.

detector baseline occurred. This was due to phase bleed, as indicated by solvent blank trials, rather than any effects such as compound decomposition. Peak symmetry appears to be quite good; however, some fronting behaviour, indicative of an concave isotherm, may be noticeable at higher concentrations. This effect gives rise to the slight shoulder on the leading edge of peak 1 in Fig. 1. There was no evidence of metal exchange between different metalloporphyrins in the gas phase, although transmetalation of certain porphyrin complexes can occur<sup>12</sup>.

Studies on silicon(IV) alkyl porphyrins, which have been reported previously<sup>6</sup>, revealed that retention indices for the Aetio and OEP bis(trimethylsiloxy) derivatives were approximately 3315 and 3440, respectively, on a methyl silicone-coated column. Clearly the conditions employed for such studies (25-m column, temperature programming to 260–280°C) would not be suitable for the chelates in Table I which have retention indices of the order of 5200–5600. For the 6-m column, the calculated resolution ( $R_s$ ) between pairs of compounds (Aetio<sup>1</sup> and OEP) of the same metal species is in the region of  $R_s \approx 6-7$  for Ni, Cu and Co under the non-optimal conditions quoted for Fig. 1 (non-optimal because the carrier gas flow-rate is far in excess of that which would correspond to a minimum on the Van Deemter curve).

The vanadyl pair were resolved to  $R_s \approx 5$ , and this is a consequence of an apparent reduction in retention volume difference between the Aetio and OEP compounds rather than any adverse chromatographic behaviour (such as band broadening or peak tailing). This may be seen by comparing the positions of peaks 2 and 6 against 3 and 7 for the Ni and VO pairs on Fig. 1. The short 2-m column afforded the nickel pair with a resolution of 2-3, with rather broad peaks resulting, though again peak shapes were symmetrical.

Some of the other metalloporphyrins, most notably the zinc porphyrins, exhibit less favourable chromatography and their elution is characterised by fronting peaks even at low injected concentrations. However, this behaviour may still be an overloading effect due to very low solubility in the stationary phase, possibly related to the lack of planarity of zinc porphyrins<sup>14</sup> (the zinc atom is out of the plan defined by the four nitrogens of the pyrrole groups, although in another crystal structure it is coplanar<sup>15</sup>). Axial ligand attachment is possible for zinc porphyrins<sup>16</sup> but no manifestation of this in peak tailing (through metal-stationary phase adsorptive interaction) is observed.

The relative retention trends of the metalloporphyrin complexes, such as Ni, Pd, and Pt, follow those usually observed for other metal-chelating systems, such as the dithiophosphates<sup>10</sup> and the tetradentate  $\beta$ -thiono enamines<sup>17</sup> and probably reflect a molecular-weight trend influencing volatility. The close similarity of molecular weights of Cu, Co and Ni porphyrins may account for the similar retention volumes of these compounds. However, no definitive work on chromatographic retention mechanisms for a range of metal chelates appears to have been undertaken. Thus, the physicochemical parameters which affect retention of the chelate are still open to speculation. Clearly some interrelation must exist between volatility and solubility (as measured by gas chromatographic retention) and the bonding status of the metal atoms within a series of metal-chelates.

For Zn, Cu, Ni and Co porphyrins, the elution order is the reverse of the molecular-weight order, though it agrees with that for the GC of other metal chelates<sup>17</sup>. The observation of the lower-molecular-weight species eluting later also holds for the VO- and TiO-porphyrins, with the latter having a molecular weight about three mass units less than the vanadyl but with a significantly longer retention. The order of increasing retention for Cu, Ni and VO is also found for other chelating systems<sup>18</sup>.

A generalised mechanism for retention behaviour of metalloporphyrins would require consideration of a variety of physical phenomena such as intermolecular attraction and volatility.

Heats of sublimation ( $\Delta H_s$ ) of a range of phthalocyanines have been determined by MacKay<sup>19</sup>, and the results correlated with calculated electron distributions around the molecules (both out-of-plane densities on the metals and the peripheral density on the *meso* nitrogens). The resulting trend predicted from distribution considerations was  $\text{Co} > \text{Cu-Ni} > \text{Zn} > \text{H}_2$ , and this agreed with experiment (thus, the cobalt has greater electron density which is manifested in greater intermolecular interaction, and therefore higher  $\Delta H_s$  value). MacKay felt that the general order of peripheral density (arising from *meso* positions) for the phthalocyanines would correspond to that for porphyrins. MacKay's order for the metallophthalocyanines agrees with that which we have obtained for the GC of metalloporphyrins, except that

the vanadyl, palladium and platinum phthalocyanines have  $\Delta H_s$  values which do not fit in with the GC trend (these were not included in the considerations of electron distributions in ref. 19). This might imply that sublimation behaviour alone cannot be reliably used to predict relative GC elution orders for the porphyrin-metal chelates.

One trend which does fit much better with our elution order is the stability order of the chelates derived from spectroscopic data. Chelate stability usually refers to stability towards demetallation by various acid treatments<sup>11</sup>. Phillips<sup>20</sup> discussed spectroscopic correlations with complex-stability for a variety of tetrapyrrole ligands, including Aetioporphyrin II (where an increasing shift to lower wavelengths in the visible and ultraviolet spectra indicated increased chelate stability). Relative stabilities decreased through the series Pt > Pd > Ni > Co > Cu > Zn. The position of Co is the only apparent anomaly when this order is compared with chromatographic retentions. Perhaps it is not surprising that spectroscopic data should give a similar order to the electron-density distributions since electronic transitions giving rise to the spectra will be perturbed by electron-density changes. Exactly why such a measure of stability should closely reflect GC behaviour is unclear.

Whilst it would be informative to have thermogravimetric results on the metalloporphyrins, such data are not yet available. It is common practice to compare such behaviour with GC retention<sup>17,18,21</sup>.

The limited GC data for metalloporphyrins do not permit us to propose a generalised mechanism for retention at this stage.

The hyperpressure procedure<sup>3</sup> gave a retention order for the Aetioporphyrin II chelates of Cu < Co < Ni < Zn < TiO < Pt < VO < Pd on an Epon 1001 column, and Co < Cu < Zn < Ni < TiO < Pt < Pd < VO on an XE-60 coated column (with dichlorodifluoromethane solvent (carrier) gas). Both these stationary phases are quite polar; Epon 1001 is an epichlorohydrinbisphenol resin (McReynolds index 2319) and XE-60 is a 25% 2-cyanoethyl silicone rubber (index 1785). Generally such polar phases are not favoured for the GC of metal chelates<sup>7</sup> (with the exception of fluorinated phases for F-containing metal-derivatives). These orders differ greatly from that which we report here, and are at variance with generally observed GC relative retentions. The metal acetylacetonates, also studied by Karayannis and Corwin<sup>22</sup> using hyperpressure GC, likewise gave retention orders not consistent with those usually expected for GC and again, as with the porphyrins, the peak shapes and column efficiencies appear rather unattractive. Evidently, supercritical chromatography must involve different physicochemical interaction mechanisms than those operative in gas-liquid chromatography.

## CONCLUSIONS

This paper has demonstrated GC analysis of a wide range of metal-porphyrin complexes. Capillary columns (of either glass or fused silica) provide the necessary low-activity support surface and high temperature stability required for compounds with retention indices in the region of 5200–5600. The self-association phenomenon of these macrocyclic compounds may contribute to such high retention volumes.

Results are reported for C<sub>32</sub> and C<sub>36</sub> fully alkylated porphyrins (Aetio<sup>1</sup> and OEP respectively); however, an extension into the "biological" porphyrins, which usually possess acidic side-chains, appears possible after appropriate derivatisation.

The ability of the porphyrin ligand to complex a wide variety of metal species (with successful chromatography of just a few of these reported here) could give this ligand a unique position within the field of metal-chelate GC.

Significant improvements in the chromatographic results would be made if increases in both resolution and overall efficiency could be effected by increasing the length of the column and/or using a carrier flow-rate closer to optimum. Both of these options would necessitate programming to higher temperatures, perhaps in the region of 340°C, and continued cycling of columns to such high temperatures would probably reduce column lifetime. Narrow-bore columns ( $\approx 50 \mu\text{m}$  I.D.) and/or the use of very thin-film phase coatings are both possible areas which could be studied, however, the former precludes the use of the on-column injection system and the latter would place an increased importance on deactivation of the glass surface, and also limit the capacity of the GC capillary system. We are currently investigating various ways of improving upon the results presented herein.

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