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GAS CHROMATOGRAPHY OF SOME METAL DIALKYLDITHIOPHOSPHATES WITH PACKED AND CAPILLARY COLUMNS USING FLAME PHOTOMETRIC DETECTION

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SUMMARY

Metal dialkyldithiophosphates are suitable for selective detection with a flame photometric detector operated in either the S_2 or HPO emission mode. Comparison of data for packed and capillary columns shows that the sensitivity in the HPO mode is only slightly greater than, and in the S_2 mode comparable with, that in the flame ionization detector. In addition, it is notable that the sensitivity to the chelates in the HPO mode is inferior to that for simple organophosphorus compounds by an order of magnitude. Background permeation of CS_2 leads to some improvement in detection limits for nickel dithiophosphate. Baseline resolution of palladium and platinum derivatives is readily achieved on wall-coated open-tubular columns.

INTRODUCTION

The search for new derivatising chelating agents that yield volatile metal compounds still continues, although the number of new systems that have been introduced in recent years does not match the rapid advances made in the early 1970's. The first metal chelates to come under gas chromatographic (GC) scrutiny were the acetylacetonates and their fluorinated analogues. Several review articles and books adequately cover this area[1-4].

Limitations associated with the β-diketonates resulted in efforts to increase the number of metals that could be suitably chromatographed by any one chelating system. Thus, ligands containing oxygen and/or sulphur or nitrogen have attracted considerable interest, specifically the thioacetylacetonates, bidentate and tetradentate β-ketoamines and their thio analogues, and dialkyldithiocarbamates. Such work, up to 1977, has been reviewed[5,6].

The exploitation of technological advances in chromatography must be expected to have some relevance to work on metal chelates, in which column adsorption

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effects may lead to significant on-column losses of compounds and render various derivatives unsuitable for GC analysis[3,7]. The intense efforts directed towards the preparation of capillary columns[8,9], especially with respect to the manufacture of neutral and non-adsorptive surfaces, offer a new vista in metal chelate chromatography; glass-surface preparations such as deactivation with Carbowax 20M[10], silylation[11] and polysiloxane degradation[12] appear to be foremost in this area. The acclaimed fused-silica flexible columns have been used to generate extremely good chromatograms of "difficult" compounds[13], including the bis-trimethylsilyl (bis-TMS) derivatives of the silicon(IV) porphyrins, Aetio[1] $Si(IV)(OTMS)_2$ and $OEPSi(IV)(OTMS)_2$ (ref. 14).

Thus, the whole range of metal chelate derivatives needs to be re-evaluated in the light of such advances. Consequently, several papers have appeared on capillary chromatographic analysis of metal chelates. These have primarily featured the dithiocarbamates[15-17], but recent communications by Sucre and Jennings[18] and by Uden et al.[19] have involved studies of a broad range of derivatives. Thermal lability may still be a problem when flash-vaporisation injection techniques are used, but on-column capillary chromatographic methodology may overcome this.

Selective GC detection of metal chelates has not been widely employed, apart from the use of the electron-capture detector (ECD). Although the flame ionisation detector (FID) usually suffices for most analyses, some investigations involving use of atomic absorption, plasma emission sources, mass spectrometry and flame photometry have been reported. For the last-named technique, work has been concentrated on spectral emission (line or band) from the metallic species, and relatively high-temperature flames have been used[20-23], whereas little has been reported on flame photometric detection based on emission from elements in the ligand.

Recently, in continuation of earlier work[24], we reported a successful GC study of some volatile bis(dialkyldithiophosphato)metal(II) chelates on inert diatomaceous earth supports, with use of FID[25]. The suitability of specific detection of dithiophosphates by a flame photometric detector (FPD), with use of S_2 and HPO emission, was recognised and is investigated in the present study. Capillary column analyses of these derivatives was an important objective, since it was expected that significant improvements in the overall chromatographic behaviour could be realised. Apart from the paper by Sucre and Jennings[18], we are aware of no other reports on GC–FPD of thiochelates. It is intended, herein, to illustrate the general characteristics of the FPD as applied to metal dithiophosphates in comparison with simple organic compounds. The GC behaviour of the metal chelates on glass capillary columns will also be discussed for both the FID and the FPD.

EXPERIMENTAL

Metal chelates and organic standards

Metal dialkyldithiophosphates were prepared as described previously[25]. The abbreviations dedtp, dpr'dtp, dprdtp and dbu'dtp correspond to the diethyl-, diisopropyl-, di-n-propyl- and di-sec.-butyldithiophosphate ligand anions, respectively.

Organic standards used were triphenyl orthophosphate (TPOP), diphenyl disulphide (DPDS) and triphenylphosphine sulphide (TPPS).

The GC–FPD system

A Perkin-Elmer Model F30 gas chromatograph was used for these studies, with either a FID or a Perkin-Elmer single-flame (FPD) of spectral characteristics listed elsewhere[26]. The FPD was optimised for nickel di-isopropyldithiophosphate in the same manner as that reported for SO_2 and TPOP[26], and similar optimal conditions were obtained for the chelate and the appropriate standard in each detection mode. Thus, O–H ratios of 0.3–0.35 were generally used.

Columns

The individual columns used are indicated in the relevant chromatograms. Capillary-column analyses are reported for soda-lime-glass columns of length not exceeding 10 m. Surface preparations included etching with gaseous HCl, deactivation with Carbowax 20M, mild silylation with a dimethyldichlorosilane–trimethylchlorosilane solution, and dynamic coating with OV-101 or PS-300. A Perkin-Elmer injection splitter was used in the split mode. The F30 "plumbing" was modified by a length of glass-lined tubing (GLT) (0.3 mm I.D.) shaped to carry effluent to the detectors through the manifold; relocation of detectors was not undertaken. For the FPD, the GLT was pushed into the detector body as far as possible to help overcome void-volume problems. Make-up gas was added at the capillary–GLT connection as required.

Permeation tubes

The preparative procedures of O'Keeffe and Ortman[27] and of Kirsten[28] were used to make the permeation tubes; details have been given elsewhere[26].

The Carlo Erba capillary GC instrument

A Carlo Erba Model 4160 chromatograph was used to obtain some of the chromatograms of metal chelates. Columns used were a 10-m OV-1 statically coated capillary of persilylated borosilicate glass and a Hewlett-Packard flexible silica column (25 m × 0.3 mm I.D.) siloxane deactivated and coated with OV-1. The glass column was used in the split–splitless injection mode, whereas the fused-silica column was used with the on-column injector supplied as standard with this instrument.

RESULTS AND DISCUSSION

Except for the section *Capillary column analyses*, all results refer to data obtained with packed columns.

Examples of chromatography of metal dithiophosphates

A chromatogram of Ni, Pd and Pt diisopropyldithiophosphates with the FPD in the sulphur mode is shown in Fig. 1B; for comparison, flame ionisation detection of a mixture of the palladium and platinum chelates under the same experimental conditions produced the resolution shown in Fig. 1A. It is apparent that the peak-to-valley heights for Pd–Pt resolution are different for the two detectors. This effect has been discussed and quantified elsewhere[29] and will be further illustrated by the results for capillary columns (see below).

Examples of nickel chelate elution in which both the S_2 and HPO emission
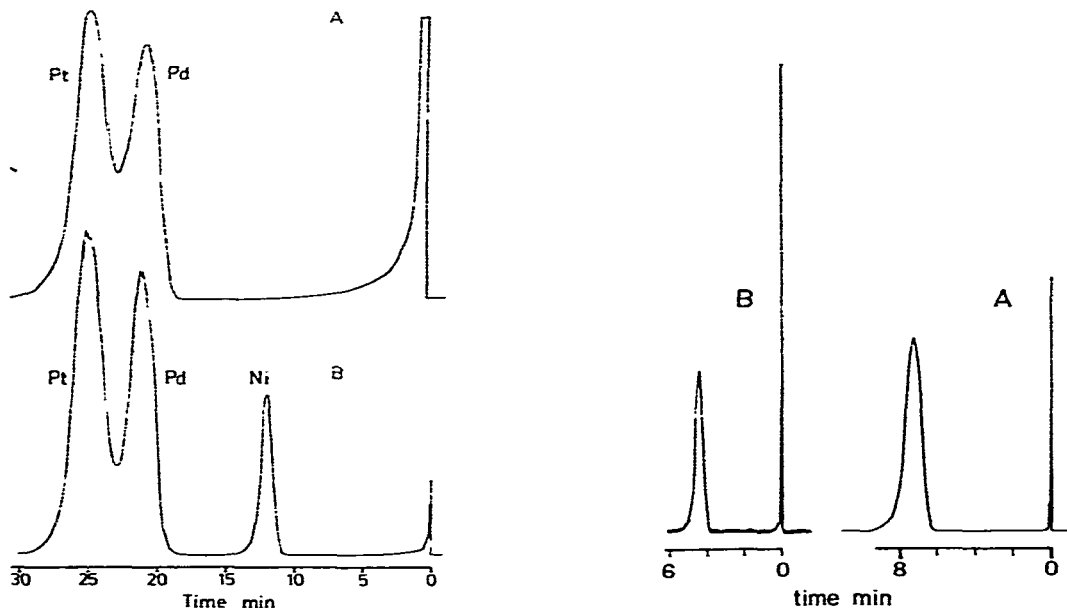
Fig. 1. Gas chromatographic traces of some metal dithiophosphates. Column: 0.4"₀ of OV-101 on DMCS,TMCS-treated glass microbeads (60–80 mesh); stainless-steel column (40 cm × 2.2 mm I.D.: 170 C oven; N₂ carrier gas. flow-rate *ca.* 10 cm³ min⁻¹. A, FID; B, FPD (S₂ mode), air = 14 p.s.i., H₂ = 24 p.s.i.; O H = 0.32.

Fig. 2. Chromatography of Ni(dpr′dtp)₂ with FPD. Column: 2 "₀ of PS-300 on Chromosorb 750; stainless-steel column (40 cm × 2.2 mm I.D.): N₂ carrier gas. flow-rate *ca.* 25 cm³ min⁻¹. A, HPO detection mode: air = 15 p.s.i., H₂ = 22 p.s.i.; O H = 0.35: oven = 155 'C. B, S₂ detection mode: air = 15 p.s.i., H₂ = 24 p.s.i.; O H = 0.33; oven = 160 C.

modes were used for the FPD are presented in Fig. 2; the solid support used was Chromosorb 750. The peak symmetry is good for this sample. being better than that obtained for the glass microbead column used in Fig. 1. Solvent (chloroform) response varies markedly with change in the component gas flow-rates to the FPD. and appears to decrease with increasing hydrogen or decreasing air flow-rate to the detector (*i.e.* for a decreasing O–H ratio). This is probably a consequence of carbon formation, with subsequent luminescence in the flame, as the largest peak responses for solvent were invariably accompanied by venting of smoke from the detector. Emission from decomposition products of the organic molecule (such as C–H emission) may also occur, although we have not established this fact. Thus, a flame supported by hydrogen and air flow-rates of 66 and 125 cm³ min⁻¹ gave a solvent peak of 41745 integrated peak units, whereas a flame with respective flow-rates of 116 and 125 cm³ min⁻¹ gave an area of only 80 units. The solvent response appears to change monotonically with changing FPD component-gas flow-rate. For example, in the range of hydrogen flows listed above, the response uniformly decreases with increasing flow-rate. Within this range, however. S₂ emission response for diphenyl-disulphide (DPDS) maximises then decreases.
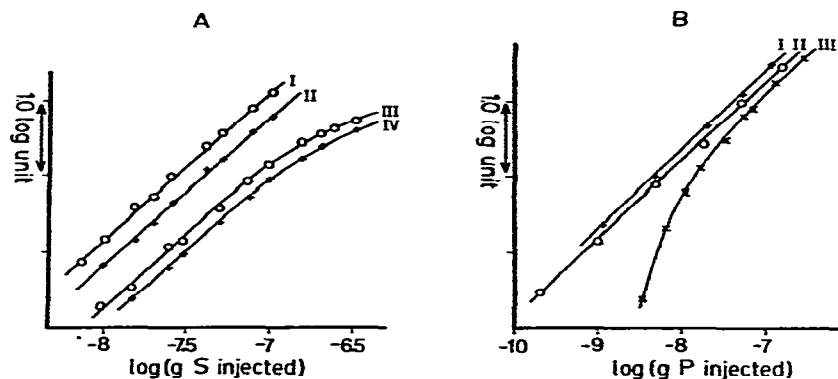
Fig. 3. Calibration curves for various compounds using FPD. A, S_2 detection mode: I. DPDS. response height data; II. DPDS. response area data; III. Ni(dpr'dtp)$_2$. response height data; IV. Ni(dpr'dtp)$_2$. response area data. B. HPO detection mode: I. TPPS; II. TPOP; III. Ni(dpr'dtp)$_2$.

Calibration curves and detection limits

The applicability of the FPD to the analytical determination of dithiophosphate chelates will be reflected by both the linearity of calibration curves and the absolute detection limits. Graphs of response against amount of sample injected are illustrated in Fig. 3; results for Ni (dpr'dtp)$_2$ in both S_2 and HPO emission modes are presented, together with curves for organosulphur and organophosphorus compounds. In the S_2 mode, the chelate shows good linearity of response, with a slope of *ca.* 1.97, although its relative response is lower when compared with the same injected mass of DPDS. This is due to the longer retention time of the chelate, with subsequent lower mass flow-rate into the detector. Log–log curves for the chelate tend to flatten (non-linearity) above *ca.* $2 \cdot 10^{-7}$ g injected sulphur. Since the organosulphur compound does not exhibit this phenomenon until much higher amounts have been injected, there could be increased contribution to interference from the non-organic component of the chelate during combustion of the compound in the FPD.

The HPO monitoring (Fig. 3) shows somewhat anomalous behaviour, with a negative deviation towards the ordinate at lower amounts of injected chelate. This contrasts with the rectilinear graphs obtained for the two organic compounds. This behaviour is attributed to interference in the production of HPO emission arising from either combustion products released when the chelate enters the flame or to formation of a refractory phosphorus-containing compound, which inhibits occurrence of the more usual decomposition processes. There must also be some degree of concentration dependency operating to cause this deviation.

Interest in the FPD was also directed towards determination of detection limits and comparison with those for FID. Results for minimum detectable quantities (MDQ), calculated for an injected mass that elicited a response equivalent to twice the noise level, are shown in Table I. MDQ values are quoted in terms of both nickel and the element responsible for the emission in the detector. For S_2 emission, similar results are obtained for both the chelate and the DPDS reference compound. In contrast, when HPO emission is monitored with triphenylphosphine sulphide (TPPS) as reference, the chelate gives a detection limit inferior by an order of magnitude (consistent with the shape of the calibration curve noted above).

TABLE I

LOWER LIMITS OF DETECTION FOR PACKED COLUMNS WITH THE FPD

Compound	Column*	Emission mode	Amount injected	MDQ
Ni(dpr'dtp)$_2$	I	S$_2$	$6 \cdot 10^{-9}$ g Ni	$8.3 \cdot 10^{-11}$ g Ni sec^{-1} ($1.8 \cdot 10^{-10}$ g S sec^{-1})
DPDS	II	S$_2$	$7.5 \cdot 10^{-9}$ g S	$1.6 \cdot 10^{-10}$ g S sec^{-1}
Ni(dpr'dtp)$_2$	I	HPO	$2 \cdot 10^{-9}$ g Ni	$2.2 \cdot 10^{-11}$ g Ni sec^{-1} ($2.3 \cdot 10^{-11}$ g P sec^{-1})
TPPS	I	HPO	$2 \cdot 10^{-10}$ g P	$1.9 \cdot 10^{-12}$ g P sec^{-1}
Ni(dpr'dtp)$_2$	III	—**	$4.5 \cdot 10^{-9}$ g Ni	$7.5 \cdot 10^{-11}$ g Ni sec^{-1}

* Column I, 2 % of OV-101 on Chromosorb 750; II, 2 % of PS-300 on Chromosorb 750; III, 1 % of OV-101 on Chromosorb 750.
** FID result.

The MDQ values obtained for the reference compounds are similar to those specified by the manufacturer. The values reported for the S$_2$ mode are at the upper limit expected[30-32] and other detectors may give better (i.e., lower) limits. Comparison of MDQ values for sulphur compounds may be tenuous, as adsorption problems may persist[7]. The MDQ value for the dithiophosphate in the HPO mode is greater than expected. Sucre and Jennings[18] reported detection limits in the region of 20–30 pg of P sec^{-1} in the HPO mode, and, although no comment was made on this level, their results would appear to support our observations.

A small improvement in MDQ (about 3-fold) is possible when the HPO mode is used rather than FID, but the S$_2$ mode is similar in sensitivity to FID. The overall gain in sensitivity with FPD is not significant, but the enhanced selectivity towards sulphur and phosphorus may be considered as most desirable.

The use of permeation tubes with Ni(dpr'dtp)$_2$

Enhancement of detection limits by chemical means for sulphur compounds in photometric detectors is well recognised[32]. By pre-establishing a sulphur background in the detector, its additive effect on total sulphur concentration within the detector is subjected to a square-law response, which effectively increases the response to eluted sulphur-containing solutes. Response linearisation is also possible[33]. This phenomenon was investigated to observe if improvements in detection limits could be achieved and also to compare qualitatively the response of the chelate with those of organosulphur compounds.

Calibration curves were obtained with use of permeation rates of CS$_2$; response data with no permeation tube present were also collected. In Fig. 4 are shown the three curves, and relative background permeation levels are indicated (detector offset caused by the constant permeation rate). It is clear that absolute response levels at lower nickel concentrations are considerably increased at higher permeation levels, and this leads to an improved detection limit of $8 \cdot 10^{-11}$ g S sec^{-1} from curve II (noise increase results in lower signal-to-noise ratio at the higher permeation rate). The shape of the curves is rather unusual, as the slope in the lower concentration region is expected to be "linearised" to give a slope close to unity (i.e., concave rather than convex shape)[34]. Again, it is necessary to postulate an interference effect when in-
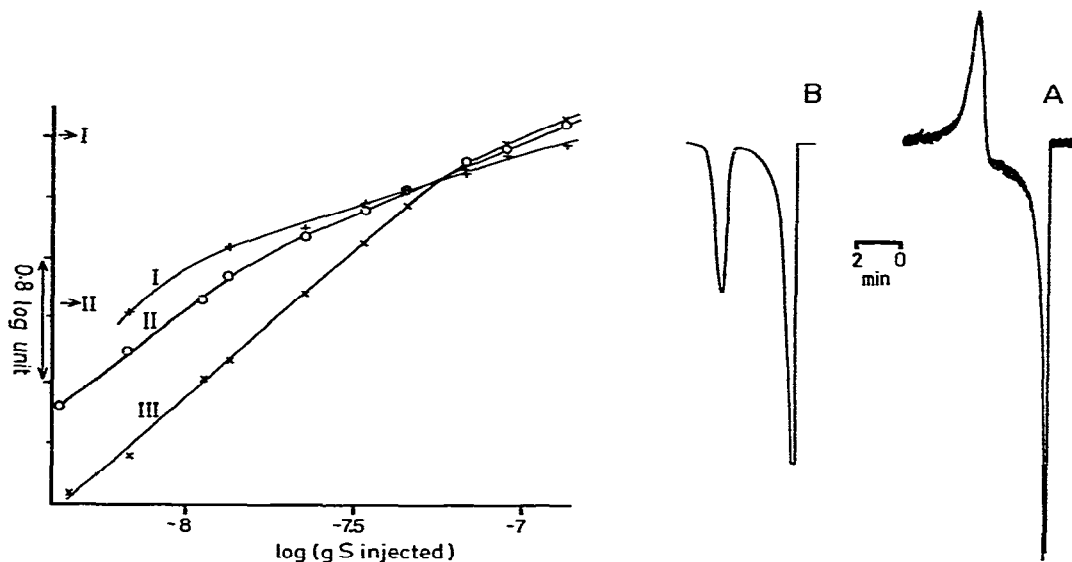
Fig. 4. Calibration curves for response against mass of sulphur [in Ni(dpr·dtp)₂] using a number of different CS₂ backgrounds as indicated. I, 'moderate' sulphur background; II, 'low' sulphur background; III, no background permeation.

Fig. 5. Representative chromatographic responses for Ni(dpr·dtp)₂ with different permeation rates of CS₂. A, 'moderate' CS₂ permeation (*ca.* 20% f.s.d. at 100 × 64 attenuation), 45 ng of Ni injected; B, 'high' CS₂ permeation (*ca.* 20% f.s.d. at 1000 × 128 attenuation), 68 ng of Ni injected.

creasing amounts of chelate enter the detector. The response with a high permeation rate adds support to this, as the chelate quenches the background to give a negative peak in a manner similar to that for a hydrocarbon[34], as shown in Fig. 5. Aue and Flinn[33] have touched on this point briefly by acknowledging that when both dopant (background gas) and analyte contain carbon, quenching of the S₂ emission must occur to some extent. The absolute degree of interference of this nature does not seem to have been studied in detail.

The peaks produced in the above experiment were analysed in an attempt to establish a correlation between mass of chelate injected (or relative level of background) and resulting peak width. We have previously shown[26] that this form of analysis may indicate the extent of linearisation of response for sulphur compounds and can also be used to estimate the exponential response factor, *n*. Generally, greater permeation rates produce broader peaks; however, as implied by the shape of the calibration curve for any one permeation rate, the greater amount of injected chelate produces a broader (and hence more linearised) peak response. This is manifested by a slope closer to unity in the upper regions of the curve, and this distinguishes the behaviour of the chelate from that of organosulphur compounds. Thus, it appears that interference associated with the metal chelate, from an as yet unidentified source, is much greater than any that could be ascribed to simple organosulphur compounds.
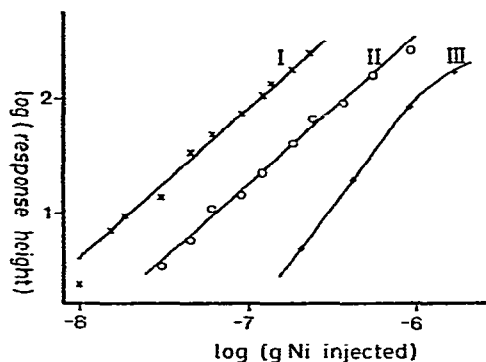
Fig. 6. Calibration curves for Ni(dpr'dtp)$_2$ with an HCl-etched, Carbowax 20M deactivated glass-capillary column dynamically coated with PS-300. I. FPD, (HPO mode), 100:1 split ratio. II. FID, 20:1 split. III. FPD, (S$_2$ mode), 30:1 split.

Capillary column analyses

Investigations on calibration response, detection limits and chromatographic-peak shapes were repeated using open tubular columns; Fig. 6 presents calibration curves of the nickel chelate using FID and both FPD modes. The HPO mode does not show the convex behaviour seen for packed columns (cf. Fig. 3), perhaps implying that some adsorption of chelate may have occurred in the packed column. Over the narrow range illustrated, the S$_2$ mode gives a slope of ca. 2.0 on the log–log graph, whereas the FID and the FPD /HPO mode calibrations both have slopes of ca. 1.2–1.3. Detection limits (Table II) show a definite improvement over those reported for packed columns. These values were obtained under conditions of split injection, and it is assumed that the amount of chelate delivered to the head of the column may be calculated on the basis of relative carrier flow-rates through the column and the splitter control. Again the MDQ values indicate that chelate detection based on HPO emissivity is about 5-fold poorer than Perkin-Elmer specifications and is about one order of magnitude inferior to that for triphenylorthophosphate (TPOP). Use of the S$_2$ mode leads to an MDQ of $3.8 \cdot 10^{-11}$ g Ni sec^{-1} ($8.4 \cdot 10^{-11}$ g S sec^{-1}) and this is comparable with that for the FID and also agrees with Sucre and Jennings' value[18].

TABLE II

LOWER LIMITS OF DETECTION FOR A CAPILLARY COLUMN WITH THE FPD AND INJECTION SPLITTING

Column as in Fig. 6.

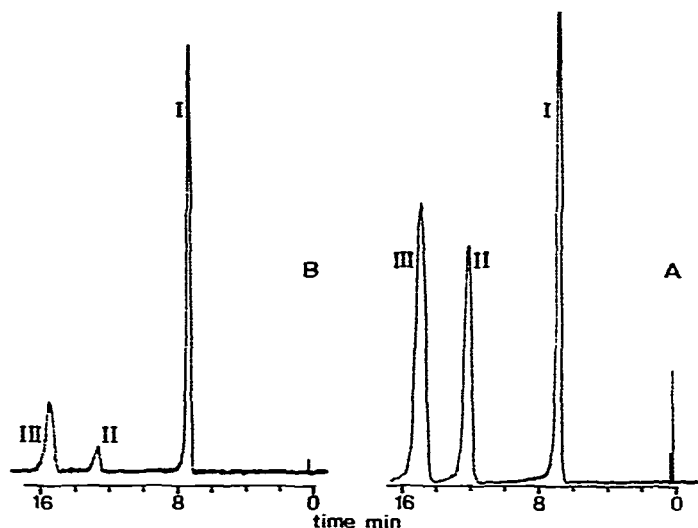| Compound	Emission mode	Amount injected	Split ratio	MDQ
Ni(dpr'dtp)$_2$	S$_2$	$1.8 \cdot 10^{-7}$ g Ni	1:133	$3.8 \cdot 10^{-11}$ g Ni sec^{-1} ($8.4 \cdot 10^{-11}$ g S sec^{-1})
Ni(dpr'dtp)$_2$	HPO	$4 \cdot 10^{-8}$ g Ni	1:100	$1.1 \cdot 10^{-11}$ g Ni sec^{-1} ($1.2 \cdot 10^{-11}$ g P sec^{-1})
TPOP	HPO	$9.7 \cdot 10^{-9}$ g P	1:100	$1.8 \cdot 10^{-12}$ g P sec^{-1}
Ni(dpr'dtp)$_2$	—*	$6 \cdot 10^{-8}$ g Ni	1:35	$3 \cdot 10^{-11}$ g Ni sec^{-1}

* FID result.

Fig. 7. Capillary chromatograms of a mixture of metal diisopropyldithiophosphates using FPD. Column: HCl-etched, dynamically coated with PS-300. Oven, 170°C isothermal; carrier gas flow-rate 67 cm sec^{-1}. A, HPO detection mode; B, S$_2$ detection mode. Chelates: I = Ni; II = Pd; III = Pt.

The compound dependency noted for the HPO mode may well be overcome by use of a double-flame photometric detector.

The favourable peak shapes produced by Ni, Pd and Pt chelates are illustrated in Fig. 7 for both FPD modes. The most noteworthy feature is the successful resolu-
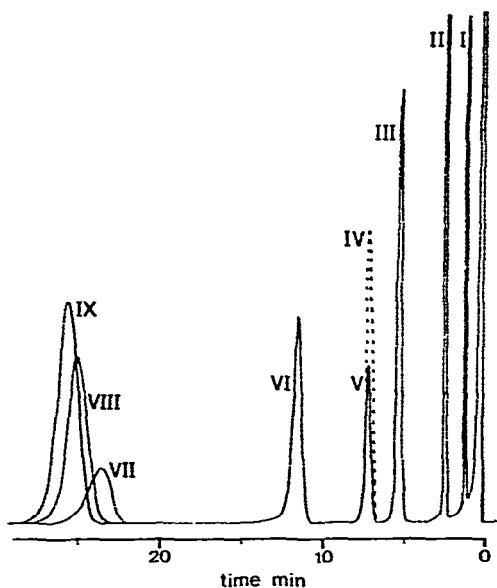

Fig. 8. Resolution of various Ni dialkyldithiophosphate chelates and n-alkanes using FID. Column as in Fig. 7; oven at 170°C; carrier gas flow-rate $ca.$ 80 cm sec^{-1}. I = n-C$_{20}$; II = n-C$_{22}$; III = n-C$_{24}$; IV = Ni(dedtp)$_2$; V = Ni(dpr^{i}dtp)$_2$; VI = n-C$_{26}$; VII = Ni(dprdtp)$_2$; VIII = Ni(dbu^{s}dtp)$_2$; IX = n-C$_{28}$. Peak IV and peaks VII, VIII and IX were obtained on separate chromatograms.
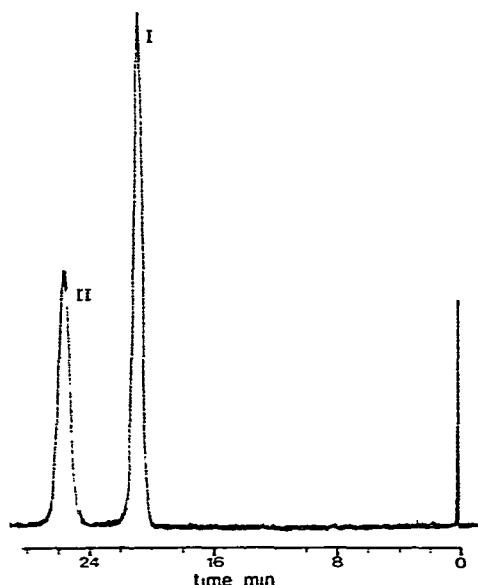
Fig. 9. Resolution of Pd and Pt chelates using FPD (S_2 mode). Column as in Fig. 7; carrier gas (He) flow-rate ~45 cm sec^{-1}. I = Pd(dpr'dtp)$_2$; II = Pt(dpr'dtp)$_2$.

tion of the palladium and platinum compounds. Since baseline resolution on packed columns was not achieved[24], this positive result is significant and indicates the prospects for resolution of derivatised metals of different chelating systems previously considered unresolvable. It is apparent that there is little difference in efficiencies and peak shapes for chelates and hydrocarbons that are eluted with similar retention volumes, as shown in Fig. 8 for a mixture of nickel chelates and some n-alkanes. The ethyl and isopropyl homologues essentially co-elute, and the n-propyl and sec.-butyl derivatives also show considerable overlap. These pairs have the same number of methylene units on their longest chain alkyl group, and, since the longest chain is directed towards the periphery of the molecule, the similar retention characteristics are not entirely unexpected (this consideration is based on expected solubility in the liquid phase). Baseline resolution of these chelate pairs would appear to be difficult and may require greatly improved column efficiencies.

The resolution of the Pd and Pt chelates with dpr'dtp (Fig. 9) allows us to test the resolution equation (Eqn. 1) previously derived for the S_2 mode of the FPD[29].

$$R_S = \frac{2\,\Delta t_R}{\sqrt{n_1}\,W'_{bn1} + \sqrt{n_2}\,W'_{bn2}} \tag{1}$$

Exponential response factors of $n_1 = n_2 = 2.0$, when substituted into Eqn. 1 with the respective experimental values for Δt_R (the difference in retention time between solutes 1 and 2) and W'_{bn1} and W'_{bn2} (the basewidths of peaks 1 and 2 in the same units as retention time), produce a value for R_S of 2.32; n_1 and n_2 were assumed to have values of 2.0 on the basis of the observed response factor for the Ni chelate of 2.0. A successive trial of the same mixture with HPO monitoring was made to de-

termine the peak resolution by using the normal resolution equation (which is obtained by substituting n values of unity into Eqn. 1), and produced a calculated resolution of R_S = 2.31. This excellent agreement further illustrates, along with our previous supporting evidence, the applicability of our non-linear detection response model[26,29].

Stationary phase PS-300, a phenyl silicone, was used primarily in the capillary-column studies because it showed greater discrimination between the Pd and Pt chelates than was obtained with OV-101. Kovats retention indices for the Ni, Pd and Pt chelates of dpr'dtp were calculated as 2480, 2615 and 2665 at 170°C on a PS-300 capillary column; those for a column packed with 1 % of OV-101 on Chromosorb 750 were 2292, 2417 and 2457, respectively, at 155°C. Values of 2261, 2326 and 2474 have been quoted for Zn, Ni and Pd on a SE-30 coated capillary at 175°C[18]. The greater retention index difference, along with better column efficiency, certainly contributes to the enhanced (baseline) resolution observed with capillary columns. Overall, the number of effective plates obtained with the latter columns were not as good as expected; various instrumental considerations with the Perkin-Elmer F-30, requiring more extra-column connections than desired, probably account for this. Although there is considerable scope for improvement in the results reported above, this does not detract from the significance of the observations made.

Our limited experience with an improved capillary system (Carlo Erba Fractovap Model 4160 Chromatograph) incorporating on-column injection on to fused silica columns supports the above assertion. A representative chromatogram for a mixture of metal chelates and some hydrocarbons is illustrated in Fig. 10. Isothermal operation at 185°C after temperature programming from 60°C leads to an observed resolution of Pd and Pt chelates in excess of 10.0, and the peak shapes bear close resemblance to hydrocarbon standards of similar retention volumes.
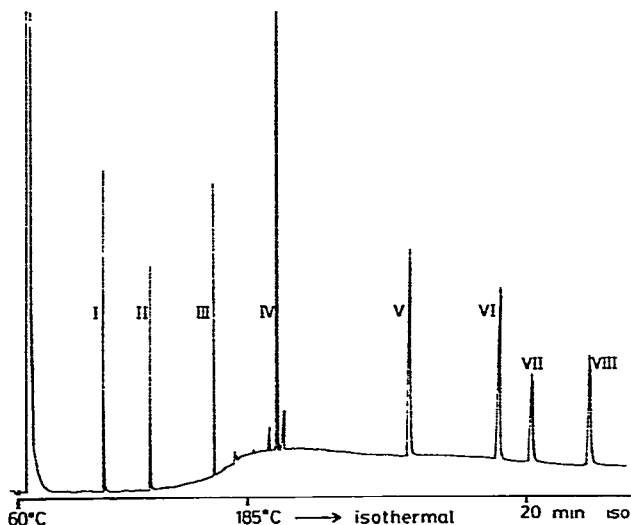

Fig. 10. Fused-silica capillary chromatogram of a mixture of n-alkanes and some metal dpr'dtp chelates. Carlo Erba 4160 instrument, with on-column injection. Carrier gas (H_2) 0.4 kg cm^{-2}; flow-rate, ca. 57 cm sec^{-1}; FID. I = n-C_{12}; II = n-C_{14}; III = n-C_{17}; IV = n-C_{20}; V = Ni(dpr'dtp)$_2$ (ca. 50 ng); VI = n-C_{24}; VII = Pd(dpr'dtp)$_2$ (ca. 20 ng); VIII = Pt(dpr'dtp)$_2$.

CONCLUSIONS

The results reported in this paper illustrate that metal dithiophosphates are well suited to selective detection based on either their S_2 or HPO molecular emission stimulated in fuel-rich reduced-temperature diffusion flames. The behaviour of the chelates in the S_2 detection mode appears to be similar to that for simple organosulphur compounds, whereas the HPO mode reflects that the process probably responsible for the emission is more complex (degradative) than that operative for organophosphorus compounds.

Analysis on open-tubular columns shows that the chromatographic integrity of the chelates is good in such systems, and improved capillary technology should enhance the analysis of the range of dithiophosphates with different alkyl substituents.

ACKNOWLEDGEMENTS

REFERENCES

1 R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.
2 G. Guiochon and C. Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Sci. Publ., Ann Arbor, MI, 1973.
3 V. P. Mihkailenko, I. P. Sereda and A. N. Korol, *J. Anal. Chem. USSR*, 34 (1979) 1755.
4 J. A. Rodriguez-Vasquez, *Anal. Chim. Acta*, 73 (1974) 1.
5 P. C. Uden and D. E. Henderson, *Analyst (London)*, 102 (1977) 889.
6 D. N. Sokolov, *Russ. Chem. Rev.*, 46 (1977) 388.
7 M. Thompson and M. Stanisavljevic, *Talanta*, 27 (1980) 477.
8 W. Jennings, *Gas Chromatography with Glass Capillary Columns*, Academic Press, New York, 2nd ed., 1980.
9 M. L. Lee and B. W. Wright, *J. Chromatogr.*, 184 (1980) 235.
10 D. A. Cronin, *J. Chromatogr.*, 97 (1974) 263.
11 K. Grob, G. Grob and K. Grob Jr., *J. High-Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 31.
12 G. Schomburg, H. Husmann and H. Borwitzky, *Chromatographia*, 12 (1979) 651.
13 G. Schomburg, H. Husmann and H. Behlau, *Chromatographia*, 13 (1980) 321.
14 R. Alexander, G. Eglinton, J. P. Gill and J. K. Volkman, *J. High-Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 521.
15 A. Tavlaridis and R. Neeb, *Z. Anal. Chem.*, 292 (1978) 199.
16 J. Krupčik, P. A. Leclercq, J. Garaj and J. Masaryk, *J. Chromatogr.*, 171 (1979) 285.
17 M. L. Riekkola, *Finn. Chem. Lett.*, (1980) 83.
18 L. Sucre and W. Jennings, *J. High-Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 452.
19 P. C. Uden, D. E. Henderson, F. P. DiSanzo, R. J. Lloyd and T. Tetu, *J. Chromatogr.*, 196 (1980) 403.
20 R. S. Juvet and R. P. Durbin, *Anal. Chem.*, 38 (1966) 565.
21 F. M. Zado and R. S. Juvet, *Anal. Chem.*, 38 (1966) 569.
22 H. H. Hill, Jr. and W. A. Aue, *J. Chromatogr.*, 74 (1972) 311.
23 W. A. Aue and H. H. Hill, Jr., *Anal. Chem.*, 45 (1973) 729.
24 T. J. Cardwell and P. S. McDonough, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 283.

25 T. J. Cardwell, P. J. Marriott and P. S. McDonough, *J. Chromatogr.*, 193 (1980) 53.
26 T. J. Cardwell and P. J. Marriott, *J. Chromatogr. Sci.*, in press.
27 A. E. O'Keeffe and G. C. Ortman, *Anal. Chem.*, 38 (1966) 760.
28 W. J. Kirsten, *Anal. Chem.*, 51 (1979) 1173.
29 P. J. Marriott and T. J. Cardwell, *Chromatographia*, 14 (1981) 279.
30 J. F. McGaughey and S. K. Gangwal, *Anal. Chem.*, 52 (1980) 2079.
31 R. Greenhalgh and W. P. Cochrane, *J. Chromatogr.*, 188 (1980) 305.
32 J. M. Zehner and R. A. Simonaitis, *J. Chromatogr. Sci.*, 14 (1976) 348.
33 W. A. Aue and C. G. Flinn, *J. Chromatogr.*, 158 (1978) 161.
34 A. R. L. Moss, *SCAN (Pye-Unicam)*, 4 (1974) 5.