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APPLICATIONS OF DEXSIL AND OTHER GAS CHROMATOGRAPHIC POROUS-LAYER OPEN TUBULAR COLUMNS TO METAL COMPOUND SEPARATIONS AND PYROLYSIS

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SUMMARY

Stainless-steel porous-layer open tubular (PLOT) columns have been made with Dexsil and other stationary phases suitable for the separation of a range of volatile metal chelates and organometallic compounds. Integrity of the substrate is assured by multiple coating of the stationary phase. Structural isomers of chromium β -diketonates and mixed ligand redistribution products are resolved and eluted without sample loss to flame ionization detection limits. A family of tetradentate copper β -ketoamine chelates are separated and the pyrolysis products of analogous tetradentate salicylaldehyde complexes are resolved. Vapor phase infra-red spectrophotometry is used on-line with the PLOT column eluent for peak identification. A range of metallocene organometallics are separated including ferrocene, ruthenocene and osmocene, and substituted ferrocenes are resolved with iron specific detection by d.c. argon plasma emission spectroscopy. Cyclopentadienylmanganese tricarbonyls and cyclopentadienylchromium nitrosyl carbonyl species are also chromatographed.

INTRODUCTION

Porous-layer open tubular (PLOT) capillary columns, first developed by Halász and Horváth¹ and coated by the dynamic method are easily made in the laboratory and their applications have been widely developed, particularly by Nikelly². They are particularly attractive in the general chromatographic laboratory since column parameters may be readily optimized, columns may be easily cleaned and repacked thus reducing the difficulties experienced by degradation of performance of wall-coated open tubular (WCOT) columns by sample decomposition or deposition of involatile residual materials. Their inherently higher capacity factors allow direct sample injection in the 0.1–1.0 μ l range without complex splitting systems. It is easy to experiment with new stationary phases and packing conditions. Also important is the compatibility of PLOT columns both with preceding analytical devices such as pyrolysis units which may be directly interfaced with total sample transfer, or with subsequent identification devices. Mass spectrometric (MS), vapor phase infrared

(IR), molecular weight, emission spectroscopic and other instrumental systems may be interfaced with little sacrifice of resolution and also with the capability to receive sufficient sample in eluted peaks to allow adequate characterization.

The development of stable stationary phases usable at high column temperatures has also been much in evidence in recent years. Prominent here have been the carborane-silicone Dexsil phases which have been widely used in packed columns and have also been utilized in commercial support-coated open tubular columns. It has been reported however that Dexsil coatings on WCOT columns have limited mechanical stability above 200°C³ although some applications have been noted⁴. The use of Dexsil 300 GC, 400 GC and 410 GC have been particularly encouraging in metal chelate gas chromatography^{5,6}, particularly for β -ketoamine and salicylaldimine complexes where stability, peak shape, resolution and available temperature range are all favorable. PLOT columns have not previously been utilized with Dexsil phases.

There appear to be no reported examples of open tubular column gas chromatography (GC) of metal chelates and little attention to organometallics^{7,8}. We give examples of various metallic systems resolved on Dexsil and other PLOT columns and also consider the application of the interfaced Pyroprobe pyrolysis unit to direct chelate pyrolysis and interfaced rapid-scan IR spectrophotometry for PLOT column peak identification.

EXPERIMENTAL

Metal chelates and organometallic compounds

Chromium trifluoroacetylacetonate, Cr(TFA)₃, was prepared from trifluoroacetylacetonone and chromium(III) nitrate by standard procedures and a sample enriched with respect to the *cis* isomer prepared by silica gel column chromatography⁹.

The mixture of mixed ligand chromium hexafluoroacetylacetonate-trifluoroacetylacetonate chelates was prepared by photochemical redistribution between Cr(TFA)₃ and Cr(HFA)₃ in benzene followed by silica gel column chromatography.

The copper(II) tetradentate β -ketoamine chelates were prepared as reported previously¹⁰. N,N'-Ethylenebis(salicylaldimine) was prepared by condensation of ethylenediamine and salicylaldehyde and the copper and nickel chelates prepared by established procedures¹¹.

The metallocenes were obtained from Professor M. D. Rausch (University of Massachusetts, Amherst, MA, U.S.A.) as were the cyclopentadienyl-dicarbonylnitrosyls. The cyclopentadienylmanganese tricarbonyl compounds were obtained from Strem Chemicals (Danvers, MA, U.S.A.).

Coating procedure for the PLOT columns

The stainless-steel tubing used was 0.03-in. I.D. 316 grade (Handy and Harman Tube Corp., Norristown, PA, U.S.A.) and the coating apparatus was based on that described by Nikelly². Chromosorb R-6470 (Johns-Manville, Denver, CO, U.S.A.) was used as the substrate although Tullanox 500 (Applied Science Labs., State College, PA, U.S.A.) was also assessed. The following procedure was found best for coating OV-101 and particularly Dexsil 300 GC. As noted subsequently, adequate coating is especially important for successful chromatographic elution of the metal chelates. A mixture consisting of 5% (w/v) Chromosorb R-6470 was prepared in

6 ml of methylene chloride. The slurry was first shaken for 30 min, any lumps of support material being dispersed as far as possible with a spatula. The slurry was then left to stand overnight, during which time a free flowing uniform milky suspension was obtained. The use of larger amounts of support gave too viscous non-uniform slurries yielding less efficient columns. The empty column was filled with methylene chloride, the agitated slurry poured into the column packer tube and nitrogen tank pressure applied at 30–40 p.s.i. The emergent clear methylene chloride was discarded until excess slurry emerged which was collected. The process was repeated until the slurry emerged as a viscous uniform flowing liquid which gave smooth complete coverage of a clean metal spatula dipped into it. The number of cycles necessary depended upon the initial viscosity of the slurry and ranged from one to four. Nitrogen pressure was then reduced to about 10 p.s.i. and the column allowed to dry under nitrogen for 45 min. Conditioning was particularly important for the Dexsil 300 GC column, the method used being similar to that described by Burgett¹². The column was heated for 1 h at 80°C with no flow and the temperature then programmed at 4°C/min to 180°C with a helium flow of 10 ml/min and held there for 12 h. Finally, the temperature was programmed at 4°C/min to 250°C and held for 4 h.

Gas chromatography

Varian 1200, 2760 and Perkin-Elmer 990 instruments were used as noted with flame ionization detection except where otherwise indicated.

Pyrolysis unit

A Pyroprobe 100 pyrolysis unit was employed (Chemical Data Systems, Oxford, PA, U.S.A.) in conjunction with Perkin-Elmer 990 and Varian 2760 gas chromatographs using a specially designed cooled probe interface to preclude prior volatilization and degradation of the complexes before firing of the probe¹³.

Vapor phase infrared spectrophotometry

A Norcon 201 rapid-scan vapor phase IR spectrophotometer (Norcon, South Norwalk, CT, U.S.A.) was used, interfaced with a Varian 2760 gas chromatograph, the full instrumental system having been described previously^{14,15}. 6-sec scans were taken and digital filtering, background subtraction and normalization carried out by an interfaced PDP 11 10E minicomputer.

Direct-current argon plasma emission spectroscopic detection

A prototype Spectraspan III echelle spectrometer (Spectrametrics, Andover, MA, U.S.A.) incorporating a high temperature argon plasma jet was interfaced through a heated transfer line to a Varian 1200 gas chromatograph. Full details of the system have been described^{16–18}.

RESULTS AND DISCUSSION

GC of volatile metal chelates has been well established and reviewed by various authors^{19–22}.

The isomeric *mer(trans)* and *fac(cis)* trifluoroacetylacetonates of trivalent transition metals such as chromium and rhodium provide a good example of the

separatory power of GC. These species formed as an equilibrium mixture on reaction of metal with ligand may be interconverted at elevated temperatures in both liquid and vapor phases²³ and the latter reaction in fact dictates the maximum column temperature that may be used for their separation. $\text{Cr}(\text{TFA})_3$ has been used as the species of choice for trace chromium analysis^{24,25} but care must be taken either to choose a stationary phase which will not separate the isomers, or to take careful account of the isomer ratio present. Probably the best packed column resolution for this system was obtained by Kutal and Sievers²³ on a glass column containing open-pore polyurethane although column efficiency was not very high due to the short column used. Among classical stationary phases employed for this separation, fluorosilicones are the best.

A 33-ft. Dexsil 300 GC PLOT column was used to obtain the isomer separation shown in Fig. 1.

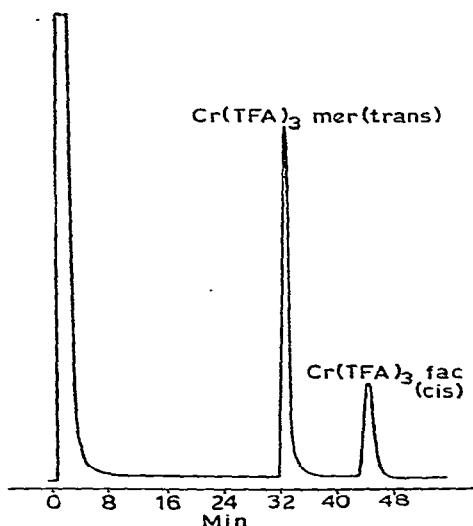


Fig. 1. Separation of *mer(trans)* and *fac(cis)* chromium trifluoroacetylacetonate. Column, 33 ft. \times 0.03 in. I.D. stainless steel PLOT Dexsil 300 GC. Temperature, 100°C. Helium flow-rate, 3.6 ml/min.

Plate numbers of around 4000 for the *mer* and 5000 for the *fac* isomer are observed and the resolution factor is close to 5. This resolution is exceptional when it is noted that a 2-m packed 2% Dexsil column shows virtually no resolution. In contrast an OV-101 PLOT column of similar dimensions gave a resolution factor of approximately 1.5. Although plate numbers obtained are substantially smaller than those noted subsequently for organometallic species, this is not atypical for metal chelates generally and the effectiveness of the column is still well indicated. The small degree of tailing noted for the *mer* isomer may be due to slight on-column isomerization to the *fac* isomer with consequent lengthening of retention time.

An example of the effectiveness of the PLOT column in the temperature programmed mode is shown in Fig. 2 which shows a separation of ligand redistribution products of trifluoroacetylacetonate and hexafluoroacetylacetonate on Cr(III).

For these mixed ligand species there are seven possible complexes of the

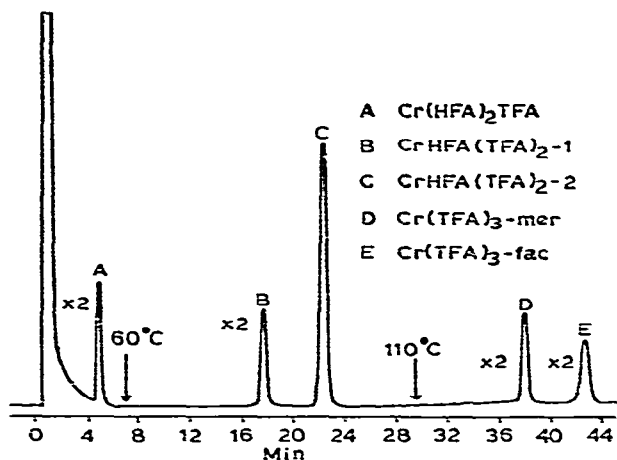


Fig. 2. Separation of trifluoroacetylaceton and hexafluoroacetylaceton redistribution products on chromium(III). Column and conditions as in Fig. 1, except temperature: programmed from 60 to 110°C at 2°/min.

formula $\text{Cr}(\text{TFA})_x(\text{HFA})_{3-x}$ obtainable from reaction of Cr(III) with a ligand mixture²⁶. Moshier and Sievers¹⁹ reported preliminary studies showing separation of all seven species but detailed chromatographic study has not been reported. The separation depicted shows good resolution of five peaks. $\text{Cr}(\text{HFA})_3$, present only at a very low level is unresolved from solvent, but the remaining chelate groups are well separated. Peak C probably contains two unresolved components of the three possible geometrical isomers of $\text{Cr}(\text{HFA})(\text{TFA})_2$. As calibration curves are linear to detection limits at nanogram levels, as for hydrocarbon standards, it appears that these compounds do not degrade on the multicoated PLOT column, although noticeable peak shape deterioration and sample loss were seen below the microgram level for singly coated columns. Since it has been shown for these β -diketonates and β -aminoketonates that elution is possible to picogram levels on packed stainless steel columns^{27,28} with sufficiently deactivated substrates, it is probable that degradation on PLOT columns occurs largely on incompletely covered diatomite substrate. For the metal complexes discussed here there is little evidence of catalyzed on-column degradation on stainless steel although there are many other instances where this does occur^{7,29}.

As an example of the effectiveness of the Dexsil PLOT column for less volatile metal chelates at higher column temperatures, Fig. 3 shows a separation of the copper chelates of *N,N'*-ethylenebis(trifluoroacetylacetonimine) and its propylene and butylene analogues [$\text{Cu}(\text{enTFA}_2)$, $\text{Cu}(\text{pnTFA}_2)$ and $\text{Cu}(\text{bnTFA}_2)$]. The latter exhibits racemic and meso geometrical isomers³⁰.

The resolution factors between successive peaks are in the range 4–5, this being greatly superior to the best packed column resolution obtained on a QF-1 fluorosilicone column³⁰ where baseline resolution is only just obtained for the latter three chelates. Plate numbers are again in the 4000–5000 range, this still comparing favourably with the typical values of around 1000 plates obtained on packed columns.

The data which we have obtained so far on these PLOT columns suggests that they have considerable potential for metal chelate analysis particularly for the

separation of difficultly resolvable chelate pairs such as copper and nickel β -ketoamine complexes. We intend to evaluate Dexsil and other high temperature PLOT and also WCOT columns for a variety of chelate systems.

Metal chelate pyrolysis

Central to the study of volatile metal compound GC is an understanding of the relative volatilities and thermal stabilities of different species. An example of a system studied in this context is that of the tetradentate salicylaldimine complexes shown in Fig. 4.

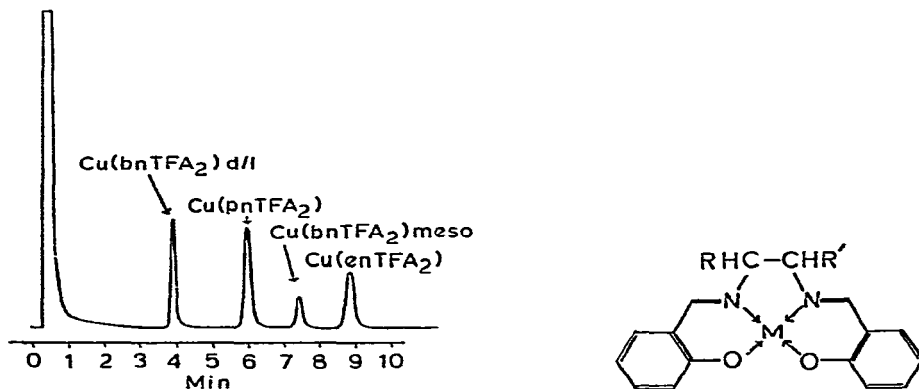


Fig. 3. Separation of copper(II) N,N' -alkylenebis(trifluoroacetylacetonimine) chelates. Column as Fig. 1 at 225°C.

Fig. 4. Structure of N,N' -alkylenebis(salicylaldimine) complexes. $M = \text{Cu, Ni, Pd, etc.}$ R and $R' = \text{H, CH}_3$.

These are analogous to the tetradentate β -ketoamine complexes and their bidentate analogues may also be gas chromatographed³¹. However, the tetradentate complexes appear to have marginally insufficient volatility for GC and their thermal degradative behaviour has been the subject of considerable study. These complexes additionally are being investigated as possible fire retardant additives for polymers. Pyrolysis was carried out with a Pyroprobe coil probe unit which forms part of the thermal analysis system described elsewhere^{14,15}. In this study we wished to establish the reproducibility of pyrolysis patterns for the interfaced PLOT column for both ligand and complexes for repeated pyrolyses over an extended period. The capacity advantages of the PLOT column in the interfaced pyrolysis mode are evident as stream splitting may be avoided, thus precluding any fractionation of the wide boiling range of products. Since a considerable range in polarities of pyrolysis fragments was encountered, a Carbowax 20M PLOT column was used for this study. Further identification of pyrolysis fragments was carried out by GC-MS and by GC-IR in order to elucidate degradation mechanisms as far as possible. The full study will be published subsequently³² but some chromatographic and IR data are presented here.

Fig. 5 illustrates a fingerprint PLOT pyrogram of the free ligand N,N' -ethylenbis(salicylaldimine), $\text{H}_2(\text{enSal}_2)$, the column being temperature programmed from 80 to 200°C.

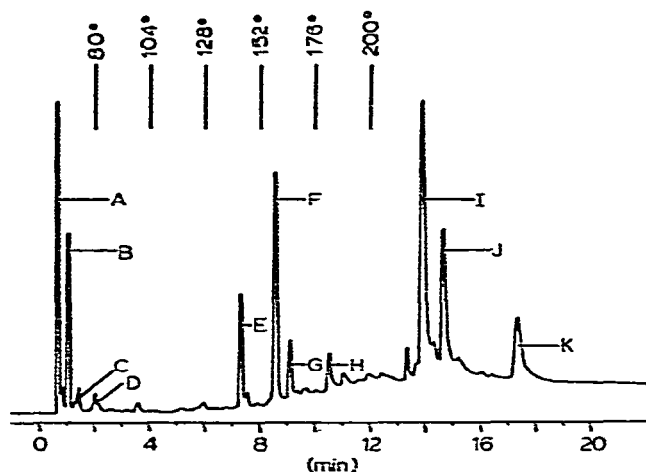


Fig. 5. Pyrogram of $H_2(enSal_2)$. Pyrolysis ramp = $20,000^\circ C/sec$. Final temperature, $900^\circ C$. Column, 100 ft. \times 0.03 in. I.D. stainless steel PLOT Carbowax 20M.

This ligand itself is sufficiently volatile to vaporize at the injection port temperature of the gas chromatograph thus preventing any reproducible pyrolysis unless the cooled version of the Pyroprobe¹³ is used to hold the sample at ambient temperature until the probe is fired. Both reproducibility of pyrolysis and of PLOT column chromatography are found to be excellent under the stated conditions. Fig. 5 shows a pyrogram obtained after approximately 50 pyrolyses and it is essentially superimposable upon a pyrogram obtained on the column when first packed. In general the column efficiency of this Carbowax 20M column when employed in the pyrolysis mode was closely similar to that shown for direct injection.

To further indicate the reproducibility of pyrolysis, Fig. 6 shows comparison chromatograms obtained under the same pyrolysis conditions for $Cu(enSal_2)$ and $Ni(enSal_2)$. While some pyrolysis peaks are common to ligand and complexes, there are considerable differences in both distribution and intensity for each compound. Peaks labelled A to K have been examined both by interfaced vapor phase IR spectrophotometry and also by GC-MS. Tentative assignments are: A = methane; B = benzene; C = toluene; D = benzylamine; E = methylbenzylimine; F = ethylenebenzylimine; G = *o*-hydroxycyanobenzene (?); H = unknown; I = *o*-hydroxybenzylimine; J = *o*-hydroxyethylenebenzylimine; K = *N,N'*-ethylenebis(salicylal-dimine) (?).

Fig. 7 illustrates a vapor phase IR spectrum of peak I in the pyrogram. The sample level which can be separated on the PLOT column without appreciable loss in efficiency is compatible with the acquisition of informative IR spectra of individual peaks. The spectrum shown corresponds to a few micrograms of component I and the assignments made in Fig. 7 correspond well to the hydroxy-imine structure shown which is further substantiated by MS analysis.

The peak width obtained from the PLOT column is entirely compatible with the IR scan time and computer programs are under development to facilitate identification of unknown species.

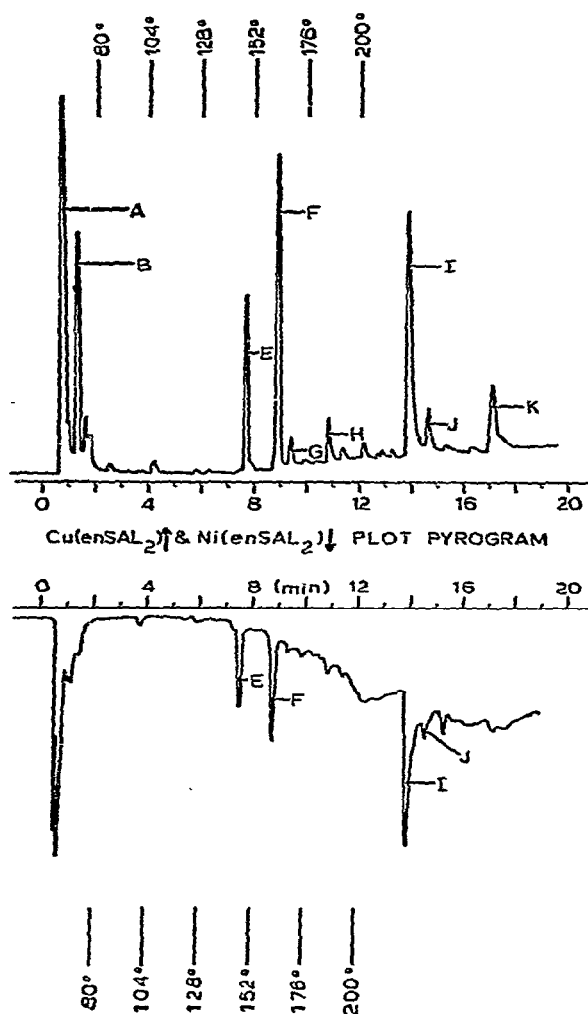


Fig. 6. Pyrograms of Cu(enSal₂) and Ni(enSal₂). Conditions as in Fig. 5.

Organometallic compounds

In general there have been relatively few organometallic chemical systems which have been gas chromatographed, and in particular transition metal compounds have received restricted attention because of the lower thermal stability of many of them and their greater sensitivity to oxygen and water. Guiochon and Pommier⁸ discuss the literature available on metallocenes, particularly ferrocene and its derivatives. A number of transition metal carbonyl compounds have also been gas chromatographed including arene and cyclopentadienyl systems. No capillary column separations are in evidence however.

We have assessed a number of transition metal organometallics on stainless steel PLOT columns and found excellent column efficiencies. As is noted from the following examples, plate numbers in the range of 10,000–20,000 are easily obtained

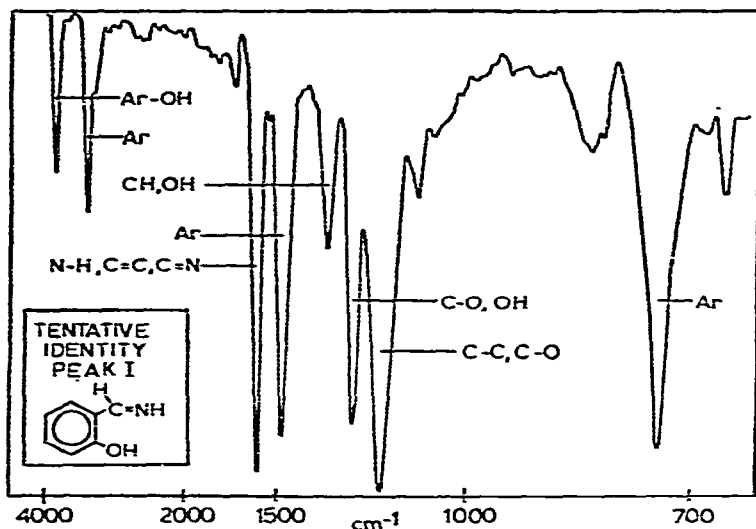


Fig. 7. Vapor phase IR spectrum of peak I in salicyaldimine pyrograms (Figs. 5 and 6). 6-sec scan with computer filtering, background correction and normalization.

for thermally stable compounds, efficiencies comparable with inert organic compounds such as paraffins. It is also important to be assured of the integrity of the eluting peaks particularly for potentially rapidly degradable compounds.

Fig. 8 illustrates the separation of analogous metallocenes in the iron group.

Plate numbers between 6000 and 12,000 were found for these compounds with very slight peak tailing. As expected, elution order follows the order of molecular weight increase.

Fig. 9 shows the separation of a series of substituted ferrocene derivatives. The presence of the various halogen substituent groups has minimal effect on peak shape or column efficiency emphasizing that the good chromatographic behaviour depends primarily on the stability of the ferrocene moiety. In addition to the flame ionization detection trace shown, the d.c. argon plasma emission detector trace monitored at 372.0 nm is shown. This serves to verify in this chromatogram that the eluted peaks correspond to iron compounds and that the relative response factors are very closely similar to those seen in the flame ionization trace.

The column efficiency as monitored by the d.c. plasma detector is identical to that noted for the flame ionization detector indicating that the low volume interface constructed for this purpose has a minimal band broadening contribution. (Optimal plate numbers were also maintained by using argon make-up gas.) For the iron complexes detection limits are in the low ng region.

The separation of three novel organometallic compounds is shown in Fig. 10. The cyclopentadienyl-dicarbonylnitrosyls of chromium, molybdenum and tungsten show good peak shape with the exception of slight tailing of the tungsten peak. Direct-current plasma emission monitoring of this peak shows the tail to result from column characteristics rather than from band broadening in the interface. Plate numbers in excess of 10,000 are again obtained, emphasizing the excellent behaviour

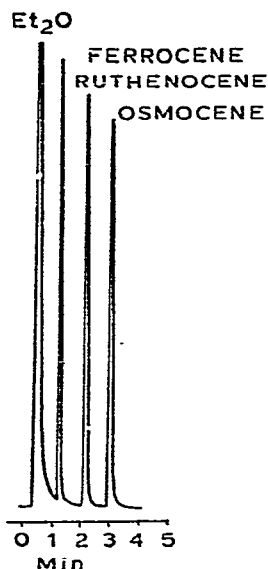


Fig. 8. Metallocene separation. Column, 33 ft. \times 0.03 in. I.D. stainless steel PLOT OV-101 at 150°C.

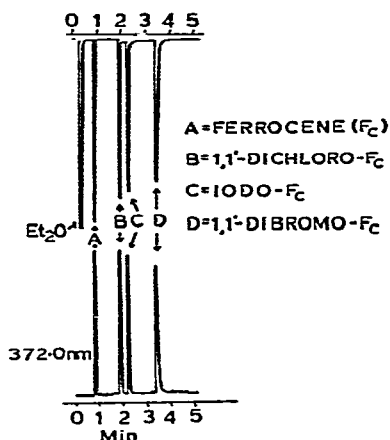


Fig. 9. Separation of halogenated ferrocene derivatives. Column as in Fig. 8 at 170°C. Upper trace, flame ionization detection; lower trace, emission at 372.0 nm. Sample split 1:1.

of compounds of this type on PLOT column, quantitative response being maintained to the ng level.

An example of an organometallic system of considerable current analytical interest is cyclopentadienylmanganese tricarbonyl, used widely as an alternative anti-knock gasoline additive to lead alkyls. In particular the methylcyclopentadienyl

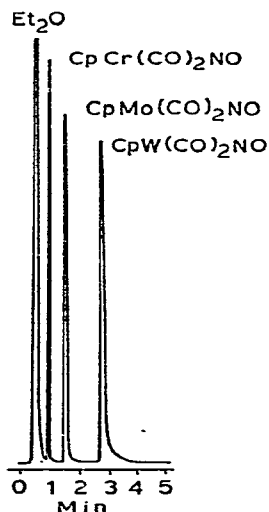


Fig. 10. Separation of chromium, molybdenum and tungsten cyclopentadienyl-dicarbonylnitrosyls. Column as in Fig. 8 at 155°C.

compound is important and may be determined readily by means of specific manganese determination in the GC-d.c. argon plasma spectroscopic mode. The simple resolution of the manganese species from gasoline components is not straightforward even by open tubular GC. A simple quantitative method utilizing the addition to the sample of cyclopentadienylmanganese tricarbonyl as an internal standard and GC-d.c. argon plasma detection has been reported³³ and analysis has also been carried out by a hydrogen atmosphere flame ionization detector³⁴. The PLOT resolution of these two manganese compounds is illustrated in Fig. 11.

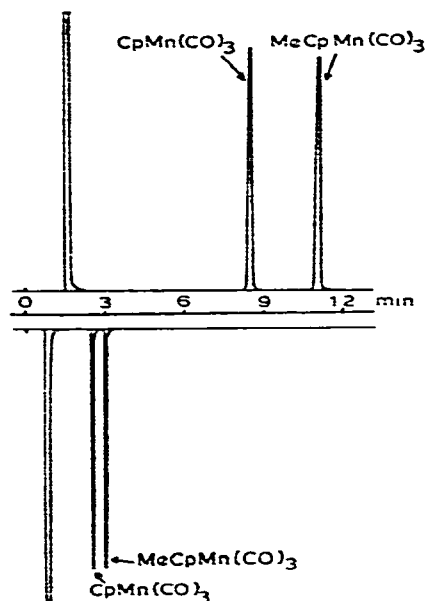


Fig. 11. Separation of cyclopentadienylmanganese tricarbonyl compounds. Upper trace, Dexsil 300 GC; lower trace, OV-101. Columns, 33 ft. \times 0.03 in. I.D. stainless steel PLOT at 120°C. Injector temperature, 150°C. Detector temperature, 180°C. Helium flow-rate, 3.5 ml/min.

The behaviour of these compounds on OV-101 and Dexsil 300 GC are compared, column conditions being set identically. Both columns show theoretical plates for both compounds in the region of 20,000. However, the Dexsil column retains them more than the OV-101 column and gives greater resolution (16 vs. 12). It is also apparent that the Dexsil phase gives somewhat more symmetrical peaks and the slight tailing on OV-101 is absent. The high efficiency obtained on the Dexsil 300 GC column in this case emphasized it to be greatly dependent on compound type since plate numbers are four or five times larger than those obtained for the chelates.

The examples considered in this paper emphasize that PLOT columns have much potential for the chromatography of metal compounds. Further, the ready compatibility they exhibit with interfaced pyrolysis and novel detection systems such as vapor phase IR and plasma emission spectroscopy serve to make their future application for metallic species of considerable interest.

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